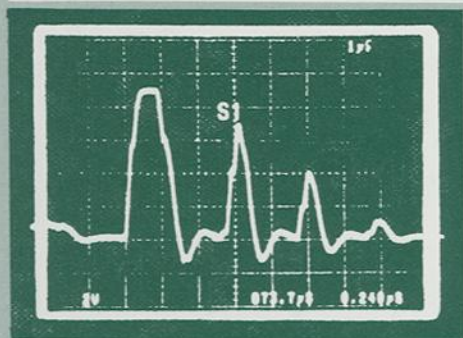

Corrosion Monitoring in Industrial Plants Using Nondestructive Testing and Electrochemical Methods

Moran/Labine, *editors*



STP 908

CORROSION MONITORING IN INDUSTRIAL PLANTS USING NONDESTRUCTIVE TESTING AND ELECTROCHEMICAL METHODS

A symposium sponsored by ASTM Committee
E-7 on Nondestructive Testing and Committee
G-1 on Corrosion of Metals
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Foreword

The symposium on Nondestructive Testing and Electrochemical Methods of Monitoring Corrosion in Industrial Plants was presented at Montreal, Canada, 22–24 May 1984. The symposium was sponsored by ASTM Committees E-7 on Nondestructive Testing and G-1 on Corrosion of Metals. George C. Moran, PSE&G Research Corp., and Paul Labine, Petrolite Corp., served as symposium chairmen and are editors of the publication.

Related ASTM Publications

Corrosion Fatigue: Mechanics, Metallurgy, Electrochemistry and Engineering, STP 801 (1983), 04-801000-30

Atmospheric Corrosion of Metals, STP 767 (1982), 04-767000-27

Electrochemical Corrosion Testing, STP 727 (1981), 04-727000-27

Acoustic Emission Monitoring of Pressurized Systems, STP 697 (1979), 04-697000-22

Nondestructive Testing Standards—A Review, STP 624 (1979), 04-624000-22

A Note of Appreciation to Reviewers

The quality of the papers that appear in this publication reflects not only the obvious efforts of the authors but also the unheralded, though essential, work of the reviewers. On behalf of ASTM we acknowledge with appreciation their dedication to high professional standards and their sacrifice of time and effort.

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Introduction

Corrosion is responsible for an enormous economic drain in the industrialized nations of the world. The National Bureau of Standards (NBS) estimates that the economic loss in both direct and indirect costs caused by corrosion in 1985 alone amounted to \$167 billion. Direct costs include replacement of equipment and the application of corrosion prevention methods (for example, cathodic protection, protective coatings, and so forth); while indirect costs are associated with loss of product, plant shutdown or reduced efficiency, and failure of components and equipment. The NBS further estimate that 15%, or \$25 billion, of these losses are avoidable by using the best currently available practices.

It should be noted that not included in the above estimates are other costs associated with corrosion related failures: losses, such as those resulting in injury to employees, hazards to the general public as a result of spills and leaks, the real although unmeasurable hardships that come about from forced plant shutdowns, and the like. Some of these losses could also be avoided with good practices.

In an effort to mitigate these indirect costs, ASTM Committees E-7 on Nondestructive Testing and G-1 on Corrosion of Metals jointly sponsored a three-day symposium in May 1984 in Montreal, Canada, where selected authors were invited to present papers that represented the state of the art in corrosion monitoring techniques. Through these 39 presentations and the 34 papers included in this STP, it is anticipated that the plant operator will have a better knowledge of the latest corrosion detection and monitoring techniques.

If more detailed information regarding the forms of corrosion is needed to supplement this volume, it is suggested that the reader refer to the following:

- *Forms of Corrosion—Recognition and Prevention*, C. P. Dillon, Ed., National Association of Corrosion Engineers.
- *Corrosion Engineering*, M. Fontana and N. Greene, Eds., McGraw Hill, New York.

In addition, the following ASTM publications may be of interest:

- STP 624—*Nondestructive Testing Standards—A Review*
- STP 697—*Acoustic Emission Monitoring of Pressurized Systems*
- STP 727—*Electrochemical Corrosion Testing*
- STP 767—*Atmospheric Corrosion of Metals*

It should be noted that ASTM Committees E-7 and G-1 are concerned with the development of voluntary consensus standards, the promotion of knowledge, and the stimulation and sponsorship of research in the areas of nondestructive testing and corrosion of metals, respectively. Within these committees reside the recognized experts of their respective technical communities of nondestructive testing and corrosion of metals.

The standard test methods developed within ASTM are by design rigorously detailed, precise, and of the highest technical quality. These standards are recognized internationally and remain current since they must be regularly revised to reflect technological advances and demands of changing markets. The benefits of using ASTM standards are widely recognized, and include eliminating the need to develop individual specifications and test methods, while providing a common means of agreement between plant owners or operators and contractors. Standards are thus used to obtain and compare results, which can be considered uniform and reproducible. They may further be used to judge what is acceptable and what is not.

ASTM Committees E-7 and G-1 are comprised of people who have a common interest in promulgating the aforementioned benefits of committee participation. Membership is open to anyone who has expertise in any particular area of nondestructive testing or corrosion of metals.

Although the symposium has covered numerous applications of nondestructive testing and electrochemical techniques of monitoring corrosion, the reader is encouraged to search the literature for additional areas of application of these techniques. ASTM, the American Society for Nondestructive Testing (ASNT), the National Association of Corrosion Engineers (NACE), and the American Society of Metals (ASM) are excellent sources for this information.

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Nondestructive Testing of Corrosion Monitoring

Neutron Radiographic Detection of Corrosion

REFERENCE: Berger, H., "Neutron Radiographic Detection of Corrosion," *Corrosion Monitoring in Industrial Plants Using Nondestructive Testing and Electrochemical Methods*, ASTM STP 908, G. C. Moran and P. Labine, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 5-16.

ABSTRACT: Many nondestructive testing (NDT) methods for corrosion detection depend on the reduced thickness of the component following corrosive attack. This is normally the underlying concept for corrosion detection by NDT methods such as X-radiography, ultrasonics, and eddy currents. For neutron radiography, however, the basis for the detection is the neutron attenuation by the hydrogen in the corrosion product itself. This difference in the approach gives neutron radiography an advantage over many other NDT methods because of the potential for early detection of corrosion, before extensive attack and thinning of the material have occurred. Neutron radiographic methods are reviewed and some initial results are given for corrosion detection in aluminum. Practical neutron sources are becoming available and can be combined with established image detectors, including real-time detection systems. Corrosion in aluminum resulting from a 6.5-h supersaturated salt-water spray is shown to be detectable.

KEY WORDS: neutron radiography, nondestructive testing, corrosion, neutron sources, neutron detectors, hydrogen

Corrosion is a serious problem as was clearly brought out in the comprehensive report by the National Bureau of Standards (NBS) [1] and a recent Air Force Workshop [2]. The NBS report indicated that the economic loss due to corrosion in the United States amounted to \$70 billion per year. Although the presence of corrosion is sometimes detectable only after there are obvious signs of deterioration, it is desirable to detect corrosion at an early stage so that remedial action can be taken.

Nondestructive testing (NDT) techniques offer the potential for early detection of corrosion. Many NDT methods [3-11] may be used; visual techniques have been used for many years for this purpose. When surfaces are accessible, either directly or by special equipment such as boroscope or video techniques,

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the visual method can be useful. Ultrasonics [12–15], radiography [16], and eddy current [17] techniques are also used for field inspections to detect corrosion, and acoustic emission methods are now coming into use. In ultrasonics, a thickness test approach is used either by causing the material to resonate or by reflecting an ultrasonic pulse off the back surface. Both ultrasonics methods are sensitive, especially when applied to a surface with two flat faces. Resonance methods are capable of detecting thickness changes in the order of 0.1%. Pulse-echo methods claim sensitivities as small as 0.025 mm in materials 1 to 250 mm thick. However, in a typical corrosion situation where one side is not flat or where there is intervening structure, the sound is scattered and accuracy is reduced.

The eddy current technique is sensitive both to the change in thickness caused by corrosion thinning and also to the different electrical and magnetic properties of the corrosion product. Typical sensitivities to changes in thickness are of the order of 1% to 2% thickness changes; Bond [17] claims sensitivities to changes in thickness as small as 0.2% of the wall thickness for the eddy current technique. Phase sensitive and low frequency eddy current methods offer potential for deeper penetration and far-side detection of corrosion.

Acoustic emission is being applied to the detection of corrosion in aluminum honeycomb aircraft parts at McClellan Air Force Base [18]. The technique has also been studied for large structures [19] and turbine blades [20]. The phenomenon appears to depend on hydrogen evolution and the stress waves that result.

Conventional radiography [21] offers the advantage that large areas can be inspected at one time. Differences in thickness on the order of the 1% to 2%, including small corrosion pits, can be visualized under good conditions (for example, when overlying structures do not mask detail).²

Neutron radiographic methods [22–29] differ from these other NDT approaches in that the primary mechanism for detection involves not the change in thickness of the basic structure but the accumulation of the corrosion product. The corrosion product contains hydrogen and is typically in the form of a hydroxide deposit. Slow neutrons are highly attenuated by hydrogen and yet are transmitted relatively easily through most metals, a situation directly opposite to that for X-rays. The graph showing both X-ray and neutron mass attenuation coefficients versus atomic number of absorber material in Fig. 1 illustrates the complementary nature of the attenuation characteristics for X-rays and slow neutrons [30]. The high neutron attenuation of hydrogen, mainly due to scattering, is shown.

Neutron Radiographic Methods

Typically neutron radiography is accomplished in a through-transmission geometry as in X-radiography. Like other radiations, neutrons exist in differ-

²Advances in all these currently applied NDT methods are discussed elsewhere in this volume.

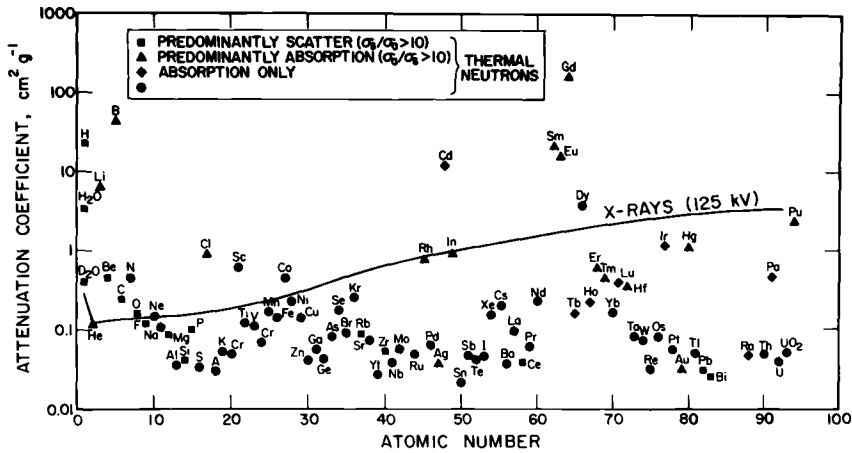


FIG. 1—Mass attenuation coefficients for thermal neutrons (dots) and X-rays (125 kV, solid line) plotted as a function of atomic number. (After Matfield, Ref 30.)

ent energies, as outlined in Table 1. The attenuation (cross section) for hydrogen and therefore the prospect for detection of corrosion products is most favorable in the cold and thermal energy portions of the neutron energy spectrum. Neutrons are typically born in the fast neutron energy range. However, the neutrons can be slowed and reduced in energy by collisions with surrounding nuclei. The material surrounding the neutron source, called a moderator, is typically a low atomic number material such as water, plastic, metal hydrides, beryllium, graphite, etc. The relatively large moderator itself becomes a source of lower-energy neutrons. To be most useful for radiography, the neutrons must be collimated into one or more neutron beams. The concept is illustrated in Fig. 2.

This moderator-collimator approach is used for most neutron radiographic sources (except fast neutrons). Reactors have been used for much of the development work, but other sources more practical for most industrial use have also been used. This includes radioactive sources, notably Cf-252, and accelerator sources. The latter sources mainly include Cockroft-Walton accelerators that produce neutrons by the reaction of accelerating deuterons on a tritium target (d, T reaction), Van de Graaff accelerators using protons or deuterons on beryllium or lithium targets, and linear accelerators where neutrons result from high energy X-ray reactions on targets such as beryllium or uranium.

Detection methods include all those normally used in X-radiography: film, radiographic paper, instant processing film, real-time methods, etc. The major difference is that special intensifying screens sensitive to neutrons are used. For film work metal screens of gadolinium or fluorescent screens of gadolinium oxysulfide are most used. The same fluorescent material can be used for real-time neutron radiographic detection either built into a neutron

TABLE 1—*Neutrons classified according to energy.*

Term	Comments	Energy Range
Slow Cold	Slow neutrons are low energy neutrons Materials possess high cross-sections at these energies, which decrease the transparency of most materials but also increase the efficiency of detection. The cross section for hydrogen is increased beyond that for thermal neutrons, so corrosion detection is enhanced. A particular advantage is the reduced scatter in materials at energies below the Bragg cutoff.	0.00 eV to 10^3 eV less than 0.01 eV
Thermal	Produced by slowing down of fast neutrons until the average energy of the neutron is equal to that of the medium. Thermal neutrons provide good discriminatory capability between different materials; sources are readily available.	0.01 eV to 0.5 eV
Epithermal	Produced at energies greater than thermal, for example, fission energies, and surrounded by a moderator. Neutrons are slowed down until they have energies in thermal equilibrium with the moderator molecules. At any location where thermal equilibrium has not been achieved the distribution of neutron velocities will contain velocities that exceed that permitted by a Maxwellian distribution of the moderator temperature. Such neutrons are referred to as epithermal.	0.5 eV to 10^4 eV
Resonance	Certain nuclei exhibit strong attenuation characteristics at well-defined energies called resonances. Neutrons in these specific energy ranges are referred to as resonance neutrons and provide excellent discrimination for particular materials by working at energies of resonance. Greater transmission and less scatter occur in specimens containing materials such as hydrogen and enriched reactor fuel materials.	1 eV to 10^2 eV
Fast	Fast neutrons provide good penetration. Good point sources of fast neutrons are available. At the lower energy end of the spectrum, fast neutron radiography may be able to do many of the inspections performed with thermal neutrons, but with a panoramic technique. Poor material discrimination occurs, however, because the cross sections tend to be small and similar.	10^3 eV to 20 MeV

image intensifier tube or as a separate screen viewed by means of a sensitive light detection system.

Thermal neutron film images typically require total thermal neutron (n) exposures in the range 10^5 n/cm² for fast films and scintillators to 10^9 or 10^{10} n/cm² for slow films with gadolinium metal screens. Real-time neutron radiography requires an incident thermal neutron intensity of about 10^4 or 10^5 n/cm² per frame. For a conventional 30 frame /s TV system, neutron intensities in the range of 10^5 to 10^6 n/cm² s will provide useful real-time results. Lower neutron intensities can be used by using integration or slow-scan TV systems. Recognizing that 10^9 thermal n/cm² is approximately 0.01 sievert

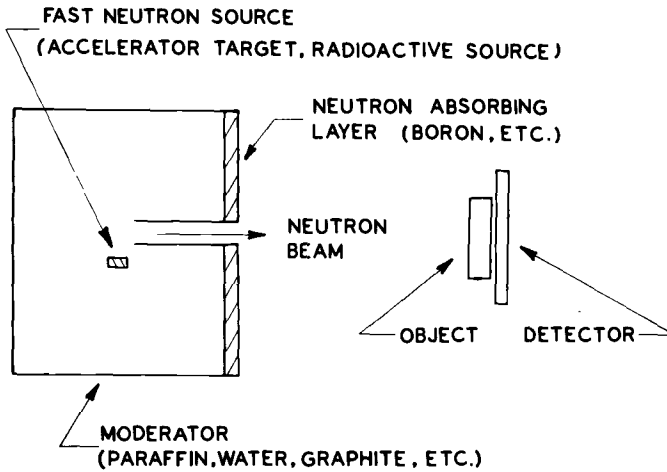


FIG. 2—Typical geometry for thermal neutron radiography showing neutron source, moderator, collimator, and imaging arrangement.

(sv; $0.01 \text{ sv} = 1 \text{ rem}$, Ref 31), this means that neutron images can be prepared with exposures in the order of 0.01 msv (1 mrem) or more.

Neutron Radiographic Detection of Corrosion

Many neutron radiographic application studies to image hydrogenous materials such as adhesives, plastics, fluids, or rubber help confirm that neutron radiography can be used to image corrosion products. The attenuation of slow neutrons by hydrogen, as indicated previously, is primarily a scattering process. The half-value-layer for water in a typical thermal neutron radiographic beam is about 2.7 mm (about 0.11 in.), thus the sensitivity to water and hydrogen is high.

An example of a neutron radiograph to show hydrogenous material, Fig. 3, is a double-cantilever beam specimen of 7075-T6 aluminum. It was pre-cracked and cathodically polarized in hydrochloric acid. The neutron radiograph shows the hydrogenous coating on the screws (upper), and below the area where the screws meet, the white line image shows the presence of hydrogen along the crack face.

A corrosion product itself will usually contain hydrogen in several forms, typically as hydroxides. The sensitivity of neutron radiography to the corrosion product will depend on its chemical form, density, and thickness and on the characteristics of the intervening structure. Confusion can sometimes result from the presence of other neutron-attenuating materials such as adhesives or plastics. However, the regular radiographic appearance of these ma-

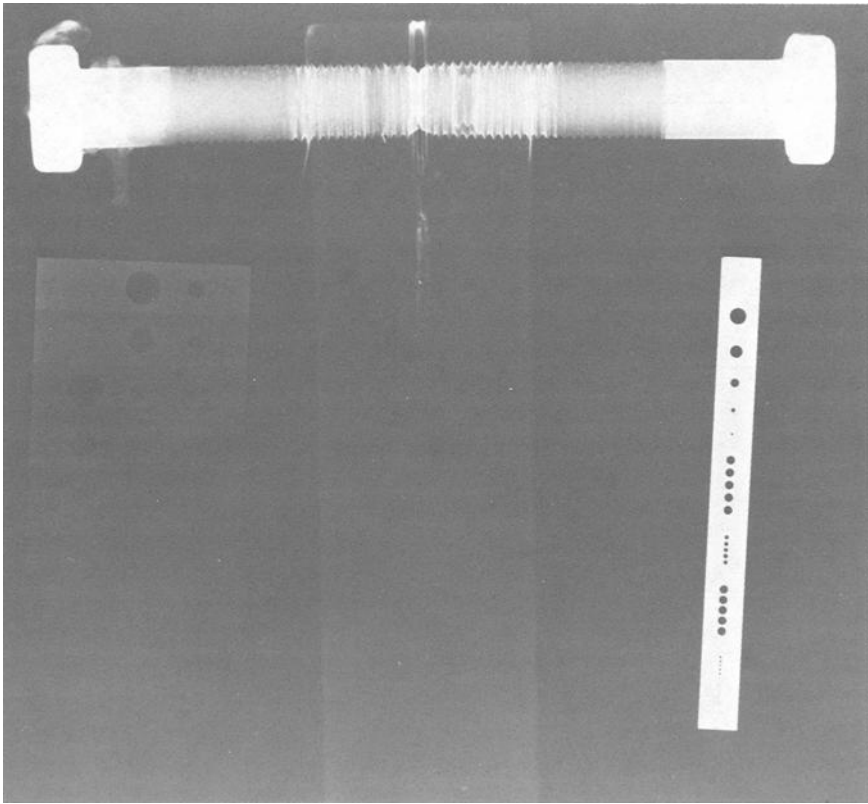


FIG. 3—Thermal neutron radiograph of an HCl-treated, aluminum, double cantilever beam specimen. White areas outlined on the screws and crack show hydrogenous material. Sharply imaged test specimen at the right is cadmium; smallest hole imaged is 0.25 mm (0.010 in.).

terials, as opposed to the irregular, salt and pepper-like neutron radiographic indications of corrosion products, often simplifies interpretation.

One of the first neutron radiographic application studies that specifically included corrosion detection was the Navy-supported work at the IRT Corporation. John and colleagues [32] used Cf-252 to demonstrate field capability for neutron radiographic inspection. Corrosion detection in wing tanks, landing gears, and other aircraft structures was demonstrated. The neutron source was housed in a large shielded container which could be brought to the site by truck. A small moderator-collimator head was positioned at the radiographic location. The radioactive neutron source was transferred from the shielded container to the exposure head by a crank-driven cable. The source used was 5.8 mg Cf-252 (neutron yield about 1.7×10^{10} n/s). In a typical inspection, about 0.58 m² (6.25 ft²) of aircraft wing was inspected in a single exposure of about two hours.

A quantitative study of neutron radiographic detection of corrosion was undertaken at NBS [33], where the NBS reactor was used as a neutron source. An example of corrosion detection from the NBS study is shown in Fig. 4. The thermal neutron radiograph shows the image of an aircraft-grade aluminum specimen [3.18 mm (0.125 in.)] thick subjected to a 6.5-h supersaturated salt spray to create corrosion. The neutron image shown is primarily due to the corrosion product. The aluminum itself is essentially transparent to the neutron beam. The nonuniform nature of the image is characteristic of corrosion images prepared by neutron radiography. It can be seen that this is not easily confused with the more regular images produced by adhesives, sealants, rubber, etc. In the NBS study successful neutron images were also prepared of specimens with less apparent corrosion, prepared by subjecting aircraft grade aluminum to an eight-day salt-water/sulfur dioxide gas environment.

A recent investigation at McClellan Air Force Base [34] also showed neutron detection capability for aircraft corrosion. The study involved aluminum skin-aluminum core adhesively bonded honeycomb aircraft assemblies. A drop of water was inserted into each of several honeycomb cells in a panel and

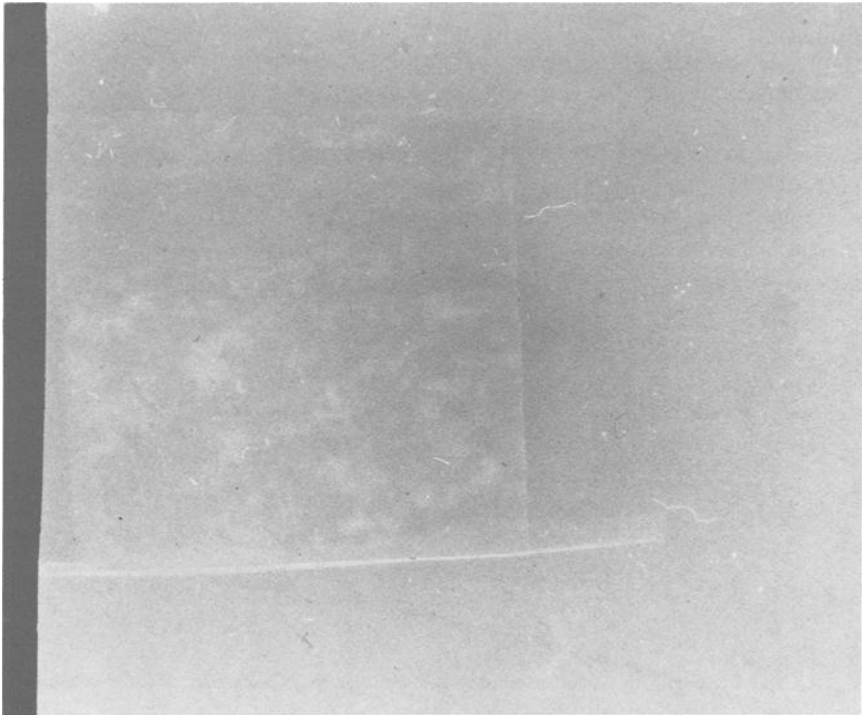


FIG. 4—Thermal neutron radiograph of a corroded aluminum specimen (courtesy of M. Ganoszy, National Bureau of Standards).

the panel was put away in an office for a year. The neutron radiograph shows the broadened corrosion that resulted. Several such corrosion areas are shown in the neutron radiograph in Fig. 5; one large area is indicated by the arrow.

Discussion

It is apparent from the results that neutron radiography can be effective in showing corrosion in metallic structures. One would like to be able to state the sensitivity of this NDT method for corrosion detection. One problem to be faced in formulating such a statement concerns a universally accepted way to discuss corrosion. Common methods such as references to weight loss are less useful for neutron radiography since detection does not depend directly on weight loss. The NBS study referred to earlier [33] attempted to address this problem by using aluminum samples subjected to specific corrosive treatments. That may be reasonably reproducible.

Since neutron radiographic detection depends on the hydrogen content of the corrosion product, another approach may be to determine the detectability of a common hydrogen-containing material such as water and to depend upon the user to relate that to the relative hydrogen content of the corrosion product of interest. With this approach, one would calculate that a layer of water of about 0.078 mm (about 0.003 in.) would attenuate a typical thermal neutron radiographic beam about 2%. This should be marginally detectable. In experimental studies of fluids in pipes, Winn [35] claimed detectability of fluids of a thickness of about 0.1 mm (0.004 in.). Therefore, these detection limits obtained by calculation and experiment appear reasonably compatible.

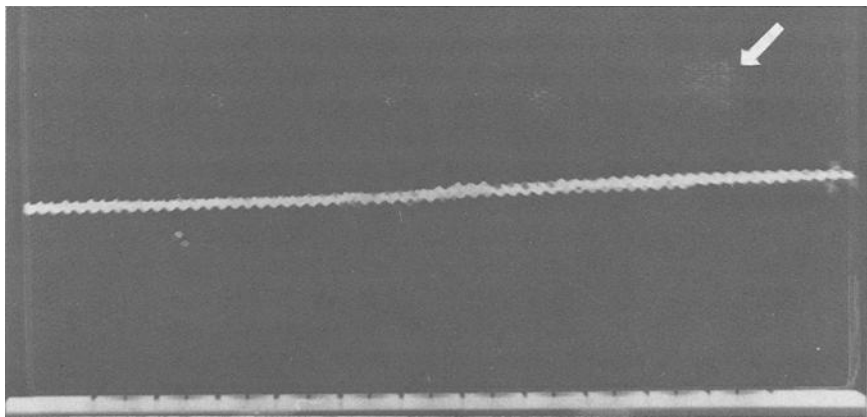


FIG. 5—Thermal neutron radiograph showing corrosion in an aluminum honeycomb panel. Central white linear indication is the image of adhesive. Broad white images, such as the one indicated by the arrow, show corrosion that resulted over a period of a year from a drop of water inserted into the assembly (courtesy of D. Froom, U.S. Air Force).

Similar numbers for hydrogen detectability have also been reported using layers of cellulose [36] and hydrogen in zirconium alloys [37]; in the latter case, the limiting value reported was 0.66 mg H/cm². A 30 to 40 times improvement in neutron sensitivity to hydrogen has been demonstrated using a scattering and filtering technique [38], but this low spatial resolution method offers only limited applicability for corrosion work because of sensitivity to any other hydrogen present and difficulty of practical field application.

In any case, complications due to other neutron-attenuating materials such as rubber, plastic or adhesives, and the metal substrate itself must be considered. As pointed out earlier, it should be possible to recognize these other neutron-attenuating materials by their shape and location. However, if it were necessary to image corrosion through such materials, sensitivity would be reduced because the relative attenuation of the neutron beam due to the corrosion would be reduced.

This reduced contrast would also be the case for some metal substrates. The examples shown have mostly involved aluminum which is relatively transparent to neutrons. The half-value-layer (HVL, thickness of material that attenuates the radiation intensity by a factor of two) for aluminum for thermal neutrons is about 7.9 cm (3.1 in.). For stainless steel, on the other hand, the HVL is about one-tenth that value (0.77 cm, 0.3 in.). Therefore, detecting corrosion in steel would be somewhat more difficult.

For problems involving steel, one approach is to use lower energy neutrons. Neutrons of energy less than 0.01 eV, cold neutrons, offer increased sensitivity to hydrogen and increasing transmission for iron-based materials because the neutron wavelength becomes too long for Bragg diffraction. This reduces scatter in the iron, as pointed out in Table 1. Using thermal neutrons it is difficult to obtain useful radiographs of steel having a thickness greater than 5 cm (2 in.). With cold neutrons, however, Hawkesworth and Walker [39] have demonstrated the observation of 1 mm (0.040 in.) of plastic through 15.3 cm (6 in.) of steel.

The neutron sources discussed can yield cold neutrons by means of filters or in the more efficient manner of cooling the moderator. In order to optimize the yield of neutrons in the energy range of 0.005 eV, the Bragg cutoff energy for iron, the moderator temperature must be about 20 K. Solid methane has been used as a moderator for such sources [40].

Another factor to consider for neutron radiography is the practicality of applying the method in typical industrial environments. As discussed, film techniques with sources of Cf-252 have been shown to be useful in field situations [32, 41]. Accelerator sources for neutron radiography are also available for field use. Sources built around small accelerators using the (*d*, *T*) reaction have been put on wheels with movable supports so the source can be moved and positioned easily. One such source has been developed by the Vought Corp. with support from the U.S. Army. An advanced unit is under development at Science Applications International Corp. through joint U.S. Air Force/Navy sponsorship.

Although film detection methods have been emphasized, it is also practical to consider television type detection systems employing neutron image intensifiers. These real-time systems offer convenient, fast response remote from the radiation area. Neutron television systems [42,43] employing integration or slow scan techniques can be successfully used with the relatively low neutron intensities often encountered with maneuverable neutron sources.

Conclusions

Neutron radiography has been shown to offer sensitivity to the hydrogen in corrosion products, a fact that makes the method attractive for early detection of corrosion. In terms of sensitivity, corrosion in aluminum resulting from a 6.5-hour supersaturated salt water spray can be readily detected. In other terms, a material having a hydrogen content equivalent to that of water having a thickness of less than 80 μm can be detected under good circumstances.

Neutron sources suitable for field use of neutron radiography are available and can be combined with real-time detection systems to create a practical inspection approach for corrosion problems.

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Advanced Ultrasonic Examination Methods for Corrosion Detection and Assessment in Industrial Components

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ABSTRACT: Ultrasonic examination techniques and equipment have been improved in recent years and have become indispensable in many industrial applications where undetected corrosion can result in unscheduled downtime. Likewise, microprocessor technology has advanced in versatility and cost efficiency so that many practical applications have become possible. The resulting combination of improved examination hardware and microprocessor-based data acquisition and analysis devices has revolutionized nondestructive examination as applied to the detection and assessment of corrosion. This paper presents information concerning three recently developed ultrasonic systems which have been proven effective in the detection of thinning, pitting, and methane-type hydrogen damage. Each of these systems utilizes manual placement of the ultrasonic search unit, as opposed to totally automated systems which rely on complicated electromechanical systems for movement and position readout. As a result, greater versatility, reliability, and speed are achieved with no loss in accuracy.

KEY WORDS: boiler tubing, computer data acquisition, computer data processing, corrosion detection, hydrogen damage, pitting detection, thickness measurement, ultrasonic evaluation.

Conventional ultrasonic (UT) equipment and techniques have been successfully used throughout industry since the end of World War II to nondestructively assess the integrity of critical plant components. An important application of UT has been the repetitive measurement of material thickness to

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detect and monitor general thinning; another has been the detection of localized thinning or pitting. UT measurement of the thickness at periodic time intervals allows determination of the thinning rate and prediction of the remaining useful service life of the component.

These applications have become widespread as relatively inexpensive ultrasonic thickness measurement devices have become readily available to industry and have gained acceptance as a basic industry tool. However, misunderstandings concerning the operating characteristics and limitations of these devices have resulted in their misapplication and misinterpretation.

Innovations have overcome these challenges with recent advances in computer technology. State-of-the-art electronics has been applied to develop and fabricate advanced devices that provide for more accurate and reliable industrial ultrasonic detection and monitoring of corrosion degradation. Three of these devices and the specific techniques used with each device are the subject of this paper. A specialized ultrasonic technique recently developed for detection of hydrogen damage in boiler tubing is also discussed.

Background

In measuring the thickness of materials using ultrasonics, high-frequency energy (typically in the 2- to 10-MHz range) is introduced into the material through an exposed surface using a transducer fired by an ultrasonic instrument. The instrument is basically an electronic device consisting of a power supply, a pulser, a receiver, a clock, and a cathode ray tube (CRT). The ultrasonic energy propagates through the material until it reaches the opposite surface, at which point some portion of the energy is reflected back toward the entry surface. The transducer (in the listening mode between pulses) then detects the reflected pulse or first backwall signal when it reaches the front surface. Like a ball being bounced between two walls, the pulse continues to be partially reflected between the boundaries of the material until it has been attenuated to the point where it can no longer be detected. Each successive return of the reflected pulse to the front wall produces a spike on the CRT screen and is referenced as another backwall (for example, second, third, etc.).

The amount of time between the reception of two successive backwall signals is the amount of time required for the ultrasonic pulse to traverse the thickness of the material twice. This time interval is directly proportional to the amount of time required to traverse the material once. Therefore, since the velocity of the ultrasonic energy is constant in a homogeneous material, the amount of time between the reception of two backwall signals is directly proportional to the thickness of the material. Thus, if an electronic circuit can be produced that will measure an unknown time period, equate it to a known distance (thickness), and translate this information into an understandable format, unknown thicknesses can be measured nondestructively.

Advanced Ultrasonic Systems for Corrosion Detection

Thickness Printer

One of the difficulties involved with the task of measuring material thickness with a CRT-type presentation is the need for a second person to record the data. For a large-volume, high-speed examination, this requirement adds to the cost of the examination and increases the possibility of human errors in the data. To eliminate the need for manual data recording, a device that prints the thickness measurement was recently developed, as shown in Fig. 1 [1]. This was accomplished through the use of interface electronics that provides direct digital conversion of the UT instrument's CRT presentation. A hardcopy printout of the converted signal in direct measurement terms is available upon the command of the operator. The device uses the basic ultrasonic signal produced within the UT instrument circuitry. However, the new device is calibrated separately so that inadvertent changes in either the device or the UT instrument do not affect the other. The UT instrument and thickness printer device each contain linearity and delay controls such that misalignment of either set of controls affects only the calibration of the respective device. Any signal changes can be readily identified and corrected since the changes will result in a disparity which will be obvious to the operator. The battery-powered device is typically positioned in the examination area so that



FIG. 1—Thickness printer mounted on ultrasonic instrument.

the operator is able to view the UT instrument CRT from a distance while placing the UT transducer on the examination surface. A 7.5-m (25 ft) dual coaxial cable connects the transducer to the UT instrument.

A remote print switch provides the operator with the ability to print the digitized thickness measurement data when he judges the CRT backwall signal acceptable. Even though a large LED display is on the face of the device, experienced operators rarely read this information except during calibration. To read this information and carefully observe the CRT trace would be much too time-consuming and would serve no useful purpose. Instead, the operator views the backwall signal in the CRT, thereby assuring that good transducer contact and proper UT instrument gain level are present. When a signal of appropriate amplitude with a clean, straight leading edge is observed, the print command switch is depressed and the hardcopy digital thickness reading is printed. This process is rapidly repeated along each examination elevation with far less physical and mental fatigue for the operator because the equipment is not carried and because actual interpretation of the CRT screen is not required.

Data records can be remotely formatted for separation of various subsets by use of the remote paper advance switch or by printing a zero reading through depressing the print switch for one-half second or more. Several full-scale boiler examinations have proven the concept to be quite successful on 38- to 76-mm (1.5- to 3-in.) diameter tubing. Average accuracy of the measurements appears to be within 0.05 to 0.08 mm (0.002 to 0.003 in.), with mistaken readings all but eliminated. Of course, this accuracy can only be maintained through surface preparation that provides bare metal at each measurement location. Handwritten notes are provided by the operator on the tape at the beginning of each string of data to identify the tube measurement locations. Verbal and handwritten communications of the thickness readings are not required when using the equipment, so the possibility of human error in the data recording process is substantially reduced.

During the design effort, there was some concern that the speed with which thickness measurements could be recorded might be reduced. However, with continued operator training and experience, data recording speed has, in most cases, surpassed that of two-person thickness measuring crews. Depending on many factors, including surface conditions and logistics, operators have been able to consistently record 3000 measurements per shift, and more than 5000 measurements recorded in several instances.

The thickness printer device was originally intended for application in industrial boiler tube wall thickness surveys; however, it may be of significant advantage in any application where numerous thickness measurements are to be recorded over a short period of time.

Thickness Data Acquisition System

Development of the thickness printer device fulfilled the immediate need to reduce the number of data-taker personnel on boiler tube wall thickness sur-

veys and also provided an effective building block in the development of a more versatile and sophisticated system, shown in Fig. 2. Even though development costs were greater, this step-by-step approach to final system design was chosen to avoid pitfalls with unproved sophistication. Modifications and improvements have been incorporated through extensive tests and field use of the thickness printer device.

A thickness data acquisition system was developed to take rapid thickness measurements and to store the data for later processing. The data acquisition system is portable and lightweight, and has three components—an electronic data memory bank, a data acquisition interface, and a UT instrument. The data memory bank is periodically connected to a microcomputer for further data processing and permanent storage and is capable of recording over 3400



FIG. 2—Thickness data acquisition system.

thickness measurements and related information. The data bank provides the software capability for continuous monitoring of the data as they are recorded, review of the stored data, and data correction.

The data acquisition interface and the data memory bank attach to the UT instrument and require less than 250 mA of current through an existing auxiliary power jack on the UT instrument. The data memory bank can transmit its entire data file to the microcomputer through the serial interface. The data are stored on a fixed disk or floppy diskettes or both where they can be edited.

The microcomputer software capabilities allow extensive operator flexibility for analyzing the data. An entire file can be scanned to search for those measurements that are above or below the operator's chosen limits. The operator can correct or change any piece of information in the file including the measurement location identifiers and thickness data. Printouts of the data measurements can be made in several formats including color coded thickness maps. The printouts also provide data such as the site location, date and time of examination, and scanning limits.

Thickness Measurement System

A thickness measurement system has been developed that performs both the data acquisition and data processing functions as two basic subsystems, as shown in Fig. 3 [2]. The data acquisition subsystem consists of a receiving array, a transducer and locator assembly, a thickness measurement instrument, and a data acquisition unit.

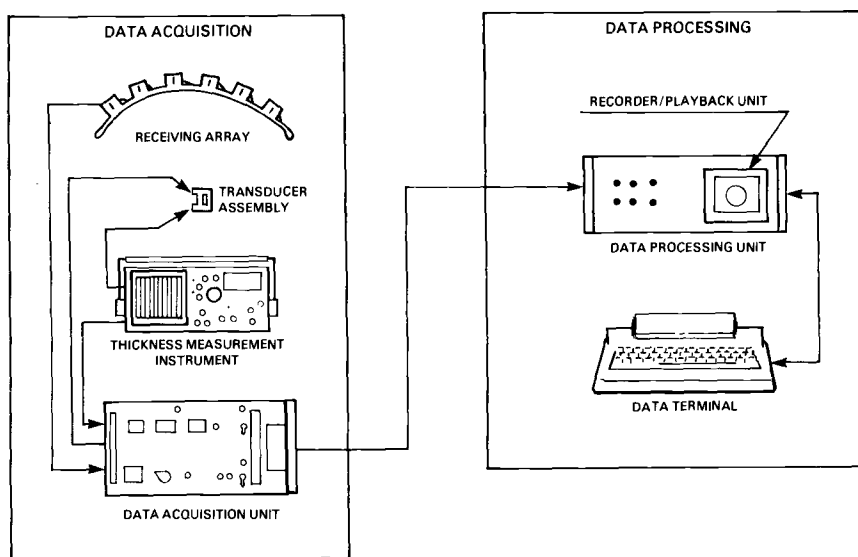


FIG. 3—Thickness measurement system.

ment, and the data acquisition unit, which has a microprocessor for X - Y coordinate locations. This subsystem is coupled with the data processing unit, the data terminal, and the recorder/playback unit. The data acquisition subsystem is taken to the inspection site; the data processing subsystem can be located up to 152.4 m (500 ft) from the data acquisition subsystem.

Data Acquisition Subsystem

Prior to the start of an examination, the data acquisition subsystem microprocessor must be programmed. It must be told the radius of the pipe, the number and spacing of the sensors, and the minimal and maximal thicknesses that would be considered valid. This is to eliminate erroneous signals that may occur, for example, from the couplant or an improperly angled transducer. Once these required parameters are entered into the data acquisition unit and the subsystem is energized, the following sequence of events takes place (Fig. 4).

First, the subsystem looks at the measured thickness to determine that it is above the minimum and below the maximum that have been entered as low/high limits. When a valid thickness is in the gate, the locator signal is initiated and the timer starts. Upon receipt of the signal by the first sensor to

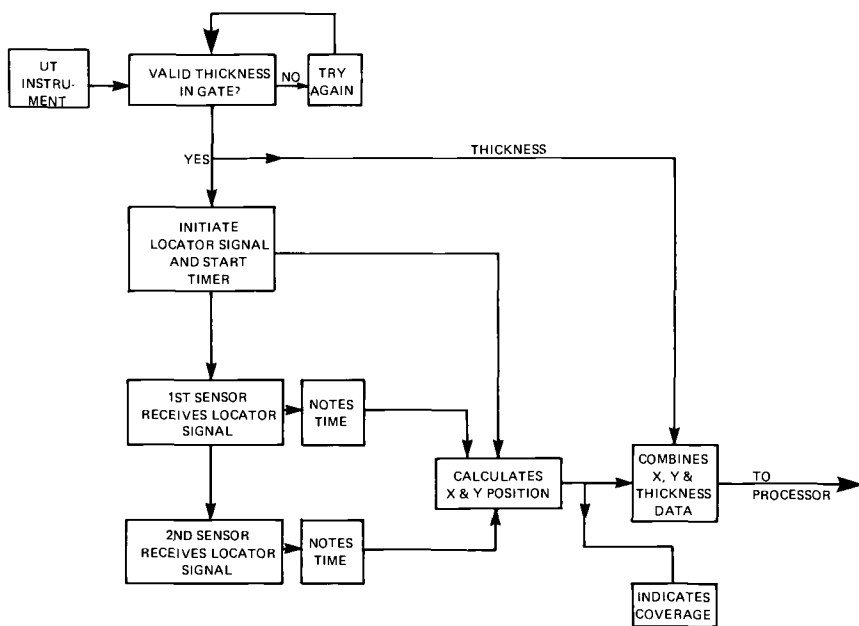


FIG. 4—Data acquisition.

“see” the signal, that sensor notes the time and sends this information to the microprocessor. The second sensor receiving the signal notes the time and also sends the information to the microprocessor. The microprocessor then calculates the X and Y position of the transducer, combines this information with the measured thickness data, and transmits both pieces of information to the data processor.

Additionally, the microprocessor indicates coverage of that 0.5- by 0.5-mm (0.2 by 0.2-in.) cell on the coverage plot. The cell size is a function of the X - Y indexing of the system. The coverage plot is a visual confirmation that a valid thickness is in a given cell. The visual confirmation is accomplished through a series of dots representing both the coverage area and sensors on the face of the CRT, an ultrasonic instrument. The instantaneous location of the transducer is also indicated by an active (brighter) dot on the coverage plot. This entire process is repeated 30 times every second until the data acquisition subsystem is deenergized. (Normally this is after complete coverage has been indicated.)

Data Processing Subsystem

As shown in Fig. 5, the data processor has two data storage areas and one area for data processing. One of the storage areas is for data from the terminal, or tape playback. This inputs into memory the header information, which includes the subsystem, piping system, location, operator, and all of the essential data to identify the specific area or component that is being inspected. The other storage area is for all of the thicknesses and is divided into 0.5- by 0.5-mm (0.2 by 0.2-in.) cells. Each cell will contain the measured thickness for a particular X and Y location. The data for the thickness stor-

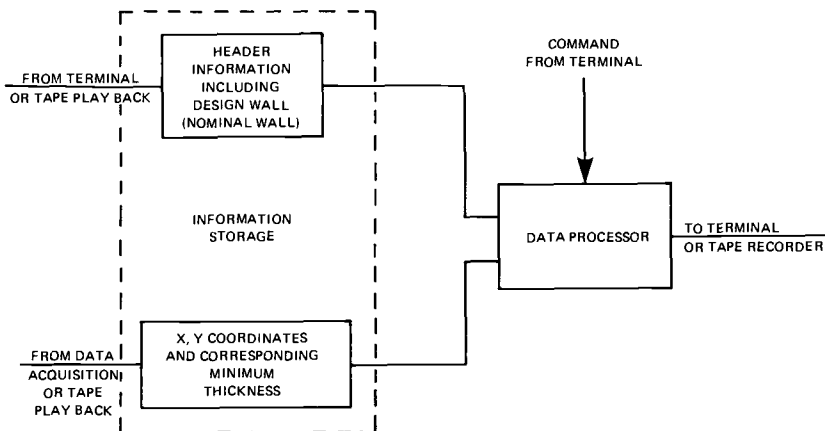


FIG. 5—Data processor operation.

age section come from either the data acquisition unit or from the tape in the playback mode.

During acquisition of raw data from the data acquisition subsystem, the thickness data storage area of the data processor operates as shown in Fig. 6. Upon receipt of data from the data acquisition unit, the data processor locates the X - Y cell. Then it asks, "Are previous thickness data in that cell?" If the answer is no, the data processor stores the thickness data in that cell. If there are thickness data in the cell, it compares the two thicknesses. If the new thickness is less than the original thickness, it will store the new thickness. If the new thickness is equal to or greater than the original thickness, it will disregard the new thickness and maintain the original thickness. This process of storing data is repeated 30 times each second as long as data are being received from the data acquisition subsystem. The data processor area operates on commands from the terminal, and its output can go either to the terminal or to the tape recorder. The subsystem has several options for handling the data that it has stored.

Option 1 is a command from a terminal to print a coverage map. The header information, as well as high limit, low limit, pipe radius, number of sensors, sensor spacing, and other information, is printed on the printer portion of the terminal. The nominal wall thickness is then used to calculate the percent wall degradation from each of the cells. The data processor retrieves the measured thickness from each of the cells, calculates the percent wall degradation for each cell, and prints a plot of the X and Y location and percent degradation. The printout is a series of pluses and numbers allocated to cell locations. Blank areas in the coverage plot indicate that no measurement was recorded for that cell. Pluses mean that the measured wall thickness is equal

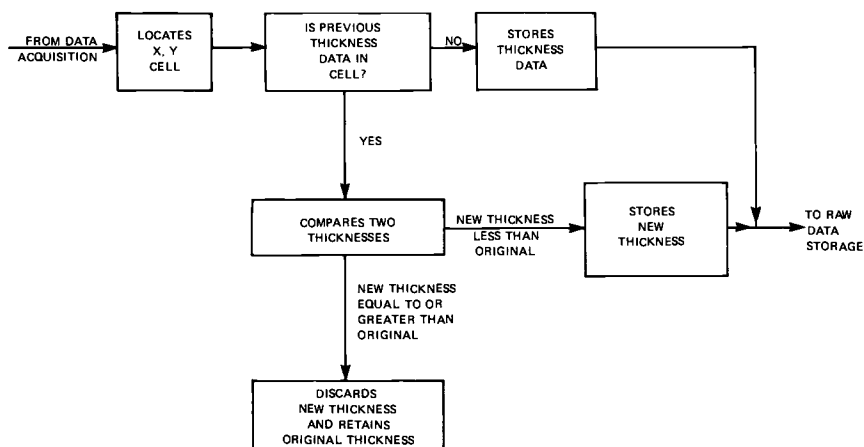


FIG. 6—Data processor thickness storage operation.

to or greater than 100% of the nominal wall thickness. Ones indicate that the wall thickness is from 90 to 99.9999% of the parameter wall thickness. Twos indicate that the wall thickness is 80 to 90% of the nominal wall thickness. Threes indicate that the wall thickness is 70 to 80% of the nominal wall thickness, etc. It is easy to determine thin portions of the piping system from the thickness measurement printout. This printout, however, does not provide actual thickness readings.

Option 2 is a command from the terminal to print a table. Upon receipt of this command, the microprocessor will ask what percent of degradation is required. The data processing operator must answer this question by specifying all or some percent of degradation. The microprocessor then calculates the thickness specified if a percent degradation is so stated. It then compares the calculated thickness to the thickness in each cell as stored in the data acquisition subsystem and sends to the printer all of those thicknesses that are equal to or less than the calculated thickness. Other variations of Option 2 are available: actual thicknesses can be specified, in which case the data processor searches through each of the cells and prints the *X*, *Y*, and actual measured thickness of each thickness that is equal to or less than the thickness specified. Another variation is that a particular *X* and *Y* location can be specified; the microprocessor will locate the coordinate *X* and *Y* cell and print that *X* and *Y* and the recorded thickness for that cell.

The last option of the data processing subsystem, Option 3, is a command from the terminal to record all of the data on magnetic tape. The header information, including high limit, low limit, pipe radius, number of sensors, etc., along with the *X*, *Y*, and thickness data, are combined as raw data and recorded on magnetic tape. A variation of this option is that the data can be taken from magnetic tape on command from the terminal. This information would then be transferred back into the data processor, at which time any of the options available under Option 2 could be exercised. Normally, the data are recorded on magnetic tape for ease of storage and retrieval. However, having the data on magnetic tape opens the possibility that the recorded data could be utilized by a computer to compare thickness readings from subsequent examinations to determine the rate of wall thinning, and thus predict the point at which the piping system would have to be replaced. This could be a very cost-effective method that would preclude replacing the entire line prior to the end of the useful life of the system or replacing the system prior to failure of the line, which could conceivably be extremely expensive or dangerous or both.

The ultrasonic section of the system is calibrated by placing the transducer on a reference block of known thickness and material which is acoustically similar to the examination material and adjusting the digital thickness reading with a single knob control. The instrument blocking gate is then adjusted to allow the acquisition of reasonable thickness readings while blocking out spurious signals such as couplant noise. The data acquisition subsystem can

be operated by anyone who has sufficient eye-hand coordination to direct the active element dot to the area of the coverage plot where insufficient coverage is indicated. Programming the data acquisition subsystem is straightforward. The software development for the system is such that, with minimal training, anyone who can read and "two-finger" a typewriter can operate the data processing subsystem.

Detection of Hydrogen Damage in Boiler Tubing

With acidic boiler water chemistry conditions and heavy internal surface deposits, hydrogen can be generated by the corrosion reaction of the metal. The hydrogen will diffuse through the steel because of its small atomic size. The hydrogen reacts with the carbon in the cementite to decarburize the steel and produce gaseous methane (CH_4). This larger molecule can no longer diffuse and becomes trapped between the grain boundaries. As more methane is produced, the internal gas pressure increases and causes discontinuous intergranular voids along the grain boundaries. Severely degraded steel will fracture in a brittle manner when any additional outside force increases the stress along the partially separated grain boundaries.

A variation in the thickness measurement technique has been employed to detect tubes that have been damaged by the hydrogen/methane process. Early discussion pointed out that successive backwall signals are obtained when ultrasound is introduced into the material. The ultrasound energy will eventually attenuate as the wave travels through the material. Hydrogen-damaged material attenuates the sound energy faster than undamaged material and thus reduces the number of backwall reflections that can be detected. The technique for detection of hydrogen-damaged steel involves the use of a 10-MHz straight-beam ultrasonic transducer with a UT instrument. The UT instrument gain controls are adjusted by placing the transducer on a section of undamaged material with surface preparation which is essentially identical to that of the suspected damaged material. The fourth backwall reflection is maximized at approximately 100% of full screen height (FSH). The presence of hydrogen damage in the material is indicated when the attenuation produces a fourth backwall reflection signal below approximately 20% of FSH.

Since the surface condition of the material being examined can also result in the reduction in amount of reflected ultrasound, this technique is not considered to be absolute. For boiler tube examinations, the presence of hydrogen damage can be rapidly detected with a high degree of accuracy when the technique is applied with good technical judgment concerning the irregularities with the surface finish. Confirmation of hydrogen damage is achieved after carefully observing the surface condition through which the ultrasound has been transmitted.

In a boiler tube, hydrogen damage progresses through the material from the internal surface to the point of fracture. While the technique described

can detect some amount of damage, the relative amount of degradation that has occurred cannot presently be established. Further development of the technique is necessary to achieve a correlation between the amount of attenuation and the percentage of damage.

Discussion

The underlying cause of failure and principal mode of degradation of many industrial and power piping system components is often some form of wall thinning. Piping systems transporting saturated steam or water containing abrasive materials or localized areas where mixed phase flow or cavitation occurs are subject to erosion. Systems containing highly oxygenated water or corrosive fluids are subject to wall thinning by virtue of general erosion or pitting corrosion. In power plants, wall thinning has been evidenced in extraction steam and service water piping. There are a multitude of wall-thinning problems in fossil-fired power plant and other industrial plant piping. In such cases, accurate determination of component wall thickness and rate of deterioration is vital to service life prediction and preventive maintenance programs.

Point measurements of installed piping wall thickness can be made accurately and conveniently using appropriate ultrasonic instrumentation and techniques. However, conventional examinations have two major deficiencies. Manually recording the thickness readings and their measured locations on the component is extremely time-consuming. Therefore, it is virtually impossible to record enough data points to profile a modest area of the inside surface. Sufficient information is not available to the engineer responsible for evaluating the component and specifying corrective action to discriminate between various corrosion and erosion mechanisms. In many cases, it is even difficult for the examiner to visualize a broad inside surface topography while performing the examination.

The second shortcoming of conventional thickness examination methods is related to using the manually recorded data of successive examinations to accurately determine a corrosion or erosion rate and to predict service life of the component. The most efficient approach to such a surveillance program is to perform an initial baseline examination followed by an identical examination after some relatively short (perhaps one year) period of system operation. The first surveillance examination interval is short to ensure that any severe cases of rapid component degradation are detected prior to failure. In most cases, however, the rate of degradation is low and the changes in wall thickness during the first examination interval are less than the tolerances of the examination technique and cannot be identified. Hence, a third or fourth surveillance examination must be performed at some increased interval before trends and life predictions are possible. Many of the test variables which affect the overall tolerance of the thickness measurement examination can be controlled.

Experience has shown, however, that the most significant hindrance to repeatability is in relocating the ultrasonic transducer at precisely the same location during subsequent examinations. Because a minute change in transducer location results in appreciable variation in the measured thickness, even the use of templates and permanent location benchmarks has not resolved this deficiency with conventional examinations.

Conclusion

Advancements in ultrasonic examination methods have been achieved which overcome some of the difficulties in obtaining rapid yet accurate thickness measurements of components that are subjected to erosion and corrosion. Improvements in ultrasonic instruments coupled with modern computer data acquisition equipment can reduce the cost of thickness surveys while enhancing the operator's capabilities for data analysis. Thickness measurements can now be obtained by one instrument operator who can electronically record the data for transfer to a computer for manipulation and storage. Trend analysis can be rapidly performed to indicate the most significant locations of erosion and corrosion and to predict when the degraded component will have to be replaced. Statistical data analysis can also be performed to reveal probabilities of failures at certain locations on specific components so that only the most severely degraded material will be replaced.

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Acoustic Emission Capabilities and Applications in Monitoring Corrosion

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ABSTRACT: The physical processes of corrosion are examined as possible sources of acoustic emission (AE). Detectable emission is produced by film cracking, gas evolution, hydrogen-induced microcracking, plastic zone growth, and discontinuous crack movements in stress-corrosion cracking (SCC) and hydrogen-assisted cracking. By these mechanisms corrosion can be detected while it is occurring. Practical applications include rapid evaluation of the susceptibility of materials to corrosion, particularly to SCC. Apart from real-time monitoring of the corrosion process, the structural damage caused by corrosion can be detected after it has occurred by AE monitoring during application of stress. In this testing mode, emission is enhanced by surface degradation and corrosion products. Pipelines and aircraft structures have been tested in this way. In large structures it is generally more practical to detect the results of corrosion than to monitor the corrosion process itself. For success in field applications attention must be paid to issues such as background noise and wave attenuation, and operator training and experience is an important factor.

KEY WORDS: acoustics, emission, corrosion, crack propagation, nondestructive tests

The phrase "acoustic emission" (AE) refers to the process of elastic wave generation during deformation of stressed materials, and also to the nondestructive testing technology based on this phenomenon.

How can AE be useful in detecting or monitoring corrosion? There are two approaches. First, the corrosion process may generate detectable acoustic emission while the damage is actually taking place; second, the results of corrosion may be detected and assessed by an AE test after the damage has occurred. In this paper, these approaches will be discussed in turn. We begin

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with a short review of the physical processes of corrosion, as a base for understanding the relevance of AE and its relationship to other monitoring technologies.

Corrosion Processes and Their Detectability by AE

The word "corrosion" can be used to cover all transformations in which a metal passes from elemental form to a chemically combined state [1]. Principally it refers to the wide variety of processes that occur when a metal is in contact with a liquid environment. High-temperature oxidation in a gas environment can also be considered as a form of corrosion; as in many liquid-environment reactions, the process involves the formation of a film of corrosion product on the surface of the part under attack.

In high-temperature oxidation, this film will grow rapidly at first, then more slowly as it gets thicker. Typically the mechanism of film formation involves migration of metal ions and oxide ions within an imperfect lattice of imprecise chemical constitution. Gaps may develop at the interface between film and metal, due to this ion migration. Stresses develop within the film and may be relieved by cracking, which typically takes place when the film exceeds a critical thickness. Cracking also takes place during cooling, due to differential thermal contraction. The cracking may lay the underlying material open to the environment again, leading to a surge in the corrosion rate. Alloy design is often targeted at finding a composition whose oxide film will give good protective properties while it is still thin enough to be relatively immune to cracking.

In liquid environments, a classic site for corrosion is a break in the protective oxide film. An electrochemical cell is set up between the exposed metal (anode) and the nearby film surface (cathode). Metal ions go into solution at the anode, and dissolved oxygen reacts to produce negative ions at the cathode; the positive and negative ions combine at intermediate locations to form solid precipitates such as rust. There is no protection at the break, so corrosion can be intense if the break is small and the cathodic film large. The corrosion site may develop the form of a pit, and the attack may be aggravated by acidity developing there. This is a very common type of electrochemical corrosion, but it is by no means the only one: electrochemical cells can also be set up when dissimilar metals are present, or even when there are differences in oxygen concentration within the liquid. Differential concentrations of oxygen (or other materials) are responsible for corrosion reactions occurring in crevices or crannies; oxygen becomes depleted inside the crevice, which then becomes the anode of the electrochemical cell. In crevice corrosion, the build-up of voluminous corrosion products can have serious structural effects, with the corrosion products in the crevice acting like a wedge driven into the material.

The whole course of corrosion may be determined by the orientation of the surface under attack, as the solid corrosion products either build up or fall away under the influence of gravity.

Externally applied currents can drive the corrosion reaction faster and influence the chemical balance at the electrodes. For instance, an iron anode in sulfate solution dissolves at low current densities, but is rendered passive at high current densities. In the passive state, the iron is covered with an oxide layer and the anode reaction is evolution of oxygen gas.

Of the many chemical species that can be produced in corrosion reactions, hydrogen is one of the most important. Hydrogen atoms liberated at a steel cathode may pass either into the gas phase or into the interstices of the solid lattice. Hydrogen in the lattice can diffuse rather freely since the hydrogen atom is so small. Hydrogen uptake often occurs during electrochemical processes associated with pickling and plating, or during welding when water is present, or during exposure to hydrogen sulphide in sour oilfields or to hydrogen compounds in refineries and chemical processing plant. Migrating through the lattice, the hydrogen atoms can either cause a general embrittlement of the material, or combine to form molecular hydrogen in small pores, internal cracks, or large blisters, causing major structural damage.

Corrosion often starts at a region of high local stress, and stays focussed there because of the way the electrochemical cell works. This is one way a corrosion pit can start; pits can also initiate at microstructural irregularities such as copper-rich segregates in aluminum, or sulphide stringers in stainless steel.

Pits can serve as starters for the process of stress-corrosion cracking (SCC). Here we see the combined effect of a corrosion reaction and an applied stress concentrated at a geometrical discontinuity. The stress at the crack tip reduces the energy required for an atom to pass into solution as an ion. Thus crack growth which would not take place due to either stress or corrosive environment alone, takes place when they are present together.

Corrosion reactions also combine with fatigue (the effect of cyclic stress), lowering the fatigue threshold and causing damage worse than either corrosion or fatigue would produce in isolation. As advancing technology began to master the problems of designing against ordinary fatigue and stress corrosion cracking, corrosion fatigue became the major unsolved threat to structures such as aircraft and offshore structures.

So corrosion is an intricate process, manifesting in a wide variety of forms and influenced by a complex of factors including

- chemical and metallurgical nature of the material under attack;
- chemical species in the liquid environment, including dissolved oxygen and a variety of catalyzing or inhibiting agents;
- solubility or insolubility of the corrosion products;
- electrical conduction paths and impressed electric currents;
- layout, orientation, and geometry of the parts; and
- stresses, both macroscopic and microscopic, both residual and applied.

There are many strategies for avoiding corrosion in engineering construction. One path is to choose metals that have insoluble corrosion products, or

that form protective oxide films in the designated environment; another is anodic or cathodic protection [control of the electrical potential by an applied electromotive force (emf)]; another is control of the chemical environment by removal of dangerous species or addition of inhibitors. Protective paints and coatings of many kinds may be used. Preventive efforts are often defeated by the insidious variety of the possible corrosion mechanisms, or by undesirable side effects: for example, cathodic protection currents in one set of pipes may promote corrosion in another set of pipes lying nearby. Thus corrosion remains a major engineering problem, and its control has become a major technology striving to keep pace with the constant demand for higher performance and lower cost in general engineering practice.

The AE phenomenon is the production of an acoustic wave through the sudden release of local stresses in a solid medium (Fig. 1). Actually, one can imagine this process accompanying just about any physical change; the salient question is not whether there will be emission, but rather, whether the emission will be large enough to be detected. Detectability depends on three factors: the amplitude of the wave at the source; the loss of amplitude as it travels to the sensor; and the sensitivity of the detecting apparatus. Loss of amplitude during wave propagation ("attenuation") depends on the distance between source and sensor, so it is a critical factor in monitoring large structures and a major point of difference between laboratory studies and field applications.

In laboratory studies of AE from mechanical deformation, the smallest detectable processes involve a number of dislocations in cooperative movement; that is, the scale of the smallest detectable process is intermediate between the scale of the atom and the scale of the crystal grain. Let us consider the physical processes of corrosion described above, as candidates for detection and maybe measurement by AE. Table 1 summarizes the situation.

Four of the listed corrosion processes do not produce detectable emission. Electric currents do not, because moving electrons do not stress the lattice.

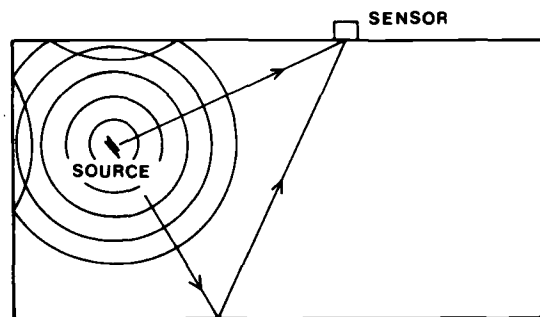


FIG. 1—The acoustic wave, generated at the source, propagates through the structure to the sensor, where it is converted to an electrical signal.

TABLE 1—*Principal processes of corrosion and their detectability of AE.*

Process	Detectable by AE?
Passage of electric current	no
Dissolution of metal	no
Film formation	no
Film cracking	depends on thickness
Evolution of gas	yes—low amplitude
Hydrogen migration/microcracking	yes—low amplitude
SCC—active path	no (except plastic zone)
SCC—discontinuous cracking	yes—high amplitude
Hydrogen cracking	yes—high amplitude

Migration of atoms during film growth will stress the lattice and might be expected to produce continuous AE, but in slow-growing films the acoustic energy would be very low and the effect has not been reported to date. Dissolution of metal and active path corrosion (in SCC) are equally silent: the forces involved in the passage of individual atoms into solution are negligible at ordinary rates of dissolution.

Secondary effects may produce apparent exceptions to these guidelines. Although the crack-tip process is silent in active path corrosion, there may be emission from the cracking of nonmetallic inclusions in the plastic zone that surrounds the tip of the advancing crack. Likewise, there may be emission when the dissolution of a surface layer releases subsurface residual stresses; in early work by Sedgewick [2], dislocations piled against a surface layer on a lithium fluoride (LiF) single crystal were released, with emission, when the surface layer was etched away.

The first process in Table 1 that does produce detectable emission is cracking of the corrosion-product film. The energy source is the elastic stress field that develops during film growth or temperature change and that releases during sudden cracking, spalling, or exfoliation. Thick, brittle, tenacious films will in general produce higher amplitude emissions than thin, soft or weak films; emission may not be detectable for the latter type. Emission from oxide spalling in high-temperature superalloys during cooling has been studied by Ashary [3] at the University of Pittsburgh.

The evolution of gas is a recognized source of low-amplitude emission during corrosion in liquid media. Heiple identified the sound-producing mechanism as the bursting of bubbles at the liquid surface [4]. The energy associated with a bubble of radius r in a liquid of surface tension γ is $4\pi r^2\gamma$ in surface energy, plus a further $8\pi r^2\gamma/3$ due to compression of the contained gas. Virtually all this energy is converted into kinetic energy when the bubble bursts. By simple theory the collapse should be complete in 10 to 100 μ s, so we can expect useful energy to appear as emission at low ultrasonic frequencies.

Bursting of gas bubbles may be the actual source of acoustic energy in the experiments of Grabec [5], where the AE amplitude (in aluminum) or count

rate (in steel) were found to be proportional to the corrosion rate. Grabec pointed out that corrosion rates could be quickly measured with this technique. Bursting of bubbles is also the source of AE in the routine testing of aerospace composites, discussed later.

It is not certain that the bursting of the bubbles accounts for all the emission associated with gas evolution, but no alternative mechanisms are in view at present. The sudden release of restraining force, as the bubble separates from the solid, might seem to be a plausible mechanism; but calculations indicate that the amplitude of this wave would be one to two orders of magnitude below the threshold of detectability.

Hydrogen migration plays an important part in some corrosion problems, and is a known source of emission. In a simple demonstration by the late M. R. Chance, a strip of mild steel, suitably polarized in dilute acid overnight, gave millions of emission counts without visible gas evolution. The individual emissions had very low amplitudes. This effect was probably caused by finely distributed microcracking; mere movement of hydrogen atoms could hardly cause this type of emission.

Cracking on a grosser scale produces emissions of larger amplitudes, and this is therefore the best candidate mechanism for structural applications of AE. Here the AE technique is nicely complementary to electrochemical methods, which correlate with volumetric dissolution and therefore are insensitive to small-volume discontinuities such as cracks.

Stress-corrosion cracking, hydrogen embrittlement cracking, and corrosion fatigue have all been detected and studied using AE. Even before AE became a recognized technology, van Rooyen used the phenomenon to study discontinuous cracking in aluminum alloys [6]. He correlated the emissions with sudden changes in electrochemical potential as newly created surface regions met the liquid environment. Later, as AE came to be recognized as a future nondestructive testing (NDT) method, several classic investigations focussed on SCC and hydrogen embrittlement for AE feasibility studies and quantitative modelling [7-9]. AE was recognized as a rapid way to assess the SCC susceptibility of materials, both aluminum alloys [10] and steels for oil field equipment [11].

The energy of AE during crack growth is drawn from the stress field around the crack, which relaxes momentarily as the crack jumps forward. The stress field is created by the external forces, in combination with internal pressure if hydrogen is involved.

Emission is the result of a momentary instability and a sudden movement of the crack tip to restore equilibrium. Advance of the crack under quasi-static conditions, as by a steady dissolution process, does not produce emission. Thus emissivity depends on the details of the crack growth process and on the nature of the material. In high-strength aluminum and steel alloys, discontinuous crack movements play a large part in the crack growth process and the main role of the corrosive environment is "to demolish the obstruc-

tions which would otherwise arrest the advance of the crack" [12]. In some lower-strength steels, AE monitoring has been disappointing because the crack growth process is more chemical than mechanical, and the emission is sporadic and low in amplitude. Stainless steels [13] and titanium alloys are borderline cases. In early work on SCC in 8-1-1 titanium, material that was heat-treated to a low strength level showed major crack movement without detectable emission; but material heat treated to a higher strength level gave substantial quantities of emission that could be correlated with crack velocity, load drop, and stress-intensity factor [14].

In high-strength steel and aluminum alloys, the emission is directly linked to the major crack growth process and the emission amplitudes are large; so these are the best materials for AE monitoring in the field. Semi-quantitative models of the crack growth process and associated emission have been proposed by several authors. For hydrogen-assisted cracking in 4340 steel, both Dunegan and Tetelman [8] and Oriani and Josephic [15] found that the emission rate was a sensitive function of stress intensity factor. Testing similar steels both in hydrogen gas and in sodium chloride (NaCl) solution, McIntyre and Green [16] measured amplitude distributions and found that a group of high-amplitude emissions was present only when the environment was hydrogen gas. They also found that increasing the grain size increased the emission amplitude during intergranular cracking; and they found that intergranular cracking gave higher amplitudes than transgranular cracking. Unlike Dunegan and Tetelman, McIntyre and Green found that the AE rate per unit of crack area was fairly independent of stress intensity. Results may have differed because McIntyre and Green used much higher sensitivity, or because the hydrogen was differently distributed in the material: it passed to the crack tip from the gaseous environment whereas the other authors' specimens were cathodically charged. So while a number of interesting relationships have been reported, we do not yet have a comprehensive model taking all the variables into account.

Crack growth processes give the largest emission amplitudes and are therefore the best candidates for detection on large structures. By and large, the other processes can only be detected under laboratory conditions. A valuable tool for assessing detection prospects is the amplitude distribution function characterizing the source mechanism [17]. Figure 2 shows an amplitude distribution for stress corrosion cracking in high-strength 4340 steel. The number of emissions with amplitude greater than A is plotted as a function of A . In this material a good fraction of the emission is of very high amplitude, and would still be detected even if the sensor were placed at a great distance and the wave were much attenuated in reaching the sensor. AE monitoring will work very well on such a material. For materials or deformation processes where the slope of the amplitude distribution plot is steeper, the results depend more critically on sensitivity, and the prospects for large-structure monitoring are not so good.

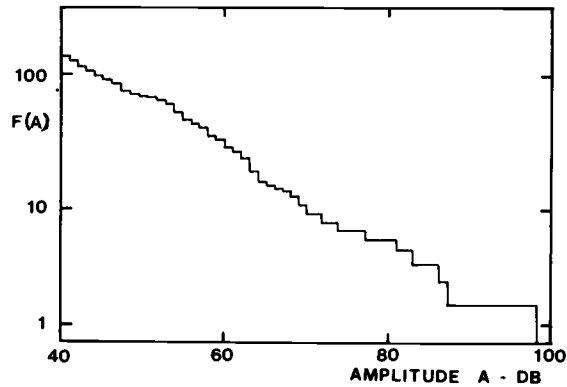


FIG. 2—Amplitude distribution function for SCC in 4340 steel; this material produces a substantial number of large emissions.

Detecting the Results of Corrosion

As an alternative to measuring corrosion processes while they are occurring, AE can often be used to detect the damage after it has occurred. For this, an external load must be applied to the structure; typically this takes the form of a proof test. The strategy for detecting corrosion damage depends heavily on the Kaiser effect, that is, the principle that material emits only under unprecedented stress. Dunegan's strategy for damage detection based on the Kaiser effect [18] is shown in Fig. 3. On a structure's first loading to a proof load L_p , emission follows the line OA. On unloading and reloading no further emission is generated, line ABA. Next the structure is put in service for a while, unmonitored but with the load never exceeding the working load

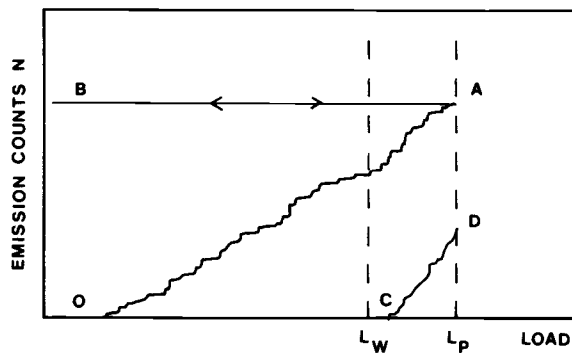


FIG. 3—Dunegan's strategy for damage detection based on the Kaiser effect. Emission during an inservice proof test (CD) indicates damage during the previous working period.

L_w . Finally it is subjected to another overload to L_p , with AE monitoring. If no damage occurred during the preceding service period, it should be silent during the proof test. But if damage occurred through time-dependent processes such as fatigue or corrosion, the new proof test will bring the local stresses in the damaged areas to unprecedentedly high levels, and emission will be observed (line CD).

Under the Dunegan strategy, the same proof load can be applied at intervals during the structure's working life; in each proof test, emission indicates the damage that occurred since the previous proof test. This is a classic procedure for materials and processes that show the Kaiser effect. For other materials and processes the Kaiser effect may not be followed, and this leads to alternative loading strategies and interpretive procedures.

Time-dependent corrosion processes produce the results listed in Table 2, which are the basis for application of the Dunegan strategy. When corrosion results in a thinning of load-bearing metal, a proof test will put a higher stress on the material than it saw on the previous proof test. The Dunegan strategy applies in principle, but in practice the margin of overstress may be very small and the bulk material may still be quiet, unless the damage is so severe that the material yields.

The surface of corroded metal is often rough with pits, debonded grains, and entrained corrosion products. This makes the surface emissive. Under increased load, emission may come from friction or separation of loosened grains, from deformation at microscopic stress concentrations, or from debonding or breaking of the corrosion products. In tension tests on 316L stainless steel, a control specimen was very quiet, but a corroded specimen gave a large amount of emission during plastic deformation.

Corrosion products on a metal surface are liable to break or debond when an overstress is applied to the underlying material. A buried pipeline tested in 1979 had many large, shallow corrosion pits filled with hard deposits of black oxide (magnetite). During pressure tests to failure with 152-m (500 ft) sensor spacing, the emission rate was high at all sensors and it was hard to predict the failure locations. The source of this emission was believed to be fracture

TABLE 2—*Results of corrosion and basis of associated AE behavior.*

Result	Basis for AE
Thinning of metal	global stress change
Rough surfaces	local stress change
Corrosion products	
on surface	new material to emit
in fissures	new material to emit
Cracks	local stress change

and debonding of the oxide deposit, stimulated by plastic deformation of the thinned metal underneath.

In the case of crack growth the solid corrosion products are likely to remain trapped between the crack surfaces, especially if gravity assists. If the stress is removed and the cracked area is allowed to dry out, the corrosion products can bond to the metal surfaces and give emission when stress is reapplied. This is illustrated in Fig. 4, which shows emission versus load for two SCC cracks in a test section of pipeline pressurized in 1981 [19]. These defects had been previously exposed to pressures above 7.6 MPa (1100 psi), and they were eventually tested to failure at pressures above 8.3 MPa (1200 psi). Based on the Kaiser effect, the emission beginning at 1.9 MPa (270 psi) could not have come from crack growth, and can only be attributed to crack face separation and the fracture of corrosion products bridging to the crack surfaces. It is interesting that the slope of the emission/pressure plot decreases with increasing pressure; this is intuitively compatible with the proposed mechanism but contrary to the usual behavior of emission from cracks.

Solid corrosion products between the faces of a crack might also be expected to emit during unloading of the part, when the crack faces come together. This effect has not been reported, but it could be important since such products can form a solid wedge that increases the stress at the crack tip and actually helps to drive the crack forward. Emission during unloading is relatively uncommon and does not fit the classic Dunegan/Kaiser approach.

Cracks themselves may emit as they grow during an overpressure test. Two mechanisms for emission may be distinguished: the growth of the plastic zone, and the advance of the crack front itself. The former mechanism gives emission of relatively low amplitude and may be difficult to detect in a large structure. The latter gives large-amplitude emission if the crack advances in discrete jumps. Detection of cracks in this operating mode is part of the routine business of AE field testing of pressure vessels and piping.

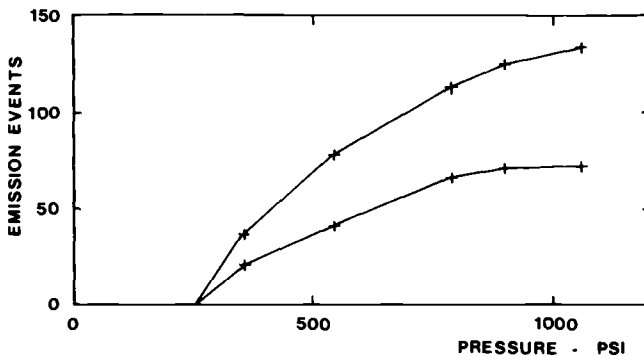


FIG. 4—Emission from two stress corrosion cracks in a 660-mm (26-in.) pipeline: each event was detected and located by two sensors 20.7 m (68 ft) apart.

AE testing always requires a stress, but the stress does not have to be applied mechanically. In an interesting variant, Rodgers and Moore applied thermal stress to detect corroded regions in aluminum structure and honeycomb composite in aircraft [20]. The emission came partly from renewed corrosion under the influence of heat and partly from the breaking of moisture-degraded adhesive bonds. The AE procedure was established as a routine test offering substantial savings in inspection time and cost.

Considerations for Successful Field Application

A well-conceived test procedure, good equipment, and adequately skilled personnel are prerequisites for successful application. The test procedure must take into account probable sources of emission, possible background noise, and load history of the structure.

Background noise sources can be reduced or eliminated by proper action before the test. Noise is more easily controlled during a proof test than during continuous service, which is one reason why the proof test mode has generally been more successful than continuous monitoring.

The load history of the structure is taken into account while determining the loading program for the test. Usually the test includes an overload whose margin must be compatible with safety and applicable code practices. The loading rate must be compatible with data recording capability and with the AE operator's commitments to observation and feedback while the test is proceeding.

In determining sensor placement and spacing, wave propagation and attenuation must be taken into account to ensure that all necessary regions will be monitored with adequate sensitivity. Sometimes the requirements can be judged in advance, but at other times (such as on unfamiliar structures) special measurements may be necessary. Attenuation should be considered together with the expected source mechanisms and amplitudes. Specification of equipment for the test follows from this analysis of structural monitoring requirements. Widely ranging equipment and services are available, with and without source location capability. If the system has source location capability, the AE test is typically followed up with other nondestructive inspections of the located sources. The advantage of AE is the ability to test the whole structure in a single operation, so that the other inspections can be precisely targeted rather than volumetric.

Operator skill is very important in AE testing. Training courses and formal qualification procedures are somewhat established, though not as well as in the older NDT technologies. Worldwide, there are probably only 100 to 200 individuals with competence and substantial experience in AE field testing (though far more have engaged in research and laboratory testing). The experienced tester will be more likely to anticipate problems, manage the test smoothly and interpret the data accurately; so experience contributes a lot to the likelihood of a successful AE test.

Conclusions

There are several mechanisms that generate low-amplitude acoustic emissions during corrosion; these are useful in the fundamental study of corrosion processes, and also in evaluating materials. In SCC and hydrogen-assisted cracking, discontinuous crack jumps generate high-amplitude emissions so these processes can be well-detected, even on large structures where the acoustic wave is much attenuated before reaching the sensor. But some processes, notably dissolution and active path corrosion, do not of themselves generate detectable emission.

The strategy of AE monitoring during periodic proof testing allows prior corrosion damage to be detected even when active corrosion is no longer occurring. In this test mode, emissivity is enhanced by surface degradation and corrosion products.

The corrosion processes most readily detected by AE, that is, processes involving cracking, are just those processes that are not well-detected by electrochemical techniques. Thus AE is a natural complement to electrochemical methods.

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Fundamental Aspects of Acoustic Emission Applications to the Problems Caused by Corrosion

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ABSTRACT: This paper describes the utility of acoustic emission (AE) for the detection and monitoring of corrosion, stress corrosion cracking (SCC), and corrosion fatigue (CF). It comprehensively surveys laboratory studies and field applications that have been made to date. How to apply the technique to fundamental studies in the laboratory and continuous monitoring in engineering structures are discussed in detail. Various microprocesses that can produce detectable AE are shown and their relative energy levels, emanated as AE, are discussed in terms of peak amplitudes measured on laboratory specimens by a conventional piezoelectric sensor. All the available information clearly demonstrates the potential usefulness of the AE technique.

KEY WORDS: acoustic emission, corrosion, stress corrosion cracking, corrosion fatigue, nondestructive tests, continuous monitoring, hydrogen embrittlement, active path corrosion

Corrosion studies are very important in the areas of economics, improved safety, and conservation. Losses sustained by corrosion in industry, in the military, and in municipalities amount to many billions of dollars annually. In the event of loss of health or life through explosion, unpredictable failure of chemical equipment, or wreckage of airplanes, trains, or automobiles through sudden failure by corrosion of critical parts, the indirect losses are difficult to assess and are beyond interpretation in terms of dollars. This has led to an increased effort in developing techniques for detecting and monitoring corrosion and subcritical crack growth caused by corrosion. Most conven-

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tional nondestructive testing techniques require manual inspection of a structure, which can be both time-consuming and expensive, especially if plant shutdown is involved. Such disadvantages can be overcome using acoustic emission (AE) techniques which have developed to the stage where continuous in-situ monitoring of large areas of structure is being performed to detect and locate subcritical crack growth.

Since AE provides a unique method of recognizing when and where defect is growing, it has been widely utilized in both laboratories and field applications [1-3]. There are several studies which demonstrate the potential usefulness of AE technique for the detection and monitoring of active corrosion of aluminum and aluminum alloys [4-8]. The AE produced in this process appears to be related to bubble motion of hydrogen evolved by cathodic reaction. The AE count rate has been reported to be linear with the reaction process as measured by hydrogen formation [4]. AE has been also applied to detect active corrosion in aluminum structure and moisture-degraded adhesive bonding in composite honeycomb used for aircrafts [6]. It was possible to reveal the true extent of corrosion damage in wings by AE. Stress corrosion cracking (SCC) of aluminum and magnesium alloys has been investigated through the extreme sensitivity of the AE technique to slow crack growth [9-13]. The results show that AE can detect the crack initiation and growth process most clearly. As for AE applications to steels, we can find much more investigations in the literature. The AE technique has been employed both for the study of cracking mechanisms [14-16] and for the detection and monitoring of the crack initiation and growth [17-22]. This technique is particularly effective to investigate the hydrogen embrittlement (HE) of high-strength steels such as 4340 and maraging steels. The relationship between the cracking mechanism and the AE source mechanism has been established in this case. The AE produced during SCC and CF (corrosion fatigue) of a 304 austenitic stainless steel which exhibits very high corrosion resistance has been studied intensively, and the usefulness of this technique is demonstrated [3,23-25]. In simulated BWR water environment, the feasibility of continuous AE monitoring for IGSCC (intergranular SCC) has been examined by several workers [26-31]. Most of the results show distinct AE response throughout the progress of IGSCC from initiation to pipe-wall penetration. The AE technique has been utilized also for the investigation of other alloys such as copper and its alloys, uranium alloys, titanium and zirconium alloys, and has proven successful [2,32-40].

AE signals are generated mainly by crack initiation and growth induced by SCC or HE. However, the evolution of hydrogen (H_2) gas via cathodic reaction in acid solutions and the breakdown of thick surface oxide film formed under certain circumstances are also important sources of significant AE. In addition, the fracture or decohesion of phases such as precipitates, second-phase particles, and nonmetallic inclusions and the twinning in the plastic zone of a crack are expected to produce detectable AE. On the other hand, dissolution

of metals can hardly be detected by AE technique. These mechanisms that can produce AE are schematically illustrated in Fig. 1 [3].

It is known that AE activity observed during cracking depends strongly upon the following three factors: (1) environmental conditions (existence of local dissolution or hydrogen); (2) mechanical conditions (triaxial stress in the crack tip plastic zone); and (3) materials characteristics (heat treatments, nonmetallic inclusions, etc.). It has been shown that the cooperation of these factors can provide very high AE activity in terms of AE event counts, peak amplitudes, and energy [42].

Since environment is very noisy during regular operation of chemical or nuclear equipment, the discrimination of valuable AE signals from environmental noises is most important for field applications in this area. The noise has three effects. First, it establishes the amplitude threshold for signal detection and hence limits the number of emissions detectable. Second, in adding to an emission signal, it modifies the measured arrival time and thus creates location errors. Third, it produces a background of events on a map of AE sources. It is therefore of the utmost importance to minimize the effect of the irreducible noise present on the structure.

Setting the proper threshold is an important first step for the discrimination of AE from noise. Further improvement may be possible by applying suitable frequency filtering, signal recognition techniques and spatial filtering. Combination of these techniques will render possible the monitoring of the equipment that has been quite intractable because of environmental noises.

Practical limitations of AE are that the AE must be discriminable from background noise and that the AE signals must be correctly interpreted. This

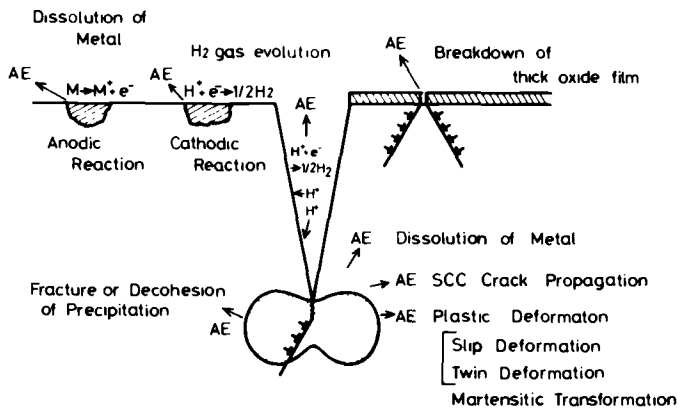


FIG. 1—Schematic AE sources during corrosion, stress corrosion cracking, and corrosion fatigue processes [3].

paper comprehensively surveys laboratory studies and field applications which have been made to date and demonstrates the potential usefulness of the AE technique. Practical methods to apply the technique to fundamental studies in laboratory and continuous monitoring in engineering structures are discussed in detail.

Laboratory Studies

Corrosion

Rettig and Felsen [4] measured AE generated during the corrosion process of aluminum wire in salt water. In this test, the AE count rate was linear with the reaction process as measured by hydrogen formation (Fig. 2). While it was suggested that an explanation for the AE associated with corrosion phenomena would include macroscopic motion of hydrogen bubbles, some AE signals were monitored in cases in which no bubbles were detectable even at $\times 10$ magnification. It is possible that other physical/chemical mechanisms are involved. Rettig and Felsen concluded that by measuring the AE count rate, cumulative AE counts, and the pulse amplitude, correlation may be made with empirically obtained corrosion data to permit failure prediction and that these AE parameters can provide a nondestructive inspection technique for monitoring invisible or hidden corrosion.

Mansfeld and Stocker [5] have recently reported the experimental results on AE from corroding electrode. They found that the AE count rate seemed

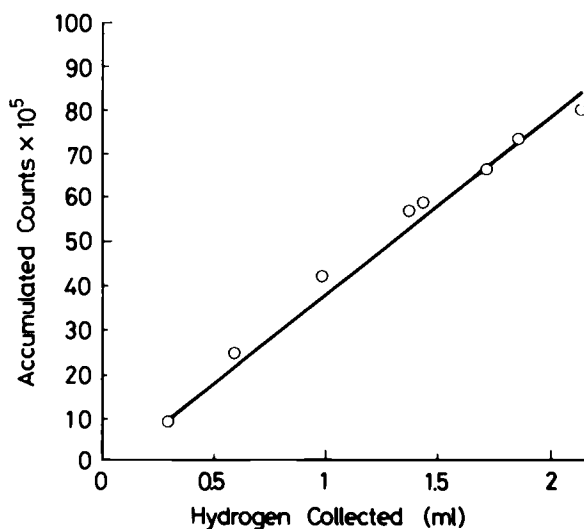


FIG. 2—Corrosion reaction monitoring of aluminum wire in salt water [4].

to be qualitatively related to the corrosion rate and that in the case of localized corrosion of aluminum alloys freely corroding or coupled to dissimilar metals, AE count rate accurately reflected the corrosion behavior of these alloys (Fig. 3). It is mentioned that additional information becomes available about the statistical nature of the pitting process for aluminum alloys and stainless steel and that hydrogen bubbling plays an important role during these processes because its evolution due to cathodic polarization increases the AE count rate significantly.

Procedures have been developed by Rodgers [6] to detect active corrosion in aluminum structure and moisture-degraded adhesive bonding in composite honeycomb using AE monitoring. Simple heating methods employing a hot-air gun or heat lamp are used to increase emissions from active corrosion sources, and to create the stress necessary to break moisture-degraded adhesive bonds. Corrosion detection in aluminum skin and honeycomb has proven successful. In this case, the AE source is thought to be the formation and bursting of hydrogen bubbles from cathodic half-cell of the corrosion reaction. It is noted that the true extent of corrosion damage was revealed by AE and that the ability to detect even the early stages of corrosion activity, before extensive structural damage has taken place, is clearly an advantage in the maintenance environment.

Druchenko et al [7] have given a qualitative description of AE generated in metals by SCC, pitting, hydrogen absorption and desorption, and electroplating. They checked calculated values for the fundamental wave frequencies for bubbles in the aqueous solution experimentally with hydrogen bubbles evolved during corrosion of D16AT aluminum alloy in 10% ferric chloride solution. The excellent agreement between the calculated and measured results showed that the wave frequency of the visible bubbles did not exceed 40 to 50 kHz. They also performed SCC test on the cantilever specimens with microscopic observation and revealed that visual appearance of the crack is always preceded by AE signals which often follow one another and are visible on the oscillographic screen as superimposed afterimages.

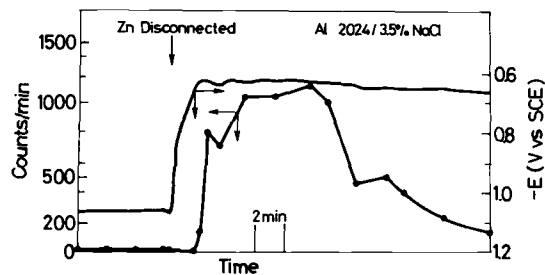


FIG. 3—Count rate and potential of Al 2024 coupled to zinc and freely corroding in 3.5% NaCl [5].

Scott and Wilson [8] used 2024 aluminum alloy specimens, polished to a 600 grit finish and degreased, to demonstrate the potential usefulness of AE technique for the detection of active corrosion. Specimens were tested in pairs for a period of four days after which a different specimen-corrodent combination was examined. It was observed that the specimen in tap water started to corrode immediately; the specimen in distilled water corroded two to three hours after immersion; and the specimens immersed in the various disinfectant solutions emitted no signal even after four days' immersion. These results were confirmed by visual and weight-loss corrosion tests.

Recently, the author and co-workers have used AE to detect the crevice corrosion process of a 304 austenitic stainless steel in a 3% sodium chloride (NaCl) solution [3, 43]. They prepared a small specimen with a 10-mm-diameter drilled hole to simulate the bulk environment, and with an artificial crevice introduced by spark machining. Figure 4 indicates the AE cumulative event counts during the crevice corrosion process induced by the polarization scan. The gradient of the AE curve changes greatly at about 3.9 ks, which suggests that the pH value of the solution contained in the crevice becomes sufficiently low and the potential falls below $E^\circ(\text{H}_2)$, so that hydrogen gas begins to evolve inside the crevice at this time.

Thus, AE has been used quite often in laboratory experiments on corrosion, although not much is known about source characteristics or AE-reaction relationships. It has been demonstrated, however, that the AE produced during corrosion process is generally associated with the actual formation of hydrogen bubbles [44]. The significant AE due to the evolution of hydrogen bubbles has been also observed during electro and electroless plating [45]. The rate of hydrogen evolution in the same solution as that for electroless nickel plating except that no nickel ion was present, was found to be $0.5 \text{ cm}^3/$

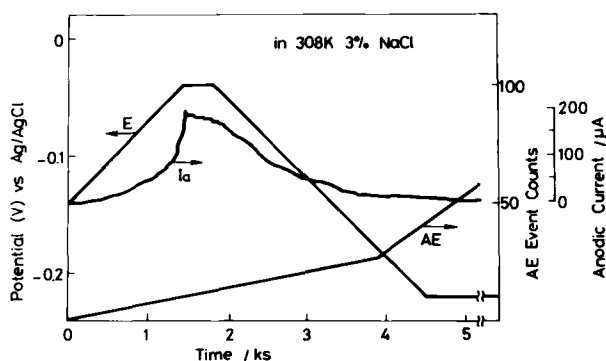


FIG. 4—AE cumulative event count during the crevice corrosion process [43].

min, which was comparable to that during electroless nickel plating. It was obvious that AE in this case was a result of the hydrogen evolution.

AE behavior of a 304 austenitic stainless steel during polarization scan has been reported by the author and co-workers [3,23,43]. Figure 5 shows the relationship between the polarization curve and AE count rate. The specimen was polarized in the passive region at first. The potential was then swept at a rate of $3 \times 10^3 \text{ s V}^{-1}$ to the cathodic region or to the pitting region in 298 K 1N sulfuric acid (H_2SO_4) + 0.5 M sodium chloride (NaCl) solution. As shown in it, AE is detected only when the reductive breakdown of passive film occurs and hydrogen gas evolves on the specimen surface. However, no AE is detected when the oxidation breakdown occurs and metal dissolves into the solution. From this result, it was concluded that the breakdown of passive film ($< 1 \text{ nm}$) and dissolution of metal do not provide AE energy sufficiently high to detect.

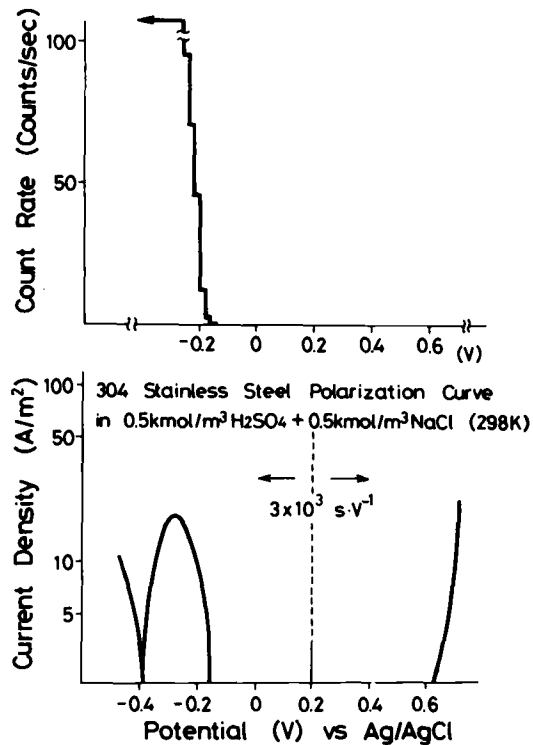


FIG. 5—Relationship between the polarization curve and the AE count rate [23].

Stress Corrosion Cracking

Steels

Austenitic stainless steels, such as Types 304 and 316, are important structural materials in chemical plants and nuclear power stations. Attempts have been made from early days to apply AE techniques for the detection of SCC, which is one of the main problems in the use of these steels.

Okada et al [14] carried out SCC tests for Type 304 stainless steel in $5\text{ N H}_2\text{SO}_4 + 5\text{ M NaCl}$ at 25°C , and for ferritic and high-strength martensitic stainless steels in boiling magnesium chloride (MgCl_2) aqueous solution at 143°C . They measured AE and changes of the electrical resistance or displacement of cantilever beam specimens. They used a high-frequency band-pass filter between 1 and 2 MHz for the tests in boiling MgCl_2 to eliminate the noise due to boiling. The results showed that the significant AE could not be detected during the SCC propagation of Type 304 and ferritic stainless steels, in which case active path corrosion (APC) was dominant as the SCC process. The high AE activity, in contrast, was observed during the SCC of high-strength martensitic stainless steel and in this case it was concluded that the SCC was caused by HE. This aspect—the difference of AE activity between APC and HE—is discussed in detail later.

Brihmadessam and McCormic [46] performed proof tests for Type 304 stainless steel to demonstrate the feasibility of using AE analysis to detect SCC growth. The precracked specimens were employed to produce a linear compliance change with increasing crack length and to simplify the study of the long cracks. Specimens were proof-loaded cyclically with an operating load of 2000 kg ($K_1 = 48.4\text{ ksi in.}^{1/2}$) and proof load of 3000 kg ($K_1 = 87.6\text{ ksi in.}^{1/2}$). During the holding cycle portion of the operating load, a 3.5% NaCl solution was used to simulate the corrosive nature of an atmosphere above seawater; such an atmosphere is encountered in many ocean-front or floating power plants. It was shown from these tests that crack growth during proof cycle could be detected by AE. Copious AE seemed to result from rapid crack growth, and large amplitude AE was observed prior to failure. Reproducibility of the AE total counts at a given stress-intensity factor K_1 could not be expected in such tests, since AE was dependent upon the metallurgical structure, heat treatment, etc., as well as variabilities in fabrication.

The author and co-workers have measured AE during a crevice corrosion SCC process of a 304 austenitic stainless steel in a 3% NaCl solution, using a double cantilever beam (DCB) specimen with an artificial crevice [3,23,43]. Figure 6 shows the AE cumulative event counts and energy during the test. After inducing crevice corrosion by the polarization scan, the potential of the specimen (E_{corr}) remains about -0.22 V and hydrogen gas evolves for some hours, but it increases suddenly to about -0.10 V at the end of this period, and then it decreases gradually. It is speculated that the sudden increment of E_{corr} corresponds to the time when the hydrogen ions have been consumed

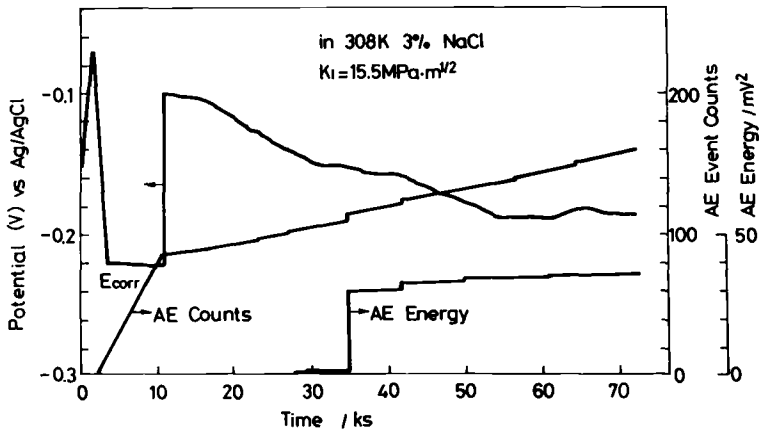


FIG. 6—AE cumulative event count and energy during the SCC test [43].

during the completion of the cathodic reaction inside the crevice. The gradient of the AE cumulative event counts curve changes greatly when E_{corr} increases, but remains constant when E_{corr} decreases gradually. The AE cumulative energy, however, increases greatly at about 35 ks, in contrast to the above. Figure 7 gives the AE amplitude distribution for this test. As shown in this figure, some high-amplitude emission (of about millivolt range) were observed. A large amount of AE energy was found in the middle of the measured zone, namely, at the crack tip. Therefore, it was concluded that the high-amplitude AE in Fig. 7 caused the sudden increment of the AE energy at 35 ks and that the SCC crack initiated at this time.

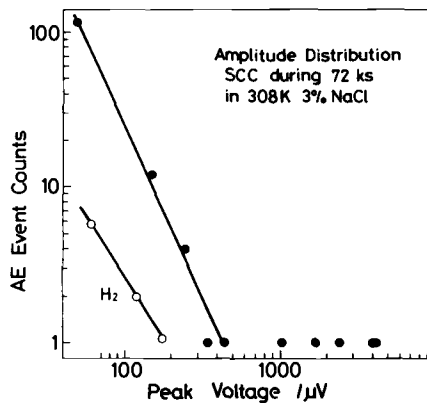


FIG. 7—AE amplitude distribution during the SCC test [43].

As for AE applications to the problem of SCC and HE in (high strength) steels, we can find a number of investigations in the literature.

Okada et al [14,15] used AE techniques to differentiate the two mechanisms (APC and HE) in environmental cracking of high-strength steels and stainless steels. It was possible to detect high-amplitude AE signals accompanying hydrogen-induced microcracking at the tip of an advancing crack. In contrast to HE, significant AE could not be observed in APC where cracks propagate by anodic dissolution along preferential paths. In their study, it was revealed that APC and HE could be differentiated during environmental cracking process of steels by AE technique (Fig. 8).

Recently, Monden et al [16] have investigated environmental failure processes in mild and high-strength steels. They studied AE characteristics during these processes in terms of AE count rate, waveform, and its mode (longitudinal or shear wave). As summarized in Table 1, APC failure could be distinguished from HE by studying AE characteristics from these viewpoints.

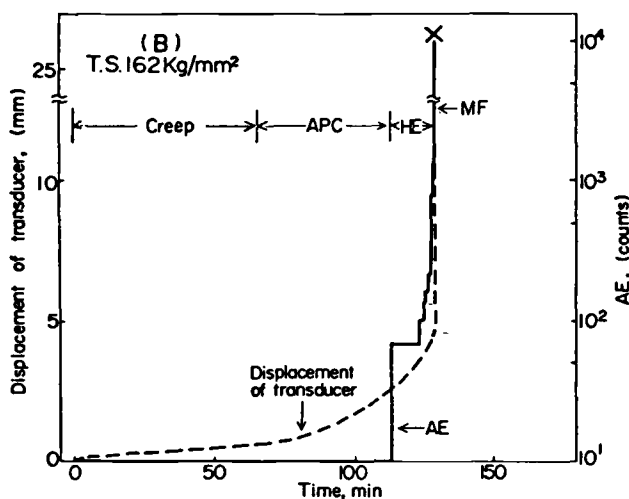


FIG. 8—AE counts and displacement of transducer with time during crack growth in low-alloy steels in 60% $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + 3\% \text{NH}_4\text{NO}_3$ solution at 110°C [14].

TABLE 1—AE characteristics during APC and HE processes in steels [16].

AE Characteristics	Failure Process in APC and Incubation Period in HE	Macroscopic Crack Propagation in HE
Amplitude Mode	small shear wave (second arrival wave)	large longitudinal wave (first arrival wave)
Waveform	smooth wave packet or continuous type	sharp waveform or burst type

Nakamura et al [17] demonstrated that the D6aC steel specimens, stressed by interference fit bolts, gave AE signals at rates which were directly related to their stress state and the amount of hydrogen charging they had previously received. The addition of water to a stressed but uncharged specimen produced a pattern of AE signals similar to that of the hydrogen-charged specimens suggesting their initiation of SCC. It is concluded from their preliminary study that the AE monitoring technique would be a useful tool for studying delayed cracking because of its high sensitivity and ability to provide immediate indications of crack growth.

AE associated with SCC of 817M40, 897M39, and AISI 4340 steels in 3.5% NaCl and gaseous H_2 at 190 to 760 torr was studied by McIntyre and Green [18]. The experimental result indicated that the AE level was more intense during intergranular than transgranular cracking. Increasing grain-size also significantly increased the emission level, and environmental effects were strongly dependent on the fracture path. The emissions were highly sensitive to crack initiation and growth, and in many cases detected the initiation earlier than any indication from electrical-resistance determinations.

A commercially available system was employed by Chaskelis et al [19] to detect and count AE emanating from the aqueous SCC propagation in 4340 steel. Standard (ASTM Test Method for Plane-Strain Fracture Toughness of Metallic Materials [E 399]) CT specimens with short notches were prepared in four tempering temperatures: 204, 316, 427, and 538°C. Crack length was monitored with a notch-opening clip-gage. Comparisons showed the time rate of AE events to increase with stress intensity in rough correspondence to, but much more rapidly than, the crack velocity.

Dunegan and Tetelman [20] have used AE techniques to determine the rate of cracking in 4340 steel due to HE, making it possible to predict failure in certain structural components undergoing environmental cracking. The linear-compliance specimens were employed under a deadweight load condition. They were cathodically charged with hydrogen, cadmium plated and baked for 3 h at 150°C, fatigue cracked and placed in a deadweight-load frame. The data for several values of K showed that the crack growth rate varies linearly with K . The slopes of the cumulative AE counts curves were taken for several values of K . A best fit of these data indicated that $K_0 = 7.0$ ksi-in.^{1/2} was the threshold stress-intensity factor below which no cracking occurred. These results suggest that continuous AE monitoring of certain structures containing an advancing HE crack will allow prediction of impending failure. The most important conclusion reached in this study is that regardless of the initial loading, nucleation time for cracking to begin, or any other factors connected with geometrical differences in specimens, the AE rate can be used to determine the time for and stress-intensity factor at the onset of rapid fracture.

Nozue and Kishi [21] have recently carried out HE tests in 4340 steel to establish the source mechanism of discontinuous AE produced during HE

process of high-strength steels. They revealed that the cumulative AE event count was proportional to the number of the microscopic intergranular cracking observed on the fracture surface by scanning electron microscopy (SEM) (Fig. 9) and that the cumulative AE energy was proportional to the new crack area developed as a result of intergranular crack extension. These results show that the dominant AE source in this process is the individual intergranular cracking induced by hydrogen.

Reuter and Hartbower [1,22] analyzed AE during subcritical cracking (SCC) process in two heats of 250 grade 18% nickel maraging steel exposed to circulating water at 21 and 74°C. The SCC tests were conducted using fatigue precracked, single-edge notched, tension specimens in conjunction with linear elastic fracture mechanics (LEFM) to determine the effect of melting practice and long exposure time. Figure 10 is a schematic of the crack jump progression during this process in terms of cumulative AE counts versus time at constant load. As indicated in the figure, the primary incubation time was defined as the time from the start of hold to the first rapidly increasing slope (jump) in the plot of cumulative AE counts versus time. Secondary incubation time was defined as the average time between successive rapidly increasing slopes (jumps) after primary incubation. The behavior at 21°C, in contradistinction to that at 74°C, consisted of a gradually increasing slope until just prior to failure; that is, there was a single jump at failure.

Aluminum and Magnesium Alloys

SCC tests of aluminum-zinc-magnesium (Al-Zn-Mg) alloy with a zinc/magnesium ratio of about 0.5 in a state of high sensitivity to cracking were carried out by Bukulin and Malyshev [9]. The specimens were flexurally de-

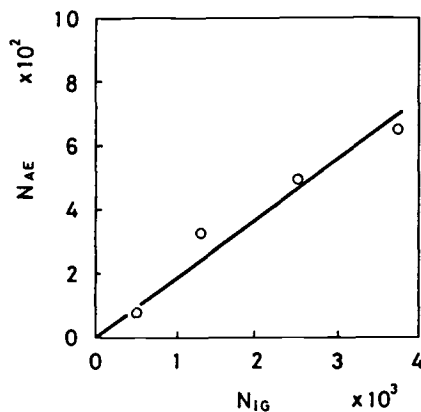


FIG. 9—Relationship between the number of intergranular cracking and detected AE event counts [21].

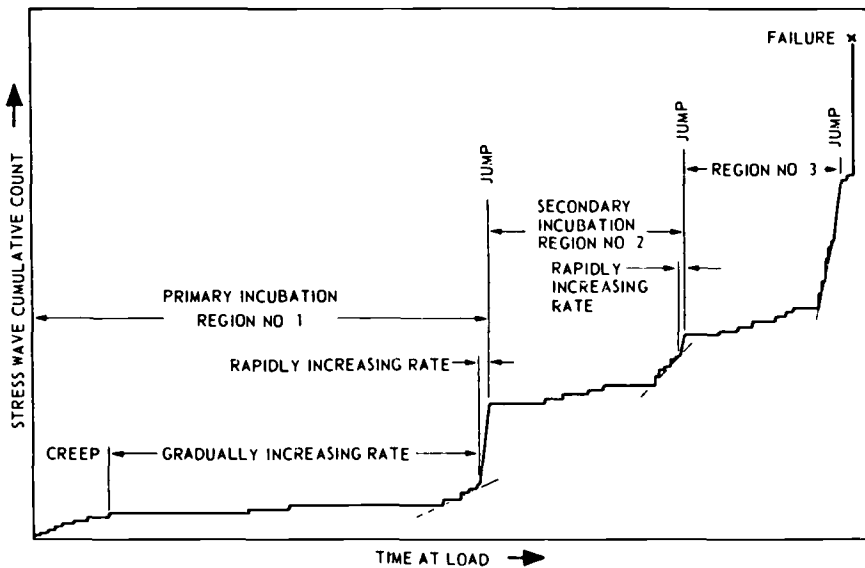


FIG. 10—Schematic diagram showing subcritical crack growth process and terminology [1].

formed in a Textolite (resin-impregnated laminated cloth) frame which was half-immersed in 0.5 M NaCl with admixtures of hydrogen peroxide (H_2O_2) and nitric acid (HNO_3) to accelerate cracking. It was found that about 20 min after the appearance of AE signals, a crack could be seen on the surface of the specimen. As the crack advanced, the character of the AE was preserved, but then the emission gradually died out and stopped at the same time as the crack halted. In all cases, it was possible even to record the moment of appearance of the crack by AE earlier than by direct observation. It was supposed that AE arises as the crack grows and continues for short period of time during which the crack executed an elementary jump.

Sugimoto and Sakai [10] used AE technique to detect the initiation of SCC in Al-Zn-Mg alloy which was aged at $150^\circ C$ for various hours. The SCC tests were carried out in 1 M NaCl solution monitoring AE cumulative event counts, elongation of the specimen, and current change. The result indicated that the AE can detect the crack initiation clearly and earliest of all these monitoring parameters applied in this test (Fig. 11).

Chakrapani and Pugh [11,12] made a study of the propagation of transgranular SCC cracks in a Mg-7.5 Al alloy tested at room temperature in an aqueous NaCl-potassium chromate (K_2CrO_4) solution. The SCC fracture surfaces were cleavage-like in appearance, containing shallow steps which were matching and interlocking on opposite faces. Discrete AE was emitted during crack propagation, and these are considered to result from discontinuous crack advance (Fig. 12). Analysis of corroded specimens indicated that hy-

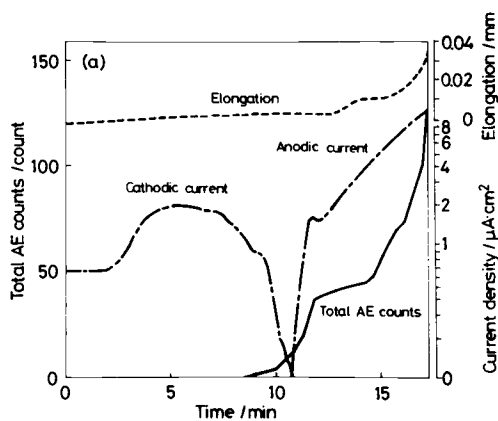


FIG. 11—AE cumulative event counts with time during SCC test of Al-Zn-Mg alloy polarized at -1.02 V (SCE) in 25°C 1 M-NaCl solution, $\sigma = 0.6 \cdot \sigma_{0.2}$.

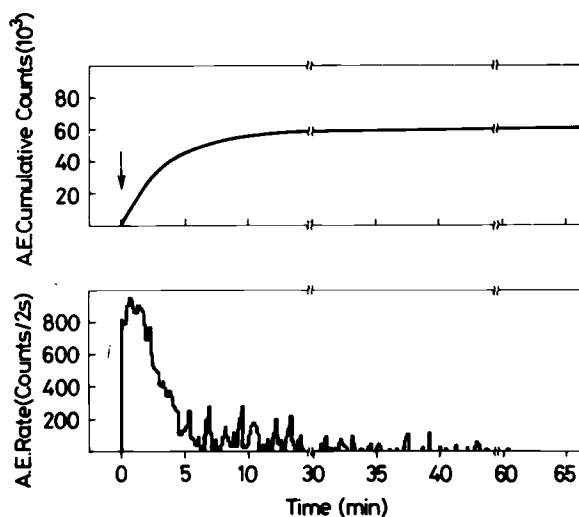


FIG. 12—AE parameters against time that a bend specimen is stressed in air after 8 h immersion (unstressed) in the test solution. The arrow indicates the time at which the stress was applied [11].

drogen absorption occurs, and there is little doubt that the reversible embrittlement in immersed specimens results from the presence of hydrogen. These experimental results thus made it possible to argue that cracking involves repeated cycles of hydrogen diffusion to the region ahead at the crack tip (a slow process) followed by cleavage through the hydrogen-rich zone (a rapid process).

The AE activity associated with cracking in a variety of SCC and HE systems of aluminum and magnesium alloys, brass, and mild steel has been studied by Pollock et al [13]. The results demonstrated that different SCC and HE systems can be compared using the same AE equipment and that AE ring-down counting provides a satisfactory method for comparing their relative acoustic activities. Since the AE ring-down count rate in a given system depends very much on the crack growth rate, it was concluded that this approach provides the engineer with a useful guiding parameter for assessing the suitability of AE for monitoring crack growth in such situations.

Copper and Its Alloys

There are only a few results obtained by using AE technique concerning the studies of SCC in pure copper (Cu) and copper alloy. Suzuki et al [32] carried out transgranular SCC tests on pure copper in 0.05 *M* ammonium hydroxide (NH₄OH) solution at 70°C. They detected the onset of tarnish film fracture which occurred at regular intervals by monitoring corrosion potential change, current change after 23 h polarization at -50 mV saturated calomel electrode (SCE), and AE signals observed during constant extension rate SCC test. The detected AE was attributed to the brittle tarnish film rupture from the correlation between the AE data and the corrosion potential or current change. They concluded that the result described above and the fact that the fracture surface was all covered with thick and black tarnish film even at the propagating crack tip indicate that the SCC mechanism in this case is consistent with the brittle tarnish rupture model.

Recently, Beavers and Pugh [33] studied the propagation of transgranular SCC in Admiralty metal (Cu-30Zn) by means of AE technique. They performed SCC tests on bend specimens under constant deflection in a 15 N tarnishing solution, while monitoring AE. In this study, while not generally resolvable with the SEM, crack-arrest markings could be detected on the fracture faces under certain conditions, and this, together with the occurrence of discrete AE which is considered to be associated with crack propagation, indicated that the SCC propagation is discontinuous. They concluded that transgranular SCC in this system occurs by discontinuous cleavage on {110} planes, and that a bulk-embrittlement model (which might be hydrogen embrittlement) is probably operative.

Uranium Alloys

Magnani [34] monitored SCC propagation of uranium (U-4.5Nb) alloy by crack-opening displacement and AE technique in dry laboratory air with some tests conducted in oxygen and water vapor. The SCC crack-velocity data and the AE behavior tested in dry laboratory air showed that three stages of crack growth existed (Fig. 13). Excellent correlation could be obtained be-

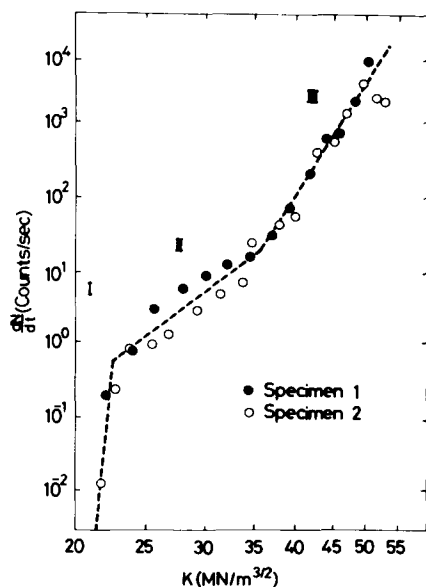


FIG. 13—Relationship between AE count rate and applied stress-intensity factor [34].

tween the directed cracking velocity measurements and AE count rate at all stress intensities. The experimental data indicated that as the cracking velocity increases, the counts per unit area of new crack surface increase, and these results above revealed the feasibility of AE detection techniques as a useful SCC testing tool.

Mah et al [35] performed corrosion and SCC tests on the same alloys as used in Magnani's study in oxygen-saturated water containing chloride ions using rectangular corrosion coupons and smooth four-point bend specimens. It was found from this study that SCC monitoring of the alloy was successful and that corrosion monitoring showed a direct correlation between corrosion rate (based on weight loss) and total AE counts.

The AE accompanying SCC in air, at ambient temperature, of a U-10Mo alloy was investigated by Bedere and Miannay [36] using a counting technique. The AE detected was due to the plasticity and microcracking which accompanied macroscopic cracking. The AE increased slightly in the course of a test but was not a unique function of the stress-intensity factor in contrast to the results obtained by Magnani.

Titanium and Zirconium Alloys

The author and co-workers [37,38] have recently investigated the SCC process of Ti-6Al-4V alloys which have different heat treatments in methanol-0.5% iodine (CH₃OH) + 0.5 I₂ solution, measuring crack-opening displace-

ment and AE. Fatigue precracked CT specimens with a thickness of 7 mm were tested under constant load. The experimental data showed that the main AE source during this process is SCC crack growth and that there exists a good correlation between the SCC crack-growth rate and the detected AE count rate. Both of them represented three stages against stress-intensity factor K (Fig. 14). The detailed observations of microstructure along the cracking path and the analysis of AE detected discontinuously during the crack growth revealed that the cracking was obviously discontinuous and occurred in jumps of some α -grain diameters on a small scale and of a prior β -phase grain diameter on a large scale. Thus, the AE technique can be a powerful tool to monitor SCC process of titanium alloys, and there is no doubt that it will find increasing use for establishing quantitative information in this area.

Using metallographic, fractographic, and AE techniques, Koch et al [39] have shown that failure of a Ti-8Al-1Mo-1V alloy occurs on (1010) planes across the α -plates in an NaCl solution and in hydrogen gas. In both cases, titanium hydride was detected at the fracture surfaces and, from AE studies, crack growth appeared to be discontinuous. From these observations, they suggested that the failures occur by the hydride-rapture model first proposed by Nelson [41], that is, the repeated formation and rupture of the hydride phase.

Cox [40] studied AE during the SCC of Zircaloy specimens comparing with the metallographic and fractographic evidence for the events occurring at dif-

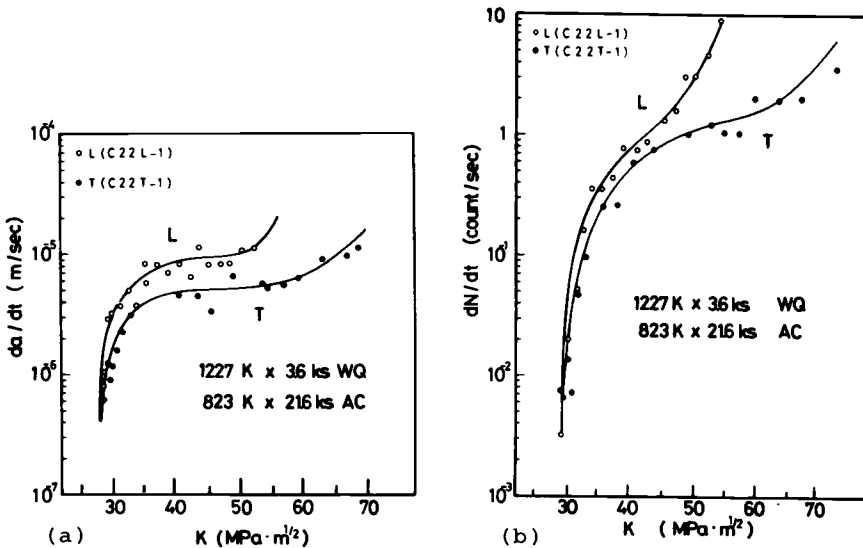


FIG. 14—Relationship between crack growth rate (a) or AE count rate (b) and applied stress-intensity factor during SCC tests of Ti-6Al-4V alloy in $\text{CH}_3\text{OH} + 0.5\% \text{I}_2$ at room temperature [37].

ferent stages in the cracking. Self-stressed DCB specimens and 12.7-mm ($1/2$ in.) lengths of standard fuel cladding tube were tested in methanol-1% hydrochloric acid solution, methanol-1% iodine solution, and 5% NaCl solutions at room temperature, and in a nitric-iodine salt mixture at 300°C. AE during testing was monitored by using a differential transducer mounted either directly on the DCB specimen or on the stressing block of the split-ring specimen for room temperature test. For tests at elevated temperature (300°C), a 152-mm-long (6.08 in.) Zircaloy rod [3.2 mm (0.12 in.) diameter] was screwed into the end of the DCB specimen near the stressing bolts, and the transducer was mounted on a platform on top of this rod, which could be cooled by an air flow if necessary. From the results, two types of AE (continuous and discontinuous) were readily distinguishable, but no unique explanation of either was possible. It was speculated that the continuous, swishing type of AE may arise from either electrochemical dissolution processes or the generation of mobile dislocations, whereas the discontinuous, cracking type of AE may result from either discontinuous propagation of a brittle crack, twinning of the hexagonal metal, or cracking of the protective oxide (at elevated temperatures).

Corrosion Fatigue

Hartbower et al [47] made an investigation of CF processes in D6aC steel, Ti-6Al-4V alloy, and 7075-T6 aluminum alloy using the precracked, single-edge-notch tension specimens and AE techniques. The SCC process during low-cycle, high-stress-intensity fatigue was readily detected by a marked increase in the AE count rate. From this investigation, the utility of AE as a precursor of imminent failure was shown for the environmentally assisted fatigue (corrosion fatigue).

Mehdizadeh [48] has monitored the progress of CF damage of quenched and tempered carbon/manganese (C/Mn) steel in 3% NaCl solution by AE generated during corrosion fatigue test and periodic proof loadings. The result showed that periodic proof testing combined with AE monitoring could be a sensitive method for assessing the progress of CF damage. This method can be utilized to establish the initiation of incipient fatigue cracks after as little as 5% of the total fatigue life. A qualitative method based on the saturation of AE during periodic proof loading was used to predict the remaining fatigue life and it was demonstrated that this scheme can predict the remaining fatigue life up to 70% of the actual values.

Crack growth and AE behavior during CF process has been studied in a high-strength Ti-6Al-4V alloy [38]. Compact tension specimens were prepared so that the cracking direction was parallel (T-L) or normal (L-T) to the direction of the prior hot rolling. The tests were carried out in air and at several electrochemical potentials in a 3.5% NaCl solution under cyclic load. Although significant difference of crack growth rate was not seen between

different environments, much greater AE activity in terms of detected AE event counts and peak amplitudes was observed in the NaCl solution than in air. This result demonstrates that AE can be a very useful method to monitor CF crack growth. Optical and SEM observations of cracking path and fracture surfaces found the fracture morphology to be a mixture of intergranular cracking along prior β -phase grain boundaries, α/β interface (interphase) cracking due to hydrides formed along the interfaces, and transgranular cleavage or hydride fracture. It was shown that different cracking mechanisms can be distinguished with respect to the energy levels of the emanated AE and the fracture morphology by using amplitude distribution (Fig. 15).

Jax and Richter [49] have recently reported AE behavior during CF process of a mild steel used for offshore platforms. Measurements were made with flat specimen of TTStE 36 steel (ultimate strength 360 MPa), which were exposed to vibration loads under seawater conditions. Systematical analysis on the load levels at which AE signals are detected found that, except for a limited rupture phase, friction in the crack area is the dominant cause of identified crack signals. It was shown that AE enables incipient cracks to be detected in several ways at any early stage, that is, generally earlier than would be possible by visual inspection methods.

The author and co-workers have made systematic studies of AE produced during CF of a 304 austenitic stainless steel potentiostatically polarized in 1

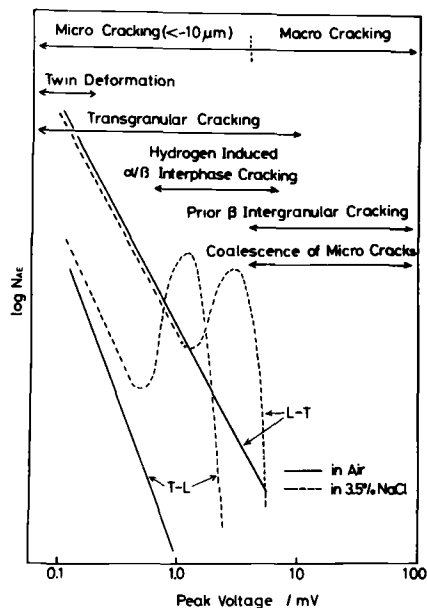


FIG. 15—Various AE sources and their relative energy levels during CF of a high-strength Ti-6Al-4V alloy [38].

$\text{NH}_2\text{SO}_4 + 0.5 \text{ M NaCl}$ or $1 \text{ M NH}_2\text{SO}_4$ solutions, using compact tension specimens [3,23–25,42]. The crack growth rates at -0.8 V , E_{corr} , and -0.28 V were accelerated significantly compared with those observed in air or $+0.01 \text{ V}$ (noncorrosive environments) when ΔK is less than about $37 \text{ MPa m}^{1/2}$, where the transition of the deformation patterns in the crack-tip plastic zone from hinge-type to shear-type takes place, and through-thickness yielding is accomplished. Both AE cumulative event counts and AE energy represented step-like curves, and their increasing rates were found to become greater with the acceleration of crack growth rates. Figure 16 indicates the relationship between ΔK and AE activity. AE activities at -0.8 V , E_{corr} , and -0.28 V (hydrogen evolution) continued to increase even after the plastic zone transition. On the other hand, AE activities in air or at $+0.1 \text{ V}$ clearly decreased after this transition. Cleavage-like cracking on (111) planes, was observed on the fracture surfaces by SEM when ΔK is less than $37 \text{ MPa m}^{1/2}$, where the plastic zone transition occurred. Since the number of the (111) planes was proportional to the event counts detected in air or at $+0.1 \text{ V}$, the main AE source during the fatigue process under plane strain condition in noncorrosive environment was attributed to this cleavage-like cracking.

In addition to the (111) cleavage-like cracking, many separations were nucleated, under corrosive conditions, perpendicular to the main crack surface at stringer-type nonmetallic inclusions precipitated continuously in the direction of hot rolling (Fig. 17). As shown in Fig. 18, since the high density of the separations is seen in the mid-part of the specimens, and it decreases as the K_{max} increases and the crack growth rate becomes greater in comparison with

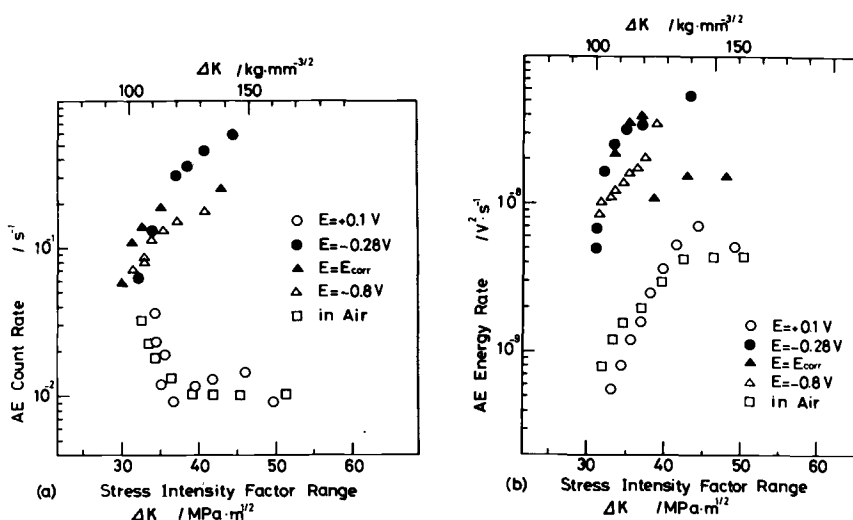


FIG. 16—Relationship between stress-intensity factor range and AE activity: (a) AE count rate, (b) AE energy rate (solution-treated case) [3,24].

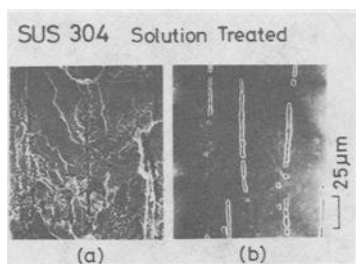


FIG. 17—(a) Microcracks perpendicular to the main CF crack surface at E_{corr} ($\Delta K = 36.6 \text{ MPa} \cdot \text{m}^{1/2}$). (b) Chain-like nonmetallic inclusions precipitated continuously in the direction of hot rolling [3,24].

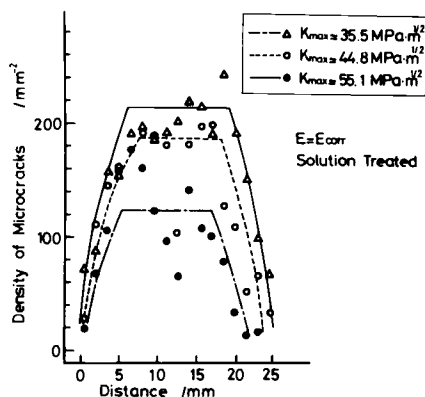


FIG. 18—Density of microcracks (separation) perpendicular to the main crack surface as a function of the distance from the specimen surface (specimen thickness $B = 25.4 \text{ mm}$) [3,24].

the hydrogen diffusion rate, it is obvious that the nucleation of the separations is due to the triaxial stress in the crack-tip plastic zone and that it depends strongly upon stress triaxiality and hydrogen diffusion process in the plastic zone. Intergranular-like cracks were observed on the sensitized fracture surface produced at $+1.1 \text{ V}$ (Fig. 19). A higher crack density was found in the mid-part of the specimen and it decreased as the stress triaxiality in the crack-tip plastic zone decreased with the increase of K value. As the effect of intergranular corrosion decreased with the acceleration of the crack-growth rate, this cracking was evidently due to cooperation of triaxial stress and intergranular corrosion caused by the preferential dissolution of carbides precipitated along grain boundaries during sensitization. Figures 20 and 21 summarize the results and schematically illustrate the relationships among AE sources, AE activity, mechanical conditions, environmental conditions and materials factors. It is demonstrated that the AE sources which provide large

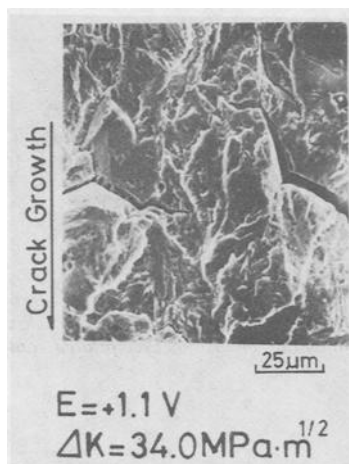


FIG. 19—Intergranular-like cracking observed on the sensitized fracture surface tested in transpassive region: $\Delta K = 34.0 \text{ MPa} \cdot \text{m}^{1/2}$ [3,24].

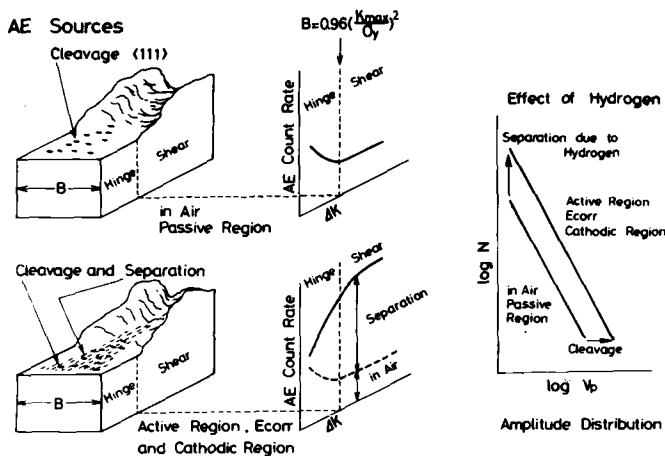


FIG. 20—Schematic representation of the effects of environmental conditions and mechanical conditions on AE activity obtained during the CF processes of solution treated 304 stainless steel [3,24].

AE activity during the CF crack growth of Type 304 austenitic stainless steels are microcracking processes such as cleavage-like cracking, separations, and intergranular-like cracking. These are caused by the cooperation of triaxial stress (mechanical conditions), corrosive environments (intergranular corrosion or hydrogen evolution), and materials factors (nonmetallic inclusions or sensitization).

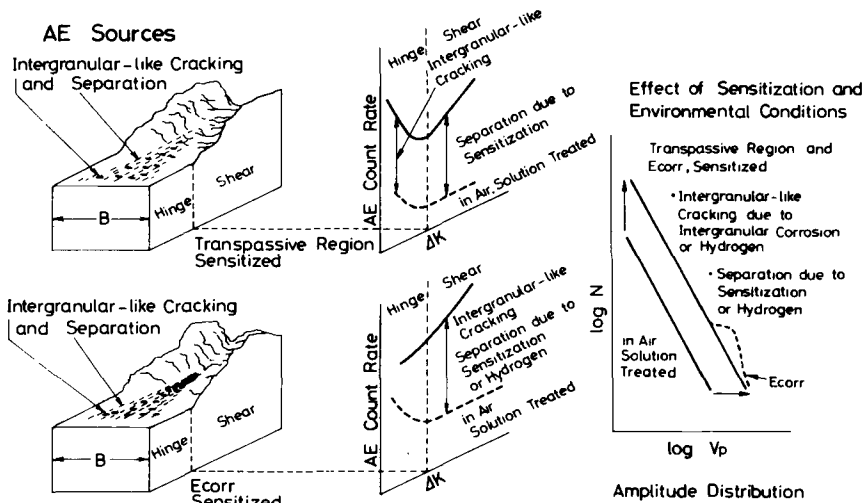


FIG. 21—Schematic AE sources and explanation for the cooperation of environments (intergranular corrosion and hydrogen), triaxial stress (mechanical conditions), and sensitization which provide high AE activity during CF processes [3,25].

From these studies described above and other tests such as fracture toughness tests and tension tests using specimens that have passivation film (thick oxide film) formed in the simulated boiling water reactor (BWR) environment, a representative map is drawn on the AE amplitude distribution (Fig. 22). Relative AE amplitude levels produced by the microprocesses that may operate in connection with each recognized CF or SCC mechanism are indicated in the figure. Since the AE generated by several of these microprocesses can occur at amplitude levels comparative with those produced by hydrogen gas bubble evolution, it is suggested that further characterization of the AE signals is required before positive mechanistic identification can be made concerning CF or SCC mechanisms operative in stainless steels.

Application-Oriented Studies

Some useful results from field applications using autoclaves have been reported relating to the IGSCC problems in nuclear power plants.

The AE behavior during SCC process in Type 316 stainless steel was studied by Bentley [26]. The AE count rate was measured during SCC test in high-temperature 10% sodium hydroxide (NaOH) solution by using U-bend specimens with waveguide. As shown in Fig. 23, high emission rate was observed as the solution temperature increased.

Stahlkopf et al [28] performed the SCC tests of Type 304 stainless steel pipe that had four pipe sections prepared by welding in a refreshed loop of high

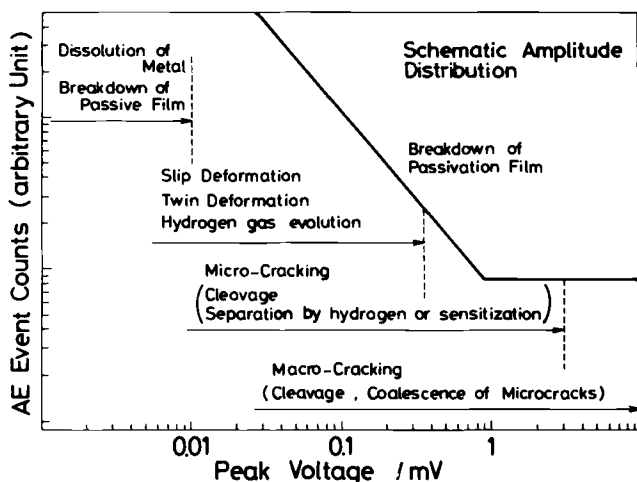


FIG. 22—Various AE sources during SCC or CF processes and their energy levels drawn on amplitude distribution [23].

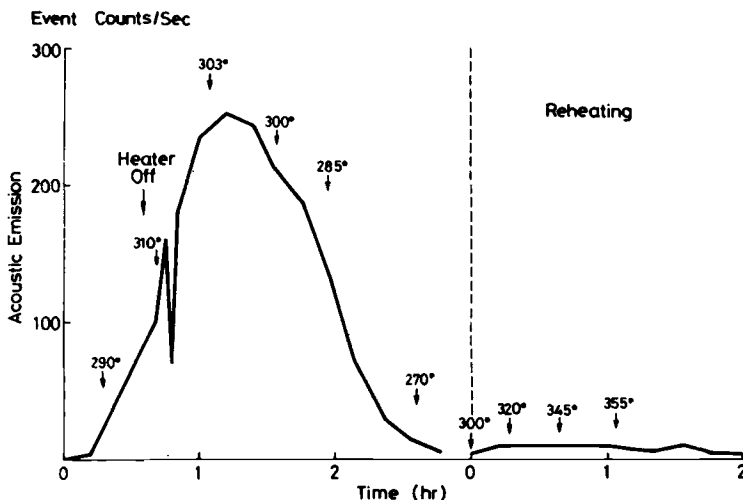
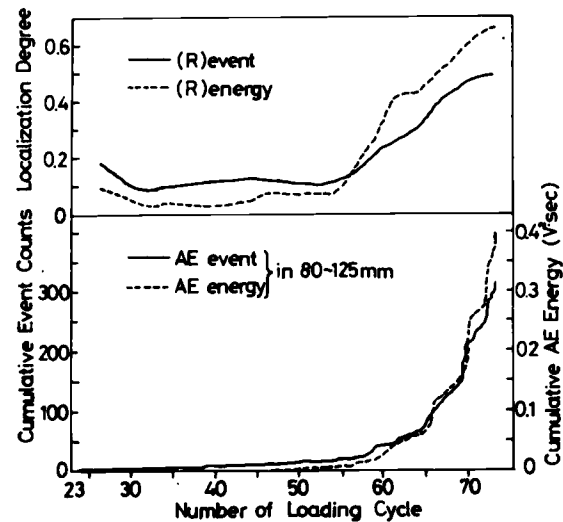


FIG. 23—AE count rate versus time during SCC test of Type 316 stainless steel in high temperature 10% NaOH solution [26].

purity water at 289°C with an externally applied bending moment. The results showed distinct AE response throughout the progress of IGSCC from initiation to pipe-wall penetration. In the course of the 23-day test period, a sustained increase in ambient AE occurred on the fourth day, apparently indicating initiation or acceleration of the IGSCC. On the fourteenth day, inter-

mittent high AE periods began to appear indicating more extensive crack increments.

The feasibility of continuous AE monitoring has been examined by Komura et al [31] to monitor SCC process of Type 304 stainless steel in a refreshed loop of high-purity water containing 8-ppm oxygen (O_2) at 289°C under a cyclic tensile loading condition. AE monitoring was carried out on the pipe test specimens. Each of them had one welded joint to obtain detailed AE characteristics from the initiation or the progress of IGSCC. The AE cumulative event count and energy showed the obvious transition during this process representing the significant and step-like increase of AE activities with the initiation and progress of IGSCC. High AE activities were found to be concentrated near the welding line by the AE source location using inner two sensors and outer two sensors to prevent the location error caused by mechanical noises which come from the loading fixture. In Fig. 24, two ratios are defined. These are an event count ratio, $(R)_{event}$, showing the extent of location of AE event, and, an energy ratio, $(R)_{energy}$, showing the extent of localization of released AE energy. These ratios are very useful in monitoring IGSCC as demonstrated in Fig. 24.



$$(R)_{event} = \frac{\text{Event count located in watched zone}}{\text{Total event count located between two inner sensors}}$$

$$(R)_{energy} = \frac{\text{Released AE energy in watched zone}}{\text{Total released AE energy between two inner sensors}}$$

FIG. 24—Degree of localizations of source location; practical parameter to represent the AE activity in a known area of interest [31].

Nakajima et al [50] have recently made an attempt to detect and analyze AE from CF process of A533B in a simulated BWR water environment using the linear-compliance specimens (T-DCB specimens) with stainless steel waveguides. The discrete AE signals could be identified by reducing the frictional noises from the loading pins and the specimen, and characterizing the spectrum of signals emitted from various sources. The empirical relationship between the AE energy and the crack-growth rate (Fig. 25) supported the conclusion that the AE technique can provide semiquantitative means of detecting and monitoring the CF process in the simulated BWR environments. This process would be quantitatively monitored in real plants if other technical difficulties associated with estimating the crack-growth rate are solved.

SCC of a structural steel used in the construction of blast furnace domes has been monitored by AE [51]. The initial feasibility study led to a 32-sensor matrix being established across the area of each dome apart from the crown nozzle and lower transition weld areas. Location of the discrete packets of sound generated by incremental crack extensions was done by timing with respect to the first threshold crossing or peak amplitude of the signal. The AE

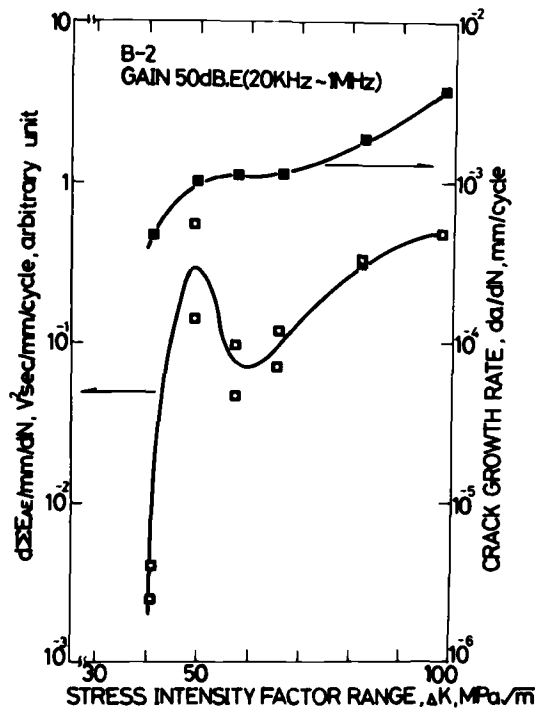


FIG. 25—Dependence of crack growth rate and AE energy as functions of stress-intensity factor range for material with martensite [50].

monitoring system was designed to operate continuously for at least the campaign life of the furnace (eight years) and was finally installed on the four stoves at Redcar, U.K.

Since boiling water reactor (BWR) environment is rather noisy, the discrimination of valid AE signals from environmental noise seems to be most important for AE monitoring of IGSCC process. It is known that the noise emission level at sensor output during the normal operation of BWR is several hundreds μV , but the peak amplitudes sometimes reach millivolt order during shutdown or start-up of a reactor as a result of mechanical vibrations, impacts, friction, hydraulic flow, cavitation, etc. On the other hand, as shown in Fig. 22, the largest amplitudes of valid AE signals from IGSCC crack growth or mechanical breakdown of thick oxide film are expected to be some mV [3,29,30]. Therefore, IGSCC process can be monitored by AE if valid AE signals are discriminated from environmental noise by setting the proper threshold level. While there are few investigations in the literature, AE should also find its large applications in chemical plants. It is well known that localized corrosion, such as crevice corrosion, SCC, and CF, is a pressing problem in using stainless steels in chemical plants. AE will be a powerful tool to monitor these processes and incipient failures. Practical limitations and problems to apply AE are believed to be almost identical to those in the case of nuclear power plant.

Discussion

It is important to identify each AE source and its energy level for better understanding and analysis of such complicated phenomena as corrosion, stress corrosion cracking, and corrosion fatigue by means of AE techniques.

Among those illustrated in Fig. 1, stronger AE sources are hydrogen evolution by cathodic reaction, crack propagation, mechanical breakdown of thick oxide film, martensitic transformation induced by strain or hydrogen, twin or slip deformation, microcracking, and fracture or decohesion of inclusions in the plastic zone. At present, it is difficult to determine the absolute values of AE energy because of the attenuation or reflection during the wave propagation, and the modulation of the waveform and frequency spectrum, which arises from the characteristics of the sensor [52]. However, relative AE energy level can be roughly rated by comparisons of AE amplitudes measured on laboratory specimens by conventional piezoelectric (PZT) sensors. Herein, the respective AE sources are illustrated and discussed from the viewpoint of their energy levels (peak amplitudes at sensor output on laboratory specimens).

Hydrogen evolution is one of the most important AE sources during corrosion process under some circumstances such as in acid solutions where the reduction of hydrogen ion is predominant as cathodic reaction [3-8,44]. Although the AE source mechanisms are not yet clear, hydrogen bubble forma-

tion, hydrogen absorption or desorption, blister formation due to hydrogen gas as a precursor of pitting [53], and hydride formation in some alloys appear to provide sufficiently high AE energy to detect. The highest AE energy level from these sources is shown to be some hundreds of μV [3]. Thus, though the precise AE source mechanisms are not yet known, it has been demonstrated that the AE techniques have the potential usefulness for the detection and monitoring of active corrosion.

Another most important AE source during localized corrosion processes such as stress corrosion cracking and corrosion fatigue is crack initiation and extension induced by corrosive environment. This type of AE is usually deeply related to the so-called "crack-jump," the transient local elastic energy release during the crack movements. It has been found that there exist quantitative relations between AE associated with crack-jump and the new crack area developed as a result of crack extension [54,55]. It appears that this crack-jump can be classified into two categories. The first one is microjump caused by microvoid coalescence or transgranular or intergranular cleavage. The scale is typically of the order of a grain size. The second one is macrojump caused by large-scale void coalescence or cleavage. The scale is much larger than grain size. The AE energy level from crack-jump seems to be dependent on the mechanical properties (microstructure) of the materials, the stress triaxiality ahead of the growing crack, etc. The elastic energy release from microjump is considerably smaller compared with that of macrojump. The highest energy level from the former is expected to be mV order [56]. The macrojump, in contrast, can provide higher AE energy because of its large energy release during the crack movements. The measured AE amplitudes in this case sometimes reach several tens of mV in high-strength titanium or aluminum alloys, high-strength steels, etc. [21,37,38]. Corrosive environments, especially the existence of hydrogen near the crack tip, will provide higher AE activities in terms of emission amplitude, count rate, and energy rate in some steels and alloys.

In the crack-tip plastic zone ahead of the growing crack, there are some phenomena which can be AE sources. They are slip or twin deformation, martensitic transformation, fracture or decohesion of inclusions, and microcracking.

During slip deformation, continuous type AE is observed and its amplitude is no higher than several tens of μV [57-59]. On the other hand, during twin deformation, burst-type AE is observed and its amplitude sometimes reaches one or two hundreds μV [37,38].

In metastable austenitic stainless steels such as Type 304 and 316 steels, it is known that martensitic transformation is induced by strain or hydrogen. This transformation has been shown to provide two or three hundreds μV emission amplitudes [60,61].

The AE energy level produced by fracture or decohesion of inclusion (and second-phase particles), such as elongated manganese sulfide (MnS) in

steels, iron-rich inclusions in aluminum alloys, and carbides precipitated at grain boundaries in stainless steels, appears to depend on its size, geometry, orientation, etc. [62-67]. Fairly high amplitude AE, whose amplitude is larger than 1 mV, can be expected from this source in some cases. As for MnS inclusions, it has been reported that hydrogen-induced blisters that may develop into cracks in line-pipe steels initiate at elongated MnS inclusions in hydrogen sulfide environments [68,69]. This hydrogen-induced cracking should provide sufficiently high AE amplitude to detect.

The maximum AE amplitude from microcracking in the plastic zone is reported to be mV order [21,37,38]. Since this microcracking is considered to be a precursor of the main crack extension and observed during incubation period of environmental cracking, AE technique can be used to predict and detect the occurrence of stress corrosion cracking or corrosion fatigue in the early stages.

Relatively high amplitude AE, whose level may reach mV order, is emitted from the mechanical breakdown of passivation (thick oxide) film [3,30,32]. It is known that the thickness of this passivation film can be μm order and the film is formed during SCC process of copper alloys in tarnish solutions, and that of stainless steels in high-temperature high-purity water or polythionic acids, etc. Therefore, it may be possible to detect and monitor this type (tarnish-rupture) of SCC by using the AE technique. It has been revealed, however, that the breakdown of passive film, whose thickness is nm order, does not provide sufficiently high AE energy to detect [3]. The maximum emission level from this source appears not to exceed $10\ \mu\text{V}$, because the lowest detectable emission level of current AE instruments is thought to be more or less $10\ \mu\text{V}$.

It has been also shown that the AE energy from dissolution of metal is so low that it is not detectable. It seems that in this case, even the highest AE amplitude does not exceed $10\ \mu\text{V}$.

Conclusions

AE can be applied to study localized corrosion in two ways. The first approach is to study the process fundamentally and analyze the mechanism by AE technique. This technique has proven successful in laboratory studies on localized corrosion where the extreme sensitivity of AE to hydrogen evolved by corrosion and crack growth induced by stress corrosion cracking or corrosion fatigue has been demonstrated. The second approach is to detect and continuously monitor localized corrosion in-service on engineering structures. AE analysis, coupled with proof testing, has been beneficially used in testing pressure vessels, piping, and other components. Since AE provides a unique method of recognizing when and where localized corrosion is taking place, it can be also used as a tool to detect and continuously monitor this process in such components.

Practical limitations are that AE must be discernible from background noise and that AE signals must be correctly interpreted. Spatial filtering has been of the greatest value in eliminating noises which come from sources outside a known area of interest. Amplitude distributions are particularly useful to interpret the AE signals and discriminate between different source mechanisms, since it is the amplitude that reflects, though roughly, the energy level of an AE signal. Other techniques based on signal characteristics [70] such as waveform or frequency spectrum can also be effective, although as yet they are not widely used.

In conclusion, AE techniques will promise fruitful results for the detection and monitoring of localized corrosion in both laboratory specimens and engineering structures. Care must be exercised, however, to discriminate valid AE signals from background noise and to interpret the results correctly.

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Monitoring Stress-Corrosion Cracking by Acoustic Emission

REFERENCE: Martin, P., Dickson, J. I., and Bailon, J.-P., "Monitoring Stress-Corrosion Cracking by Acoustic Emission," *Corrosion Monitoring in Industrial Plants Using Nondestructive Testing and Electrochemical Methods*, ASTM STP 908, G. C. Moran and P. Labine, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 75-88.

ABSTRACT: Acoustic emission (AE) is well suited for laboratory studies of stress corrosion cracking (SCC) since the crack velocity is often approximately proportional to the AE rate. For 7075-T6S1 and 2024-T3S1 aluminum alloys, this proportionality is shown to be particularly good. For 7075-T6S1, less scatter is obtained in SCC crack velocity when these are based on the cumulative AE counts than on surface crack length measurements. The curve of AE rate versus time after addition of fresh solution into the crack depends on the type of transducer employed. Using either a broad-band or a resonant transducer, it was possible to distinguish between SCC and corrosion signals from their frequency spectrum.

The applicability of employing AE to detect SCC in an industrial environment is considered. Possible solutions to some of the difficulties expected in cases where SCC produces low-amplitude AE signals are discussed.

KEY WORDS: acoustic emission, stress corrosion cracking, corrosion, aluminum alloys, industrial applications

The utilization of acoustic emission (AE) to study stress-corrosion cracking (SCC) in the laboratory is increasing in popularity as researchers better realize the potential of this technique. AE can also be employed to monitor or to inspect real structures, and its applicability in detecting SCC under service conditions is of obvious practical interest. The applicability of employing AE for studying or monitoring SCC can be appreciated from the number of materials for which it has been shown the AE rate is at least approximately proportional to the SCC velocity, v . These materials include high strength steels

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[1,2], mild steel [3], aluminum alloys [3-6], a uranium alloy [7], and brass [3].

To more clearly show the relationship between v and the AE rate in 2024-T351 aluminum alloy, Blain et al [4] considered the number of AE counts, N , per unit of crack advance, Δa , for the crack immersed in 3% sodium chloride (NaCl) aqueous solution. Their results (three specimens) are reproduced in Fig. 1 as $N_a = N/\Delta a$ plotted against the stress intensity, K . The increased value of N_a above $K \approx 23$ MPa was associated with increasing amounts of crack branching and secondary cracking. For 7075-T651, the present authors [5] obtained similar results (Fig. 1) for tests in which 3.5% NaCl solution was periodically added to the crack mouth (three specimens). This periodic addition, moreover, resulted in a pronounced maximum in AE rate and in SCC velocity several hours later.

The objectives of the present paper are to present further results which show that AE is particularly well-suited for studying SCC, to show that the AE signals produced by this SCC have recognizable signatures, and to discuss the applicability of employing AE to detect or monitor SCC in real structures.

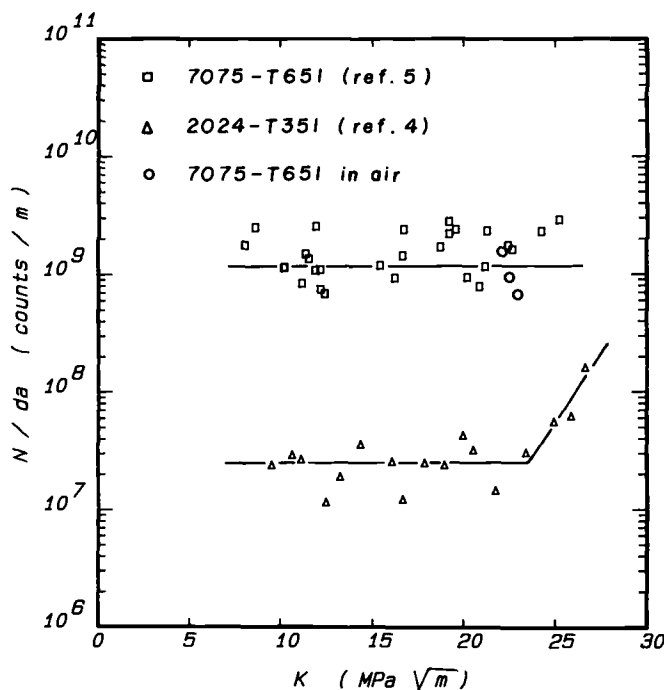


FIG. 1—Curves of N_a , number of AE counts per unit of crack advance, versus K for 2024-T351 fully immersed in 3% NaCl solution [4] and for 7075-T651 tested both with periodic addition of 3.5% NaCl solution [5] and for cracking in air.

Experimental Procedures

The materials studied were 7075-T651 and 2024-T351 aluminum alloys, purchased as 19-mm-thick plate. Bolt-loaded precracked double cantilever beam (DCB) specimens, 126 mm in length, and of 19-mm² cross section were employed. The crack propagation orientation was SL, that is, propagation parallel to the plate surface and parallel to the rolling direction.

SCC tests were performed by periodic addition of a 3.5% aqueous solution of NaCl into the crack mouth. Optical crack length measurements were performed prior to each addition. The transducer was positioned near the bottom of the specimen on a face perpendicular to the crack plane. Corrosion experiments were performed in the same solution employing uncracked DCB specimens without any applied load. The portion immersed in solution was covered with protective varnish except for a 19 by 30-mm section on one face. The transducer was placed on the opposite face above the solution.

Acoustic Emission Technology (AET) Corp. equipment was employed, and a 60-dB preamplifier was used for all tests. SCC velocity tests were performed employing a 201 signal analyzer with 99 dB of total gain. A 204 BR analyzer was employed for comparing the different transducer-band pass filter combinations and for recording signals for analysis. The transducers employed were a AC 375 resonant transducer and a 0.1 to 2-MHz FC 500 broad-band transducer. Either a narrow (250 to 500 kHz) or a broad (0.125 to 2 MHz) bandwidth filter was employed. The cumulative count over a fixed threshold was recorded as a function of time on a strip-chart recorder. Signals of interest were sent to a digital oscilloscope (Nicolet Scientific model 204) for sampling and storage on floppy disks. The frequency content of individual signals was analyzed employing a fast Fourier transform computer program.

The values of K applicable to a given crack length and load-point opening displacement were determined as described by Blain et al [4,8]. These authors [8] have also discussed factors causing the effective K -value to differ from the calculated value in bolt-loaded specimens.

Results

SCC Velocity Measurements on 7075-T651 Aluminum Alloy

Three measurements of N_a obtained on two specimens of 7075-T651 tested in laboratory air ($\approx 45\%$ relative humidity) have been added to Fig. 1. The value of N_a obtained under similar AE monitoring conditions appears very similar in air and in 3.5% NaCl solution.

Figure 2 compares, for 12 h of SCC after addition of solution, the dispersion between values of v obtained by optical crack length measurements and between values based on the cumulative AE count and N_a ($10^9/\text{counts/m}$). The latter shows significantly less dispersion, probably because they represent a measure of SCC occurring in the entire specimen and not only at the

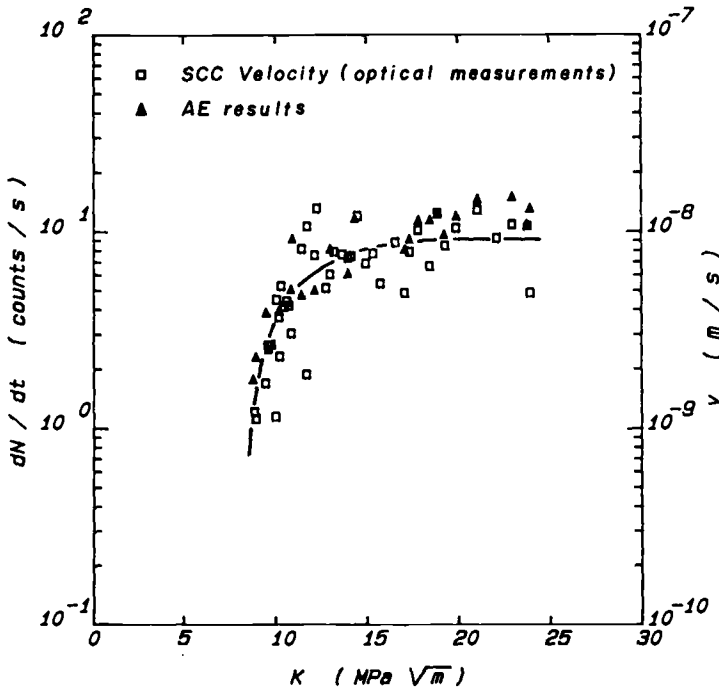


FIG. 2—Average AE count rate and average SCC velocity measured optically and calculated from the AE rate for periods of 12 h after addition of fresh solution into the crack (7075-T651 alloy).

surface. These results indicate that the use of AE can actually improve precision for monitoring SCC in the laboratory. With the form of the AE rate or v versus time curve of Fig. 3, low dispersion in the measurements will be obtained only for tests carried out at or based on a constant time interval after the addition of fresh solution. As well, the time to the maximum velocity is seen to increase with increasing crack length. This time also appeared to be somewhat sensitive to the amount of solution added as well as to the elapsed time since the previous addition.

Because of the occurrence of this maximum in SCC velocity, it was decided to verify whether a vertical crack running upward would propagate as rapidly as one running downward. A test was performed in which the DCB specimen was inverted several minutes after the solution addition. This procedure had little influence on v or on the AE rate versus time variation. The indication is that capillary action at the crack tip tends to prevent the crack direction from having a major influence after wetting.

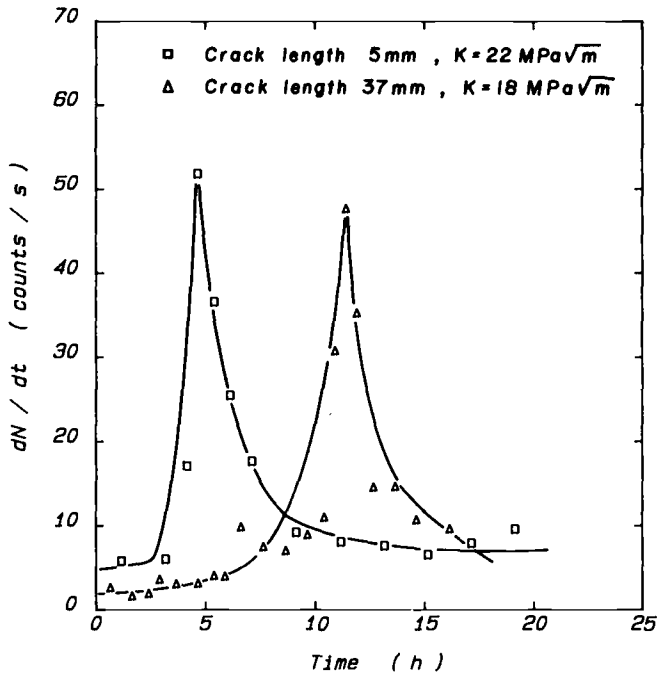


FIG. 3—Variation in AE rate as a function of time after solution addition (7075-T651 alloy).

Influence of Transducer-Band Pass Filter Combination

Tests were carried out to compare the influence on the N versus time recordings of the use of a resonant and a broad-band transducer, each employed with either a narrow (250 to 500 kHz) or broad (0.125 to 2 MHz) band-pass filter (BPF) as well as of the gain and the threshold level employed. The possible interest in using the 0.125 to 2 MHz BPF with the resonant transducer is that while this transducer is most sensitive at the resonant frequency (377 kHz according to analyses of signals), it is not completely insensitive at other frequencies and can be of some use in signal recognition. In particular, the second most sensitive frequency response of the transducer employed was ≈ 117 kHz [4]. The possible interest in using the narrow BPF with the broad-band transducer is for noise elimination; however, this combination seriously reduces the usefulness of this transducer for recognizing signals by their frequency spectra.

In previous tests using several broad-band transducers including the FC 500, a similar 0.125 to 2 MHz BPF and similar, but not identical equipment, Blain et al [4] had not been able to detect AE signals from SCC of 2024-

T351 aluminum alloy for conditions of constant immersion of the crack in 3% NaCl solution. In the present tests, signals from SCC produced by periodic wetting of the crack were detected for proper gain and threshold settings on 7075-T651 and 2024-T351 aluminum alloys. Signals produced by corrosion were similarly detected during a certain period, after which such signals could no longer be detected in new tests, typifying possible problems associated with employing such a transducer to detect low amplitude AE signals.

The chosen settings of total gain and threshold levels for the different transducer-filter combinations are given in Table 1, which also lists the resulting approximate signal-to-noise ratio for SCC in 7075-T651. This signal-to-noise ratio was measured by taking the average count rate corresponding to the K independent (Stage 2) portion of the v versus K curve (that is, the portion in Fig. 2 for $K \geq 14 \text{ MPa} \cdot \text{m}^{1/2}$) and dividing it by the count rate obtained with the transducer placed on a dry uncracked specimen.

The less sensitive response of the broad-band transducer results in having to accept relatively low values of signal-to-noise ratio (Table 1). The broad BPF tends to increase the noise level and therefore to decrease this ratio. Especially with this transducer-filter combination, proper judgment must be employed to choose the optimum combination of gain and threshold settings so as to best be able to follow the SCC. This depends on obtaining a sufficient signal-to-noise ratio and on still detecting a sufficiently high percentage of the signals of interest.

The cumulative count as a function of time after solution addition was measured for the four transducer-filter combinations. For the AC 375 transducer with the broad BPF (Fig. 4), signals were received at a fairly continuous rate and even for the slower velocities the waiting time between signals was gener-

TABLE 1—*Influence of transducer and filter on AE results, 7075-T651.*

Transducer Band-Pass Filter	AC 375		FC 500	
	250–500 kHz	0.125–2 MHz	250–500 kHz	0.125–2 MHz
AE settings				
total gain	100 dB	94 dB	100 dB	94 dB
threshold setting	0.96 V	1.22 V	1.15 V	1.27 V
SCC Velocity results				
SCC signal/noise ratio	$\cong 250$	$\cong 250$	$\cong 16$	$\cong 12$
N_a counts/m	14.9×10^8	9.1×10^8	9.4×10^7	6.5×10^7
Principle frequency peaks				
Type A corrosion signals	NS ^a	117	NS	174
Type B corrosion signals	NS	377	NS	436
SCC signals	NS	377 and 117	NS	174 and 436–500

^aNS = not studied.

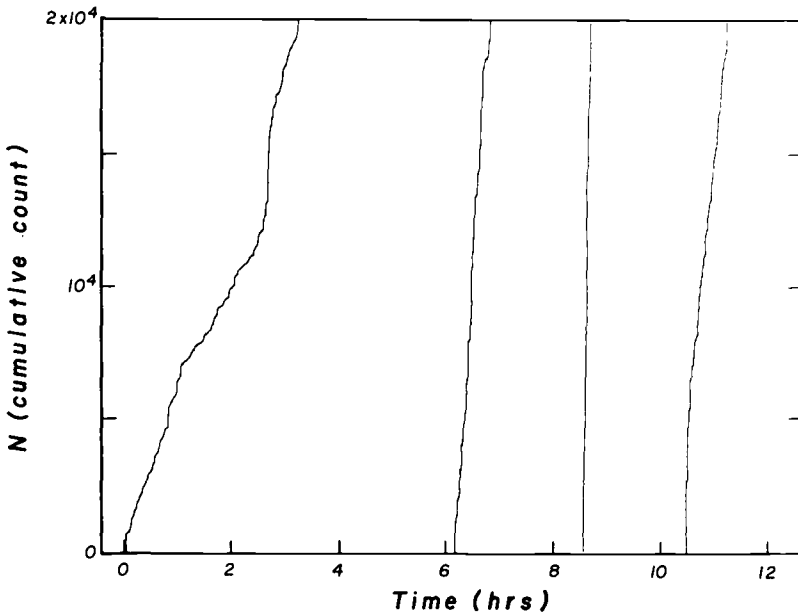


FIG. 4—Example of portions of strip-chart record of cumulative count versus time after addition of solution obtained with a resonant transducer in combination with broad-band pass filter.

ally short. Many of the signals detected were of relatively low amplitude since the count rate between the numerous jumps in the cumulative count curve was still considerably higher than the noise rate. The curve obtained employing this transducer with the 250 to 500 kHz filter was very similar. Changing to the broad-band transducer indicated a much more discontinuous phenomenon since the cumulative count versus time curve (Fig. 5), the form of which did not depend on the BPF, consisted of discrete jumps in N with the count rate between jumps equal to the noise rate. The typical waiting time between jumps in N was 10 to 15 min at the lower velocities and a few seconds at the highest velocities. The height of the discrete jumps in N were comparable to those observed with the resonant transducer, which, however, also detected many of the lower amplitude signals associated with SCC. The measured values of N_a for these different tests are found in Table 1.

A few preliminary tests were also performed on 2024-T351, although from a different plate than employed by Blain et al [4], to compare its behavior to 7075-T651. The Stage 2 (K -independent) velocity was 10% to 20% lower in the 2024-T351 material. The number of counts per unit crack advance in Stage 2 ($K \approx 19 \text{ MPa} \cdot \text{m}^{1/2}$) was approximately half of the N_a for the 7075-T651 alloy. However, for $K \geq 23 \text{ MPa} \cdot \text{m}^{1/2}$, Blain et al [4] found a considerable increase in N_a associated with the occurrence of crack branching and

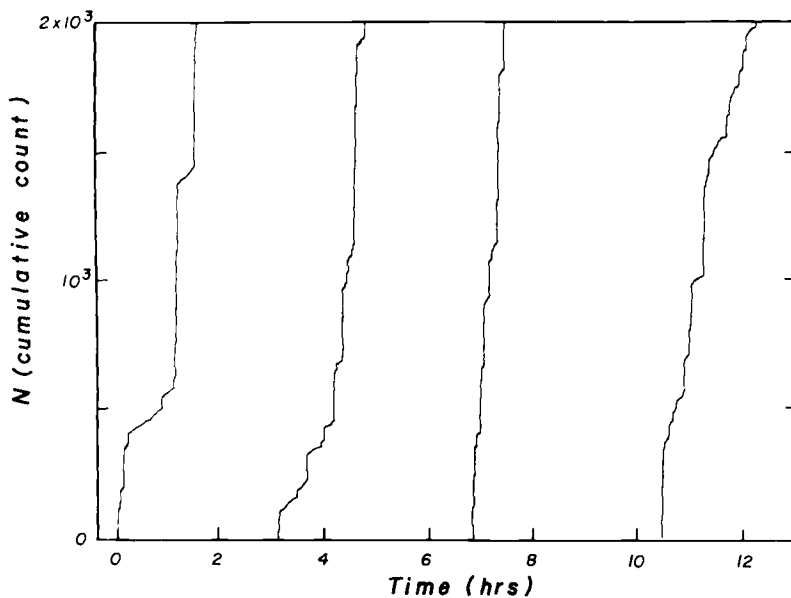


FIG. 5—Example of portion of strip-chart record of cumulative count versus time after addition of solution obtained with a broad-band transducer in combination with broad-band pass filter.

secondary cracking, while such behavior was not observed in the higher-strength 7075-T651 alloy [5]. SCC is generally considered to result from hydrogen embrittlement in the 7075 material [9-11] and from anodic dissolution in the 2024-T351 alloy [11-14]; nevertheless, the shape of the cumulative count versus time curve, employing either transducer, was rather similar. In a few tests on 2024-T351, however, the maximum count rate obtained a few hours after the addition of solution was less clearly observed, although this may be due to other factors and is being investigated further.

The noninfluence of K on N_a in the absence of significant crack branching effects can be related to the observations that the signature of the AE signals produced by SCC was independent of K as observed in the present experiments and as observed previously on 2024-T351 [4]. However, the rate at which AE events occurred was dependent on the SCC velocity.

Signal Recognition

Analyses were performed on individual signals obtained on both alloys in an attempt to differentiate between signals produced by SCC and those produced by corrosion. An earlier attempt by Blain et al [4] to differentiate between such signals on 2024-T351 employing the AC 375 transducer and a

0.125 to 2 MHz BPF with constant immersion of the crack in the solution had been unsuccessful. The problem there was that the recorded signals were of quite similar amplitude and the average frequency content of series of signals were also very similar. In the present tests this type of transducer-BPF combination was employed, as well as this type of filter with the FC 500 transducer, and individual signals were analyzed.

The frequency response of the AC 375 transducer employed has been given by Blain et al [4]. The essentially flat response of the FC 500 transducer in combination with the BPF for frequencies above ≈ 125 kHz has been verified by Blanchette [15].

Two types of signals were recorded during corrosion tests employing either transducer. Examples of these and of signals produced by SCC are compared in Fig. 6. The two types of corrosion signals were (similar to previous results [4]) a signal (Type A) containing a more important lower-frequency content and a signal (Type B) containing a higher-frequency content. Both types of signals generally contained a single principal frequency peak (Fig. 7, Table 1). In contrast, individual signals associated with SCC contained both as principal peaks (Fig. 7, right), with the lower frequency peak generally higher for signals recorded with a broad band transducer and vice versa for the AC 375 transducer, in agreement with their differences in response. In addition, the AE signals produced by SCC and recorded employing the broad-band transducer contained the multiple reflection peaks. Their presence up to frequencies of 600 to 750 kHz was still slightly noticeable with the AC 375 transducer, but was not a feature of the frequency spectrum of corrosion signals.

Signals similar to the Type B corrosion signals appeared associated with the increased AE activity immediately after the addition of fresh solution to the crack. The Type B signals also dominated at the start of the corrosion experiments, in agreement with previous results [4], as well as following stirring of the solution.

The amplitude of the AE signals produced by corrosion and by SCC also differed. The amplitudes obtained with the AC 375 transducer-broad BPF combination were generally less than 4 V for the corrosion signals and 4 to 6 V for the SCC signals. Some of the latter occasionally saturated the equipment (> 8 V). Only very occasionally and only at the start of tests did corrosion signals also saturate the equipment.

No significant difference was found in the characteristics of the SCC or of the two types of corrosion signals produced on 2024-T351 compared to those on 7075-T651.

These results thus showed that corrosion signals could be distinguished from SCC signals, even when a resonant transducer was used in combination with a broad BPF. When used with signal recognition techniques, this combination, still should be more practical to use to detect low amplitude signals on a real structure than a broad-band transducer.

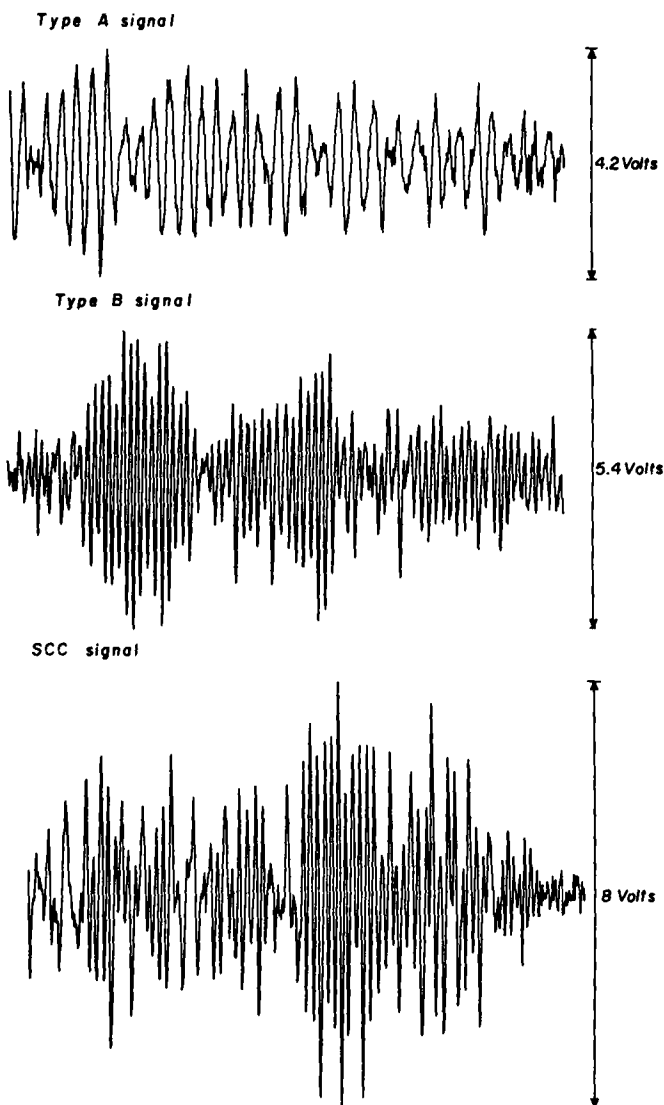


FIG. 6—Typical low (Type A) and high (Type B) frequency signals recorded during corrosion and typical signal recorded during SCC.

AE Applied to Detecting SCC in Industry

A number of problems can be envisaged in applying AE for detecting SCC in industrial applications, especially in the case of materials for which the AE signals produced by SCC are of low amplitude. In the case of high amplitude signals which are emitted in sufficient numbers and sufficiently frequently,

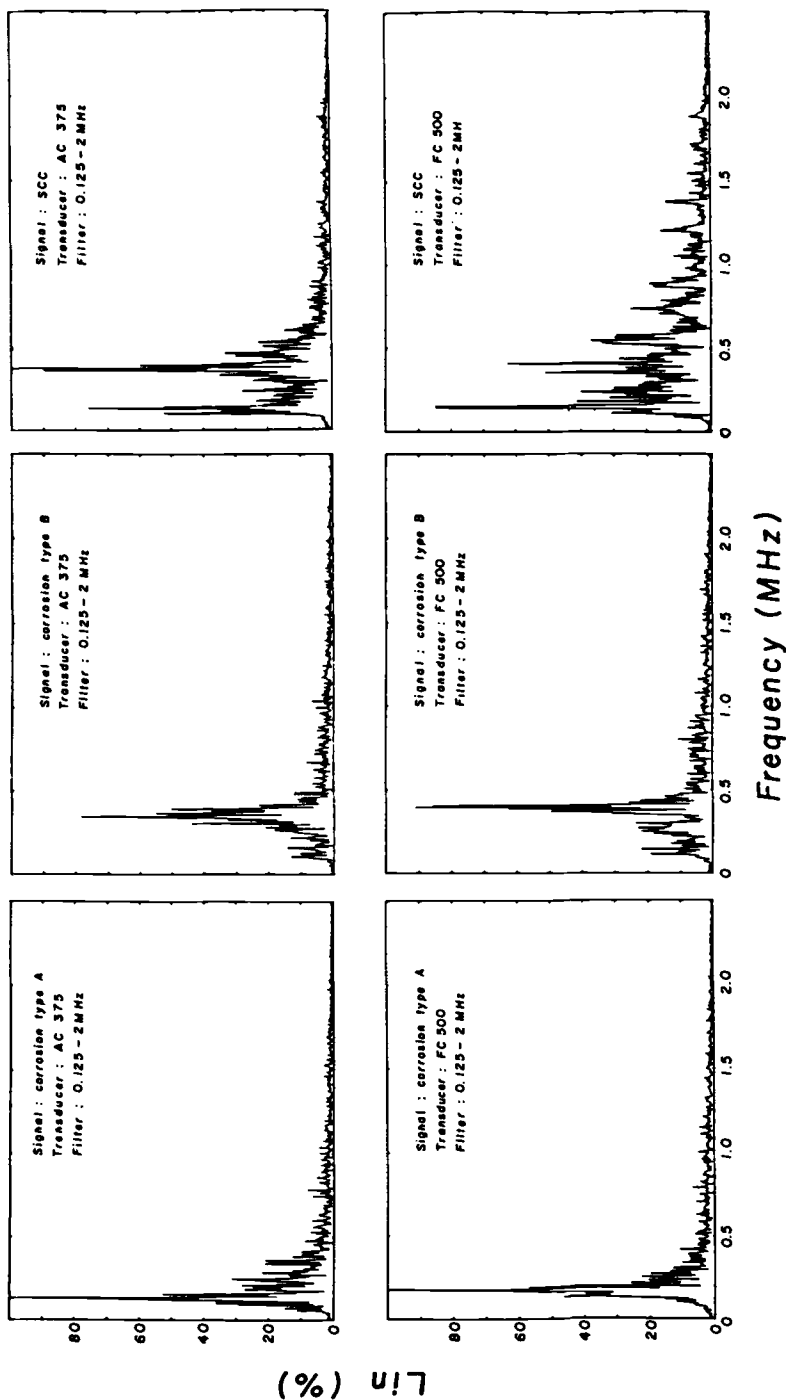


FIG. 7—Frequency spectra given as percentage of highest peak in spectra (at times a noise peak is present at 0 MHz and is not shown) for typical corrosion and SCC signals for two transducers in combination with broad band-pass filter.

the use of AE to detect and locate SCC can be expected generally to be reasonably straightforward. Some problems may be encountered in monitoring SCC velocities since this necessitates knowing N_a for the monitoring conditions and distinguishing between a large crack giving a high count rate and a large number of small cracks producing a similar count rate, which may be possible in materials where the signature of the signals including the amplitude are a sufficiently reproducible and well-identified function of K .

Some studies [1,2,16] suggest that this may be the case for SCC hydrogen embrittlement cracking of high-strength steels. This procedure would first involve obtaining an indication of K from the signatures of the acoustic emission signals. If the stress levels and expected crack shape and orientation are reasonably well known, it should be possible to estimate the crack length associated with the indicated K level. The presence of residual stresses, of course, could considerably complicate this procedure. Sufficient prior testing would also be required to determine the reliability with which crack lengths could thus be estimated. The study of the signatures of the AE signals should always be useful to reduce the number of false indications where another phenomenon produces AE signals which are mistaken for those produced by cracking. This requires knowledge of the expected signatures of signals for the different AE sources with respect to the AE equipment and setup employed and for the material and structure being studied (rather than for laboratory specimens not geometrically representative of this structure).

In the case of SCC producing lower-amplitude signals, the use of signal recognition techniques [17] should become particularly important in separating SCC signals from noise or from signals produced by other phenomena such as corrosion. The choice of the transducer, band-pass filter, amplification gain, and threshold setting can then become particularly critical to being able to reliably identify the signals produced by SCC. In such cases, a considerable amount of preliminary testing will generally be required to identify the signatures of the different signals for that material and structure and to optimize the monitoring conditions so as to be able to reliably detect the signals produced by SCC.

For low-amplitude SCC signals it may be necessary to position transducers considerably closer to the SCC crack than for higher-amplitude signals, which may make it impractical to monitor entirely a large structure. Knowledge of the sites at which SCC is particularly susceptible of occurring, for example, at or near weldments or at particular geometrical features, may still permit the monitoring of these more critical regions. In such a case, a multi-channel AE system with a number of transducers can be employed first to detect the possible occurrence of SCC. The transducers can then be repositioned at shorter spacings about that at which SCC was suspected, with the possible use of spatial discrimination to verify the occurrence of this cracking and to locate the crack-tip sites. Again, sufficient preliminary tests must be performed to properly choose the spacings between the transducers, espe-

cially in the initial monitoring, so that a high degree of probability exists that any SCC occurring in the region of the structure being investigated will in fact be detected. Signal recognition techniques should be employed during one or both of these monitoring steps to verify the nature of the AE sources located.

In the case of at least some aluminum alloys and intermittent wetting, use can be made of the occurrence of a maximum crack velocity several hours after wetting to temporarily remove the part from the service environment and to monitor for the occurrence of SCC under conditions where noise is less of a problem. This may, for example, be applicable in the case of aircraft parts. It is also possible to consider artificial wetting of the part with salt solution prior to doing the AE monitoring, if there is sufficient assurance that this intentional wetting will not reduce to any significant extent the service life and especially that it will not initiate any new stress corrosion cracks. It should be noted that the present tests indicate (Fig. 3) that the time to this maximum is significantly influenced by the crack depth, which suggests that this procedure may be difficult to apply to detect the presence of very short cracks.

The maximum in AE and SCC rates some time after wetting should reflect changes with time in the characteristics of the solution in contact with the crack tip. Accordingly, it should not be expected to occur for all combinations of material and environment. For the combinations in which it does occur or in which cracking continues for some time at a sufficient rate after removal of the solution from contact with the structure, such a procedure may often permit the detection of SCC by AE under conditions in which problems with extraneous noise have been considerably reduced.

Conclusions

From the present study, it can be concluded that acoustic emission is a technique particularly well-suited for studying SCC in the laboratory. It should also be well applicable to detecting or monitoring SCC in real structures when the resulting AE signals are of high amplitude. However, when the signals produced by SCC are of low amplitude, as in the present study, the reliable detection or monitoring of such signals in real structures will be much more difficult. Detection and monitoring may still be feasible if sufficient background information on the characteristics of the SCC in the structure under consideration and on the characteristics of the AE generated by this SCC in this structure is available. In some situations, it may be possible to increase the probability of reliably detecting and monitoring these low amplitude signals by making the monitoring conditions more similar to those typical of laboratory studies.

In general, to reliably detect SCC by AE in real structures will require considerable preliminary testing, especially when the AE signals produced are of low amplitude.

Acknowledgments

The authors are indebted to Yves Blanchette, M. N. Bassim, and D. R. Hay for helpful discussions. Financial support from the NSERC (Canada) and FCAC (Québec) programs is gratefully acknowledged.

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Nondestructive Inspection with Portable Ultrasonic Imaging System

REFERENCE: Grills, R. H. and Tsao, M. C., "Nondestructive Inspection with Portable Ultrasonic Imaging System," *Corrosion Monitoring in Industrial Plants Using Nondestructive Testing and Electrochemical Methods*, ASTM STP 908, G. C. Moran and P. Labine, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 89-101.

ABSTRACT: The device described herein is a microprocessor-controlled ultrasonic imaging system, the Ultra Image III, originally developed for the inspection of corrosion/erosion inside seawater pipelines. It has been used successfully for many other types of non-destructive testing (NDT) applications, including intergranular stress corrosion cracking detection in nuclear piping systems. It consists of four packages each with a weight of less than 13.6 kg (30 lb): the microprocessor, the dual-diskette drive, the ultrasonic pulser/receiver/gate package, and the display package that consists of an A-scan scope and a two-dimensional imaging scope. The scanner, equipped with pulse/echo or pitch/catch transducers, can function automatically or manually. Information for operational controls is input using a hand-held terminal that can be placed at remote distances from the test site. Output results are displayed in two-dimensional format in gray scale indicating the thickness of the pipe wall after corrosion/erosion effects. Test results are stored permanently on floppy diskettes for on-site overview and off-site detailed analysis.

The system is further equipped with a variety of software packages providing capabilities for a multicolor display of the size, configuration, and distributions of erosion patterns or flaw and crack orientations or both inside the tested material. The portability and versatility of the system is demonstrated with examples of different applications.

KEY WORDS: corrosion, cracks, erosion, imaging, microprocessor, nondestructive testing, portable, tomography, transducer, ultrasonic testing (UT), hydrogen blistering

One of the major advantages that a conventional, hand-held ultrasonic testing (UT) system possesses is its portability. The basic equipment used in conventional UT is a flaw detector plus one or two transducers. The flaw detector built in with an oscilloscope can be as small as a lunch box and as light

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as a small bag of apples. By moving a transducer on top of a suspected structural material, an inspector interprets his or her findings as to the existence of flaws deep inside the material and the size of these flaws equivalent to certain sizes of standard flat-bottom-holes. The portability of the conventional handheld UT system, often taken for granted, has made it a favored choice over many other nondestructive testing (NDT) methods used in the field for testing structures wherever sound can penetrate. Engineering applications are so numerous that the method is considered adequate, so when only "go" and "no-go" decisions are required.

However, because of increasing public awareness of potential technological, economical, or legal problems, criteria for engineering considerations are more stringent now than ever before. Integrity is now a critical factor in structure design and construction, because many human lives, millions of dollars, and corporate reputation often depend on them. Furthermore, mechanical systems and installations are evaluated in terms of cost-effectiveness and merit of profit return. For maximum profit return per capital investment, it is essential to maintain a high level of integrity for all components during the entire designed life span of the installation. In the face of this demand, the conventional UT method, by means of spot checking with hit-and-miss results, appears just short from what is desirable. The Ultra Image III system [1], which uses modern electronics and microprocessor technology, was developed to fill the gap in the market.

Equipment and Calibration

The equipment used in the present study is the Ultra Image III system, a portable, microprocessor-controlled ultrasonic imaging and analysis system, shown in Fig. 1. The system consists of four units: the microprocessor, the ultrasonic pulser/receiver/gate package, the dual-diskette drive, and a display package of a 12.7 cm (5 in.) black-and-white monitor and a 8.9 cm (3½ in.) cathode-ray tube (CRT). Each package weighs less than 13.6 kg (30 lb), and the system can be set up for operation by trained personnel in 15 min.

The microprocessor with 8-bit central processing unit (CPU) operates at 4 Mhz. It has a memory of 576 K bytes and is expandable to 1 M bytes. The ultrasonic package consists of a pulser powered at maximum 400 V and a receiver with broad band filter up to 12 Mhz. The maximum gate delay is 999 μ s. Each of the two floppy diskettes has a formatted capacity of 628 K bytes.

A transducer, mounted on a scanner arm, can scan an area of 5.08 by 10.16 cm (2 by 4 in.) with a pixel size of 0.05 by 0.05 cm (0.02 by 0.02 in.), expandable to 50.8 by 101.6 cm (20 by 40 in.) with a pixel size of 0.508 cm by 10.16 cm (2 by 4 in.). The maximum scanning speed is 15.2 cm/s (6 in./s). Transducers with frequencies between 0.5 and 15 Mhz have been commonly used with this system for different applications. Depending on the geometry of the structure to be inspected, the scanner can be operated manually or automati-

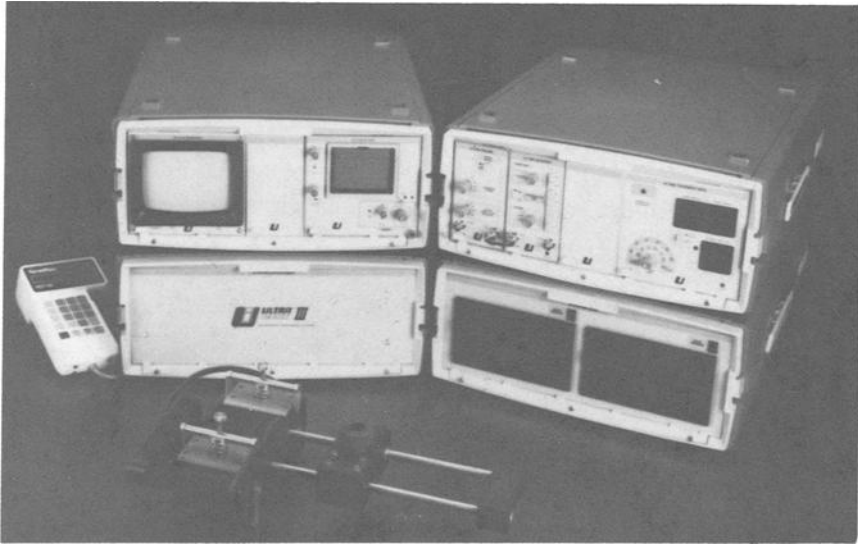


FIG. 1—*Ultra Image III system.*

cally. Information of the transducer location, the ultrasonic signal amplitude, and its time-of-flight are recorded for each pixel. Various software algorithms are programmed in the microprocessor, permitting analyses of the top, front, and side views of discontinuities inside the tested structure.

Calibration of the system is performed on a step block with known thicknesses. Using the second multiple of reflections in the calibration block, the system eliminates errors due to variance in transducers, delay lines, couplant, and electronics. System controls are monitored by the microprocessor to ensure that the system is and remains in calibration throughout the data acquisition period. All set-ups and the result data are permanently recorded on a dual-sided, double-density floppy diskette which can contain information from up to 15 tests.

The inspection results are easily analyzed through an interactive color graphics system which provides instant viewing of the ultrasonic signal amplitude and depth over the scanned area immediately after the scanning process is completed. The image can be sliced in X or Y direction and enlarged to many times its original size to aid in analyses of defect shape.

Applications

The portability and versatility of the Ultra Image III system can be illustrated in a few examples.

The corrosion of a seawater pipeline in a power plant or in a ship is a serious problem. To monitor the corrosion of these pipes inside an engine room

where space is limited, the equipment must be small in size and light in weight. Figure 2 shows a seawater pipe being examined by the Ultra Image III system. The scanner track is attached on a flange. Mounted with a spring on the scanner, the transducer is kept in uniform contact with the pipe surface to be inspected. A designated area on the pipe, including part of its elbow section, has been successfully examined. By periodically examining the same area of the pipe with this equipment, the corrosion growth inside the pipe can be monitored confidently.

The corrosion of the fuselage in an airplane is another serious problem. Although the space outside the airplane wing is unlimited for any size of inspection equipment, the Ultra Image III system is compact enough to be carried by a small airplane to a remote airfield where other airplanes on the ground were examined by this equipment [2]. The scanner was mounted on a fixture attached underneath the airplane wing by two suction cups, and the bottom fuselage panel was successfully inspected with this set-up.

For large areas to be examined, the system is versatile enough to be equipped with an automatic scanning system. The system was put through a manhole and set up inside a large oil storage tank where a large section of the bottom plate was inspected. The scanner was motor-controlled, and 50.8 by

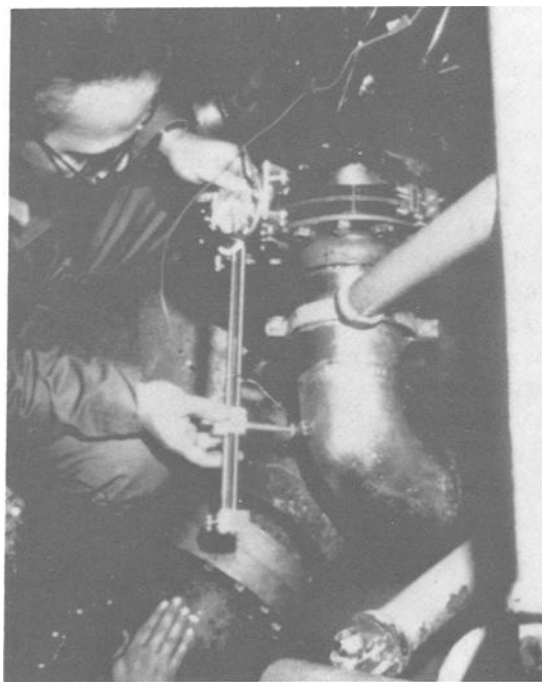


FIG. 2—Manual scanning a seawater pipeline inside an engine room.

101.6 cm (20 by 40 in.) areas were examined in successive scans to cover the entire area of interest.

Another important feature of the system is its analyzing power. Images can be evaluated as soon as the scanning process is completed. This capability enables the operator to examine the results in situ. Such applications occurred in examining corruptions of several choke valves in an oil field where decisions for more tests were to be made on-site.

Results

The display of the Ultra Image III results is designed so that the top half of the picture is reserved for mapping the internal flaw shapes and the bottom half is reserved for analysis of the cross-sectional pattern of the tested specimen. The fidelity of the ultrasonic images is compared with results from open and visual examination.

Figure 3 shows the corrosion/erosion on the inside wall of a seawater pipe which was later cut open for visual inspection. Figure 6 gives the results tested on the outside of the pipe wall with the Ultra Image III system. The bolt holes of the pipe and the corrosion pattern of the pipe wall are shown on top of the picture, which shows good agreement with that shown in Fig. 3. The depth of corrosion cannot be measured photographically, but the depth at any section of the tested area can accurately be viewed ultrasonically, as in the lower part of Fig. 6.

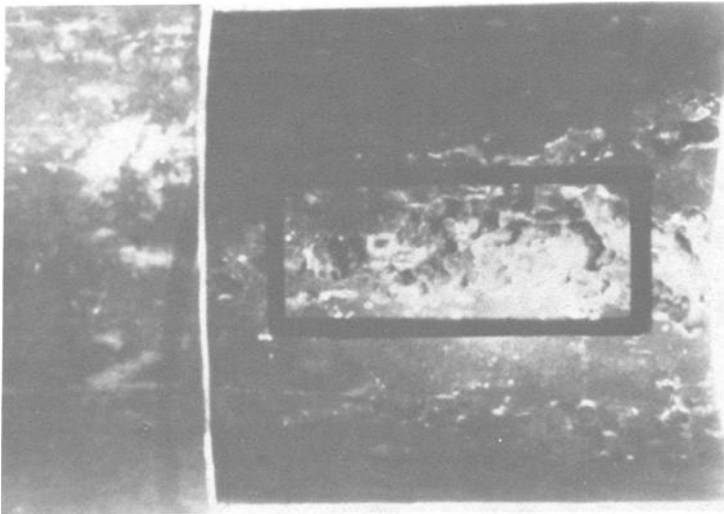


FIG. 3—*Photo of corrosion on inside wall of a seawater pipe.*

Figure 4 shows a corroded specimen from the fuselage of a commercial aircraft taken out of service, and Fig. 7 the ultrasonic imaging of the specimen. The cursor is located at pixel location (57,29). The bottom graph shows the corroded depth relative to panel thickness at section $y = 29$. From the top figure, we can see that actual corrosion has propagated underneath the rib. The corrosion underneath the rib could not be seen photographically, even though a liquid penetrant had been applied.

Figure 5 shows erosion inside a choke valve. The valve was used for regulating flows of crude oil from a well to its manifold system. Figure 8 shows an ultrasonic image of erosion of the valve wall due to solid particles in the flow. The bolt holes in the valve and the erosion pattern of the valve wall are shown clearly in the picture. The cursor is located at pixel location (123,67). The bottom graph shows the corroded depth relative to the valve thickness at section $y = 67$.

Figure 9 shows the ultrasonic image of a part of the welded region of a copper nickel pipe. On the bottom of the figure, a sectioning plot across the welds through the cursor location (101,36) indicates no corrosion in the welds itself, but does indicate significant corrosion in the heat-affected zone next to the welds. The distribution of corrosion relative to the welds in the pipe can be very useful for evaluating the strength of the welded joints.

Figure 10 shows an ultrasonic image of a steel plate taken out of a heavy water processing tank in which hydrogen sulfide and water were contained. Hydrogen migration from the inside surface of the tank through the steel has been suggested to have caused the stair-stepped cracking as shown on the bottom of the picture near the slice at section $y = 1$. Different color patterns demonstrate that cracks have propagated over several regions in the tested plate.



FIG. 4—Photo of corroded aircraft fuselage panel.

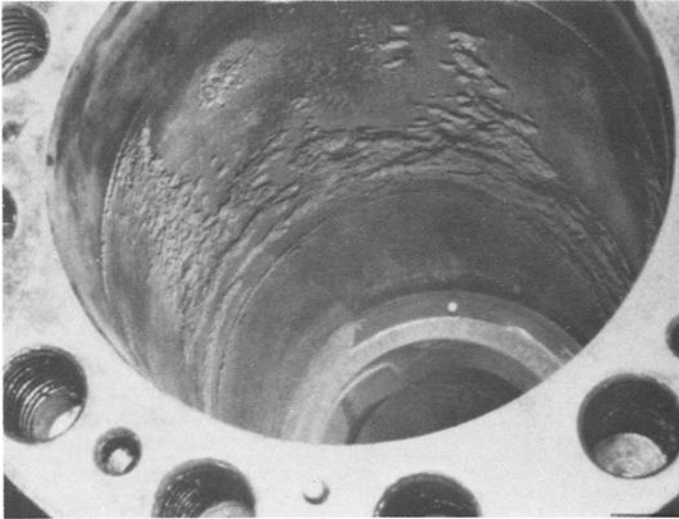


FIG. 5—*Photo of erosion inside choke valve.*

Although the Ultra Image III system was designed to image corrosion patterns of metallic materials by contact test, it has been used to examine the bonding structures of composite materials in immersion tests as well. Unlike metallic materials, which are mostly homogeneous for sound to propagate through, composite materials in general are very nonhomogeneous, making it difficult for conventional UT methods to obtain repeatable results. The ultrasonic imaging technique, however, offers a potential solution for reliably inspecting composite materials. Figure 11 shows an image of a fiberglass composite flywheel by immersion test. The color at the center of the flywheel shows the location of the aluminum hub; blue indicates good bonding structure of the flywheel disk. Figure 12 shows an ultrasonic image of a flywheel spun-tested to its ultimate speed of 35 000 rpm when the aluminum hub was detached from the flywheel. The yellow and pink are due to microvoids induced to the structure during the spin test. Detailed results of the flywheel tests can be found in Ref 3.

Comparison of C-scan and Ultra Image III

In a regular C-scan, the signals received in the gate with amplitudes greater or smaller than a preset value are separated. The results are displayed in a two-dimensional map, that is, dark areas are plotted denoting signal amplitude exceeding the threshold level, in contrast to the white areas where signals are below the threshold level. Neither of these areas provides any depth infor-

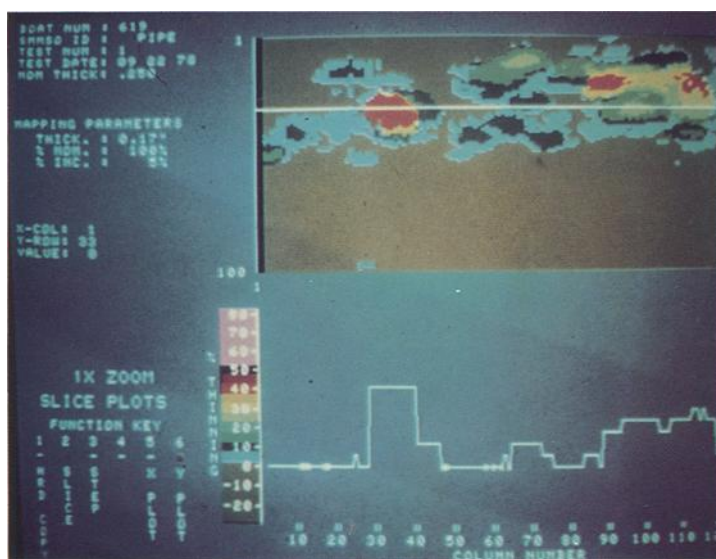


FIG. 6—Ultrasonic image of corroded pipe wall.

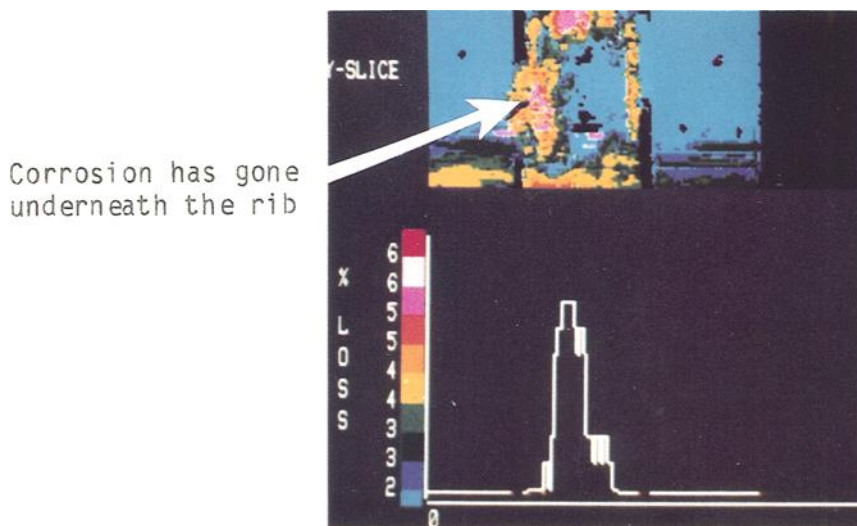


FIG. 7—Ultrasonic image of corroded fuselage panel.

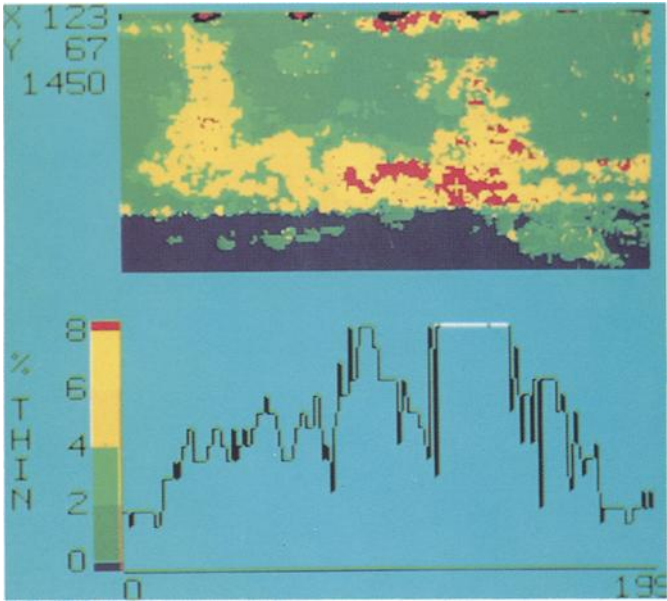


FIG. 8—Ultrasonic image of eroded valve.

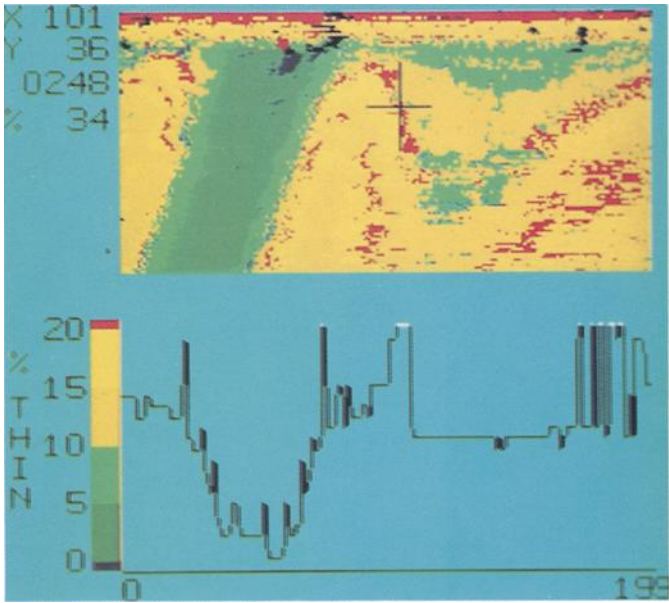


FIG. 9—Ultrasonic image of welded region.

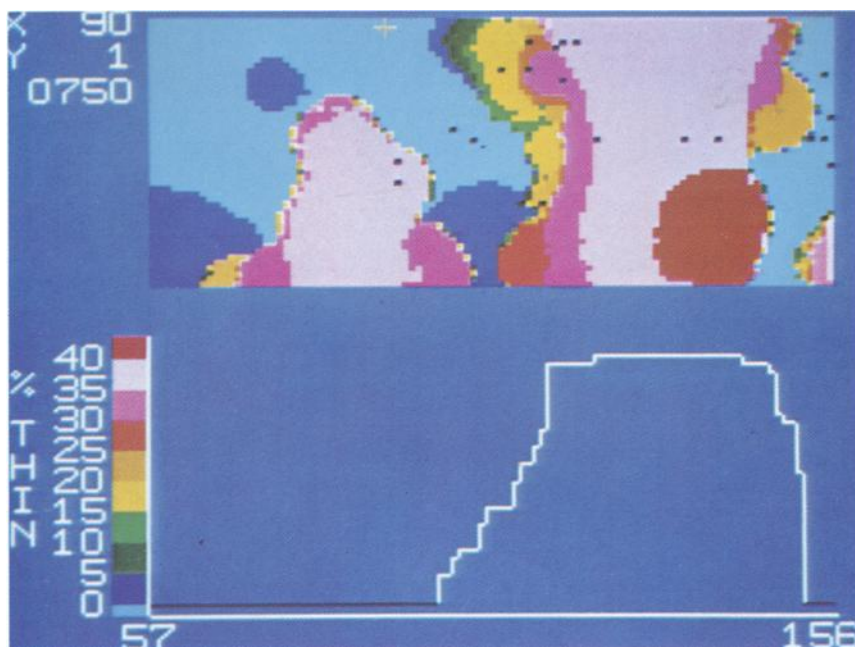


FIG. 10—Ultrasonic image of steel plate cracks due to hydrogen blistering.

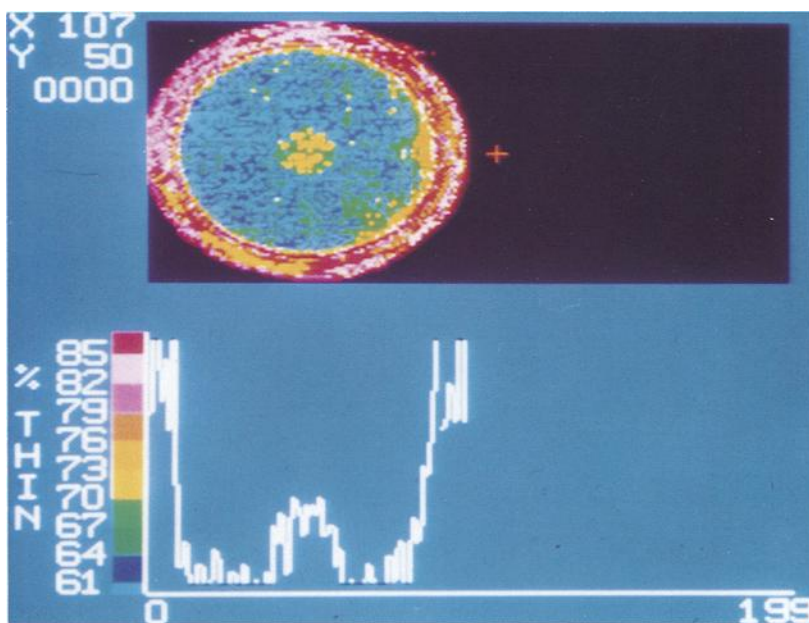


FIG. 11—Scanning of fiber glass composite flywheel, before spin test.

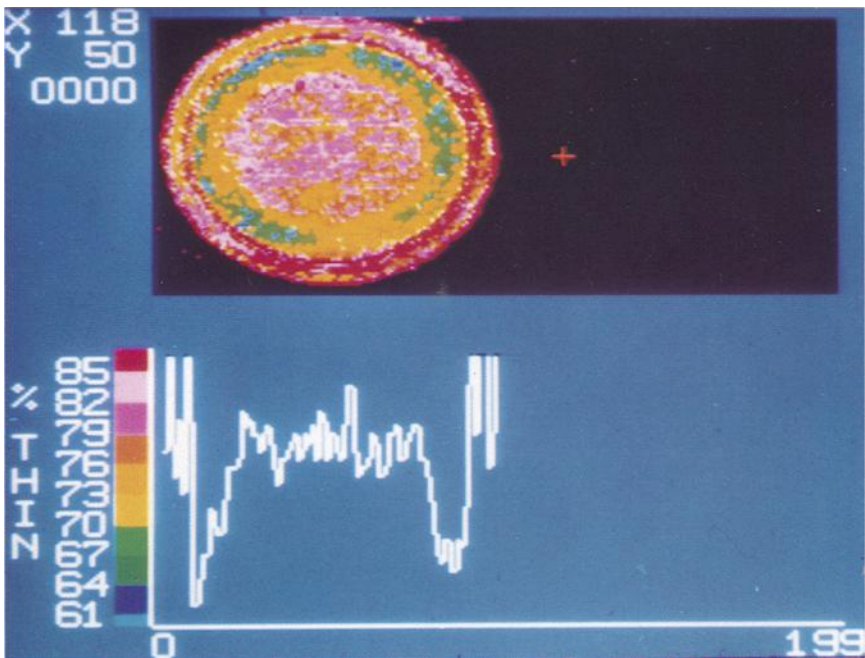


FIG. 12—Scanning of fiber glass composite flywheel, after spin test.

mation. The C-scan signal is in analog form, which cannot be displayed again in other formats or at a later date.

For the Ultra Image III system, the scanned area is divided into 100 by 200 picture elements or pixels. Each pixel represents a corresponding location in the scanned area. Every pixel contains simultaneously one depth and one amplitude information. Each depth and amplitude information is an average of four sets of measurements taken at the pixel location. When scanning is completed, the results can be reviewed either by depth or amplitude distribution. A suitable color scale can be selected to enhance feature extractions for better characterization of flaws in the tested material.

The process of forming the image by Ultra Image III system is similar to that of the tomography process which became well-known after X-ray tomography technique was introduced [4]. With this process, the image is reconstructed from physical quantities measured for each pixel in the scanned area. The image reconstructed for X-ray tomography is from measured and calculated absorption coefficient at each pixel. It is this single parameter, the absorption coefficient, distributed over the scanned area, that is used for characterizing the materials. The results obtained using Ultra Image III have two parameters, depth and amplitude, in each pixel. Depending on the nature of the material under test, certain parameters are effectively used for describing the conditions of the tested structures.

Since the ultrasonic imaging obtained here is reconstructed, the accuracy of the image depends on the accuracy of the raw data collected at each location. The accuracy of these ultrasonic signals depends on the property of the material tested, the frequency of the transducer used, the scanning time, processing time limit, and other factors. Hence, the exact tolerance of accuracy of the method depends on specific applications.

The colors appearing in a computer-reconstructed image represent assigned values. The color distribution of an ultrasonic image is used for immediate identification and characterization of defects inside a structure. Therefore, various color patterns can be arranged to represent one corrosion pattern.

If the ultrasonic signals are reliably obtained, the image reconstruction by computer is consistent. In fact, the consistency of a computerized system allows the operator to use the image results in checking and maintaining precision of the ultrasonic data collecting process. It should be noted, however, that inspection by imaging method is based on an operator/system interaction approach and that the ultimate accuracy of the results depends on the data acceptance from the operator.

Summary

The portability of a conventional UT system is a major factor in its being commonly used in the field. But because of its lack of accuracy and repeat-

ability in determining the crack shape and sizes, it cannot meet the increasing demand for product reliability and component integrity. The ultrasonic imaging method is born to meet this challenge. In this study, a portable, microprocessor-controlled ultrasonic imaging system, the Ultra Image III, is described. This equipment is shown in use, from tests of pipes in an engine room in a ship to fuselage in an aircraft wing, and from contact test of metal corrosions to immersion test of fiber glass composite structures. The system provides results as soon as tests are completed so that decisions of further tests at different locations, with different levels of resolutions, can be made in situ. The portability and versatility of the system is described. This system is proven tested and is ready for ensuring component integrity in the NDT world.

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An Automated Ultrasonic Data Acquisition and Evaluation System

REFERENCE: McGarvey, T. J., Murray, J., and Roller, D., "An Automated Ultrasonic Data Acquisition and Evaluation System," *Corrosion Monitoring in Industrial Plants Using Nondestructive Testing and Electrochemical Methods*, ASTM STP 908, G. C. Moran and P. Labine, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 102-111.

ABSTRACT: A computer-based ultrasonic (UT) inspection system has been developed which provides a method for locating and sizing flaws in the near-bore region of steam turbine rotors. Components from various manufacturers were integrated to make up this unique test system.

Shear wave inspections are performed utilizing an expandable test head coupled to a positioner via geared extension bars. The head accepts up to three transducers while the positioner provides the axial indexing and circumferential rotation of the transducers.

A microprocessor is supplied with signal information from a multichannel UT instrument and location information (axial and circumferential for each transducer) from the positioner. All recorded data are transferred from the computer memory to floppy disks, thus maintaining a historical record of all test results.

Upon completion of each UT inspection scan, a color video monitor with graphic display allows for evaluation of test data utilizing several software programs which are presently available. A color printer supplies a hard copy of inspection results.

A visible magnetic particle (MT) examination is performed from the bore to provide additional information on surface and near-surface flaws. This boremag inspection is accomplished using the positioner with extension bars and a miniaturized TV camera with a light source and mirror. The camera outputs to a video recorder and a video monitor.

The UT and MT inspections provide a data base which can be used for evaluating turbine rotor integrity and monitoring flaw propagation. With the addition of new software and a different type positioner, the basic ultrasonic hardware can be used for inspection of brazed joints in sleeved steam generator tubes. Other possible applications of this system (UT on piping, eddy current in tubing, etc.) are discussed.

KEY WORDS: boresonic, boremag, data acquisition hardware and software, turbine rotors

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Prior to 1982, all magnetic particle (MT) and ultrasonic (UT) inspections of Public Service Electric and Gas Company (PSE&G) turbine generator rotors were performed by outside contractors. The costs for these services was substantial, and since PSE&G personnel had performed nondestructive examinations (NDE) or inspections on rotor peripheries and other system components, it was resolved that it would be more cost effective for the PSE&G Research and Testing Laboratory to:

1. Investigate system components available on the market to perform MT (boremag) and UT (boresonic) from the bore surface.
2. Purchase system components and design a boremag inspection system, perform inspections and evaluate test results.
3. Purchase systems components and a boresonic data acquisition system for manual scanning.
4. Acquire and interface a computer with the boresonic system to provide for automated inspection scans and data retention.
5. Perform in-house rotor stress evaluation utilizing fracture mechanics, computations, or computer codes (that is, Safer Computer Code [1]), or all three.

Before reporting details of our equipment and design; let us review a few initial work efforts prior to computer utilization. The automated boremag inspection system has been operational since February 1982 and has been utilized for inspections of 12 turbine rotors and several rotor reinspections after machining operations were performed to remove defect areas of the bore region. Initial inspections on five rotors in February 1982 were performed with the KB 6000 UT flaw instrument coupled to probing via an automated probe positioner. Evaluation of UT test results was performed during the inspection, but this proved to be a very time-consuming process.

In 1983, a computer was interfaced with our existing boresonic system and our Research and Testing Laboratory in parallel tests with rotor manufacturers inspected seven turbine rotors. PSE&G inspection results when compared to manufacturer's test results of the same rotor had good correlation. The boremag inspection system will now be discussed, followed by a description of the hardware and software capabilities of the Ultrasonics Data Acquisition System.

Boremag System

Magnetization of the rotor from the bore is accomplished using a Magna-flux unit as a d-c current source, an aluminum rod for a center conductor, and a spray head to apply the visible magnetic particle material. While the conductor is energized, the spray head is withdrawn at a constant speed and visible magnetic particle material is sprayed onto the bore surface. The inspection is accomplished using a miniature black-and-white television cam-

era housed in a fixture which is equipped with a mirror and light source. The fixture attaches to an extension bar which is rotated at a constant speed. The fixture (Fig. 1) rotates clockwise from 0 to 370 deg, then moves forward at a predetermined increment [that is, 6.35, 12.7 mm, 0.25 in., 0.5 in], reverses direction, and then completes a 370 deg to 0 deg counterclockwise scan. This procedure continues until the entire length of the rotor bore has been inspected. The rotational speed (circumferential) and the indexing increment (axial) are adjustable.

All inspections are videotaped and can be viewed on a TV monitor at any time (Fig. 2). A voice channel provides for input of inspection information including axial location for each inspection scan. This system can be modified

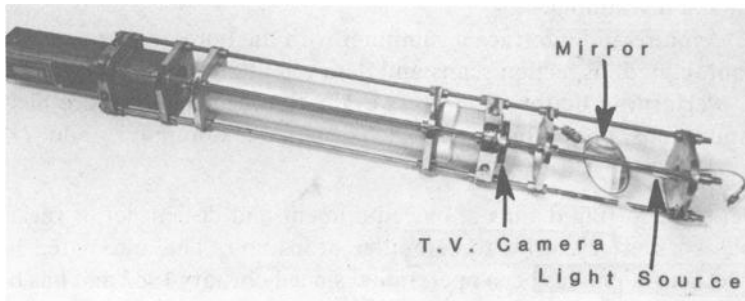


FIG. 1—*Boremag inspection fixture.*

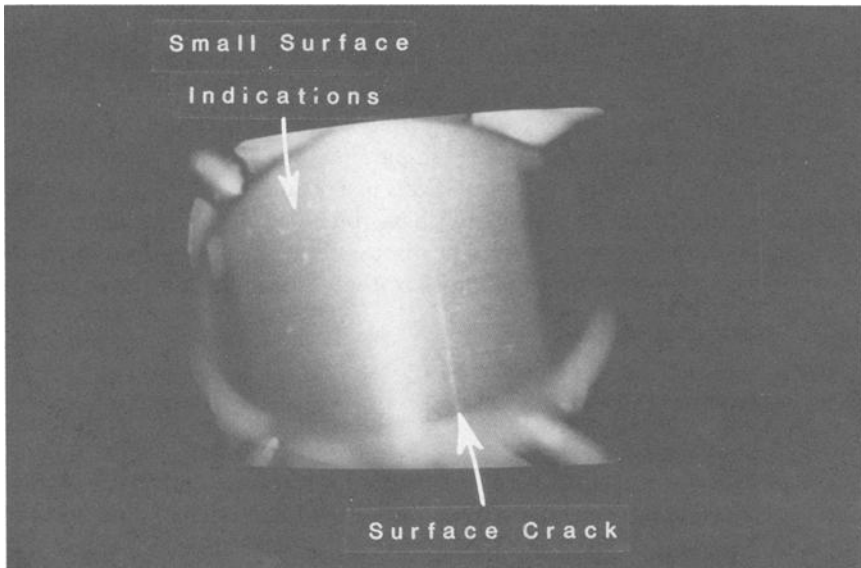


FIG. 2—*Reproduction of a video playback.*

to provide digitized axial and circumferential location information which would be displayed on the TV monitor.

Boresonic Data Acquisition System

Aware now of some reasons for developing an automated inspection system, we can now study the specific test system utilized for the boresonic inspection. In Table 1, the methodology used during development of the inspection system is outlined. This philosophy is taken from Roller and Rose [2], where computer-controlled data acquisition methodologies on inspections of turbines, composite materials and stainless steel piping are discussed. Alternate boresonic inspection schemes are presented by Ammirato [3].

The proposed boresonic inspection problem addressed here is that of examining the bore region of a turbine generator rotor, to detect and locate near bore indications. In order to achieve this inspection goal, an automated testing system was designed to perform an ultrasonic examination of the rotor bore using the shear wave mode of testing to detect and locate axial and circumferential indications in a rotor.

Shown in Fig. 3 is a block diagram of the computer-based automated data acquisition and analysis system for boresonic inspection. This system was built by PSE&G Research Corp. and Ultrasonics International to inspect turbine and generator rotors as required during periodic in-service inspection maintenance. As shown in the block diagram, the system is composed of an expandable test head which accepts up to three contact type transducers and is coupled to a positioner via geared extension bars. The scanner position displays are interfaced to a DEC LSI-11/23 microcomputer. The microcomputer is also interfaced to a KB 6000 computer-controllable flaw detector to record ultrasonic information.

TABLE 1—*Computer-controlled inspection system methodology.*

Proposed inspection problem	steam turbine and generator rotor
Problem definition	detection and location of a subsurface indications in the rotor's bore (boresonic inspection)
Approach (physics)	multiple transducer contact test inspection with shear wave transducers
Mechanics	automated rotational and axial drive scanner with a three-transducer probe fixture
Ultrasonics equipment	multichannel, multiplexed computer-controlled flaw detector
Software requirements	(1) record scanner position (2) flaw detector control (3) data collection (4) display (5) data analysis
Display and recorder	color graphics display with a color printer

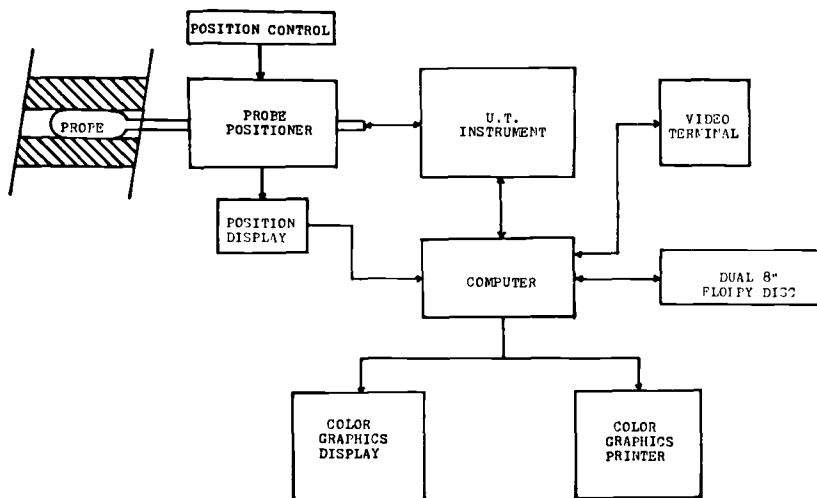


FIG. 3—Block diagram of PSE&G Ultrasonic Inspection System.

This microcomputer based system also contains the following components: dual 8-in. floppy diskette drives; color graphics video unit with 512 by 512 pixel resolution and eight displayable colors; color hardcopy printer; and alphanumeric video display terminal.

The floppy diskettes are used to record ultrasonic data obtained during inspection of a bore, and they also contain the inspection and analysis programs. A color graphics display unit was selected for this system to provide a display media for the collected ultrasonic data to allow easy interpretation by the test operator. A description of the types of color displays that the system provides will be discussed later. To preserve the information on the display unit, a color printer was included in the system to provide hardcopy printouts of the ultrasonic scans. The alphanumeric video display is used as the input/output link between the test inspector and the inspection system. Through the unit's keyboard and display, the test inspector interacts with the system with a user-friendly, menu-driven series of commands and messages.

The computer software package developed for this system included programs to record ultrasonic amplitude and depth information at specified scanner positions, to recall stored scan data, and to allow the test inspector to analyze this information through a number of possible presentations. It also offers complete control and setup of the computer controlled flaw detector, assisting in calibration of each channel. In all, the software package provides the inspection system with a comprehensive operating procedure to achieve reliable and repeatable operation of the system by a number of testing inspectors. A photograph of the computer-based inspection system developed for boresonic testing is shown in Fig. 4.



FIG. 4—Ultrasonic inspection system housed in three portable cabinets (exclusive of probe assembly and positioner).

Ultrasonic Evaluation

There are three key features of the inspection system implementation: automatic setup of the flaw detector and an operator interactive method for adjusting the settings of the flaw detector; automated data acquisition and storage of ultrasonic data in the form of amplitude and depth measurements obtained from the flaw detector; and data reconstruction potential of the system to produce an image of the indications in the near bore region from the ultrasonic data.

The data analysis software in the system provides the test inspector with the flexibility to analyze all or selected portions of the data recorded during scanning at different amplitude thresholds and for different depth regions as measured from the surface of the bore. In order to further discuss the various formats available for analyzing the scan data, we will review a simple scan (see Figs. 5 and 6).

In Fig. 5 is a sample of an axial scan plot (unfolded cylinder) of a calibration block. The location of the indications are shown in the left-hand portion of the figure in terms of the position around the bore in degrees and the axial position along the axis of the bore as measured from the end. The depth of the indications are shown in the right-hand portion of the figure in terms of the depth from the ID of the bore, as a function of axial position for the selected angular segment of the bore.

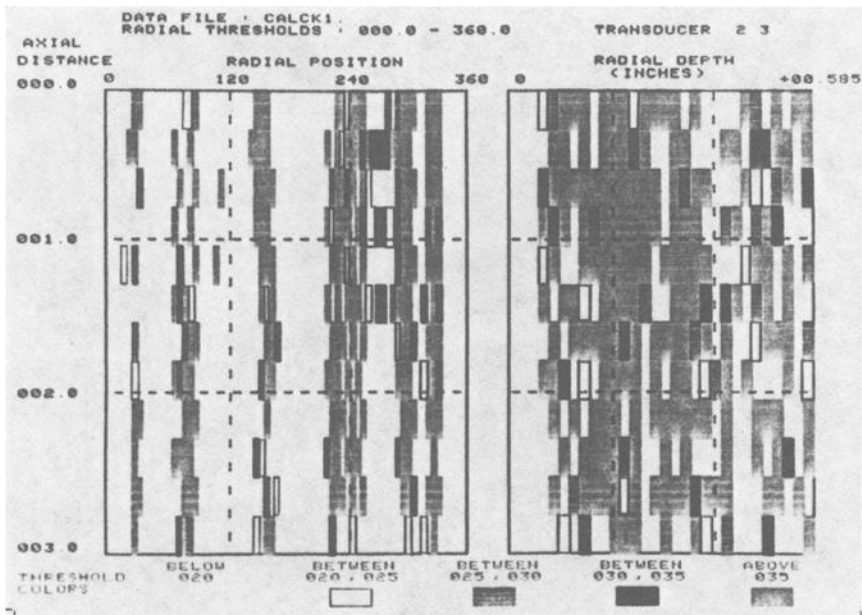


FIG. 5—Axial scan plot (unfolded cylinder) of the test block.

The test inspector can analyze data recorded from the shear wave scan by selecting a transducer or any combination of the three transducers used during the inspection. Once choices have been made, he chooses the axial range of the scan, the angular segment of the bore, the depth region, and the threshold levels for presentation in the plot. All of these variables are selected by the inspector through interactive prompts and responses by the system.

Figure 6 shows the end view scan plot (scatter plot) of the test block scan data. As in the case of the axial scan plot, the inspector can also select a number of plotting parameters. The test inspector can choose to display shear wave results, the transducer or combination of transducers, the axial range over which the data will be displayed, and the amplitude threshold for the colors plotted. For this set of parameters, the system will produce a polar plot showing the depth and radial locations of all indications occurring in the selected axial region of the bore with the chosen color thresholds.

This analysis software flexibility allows an inspector to select any section of the bore scan and to set sensitivity levels for a detailed analysis of the acquired scan data.

Boresonic Mechanics

The probe fixtures are equipped with three contact type transducers and have expandable arms (air pressure controlled) for accommodating various

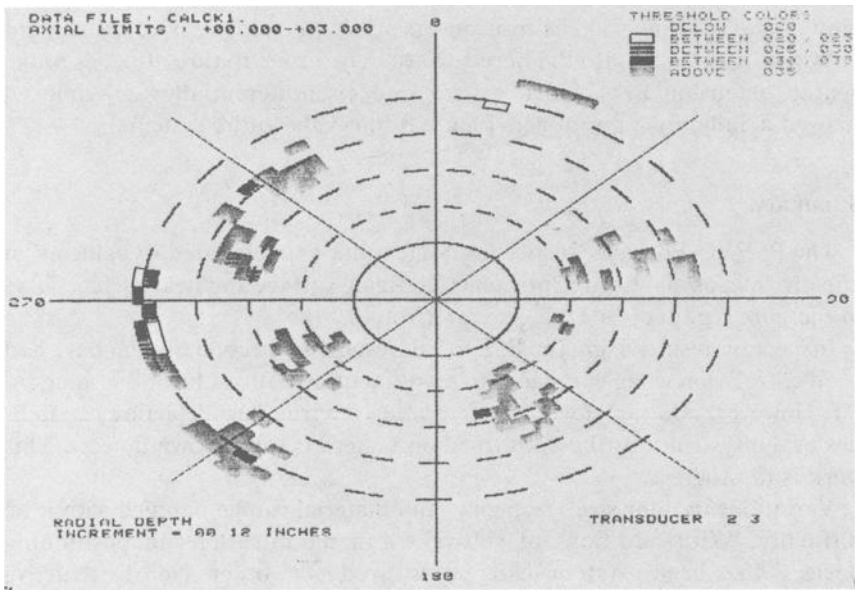


FIG. 6—End view of indications over an axial range of 0 to 7.62 cm (3 in.) and a radial range of 0 to 1.48 cm 0.585 in.).

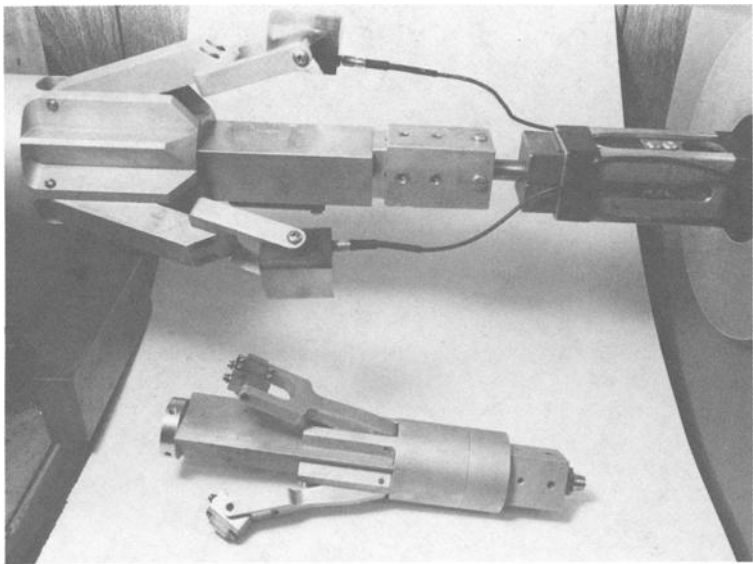


FIG. 7—Probe fixtures for boxes of various sizes.

bore diameters (Fig. 7). The transducers are coupled to the bore with a light oil which is sprayed onto the bore surface. The probe fixture attaches to the geared extension bars which are rotated circumferentially and indexed (moved axially) by a positioner. Figure 8 shows the entire system.

Summary

The PSE&G Boremag Inspection System has demonstrated its value as an effective means of detecting and characterizing surface and near surface flaws in the bore region of turbine generator rotors.

Inspection results using the PSE&G Boresonic Inspection System have had good correlation when compared to manufacturer test results of the same rotor. However, additional work to determine the true flaw detection capabilities of the system must be performed on materials with known defects. This work is in progress.

Variations in rotor size, geometry, and material can be handled with little difficulty. With additions of software and modifications in positioning devices the basic system can be utilized for other Non-Destructive Examinations.

Flexibility in the boresonic and boremag inspection system design, along with features such as portability and quick setup time, will provide a viable method for Public Service Electric and Gas to meet its rotor inspection commitments for the future.

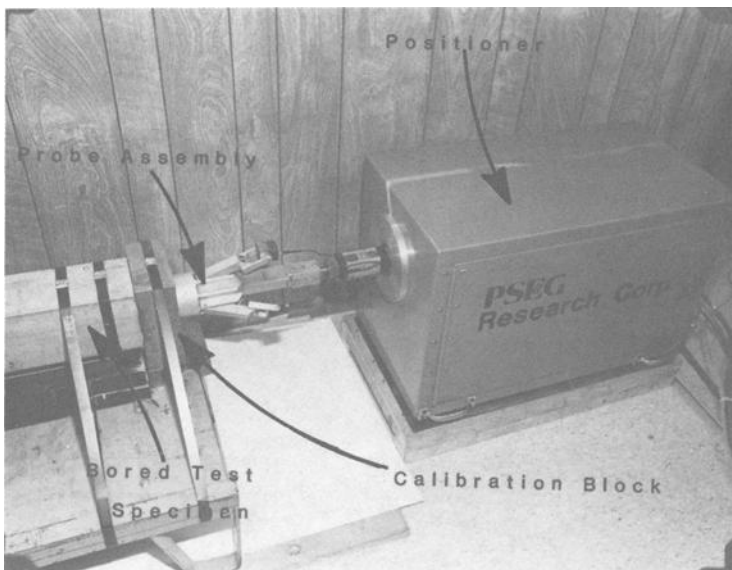


FIG. 8—Boresonics mechanics.

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Detection of Intergranular Stress-Corrosion Cracking Using Automated Ultrasonic Techniques

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ABSTRACT: Intergranular stress-corrosion cracking (IGSCC), which has occurred in nuclear power plant piping systems, is detected ultrasonically. The principal problem is discrimination between the few acoustic reflections from flaws and the large number from geometry of the weld root and counterbore. This paper discusses two areas of recent work on the IGSCC problem: the development, fabrication, and initial testing of a miniature automated ultrasonic search head, and the detection and characterization of IGSCC using an imaging technique.

The search head contains a toroidal-axicon-lens system with folded acoustic optics. The resulting beam is remotely controlled to produce a small-diameter beam that is near parallel or defocused 2.5° or 5°. The transducer's linear and two angular motions and nearly all field operation steps are automated. This allows certified Level II inspectors, who are in short supply because of radiation "burnout," to operate primarily from the radiation-free computer console area.

The imaging technique consists of comparing multiple images that present amplitude, position, and reflector "texture" information. The surface of IGSCC has small and highly irregular facets which scatter strongly in all azimuths at high frequencies. Other classes of targets have similarly distinctive characteristics.

KEY WORDS: inservice inspection, weld inspection, piping inspection, ultrasonics, ultrasonic scanner, ultrasonic imaging, automated ultrasonics, robotic inspection, acoustic optics, intergranular stress corrosion cracking (ISGCC)

During the past decade, nuclear reactors have experienced increasing incidents of intergranular stress-corrosion cracking (IGSCC) in the heat-affected

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zone (HAZ) adjacent to stainless steel welds within the primary piping system. Development of improved ultrasonic testing methods for detection and sizing IGSCC has received considerable attention in the United States through work funded by the U.S. Nuclear Regulatory Commission, U.S. Department of Energy, and the Electric Power Research Institute. These programs have included evaluation of the current industry capabilities and development in various areas of automated ultrasonic inspection.

The ASME Code Section XI requires periodic volumetric examination of the critical welds located in the primary piping system of nuclear reactors. The ultrasonic method is normally used to meet this requirement. The Code requires that the plant be designed to provide adequate access for the examination, although in many instances access is severely limited. Current examinations of piping are largely accomplished using the manual hand-scan method. Although this approach is the most versatile in confronting the accessibility limitations, it has other drawbacks. Reliability of the manual method is strongly operator- and technique-dependent as has been shown in numerous round-robin tests. This adversely affects the use of the method for periodically monitoring a known flaw for evidence of growth. Another concern within the industry is the limited number of experienced personnel that can qualify as certified Level II inspectors.

This paper discusses two recent areas of work directed toward improved inspection performance. These are the development, fabrication, and testing of a miniaturized computer-controlled ultrasonic search head, and the detection and characterization of flaws, including IGSCC, using an imaging technique.

During 1976, an automated ultrasonic inspection system was developed for examination of the primary piping within the Loss-of-Fluid Test (LOFT) reactor located at the Idaho National Engineering Laboratory (INEL). The scanner contained an immersion-type search head which provided axial travel and two angular motions for positioning the acoustic beam, all under computer control. This Mark I configuration was periodically field-operated over a six-year testing cycle. During this time, extensive experience was gained in implementing automated ultrasonic inspections and the importance of various performance characteristics was evaluated. All of the images shown in this report were constructed with data collected with this search head.

Based on this background, a program was initiated in 1980 to develop and fabricate a prototype search head with improved performance characteristics and smaller physical size. The resulting unit incorporates much that was learned through the use of the Mark I, but is a completely new design. It includes a unique folded acoustic system that produces a small diameter beam which can be either nearly parallel or optionally defocused under computer control. The folded acoustic path permits miniaturization of the search head while providing a long fluid path to the first interface, thus eliminating multiple interface echoes during the inspection period. The operational steps

during the equipment installation and scanning were evaluated and nearly all were automated. This allows the certified Level II inspectors, who are in short supply because of radiation "burnout," to operate primarily from the computer console, which is located out of the radiation zone.

The imaging technique to be presented here has evolved over a ten-year period through work on both the LOFT reactor piping and numerous flaw samples. A primary problem in analyzing ultrasonic data taken on piping weldments is discrimination between acoustic reflections from geometric targets and those from real flaws. The method discussed separates these targets by evaluating their surface texture and presenting the amplitude and spatial relationship information in graphic form. The texture information may also provide a method for determining if a flaw is IGSCC or a fatigue crack.

Search Head Design

The Mark II search head is a small, lightweight prototype unit designed for computerized ultrasonic inspection of welds in primary piping of nuclear reactor plants. The immersion technique used has significant advantages over the more commonly used contact method in versatility, repeatability, and ability to computerize the operation. The broad performance capabilities of the equipment may also be useful in other ultrasonic inspection applications.

The search head is approximately 10 by 10 by 11 cm (4 by 4 by 4½ in.) in overall dimensions and weighs 1½ kg (3½ lb). Its size is slightly larger than a gloved hand of an inspector holding a contact transducer; therefore, most areas that can be inspected by the contact method may also be examined with the automated equipment.

The Mark II search head is designed to minimize radiation exposure of the certified Level II inspectors, who are in short supply, by placing all key operating and decision-making functions at the computer console, which is located in a radiation-free area. This results in moving the Level II function out of the radiation area and reducing the skill needed for handling the scanner to that of the more available Level I inspectors.

Acoustics

The acoustic design produces one of three optional beams that are approximately 7 mm (0.3 in.) in diameter upon entering the part surface. The beam may be symmetrical and near parallel or cylindrically defocused 2.5° or 5°. The symmetrical beam provides better resolution, but is more angle-sensitive. The defocused beams improve off-angle detection during shear wave inspection without decreasing the resolution in the weld-depth direction. A long fluid path results in elimination of first interface multiple echoes in the time frame required for the inspection.

The nominal fluid path of 15 cm (6 in.) in mineral oil is achieved by folding

the focused beam with two right angle reflecting mirrors (Fig. 1). The third mirror component, the ball mirror, provides the three different shapes of incident beam. It contains a flat surface and two cylindrical defocusing surfaces that produce the divergent beam. By rotating the ball on its centerline, the desired mirror and the incident angle can be selected.

The transducer is a 3.8-cm (1.5-in.) diameter, 2.25-MHz unit with a toroidal-axicon lens. The functional advantage of the toroidal lens, so named because its surface is part of a toroid, over more conventional spherical ones is that it produces a very narrow, long range (depth of field) sound beam. References 1 through 4 provide detailed discussions on the functioning and performance of both the axicon and other lens types. A flexible convex diaphragm retains the oil in the housing, and commercial ultrasonic couplants serve as

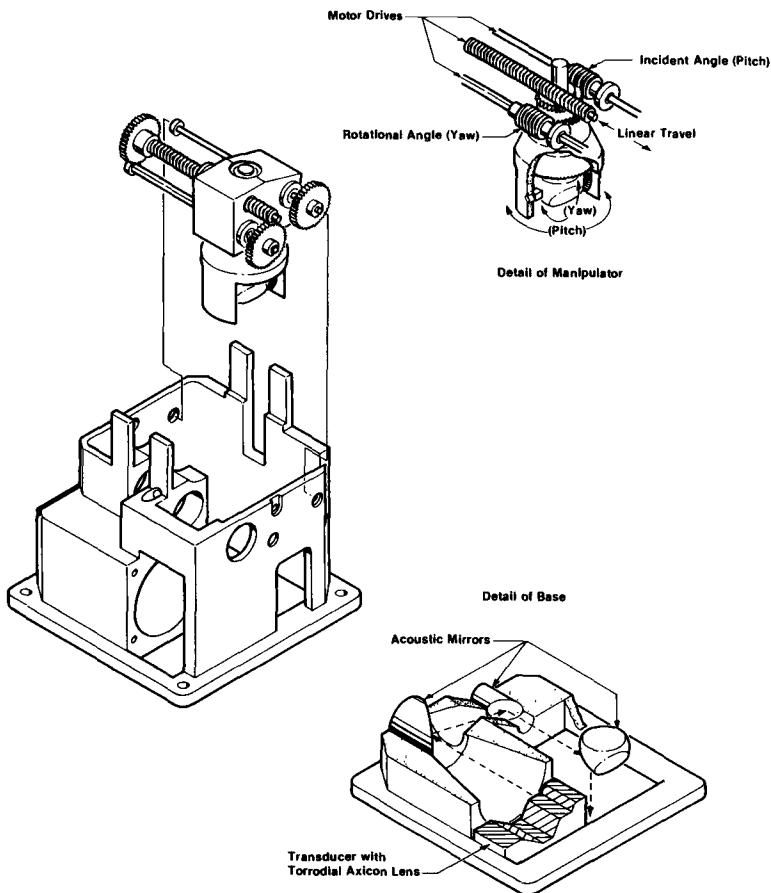


FIG. 1—Perspective and cutaway views showing the three mechanical drives and folded acoustic path. Cover, diaphragm, and motor drives have been omitted for clarity.

the interface material. The pitch and yaw angles and precision axial travel are produced by stepper motors that are controlled from the computer-console.

The acoustic performance of the search head may be evaluated using RF waveform analysis derived from the normal-incident flat surface of the ball mirror and x-y beam profiling of a 3.18-mm (0.125-in.) diameter spherical target contained within the search head.

Mechanical

The Mark II search head differs from previous designs such as P-scan [5], Amaps [6], ALN [7], and Sutar (Product of Southwest Research Institute, San Antonio, TX), in that virtually all operating functions are automated to minimize the radiation exposure to the Level II ultrasonic inspector. The search head consists of three major components: a cover, diaphragm, and frame assembly. The aluminum cover provides physical protection of the mechanism, retains the oil, and is anodized to dissipate the internal heat generated by the three stepper motors. The diaphragm is molded of clear, flexible polyurethane. The overall convex shape assures adequate contact with the part surface, even on the inside radius of pipe elbows. The frame assembly, shown in Fig. 1, consists of a molded polyurethane frame and all acoustic and mechanical components. The acoustic portion of the assembly contains an integral acoustic collimator, a transducer with toroidal axicon focusing lens, and mirrors to fold and shape the beam.

The mechanical portion of the assembly contains three stepper motors and related drive trains to provide the pitch and yaw angular motions and axial travel of the incident beam. The angular motions are continuous and are initialized by normalizing the beam with the final mirror. The axial travel limit is 2.5 cm (1 in.) and is initialized at the end of travel. The number of motor pulses from initialization is used to determine relative positions for all motions. A miniature position detector provides a highly repeatable circumferential benchmark for scanning horizontal pipe. The device also allows verification of the pipe diameter by counting motor pulses for each quadrant of travel on the pipe.

Materials

Molded polyurethane components have been used extensively to improve performance, simplify the design, and reduce cost. This material reduces the acoustic reflectivity within the search head, simplifies the mechanism by reducing the number of parts, and results in a low unit cost after only a modest investment in gravity-type molds. The material is flexible in thin sections, permitting parts to be snapped together rather than assembled with fasteners, and bearing surfaces are produced by simply boring the material rather than installing bushings. A rigid, machinable polyurethane of 75 D hardness was used for all parts except the diaphragm.

The frame is molded with an integral collimator consisting of two adjacent conical cavities and a cylindrical cavity. The only practical method of fabricating the collimator was by molding.

The diaphragm is molded of clear, flexible polyurethane with a hardness of 65 A. The clarity provides good visibility of the mechanism while the flexibility assures good part surface contact. The material also exhibits excellent tear and abrasion resistance.

The aluminum cover has been black anodized to achieve high emissivity, since dissipation of the heat from the three internal motors is essential.

Automation

Automation provides a high degree of repeatability in mechanically positioning the acoustic beam. Additionally, periodic measurements of certain acoustic characteristics can be used to standardize the inspection and verify system performance. The search head design considered each operational step of the inspection and included functional features that placed under computer control virtually all factors affecting overall performance. These include the following:

1. Initialization of each of three mechanical motions.
2. RF waveform and power spectrum measurement.
3. Beam profiling measurement.
4. Reference amplitude measurement.
5. Setting of the incident angle.
6. Acoustic-velocity measurement of internal fluid (permits periodic adjustment of incident angle so as to maintain constant refracted beam angle regardless of search head operating temperature).
7. Verification of adequate interface couplant.
8. Verification that the scanner is normal to pipe centerline.
9. Verification of the pipe diameter.
10. Identification of a benchmark on horizontal pipe.
11. Measurement of mechanical backlash in each of three motions.

Typical Observations of IGSCC

The search head has the capability to point a well-collimated sound beam in any desired direction within the part being examined, combined with precise computer control and reproducibility of the resulting linear and angular positions. The usefulness of these characteristics is illustrated by an imaging technique being developed for classifying ultrasonic targets found during in-service inspection of austenitic steel nuclear piping.

One of the major problems in this type of inspection is that of distinguishing with high reliability between benign "geometric" targets and the very small percentage of targets which are real defects. Targets representing weld

root, counterbore, or grain scattering or all three are nearly always present within a transducer's field of view; each must be classified correctly if the inspection is to be fully reliable. A number of techniques for this classification have been reported [7,8]. The one described here as an illustration of the use of the search head for imaging.

The spatial relationships of the various targets, that is, their size, shape, general appearance, and relative locations, are important visual clues easily revealed by imaging. Image characteristics have been found to correlate, even in the presence of comparatively poor resolution, with physical descriptions of the target. As an example, a machined surface such as a counterbore yields a straight image of nearly uniform amplitude, while a weld root image is rounded and lobate in appearance and not as uniform in shape or in amplitude. The differences in images of the machined surfaces and weld root, when each is viewed with the sound beam perpendicular to its trend, reflect the differences in physical configuration left by the machining and welding processes. These relationships are not always sufficient for complete characterization, however. Figures 2 and 3 show two cases in which the nature of parallel targets cannot be determined from the single images shown. In each case, one of the targets is the weld root, but the nature of the adjoining indication is ambiguous. Additional information is needed to characterize the targets fully.

With its ability to point the sound beam in arbitrary directions (not simply

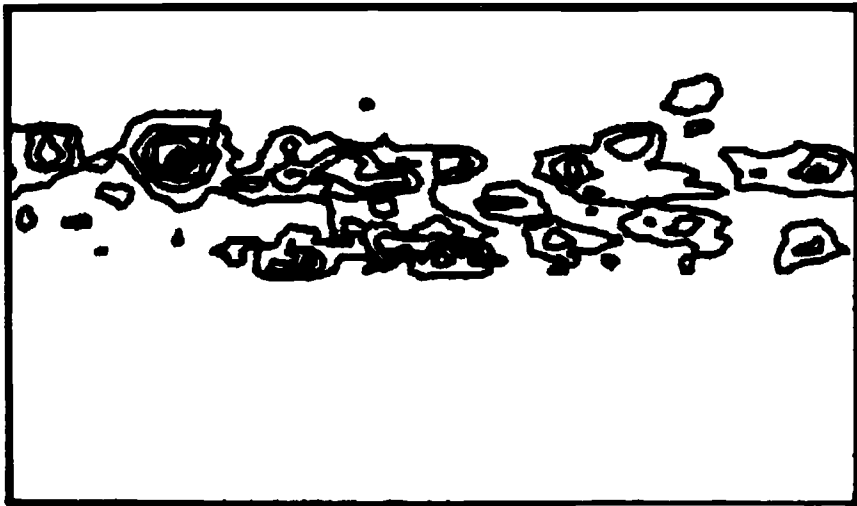


FIG. 2—View from shear wave data illustrating the difficulty of discriminating between geometric and real flaw targets without the use of supplemental views. Contour intervals are 10% of DAC; scan increments in both directions are 2 mm (0.08 in.); image is presented at $\times 0.9$; and $F_c = 1.8$ MHz.

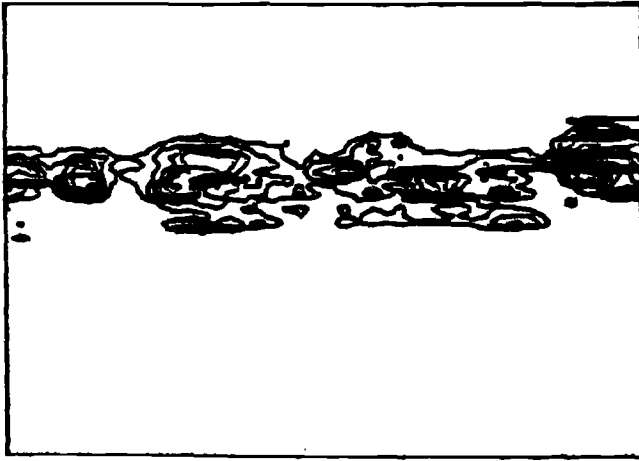


FIG. 3—View from shear wave data illustrating difficulty of discriminating between geometric and real flaw targets without use of supplemental views. Contour intervals are 10% of DAC; scan increments in both directions are 2 mm (0.08 in.); image is presented at $\times 0.9$; and $F_c = 1.8$ MHz.

in the axial or circumferential directions on a pipe), the search head helps provide the additional information needed. The present technique relies on a visual comparison of several images of the same target area, the set of images being made under conditions which emphasize the distinctive differences in the “texture” of the surfaces of each of the major classes of ultrasonic targets being considered. The development effort is showing that there is a good correlation between physical descriptions of the target surfaces and what one would expect the ultrasonic response to be under appropriate conditions, in addition to the correlations noted above with respect to spatial relationships.

Continuing with the same example, a machined surface is smooth at all practical ultrasonic frequencies. On the other hand, a weld root is rounded in three dimensions, and may have small irregularities and asperities. When viewed in images at sufficiently large angles to the trend of these targets, distinctive changes occur in the two kinds of images. That of a machined surface simply disappears due to specular reflection that does not return sound to a pulse-echo transducer. The image of the weld root remains; its curved surfaces act locally as spherical reflectors which allow an image to be obtained. Figure 4 is such a case. The images are from a section of 35.56-cm (14-in.) nominal pipe size (NPS) Schedule 160 stainless steel pipe imaged at 1.8 MHz with a shear-wave beam angle of 45° with respect to the surface normal. The missing portion of the weld-root image in the off-angle view identifies specular reflection from a machined surface, later determined from radiography to be lack of fusion at the weld root.

The correspondence between physical descriptions and images seems, from

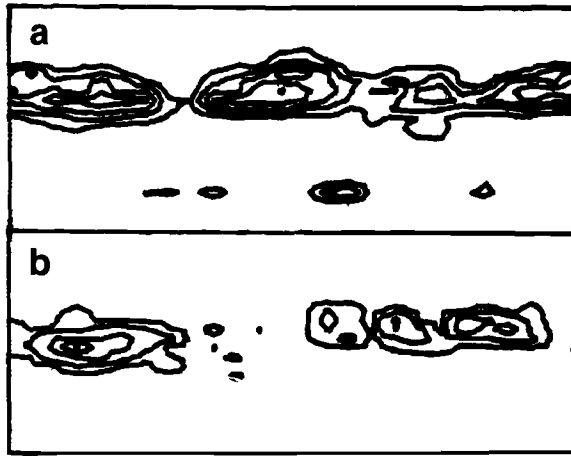


FIG. 4—Comparison of normal and off-angle views illustrating lack of fusion that was later verified by radiography. (a) Yaw angle = 0 deg. (b) Yaw angle = -15 deg. "Missing" area in (b) is lack of fusion.

the work to date, to carry over to such service-induced flaws as fatigue cracks and IGSCC. Again, distinctive image characteristics are found.

In general, the surface textures of cracks can be described as significantly rougher on a microscopic scale than those of geometric targets. This roughness is emphasized when the images are made at beam azimuths which de-emphasize specular reflections and corner-trapping, and at ultrasonic wavelengths which are at least roughly comparable to the characteristic scale of the surface roughness. Under these conditions, the images of cracks are formed primarily with diffractively scattered sound. There is less diffractive scattering from the relatively smoother geometric targets.

The basic technique developed to date uses pulse-echo measurements and a 45° angle beam. Three images are made of each volume being inspected. The first is at an azimuth which is approximately normal to the trend of the suspected targets, at a nominal low frequency of 1.8 MHz. The other two images are made at $\pm 15^\circ$, respectively, from that azimuth. These last two images are made through an analog filter which confines the effective response of the system to a band at approximately 5 MHz, with an appropriate increase in system gain. (A scanning protocol to be described elsewhere [9] reduces the effects of grain scattering and permits a good signal/noise ratio.)

The low-frequency image at normal azimuth is used to define the spatial relationships of the various targets; the two high-frequency images at off-angles ("yaw") are used to elicit information on the surface textures of the targets. Differences between the three images are used for characterization.

Methods for interpretation are illustrated by Fig. 5, which shows images of a laboratory specimen containing IGSCC. The specimen is from a 30.48-cm

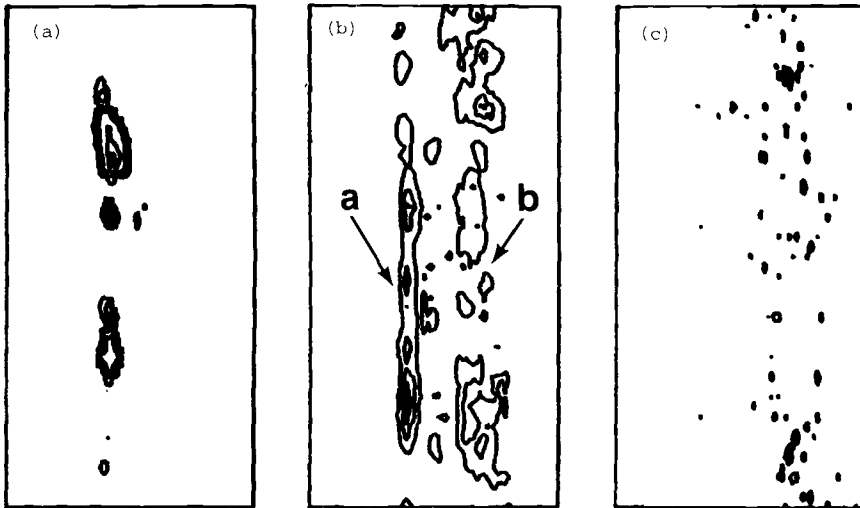


FIG. 5—Comparison of normal and off-angle views taken on same weld area allows separation of IGSCC from weld root. (a) Yaw angle = -10 deg; $F_c = 5.0$ MHz. (b) Yaw angle = 0 deg; $F_c = 1.8$ MHz. (c) Yaw angle = $+10$ deg; $F_c = 5.0$ MHz. Intergranular stress-corrosion crack is shown by Arrow a. Arrow b points to weld root.

(12-in.) nominal pipe size (NPS) Schedule 80 Type 304 stainless steel pipe. The center, low-frequency image shows the weld root and a more intense image of the IGSCC. No counterbore is present in the image. (Note that the signal-strength contours in these images are at 6-dB intervals.) The weld root has disappeared from the high-frequency, off-angle (yawed) images; its surface is relatively smooth in this case. The left-hand image shows intense scattering from a rough surface, the IGSCC. The right-hand yawed image shows only three small spots in the location of the IGSCC (and grain scattering in the weld), despite a relative increase of 30 dB in image sensitivity. It is to be noted also that the three different images of the same IGSCC are not congruent.

The IGSCC in these images has these four characteristics: it is a target that is not normally present in the heat-affected zone of the weld; it has some quite rough surfaces; scattering is more intense from one sign of yaw than from the other; and the target is highly irregular (as shown by the relative “hot spots” or “sparkles” in its image and the lack of congruence of its images). In all work to date, this combination of image characteristics has been found to be unique to IGSCC. Corresponding images of fatigue cracks, while still quite rough in surface texture, are more regular, have nearly congruent images, and do not have a strongly preferred azimuth for scattering.

This particular specimen of IGSCC is unique among those examined in that its image disappears entirely at one sign of yaw; this is thought to be

related to an early stage of IGSCC growth. All other IGSCC specimens, however, have exhibited strongly preferred scattering in varying degrees for one sign of yaw.

Except for the asymmetric scattering load for IGSCC, the physical descriptions of the various classes of targets have been found to correlate well with properties of images made as described. The combinations of image properties seem to be sufficient for unique classification, including in particular IGSCC. A summary of physical and corresponding image properties for a number of different classes of ultrasonic targets is shown in Table 1.

The process of interpreting these images has been found to be strikingly similar to that for interpreting radiographs. Also similar to radiography is the fact that the images are essentially self-normalizing in the sense that precise signal strengths do not enter into the process as long as there is enough signal (or density) to produce an image. The interpretation is based on shapes and patterns, and changes in these between the images.

The technique described here requires the ability to handle a wide dynamic range of signal strength, a high degree of reproducibility, and a precise scanning mechanism. These properties have been demonstrated by a system which was developed at the Idaho National Engineering Laboratory and used for a number of years to perform inservice inspection of the Loss-of-Fluid Test reactor.

TABLE 1—*Comparison of physical and ultrasonic image properties.*

Type of Target	Physical Properties	Image Properties
Machined reflector	smooth and uniform; usually straight	smooth and uniform; specular reflector at all frequencies
Weld root	rounded, relatively smooth; known location documented on radiographs	rounded, lobate; imaged best at low frequencies; relatively smooth
Slag	macroscopically smooth; location within weld, not (usually) connecting to surface	smooth, rounded image obtained at any frequency
Lack of fusion	machined reflector located at root or sidewall	same as any machined reflector
IGSCC	rough, highly irregular, finely branched, randomly oriented facets; not usually straight	rough, ragged, sparkly; persists at high yaw angles; preferred directivity; abrupt; (usually) narrow and changes configuration with viewing angle; imaged strongest at high frequencies and yaw angles
Mechanical fatigue crack	relatively straight; microscopically rough	properties intermediate between weld root and IGSCC; symmetric with yaw

Conclusion

The miniature immersion-type search head, developed for use in automated inservice inspection, provides for increased repeatability of data, versatility of inspection techniques, and reduction in radiation exposure for certified Level II inspectors, who are in short supply. The general-purpose nature of the design makes it easily adaptable to a wide variety of advanced methods of data acquisition.

The procedure for imaging weld flaws is self-normalizing in the sense that one uses differences, rather than measuring the absolute values of any parameter. Further, it extracts and uses information arising on a much smaller scale than the spatial resolution of the system. These properties, together with the good reproducibility shown by the system, suggest its use for detecting changes associated with growth of flaws between inspection cycles.

Acknowledgment

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An Eddy Current Technique to Estimate Dimensions of Crevice Corrosion Pits

REFERENCE: Baron, J. A., Leemans, D. V., and Dolbey, M. P., "An Eddy Current Technique to Estimate Dimensions of Crevice Corrosion Pits," *Corrosion Monitoring in Industrial Plants Using Nondestructive Testing and Electrochemical Methods*, ASTM STP 908, G. C. Moran and P. Labine, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 124-137.

ABSTRACT: A model of an eddy current probe in the presence of an open defect, such as an elongated crevice corrosion pit, is developed. Assumptions are made in respect to field shape, field width, and lift-off function, which are then justified using experimental data. The technique generates estimates of both crevice depth and width without resorting to microminiature probes; other methods tend to generate a response to "volume lost" rather than the more important geometrical parameters. The model is tested against experimental data from artificial pits in a zirconium-niobium material in the range 50 to 800 μm deep, 500 to 2000 μm wide, and 5 to 20 mm long. The technique is also useful in assessing eddy current probe performance.

KEY WORDS: eddy current, nondestructive testing, corrosion pits, crevice corrosion

The primary application of eddy current testing in the nondestructive evaluation arena is the discovery of defects and the interpretation of the electromagnetic disturbance caused by the defect. One of the most common ways of displaying the disturbance is with an amplitude phase diagram presented on a cathode ray tube (CRT) screen, Fig. 1a. Another method is to display the X and Y (or real and imaginary) components of the impedance on a two-channel plotter where a common axis is related to position, Fig. 1b. A typical setup procedure for a given probe or coil would be to adjust the test frequency so

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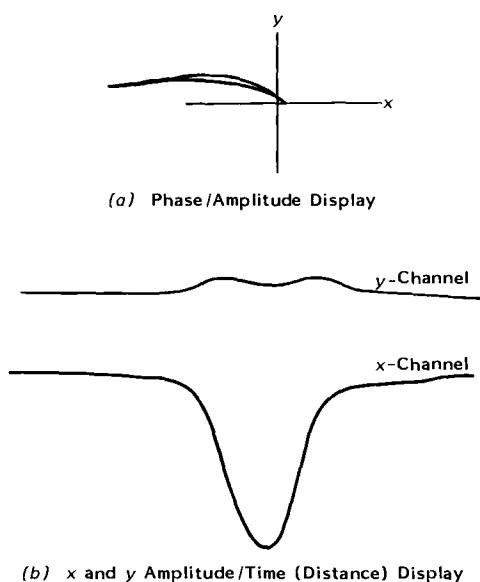


FIG. 1—Response to 1500- μm -wide, 500- μm -deep ID notch.

that there is a 90-deg phase change between shallow defects on the inside and outside of the material or component under test [1]. Usually, disturbances from defects at the same surface as the test coil are arranged to provide a response in the x , or lift-off, direction, with the phase angle from this direction being used to estimate defect depth.

Unfortunately, this technique presents difficulties when attempting to assess the geometrical extent of a defect, especially an open defect such as a corrosion pit rather than a tight crack. The following documents the derivation of geometric data from eddy current indications related to small open-type defects caused by a crevice corrosion process.

Background

A CANDU (CANada Deuterium Uranium) reactor has several hundred horizontal pressure tubes in which heat is transferred from the nuclear fuel to the primary heat transport fluid. The pressure tube material is a zirconium-niobium alloy (Zr-2.5Nb) approximately 4 mm thick. The heat transport fluid is a pH10 lithium hydroxide solution using heavy water and is pressurized at ~ 9 MPa and 250 to 300°C.

The nuclear fuel is contained in bundles of elements, Fig. 2, which rest on the inside surface of the pressure tube. Bearing pads 34 mm long, 3 mm wide, and 1 mm high support the fuel.

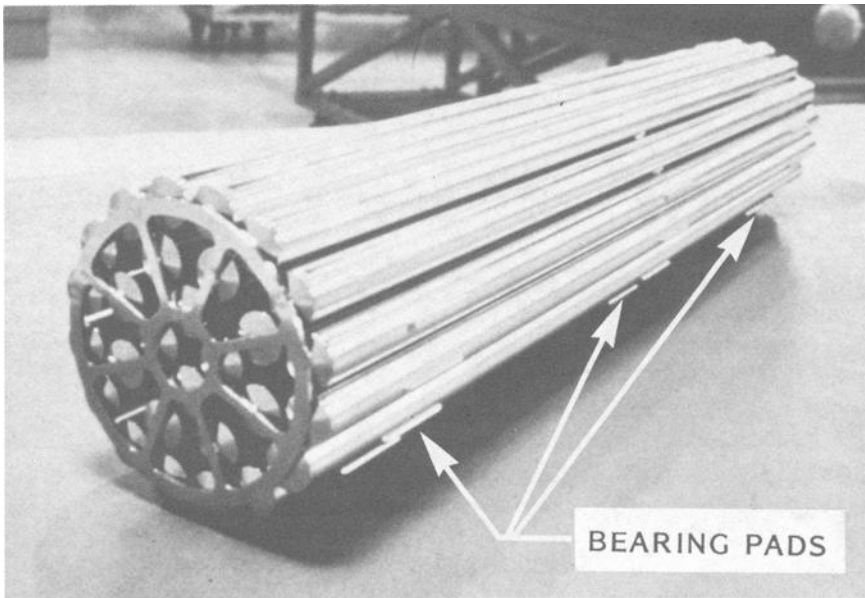


FIG. 2—Typical CANDU fuel bundle.

On-line fueling is employed, and the relative position between the pressure tube and fuel bundle string is always maintained. Further, evidence suggests that not only the axial position of the fuel bundle is maintained; frequently the angular position is maintained so that the bearing pads take up the same location on the pressure tube.

The thermal conductivity of the bearing pads is greater than the primary coolant, thus hot spots develop between the pressure tube and bearing pad, causing localized boiling. This action causes a slight increase in pH and provides an environment conducive to the formation of crevice corrosion pits. In fact, pits have been observed visually in removed pressure tubes. They vary in length from 10 to 38 mm and may occur as a single or multiple parallel pits. They may be oxide filled.

The problem, then, was to devise a technique that would provide sound geometric data, especially depth, of crevice corrosion pits in reactor. This requirement essentially precluded visual/replication methods.

Black-Box Approach

For the most part, the signal⁴ of interest when inspecting for open crevice corrosion pits is in the lift-off direction, that is, the desired signal is a function

⁴Throughout this paper, the "signal" referred to is the change in impedance of the coil, not the induced voltage and not the eddy currents so generated.

of the spacing between the eddy current coil and material surface [2]. It may be seen that the best approximation to crevice depth will occur when the eddy current probe is small compared to the dimensions of the pit, that is, when edge effects are minimized. Considerable effort could be expended to reduce the coil to microscopic dimensions and so achieve an easily identifiable indication of defect depth, but the field becomes weaker and the sensitivity to deep crevices ($\sim 1000 \mu\text{m}$) is lost in doing so. Further, although the coil itself may be minuscule, the effective field, which produces the eddy currents in the material, may be quite large with respect to the defect dimensions. It is thus difficult to interpret the response other than that related to the missing volume under the probe, rather than defect depth. Efforts to control field spread have been made and successfully applied to the detection and sizing of small, tight cracks, but these special probes may prove inappropriate where the defect of interest is open, rather than tight, with substantial volume loss [3,4].

Another approach may be taken, however. Since it is extremely difficult to build an adequate eddy current probe with an effective field width of a few micrometres, it is more productive to simulate the response of a "regular" probe to known small, open defects. The inverse problem of deducing the geometry of an unknown defect from its eddy current response can then be addressed. Note that this "black-box" approach could be applied equally well to other situations such as ultrasonic testing.

Assumptions

The approach taken is not rigorous, but it is sufficient for engineering needs and the inverse problem will not be addressed at great length. The method relies on a number of parameters derived from the voltage-position response as would be viewed, for example, on an oscilloscope screen. Although these derived parameters are a function of physical coil dimensions, orientation, frequency, and instrumentation, they are not used directly and need not be considered for the method to work. It is recognized that the quality of the signal is important, but this has not been taken into account in the following theoretical derivation. However, certain fundamental, but not necessarily critical, assumptions have to be made.

Field Strength Pattern

A disturbance, such as that caused by the presence of a long crevice corrosion pit, will have the greatest effect on the system impedance of the tangential probe used for the experimental verification when its location is at the center of the probe. Therefore, the influence function, while not exactly known, will take on a shape similar to the familiar Gaussian distribution function. In fact, an offset cosinusoidal function has been used for no other reasons except that it fulfilled the smooth maximum to minimum transition and was easy to work with. The assumed shape of the influence function is

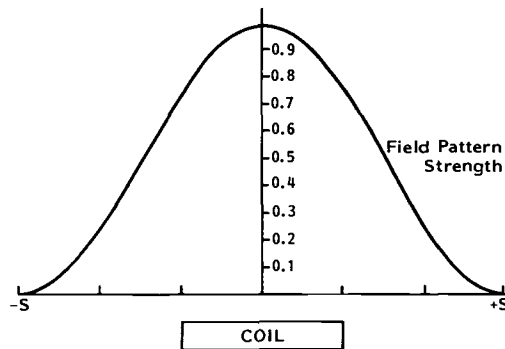


FIG. 3—Assumed field strength pattern (influence function).

illustrated in Fig. 3. This relates most closely to the field pattern generated by an absolute coil. A differential coil could be modelled using a sinusoid, the differential of the cosinusoidal function.

If it is assumed that the peak value of the influence function is unity, Fig. 3, and that the field extends from $x = -s$ to $x = +s$, then the influence function may be expressed as

$$F = 0.5 \left[1 + \cos \left(\frac{\pi x}{s} \right) \right] \quad (1)$$

Amplitude-Distance Parameter

Signals from defects of interest lie totally in the lift-off direction. It is assumed that the probe response is inversely proportional to the probe-material separation:

$$V \propto \frac{1}{H} \quad (2)$$

where V is in the lift-off direction response measured in arbitrary units on the screen of the CRT and H is the coil-surface separation. It should be noted here that H is not strictly the separation between surface and the physical coil, but rather that between the surface and the effective "magnetic zero" of the coil.

Derivation of Response

Consider the situation of Fig. 4a: the separation between the coil and the workpiece is H_1 ; and the response that would be derived in this situation is the result of the entire field acting on the workpiece, that is

$$\begin{aligned}
 V &\propto \int F dx \\
 &= \frac{A}{H_1} \int_{-s}^{+s} 0.5 \left[1 + \cos \left(\pi \frac{x}{s} \right) \right] dx \\
 &= A \frac{s}{H_1}
 \end{aligned} \tag{3}$$

where A is a constant and depends on instrument gain, etc. Thus, the response is proportional to the width of the field and inversely proportional to the coil-workpiece separation.

Where the surface contains an imperfection (such as a crevice corrosion pit found in a reactor pressure tube) within the influence of the magnetic field, Fig. 4b, the response is then derived in exactly the same manner as in Eq 3, that is,

$$V = \frac{A}{H_1} \int_{-s}^x F dx + \frac{A}{H_2} \int_x^{x+w} F dx + \frac{A}{H_1} \int_{x+w}^s F dx \tag{4}$$

Thus, within the limitation of the assumptions, the response of the eddy current probe may be predicted.

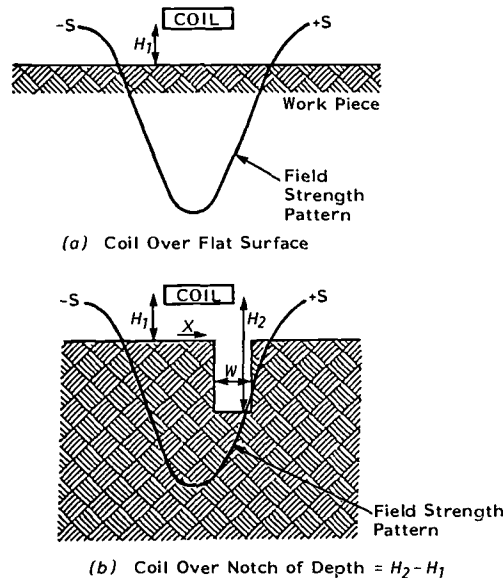


FIG. 4—Eddy current coil over flat surface and notched surface.

Testing the Model

Testing the simulation is not that straightforward because the width of the influence function for a given coil is not usually known, and neither is the position of the "magnetic zero" which is required to generate the parameter H_1 . However, sufficient data can be assembled to develop close estimates of these two parameters using observation and an iterative technique.

Experimental Data

A set of test data was generated using a 250- μm -wide tangential coil operating at 50 kHz and a set of electrical-discharge machined (EDM) notches on the inner wall of a Zr-2.5Nb pressure tube coupon. The coil used was similar in construction to a pancake coil but with its axis parallel to the material surface and perpendicular to the long direction of the notch. The eddy current instrument used was a "Forster Defectomat F" in the bridge mode. Some of the data, Table 1, were corrected by drawing a smooth curve through the points. The data may be separated according to EDM notch depth. The test

TABLE 1—Laboratory data for 250- μm -wide tangential coil at 50 kHz.

Notch, μm		Maximum Signal		
		Amplitude, mV		Theoretical
		Measured	Corrected ^a	
Width	Depth			
2000	50	8	7.0	6
2000	100	11	11.0	11
2000	200	19	18.5	19
2000	300	25	24.5	26
2000	400	28	29.5	31
2000	600	39	38.0	38
2000	800	42	43.0	44
1500	100	8	8.5	10
1500	270	22	22.0	22
1500	400	27	27.0	28
1500	525	30	34.0	31
1500	800	40	37.5	40
1000	100	7	...	8
1000	200	13	...	13
1000	400	20	...	21
1000	600	28	...	27
1000	800	30	...	31
500	100	4	...	4
500	137	6	...	5
500	200	8	...	7
500	400	11	...	12
500	800	17	...	17

^aThe measured values were corrected by drawing smooth curves through these points.

defects were limited to single notches, although it was recognized that multinotch configurations may be found in-reactor. The interest was to validate the approach, not to produce a field-hardened test system.

Determination of Field Width

Although the tangential coil had a width of only 250 μm , plus a ferrite "sandwich" of 500 μm , from Table 1 it may be observed that there was a change in response amplitude between the 1500- μm and 2000- μm -wide notches, for a given notch depth. This suggests a field width of at least 1500 μm . In fact, at a notch depth of 800 μm , the change in signal due to changing the width from 1500 μm to 2000 μm is in excess of 10% using the corrected amplitudes. By iteratively fitting the theoretical response to the experimental response for the 1500 and 2000- μm -wide notches, the effective field width was determined to be about 2600 μm ($s = 1300 \mu\text{m}$).

Determination of Lift-Off Parameter, H

The lift-off parameter is very important, as the response of the probe to a given crevice is dependent on the ratio $H_1:H_2$, Eq 4. If the initial lift-off H_1 is small, then the greatest amplitude change will be observed for a given notch. As with the determination of the influence function width, the value of H_1 was found by an iterative technique employing the values of Table 1 for the 1500- μm and 2000- μm -deep notches. It was determined that the best fit value for H_1 was 600 μm .

The appropriateness of the assumption of response being inversely proportional to separation between coil and workpiece surface is illustrated in Fig. 5 for the 2000- μm -wide notches.

Influence Function

It was assumed that the influence function had a cosinusoidal form. It was not possible to verify the appropriateness of this directly, but the comparison of actual and theoretical responses to a particular notch, Fig. 6, demonstrates the acceptability of the assumption.

Results

The derivation of the influence function width and lift-off parameter has made use of the experimental data relating only to the 2000- μm and 1500- μm -wide series of notches. To this point, the data relating to the 500- μm and 1000- μm -wide series of notches has not been used to derive the coil parameters but will be used only as an evaluation set. Figure 7 provides a comparison of calculated and experimental results as listed in the right-hand column of Table 1.

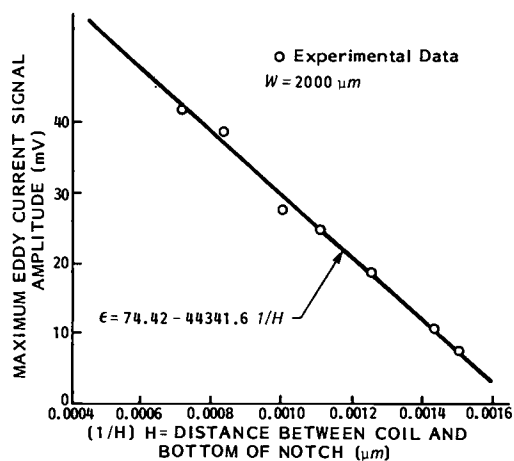


FIG. 5—Comparison of experimental data and the assumption that response $\propto 1/H$ ($H_1 = 600 \mu\text{m}$).

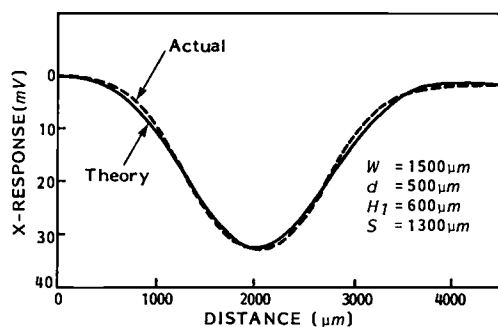


FIG. 6—Comparison of actual and theoretical response.

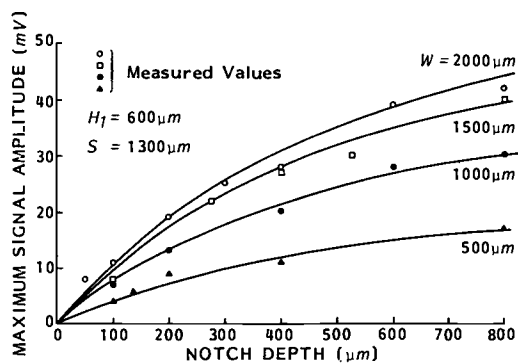


FIG. 7—Comparison of uncorrected experimental data and model response.

Observation of Fig. 7 indicates that the measurement of maximum response is a poor indicator of notch depth, unless the notch width is known. This is illustrated in Fig. 8, which depicts the theoretical response to two dissimilar notches having identical maximum responses. However, there are obvious differences between the two responses of Fig. 8, and this comparison is shown in Fig. 9.

The two principal features of the rate of change of response, Fig. 9, are the amplitude of the peak values and the separation of the two peaks. Figure 10 illustrates how the peak-peak amplitude changes with notch depth and width, and Fig. 11 depicts the separation of the peaks with notch width. In both of these figures, the flat portions are at first surprising.

Figure 12 illustrates how the response changes with notch width for a given notch depth, and Fig. 13 is the corresponding differential of the response. Note that in Fig. 12 the initial part of the curve, the left-hand side, is consistently tracked until the influence of the more remote edge is felt. Clearly, the onset of this influence is dependent only on notch width. Thus, as the coil moves over the edge of the notch, the rate of change of signal will increase.

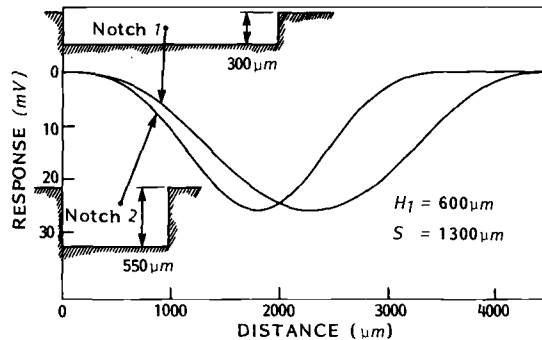


FIG. 8—Comparison of response from two notches. (Note equality of maximum response.)

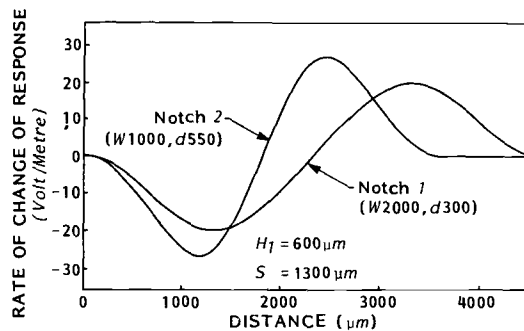


FIG. 9—Differential of response for two notches.

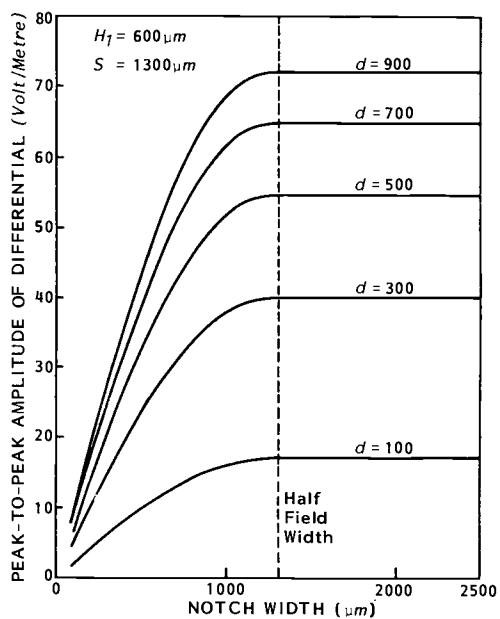


FIG. 10—Relation between peak-to-peak value of rate of change of response and notch width.

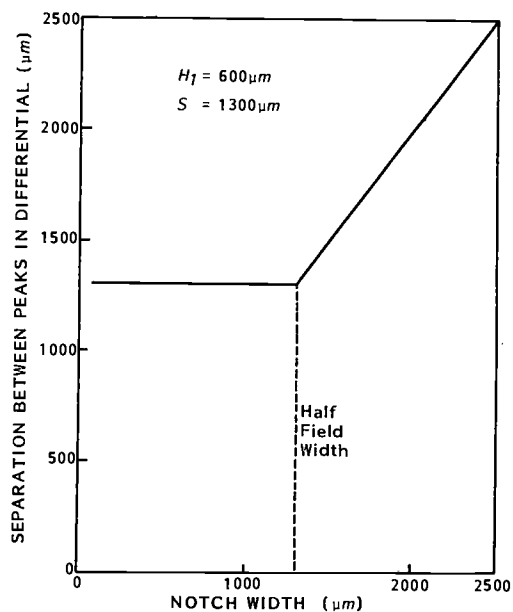
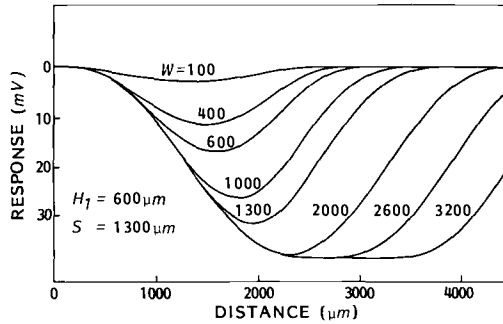
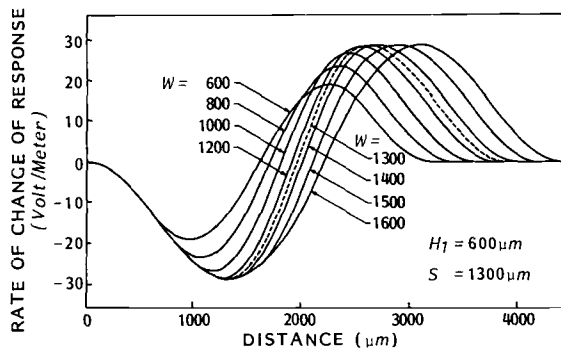


FIG. 11—Separation of peaks in differential of response for any notch depth.


 FIG. 12—Response for a notch of depth 550 μm .

 FIG. 13—Differential of response for a notch of depth 550 μm .

This is easily observed in Figs. 13 and 10. However, once the notch width is equal to the half field width (influence function), the situation will exist where the leading edge of the notch has had its maximum influence on the field and there will be no more increase in the rate of change signal, again well-illustrated in Figs. 13 and 10. If the notch depth is changed there will be a corresponding change in the derivative of the response signal, for a given notch width, Fig. 10.

Where the notch width exceeds half the field width, the coil is able to demonstrate its maximum response to a given notch. This is because the maximum rate of change will occur when the maximum of the influence function is directly over the edge of the notch. Thus, the separation of the maximum-minimum peaks in the derivative of the response will correspond to the notch width. This separation will be independent of notch depth. However, where the notch width is less than half the field width, it will not be possible to build up either the maximum response, Fig. 12, or the maximum rate of change, Fig. 13. In this instance, the separation of the peaks, Figs. 11 and 13, will be constant and equal to half the field width.

Inverse Problem

At this point, the behavior of a well-characterized eddy current probe in the presence of a notch can be predicted. The inverse problem is that, given the response of the probe, can the dimensions of the notch be derived?

The process is to derive three measurements from the response: maximum response; peak-to-peak amplitude of the derivative of the response; and separation of the maximum and minimum in the derivative of the response.

If the peaks in the derivative are separated by at least the half field width, Fig. 11 can be used to read off the notch width. A curve can be generated equivalent to Fig. 7 for the known width, and thus the depth may be found.

If the separation of the peaks is less than the half field width, the process is more complex. This will involve an iterative technique making use of both the functions illustrated in Figs. 7 and 10, and will lead to a unique solution.

Conclusions

The black-box approach can be used quite readily to model the response of an eddy current probe in the vicinity of a notch representative of an elongated crevice corrosion pit. The experimental data confirm the appropriateness of the assumptions made.

Although the simplicity of the use of the method is dependent on notch width, that is, narrow notches will dictate an iterative process, it has been demonstrated that notch dimensions may be determined even though the influence function, or field, is larger than the notch.

Throughout, it has been assumed that the notch is rectangular in cross section, whereas in reality it is more likely to be penny-shaped. This in itself does not negate the value of the technique, especially if an assumption may be made regarding the width/depth ratio of such a notch. In this case, the constant H_2 of Eq 4 is replaced by the appropriate function describing the notch. If the width/depth aspect is constant, as it typically is, this will be a function of a single variable which may be determined by a similar process.

The sole interest of this investigation has been with notches representing corrosion crevices. No attempt has been made to evaluate the situation where the crevices are short compared to the field width. Where the crevice depth varies along the width of the coil, the technique, as described, will tend to yield an average value.

Acknowledgment

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Development of a Sensor for Real-Time Detection of In-Plant Crevice Contaminants

REFERENCE: Carmichael, N. E., Leverant, G. R., and Hugg, S. B., "Development of a Sensor for Real-Time Detection of In-Plant Crevice Contaminants," *Corrosion Monitoring in Industrial Plants Using Nondestructive Testing and Electrochemical Methods*, ASTM STP 908, G. C. Moran and P. Labine, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 138-152.

ABSTRACT: Most forms of corrosion damage in electric power plants are believed to involve the concentration of corrosive species in critical crevice locations such as between disc keyways and keys. The development of an on-line, real-time sensor capable of detecting the concentration of corrosives in crevices is presented in this paper. The sensor measures the temperature and conductance of fluid films entrapped within the crevice of the sensor. The sensor crevice was designed to entrap contaminants similar to those found in actual crevices and to contain the contaminants for future analysis.

Several sensors were laboratory-tested in aqueous solutions within autoclaves and steam lines. Three sensors were evaluated at an electric power plant. These sensors were hard-wired to a steam extraction line and an autoclave in which stress corrosion cracking tests were being conducted. Although problems were experienced with the materials used in sensor construction, the field evaluation demonstrated real-time collection of conductivity and local temperature data and accumulation of crevice contaminants with subsequent laboratory analysis.

KEY WORDS: stress corrosion, contaminants, steam turbine, development, sensor, monitoring, resistive thermal device (RTD)

The problems of corrosion and corrosion-assisted cracking persist in electric power generating plants. The chemical species most frequently responsible for stress corrosion cracking, corrosion fatigue, and other forms of corrosion damage to power plant components are sodium hydroxide (NaOH), sodium chloride (NaCl), and oxygen [1-3].

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Historically, utilities have attempted to prevent corrosion damage by controlling the chemical makeup of feedwater. While this method of corrosion control relies on control of bulk feedwater chemistry, most forms of corrosion damage in power plant machinery are believed to involve the concentration of corrosive species. For example, both thermodynamics [2,3] and practical operating experience [3,4] indicate that ppb levels of NaOH in feedwater can result in localized deposition in turbines of caustic solutions ranging in concentration from a few percent to 100 percent NaOH. In the particular case of low-pressure turbine discs, deposits of hydroxides, carbonates, sulfur-containing compounds, and copper have been detected in or near locations where stress corrosion cracking has been found, for example, in crevices between blades and rim-attachment steeples, between disc keyways and keys, and between disc bores and rotor shafts [4]. It is presumed that these concentrated contaminants are related to pitting and stress corrosion cracking occurring in these creviced regions.

Currently, the first indication of deposition and concentration of corrosive species in an operating power plant is likely to be failure of a component. An on-line, real-time sensor capable of detecting the concentration of corrosives in critical crevice locations (for example, steam generators and turbines) would be of value to the electric utility industry. The development a sensor for this application in low-pressure turbines is addressed in this paper. The sensor detects the concentration of potentially corrosive species by measuring the conductivity of a liquid film condensed from steam into the sensor's crevice. The design, laboratory testing, and preliminary field evaluation of the sensor are addressed in the respective sections of this paper.

Sensor Design

Sensor Definition

The sensor consists of two pairs of electrodes and a resistive thermal device (RTD). The sensor measures the conductances of fluid films deposited in the windows between the two electrode pairs. This conductance depends on the chemical species comprising the fluid and the temperature of the fluid. A RTD responds to local temperature. The sensor is designed to be small enough for insertion, for example, between the base of a turbine blade and the disc rim, with a minimal amount of material removal from the blade or disk. The sensor materials and manufacturing processes were dictated by the environmental and strength requirements for mounting on a rotating steam turbine blade.

Design and Manufacture

The sensor design as shown in Fig. 1 consists of two alumina oxide outer plates with three platinum-gold circuits enclosed. A dielectrical material seals

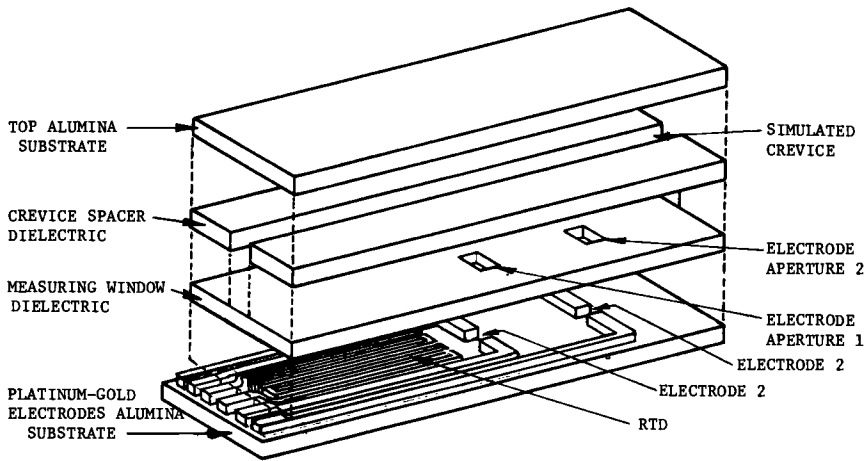


FIG. 1.—Crevice contaminant sensor.

all potential steam or moisture entry except at a designed crevice entry location of about $40\text{ }\mu\text{m}$ in depth. The crevice spacing is approximately the size of crevice spacings developed between blade roots and disc steeples as well as between some disc keyways and keys. The sensor entraps contaminants similar to those trapped in actual crevices, and contains the contaminants for future analysis. However, the sensor can also be used without the top alumina substrate to gather and detect corrosive material directly from an adjacent surface.

The platinum-gold material was chosen for its superior bonding characteristics with the alumina substrate. The dielectric was selected for its high resistance to corrosive environments. Alumina, such as that used for the sensor substrate, is a good insulating material with excellent abrasion resistance. Sensor manufacture involved a series of steps which included screening of the platinum-gold, screening of the dielectric, and several drying and firing processes. After completion, signal wires were bonded to platinum-gold pads of the sensor. High-temperature epoxy added mechanical strength to these connections and effectively insulated the leads from one another. The sensor was then ready for laboratory testing.

Laboratory Testing

Figure 2 shows the laboratory test configuration. Since a single measurement channel was used, the sensor measurement elements were manually switched. By using the meter in the ohm function at the megohm range for conductivity measurement positions, approximately a $10\text{ }\mu\text{A}$ DC current was supplied. The current polarity was switched at the frequency of the function generator to overcome polarization effects, and an oscilloscope was used to

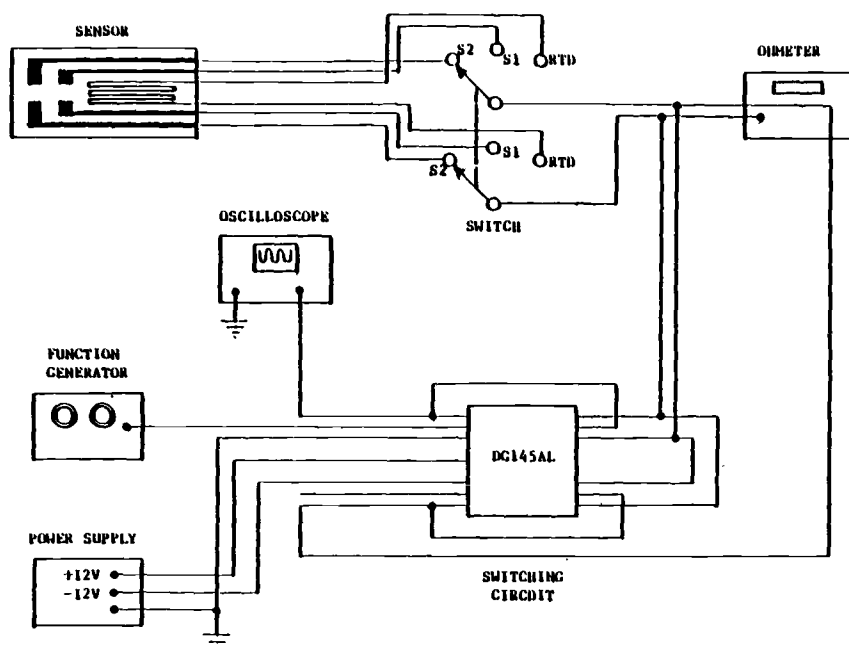


FIG. 2—Laboratory instrumentation for gathering sensor data.

observe the switching frequency and shape of the signal applied to the sensor element. At a switching frequency of one kilohertz, the ohm reading taken directly from the meter provided the sensor element resistance.

A prototype fixture to secure the sensor during laboratory testing was designed to include three basic components:

1. *Sensor Housing*: Protected sensor and soldered joints from excessive stress and fixes sensor position in all three axes while allowing steam to enter the sensor crevice.
2. *Mounting Block*: Allowed hard-wiring of sensor leads through a metal conduit and provided a mounting surface for attachment (welded or other) of the assembly.
3. *Conduit and Pressure Seal (Conax) Fittings*: Allowed wires to travel between sensor and room instrumentation completely isolated from steam.

Room Temperature Calibration

Tests were conducted to evaluate sensor sensitivity to various concentrations of NaOH, NaCl, and sodium sulfate (Na_2SO_4) in solution at room temperature. Data typical of that generated during the test series is plotted in Fig. 3. The significant result of these tests was the three orders of magnitude

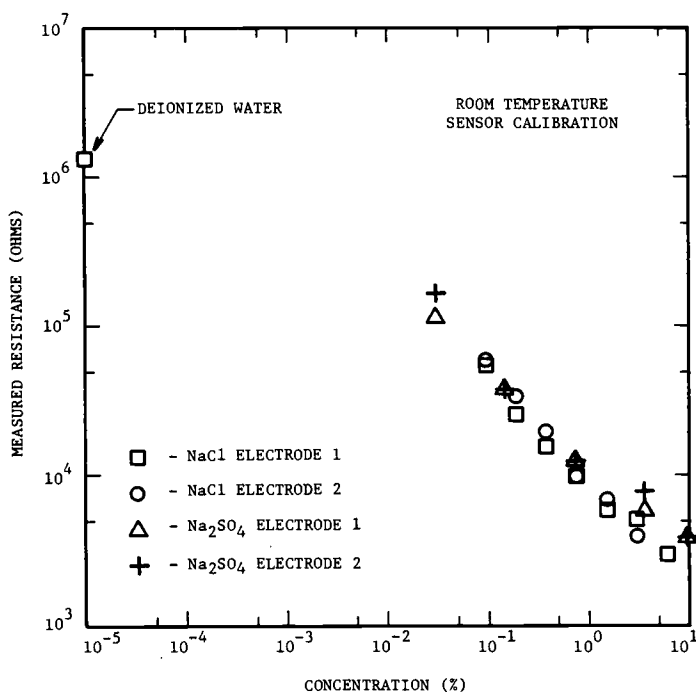


FIG. 3—CCS calibration data using room-temperature solutions of NaCl and Na₂SO₄.

drop in resistance when solution concentrations reached levels of 1% and greater.

Steam Environment Calibration and Testing

A separate series of tests was conducted to determine sensor performance in steam environments. One of the first tests attempted to answer the question of whether the flow rate through the simulated crevice in the sensor would approximate the flow rate through an actual crevice on a turbine disc or blade. A sample of turbine disk material (Ni-Cr-Mo-V steel) was fabricated into a test fixture with geometry similar to that of a sensor crevice. Both this fixture and a sensor were subjected to a set head pressure of water, and rates of flow for each system were recorded. Results of the test indicated that the flow rates for the two systems were essentially identical. Another test to demonstrate the entrapment of contaminants within the sensor crevice was performed inside an autoclave with a 408 K steam-over-water environment. The sensor was not physically damaged by this exposure, and upon dismantling the sensor after the test, it was found that contaminants in the steam had deposited along the entire length of the crevice. A similar test was performed

using a 5% solution of Na_2SO_4 at 447 K. After completion of this test, the upper and lower substrates of the sensor were separated, exposing the inner crevice for examination. Both halves exhibited a deposit along the entire length of the crevice, while a crystalline substance was found between a set of electrodes on the lower half. Energy dispersive X-ray analysis of both the deposit and the crystalline material showed strong indications of sodium and sulfur, suggesting that the deposits were in fact a consequence of the concentration and deposition of Na_2SO_4 in the crevice.

Calibration data for the conductivity sensor was also obtained at 366 K for NaCl and Na_2SO_4 solutions. The shape of these curves is similar to those obtained at room temperature.

RTD Calibration

The resistive thermal device (RTD) in the sensor was tested for its response to temperature in the range of room temperature to 447 K. The results indicated a practically linear increase in resistance with increasing temperature.

Mechanical Testing

A high-speed flywheel testing rig was constructed to evaluate the mechanical integrity of the sensors. This rig rotates the sensor at approximately 6200 rpm, which is equivalent to an acceleration of 65 km/s^2 at the sensor mounting location. This is in excess of the forces at the rim of turbine. No sensor damage was observed after completion of the mechanical testing.

Flowing Steam Tests

The following tasks were completed:

1. The design and testing of sensor attachment techniques.
2. The design and testing of a prototype wiring harness for use on an operating steam turbine.
3. Testing in a flowing steam environment while monitoring the performance of the prototype wiring harness and sensor attachment along with sensor sensitivity and mechanical integrity.

The sensor was mounted inside stainless steel piping attached to a steam generator for sensor and hardware testing under flowing steam conditions. Candidate encapsulation and insulation materials for the sensor lead wires, along with the wiring harness design, conduit and pressure seal fittings, and recording instrumentation were evaluated. Resistance data was monitored and recorded for both sensor electrode pairs and the RTD during a series of short test runs. The sensor used for these test purposes was subjected to a cumulative 55-hour period of steam environment testing.

The sensor and attachment hardware performed well throughout the test period. A conclusive check of wiring harness mechanical integrity was performed after the test series through a disassembly and inspection procedure. No sensor components showed degradation.

An initial attempt was made during this testing phase to introduce contaminant into the flowing steam line at a point just upstream of the sensor. A pipe tee 0.3 m upstream of the sensor was modified to allow a batch addition of contaminant. Sodium sulphate was used as a contaminant. A distinct transient decrease in sensor resistive readings corresponding to the addition of the Na_2SO_4 was seen. After three similar tests were run, the resistance measurements of the sensor suddenly remained near the low level “dip” characteristic of the contaminant addition. An explanation of this phenomenon was apparent after the test rig was dismantled and the sensor was subjected to X-ray analysis. Evidence of sodium, sulfur, and iron was found inside the sensor crevice; their accumulation apparently resulted in the permanent reduction in resistance. This buildup of contaminants inside the sensor was further proof of the entrapment capabilities of the design. Also, the marked effect of these contaminants on sensor resistance was a good indication of the sensor’s ability to detect the presence of corrosive material and to indicate a buildup of the material over time.

Preliminary Field Evaluation

Test Bed

Preliminary field evaluation of the sensor was conducted after completion of the laboratory development of the crevice contaminant sensor. This phase included development of sensor probes and signal conditioning equipment for the field site, calibration, sensor evaluation, and data analysis. The test bed for the sensor was a 2-gal autoclave fed from a steam extraction of a low-pressure steam turbine in an electric power generating plant. The site included a bulk chemical analysis test loop that operated in conjunction with the autoclave. The autoclave also served as a test bed for stress corrosion cracking tests [5].

Field Equipment Development

The system featured three crevice contaminant sensor (CCS) probes, associated signal conditioning, and data recording on the plants process control computer. Each probe featured a unique fixture so that the complete and open-faced sensor designs could be field-tested in various orientations, positions, and steam flow rates. Figure 4 presents a schematic of the installation of the three CCS probes. Probe C, a complete sensor with a vertically oriented crevice, was installed in a T-section in the steam supply to the autoclave.

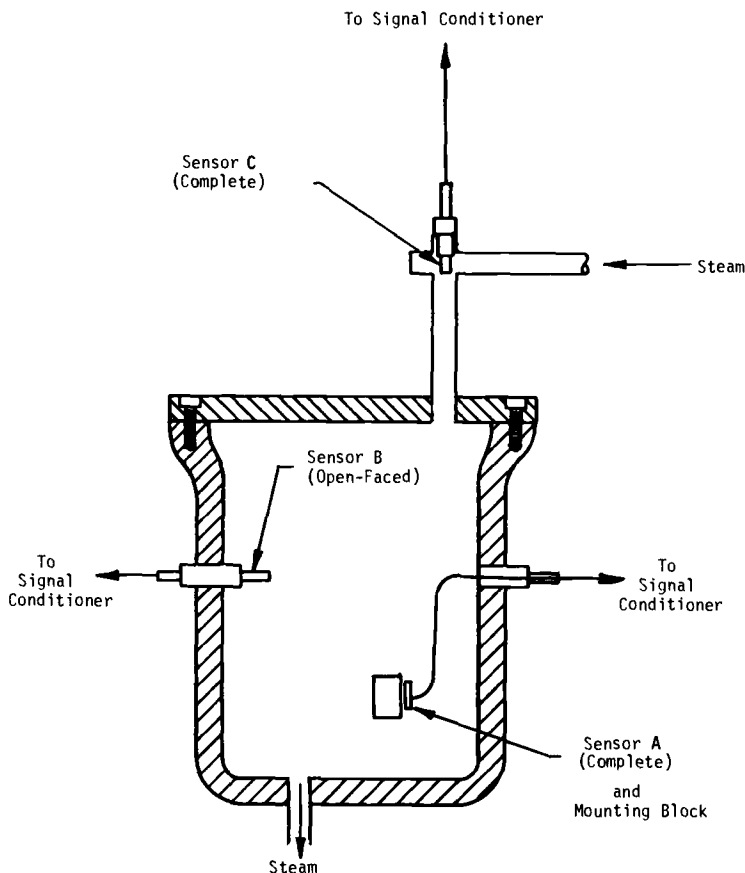


FIG. 4—Schematic of autoclave installation.

Probe B, an open-faced sensor with its face oriented upward, and Probe A, a complete sensor with a vertically oriented crevice, were installed through the autoclave wall.

The expected autoclave environments were 7.82 atm, 443 K, 2% to 3% moisture steam or 7.82 atm, 472 to 505 K, dry steam. To operate in this steam environment, the sensor was integrated into a CCS probe using high pressure fitting, welded stainless steel construction, gold paste to bond lead wires to the sensor, and high temperature epoxy encapsulant. Figure 5 shows photos of these probes after assembly.

The signal conditioner supplies excitation to the sensors and then converts the low-level sensor signals to signals compatible with the recording media. Electronics were contained within a NEMA 4 enclosure (watertight and dust-tight) with watertight cable connectors designed to operate in an area with

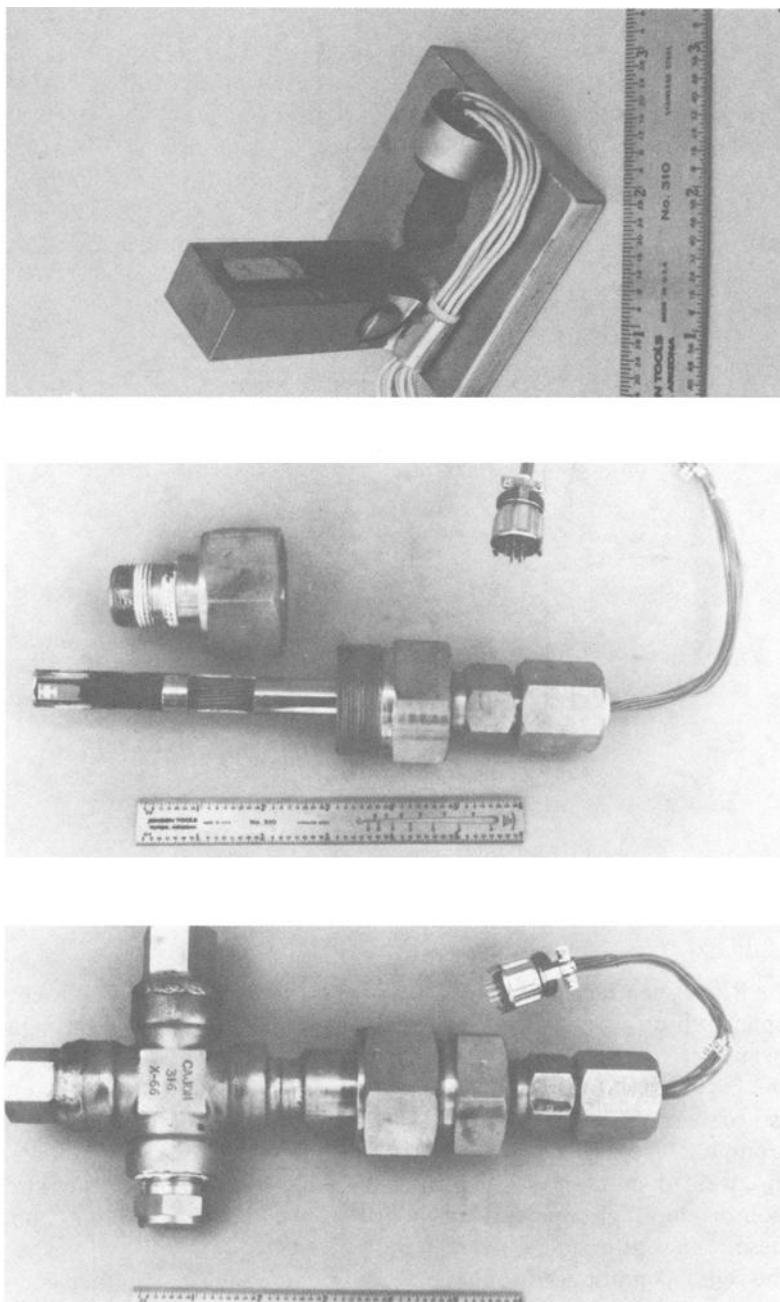


FIG. 5—Assembled probes. (a) Probe A: complete sensor. (b) Probe B: open-faced sensor. (c) Probe C: complete sensor.

overhead steam and water pipes. The front panel included a digital voltmeter and a selector switch to allow local monitoring and calibration of the sensors. The RTD signal conditioner converted the approximately linear increase in resistance with increasing temperature to a proportional 4 to 20 mA output. The RTD signal conditioner consisted of a three-wire bridge, a differential amplifier, and a voltage-to-current converter. The oscillator and demodulator provided the excitation and signal conversion from the electrode pairs of the CCS probes. The oscillator excited the sensors with a stable 1 kHz sinusoidal waveform. A sinusoidal waveform with no measurable direct current component was chosen to minimize polarization effects in the conductivity measurement. The demodulator produced an output inversely proportional to impedance between an electrode set. The signal transfer function provided for three decades of measurement with increased accuracy when measuring low resistance (high conductivities). The lowest resistance within the measurement range was 10 kilohms.

Calibration Procedures

This test program complemented the earlier testing performed during the laboratory development of the sensors. While the previous test results demonstrated the capabilities of the device for measurements in a laboratory-controlled steam environment, this series of tests generated calibration data for the specific sensors that were installed in the field, and evaluated the integrity of the CCS probes. The CCS probes, with sensors installed, were tested according to the following procedures:

1. Inspect mechanical and electrical integrity of sensor and lead wires under a low magnification binocular microscope.
2. Calibrate the RTD over the temperature range of 273 to 491 K.
3. Calibrate the conductivity electrode pairs with room temperature solutions of deionized water and Na_2SO_4 of 0.001, 0.01, and 0.1% concentration.
4. Repeat Step 3 with 366 K solutions.
5. Age CCS probe at 490 K for 12 h while checking RTD resistance.
6. Repeat Steps 3 and 4 and check RTD sensitivity.

Calibration of RTD

The RTD and RTD signal conditioner were calibrated with the sensor submerged in deionized water and in air in an environmental chamber. Given the desired accuracy of 2 K, the resistance versus temperature function was linear over the expected operating temperature range. No significant shifts in the RTD calibrations were noted following the aging of Step 5 of the test procedure.

Calibration of Conductivity Electrodes

The electrode pairs of the sensors were calibrated with room temperature solutions and with 366 K solutions of Na_2SO_4 . Sodium sulfate was chosen for its minimal corrosive nature and for its solubility in deionized water. The latter property was especially important when flushing all traces of Na_2SO_4 from the channels of the complete sensors prior to field installation. Figure 6 shows typical calibration curves. The calibration curves showed the expected increase in measured conductivity with an increase in the temperature and concentration of the solution and agreement of readings between electrode pairs of a sensor. No significant changes were noted in the calibration curves following aging.

Integrity Tests

The environmental conditions of the autoclave and the plant environment were outlined in a previous section. The environmental tests included the following:

1. Signal conditioning environmental temperature test at 322 K for one hour.

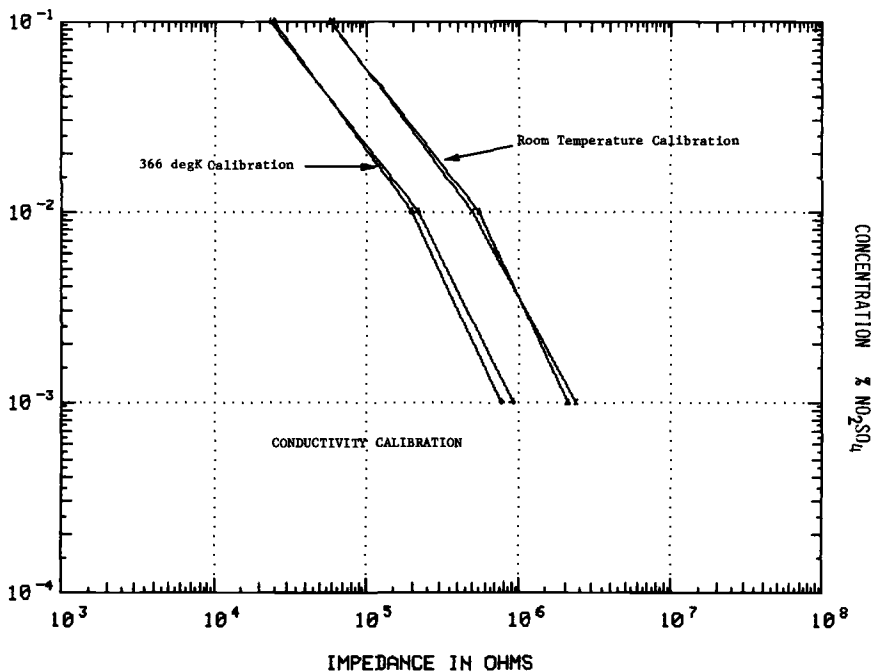


FIG. 6—Typical calibration curves for CCS electrode sets.

2. Probe temperature test at 490 K for 12 h.
3. Pull test on gold paste bond of the sensor lead junction.
4. Pressure seal test of probe using helium.

The signal conditioning equipment and probes operated successfully in all cases except in the probe test at 490 K for 12 h. The epoxy of Probe B pulled away from the stainless steel shelf on which the sensor was mounted, but Probes A and C showed no similar degradation of the bond. Discussion with the manufacturer led to the conclusion that the separation was probably a combination of the thermal expansion characteristics of the epoxy and inadequate preparation of the stainless steel surface. The decision was made to use a different epoxy and change the surface preparation of the stainless steel for Probe B alone, since the epoxy bonds for Probes A and C were mechanically sound. The second epoxy adhered to the stainless steel and to the sensor during subsequent tests.

Field Installation

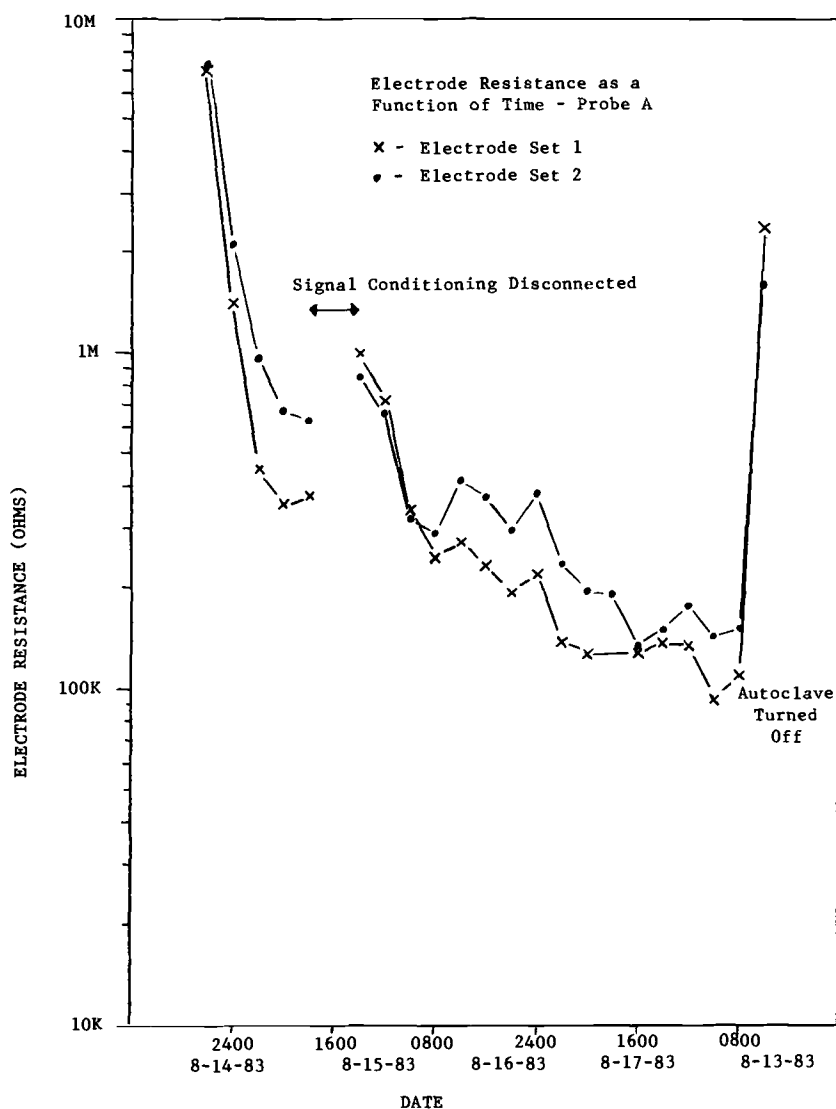
A field test setup for three CCS probes was installed in an autoclave. Following assembly of probes into the autoclave and its steam supply line as specified in the installation drawings, test and calibration signals were generated.

CCS Probe Evaluation and Data Analysis

The probes were left in the autoclave for approximately 10 weeks, after which the probes and signal conditioning were returned to the laboratory for evaluation. When the steam valve for the autoclave was opened, the response of the electrode sets of Probes A and B showed a relatively rapid increase in conductivity. This transient was probably caused by contaminants in the water that collected in the upstream vertical piping while the autoclave was shut off for the previous week. As expected from the laboratory test program, the resistivity measured by the complete sensor (Probe A) was an order of magnitude higher than the resistivity measured by the open-faced sensor (Probe B).

Initially, problems were experienced with Probe C. Further, during the first day of field test, the RTD of Probe B failed. However, the temperature measured by the RTD of Probe A tracked the recorded autoclave temperature as measured with thermocouples. Following 15 h of autoclave operation, the probes were visually inspected. No degradation of the probes was observed. The probes and autoclave were then returned to operation, and the field test continued for another 10 weeks.

The response of Probe A during the first 5 days of operation is seen in Fig. 7. The data showed a trend toward lower resistivity, which is probably indicative of the accumulation of contaminants. As discussed later, Probe A showed traces of contaminants when examined using X-ray analysis. The electrode resistance returned to a high value when the autoclave was turned off, be-



temperature was approximately 2% per degree K, as expected [5]. At the autoclave temperature of 386 K, the resistance responses translate to solution concentrations of 0.001% to 0.01% by weight. Over the same period of time, the existing total conductivity analyzer recorded an average conductivity of $6.5 \mu\Omega/\text{cm}$. When this conductivity was converted to the approximate concentration [5,6], the concentration calculated from the CCS measurements was an order of magnitude higher than the concentration calculated from total conductivity. This result demonstrates that bulk conductivity of the effluent from the autoclave does not necessarily relate to the conditions at a local site such as a crevice.

The electrode resistivity data beyond the initial five days of operation was not used in the sensor analysis. Probe failures, that were discovered when the probes were removed from the autoclave, compromised the data collected beyond this initial period.

At the conclusion of the field test the probes were removed from the autoclave, then returned to the laboratory for evaluation. Components of the sensor and the CCS probe failed during field test. The dielectric and the epoxies degraded in the steam environment of the autoclave. The capabilities of the epoxies to insulate and secure the leadwire connections to the sensors were compromised thereby resulting in sensor failures during field test.

Apart from the component problems described above, all other components performed very well throughout the field test. Specifically, no degradation of the Teflon pressure seal was observed. The stainless steel probe substructure, coupling, and unions not only performed well in the steam environment, but also provided for easy sensor insertion and removal from the autoclave. The signal conditioning functioned without component failure throughout the field test.

Summary

A crevice contaminant sensor system was developed that provides for the following:

- Installation of multiple sensors into steam vessels and piping.
- Real-time data collection in the field.
- Accumulation of crevice contaminants in the field with subsequent laboratory analysis.

Although the operation and mechanical and electrical integrity of the system was demonstrated initially in the field, degradation of the encapsulation material used in the probe manufacture under the steam conditions resulted in the eventual loss of data collection.

Field test results indicated a need for component modification and subsequent testing prior to introduction of the CCS into a long-term test bed. Specifically, the following component modifications were recommended:

1. Replace epoxy encapsulating material with a more erosion-resistant material.
2. Reconfigure sensor such that leadwire connections are made along the long sides of sensor rather than on one short side, thereby increasing the pad surface area and preventing capillary-induced attraction of encapsulating material into the crevice.
3. Add a leadwire fixture integral to the stainless steel probe substructure.

Acknowledgments

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Ultrasonic Velocity Ratio Method for Detecting and Evaluating Hydrogen Attack in Steels

REFERENCE: Watanabe, T., Hasegawa, Y., and Kato, K., "Ultrasonic Velocity Ratio Method for Detecting and Evaluating Hydrogen Attack in Steels," *Corrosion Monitoring in Industrial Plants Using Nondestructive Testing and Electrochemical Methods*, ASTM STP 908, G. C. Moran and P. Labine, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 153-164.

ABSTRACT: An ultrasonic attenuation technique has been employed in practice to detect hydrogen attack nondestructively. However, it is difficult to evaluate hydrogen attack quantitatively by this technique, because ultrasonic attenuation is influenced by the test conditions and the material itself.

In this paper, a new approach to a quantitative evaluation of hydrogen attack with an ultrasonic velocity technique is described. The longitudinal and shear wave velocities were observed to decrease more than 10% and 7%, respectively, in a steel fully attacked by hydrogen as compared with those in sound steel. This large change in velocity is sufficient to enable the thickness attacked by hydrogen to be predicted, if the wall thickness of material concerned is known.

Moreover, the ratio of shear wave velocity to longitudinal wave velocity is quite promising as a factor for evaluating the thickness attacked by hydrogen, without measuring the thickness of material tested.

KEY WORDS: ultrasonic testing, wave velocity, hydrogen attack, Young's modulus, shear modulus, Poisson's ratio, carbon steel, low alloy steel, decarburization, micro-cracks, nondestructive tests

In chemical and power plants, a large number of equipment and pipes serve in a hydrogen environment under pressure and at elevated temperature. Hydrogen diffuses into the plain carbon steel and low-alloy steel of these components and causes internal decarburization and intergranular fissuring,

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known as "hydrogen attack," accompanied by a severe deterioration of mechanical properties of materials.

In March 1982 in Japan, a window-type fracture of piping which was fully attacked by hydrogen resulted in a serious explosion in a desulfurization process unit of a petroleum refining plant. The development of a nondestructive inspection method to detect and evaluate the early stages of hydrogen attack has thus become necessary to avoid another such catastrophic accident.

Up to now, an ultrasonic echo attenuation technique has been employed to detect hydrogen attack in the field [1-3]. Acoustical absorption is strongly affected by variables such as exterior surface roughness and internal surface profile, in addition to the metallurgical structure of the material. Also, initial attenuation measurements prior to service and periodic monitoring during service are required to detect the initiation and development of hydrogen attack.

This paper discusses the possibility of using wave velocity to evaluate the hydrogen attack, based on the velocity decrease in a steel attacked by hydrogen.

Hydrogen Attack Decreases Wave Velocity

The wall thickness of the window-type fractured carbon steel pipe, in which hydrogen attack was confirmed by metallographic examination, was measured using an ultrasonic thickness gage and a dial caliper. The ultrasonic thickness gage, which was calibrated by a standard test block, indicated a thickness which was more than 10% greater than that measured by a caliper [4].

From this fact, it was anticipated that decarburization and microcracks at grain boundaries in the hydrogen attacked zone would affect the ultrasonic velocity. A test specimen approximately 10 mm thick was sectioned from this pipe in order to confirm the difference between wave velocity in the hydrogen-attacked zone and that in the sound metal. A normal transducer was located on the cross section of the test specimen, as shown schematically in Fig. 1, to observe the reflected signals in both areas simultaneously on the cathode ray tube (CRT) screen.

The multiple reflected signals of a longitudinal wave are shown in Fig. 2, in which L_S means the reflected longitudinal wave signal in sound metal, and L_A means that in the hydrogen-attacked zone. Then, a normal incidence shear wave transducer was located on the same position of the test piece as a normal transducer was. Figure 3 shows the multiple reflected signals of a shear wave.

The brief experiment makes it clear that the wave velocity decreases to a greater extent in the hydrogen-attacked zone compared with that in the sound metal.

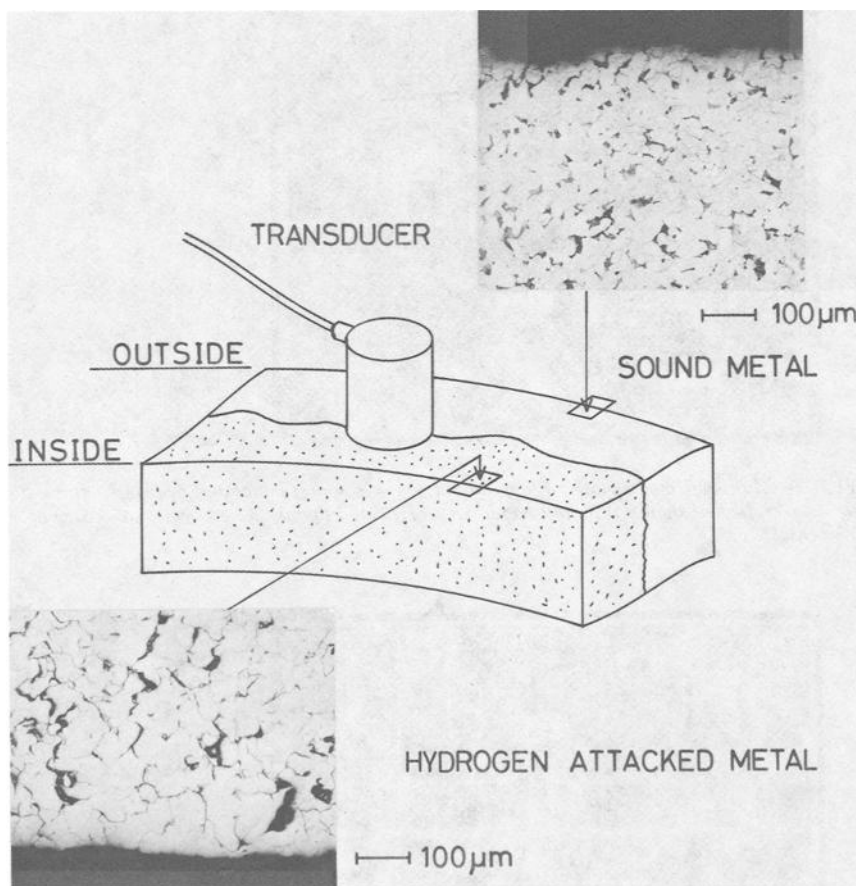


FIG. 1—Location of ultrasonic transducer to observe the difference in wave velocity between sound metal and hydrogen-attacked metal.

Application of Wave Velocity for Evaluating Thickness of Hydrogen Attack

Application of Longitudinal Wave Velocity

From the fact that the wave velocity decreases in hydrogen-attacked metal, wave velocity measurement may be employed as a nondestructive technique to determine whether or not a material has been subjected to hydrogen attack. But the wave velocity in metal is influenced by the characteristics of the metal itself; in addition, it seems to be quite difficult to measure directly the real thickness of suspicious components in service. This disadvantage can be over-

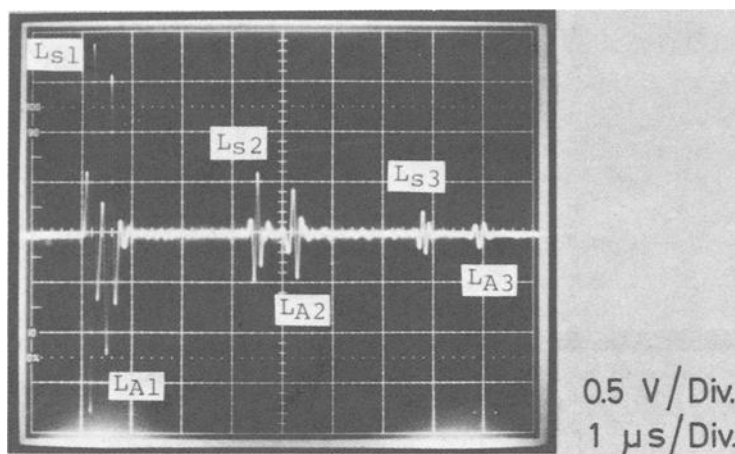


FIG. 2—Multi-reflected signals of longitudinal wave in sound metal and hydrogen-attacked zone. L_S = reflected signals in sound metal. L_A = reflected signals in hydrogen-attacked zone. 0.5 V/Div.; 1 μ s/Div.

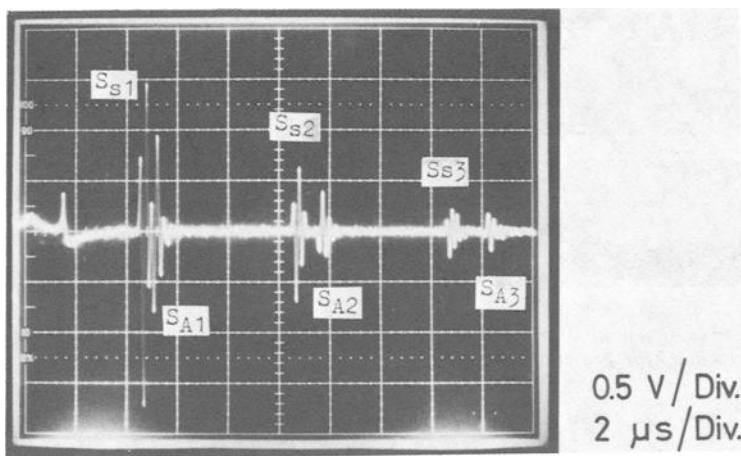


FIG. 3—Multi-reflected signals of shear wave in sound metal and hydrogen-attacked zone. S_S = reflected signals in sound metal. S_A = reflected signals in hydrogen-attacked zone. 0.5 V/Div.; 2 μ s/Div.

come by measuring the time taken for the wave to propagate and be reflected from the back wall.

In other words, hydrogen attack may be detected by a delay in the wave traveling time, which is easily measured with accuracy. However, this method still requires periodic measurement, like the attenuation method; it is also not possible to evaluate the thickness attacked by hydrogen.

Wave Velocity Ratio Method

In order to avoid these problems, the combination of shear wave velocity and longitudinal wave velocity was examined for evaluating hydrogen attack.

In comparing Figs. 2 and 3, it is clear that the decrease of the wave velocity caused by hydrogen attack is different between the longitudinal wave and the shear wave. This suggests the possibility of applying the wave velocity ratio of the shear wave to the longitudinal wave for evaluating the thickness of the hydrogen-attacked zone. Based on this idea, the relation between the wave velocity ratio V_S/V_L and the thickness of hydrogen-attacked zone was derived.

A schematic representation of a longitudinal wave and a shear wave traveling in the wall of a suspected component is illustrated in Fig. 4. Each transducer will be located at the same position on the outside surface of the component inspected.

The following basic equations can be set up:

$$T = T_S + T_A$$

$$\frac{2T}{V_L} = \frac{2T_S}{V_{LS}} + \frac{2T_A}{V_{LA}}$$

$$\frac{2T}{V_S} = \frac{2T_S}{V_{SS}} + \frac{2T_A}{V_{SA}}$$

where

T = wall thickness of a suspected component, mm,

T_S = thickness of sound metal, mm,

T_A = thickness of hydrogen-attacked zone, mm,

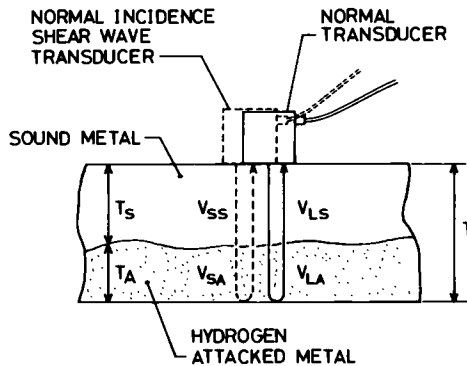


FIG. 4—Longitudinal and shear wave velocities in a suspected component.

V_L = mean value of longitudinal wave velocity through wall, mm/s,
 V_S = mean value of shear wave velocity through wall, mm/s,
 V_{LS} = longitudinal wave velocity in sound metal, mm/s,
 V_{LA} = longitudinal wave velocity in hydrogen-attacked zone, mm/s,
 V_{SS} = shear wave velocity in sound metal, mm/s, and
 V_{SA} = shear wave velocity in hydrogen-attacked zone, mm/s.

From these equations, we obtain the following equation which shows the relation between the velocity ratio of the shear wave to the longitudinal wave (V_S/V_L) and the thickness ratio of hydrogen-attacked zone to the wall thickness (T_A/T).

$$\frac{V_S}{V_L} = \frac{V_S}{V_{SA}} \left(\frac{V_{SA}}{V_{LA}} - \frac{V_{SS}}{V_{LS}} \right) \frac{T_A}{T} + \frac{V_{SS}}{V_{LS}} \quad (1)$$

Here, V_S/V_{SA} on the right side of this equation depends on the percentage of the thickness attacked by hydrogen, because V_S is the mean shear wave velocity through the wall thickness. Further, it effects still less than 0.2% the change in the value of V_S/V_L . Therefore, Eq 1 can be approximated as

$$\frac{V_S}{V_L} = \left(\frac{V_{SA}}{V_{LA}} - \frac{V_{SS}}{V_{LS}} \right) \frac{T_A}{T} + \frac{V_{SS}}{V_{LS}} \quad (2)$$

It is almost impossible, however, to measure the wave velocity in the component in service, as mentioned before. Therefore, considering the application of this technique on site, the traveling times of a longitudinal wave and a shear wave (t_L and t_S), which penetrate from the exterior surface of a suspected component and are reflected from the back wall, are more appropriate for avoiding the above difficulty. In this case, V_S/V_L is equal to t_L/t_S , and also, V_{SA}/V_{LA} , V_{SS}/V_{LS} in Eq 2 are converted to t_{LA}/t_{SA} , t_{LS}/t_{SS} , respectively.

Finally, the relation between the wave traveling time and the proportion of the thickness of hydrogen attack to the wall thickness is obtained as follows.

$$\frac{t_L}{t_S} = \left(\frac{t_{LA}}{t_{SA}} - \frac{t_{LS}}{t_{SS}} \right) \frac{T_A}{T} + \frac{t_{LS}}{t_{SS}} \quad (3)$$

Test Specimens and Experimental Results

Test Specimens

Details of all specimens and experimental results are summarized in Table 1. Several test blocks 25 mm square and 15 mm thick were taken from the window-type fractured carbon steel pipe (symbol "A"). Two more blocks

TABLE 1—Details of test specimens and experimental results.

Test Specimen	Thickness T , mm	Thickness of Hydrogen Attack, T_A , mm			T_A/T , %	Wave Traveling Time		Wave Velocity		t_L/t_S
		Min	Max	Avg		Longitudinal t_L , μs	Shear t_S , μs	Longitudinal V_L , m/s ^a	Shear V_S , m/s ^a	
A-1	10.0	0	0	0	0	3.41	6.23	5.87	3.21	0.547
A-2	15.0	10.5	12.0	11.1	74	3.41	6.24	5.87	3.21	0.546
A-3	15.0	12.7	14.1	13.4	89	5.62	9.84	5.34	3.04	0.571
A-4	15.0	13.3	14.5	13.7	91	5.62	9.90	5.34	3.03	0.567
A-5	15.0	13.2	14.5	13.7	91	5.69	9.85	5.27	3.05	0.578
A-6	10.0	10.0	10.0	10.0	100	5.70	9.99	5.26	3.00	0.571
A-7	10.0	5.5	6.3	6.0	60	5.64	9.82	5.32	3.05	0.574
G	15.0	0	0	0	0	5.66	10.01	5.30	3.00	0.565
H	10.0	0	0	0	0	5.70	9.83	5.26	3.05	0.580
I	22.3	5.5	9.0	7.1	32	5.70	9.96	5.26	3.01	0.572
S	25.0	...	...	0	0	3.94	6.70	5.08	2.99	0.588
F	10.0	...	...	0	0	3.95	6.82	5.06	2.93	0.579
						3.62	6.43	5.52	3.11	0.563
						3.62	6.45	5.52	3.10	0.561
						5.07	9.25	5.92	3.24	0.548
						5.06	9.25	5.93	3.24	0.547
						3.38	6.17	5.92	3.24	0.548
						3.38	6.20	5.92	3.23	0.545
						7.67	13.87	5.81	3.22	0.553
						7.66	13.89	5.82	3.21	0.551
						8.44	15.42	5.92	3.24	0.547
						8.45	15.42	5.92	3.24	0.548
						3.35	6.14	5.97	3.26	0.546
						3.36	6.19	5.95	3.23	0.543

^aEach entry times 10³.

having a thickness of 10 mm were taken from this pipe: one was cut from the hydrogen-attacked zone for the purpose of obtaining one specimen fully hydrogen-attacked through its thickness. The other was cut from the sound metal portion.

Specimen "G" was sampled from a carbon steel specified as same as specimen "A." Another carbon steel pipe (symbol "H") and a carbon steel nozzle of a pressure vessel (symbol "I") operated under hydrogen service were prepared for testing. Also, the IIW-type ultrasonic calibration standard block (symbol "S") and an extra-low-carbon steel of 0.007 weight % carbon (symbol "F") are supplied for reference.

The thickness of hydrogen attack is defined as the distance between the bottom edge of the specimen and the edge of the area on which microcracks can be observed by a microscope of $\times 100$ magnification. Observations were conducted on the both cross sections of the test specimens, in the range of the diameter of the transducer. The ratio of the thickness of hydrogen attack to that of the test specimen was calculated by using the average values of the thickness of hydrogen attack.

Wave Traveling Time Measurement

The block diagram for measuring the traveling time of the wave is illustrated in Fig. 5. A normal transducer and a normal incidence shear wave transducer, both 6.4-mm-diameter, 5 MHz types, were alternately coupled to the same position on the test specimens. The pulser/receiver out put signals were digitized and transferred to the central processing unit (CPU).

Signals were sampled at intervals of 10 ns, and a simple averaging method was used to increase the signal-to-noise ratio. The traveling time was calculated from the data sampling addresses on which the peaks of the first and second reflected signals are located.

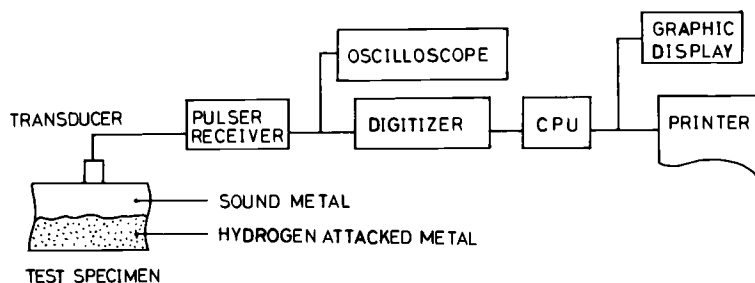


FIG. 5—Block diagram of the wave traveling time measuring system.

Experimental Results

Wave velocity measurements were made for each test specimen at two different particle motion directions of the shear wave. The experimental results are shown in Table 1. Wave velocities were calculated from the traveling times. In the case of the "A" specimens, it is found that the longitudinal wave velocity and the shear wave velocity decrease by more than 13% and by approximately 7%, respectively, in the hydrogen-attacked metal as compared with those in the sound metal.

Test Specimens A-1 and H were served in hydrogen environment, but were not attacked by hydrogen. Test Specimens G, S, and F are not exposed to hydrogen. The ratio t_L/t_S of these specimens is included in the range 0.546 to 0.548. On the other hand, the ratio t_L/t_S of Test Specimen A-6, which is fully hydrogen-attacked through its thickness, is 0.588.

The relation between the ratio t_L/t_S and the percentage of the thickness attacked by hydrogen is illustrated in Fig. 6. In this figure, the experimental data are shown by round symbols, and the broken line shows the relation represented by Eq 3, in which t_{LA}/t_{SA} and t_{LS}/t_{SS} equal 0.588 and 0.547, respectively. These data are lower than the values obtained using Eq 3. This is possibly caused by the uncertain crack distribution in the specimens.

The result of a test performed on Test Specimen I, which is a fragment

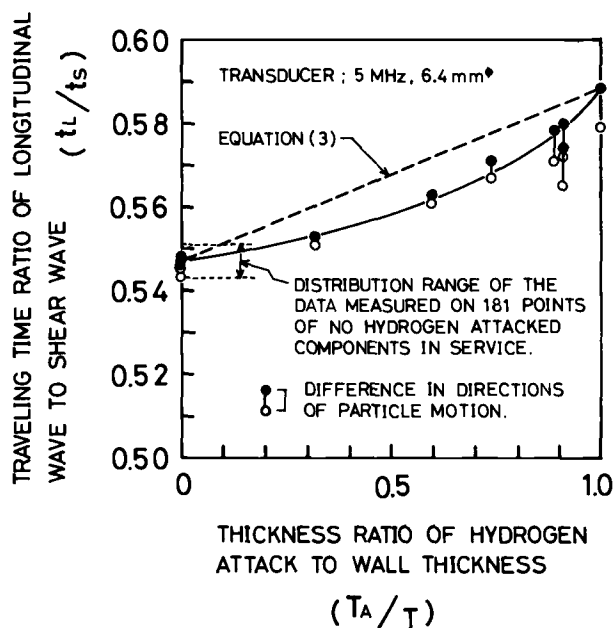


FIG. 6—Relation between hydrogen-attacked percentage of wall thickness and traveling time ratio of longitudinal wave to shear wave.

taken from a nozzle of a pressure vessel, shows good agreement with the results obtained from the "A" test specimens. Therefore, this curve will be applied for predicting the thickness of hydrogen attack in suspected components.

Discussion

A steel attacked by hydrogen involves decarburization and microcracks at grain boundaries. In this experimental work, the longitudinal and shear wave velocities in the extra low carbon steel are similar to those of the sound carbon steel specimens, but they are quite different from velocities of Specimen A-6, in which no pearlite was observed. Besides, the ratio t_L/t_S of the extra low carbon steel is 0.546. This fact indicates that the wave velocity decrease is mainly caused by the existence of microcracks, not by decarburization.

L. A. Glikman reported that the Young's modulus of carbon steels decreased after exposure to high-pressure hydrogen at elevated temperature [5]. Thus, the Young's modulus (E) and the shear modulus (G) of the sound metal (Test Specimen A-1) and the fully hydrogen attacked metal (Test Specimen A-6) were calculated using the following equations.

$$E = V_L^2 \frac{(1 + \nu)(1 - 2\nu)}{(1 - \nu)}$$

$$G = V_S^2 \rho$$

$$\nu = \frac{V_L^2 - 2V_S^2}{2(V_L^2 - V_S^2)}$$

where ρ is mass density (kg/m^3) and ν is the Poisson's ratio.

The mass density of the sound metal and the hydrogen attacked metal were $7.75 \times 10^3 \text{ kg/m}^3$ and $7.67 \times 10^3 \text{ kg/m}^3$, respectively. The calculation results are shown in Table 2. From these data, it is clear that hydrogen attack accompanied with numerous microcracks induces extreme change of the mechanical properties of a material.

Here, problems that need to be clarified are the influence on wave velocity

TABLE 2—*Young's modulus, shear modulus, and Poisson's ratio estimated by the wave velocities.*

Material	E , GPa	G , GPa	ν	ρ , kg/m^3
Sound metal (A-1)	206	79.9	0.287	7.75×10^3
Hydrogen-attacked metal (A-6)	169	68.6	0.236	7.67×10^3

due to anisotropy of mechanical properties possibly caused by microcracks and the distribution of the inherent Poisson's ratios of various kind of steels. The ratio t_L/t_S is related to the Poisson's ratio as follows:

$$\frac{t_L}{t_S} = \frac{1 - 2\nu}{2(1 - \nu)}$$

The ratio t_L/t_S of all test specimens were measured in two directions to survey the former problem. In Fig. 6, the round solid symbols show the results where the direction of particle vibration is parallel to the axis of the pipe; round open symbols represent the results perpendicular to the axis of the pipe. The difference between the ratios in these two directions was not so big. A better relationship between the ratio t_L/t_S and the thickness ratio of hydrogen attack to the wall thickness is found on the upper data.

Concerning the inherent Poisson's ratios of sound metals, however, a number of tests carried out on site indicate that they are distributed between 0.543 to 0.551 in terms of the expression of t_L/t_S , which is shown by the dotted lines in Fig. 6. These data were obtained from several chemical plants in service under the limited operating conditions defined by Nelson chart, by testing a total of 181 points of various kind of components, including piping, heater tubes, heat exchangers, and pressure vessels, the materials of which were carbon steels and low alloy steels. The fact indicates the existence of hydrogen attack in components of over 0.550 t_L/t_S .

Conclusion

It was demonstrated that the ultrasonic wave velocity of metal attacked by hydrogen decreases compared with that of sound metal. Experimental work on the test specimens taken from the pipes which incurred hydrogen attack make it clear that the decrease of the wave velocity is due to a change of mechanical properties of the material caused by microcracks at grain boundaries. Also, the degree of decrease is different between longitudinal wave and shear wave.

This fact suggests that the ratio of longitudinal wave traveling time to shear wave traveling time is applicable to predict the thickness attacked by hydrogen.

In the application of this technique, the following four points should be considered.

1. Taking into account the influence of the anisotropy of material to wave velocities, the direction of particle vibration by shear wave must be set to the larger t_S/t_L ratio.
2. The longitudinal wave transducer and normal incidence shear wave transducer should be located at the same point on the surface of the component being tested.

3. The limitation for judging the existence of hydrogen attack should be set to 0.550 in terms of the ratio t_L/t_S .

4. In this experimental work, 5-MHz transducers were used. If other frequencies are employed, it is doubtful whether or not the results in this paper can be applied.

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Detection of Hydrogen-Assisted Crack Growth by Measurement of Modulus Changes and Acoustic Emission

REFERENCE: Carpenter, S. H., Armstrong, J., and Heiple, C. R., "Detection of Hydrogen-Assisted Crack Growth by Measurement of Modulus Changes and Acoustic Emission," *Corrosion Monitoring in Industrial Plants Using Nondestructive Testing and Electrochemical Methods*, ASTM STP 908, G. C. Moran and P. Labine, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 165-178.

ABSTRACT: An investigation of new techniques to probe and study the initiation of cracks in a hydrogen environment is reported. The techniques investigated are the precise continuous measurement of changes in the elastic modulus and acoustic emission measurements. A decrease in the elastic modulus should be observed as cracks nucleate and grow in a test material. Measurements of changes in the elastic modulus while cathodically charging a number of iron base materials both at zero load and under applied load are also given.

In all cases a decrease in the elastic modulus was observed as a result of cathodic charging with hydrogen. The modulus loss was found to be permanent and could not be restored by heat treatment. Acoustic emission measurement were carried out as miniature pressure vessels were pressurized and subsequently held at pressure. Differences in the acoustic emission were observed for vessels pressurized with hydrogen gas as compared to vessels pressurized with helium. Considerably more acoustic emission was generated in vessels pressurized with hydrogen.

KEY WORDS: hydrogen, crack nucleation, crack propagation, cathodic charging, modulus measurements, acoustic emission

The ability to detect the initiation or early stages or both of crack growth in metal structures has been and is still a goal of scientists and engineers in-

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volved in nondestructive evaluation. Another important goal is to develop techniques which provide screening and evaluation of materials for their resistance to slow crack growth or embrittlement in hydrogen environments. Conventional uniaxial tension testing with measurement of changes in reduction-of-area and fracture mode in a hydrogen environment does not always provide a reliable guide to resistance to slow crack growth in hydrogen. Furthermore, postmortem examination of destructively tested specimens frequently fails to give adequate information on crack initiation and propagation. Techniques which would provide real time information would be useful not only to the engineer performing the evaluation, but also to the theorist studying fundamental aspects of crack initiation and growth.

The purpose of this paper is to provide information on two different experimental techniques which have been applied in preliminary experiments to monitoring and studying the initiation and growth of cracks in metals. The first technique involves the precise and continuous measurement of the elastic modulus as cracks initiate and grow in a test specimen. The basic premise is that a specimen of a given material containing cracks should have a lower effective elastic modulus than an identical specimen of the same material containing no cracks. Bristow [1], assuming a homogeneous material of volume V containing a random distribution of N penny-shaped cracks of radius a , has shown that the Young's modulus of the cracked material is given by

$$Y_{\text{eff}} = Y_0 \left[1 - \frac{16(1 - \gamma^2)(10 - 3\gamma)N a^3}{45(2 - \gamma) V} \right] \quad (1)$$

where

Y_{eff} = effective Young's modulus,

Y_0 = Young's modulus of the material with no cracks, and

γ = Poisson's ratio.

Using a Poisson's ratio of 0.3, Eq 1 reduces to

$$Y_{\text{eff}} = Y_0 \left[1 - \frac{1.73 N a^3}{V} \right] \quad (2)$$

Clearly, a decrease in the Young's modulus should be observed as cracks nucleate and grow in the test material.

The second technique involves the monitoring the acoustic emission emitted from a metal specimen as cracking occurs. The acoustic emission generated from stressed specimen placed in a hydrogen environment has been monitored and characterized. Preliminary results have demonstrated the capability of nondestructively detecting the initiation and growth of cracks less than 0.01269 mm (0.0005 in.) long in an austenitic stainless steel.

Experimental Procedure

The Young's modulus of a test specimen can be continuously monitored by accurately measuring the resonant frequency of the specimen while driving it in a standing wave configuration. A modified Marx composite piezoelectric oscillator [2] was used to drive the test specimen at its resonant frequency. For longitudinal standing waves, a resonant frequency of approximately 50 kHz was used, while for torsional standing waves, the resonant frequency was approximately 40 kHz. The resonant frequency could be measured to better than 1 Hz. A closed-loop crystal driver continuously maintained the specimen at its resonant frequency at a predetermined (but adjustable) vibratory strain amplitude. A microprocessor, interfaced with the closed-loop crystal driver, gave a continuous digital and analog printout of the resonant frequency.

The resonant frequency of the total wave train is the measured quantity from which the resonant frequency of the specimen is calculated. Once the resonant frequency of the specimen is known, the Young's modulus can easily be calculated. Mechanical damping measurements were also carried out to provide additional information on the mechanisms responsible for crack initiation. A more complete description of the test apparatus is given elsewhere [3].

Cracks were initiated in the test specimens by cathodic charging. Specimens for cathodic charging were machined in length to exactly one half wavelength, the center of the specimen being a displacement node. Hence, the necessary electrical connection could be made at the center of the specimen without interfering with the standing wave. A schematic of the test apparatus is shown in Fig. 1. The cathodic charging was carried out at a current density of 30 mA/cm² in a solution of one normal sulfuric acid (H₂SO₄) with slight additions. Clearly, the apparatus shown in Fig. 1 only allows for charging at zero applied load. In order to investigate modulus changes while charging a test specimen under an applied load, a specially designed test specimen was employed. Samples like those shown in Fig. 2 were used in an apparatus diagrammed in Fig. 3. The specimen is three half wavelengths in length with enlarged sections one fourth wavelength from each end. These positions are nodal points and the specimen can be gripped here without interfering with the standing wave. Gripping of these enlarged sections provides a way of applying load. A nonmetallic cup is then glued on at the center of the specimen (also a nodal point) to hold the charging solution. This technique has also been used to investigate and to study stress corrosion cracking [4].

Acoustic emission measurements were carried out using a Dunegan/Endevco HS 140B piezoelectric transducer and Series 3000 signal processing equipment. The acoustic emission from small model pressure vessels (like those shown in Fig. 4) was measured as the vessels were pressurized with high pressure hydrogen gas as well as with other gases. Measurements were also carried out as a function of time while holding the pressure at preselected levels. The vessels were pressurized to approximately 80% of their burst pressure.

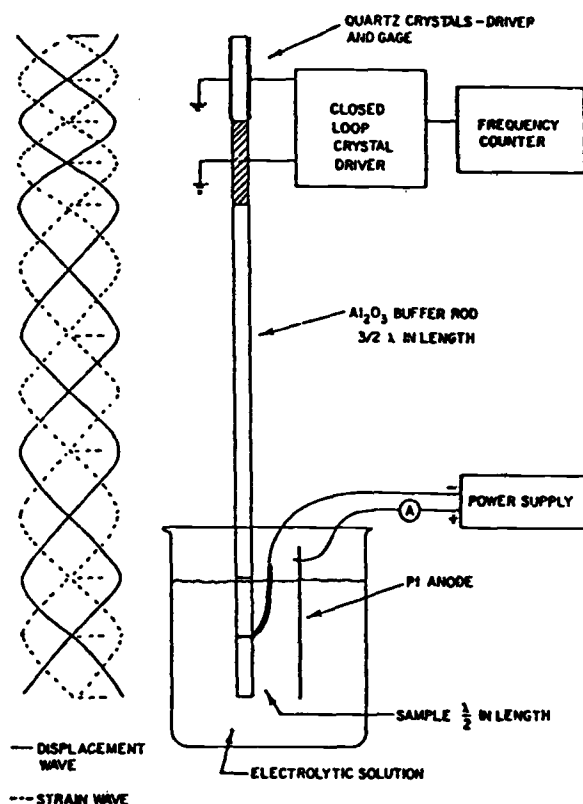


FIG. 1—Schematic of apparatus used to monitor resonant frequency of specimen while it is being cathodically charged at zero applied stress.

Materials tested to date include pure Armco iron and three grades of stainless steel. The stainless steels include AISI-304 (an austenitic stainless steel), AISI-430 (a ferritic stainless steel), and AISI-410 (a martensitic stainless steel). These materials were chosen to help identify the effects of structure on the crack initiation and our ability to detect the cracks. However, due to length limitations, the modulus measurements reported will concentrate on pure Armco iron, and the acoustic emission measurements will concentrate on the stainless steels.

Experimental Results

Modulus Measurements

A complete series of experiments has been run using pure Armco iron specimens to investigate both the initiation and growth of cracks and to also study

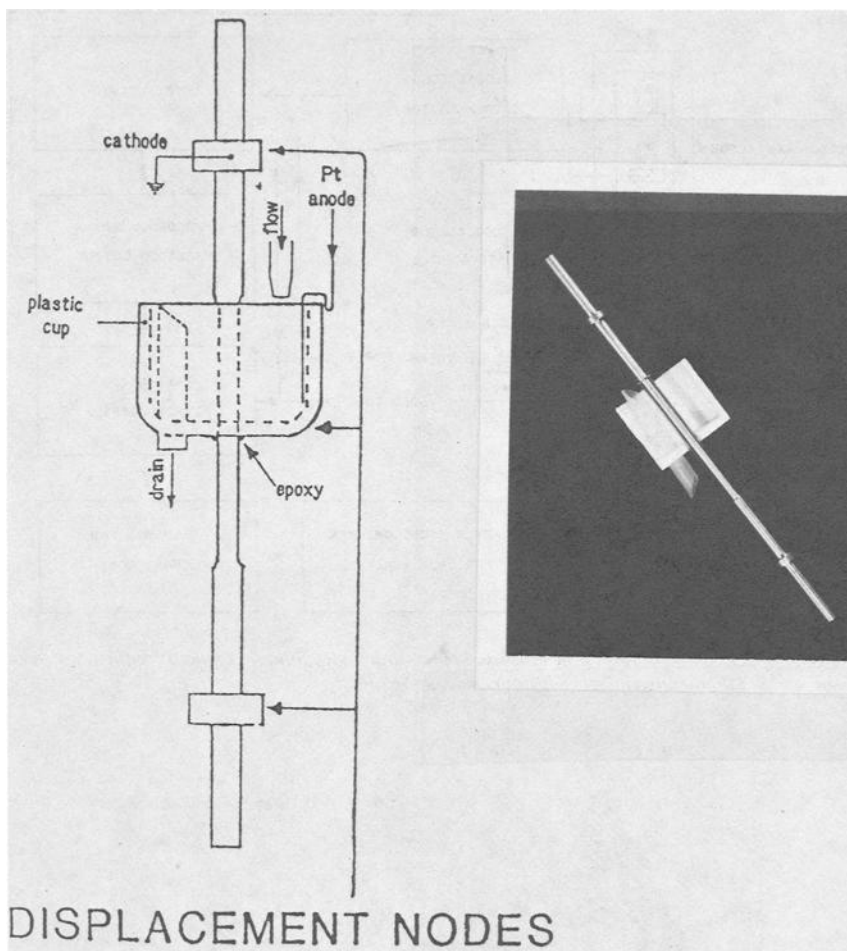


FIG. 2—Schematic and photograph of actual specimen used when resonant frequency is monitored while specimen is under an applied load.

hydrogen-dislocation interactions. The following experimental procedure was carried out for specimens cathodically charged at various vibratory strain amplitudes in a standing torsional wave mode.

1. Specimens were machined, cut to proper length, polished, and then annealed for 6 h in a vacuum of better than 5×10^{-6} torr.
2. After annealing, the mechanical damping and resonant frequency were measured both in and out of a strong magnetic field to eliminate any magnetic effects and to determine the damping due to dislocation motion alone. The lattice parameters and the peak half-widths (amount of cold work) were also measured, using X-rays.

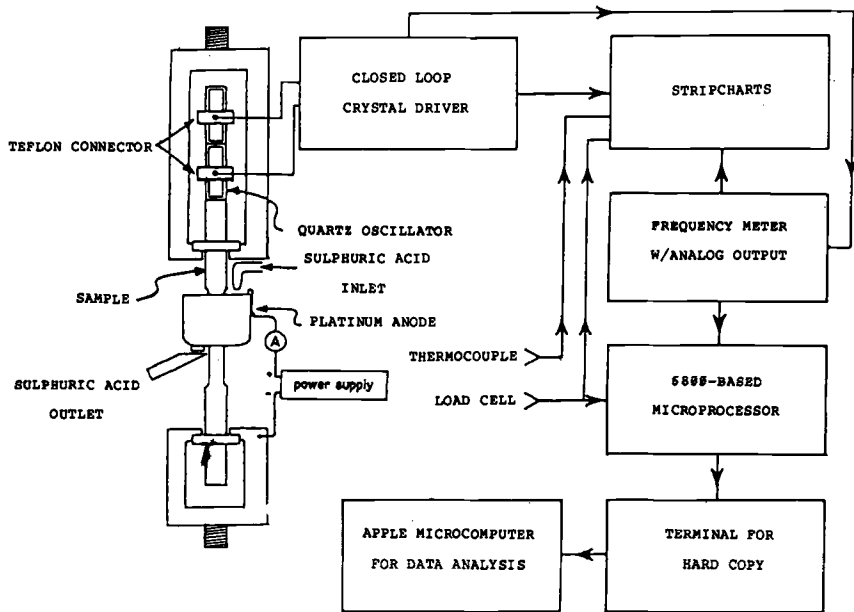


FIG. 3—Schematic of test apparatus used to continuously monitor resonant frequency of specimen while cathodically charging it under an applied load.

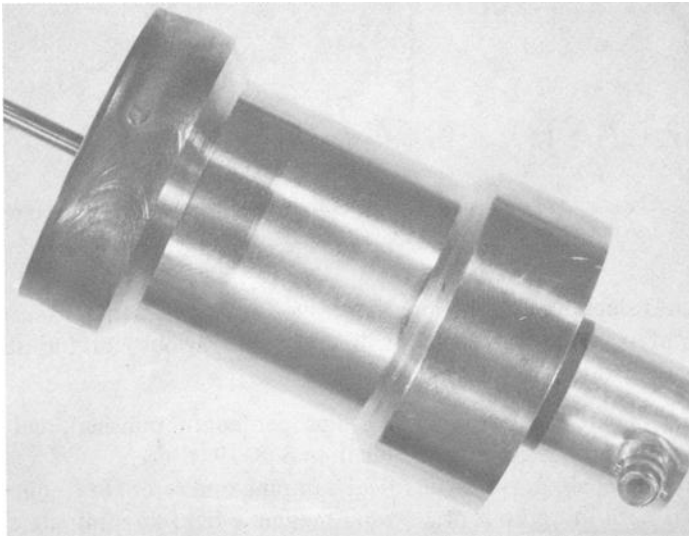


FIG. 4—Photograph of one of the miniature pressure vessels used for acoustic emission measurements.

3. The specimens were then cathodically charged at 30 mA/cm² for 15 h, during which time the resonant frequency and the mechanical damping were continuously monitored. Upon completion of the charging, all of the measurements listed in Step 2 were repeated.

4. The specimens were then given a bakeout anneal of 72 h at 100°C in a vacuum of better than 5×10^{-6} torr. Upon completion of this anneal, all of the measurements listed in Step 2 were again repeated.

5. The specimens were then given a vacuum anneal of 6 h at 500°C and the measurements listed in Step 2 were again repeated.

6. The specimens were then sectioned polished and examined to determine the crack distribution and volume due to hydrogen charging.

In all cases where pure Armco iron specimens were cathodically charged, a decrease in the resonant frequency was observed during charging. Data showing the normalized decrease in frequency as a function of charging time for specimens charged at various vibratory strain amplitudes are shown in Fig. 5 (all data taken at room temperature).

Notice that the data show no dependence on the vibratory strain amplitude used, indicating that the kinetics of the process does not depend on the strain

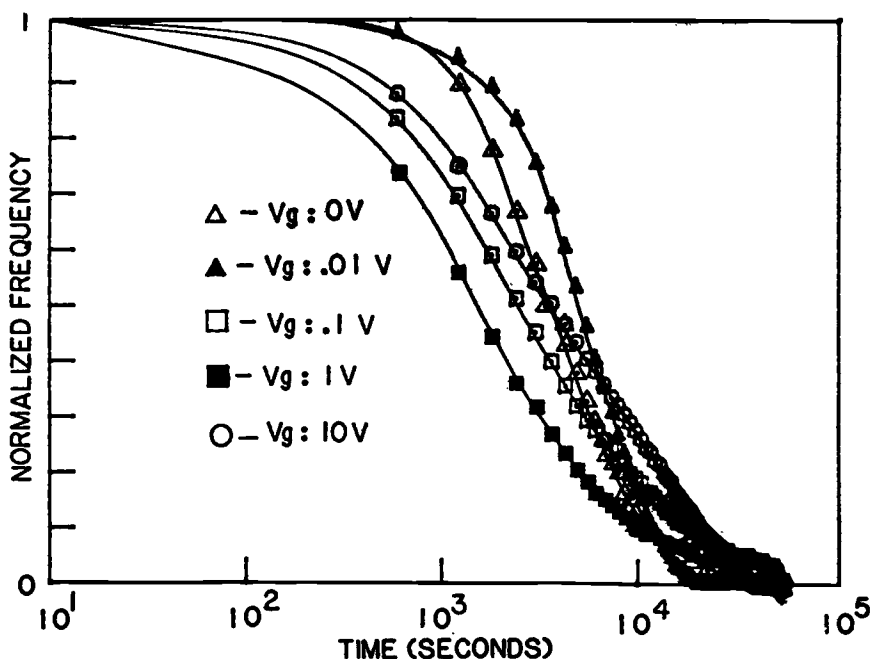


FIG. 5—Normalized resonant frequency data for loss of resonant frequency as a function of charging time. Data are for different vibratory strain amplitudes.

amplitude used. These results are puzzling, since the measured crack volume is very dependent on the vibratory strain amplitude. Table 1 provides a comparison of the magnitude of change in the resonant frequency and measured crack volume for specimens charged at different vibratory strain amplitudes. Crack volumes were measured from photomicrographs using the same techniques used to measure grain sizes.

Figures 6 and 7 are micrographs showing the type and density of cracks formed in the iron specimens when cathodically charged for 15 h at vibratory strain amplitudes of 0.01 and 10 gage volts, respectively. The difference in crack volume is clearly evident. It is difficult to compare the data in Table 1 with what would be predicted by Eq 2, since the latter depends on the characteristics of the cracks and not simply on the crack volume. Measurements are

TABLE 1—*Comparison of change in resonant frequency and measured crack volume for samples charged at different vibratory strain amplitudes.*

Gage Voltage, Proportional to Vibratory Strain Amplitude, V	Change in Resonant Frequency, Hz	Measured % of Crack Volume
0.01	—640	0.45%
0.10	—472	0.34%
10.00	—541	0.14%

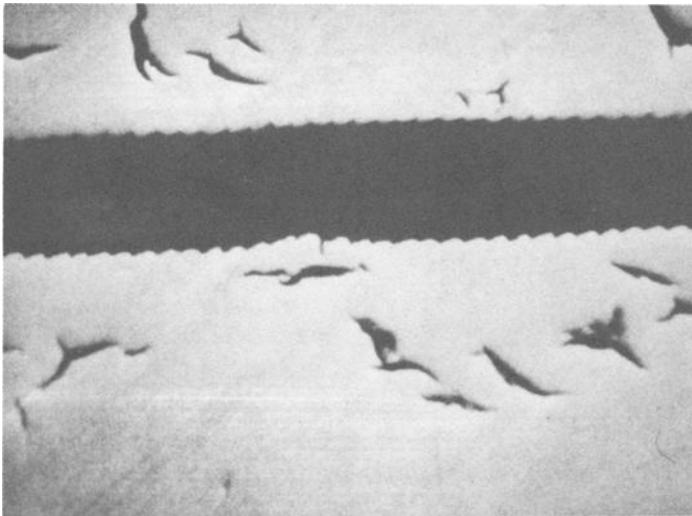


FIG. 6—Micrograph of Armco iron specimen cathodically charged at vibratory strain amplitude of 0.01 gage volts. Charged for 15 h; magnification is $\times 38$.

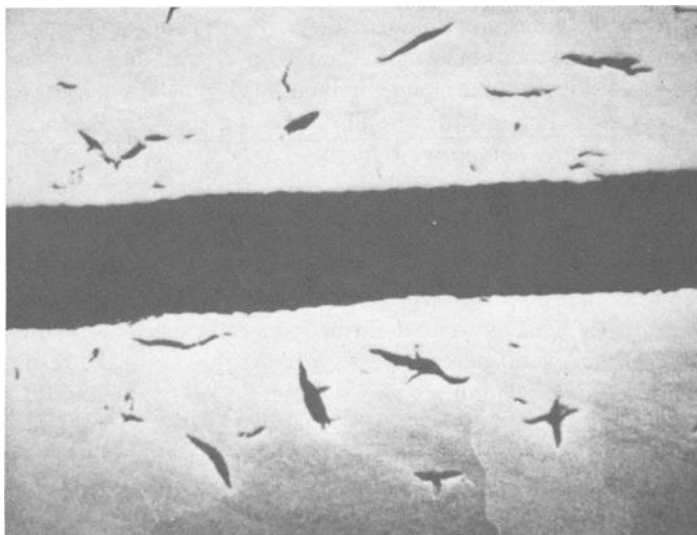


FIG. 7—Micrograph of Armco iron specimen cathodically charged at vibratory strain amplitude of 10 gage volts. Charged for 15 h; magnification is $\times 38$.

currently underway to determine the crack density and crack size so that a direct comparison with Eq 2 can be carried out. The measured change in resonant frequency is permanent and cannot be restored by annealing treatments.

Figure 8 shows data for the resonant frequency as a function of the differ-

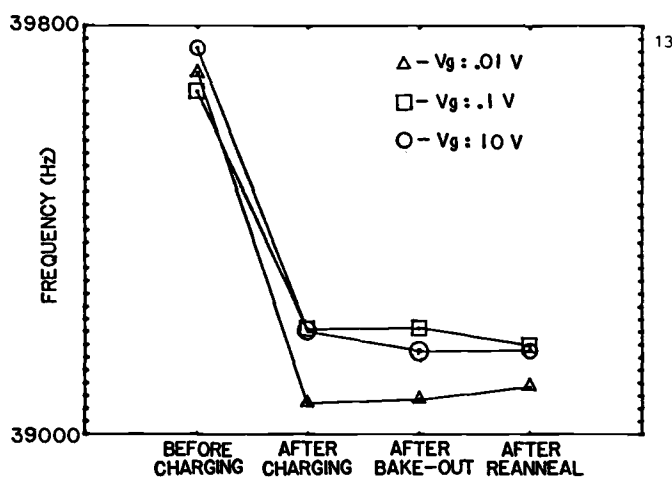


FIG. 8—Resonant frequency as function of different experimental conditions.

ent experimental conditions. Note that the cathodic charging produces a permanent effect on the modulus which is not proportional to the induced crack volume. It is possible that the change in modulus is due to a composite sample effect, that is, a specimen with a solid core and a cracked outer layer. This possibility is currently being investigated.

A number of experiments were also carried out with the specimen under an applied load. The procedure used for these experiments was as follows:

1. The resonant frequency and mechanical damping as a function of strain amplitude were measured at zero applied load.

2. The test specimen was then deformed at a relatively slow strain rate to a preselected strain several percent past yield. At this point the resonant frequency and mechanical damping as a function of strain amplitude were remeasured.

3. The specimen was then allowed to stress relax under load until it reached an equilibrium condition. After complete relaxation the resonant frequency and mechanical damping were again remeasured.

4. At this point, charging solution was introduced into the solution cup and the sample was cathodically charged while the specimen was maintained at various strain amplitudes. During charging the resonant frequency, the mechanical damping and the applied load were continuously monitored.

5. When charging was completed, the specimen was re-yielded to determine the effects of the charging on the mechanical properties of the test material.

6. The specimen was then unloaded and the resonant frequency and mechanical damping were again measured as a function of strain amplitude.

7. The specimens were then sectioned and examined metallographically to determine the crack density and volume induced by charging.

The results of the tests under applied load are similar to those obtained with zero load. However, two additional results are obtained. First, the hydrogen charging causes a significant change in the mechanical properties of the pure iron test specimens. A significant strengthening and a very definite yield point are observed on re-yielding the specimens after charging; Fig. 9 presents data which clearly shows these effects.

Second, it has been observed that upon charging, the applied load that the specimen can maintain begins to decrease. The rate of decrease and possibly the magnitude is strongly dependent on the value of the vibratory strain amplitude used during charging. Figure 10 shows data on this phenomenon. It is not clear whether this result is due simply to a reduction in area due to cracking, or if it is due to a more fundamental cause.

Acoustic Emission Measurements

Preliminary studies performed to investigate the possibility of detecting hydrogen assisted crack growth with acoustic emission, have shown that 21-6-9

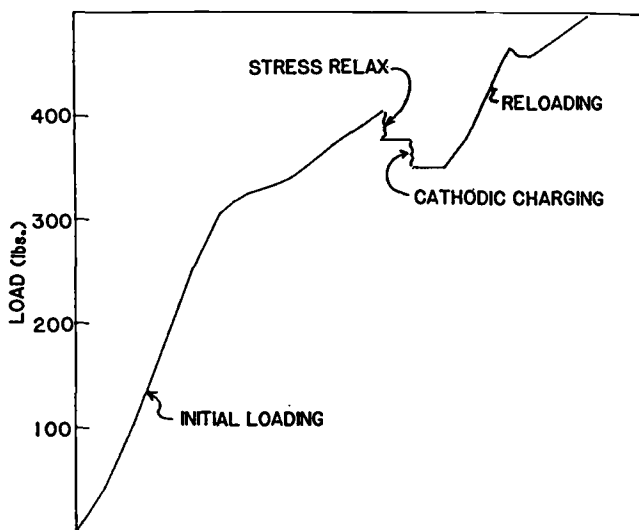


FIG. 9—Mechanical behavior of pure Armco iron before and after cathodic charging while under an applied load.

stainless steel vessels which cracked in high-pressure hydrogen could be distinguished from vessels which did not crack (either in hydrogen or in an inert gas) from the acoustic emission record. Upon pressurization beyond yield, considerable acoustic emission was produced regardless of the pressurizing gas. However, for vessels which did not crack, the acoustic emission decreased rapidly to the background noise level when held at a constant pressure. These results are expected since the plastic flow due to stress relaxation at constant pressure also decreases rapidly with time. For vessels which cracked, the acoustic emission also decreased with time, but it always stayed above the noise level—presumably because of acoustic emission from growing cracks. These results are shown in Fig. 11. It should be noted that some vessels did not crack when pressurized with hydrogen, and their acoustic emission behavior was the same as vessels tested in helium.

Model pressure vessels made from 304, 410, and 430 stainless steels have been tested in hydrogen up to 138 MPa (20 000 psi) and identical vessels have been tested in helium. The behavior during pressurization of these vessels is the same as that previously observed for the 21-6-9 vessels; however, the behavior during holds at constant pressure is significantly different. The martensitic type 410 vessels were extremely sensitive to hydrogen and failed less than one minute after the onset of detectable acoustic emission during pressurization. Failure occurred even when pressurization was stopped and pressure held constant at the point at which measurable acoustic emission was first detected. The measured acoustic emission from vessels of 304 and 430 stainless steel pressurized with hydrogen beyond yield remained well above

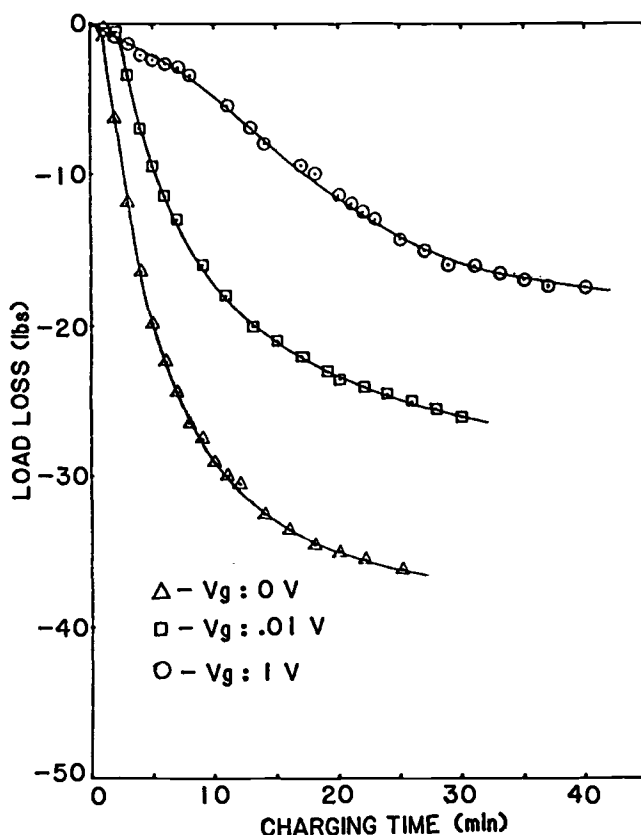


FIG. 10—Loss of applied load as function of charging time for specimens cathodically charged while under an applied load.

the noise level for up to 100 h when held at that pressure. For similar vessels tested in helium, the acoustic emission decreased to the noise level within 24 h. Typical acoustic emission behavior for vessels of 304 stainless steel is shown in Fig. 12. These results would indicate that cracking should be occurring in the hydrogen-filled vessels producing the measured acoustic emission. Optical and scanning electron microscopy was used to carefully examine the inner surface of the vessels pressurized with hydrogen, but no observable cracks were found.

Thus the continued acoustic emission at constant pressure is not necessarily due to crack growth in these materials. The origin of the measured acoustic emission from the 304 and 430 vessels held at a constant pressure of hydrogen is at present unknown. One plausible source of the additional acoustic emission from these materials is that the hydrogen driven into the lattice interacts with the dislocations in such a way as to increase the emission from

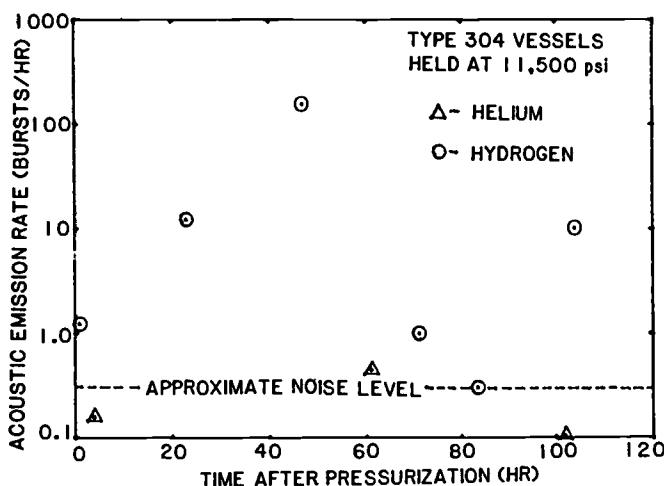


FIG. 11—Acoustic emission burst rate as function of time for a 21-6-9 miniature pressure vessels pressurized with high-pressure hydrogen and helium.

dislocation motion during stress relaxation. Tests are currently underway to evaluate this hypothesis.

Conclusions

Modulus Measurements

In all cases, a significant reduction of elastic modulus is observed for pure Armco iron specimens when cathodically charged with hydrogen. At room temperature neither the kinetics nor the magnitude of the loss of modulus are dependent on the vibratory strain amplitude imposed by the standing wave used to measure the resonant frequency. However, the induced crack volume is strongly dependent on the vibratory strain amplitude imposed during charging. Significantly more cracking is observed when the test sample is charged at a lower strain amplitude. The loss of modulus appears to be permanent and is not restored after a long time low-temperature bakeout nor after a high-temperature anneal. It is possible that the observed loss of modulus is due to a composite sample effect, that is, an outer cracked layer surrounding a solid core. If this is the case, the loss of modulus may be a direct measure of the depth of cracking.

Acoustic Emission Measurements

The acoustic emission generated during the pressurization and subsequent hold at pressure has been measured for miniature pressure vessels using both

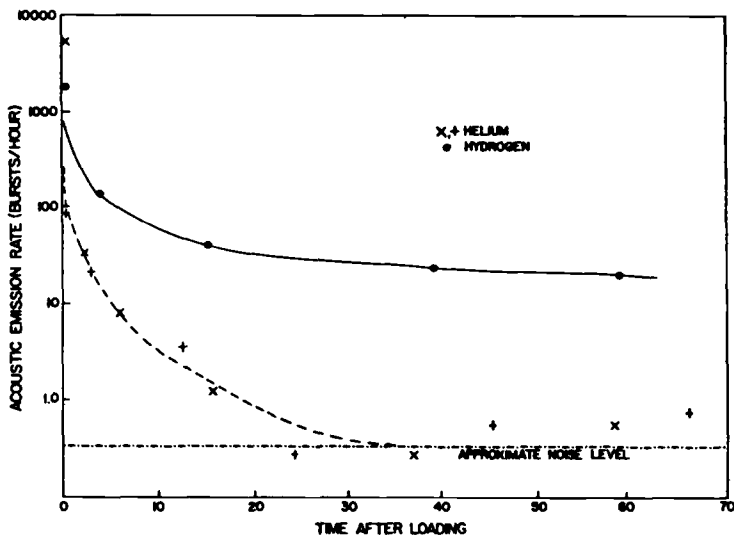


FIG. 12—Acoustic emission burst rate as function of time for 304 stainless steel miniature pressure vessels pressurized with high-pressure hydrogen and helium.

hydrogen and helium as the pressurizing gases. Significantly more acoustic emission was measured for vessels pressurized with hydrogen, and in fact, little or no emission was detected for vessels pressurized with helium. These results are as expected, except that no hydrogen-induced cracks could be found with optical and SEM methods. Hence, it has not been possible to directly relate the acoustic emission with hydrogen induced crack growth. It is not clear at present whether the acoustic emission is due to microcracks beneath the metal surface or due to some hydrogen dislocation interaction.

Acknowledgments

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Corrosion Monitoring of Underwater Steel Structures

REFERENCE: Birring, A., "Corrosion Monitoring of Underwater Steel Structures," *Corrosion Monitoring in Industrial Plants Using Nondestructive Testing and Electrochemical Methods*, ASTM STP 908, G. C. Moran and P. Labine, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 179-190.

ABSTRACT: Deterioration of underwater steel structures due to corrosion is of serious concern because it reduces thickness in structural components, which can degrade structural strength. Inspection programs are necessary to determine the remaining thickness so that action can be taken to repair the damage if required.

An ultrasonic technique using a focused transducer has been developed to find the thickness of steel plates or structures corroded from both sides and having pit sizes as large as 15 mm in diameter and 4 mm deep. The technique was implemented into a system that acquires and processes ultrasonic waveforms reflected from the corroded area and determines the thickness. The system was tested and successfully operated in a harbor environment.

KEY WORDS: corrosion, nondestructive testing, ultrasonics, underwater, ultrasonic inspection

Annual financial loss to the U.S. economy due to corrosion is over \$70 billion, according to conclusions from a recent study by the National Bureau of Standards [1]. This cost includes corrosion of offshore and waterfront structures, seagoing vessels, and underwater pipelines. Corrosion reduces the thickness of these structures and hence, their structural strength.

The thickness of these structures must be measured not only to avoid failure and save costs [2], but also to assure that necessary repairs are undertaken. Conventional nondestructive evaluation (NDE) techniques can be used to measure the remaining thickness if the surfaces are smooth; however, corrosion of offshore and waterfront structures are generally associated with pitting. Pitting can be as large as 15 mm in diameter and 4 mm deep, and con-

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ventional NDE techniques fail because of these rough-pitted surfaces [3]. A new NDE approach for use on such underwater structures is presented.

Traditional Inspection Methods

The most common method for assessing deterioration due to corrosion pitting in underwater structures is visual inspection [3]. However, information from visual inspection is limited to surface damage, and cannot provide information regarding the remaining thickness of the corroded steel plate. Another method commonly used for thickness measurement is conventional ultrasonics, which can only be used on plates with flat surfaces. Commercial ultrasonic thickness gauges use this method. To determine the plate thickness, the time difference between the front- and back-surface reflections is used. However, conventional ultrasonics will not work on corroded plates because of spurious signals caused by scattering. These signals introduce noise in the reflected signals, making it impossible to resolve the back-surface reflection. Figure 1a shows the reflection and scattering of ultrasonic energy from a corroded plate, indicating clearly that the signal reflected from the back surface cannot be resolved in the presence of noise (Fig. 1b). A commercial ultrasonic thickness gauge therefore should not be used on corroded structures, as it may indicate a false thickness reading because of spurious signals.

Thickness measurement by surface milling is another alternative system developed by the Naval Civil Engineering Laboratory [4]. The milling system

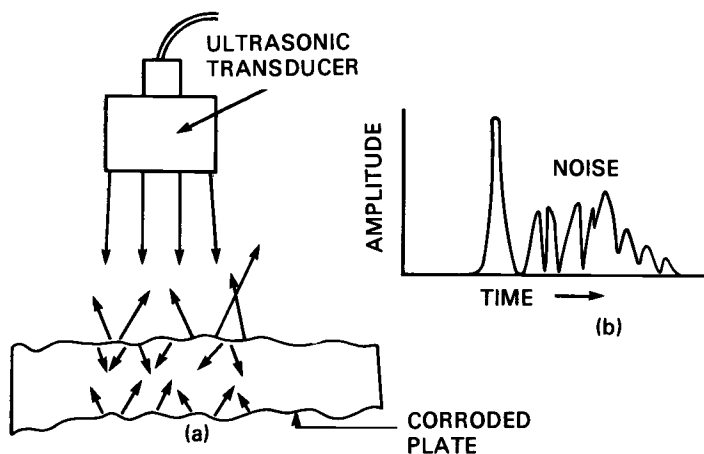


FIG. 1—Thickness measurement of corroded plate using conventional ultrasonic method. (a) Scattering is caused by corroded surface. (b) Back-surface signal cannot be resolved in scattering-generated noise.

can take accurate thickness measurements; however, the milling operation to obtain a smooth surface is destructive, which makes the technique unsuitable.

Focused Transducer Technique for Underwater Thickness Measurement

A new ultrasonic technique was developed to determine thickness of underwater corroded steel structures. Since inspection has to be performed underwater by remote control, this technique was integrated into a microcomputer-controlled system. Field tests of the system proved its capability to take thickness measurements in a severe harbor environment. The theoretical basis of the newly developed system, the operation of the system, and its field implementation in a harbor environment are presented in the following subsections.

Theory

Figure 2 indicates the focused transducer concept for thickness measurement of corroded plates [5,6]. The pit acts as a lens when the focal point of the

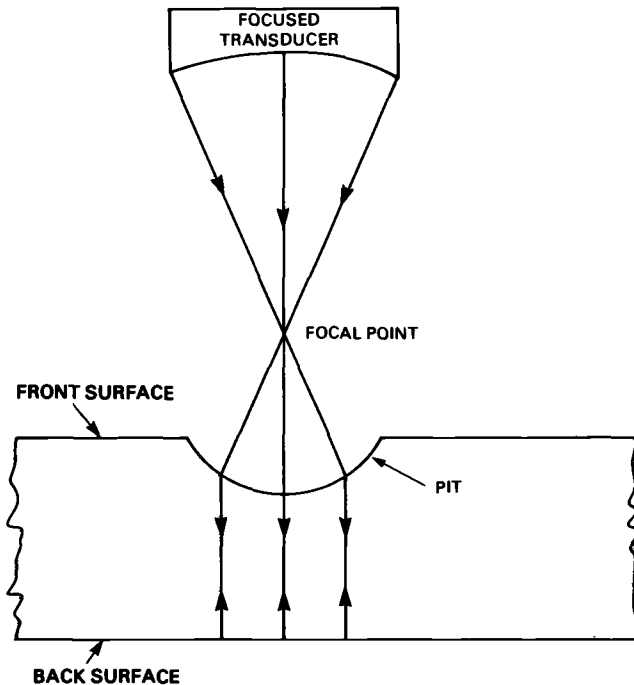


FIG. 2—Focused transducer concept. The curvature of the pit collimates the diverging beam in the steel plate, resulting in a strong back-surface reflection.

beam is placed above the pit center. As a result, the beam diverging from the focal point collimates as it enters the steel. Thus, a parallel or slightly converging beam in steel can be obtained by positioning the focal point above the pit. Significant back-surface reflection is obtained under this condition (see Fig. 3) using a 7.5-MHz, 25-mm-diameter, 50-mm focal length, piezoelectric ultrasonic transducer (made by Panametrics). The standoff distance from the transducer to the plate remains slightly greater than the focal length. Although use of the focused beam technique significantly improves the observed signal level due to the back-surface reflection, some spurious signals remain due to scattered ultrasound. These spurious signals are generated from the sidelobe mode conversion to shear waves, or by interference of the waves reflected from the front surface. An over- or underestimation of the thickness can result if these spurious signals are mistaken for back-surface signals. The cause and removal of spurious signals are described in the following paragraphs.

Figure 4a shows the spurious signal caused by a sidelobe generated from the periphery of the transducer. The sidelobe signal was incident at the side of the pit and thus traveled more in steel than did the main beam signal, which transmitted through the pit center. Because the velocity of longitudinal waves in steel is higher than in water, the spurious signal arrived earlier in time than the back-surface reflection from the main beam, as shown in Fig. 4b, and hence underestimated the thickness. An acoustic mask with a 2-mm-diameter hole placed at the focal point removed the sidelobe signal. The acoustic mask was made from a mixture of 54.5% iron oxide (Fe_2O_3) and 45.5%

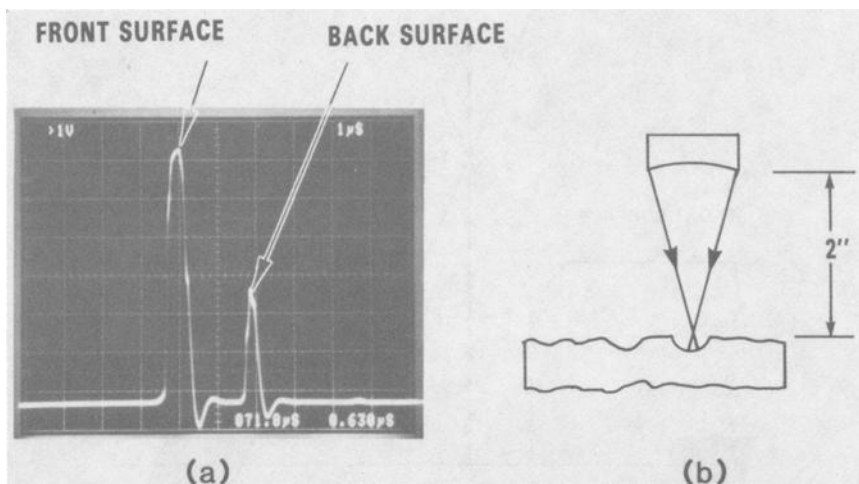


FIG. 3—Thickness measurement of a corroded surface using focused beam. Video signal shows front-surface and back-surface reflections from a pit where the metal thickness is 6.2 mm (0.24 in.).

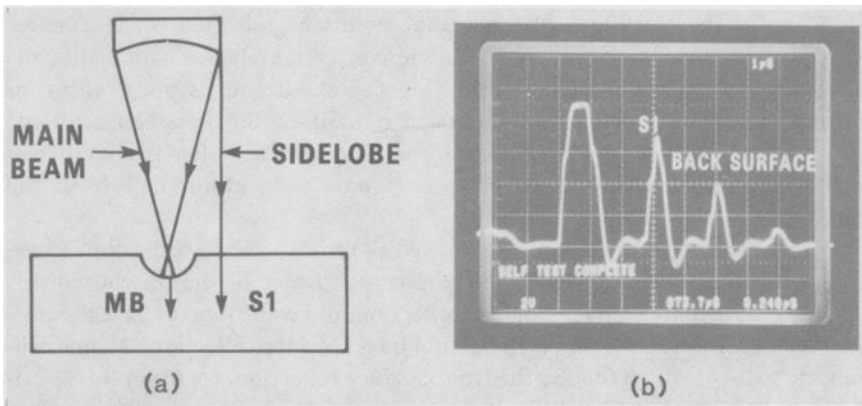


FIG. 4—Spurious signal *S1* caused by a sidelobe. (a) Sidelobe generates spurious signal *S1*. (b) Sidelobe signal *S1* traveled more in steel and hence arrived earlier in time.

RTV602 (silicons) by weight. The distance between the acoustic mask and the transducer was equal to the focal length of the transducer. The acoustic mask attenuated the sidelobe signal and removed a spurious signal.

A second source of spurious signals was the mode conversion to shear waves (see Fig. 5a). Mode conversion to shear waves occurred when the longitudinal wave was not incident normal to the steel plate. This spurious signal (*S2*) (see Fig. 5b) arrived later in time than the back-surface reflection because shear waves propagate more slowly than longitudinal waves. This resulted in overes-

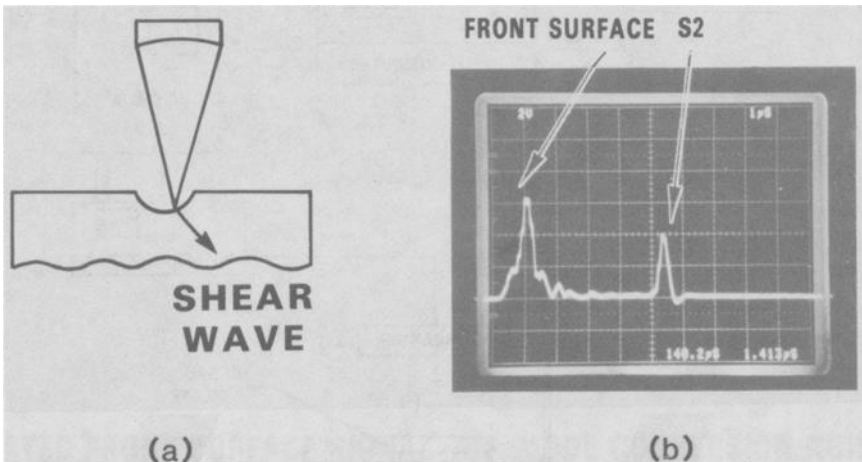


FIG. 5—Spurious signal caused by mode conversion. (a) Mode conversion to shear wave causes the generation of spurious signal *S2*. (b) Spurious signal *S2* is associated with low amplitude and large pulse width front-surface reflection.

timation of the thickness. Pattern analysis of the reflected waveforms removed the spurious signals due to mode conversion. It was found that the amplitude of the front-surface reflection decreased and its pulse width increased whenever mode conversion occurred. Based on these characteristic front-wall signal patterns, the waveforms that had a higher probability of containing mode conversion spurious signals were eliminated from the analyses.

A third spurious signal closely followed the front-surface reflection. Interference of the waves reflected from the front surface of the pit caused this signal. It looked like a back-surface reflection, but was found to have a significantly larger amplitude than the actual back-surface reflection. A time amplitude gate [8] which follows the front-surface reflection, removed this spurious signals. Upon removal of all these spurious signals, the technique was used to take accurate thickness measurements of the corroded structure.

System Operation

The scanning of the transducer over the corroded A36 steel plate and its alignment over the pit center are performed automatically by a computer-controlled data acquisition system. The schematic of the system is shown in Fig. 6. The pulser/receiver receives the signal from the focused transducer, which is digitized by a transient recorder. This signal is transferred to the microcomputer for analysis or storage in the computer memory. Alignment of

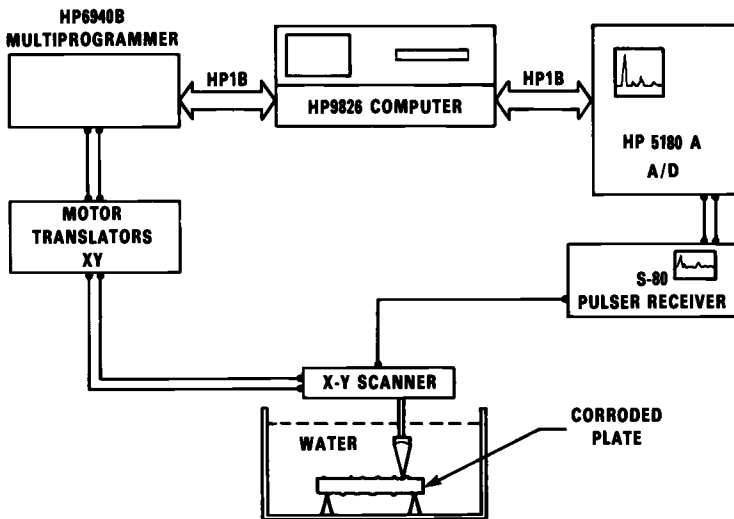


FIG. 6—Schematic of the automated thickness measurement system. The system is built using commercially available equipment.

the focused transducer directly above the pit is performed as follows: the transducer is scanned parallel to the specimen surface as shown in Fig. 7. As the transducer is moved toward the center of a pit, the arrival time of the signal reflected from the front surface will increase due to an increase in water path.

The first step to align the transducer over the pit center is to move the transducer to a pit area. A coarse x - y scan is performed using 5-mm (0.2 in.) increments and waveforms acquired at each scan position. Locations where the front-surface arrival times are relatively large are indicated as pit areas. After a pit area is located, the search for the pit center is performed by moving the device in the x - y directions with a certain step size toward increased front-surface signal arrival time. The step size is decreased by the computer as the device gets closer to the pit center. When the pit center is reached, one waveform from the center and four more in a cross-shaped (+) pattern are stored (that is, along the four directions). The five waveforms are acquired from each pit so as to have a larger data base and to more accurately measure the plate thickness. Then the search begins for the next pit center.

Waveforms acquired at pit centers are analyzed and a calculation of the average thickness is made. Waveforms having back-surface features that correlate with spurious signals are rejected. These features include large pulse width and low amplitude of the front-surface reflection. The remaining waveforms are then analyzed to find their back-surface signal, and hence, the plate thickness at the pit centers.

For example, data acquired over a 50 by 50 mm (2 by 2 in.) area of a plate included 13 pits, from which 65 waveforms were stored (5 waveforms per pit).

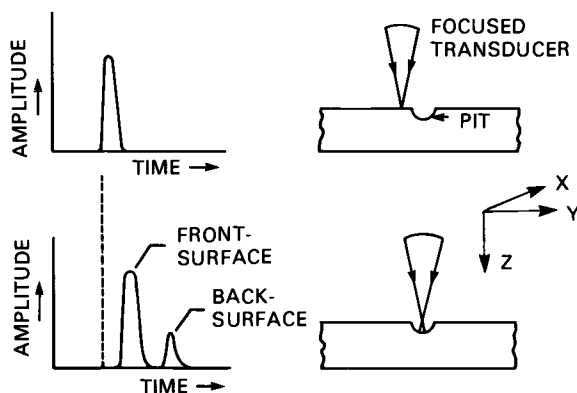


FIG. 7—Method of aligning the focused transducer over the pit center when using the focused transducer concept (see Fig. 2). The transducer is scanned in both the x - and y -directions until the arrival time of the front-surface signal is maximized. This condition occurs when the transducer is over the center of the pit where the distance between the transducer and front-surface is maximum.

From these 65 waveforms, 18 waveforms were rejected based on front-surface signal features. Even after this rejection operation, some spurious back-surface signals remained. These spurious signals were rejected by statistical cluster analysis. The thickness values corresponding to all back-surface reflections, as plotted, are shown in Fig. 8.

The display in Fig. 8 shows how signals from true back-surface reflections and from spurious signals can result in two distinct clusters. The first cluster, located around a thickness value of 4 mm, is due to the spurious signals caused by interference within the front-surface reflection. This cluster also has much fewer points (8 points) compared to the second cluster with 41 points that lie between thickness values of 10 to 15 mm. Because of the much greater number of points, the 10- to 15-mm cluster was selected for computing the thickness. The average of the thickness values found at the pit centers in the selected cluster equals the average of the minimum thickness in the plate.

To calculate the average plate thickness, the average thickness at the pit centers was added to the front-surface variation. This front-surface variation was computed from the root mean square (rms) of the arrival time of the front-surface signal measured during the coarse x - y scan.

Using the system that has been developed, the thicknesses of six samples [50 by 50 mm (2 by 2 in.)] were measured. Table 1 gives the values of the average thicknesses of corroded plates found by this method. The actual average thicknesses were determined using Archimedes' principle.

Table 1 shows that the average thicknesses of the pitted specimens varied

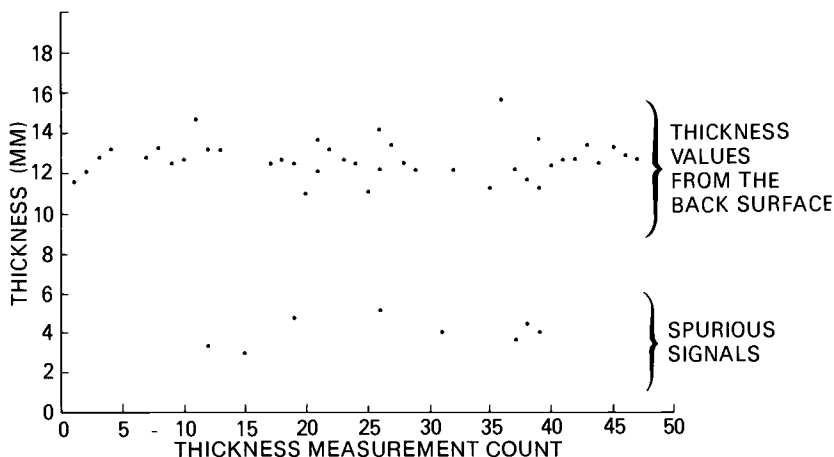


FIG. 8—Thickness plot for a corrosion-pitted steel plate. True back-surface reflections are clustered separate from spurious signals. Note that the back-surface cluster has more points (41) compared to the number of points in the spurious signal cluster.

TABLE 1—Results from average thickness measurements of corrosion-pitted plates. Thickness was measured with an average error of 4%.

Corroded Plate Test Sample	Actual Thickness Found By Archimedes' Principle, mm	Measured Thickness, mm	Error %
TNP-1	7.0	6.8	−3
TNP-2	7.0	6.8	−3
TNP-4	6.9	7.1	+3
THP-1	13.2	14.2	+8
THP-2	13.0	13.3	+2
THP-3	13.0	13.5	+4

NOTE: Average absolute error was 4%.

from 6.9 mm (0.27 in.) to 13.2 mm (0.52 in.) and that the thicknesses were calculated with an average error of 4% and a maximum error of 8%.

Tests in a Harbor [9]

Tests were done in a harbor on steel piles that have a cross section like an “H” and thus are called H-piles. The flanges of these piles were cleaned to enable the ultrasonic waves to propagate into the steel without scattering or absorption by marine growth on the surface. The scanner assembly, shown in Fig. 9, was then mounted onto the pile by divers and attached to the pile by C-clamps. Thickness measurements were taken on individual piles by taking a scan across the pile cross section. The scans were taken at depths ranging from 0.3 m to 2.2 m (1 to 7 ft) at 0.3-m (1 ft) increments along the length of the piles.

Figures 10, 11, and 12 demonstrate that the system is capable of determining both the thickness along the cross section of a pile and the variation of average thickness along the length of the pile. These data can then be used to determine the strength of the structure and to plan necessary repairs.

The time to take thickness measurements during a 250-mm (10 in.) scan across the H-piles was approximately 5 min on smooth piles and approximately 15 min on pitted piles. The inspection time can be decreased by using more powerful motors to increase the scanning speed. It is estimated that the integrated system with more powerful motors will require approximately 1 min to take thickness measurements on a rough pile and approximately 4 min on a pitted pile [10].

Conclusion

A new approach that uses focused ultrasonics has been developed that can nondestructively measure the thickness of corroded underwater structures.

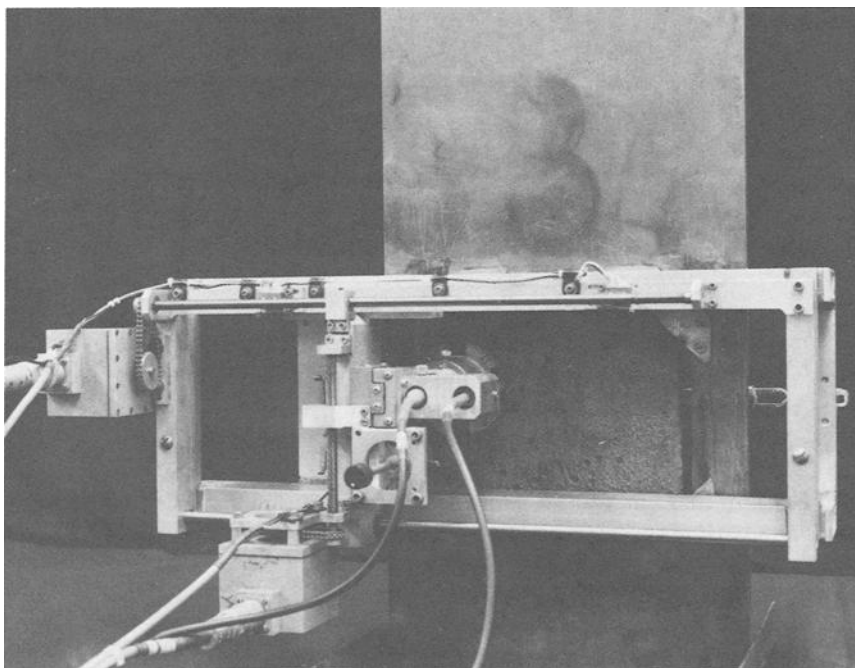


FIG. 9—Scanner assembly mounted on a simulated piling. The scanner assembly moves the ultrasonic transducers across the pile for thickness measurement.

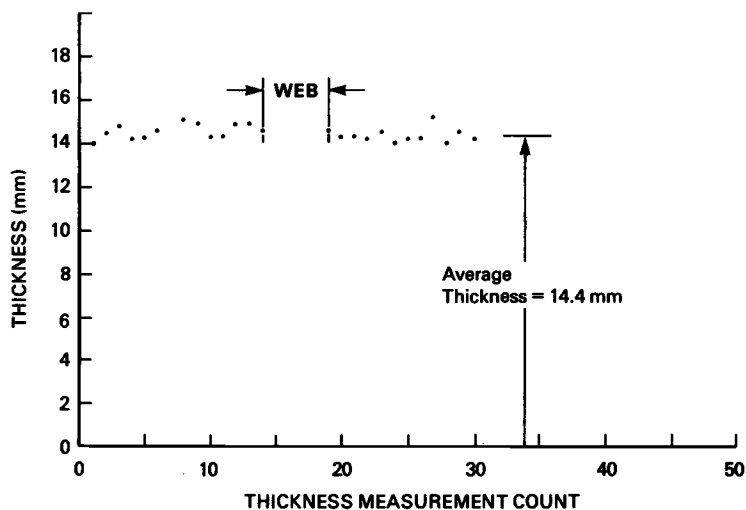


FIG. 10—Plot of thickness across the flange of a rough H-pile. Average thickness across the flange is calculated by taking the mean of the thickness measurements.

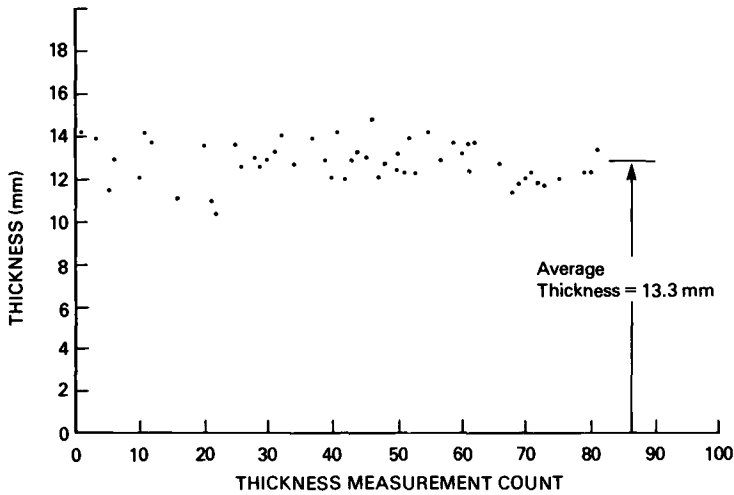


FIG. 11—Plot of thickness across the flange of a pitted H-pile. Average thickness across a pitted pile is calculated by finding the mean of the thickness measurements at the pits and adding the surface roughness.

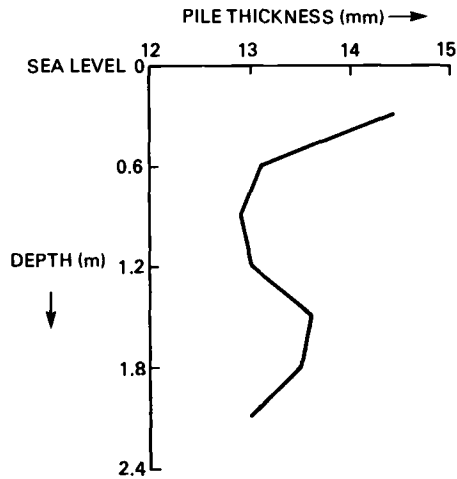


FIG. 12—Variation of mean thickness along the length of the rough H-pile. Thickness measurements along the length of the pile determine the strength.

The technique is effective in accurately measuring the thickness of heavily pitted structures. A computer-controlled system was developed that automatically scans a pile and obtains the thickness measurements. Field tests of the system in a harbor proved its capability in measuring the thickness of underwater piles.

Acknowledgments

The author wishes to thank Messrs. Ron L. Brackett and Anthony Smith, Naval Civil Engineering Laboratory, Port Hueneme, California, for their support and encouragement towards the development of this technology. Thanks also are due to R. McClintock, Yuzo Hasegawa, Floyd Bradley, and T. W. Rudwick for making this research program a success. This program was supported by the Naval Civil Engineering Laboratory, Port Hueneme, California.

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Summary of Nondestructive Testing

The nondestructive testing (NDT) section begins with a paper by Berger, which discusses the attributes of neutron radiography, and, in particular, its advantages over other NDT methods because of the potential for early detection of corrosion before extensive attack and thinning of the material has occurred.

Meredith and Lamping discuss three recently developed ultrasonic test (UT) systems that have proven effective in the detection of thinning, pitting, and methane-type hydrogen damage. The specific techniques used with each system are also discussed, along with a specialized technique for detection of corrosion damage in boiler tubes.

Acoustic emission (AE) is a relatively new although maturing NDT technique. Pollock presents two approaches to detect and monitor corrosion, and reviews the demonstrated capabilities and limitations of the technique. He discusses the basic requirements for successful field applications. Yuyama presents a survey of laboratory studies as well as field applications to describe the utility of AE for the detection and monitoring of corrosion, stress corrosion cracking (SCC), and corrosion fatigue. Both authors clearly present the potential usefulness of AE as a powerful NDT technique, if the capabilities as well as the limitations are recognized. Martin et al present further results for two aluminum alloys which show that AE is particularly well suited for studying SCC in the laboratory. They show that the AE produced by the SCC have recognizable signatures, and discuss the applicability of employing AE to detect or monitor SCC in real structures. They conclude that AE is a viable technique for detecting or monitoring SCC in real structures when the resulting AE signals are of high amplitude, although considerable preliminary testing will be required, especially when the AE signals produced are of low amplitude.

A portable, commercially available, field ready, state-of-the-art system to monitor corrosion is the subject of the paper by Grills and Tsao. The system is described, and examples of where it has been used to monitor corrosion are presented, with actual results from the examples, all in "living color."

Another illustration of state-of-the-art ultrasonic NDT systems in field use monitoring corrosion is the subject of the paper by McGarvey et al. Although not limited to only detecting corrosion damage, the paper describes how the computer based automated system is used for locating and sizing flaws in the near-bore region of steam turbine rotors. A magnetic particle (MT) inspec-

tion may also be performed with the system, and the authors note that the system also has application for piping and tubing.

Intergranular stress corrosion cracking (IGSCC) detection and characterization is a problem of particular interest to the nuclear industry. Tests have shown that reliability of manual ultrasonic testing (UT) is strongly operator and technique dependent, thereby adversely affecting and monitoring of flaw growth. Mikesell et al describe an ultrasonic imaging technique, which has been developed over a ten-year period, and an automated search head, in development for the past five years. The design of the search head is described, and the results of the imaging technique using the search head in detecting, interpreting, and characterizing IGSCC are presented.

In monitoring crevice corrosion it is necessary to have good geometric data on pit sizing. The paper by Baron et al presents an eddy current technique developed for an application, which precluded visual or replication methods. The theory together with the tests to validate the theory are presented, and the authors conclude that it is possible to use eddy current to monitor the depth of the most common types of corrosion crevices, which are long with respect to their width.

Carmichael et al point out that most forms of corrosion damage in power plant machinery are believed to involve concentrations of corrosive species in the fluid stream. They describe an on-line, real time sensor capable of detecting the concentration of contaminants that cause corrosion, and the results from both laboratory autoclaves and steam line evaluations as well as a field evaluation of three sensors in an actual power plant.

Hydrogen environments combined with high pressure and high temperatures produce hydrogen embrittlement in steels. At present, hydrogen attack may be detected nondestructively using UT, although quantitative evaluation is questionable. Watanabe et al present a new method to apply ultrasonic techniques to quantitatively evaluate hydrogen attack, thereby overcoming the shortcomings of present methods. They show in laboratory tests that the shear and longitudinal wave velocities both decrease in hydrogen affected steels, and that the ratio of shear wave velocity to longitudinal wave velocity is a promising factor to evaluate intergranular type corrosion attack.

Detection of hydrogen assisted crack growth may be possible with a new technique presented by Carpenter and Heiple. The method involves the precise continuous measurement of changes in the elastic modulus coupled with acoustic emission measurements. Results from laboratory tests of samples exposed to high pressure hydrogen gas as well as results from AE tests of small laboratory pressure vessels of the same materials while pressurized with hydrogen gas are presented.

Since many underwater steel structures are rough and pitted because of corrosion, conventional NDT techniques are of questionable value in accurately monitoring and assessing corrosion. Birring describes a focused ultra-

sonic transducer integrated with a computer-based system, which was used with the techniques presented to successfully and accurately measure underwater thicknesses of steel piling in a severe harbor environment.

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Electrochemical Methods of Corrosion Monitoring

Overview of Corrosion Monitoring in Modern Industrial Plants

REFERENCE: Dean, S. W., "Overview of Corrosion Monitoring in Modern Industrial Plants," *Corrosion Monitoring in Industrial Plants Using Nondestructive Testing and Electrochemical Methods*, ASTM STP 908, G. C. Moran and P. Labine, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 197-220.

ABSTRACT: A number of procedures and devices used to monitor corrosion damage and metal loss are discussed. The advantages and drawbacks of these methods are reviewed. The factors which need to be considered in selecting a corrosion monitoring system include the purpose of the program, the cost and availability of the equipment, reliability of the system, and the nature of the corrosive stream. The problems which accompany a plant corrosion program, including safety, potential for leaks, and misleading data, are discussed. Various commercial devices employing polarization resistance, electrical resistance, polarization behavior, and alternating current (AC) are included. Problem areas in corrosion monitoring are discussed, together with needs for future development.

KEY WORDS: corrosion monitoring, polarization resistance, stress corrosion cracking, localized corrosion, polarization diagram, ultrasonic thickness testing, hydrogen probe, AC impedance, occluded cell corrosion

Corrosion monitoring has become an important aspect of the design and operation of modern industrial plants. In view of the 1975 Battelle Memorial Institute Study which showed that corrosion was responsible for approximately \$70 billion worth of damage in that year [1], it is apparent that corrosion is a significant degradation process which must be dealt with. Modern manufacturing facilities employ a wide range of corrosive materials, so that it is no surprise that corrosion occurs.

Corrosion monitoring is important because it allows plant engineering and management to be aware of the extent of damage caused by corrosion and also to be aware of the rate at which this damage is occurring. Monitoring as described in this paper includes any technique to evaluate the progress or rate of corrosion, including the rate of attack, the penetration, or loss of load-

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carrying capacity of the elements of the plant in question [2]. These degradation factors are normally interrelated, although in some cases there may be exceptions. For example, perforation can occur by means of stress corrosion cracking or pitting, even though the overall rate of attack is very small.

This paper is a review paper and not intended to present research results. The factors which motivate engineers to include corrosion monitoring capabilities in manufacturing facilities will be discussed. A variety of different methods of monitoring corrosion will be reviewed, and some strategies for employing corrosion monitoring will be discussed. Finally, areas for future work will be identified.

Motivation for Corrosion Monitoring

Corrodents

Corrosive agents are omnipresent in modern manufacturing facilities. Probably the most common corrosive compound is water, which is used widely for cooling but is also used for heating, both as steam and as hot water. It is a reaction product in many processes; it is used for washing equipment, for extinguishing fires, and a variety of other purposes.

Corrosive chemicals are widely used in many manufacturing facilities. For example, sulfuric acid is probably the most important industrial chemical in the world, with an annual production of about 45 million tons [3]; sulfuric acid is also extremely corrosive to most materials of construction [4]. Consequently, it is essential to monitor the equipment handling this material to avoid problems. Many other corrosive chemicals, including other acids, bases, and salts, are widely used.

Combustion processes generate corrosive conditions due to the formation of water, heat, molten salts, sulfur oxides, and other corrosive combustion products. Although the techniques for avoiding corrosion in combustion processes are well-known, it is important to monitor equipment, such as boilers, condensers, etc. Atmospheric corrosion is another source of concern in many plants. Condensed moisture or rain combining with atmospheric pollutants, or both, are corrosive to many materials of construction; consequently, structures exposed to the atmosphere should also be monitored to avoid difficulties.

Materials of Construction

Industrial plants employ materials that corrode in service. Carbon steel is widely used for structural and other purposes, and a variety of measures is required to protect the steel or otherwise cope with the corrosion that occurs. The use of materials, such as steel, is justified by the cost-performance benefits that these materials provide. The risk of damage by corrosion is accepted because of the normally slow, progressive nature of the corrosion process. A

well-designed corrosion monitoring program is able to provide good information on the condition of the equipment in question and its ability to continue operation. Thus, the risks associated with the corrosion process can be minimized by this approach.

Unanticipated Conditions

The actual operating conditions which many industrial plants encounter are sometimes not fully anticipated in design of these plants. For example, the failure of components such as valves, relief devices, leaks in adjacent equipment, etc., can cause unexpected conditions to develop. Furthermore, the conditions which result from events such as plant upsets, extended startup problems, turndown, and plant shutdown all can cause corrosion problems. Even in well-designed plants, events such as leaks, spills, fires, power failures, floods, and earthquakes can cause unexpected problems. In these situations, a corrosion monitoring program can be very helpful in understanding the extent of damage and identifying potential problem areas.

Unknowns

In plants where new processes or new chemicals or both are being handled, a corrosion monitoring program can be very helpful. This is especially true in pilot plants. In such situations, corrosive species may form which were not anticipated or recognized. A corrosion monitoring program can help to identify when this situation occurs and provide solutions to the problems that it causes. In existing plants, there is often a need to find better construction materials for certain components of the plant. This may result from inadequate initial selection of materials or from changes in operating parameters which increase the corrosivity of the environment. In either case, a corrosion monitoring program can be helpful in selecting new materials as well as detecting ongoing damage.

Verification of Control

Finally, corrosion monitoring programs can be helpful in verifying the effectiveness of preventive measures. It is usually desirable to monitor the performance of corrosion inhibitor programs used in cooling water to verify that the program is adequate. In some cases, the programs can be used to signal the need for additional inhibitor addition. In addition, corrosion monitoring can provide information on the success of cathodic protection systems and on the performance of barrier layers, for example, glass-lined vessels.

Selecting a Corrosion Monitoring Method

There is a rather large variety of methods which are available for corrosion monitoring in the field. However, there are relatively few standards available

to provide guidance on selection of monitoring methods. The ASTM Recommended Practice for Conducting Plant Corrosion Tests (G 4) was designed to provide guidance on coupon type tests. Dillon, Krisher, and Wissenberg provide information on both coupons and electrochemical techniques [5]. However, in view of the growing number of methods available, selection of a corrosion monitoring method is somewhat arbitrary and largely influenced by the experience of an engineer responsible for selection. In any case, it is not unusual for engineers to experience a learning curve evolution when entering the field of corrosion monitoring.

Selection Factors

In the selection of a corrosion monitoring method, a variety of factors should be considered. First, the purpose of the test should be understood by everyone concerned with the corrosion monitoring program. The cost and applicability of the methods under consideration should be known, and it is important to consider the reliability of the method selected. In many cases, it will be desirable to include redundancy so as to provide more confidence in the information generated.

Another question of importance is whether there is access to the streams and equipment in question. If access is available, then methods which imply probes or coupons become more feasible. Otherwise, nondestructive methods may be required. An important factor in considering monitoring methods is the response time required to obtain the information from the method. Coupon methods and techniques which require plant shutdown tend to be relatively slow in generating information. On the other hand, instantaneous corrosion rate measuring equipment can provide fast results. A final consideration is one of safety and hazard potential. Will the monitoring method increase the probability of a leak or cause potential injury to personnel? A related question is whether a lack of monitoring will cause a hazard potential. These questions should be carefully considered in the selection of any monitoring approach.

Plant Versus Laboratory Techniques

It is important to keep in mind the differences between laboratory methods and applications for use in plant situations when considering corrosion monitoring programs for plant application. The consequences of an equipment failure in these situations is rather different. Usually, in a laboratory situation equipment failures are troublesome, but not catastrophic. In an operating plant, equipment failure can lead to a leak resulting in loss of product, a hazard potential, and possible shutdown of the plant. It is important for the monitoring apparatus to minimize the eventuality of such an incident.

A second important difference is that corrosion monitoring equipment in

the plant is usually not watched on a continuous basis. Automatic data gathering systems are frequently necessary, and personnel cannot be expected to devote substantial amounts of time to operating and maintaining monitoring devices. Furthermore, much of the plant equipment is located far from control rooms and it may be exposed to the weather, pollution, leaks, spills, and other environmental problems. Devices which protrude from operating vessels are often used as handholds or footrests, even though plant safety codes may forbid such practices. In any event, the equipment must be sufficiently robust to withstand rough handling during installation and adjustment.

The American Society of Mechanical Engineers code should be reviewed and any modifications made to equipment must conform with the appropriate code requirements in dealing with pressure vessels and piping. In many plant situations, electric power is not available at the site where the corrosion monitoring is to be carried out. Furthermore, intrinsically safe designs will often be required because flammable gases used in the process may result in the possibility of explosive mixtures. In addition, the presence of thermal insulation will often restrict access to the metallic components and vessels which are either above or below ambient temperature. All of these factors contribute to making in-plant corrosion monitoring a very different proposition from measuring corrosion rates in laboratory settings.

Methods Available for Corrosion Monitoring

Coupons

Probably the most widely used and simplest method of corrosion monitoring involves coupons. These are relatively small specimens of materials in question which are inserted into the process stream for a period of time, then removed and evaluated. The specimens may take the form of disks, rectangular pieces, or special devices, such as U-bends, to check stress corrosion cracking [see the ASTM Recommended Practice for Making and Using U-Bend Stress Corrosion Test Specimens (G 30)]. Figure 1 shows a typical coupon rack. Evaluation carried out at the end of the exposure period is intended to estimate the extent of damage to the coupon. One of the simplest and most straightforward approaches to coupon evaluation is to determine the mass loss by weighing the coupon before exposure and then re-weighing the coupon after the exposure period has been completed and the specimen cleaned of corrosion products. This method can provide an accurate estimate of uniform corrosion, but it is not applicable in cases where pitting, cracking, or embrittlement have occurred.

In cases where pitting has occurred, it will be necessary to determine the penetration. The ASTM Recommended Practice for Examination and Evaluation of Pitting Corrosion (G 46) provides a helpful guide in examining and evaluating pitting corrosion. If cracking is suspected, then it is often desirable

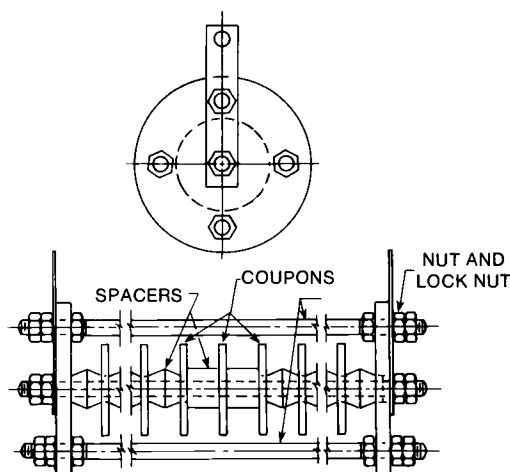


FIG. 1—Typical coupon rack—Spool Type—ASTM G 4.

to use metallographic sectioning to determine the morphology and depth of attack. In some cases, it may be desirable to use tensile specimens as coupons and then measure the breaking strength of the specimen as compared to the strength of an unexposed coupon in order to estimate the damage which has occurred. This is particularly appropriate when the major concern is loss of strength rather than penetration or general attack.

In any event, the rate of attack as determined by a coupon test is inferred by the total attack divided by the exposure period. If information is needed on how the rate of attack varies with exposure time, then it will be necessary to conduct a series of tests for different exposure times. The planned interval corrosion test [6] provides a rational approach to determining how corrosion rates vary with time using coupon testing techniques. A variety of approaches for in-plant coupon testing is described in ASTM Method G 4. The ASTM Recommended Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens (G 1) provides information on cleaning and evaluating general attack on coupons.

There are a variety of advantages and disadvantages to coupon tests. The coupon testing approach is particularly desirable when a large number of specimens of different types of material needs to be tested. The specimen designed for most coupon tests is relatively simple, and a large variety of materials of construction coupons are available commercially from several sources. The results of coupon tests can provide information on stress corrosion cracking, crevice corrosion, pitting, and galvanic effects as well as general attack. The cost of setting up and running a coupon test program is relatively low.

There are, of course, disadvantages to coupon tests. It is necessary to expose the coupons to the environment in question, thus access to this environ-

ment is required. It is necessary to have the coupons exposed to the actual conditions in question because the corrosion rate will depend on factors such as flowrate, turbulence, temperature, etc. In many cases, it is not practical to install coupons except when the plant is down; likewise, coupon retrieval may only be possible at a subsequent turnaround. Trained personnel must carefully identify, retrieve, and evaluate all coupons, and until the coupons are retrieved and evaluated, the program provides no information.

Electrical Resistance Probe

The electrical resistance probe is based upon the principle that the electrical resistance of a conductor is inversely proportional to its cross-sectional area. The approach here is to install a wire or other device made of the material in question in such a way that its electrical resistance can be measured at any convenient time [see ASTM Test Methods for Corrosivity of Water in the Absence of Heat Transfer (Electrical Methods) (D 2776)]. It is important to incorporate in such a probe a temperature compensating element because the resistance of the probe will also be determined by its temperature. Because the corrosion process reduces the cross-section of the exposed element, its electrical resistance will increase with exposure time if corrosion is occurring.

This device effectively measures the average metal thickness remaining. To obtain the corrosion rate, a series of measurements is made over a period of time and the results plotted. The corrosion rate can be determined from the slope of the resulting plot. Figure 2 provides an example of electrical resistance probe results.

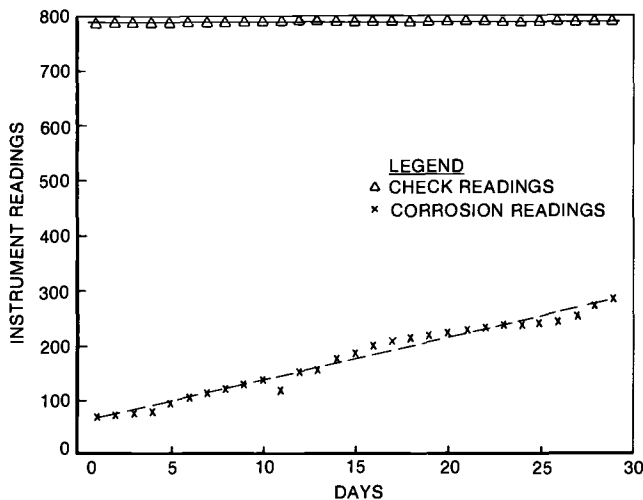


FIG. 2—Typical data plot from electrical resistance probe.

This approach has a number of advantages. Probes are relatively small and can be installed fairly easily (see Fig. 3 for a typical probe). The probe can be wired directly to a control room location or a portable resistance bridge can be used at the location of the probe to determine the metal remaining. In systems wired directly to control rooms, it is possible to employ a computer data acquisition system to obtain the data and reduce the results to corrosion rate values. Commercial electrical resistance equipment is available from several sources. This approach does not depend on the environment because only the remaining metal is measured, and because the conductivity of the corroding environment is of no consequence. Thus there is no problem with measuring corrosion occurring in liquid or vapor streams.

This approach has several disadvantages. It is necessary to penetrate the walls of vessels and piping to install the probes, and any such penetration creates the possibility for leaks. Direct wiring the probe to a control room location is expensive and must be done carefully to avoid spurious signals and errors. On the other hand, measurements at the probe site using a portable bridge are time-consuming and not always possible. The temperature compensation device reacts slowly and may cause errors if the temperature is varying at the time the measurement is made. Corrosion rate measurements obtained in short periods of time can be inaccurate because the method measures only the remaining metal and not the rate of attack, increasing the signal to noise ratio in short exposure periods. This method also provides no information on localized attack.

Ultrasonic Thickness Measurements

Ultrasonic thickness measurements (UT) can be used as an in-situ corrosion rate monitoring approach. The principle here is to place a probe against the exterior of the vessel in question. The probe contains a device which emits an ultrasonic signal which travels through the vessel wall and bounces off the

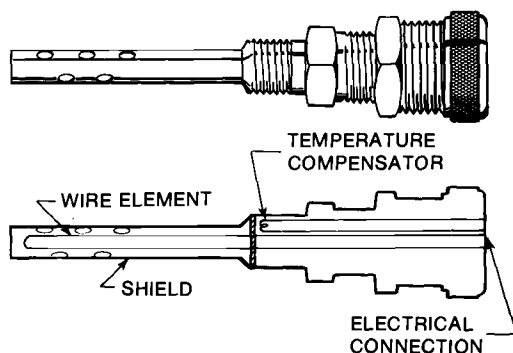


FIG. 3—Typical electrical resistance probe design.

interior surface, then returning to the probe. The time elapsed between emission of the signal and its subsequent reception is used together with the velocity of sound in the material to calculate the thickness. It is necessary to make a series of measurements over a time interval and determine the metal loss per unit time in order to obtain a corrosion rate.

This method has several advantages. It is not necessary to penetrate the vessel in order to make the measurements involved, and the results are obtained in terms of thickness. Commercial equipment such as small, hand-held probes and reading devices are available for making these measurements, and are relatively easy to use.

There are also several disadvantages. The presence of paint, thermal insulation, or adjacent equipment can make it difficult or impossible to obtain readings at desired locations. It is necessary to use a coupling agent, such as grease, petroleum jelly, or oil, in order to have the signal pass from the probe into the metal and return. There are considerable problems when vessel walls are at high or low temperatures. Although it is conceivable to apply a permanently mounted probe system hard-wired to a control room computer data acquisition system, this approach has not been widely practiced. The high cost of the equipment, together with the fragility of the probes involved, make such an installed system less than desirable. There are serious problems in equipment which has an internal lining, because it is not obvious from which surface the returning signal will originate.

In spite of these problems, the UT approach is widely practiced in turn-around situations where it is necessary to evaluate vessel life and suitability for further service. One problem with this approach occurs because the UT method tends to overestimate metal thicknesses when the remaining thickness is less than about 1.3 mm (0.05 in.). The method must be used carefully because spurious readings can occur. Surface roughness can create problems. Furthermore, pits and cracks are not readily detected unless angle beam methods are employed. Corrosion rates occurring at any point must be inferred by extent of damage divided by the exposure time.

Other NDT Approaches

A variety of other nondestructive testing (NDT) methods can be used to evaluate corrosion damage. These include radiographic methods, magnetic methods, eddy current methods, and techniques such as dye penetrant examination. All of these approaches are helpful in determining the suitability of equipment for this service. In special cases, they may be employed for corrosion monitoring purposes, but have not been widely used for this purpose.

Polarization Resistance

Polarization resistance is a technique which provides an estimate of the corrosion rate as opposed to the previous methods, all of which provide informa-

tion on remaining thickness. The method is based on the Stearn-Geary [7] analysis. The concept here is that corrosion rate of a probe is inversely proportional to its polarization resistance, that is, the slope of the potential-current response in the vicinity of the corrosion potential. In a plant situation, it is necessary to employ a probe which enters the vessel in the area where the corrosion rate is desired (see Fig. 4). The probe has electrodes made of the material in question. An electronic power supply polarizes the specimen about 10 mV from the corrosion potential, and the resulting current is recorded as a measure of the corrosion rate. This method has the advantage of providing an instantaneous estimate of corrosion rate.

There are a number of commercially available probes and analyzing systems which can be interfaced directly into control room computer data acquisition systems. Furthermore, alarms can be used to alert plant operators to situations when high corrosion rates are experienced.

There are a number of limitations to this approach. It is necessary that the corroding environment be an electrolyte with a reasonably low resistivity. High-resistivity electrolytes give erroneously low corrosion rates. It is necessary to penetrate the vessel wall, with the attendant concerns for leaks, personnel safety, and other problems. Although the ability to use direct wiring from the probe location to the control room site is desirable, the installation of such wiring systems is rather expensive. Furthermore, these systems provide no information on localized corrosion, such as pitting and stress corro-

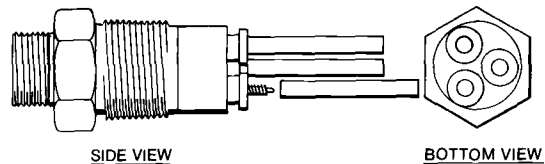


FIG. 4a—Typical three-electrode polarization resistance probe.

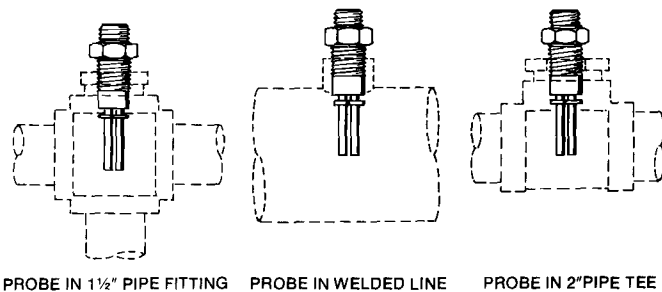


FIG. 4b—Typical installation of polarization resistance probes (1 in. = 25.4 mm).

sion cracking. In addition, corrosion rate values are approximate at best, and the method is best suited for determining periods when substantial corrosion rate changes occur.

Polarization Diagrams

It is possible to use the same electrochemical probe system as one employs in polarization resistance measurements to obtain a current density-potential response by using a portable potentiostat/ x - y recorder data acquisition system. If one of the specimen electrodes is replaced with a reference electrode, the resulting current density potential polarization diagram is comparable to what is observed in laboratory setups. This approach has the potential to provide detailed information on electrochemical reactions occurring in the environment. The results of polarization-current density analyses can be used to determine whether a plant stream may cause pitting. It can also predict whether passivating inhibitors can be used to eliminate corrosion.

Portable potentiostat devices are available with built-in x - y recording capability. This type of approach can be very helpful if used in conjunction with polarization resistance monitoring programs to determine the cause of unusually high or low observed corrosion rates. As such, this is a valuable analytical tool. This is probably not an approach which can be used on a routine basis. The results generated from such equipment require interpretation by skilled personnel. Although the equipment available for this purpose is portable, it is rather large and difficult to transport, and it is fragile, which means that it should not be shipped through commercial airlines baggage handling facilities. In addition, problems can arise because long lengths of wire required to connect the probe to the instrument introduce extra resistance into the circuit. This, of course, can be compensated for if the problem is recognized. Another problem which occurs when running polarization curves is drift of the reference electrode, which can be most troublesome when using slow scan rates.

AC Impedance

The use of AC impedance polarizing techniques is becoming more popular in electrochemical evaluation. In principle, the same probe elements can be employed for AC impedance studies as in polarization resistance or polarization diagram evaluations. The AC impedance approach permits resistive and capacitive elements of the electrochemical corrosion reaction to be separated and analyzed independently [8] (see Fig. 5). The method is particularly attractive in the case of high resistivity electrolytes, such as steam condensate. In these cases, the polarization resistance method gives erroneously low readings because the bulk resistance of the electrochemical cell adds to the measured resistance. The AC approach avoids this problem.

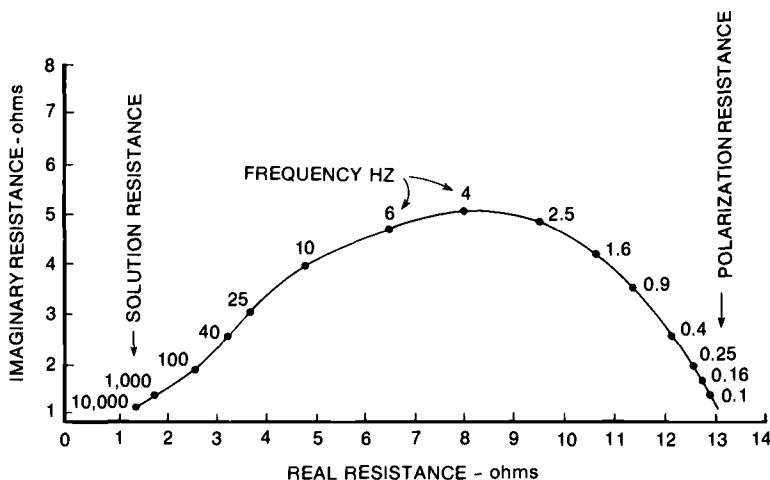


FIG. 5—Typical plot of AC data in terms of real (resistive) and imaginary resistance.

It is necessary to employ a rather sophisticated AC frequency generator and analyzer system to obtain results such as in Fig. 5. Haruyama et al [9] have suggested using only the two frequencies to characterize the AC impedance behavior. This minimizes the number of measurements, but does not reveal details of the behavior. Interpretation of the results of AC studies requires familiarity with the approach. The specimen designs employed in commercial polarization resistance probes have not been optimized for AC analysis. Therefore, it is desirable to obtain a full frequency response curve to verify that the behavior may be analyzed by conventional techniques, but obtaining a complete frequency response curve may require several hours. Thus, much more developmental work will be necessary before the AC impedance technique achieves widespread acceptance for corrosion monitoring in operating plant situations. Note that the Stearn-Geary constant or the Tafel slopes must be known in order to convert AC impedance data to corrosion rate information.

Hydrogen Probe

The hydrogen probe concept is based on the fact that in non-oxidizing acidic systems, a cathodic reaction product is hydrogen. Hydrogen atoms generated in this manner diffuse through the thickness of the vessel and are liberated at the exterior surface. A hydrogen probe is applied to the exterior surface, and in one variation consists of a piece of palladium foil which serves as collector and catalyst for the subsequent oxidation of the hydrogen [10]. The cell is attached to the palladium foil and a stainless steel working electrode is used to supply the current employed in this oxidation (see Fig. 6). The

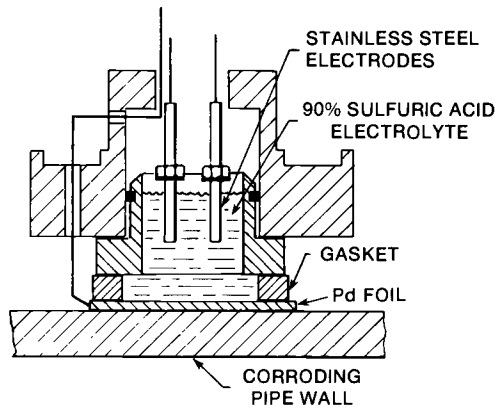


FIG. 6—Hydrogen patch probe design.

electrolyte is 90% sulfuric acid. The current required to oxidize the hydrogen is measured and is therefore directly proportional to the corrosion rate which the interior of the vessel is experiencing.

Unlike the UT and other techniques which measure the remaining wall thickness, this approach measures the corrosion rate. However, it is limited to systems in which the temperature is close to ambient and the diffusion rate of hydrogen is high. The most common application is gas pipeline service where corrosion can occur when hydrogen sulfide, water, and sometimes carbon dioxide (CO_2) are present. Another variation of this approach consists of simply attaching a chamber to the exterior of the pipe and monitoring hydrogen liberation through an increasing pressure [5].

An advantage of this approach is that it does not require penetrating the pipe wall in order to obtain the corrosion rate. This method assumes that all the hydrogen liberated in the corrosion reaction diffuses through the steel vessel wall rather than being liberated as hydrogen gas at the surface. This is true when hydrogen poisons such as hydrogen sulfide (H_2S) are present. There are commercial devices available for corrosion monitoring by this technique, but it is questionable as to whether or not such a device could be set up and allowed to run unattended for extended periods of time. It also suffers all of the problems which are associated with any electrochemical measuring device, that is, the need for complex electronic equipment and wiring, and for operators and installers with a sensitivity to the requirements of such equipment. Thus this method is practicably limited to steel, which has a high hydrogen diffusivity and low solubility of hydrogen.

Other Corrosion Monitoring Techniques

Another technique which is useful in monitoring corrosion in operating plants is an analysis of the product streams for the presence of corrosion prod-

ucts. This approach is simple and straightforward and does not usually require the installation of specialized equipment. For example, product streams from the bottom of the distillation column can be sampled at regular intervals and atomic absorption analysis techniques used to determine heavy metals such as iron, nickel, chromium, etc., at very low levels. Concentration of such impurities is then directly proportional to the corrosion rates times the area of metal corroding, providing that the only source of metal ions is corrosion and the corrosion products are not precipitating. The major problem is that the corroding area is seldom known with certainty, so the results tend to be qualitative in nature.

The Materials Technology Institute (MTI) of the Chemical Process Industries has sponsored research with Battelle Memorial Institute to develop an occluded cell corrosion monitoring device [11]. The resulting apparatus was shown to have merit in detecting when environments were conducive to developing occluded cell or crevice corrosion. This device is based on the concept of isolating the occluded electrode from the boldly exposed electrode and measuring the current between these electrodes by means of a zero resistance ammeter. The principle of this system has been demonstrated, but a commercial device has not yet been developed.

MTI has also been interested in developing a device for monitoring stress corrosion cracking conditions in process streams. The Battelle Memorial Institute has provided a device based on the cyclic slow strain rate approach which shows when stress corrosion cracking initiates [12]. However, a variety of problems have been identified and no commercial equipment yet exists based on this work.

Another approach to corrosion monitoring is to employ weep holes, also known as sentinel holes [13]. This approach is based on the concept that if a small hole is drilled through the exterior of the vessel or pipe to the corrosion allowance, a leak will result when the corrosion allowance is gone. If provisions are made to detect this leak and shut down the equipment, there can be some assurance that the vessels will not be operated when corrosion has exceeded the corrosion allowance provided for the vessel. A serious disadvantage of this approach is that it does not provide an early warning or provision for taking action to prevent the corrosion before the vessel becomes inoperable. Furthermore, the problem of leaks is often unacceptable when hazardous, flammable, or toxic materials are being processed.

Another device which has been used in the past in boiler applications is the embrittlement detector. This device was specifically developed to anticipate caustic cracking of boiler steels, and was employed to allow prompt action when caustic cracking conditions developed. This method is described in the ASTM Method of Assessing the Tendency of Industrial Boiler Waters to Cause Embrittlement (USBM Embrittlement-Detector Method) (D 807), and it was originally developed by the U.S. Bureau of Mines. Since the device was aimed primarily at riveted boilers, the method has faded from wide usage

with the development of fully welded steam boilers. The method has the advantage of exposing the test specimen to a steam environment in an external location. However, the specimen must be retrieved and inspected visually in order to determine whether cracking has occurred.

Strategies in Corrosion Monitoring

Monitoring Location

One of the key issues in any corrosion monitoring program is the decision where to locate corrosion monitoring devices. If the initial material selection for the plant has been carried out in a thoughtful manner, it is unlikely that a general uniform corrosion will occur throughout the plant. In any corrosion monitoring program, it is desirable to find sites where the highest corrosion rates will be experienced.

The dilemma facing corrosion engineers in developing corrosion monitoring programs for plants can be illustrated by considering a distillation column (Fig. 7). The most logical point for corrosion monitoring in a distillation column would be the feed point, overhead product receiver, and the reboiler or bottoms product line. These points represent the locations where the highest and lowest temperatures are encountered and also the points where the

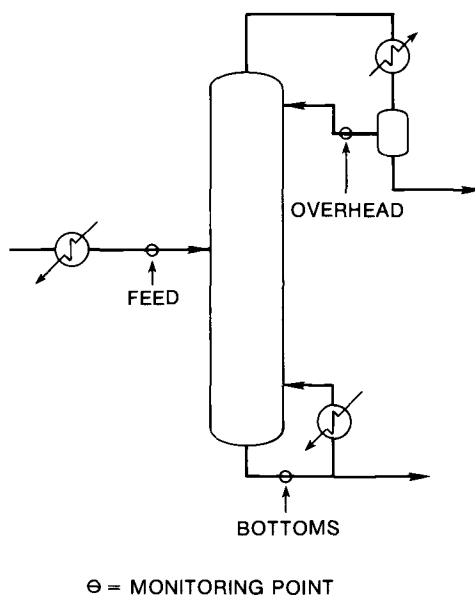


FIG. 7—Three-point monitoring for a distillation column.

most and least volatile products are concentrated. However, it is usually observed that these are not the locations where the most severe corrosion occurs.

In many cases, the species causing the corrosion will concentrate at an intermediate point in the column due to chemical changes which change its volatility within the column. Therefore, a comprehensive corrosion monitoring program involving a distillation column would require several monitoring points throughout the column if there is a possibility of concentrating a corrosive species within the column (Fig. 8). Once the most corrosive location within the column is identified, a monitoring program can be restricted to this area [14].

Another problem with distillation columns is the fact that the liquid on trays tends to be frothy, and this creates difficulties for electrochemical methods. One approach to overcoming this problem is to install bypass loops to withdraw liquid from the column, pass it over the corrosion monitoring probes, and reinject it at a lower point in the column [5]. This avoids the problem of foam and froth, and also provides a more controlled flow rate over the corrosion monitoring equipment. The use of such a loop also provides an opportunity for withdrawing liquid samples at times of high corrosion rates (Fig. 9).

The concept of sampling the process stream can be employed in locations other than distillation columns. A sample tap can be very helpful in conjunc-

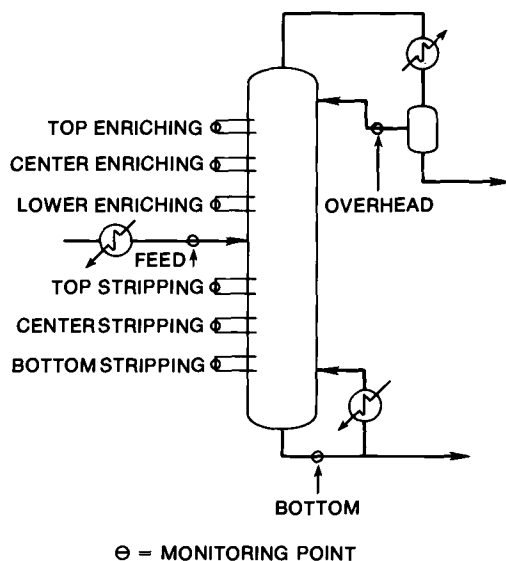


FIG. 8—Distillation column showing preferred location of monitoring probes or other devices, nine points.

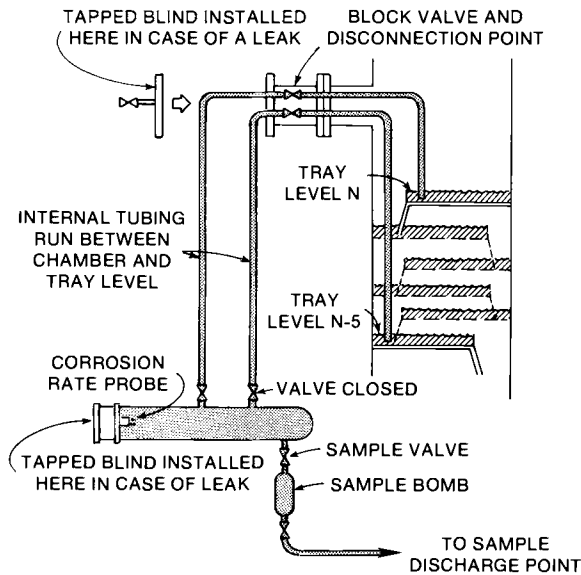


FIG. 9—Side-stream withdrawal approach to corrosion monitoring in a distillation column.

tion with polarization resistance devices. The alarm feature on polarization resistance monitoring equipment can be used to signal the need to withdraw samples, which is particularly desirable in the case of pilot plant operation where wide variations in processing conditions are experienced. It is also helpful in operating plants which employ a campaign strategy to produce different products in the same equipment.

High-velocity gas streams in pipes may cause problems with conventional monitoring systems. In this case, the presence of an aqueous phase is usually restricted to a thin layer on the surface of the pipe. A probe which protrudes into the pipe may miss the liquid layer which is present only close to the pipe wall. In this case, the use of a surface probe (Fig. 10) permits the use of polarization resistance measurements to estimate the corrosion rate of the pipe wall [15]. Storage tanks containing nonaqueous liquids provide another example where probe location is critical. In such tanks, the most corrosive location may be at the liquid level if the liquid in the tank has a density greater than that of water. In this case, it would be desirable to locate the corrosion monitoring probe on a floating platform so that it may detect the presence of a corrosive aqueous phase.

In the other case, when the liquid stored in the tank is less dense than water, it may be advisable to place the corrosion monitoring device at the bottom of the tank. In any event, an understanding of the corrosion process can be of great assistance in determining probe locations.

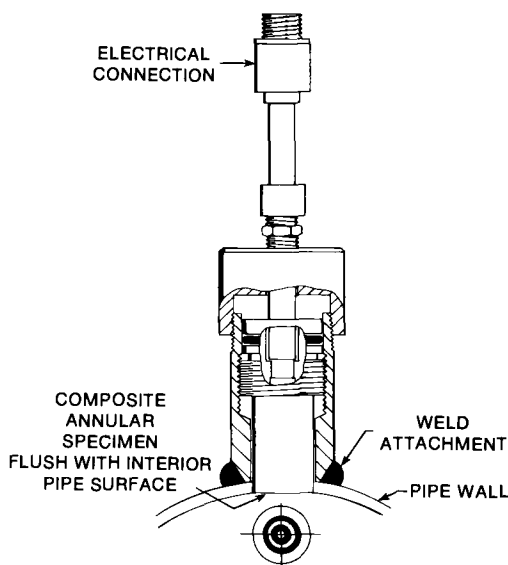


FIG. 10—Flush-mounted polarization resistance probe design.

UT Data Analysis

Ultrasonic thickness (UT) measurements are usually obtained during turn-around periods when the plant is down. A well-designed program will provide a series of thickness measurements at specified locations throughout the plant. Assuming the original thickness of a vessel was constant, a diagram similar to Fig. 11 can be drawn, which shows that the average corrosion rate and remaining thickness are inversely related. The remaining life of the vessel can then be estimated from the maximum corrosion rate and the remaining corrosion allowance. In situations where variations in corrosion rate can occur in a random manner, statistical analysis can be used to estimate the highest corrosion rate and smallest remaining thickness. This approach provides a rational method of estimating remaining life when faced with a quantity of thickness readings from a UT survey.

Redundancy

Redundancy is another issue of importance in designing corrosion monitoring programs. It is often desirable to use at least two different types of corrosion monitoring devices at any location. For example, the use of an electrical resistance probe, together with a polarization resistance probe, allows both instantaneous corrosion rates to be measured along with a longer time average corrosion rate. These two approaches can be correlated to one another, and this is very helpful in weeding out spurious or inaccurate readings.

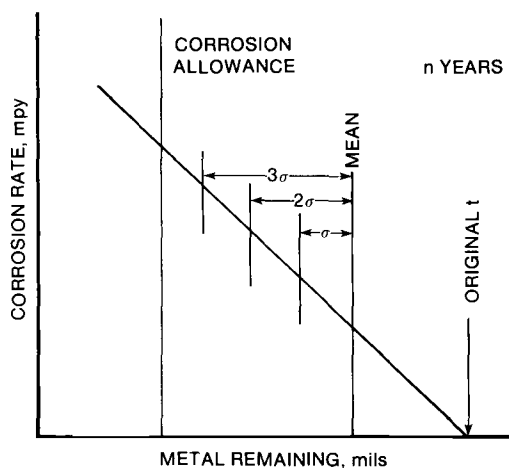


FIG. 11—Typical UT data analysis—plot of metal thickness remaining versus calculated corrosion rate.

Another approach in using polarization resistance probes is to weigh the probe before and after the test program to correlate the mass loss with the time average corrosion rate which the probe suffered. If the time average corrosion rate does not agree with the mass loss of the probe itself, there is reason to expect that the electrochemical value is in error. Independent coupons can also be installed along with polarization resistance probes in order to obtain time average corrosion rate values.

It is especially important to use a variety of corrosion monitoring approaches when designing pilot or demonstration plants. Coupon tests can be very helpful in selecting optimum materials for processes based on pilot plant experience. The use of polarization resistance monitoring is very helpful in determining if certain processing conditions cause the development of corrosive situations. Redundancy in the design of such monitoring systems is important in pilot plants, because often the mechanisms of corrosion are not well understood, and the consequence of erroneous information can be serious over-design or exposure to unexpected hazards.

Other Issues

One of the major problems with corrosion monitoring equipment is the need to install wires from the probes to the control room or to the instruments and data storage systems. Hard wire systems are frequently more expensive than the probes and electronic instruments, and wiring systems frequently are sources of problems due to breakage, moisture ingress, and connection problems. An increasingly attractive option is the use of devices to transform the signals to coded CB radio signals. These devices can be small, battery-oper-

ated units installed at probe locations to provide on command the information desired to the base station located at the control room. This approach may become increasingly attractive as the availability and reliability of such CB systems increase.

Another important issue in corrosion monitoring systems which has already been mentioned is the problem of leaks. Leaks have the potential of causing hazards and of shutting down operating plants. Any corrosion monitoring system must be installed in such a way that leaks from the probes can be handled with a minimum of interruption. It should never be assumed that a device which penetrates the wall of the vessel will not leak, so it is essential to have contingency plans available to cope with leaks before the devices are installed.

A related problem is that of packing glands on pressure vessels that have removable devices. The pressure within a system will always exert a force on any device which is removable and it is important to prevent the device from being blown out, thereby injuring the personnel attempting to remove the device, or exposing such personnel to the fluid within the vessel. The use of restraining rods, chains, etc., is very important and must not be left to chance.

Current Needs

Stress Corrosion Cracking

Probably the most serious problem we face in corrosion monitoring is that of stress corrosion cracking. Normally, in the materials of construction of chemical processing plants, stress corrosion cracking causes leaks rather than catastrophic vessel failure. However, even leaks are a serious problem, and none of the commercially available corrosion monitoring systems provides an early warning that stress corrosion cracking is initiating or progressing in the very early stages. The MTI program to develop a stress corrosion cracking monitoring device was very attractive because the device seemed to be able to accelerate stress corrosion and thereby detect it before serious damage occurred to adjacent structures. This approach would be very helpful for example, ammonia storage vessels which rely on the presence of water to inhibit stress corrosion cracking. Many other examples can be cited where stress corrosion may be a threat due to upsets or unexpected events. A reliable monitoring system which was not subject to premature positive signals would be very helpful in that it would prompt action to prevent or minimize further damage.

AC Methods

Alternating current methods are inherently more versatile than the conventional polarization resistance method because they are applicable to both low

and high resistivity environments. Some studies are currently underway at the University of Manchester Institute of Science and Technology (UMIST) [16], but more work is needed to develop probes which take advantage of these methods without introducing spurious or difficult-to-understand responses. In addition, the development of equipment which is durable and suitable for plant control room usage is essential if these systems are to be useful. It would also be helpful if this equipment were designed to be compatible with computer control data acquisition systems.

Localized Corrosion

The polarization diagram approach described above can be used to identify the potential for localized corrosion. However, this approach is time-consuming and requires a skilled operator to obtain and analyze the results. The MTI occluded cell corrosion monitoring device described above is an approach to signaling when crevice corrosion is a possibility, but much more work needs to be done to exploit this device. The problem of localized corrosion in the form of either pitting or crevice corrosion is serious, and conventional electrical resistance or polarization resistance probes are not adequate to alert plant personnel to the development of such problems.

Computer Methods

Computers are increasingly available for data analysis and storage. It is thus becoming important to have corrosion monitoring equipment that is compatible with computer systems, so that results can be displayed at will and the time normally associated with data reduction and analysis can be reduced. Furthermore, it would be desirable to have methods which are generally applicable to avoid the necessity of having each company or plant develop its own software and interfacing methods.

Standards

To date, there are very few standard methods available for corrosion monitoring in industrial plants. ASTM Method G 4 provides guidance for coupon tests and there are a few other relatively old standards relating to polarization resistance and to electrical resistance monitoring methods. In view of the expanding use and reliability of modern corrosion monitoring equipment, it would be desirable to have similar methods to avoid the repetition of trial and error in using these methods. The development of industry-wide, national, or international standards for corrosion monitoring methods provides an opportunity to increase the availability and to reduce the cost of these methods. It also provides an excellent process to eliminate shoddy or oversimplified approaches.

Conclusions

Corrosion monitoring is an important activity in modern industrial plants, insuring the integrity and continued performance of equipment exposed to corrosive environments. It is important to include provisions for corrosion monitoring in plant design and to consider carefully location and installation of corrosion monitoring equipment. It is especially important to incorporate corrosion monitoring systems in pilot and demonstration plants.

Corrosion monitoring of industrial plants allows engineers to take best advantage of materials properties without overdesign or "gold plating." The use of corrosion monitoring can help solve difficult corrosion problems, especially those of an intermittent nature.

There are a variety of approaches to choose from for corrosion monitoring. The best approach can be tailored to the needs of the process. It is desirable to employ redundancy in corrosion monitoring so that the information developed will be reliable and accurate. The problems which result from either over or underestimation of corrosion rates are important enough to warrant redundancy. The use of instantaneous corrosion rate measuring devices, along with time average devices, for example, polarization resistance and electrical resistance, provides a useful approach to obtaining reliable data.

There is an ongoing need for new methods and standards in the corrosion monitoring field. It would be desirable to have methods for monitoring stress corrosion cracking and to have better AC methods. Development of standards for existing methods will provide opportunities for increasing availability and reducing costs of corrosion monitoring in the future.

Acknowledgments

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DISCUSSION

*G. Liening*¹ (*written discussion*)—Regarding the advantages of electrochemical and electrical resistance corrosion monitors, I would like to mention that in addition to those advantages that you mention in your presentation, we have been very successful in identifying causes of corrosion in process plants by monitoring corrosion probe output continuously, and correlating changes in rate with process events. We have found this to be an important use for these monitors. This has identified factors causing corrosion that were previously unsuspected.

S. W. Dean (author's closure)—The use of electrochemical corrosion monitoring probes to assist in the determination of conditions or events which cause corrosion is certainly valid. We have used this technique, both to determine what process parameters were significant in causing high rates and to signal when process streams should be sampled to determine what corrosive species is present.

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G. Liening (written discussion)—I would like to comment on what I consider to be a serious disadvantage of the LPR-type corrosion monitors for alarming purposes. That disadvantage is their susceptibility to having the electrodes broken off in the process stream by fatigue, high flow forces, trash in the pipeline, etc. When failure occurs in this manner, the measured rate goes to zero (or nearly zero), and there is no way that the instrument can alarm in case of a corrosion upset. In addition, to the casual observer, there is nothing wrong with the system!

S. W. Dean (author's closure)—Mr. Liening is correct, and the author thanks him for his comment. This is a very important limitation of the polarization resistance probe. We have also had problems with the probes corroding at the connection point and being lost. Ultimately, a leak occurred to alert us of the failure, but it caused us to doubt all of the data from this probe. This discussion emphasizes the need for redundancy in monitoring systems.

Koji Yamakawa,¹ Harushige Tsubakino,¹ and
Shiro Yoshizawa²

A New Electrochemical Hydrogen Probe

REFERENCE: Yamakawa, K., Tsubakino, H., and Yoshizawa, S., "A New Electrochemical Hydrogen Probe," *Corrosion Monitoring in Industrial Plants Using Nondestructive Testing and Electrochemical Methods, ASTM STP 908*, G. C. Moran and P. Labine, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 221-236.

ABSTRACT: A new electrochemical hydrogen probe consisting of a thin layer of deposited nickel was developed for use in laboratory and in field tests. The principle of such a probe is based on the formation of nickel oxyhydroxide (NiOOH) which contains a mobile hydrogen. The probe was used to examine the effect of plastic deformation on hydrogen absorption and the relationship between K_{ISCC} and hydrogen content, and to monitor hydrogen contents continuously at the carbon dioxide absorption tower and line pipe.

KEY WORDS: hydrogen probe, hydrogen content, electrochemical measurement, hydrogen embrittlement, hydrogen-induced cracking, corrosion monitoring

Although various methods were developed in order to measure the hydrogen content in steels, an electrochemical method is frequently used from the viewpoints of good detection limits, simple measurements, and suitability for long-term measurement.

An electrochemical method is based on the following concept: hydrogen is introduced into one side of a metallic specimen during cathodic polarization, while the other side of the specimen is held at an anodic potential sufficient to ionize any hydrogen arriving at the surface after passage through the metal, and the hydrogen content and its diffusion coefficient can be evaluated from the resulting ionization current [1]. Normally, a thin palladium layer is deposited on the extraction side of the specimen in order to prevent the corrosion of the specimen and to promote the ionization of hydrogen atoms [2-5].

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However, because of the difficulty in getting a uniform and thin deposition of palladium microscopically, the residual current is large in order to detect a small amount of hydrogen [4].

Petrolite Corp. developed a hydrogen probe in which a thin palladium film was attached on the extraction side. Such a probe cannot apply for the thin or annealed iron specimen in the measurement of the absolute values of hydrogen content and diffusion coefficient, because the permeation rate is controlled by the palladium film [6]. After several searches, nickel was found as a new plating metal [7]. The deposited nickel metal is changed to nickel oxyhydroxide (NiOOH) in an alkaline solution under a certain anodic polarization whose hydrogen is mobile. The apparatus, the measurement of the nickel plating method, and its application for various fields are reported [8].

Experimental Procedures

Apparatus

The hydrogen monitoring system consists of electronic equipment and the electrolytic cell. A typical example of the field type is shown in Figs. 1 through 3 [9].

The electronic equipment provides the constant current source for nickel plating and the potentiostat for hydrogen extraction as shown in Fig. 1. The permeation current and temperature are recorded. Figure 2 shows the electrolytic cells of nickel plating and of hydrogen extraction for the monitoring of line pipe mentioned later. Furthermore, Fig. 3a shows the pumping equip-

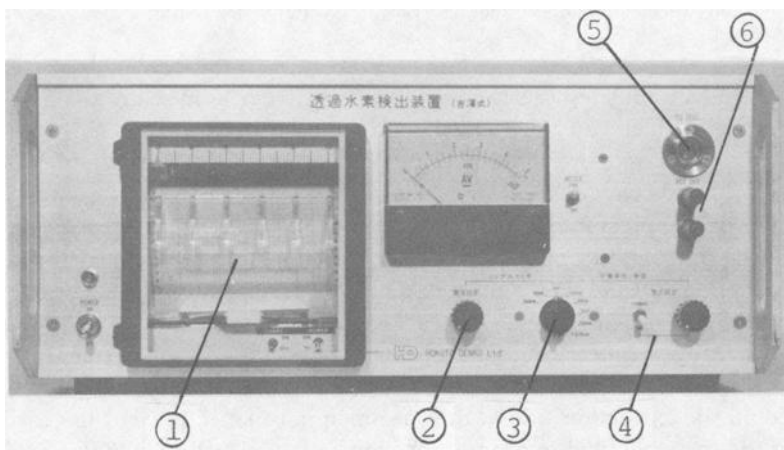


FIG. 1—Photograph of electronic equipment of hydrogen monitoring system (Yoshizawa type): (1) recorder, (2) current, (3) switching of nickel plating or monitoring, (4) potential, (5) to cell, (6) output.

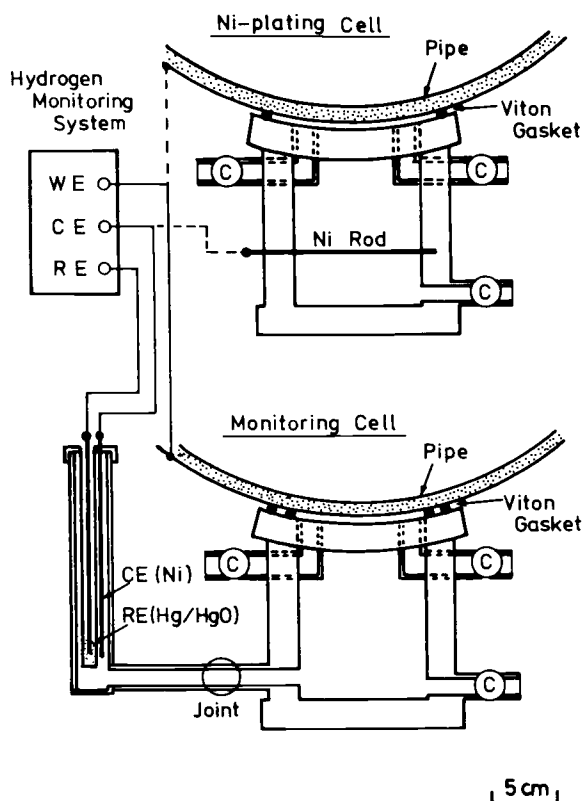


FIG. 2—Nickel plating and hydrogen monitoring cells. WE = working electrode (line pipe). CE = counter electrode (Ni), RE = reference electrode (Hg/HgO), C = cock.

ment used for the supply of electrolyte to the cell and the degassing of electrolyte.

Measurement Procedure

The three steps of surface preparation, nickel plating, and setup of the electrolytic cell are required before monitoring hydrogen.

The part of the specimen or wall of the plant to be monitored is polished with emery paper or a mechanical tool followed by an electrolytic treatment, usually using a chromiumtrioxide-phosphoric acid ($\text{CrO}_3\text{-H}_3\text{PO}_4$) solution [7,10]. The process of electropolishing can be omitted for a thick specimen. After pickling and water rinsing, the thin nickel layer is electrodeposited in the usual Watt's bath of density 0.3 A/m^2 , which corresponds to $500 \text{ \AA}$ in thickness [7]. This condition was determined from the permeation measure-

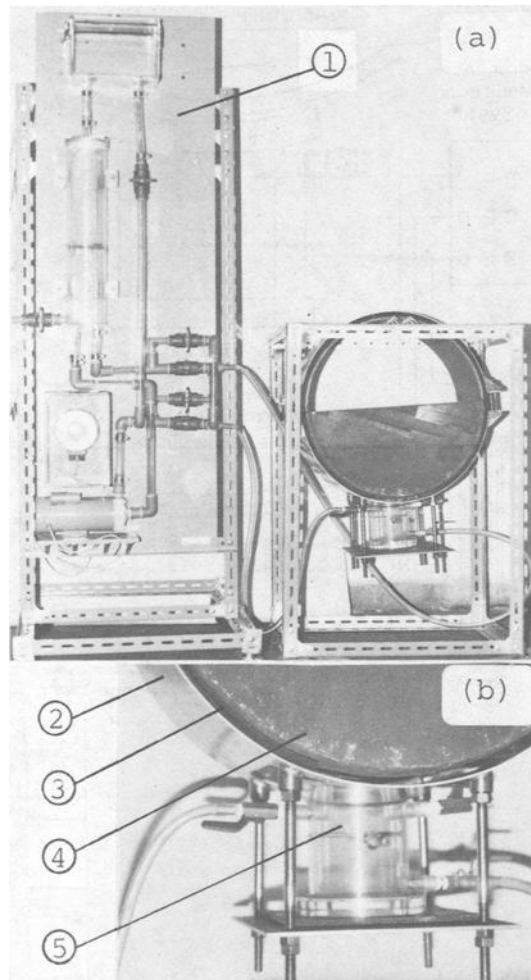


FIG. 3—Photographs of hydrogen monitoring system and pumping equipment for supply of electrolyte (a), and fixing of cell (b). (1) pumping equipment, (2) fixing belt, (3) rubber plate, (4) line pipe, (5) cell.

ments with the specimens of annealed mild steel differing in thickness of the nickel layer, as shown in Fig. 4 [7]. The steady-state permeation current density (A/m^2) and diffusion coefficient of hydrogen, D (m^2/s), appear to be independent of thickness in 100 to 1000 Å of nickel layer. Such facts mean the permeation is controlled by the iron specimen.

After nickel plating, the electrolytic cell is set and filled with 1 N sodium hydroxide (NaOH) solution and then the electronic equipment is operated under the potentiostatic condition of 0.150 V mercury/mercuric oxide (Hg/

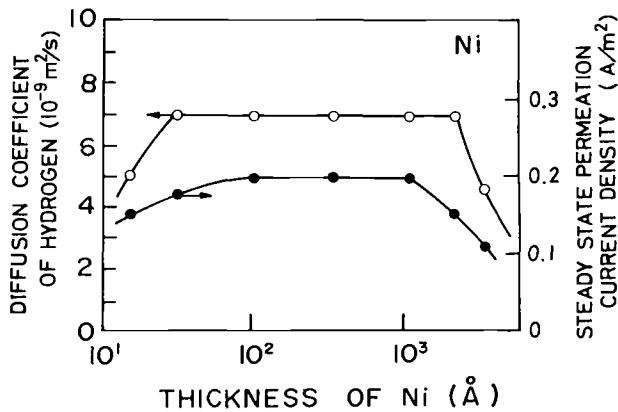


FIG. 4—Relationship between steady-state permeation current density, diffusion coefficient, and thickness of nickel.

HgO) [0.100 V silver/silver chloride (Ag/AgCl)], 0.050 V saturated calomel electrode (SCE). Such a condition was determined from Fig. 5 [7], which shows that at potentials less noble than -0.1 V and at potentials more noble than 0.3 VSCE, nickel-nickelic oxide (Ni_3O_4) and nickel peroxide (NiO_2) are formed, respectively, through which the diffusion is controlled. Also at the

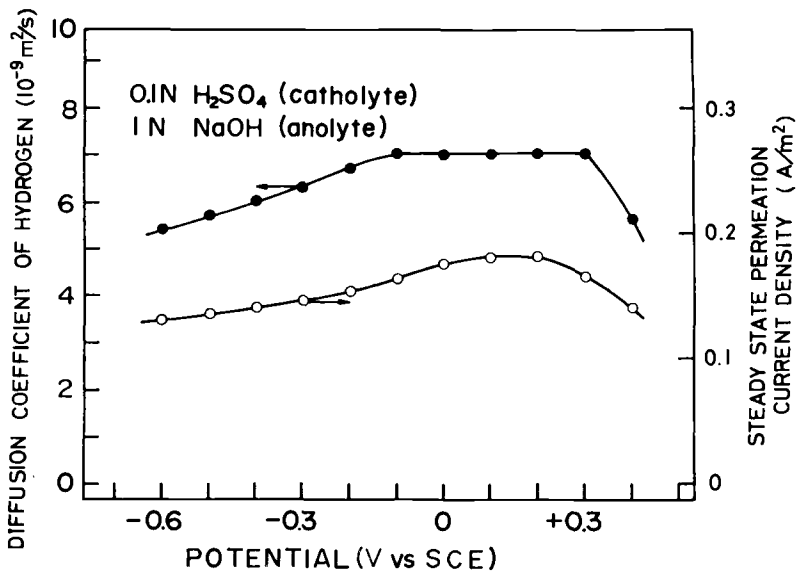


FIG. 5—Relationship between steady-state permeation current density, diffusion coefficient, and electrode potential of extraction side.

potential range of $-0.1 \sim 0.2$ VSCE, NiOOH is formed [11, 12] whose hydrogen is very mobile as understood from nickel-cadmium (Ni-Cd) battery research [11]. Just after the operation, a large anodic current is observed due to the reaction of nickel to NiOOH. Such anodic or residual current decreases gradually to reach less than 0.3 mA/m^2 within one day. After such preparations, the corrosive solution is inserted and the hydrogen permeation current is continuously measured and recorded.

Analysis

After confirming the good fit of the transient curve to the theoretical curve reported by Nanis et al [1, 13], the diffusion coefficient of hydrogen in steel, D (m^2/s), is calculated from

$$D = 0.136 \frac{L^2}{t_{0.5}} \quad (1)$$

where L is the thickness of specimen or wall of plant (m) and $t_{0.5}$ is the time (s) to the attain half-fraction of its steady-state permeation rate. A buffer solution, such as acetic acid sodium acetate ($\text{CH}_3\text{COOH}-\text{CH}_3\text{COONa}$), was used in order to avoid the variation of hydrogen content due to the occurrence of corrosion products.

Also, the hydrogen content at the entry side, C_0 (ppm), is calculated from the steady-state permeation current, J_∞ (A), by

$$C_0 = 1.316 \times 10^{-6} \frac{J_\infty L}{AD} \quad (2)$$

where A is the area of extraction side (m^2). In the case of pipe, it can be regarded as a linear diffusion, if the ratio of outer to inner radius is less than 1.1.

Applications

Measurement of Hydrogen Content as a Function of Electrode Potential

The hydrogen content of mild steel was measured in 0.1 N sulfuric acid (H_2SO_4) solution as a function of electrode potential and of degree of plastic and elastic strain, as shown in Fig. 6 [14, 15]. The circles show the degree of plastic strain in the specimens. A typical example of measurements is shown in Fig. 7 for the annealed specimen. $E_{\text{H}^+/\text{H}_2}$ is the reversible potential of hydrogen evolution reaction. At such reversible potential, the surface coverage of adsorbed hydrogen, θ_0 , can be expressed by [16]

$$\frac{\theta_0}{1 - \theta_0} = K_1 \sqrt{P_{\text{H}_2}} \quad (3)$$

	C	Si	Mn	P	S	Al	N	O
wt(%)	0.060	0.001	0.34	0.008	0.011	0.002	0.002	0.005

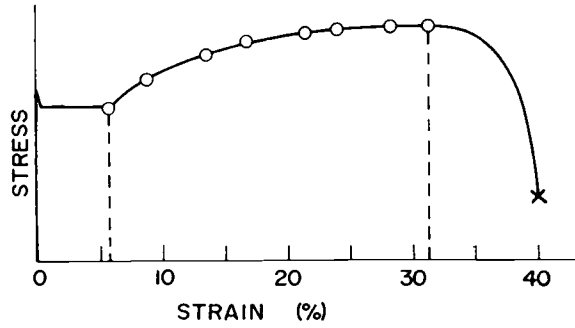


FIG. 6—Chemical composition of mild steel and degree of plastic strain.

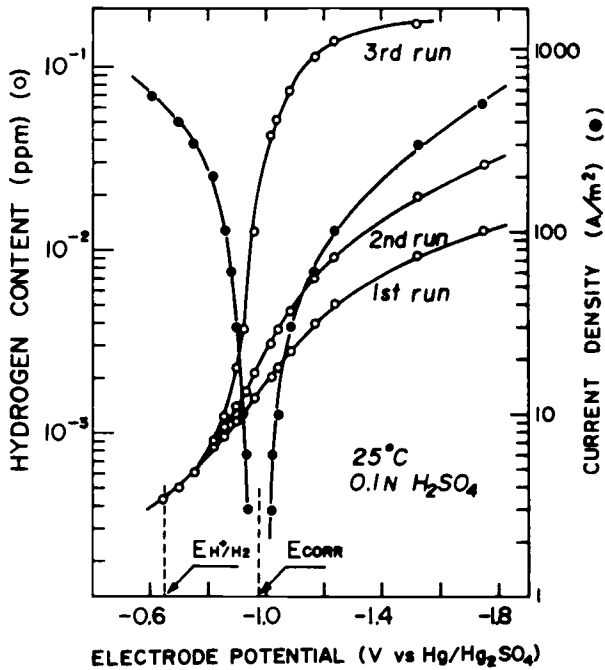


FIG. 7—Relationship between hydrogen content, polarization current, and electrode potential. E_{H^+/H_2} = reversible potential of hydrogen evolution reaction. E_{CORR} = corrosion potential.

where K is the constant depending only upon the metallic property. Also the partial equilibrium of hydrogen between the adsorbed and the absorbed states gives

$$\frac{\theta_0}{1 - \theta_0} = K_2 C_0 \quad (4)$$

From Eqs 3 and 4, Eq 5 is obtained, which is Sievert's law

$$C_0 = (K_1/K_2)\sqrt{P_{H_2}} = K\sqrt{P_{H_2}} \quad (5)$$

Such hydrogen contents were measured as a function of plastic strain with a bubbling of hydrogen gas of 1 atm and shown in Fig. 8 with the hydrogen

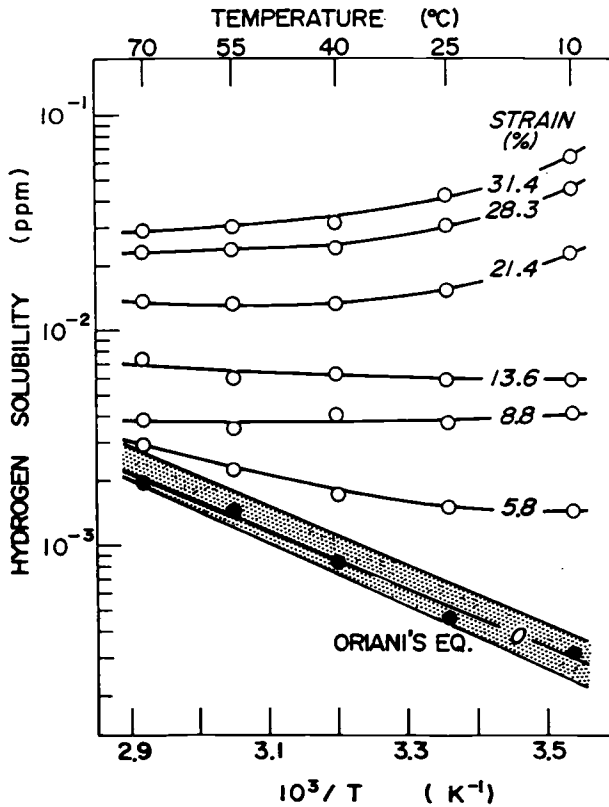


FIG. 8—Relationship between hydrogen solubility, plastic strain, and temperature.

content in Eq 6 measured as the partial pressure of hydrogen gas and summarized by Oriani et al [17,18]

$$C_0 = 4.19\sqrt{P_{H_2}} \exp\left(-\frac{6500 \pm 300}{RT}\right) \quad (6)$$

Plastic strain resulted in the significant increase of hydrogen solubility at lower temperatures and the change of occlusion mode from endothermic to exothermic. The introduction is one of the most important factors concerning hydrogen occlusion.

Measurement of K_{ISCC} as a Function of Hydrogen Content

The K_{ISCC} values were measured with a WOL-CT type specimen immersed in the various solutions with or without cathodic polarization [19]. The specimen was commercial SCM 435 steel corresponding to AISI 4135, and its strength was varied in the range of 1480 to 1800 N/m² with the tempering temperatures. The measured results are summarized in Fig. 9. The K_I value at which the crack growth rate became less than 10⁻⁸ m/s was adapted as K_{ISCC} .

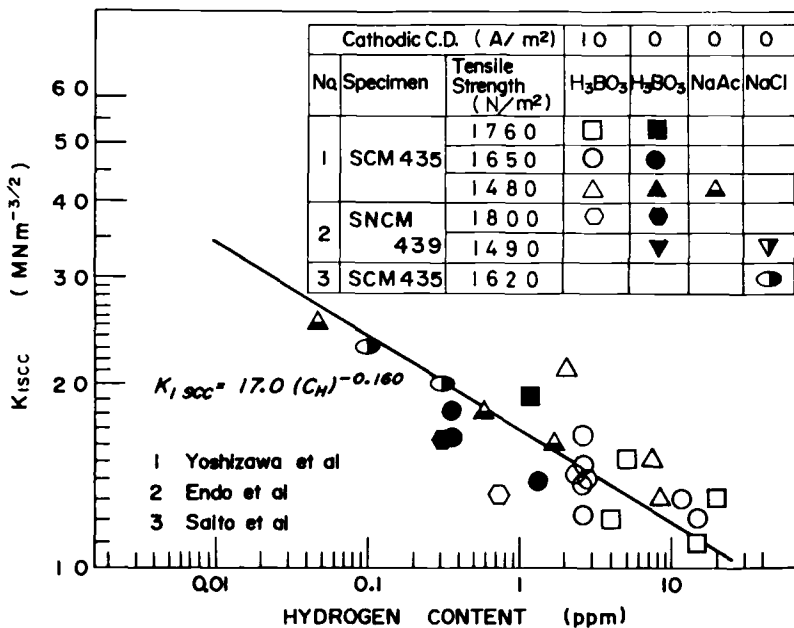


FIG. 9—Relationship between K_{ISCC} of high-strength steel and hydrogen content.

Despite other published results to the contrary, our results indicate that K_{ISCC} was found to be only a function of hydrogen content and does not depend upon the kind and strength of these steel specimens, the composition of solution, or the presence of cathodic polarization. The increased susceptibility to hydrogen embrittlement with the increased strength of low-alloy steel can be explained by the increased hydrogen content under the same environmental condition. It is very useful to prevent the failure in the actual structure and to make clear the mechanism of hydrogen embrittlement, if such a relationship is found for common steel.

From Fig. 9, the hydrogen embrittlement of high-strength steel can be protected, if an entry of hydrogen can be prevented. Such effect was observed with an addition of sodium nitrite in artificial seawater, as shown in Fig. 10 [20,21]. Also, the fractured surface revealed only a dimple pattern which indicated mechanical fracture. Sodium nitrite provides the protective film on the steel surface and shifts the corrosion potential of -0.670 VSCE to -0.113 VSCE at which the hydrogen evolution reaction is prevented.

Measurement at CO₂ Absorption Tower in Ammonia Synthesis

Okubo found numerous microcracks at a welded part of a carbon dioxide (CO₂) absorption tower made of carbon steel SB 49 corresponding to Ameri-

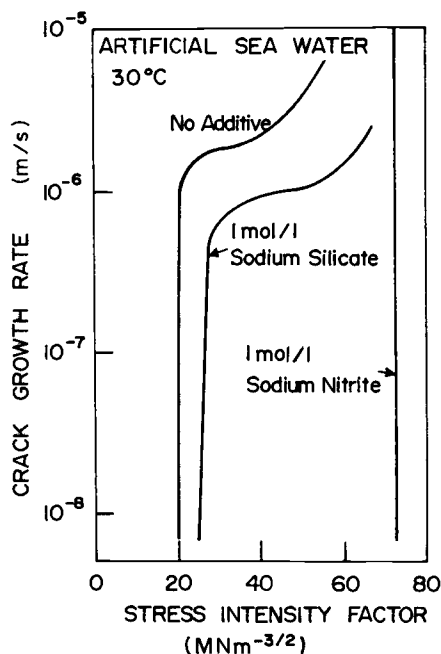


FIG. 10—Effect of addition of NaNO_2 or Na_2SiO_3 on fracture behavior of high-strength steel.

can Institute of Mining, Metallurgical and Petroleum Engineers (AIME) A515, and measured the corrosion potential and hydrogen content using our method [22]. The solution contained potassium hydrogen carbonate (K_2CO_3), ($KHCO_3$), and (As_2O_3), which was a corrosion inhibitor and accelerator for an entry of hydrogen. Okubo provided the bypass pipe from the main pipe and measurement system as shown in Fig. 11. A typical example of the measured corrosion potential and hydrogen content is shown in Fig. 12. The hydrogen content at the steady state is about 10 ppb, which is too small to cause hydrogen embrittlement. On the other hand, the corrosion potential lies in the potential range for stress corrosion cracking (SCC) reported by Poulson [23]. He adopted the addition of oxidizer for the prevention of SCC with a monitoring of the corrosion potential.

Hydrogen Monitoring of Line Pipe

The interior of line pipe shown in Figs. 2 and 3 was filled with the buffer solution of 0.2 M acetic acid (CH_3COOH) + 0.017 M sodium acetate (CH_3COONa); 12 L and 85 g of sodium sulfide (Na_2S) was added, which cor-

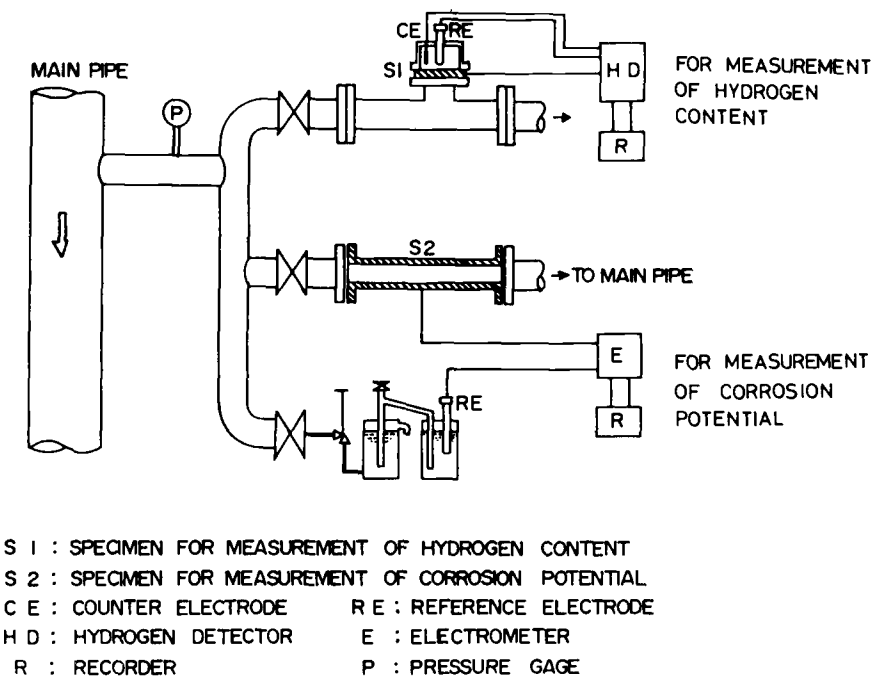


FIG. 11—Monitoring system for corrosion potential and hydrogen content of CO_2 absorption tower made of carbon steel.

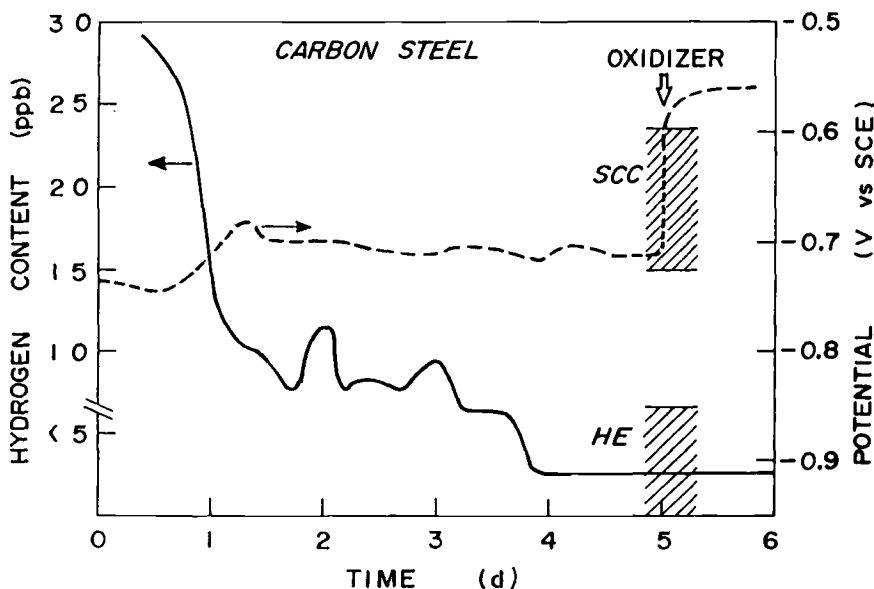


FIG. 12—Corrosion potential and hydrogen content measured with monitoring system of Fig. 11.

responded to 1000 ppm as hydrogen sulfide (H_2S) [9]. The used line pipe was API Grade 5LX-X60 (C0.07-Si0.30-Mn1.23-P0.016-S0.001-Cu0.03-Cr0.03-Ni0.03-Mo0.06-Nb0.032-Ti0.017-Al0.041-Ca0.023; yield strength 511 N/m^2 , tensile strength 576 N/m^2), and its dimensions were 0.3 m in length, 0.506 m in outer diameter, and 0.01 m in thickness. The measured permeation current and hydrogen content calculated by Eq 2 are shown in Figs. 13 and 14, where the diffusion coefficient was determined by the method mentioned already from Eq 4 [9]

$$\log D = -\frac{1.29 \times 10^3}{T} - 1.05 \quad (7)$$

Each arrow shows the addition of 5 g of Na_2S into the solution to supplement H_2S . Although the permeation current was changed with a variation of temperature, the hydrogen content kept the constant value of 0.3 to 0.5 ppm.

The detection limit is an important factor for the thick specimen in order to obtain the relationship between hydrogen content and hydrogen-induced cracking. Ikeda et al [24] tried to make clear such relationship in three different solutions of National Association of Corrosion Engineers (NACE) bath ($5\text{NaCl} + 0.5\text{CH}_3\text{COOH}$), AS bath ($0.5\text{CH}_3\text{COOH}$), and SS bath (artificial seawater). Such solutions were saturated with H_2S gas of 1 atm.

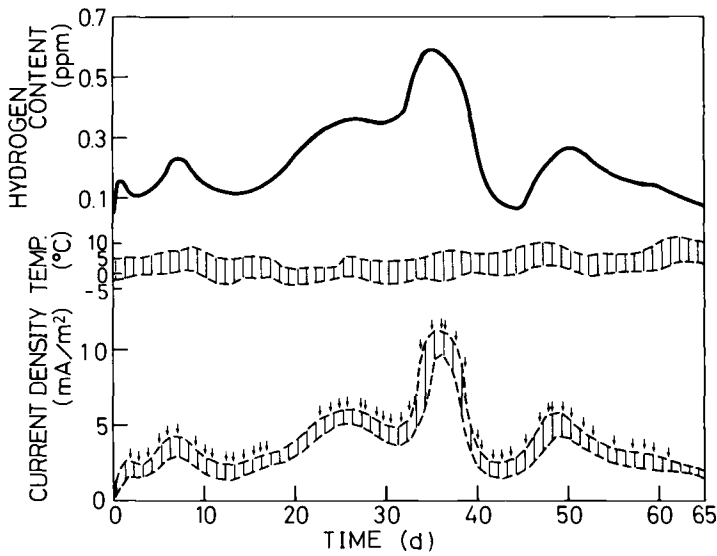


FIG. 13—Monitoring of hydrogen content of line pipe steel: long-term measurement.

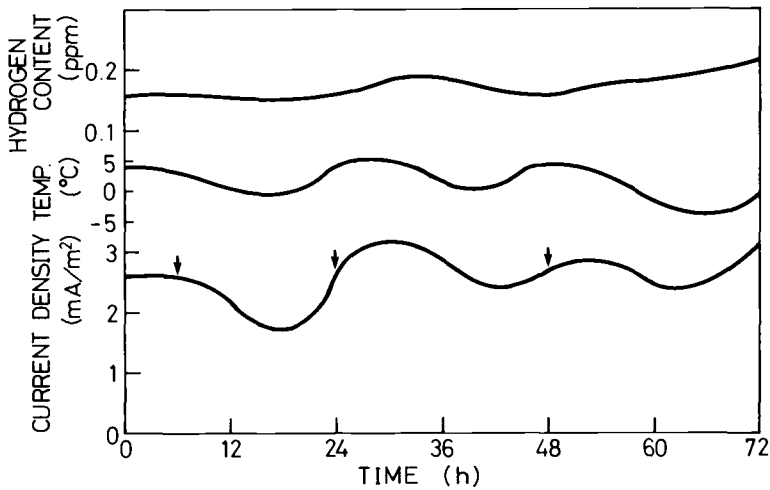


FIG. 14—Details in variation of hydrogen content after 16 days in Fig. 13.

Figure 15 shows the hydrogen permeation current as a function of temperature recalculated from the hydrogen content of common line pipes different in copper content under the dimensions of Fig. 2. The dotted line in Fig. 15 shows the minimum content inducing hydrogen-induced cracking.

Figure 16 shows the detection limit of the hydrogen probe in this work. The

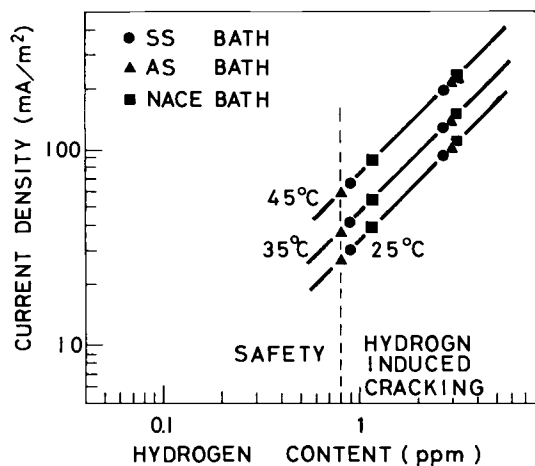


FIG. 15—Relationship between permeation current density and hydrogen content for hydrogen-induced cracking, evaluated by using data from Ikeda et al [24].

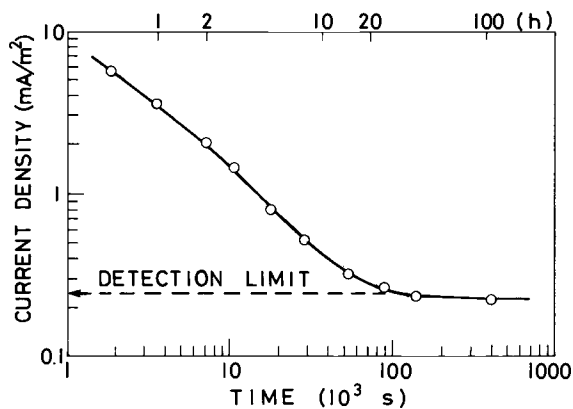


FIG. 16—Typical relationship between passive current density of nickel-plated layer and time. Arrow shows the residual current density, that is, detection limit of probe.

anodic or residual current of the nickel-plated layer decreases gradually to the value less than 0.3 mA/m^2 , which corresponds approximately to 0.01 ppm of hydrogen content, within one day. These measurements were done without supplying the electrolyte in the interior of line pipe. From this figure, the detection limit of this hydrogen probe is concluded to be quite enough to use for hydrogen-induced cracking tests.

Conclusions

1. A new electrochemical hydrogen probe, in which a thin nickel layer was deposited at the extraction side to improve the detection limit of hydrogen content, was developed and was useful for application to an actual plant.
2. The hydrogen content at the reversible potential of hydrogen evolution reaction could be measured and did agree with the solubility in hydrogen gas atmosphere of 1 atm.
3. The K_{ISCC} values measured with WOL-CT type specimens of high-strength steels were found only to be a function of hydrogen content.
4. In order to make clear the cause of corrosion cracking at a carbon dioxide absorption tower made of carbon steel, such a hydrogen probe was used.
5. Long-term measurements and detection limits of hydrogen content were checked to apply such a probe to line pipe.

Acknowledgments

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Sensing Probes and Instruments for Electrochemical and Electrical Resistance Corrosion Monitoring

REFERENCE: Cooper, G. L., "Sensing Probes and Instruments for Electrochemical and Electrical Resistance Corrosion Monitoring," *Corrosion Monitoring in Industrial Plants Using Nondestructive Testing and Electrochemical Methods*, ASTM STP 908, G. C. Moran and P. Labine, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 237-250.

ABSTRACT: Corrosion monitoring in industrial environments is facilitated by using electrochemical or electrical resistance sensing probes and instruments. This paper describes their principles of operation and practical guidelines for successful implementation.

KEY WORDS: corrosion monitoring, electrical resistance probes, electrochemical probes, corrosion probe

Electrical resistance and electrochemical corrosion probes have proven useful in industrial corrosion monitoring. Electrochemical corrosion probes can be used in aqueous environments of certain maximum resistivities to measure corrosion rate in mil/year (0.001 in./year) directly. Electrical resistance probes can be used to monitor loss in a wider variety of areas.

Corrosion monitoring instruments can be either portable, hand-held devices or automatic microprocessor-controlled units, compatible with the latest computer technology.

Corrosion is a costly problem in the United States. The U.S. Department of Commerce/National Bureau of Standards estimated the cost to be 4.2% of the Gross National Product in the United States.

Of course, certain parts of the cost of corrosion may be unavoidable, or at least beyond the scope of control with today's technology. However, the avoidable or controllable corrosion cost is estimated at about \$10 billion dollars by the same group [1].

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Industrial corrosion control is attempted using four main methods:

1. **Coatings**—Metallic systems can be protected from the corrosive environment by coatings. Paint, tape, plastics, and noble metal claddings are all common methods of coating.
2. **Materials**—Some materials are more resistant to corrosion in certain environments than others. We might include “methods of construction” in this category as well.
3. **Cathodic Protection**—This is a means of reversing a metal’s natural tendency to corrode by placing a metal element, called an “anode,” in the same environment.
4. **Corrosion Inhibitors**—These are chemicals designed to control corrosion within a given system. Of the four components of a corrosion cell (anode, cathode, electrolyte, and electronic conductor), the anode and the cathode are the primary areas affected by the inhibitor.

Of these four control methods, electronic corrosion probes have relevancy to the last three. Delving further into these three methods, inhibitors is probably the most relevant.

Electronic corrosion probe systems consist of a probe with a sensing element and an instrument. The probe sensing element is a discrete point that samples the corrosivity in its general area. Because of this, it is difficult to apply to coatings. Typically, coatings fail because of “holidays” or voids in their coverage of the protected surface. As it is difficult to ascertain where a holiday is or where one might occur, proper probe placement is problematical [2].

Materials selection is suitable for measurement with electronic probes [3] because they can provide more rapid results than the traditional coupons.

Cathodic protection can be monitored and evaluated [4] with electronic probes. The efficacy of inhibitors can also be determined [5].

The Probes

Electronic corrosion probes operate via two principles. The first is an electrochemical basis of measurement called linear polarization resistance (LPR). The second is an electrical resistance technique (ER).

Linear Polarization Resistance

Linear polarization resistance probes operate by measurement of the intensity of the transport current accompanying a corrosion cell.

In a typical corrosion cell there are two contributing sites: the anode and the cathode. As corrosion continues, metal is exchanged to ion flow through the electrolyte. This exchange current density (called I_c) if measured would correlate with corrosion directly by Faraday’s law, which states that an equiv-

alent weight of matter is altered at an electrode for a given unit quantity of electricity. Or

$$I_c/C \times \frac{K_1}{D} \times \frac{1000}{L} \times K_2 = \text{mmpy (mpy) corrosion rate} \quad (1)$$

where

I_c = Corrosion current in A/cm² (I_{corr} in A/in.²),

C = 96 487 C/equivalent weight,

K_1 = A constant for mass loss in kilograms (a constant for mass loss in pounds),

D = Density in kg/cm³ (density in lb/in.³),

L = Length in centimetres (length in inches),

K_2 = A constant for 2.433 C/A year,

mmpy = Millimetres per year, and

mpy = Milli-inches per year.

However, the direct measurement of this corrosion current is impractical because the corrosion cell sites are minute and in many cases inaccessible. Linear polarization resistance theory states that a linear relationship exists between small changes in the potential of a metal to flow current in contact with a corrodent.

The equation expressing this phenomena is known as the Stern Geary equation, after its developers [6]

$$E/I = (Ba Bc)/[(2.3I_c)(Ba + Bc)] \quad (2)$$

This equation states that at polarization E , current I will flow between the metal and corrodent, which is related to the free corrosion current I_c and to the slopes of the logarithmic local anodic and cathodic polarization curves (or tafel constants) Ba and Bc [7].

Reducing the quantities for the relation of measured current to corrosion current and Ba and Bc to constants allows us to refer to the summation of their effects as polarization resistance R_p .

$$\frac{BaBc}{2.3(Ba + Bc)} = K_2 = B \quad (3)$$

$$C_m = K_1 I_c \quad (4)$$

$$\frac{E_a}{I_m} = R_p = \frac{K_1 K_2}{C_m} \quad (5)$$

where

- C_m = corrosion rate,
- E_a = voltage applied,
- I_m = measured current,
- R_p = polarization resistance, ohm $\cdot$ cm, and
- $B = K_2$ (ASTM G 59).

If we construct an artificial electrochemical cell consisting of two electrodes (Fig. 1) and cause a current to flow from one electrode to the other by applying a small polarization voltage, that current is I_m . We can now rewrite Eq 5 as

$$I_m = E_a / (R_p + R_s) \quad (6)$$

The new parameter R_s is the solution resistance, which is in series with the polarization resistance and is summed by the instrument system for the measurement. When solution resistance is independently measured, correction curves may be used.

If R_s is much smaller than R_p , it can be ignored. But as R_s approaches R_p , it will cause a greater effect on the measured current I_m than the desired measurement R_p . As resistivity increases to significant amounts, the LPR technique is inappropriate. A practical rule of application is to use the product of

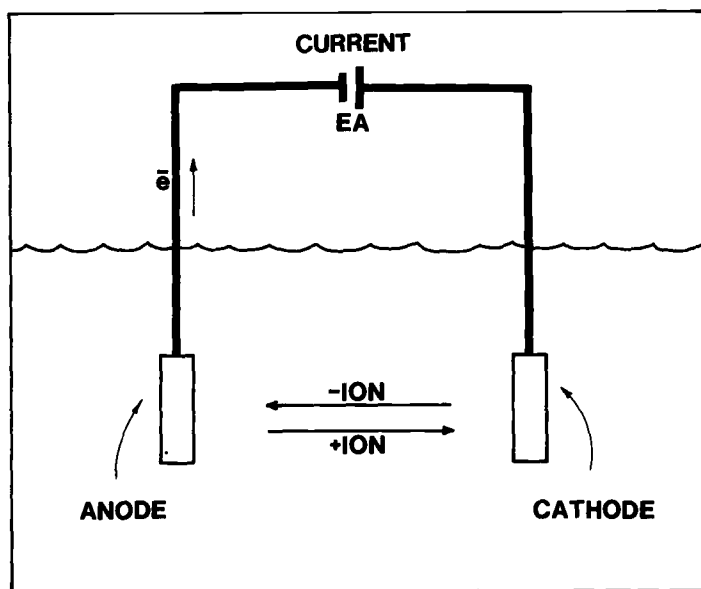


FIG. 1—Electrochemical cell consisting of two electrodes.

the corrosion rate in mil (per year) 0.001 in. (mpy) times the solution resistance in ohm-centimetres [8, 9] (Fig. 2).

If the measured sample is a unit of current I_m that passes as a result of the polarization voltage E_a , the meter of an LPR instrument can be graduated in mil per year corrosion rate directly.

Electrical Resistance Probes

Electrical resistance probes, or ER probes, as they are commonly called, were developed after observation of corrosion coupons. It was observed that as mass was lost from a metal specimen as a result of corrosion, electrical resistance would change also, because of the same mass loss. Chief among these other measurable parameters is electrical resistance.

Ohm's second law states that the resistance of a conductor is proportional to its length and area

$$R = \rho L / A \quad (7)$$

where

R = resistance, Ω ,

L = length of a conductor,

ohm-cm (RESISTIVITY) x CORROSION RATE (MPY) =

$R \times C < 10,000$:

2 - electrode without correction curves

$10,000 < R \times C < 25,000$:

2 - electrodes with correction curves

$25,000 < R \times C < 100,000$:

3 - electrode without correction curves

$100,000 < R \times C < 250,000$:

3 - electrode with correction curves

$250,000 < R \times C$:

LPR technique is not recommended

R =resistivity

C =corrosion rate

FIG. 2—Guide to using LPR technique.

A = area of a conductor, and

ρ = a factor for a conductor's intrinsic resistivity.

While it is possible to measure a conductor's resistance directly, it is not practical to do so for corrosion work. This is because the effects of other phenomena upon resistance are greater than the effects upon resistance caused by the weight loss due to corrosion.

Usually temperature has a greater effect on electrical resistance than day-to-day metal loss caused by corrosion. The resistance of a metallic conductor decreases with temperature until, theoretically, toward absolute zero it has zero resistance.

Therefore, some means must be found to measure only those resistance changes caused by weight loss. This can be done by utilizing a finely balanced set of resistors, called a Kelvin bridge (Fig. 3).

By placing one resistor in the corrodent R_M , a second hidden in the body of the probe R_R , while noncorroding, will change resistance because of temperature at the same rate as the corroding element. Thus, the ratio of their resistances as it affects the bridge is the measurement achieved

$$(R_M/R_R T_2) - (R_M/R_R T_1) = R_{\text{corr}} \quad (8)$$

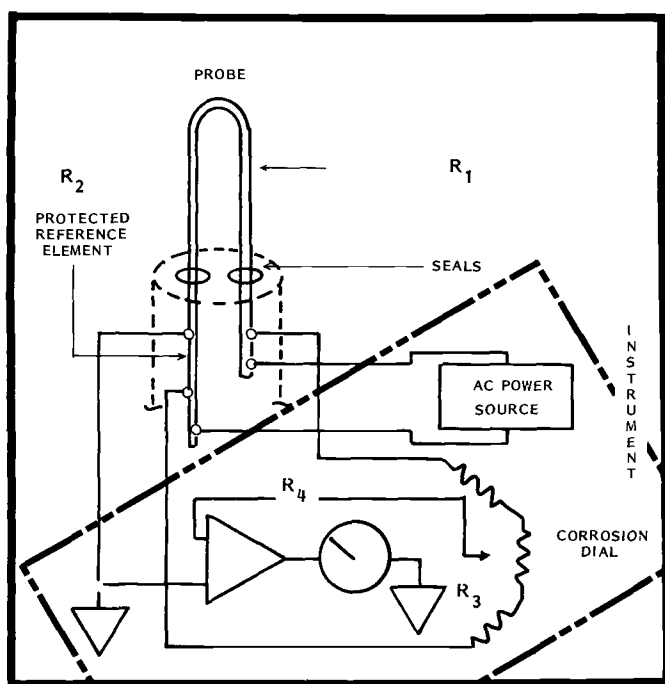


FIG. 3—Kelvin double bridge.

Practically, the Wheatstone bridge contains four elements R_1 , R_2 , R_3 , and R_4 , which when balanced

$$R_1/R_2 = R_4/R_3 \quad (9)$$

Thus, when the bridge in Fig. 3 is out of balance by the change in ratios from 8, balance can be re-established by using an adjustable resistor on the instrument. If this adjustment is made with a dial galvanometer graduated in divisions (1 to 1000), a measurement can be made comparing increased resistance expressed in divisions against a known metal sensing element span

$$\frac{\text{sensing element span}}{1000 \text{ divisions}} = \text{metal loss unit per division} \quad (10)$$

The span of an ER probe is limited to one half of its original thickness. This is because as the metal corrodes beyond one-half thickness, the ER instrument does not linearize the results. Note that the ER probes measure corrosion of their sensing elements as units of metal loss or penetration. Corrosion rate, if required, must be derived from at least two observed sampling points

$$\frac{\text{divs}_2 - \text{divs}_1}{\text{time (days)}} \times 0.365 \times \text{span} = \text{mpy rate} \quad (11)$$

Advantages of the Electronic Probes

The traditional methods of monitoring corrosion are either via visual inspections or coupons. Coupons are samples of material that are cleaned and weighed, exposed to corrosion, removed from the corrosive environment, and reweighed to find the loss of material caused by the corrosion process. The weights before and after exposure are compared to determine a rate of metal loss over the time exposure. Clearly visual methods (that is, "looking for leaks") are the greatest proof of corrosion.

Coupons, however, allow some forward-looking interpretation; but these are based upon only two sample points (Fig. 4).

The advantages of electronic probes become obvious when we compare ER probe measurement to coupon data (Fig. 5). Not only can changes in metal loss or ongoing corrosion rate be calculated, but changes in an operating system can tell the operator what system parameter most affects corrosion. For instance, a change in throughput at a refinery that over utilizes the desalters [10] can be seen and analyzed (Fig. 6).

Another advantage associated with electronic probes is the ability to take several readings in situ. Unlike a coupon, a probe need not be removed from the corroding system for information retrieval. Thus maintenance schedules built around coupon removal and replacement may be reduced, which will

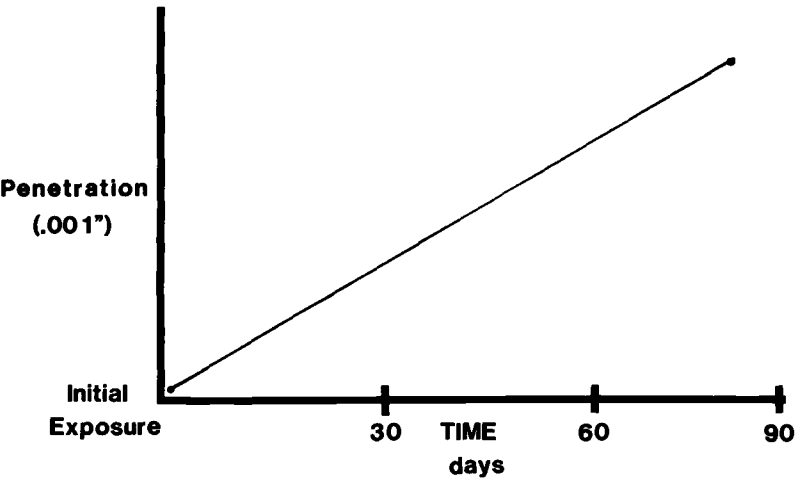


FIG. 4—Corrosion measurement by weight loss coupon.

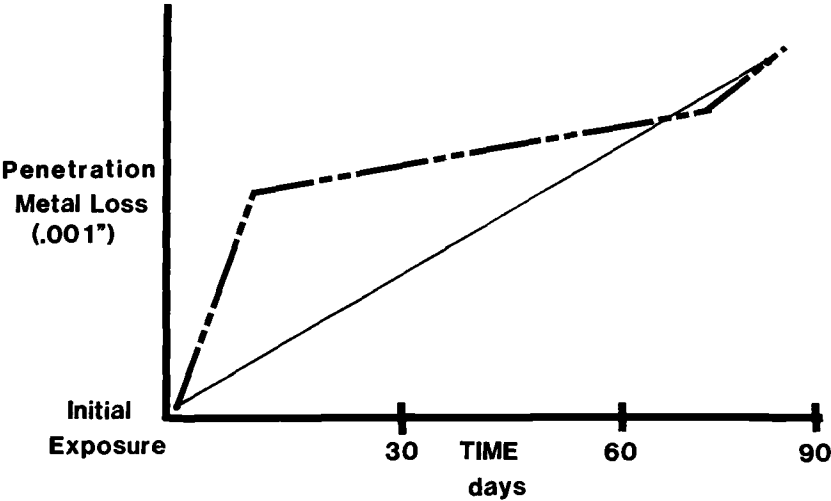


FIG. 5—Comparison measurement by weight loss coupon compared to electrical resistance probe.

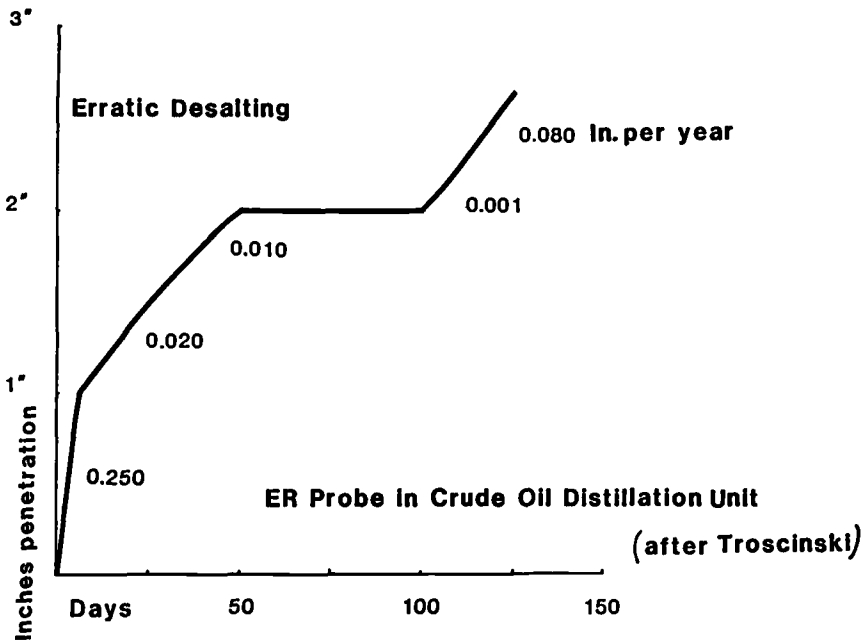


FIG. 6—ER probe in crude oil distillation unit.

lessen man-hour requirements. Further, as probe readings are made with an instrument, the delays and expense associated with the cleaning and weighing of coupons are not necessary.

Comparison of ER and LPR Probes

LPR probes require a solution of sufficient conductivity for proper operation, whereas ER probes do not. LPR probes report corrosion rate directly, while ER probes and instruments must derive corrosion rate over time.

The advantage of an ER probe is that it can monitor corrosion in virtually any environment. The main disadvantage to ER probes is that they do not read corrosion rate directly, corrosion rate is derived by comparing different penetration values over time (Table 1).

Instruments

Both types of probe can be used with either portable or full-time instrumentation.

Portable units have the advantage of low cost but sometimes do not provide a fine enough time resolution to allow discernment of swings in corrosivity.

TABLE 1—Comparison of different penetration values over time.

Parameters	LPR	ER
Corrosion rate	yes	no, must be derived over time
Environment		
water	yes ^a	yes
water/oil	?	yes
oil	no	yes
gas	no	yes

^aConductive.

Automatic units cannot only provide this finer time resolution, they can also be integrated into modern instrument systems.

Portable Instruments

A portable ER instrument has a null-needle meter and a dial calibrated from 1 to 1000 units, which were called divisions as mentioned earlier. The operator turns the dial until the meter needle is “nulled” or centered and records the value shown on the dial. This value has a relation to the sensing element span per Eq 10.

As the probe has, in a sense, “a memory” (metal once lost cannot be replaced) all the new readings illustrate what has occurred since the last reading (Fig. 7).

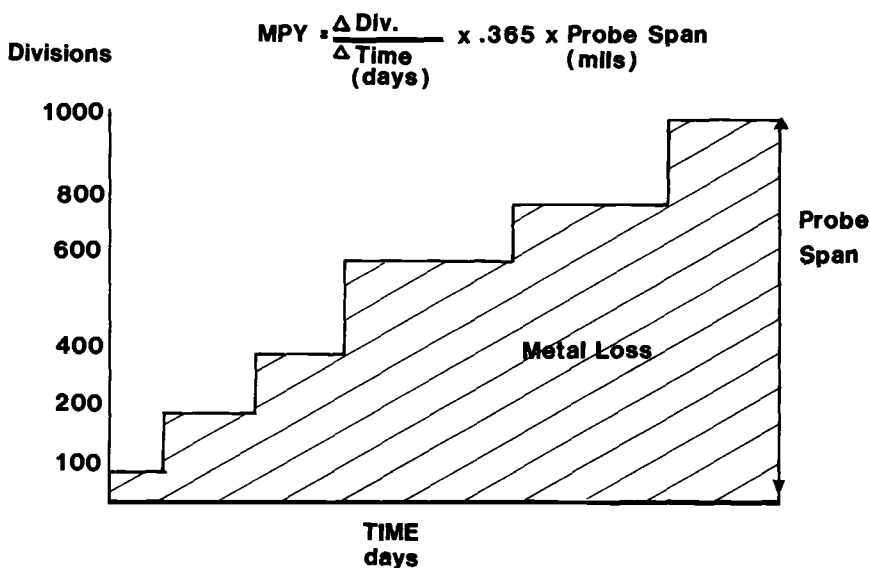


FIG. 7—Portable ER instrument reading.

As a portable LPR instrument is graduated in rate directly, the value obtained is corrosion rate directly. This is analogous to the speedometer on a car, the velocity one is traveling precisely at that moment in time. In this way there is no memory, in the sense at least of an ER probe, so what has occurred between readings is unknown and must be surmized (ASTM Test Methods for Corrosivity of Water in the Absence of Heat Transfer [Electrical Methods] [D 2776]) (Fig. 8).

Automatic Instruments

Recent advances in automatic instrumentation have made their implementation more flexible. Front-end transmitters can be used, which regulate the current draw over a 4 to 20 mA range, as an analog of the sensing element is available. The 16 mA is an analog of the probe sensing element span (Fig. 9).

Dedicated microprocessor instruments can not only power probe measuring loops, they can feed back corrosion information over a hardwired loop or microwave or even telephone connection. This allows probe "clusters" to be read by data loggers called multiplexers that can then be located miles away from the home office (Fig. 10).

Application of Electronic Probes

In order to correctly specify a probe system, several parameters must be known. The following information should be considered (Fig. 11):

- Adequate number of readings per week.
- Requirements for rapid response.

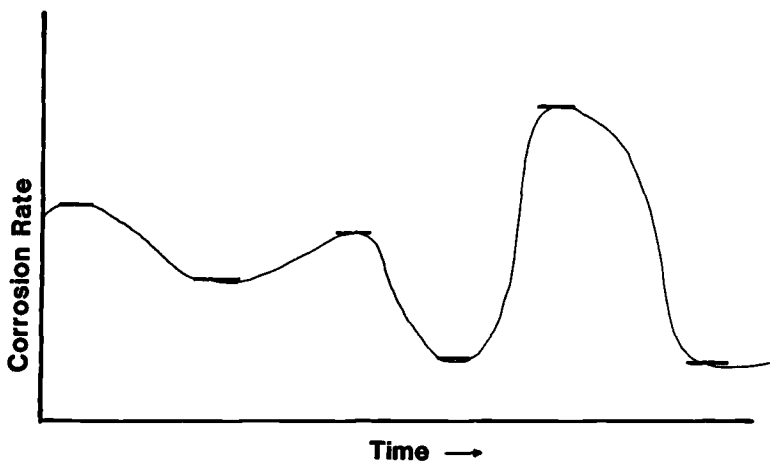


FIG. 8—Portable LPR instrument reading.

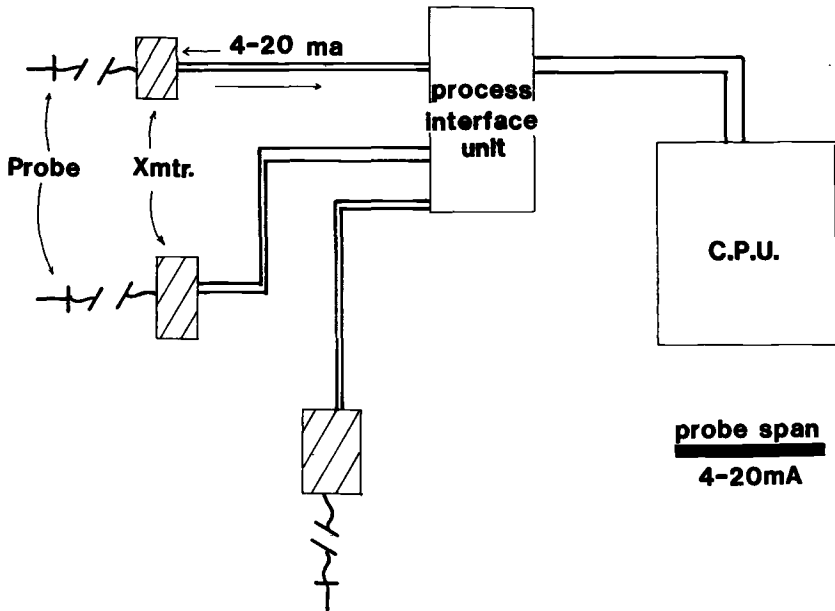


FIG. 9—ER probe two-wire transmitter.

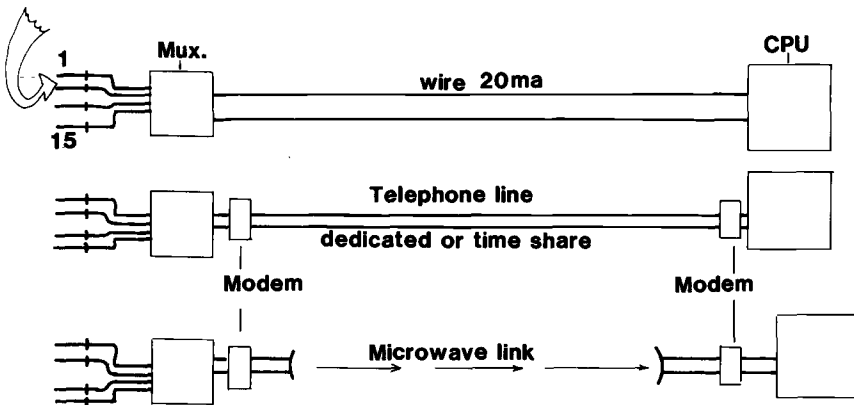


FIG. 10—Reading of probe clusters by data logger called multiplexers.

- The conductivity of the system.
- The state of the environment (solid, liquid, gas).

Conclusion

ER and LPR probes can assist an operator in a corrosion control process. Proper probe selection is based upon a knowledge of the instrument method

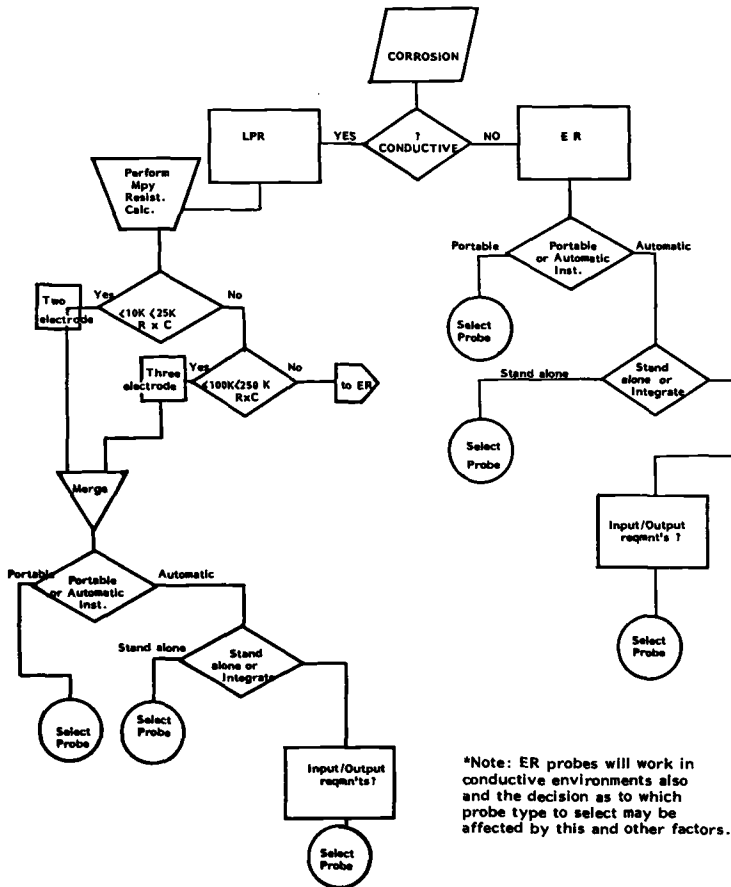


FIG. 11—Flow chart for proper instrument probe selection.

and the information desired. LPR probes require an adequate electrolyte to operate but report rate directly. ER probes have fewer restrictions in application, but rate information must be derived from observed samples.

Both types have several advantages over older methods of corrosion monitoring, such as the use of coupons.

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Oil Production Corrosion Inhibitor Optimization by Laboratory and Field Application of Electrochemical Techniques

REFERENCE: Cameron, G. R. and Coker, L. G., "Oil Production Corrosion Inhibitor Optimization by Laboratory and Field Application of Electrochemical Techniques," *Corrosion Monitoring in Industrial Plants Using Nondestructive Testing and Electrochemical Methods*, ASTM STP 908, G. C. Moran and P. Labine, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 251-265.

ABSTRACT: A multifaceted approach was used to address the corrosion inhibition program in Esso Resources Canada Limited's Redwater field. In the laboratory, inhibitor performance was measured by linear polarization and film persistency wheel tests. Both techniques produced similar inhibitor ranking, although the percent protection results were consistently higher for the linear polarization technique. In the field, corrosion rates were monitored by several devices. Metal loss measurements from flush strip electrical resistance probes best correlated to weight-loss coupons, although the instrument's calculated corrosion rates did not agree with the indicated metal loss. Inhibitor and tracer concentrations were monitored during batch-circulation well treatments to improve application efficiency. The concentration measurements showed that circulation time is the controlling factor in effectively batch-treating wells that have high annular fluid levels. The foregoing investigations, which provided vital information for corrosion control in a specific field, also point the way to improvements in corrosion inhibition technology.

KEY WORDS: inhibitors, linear polarization, wheel tests, corrosion monitoring, electrical resistance probes, inhibitor detection, batch-circulation treatments, circulation time

Esso Resources Canada Limited's Redwater oilfield, located northeast of Edmonton, Alberta, has experienced increased failure frequencies in the past five years due to internal corrosion in its production facilities. Previous efforts to control corrosion included reviewing failure history, monitoring corrosion

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by weight-loss coupons, and predicting inhibitor return using ammonium thiocyanate as a chemical tracer. These efforts met with mixed success. To better address the corrosion problem, Esso Resources Canada Limited, Esso Chemical Canada, and Exxon Chemical Company initiated a joint research project to optimize the corrosion inhibition program.

This project employed a multifaceted approach. Inhibitor performance was determined in the laboratory using film persistency wheel tests and linear polarization measurements. Then, at the wellhead, the response to the inhibition treatment was measured using common techniques of corrosion monitoring. This also provided a basis for comparing the various monitoring methods. Finally, inhibitor and tracer concentrations were monitored during batch-circulation well treatments to improve inhibitor application efficiency.

Experimental Procedure

Laboratory Measurements

The performance of four organic oil-dispersible/water-dispersible film-forming inhibitors was measured using film persistency wheel tests and linear polarization techniques. Each inhibitor was evaluated using commercially available "as sold" strengths. The test concentrations were set at 500 ppm, 1500 ppm, and 4500 ppm. Test fluids for both methods consisted of uninhibited produced brine and crude oil from Redwater. Samples were separated into oil and water fractions and stored in inert containers. For subsequent use, the oil and water phases were purged with carbon dioxide (>99.99%) a minimum of six hours. A portion of the original aqueous phase was purged with hydrogen sulfide for two hours, measured for concentration, and recombined with the carbon dioxide saturated fluids to give a final concentration of 450 ppm hydrogen sulfide and an oil/water ratio of 7%/93%.

Film Persistency Wheel Tests

The wheel tests were performed by an independent consulting firm specializing in that method of corrosion inhibitor evaluation. (The detailed procedure is included in the Appendix.) Each inhibitor was run in triplicate at each of the three concentrations for 24 h and 72 h. The percent protection results were calculated by comparison to blank (unfilmed) coupons that were also run in triplicate for each exposure time.

Linear Polarization Measurements

The test specimens consisted of AISI 1020 mild steel cylindrical electrodes (1.27 cm in length and 1.27 cm in diameter) with a 600 grit surface polish. The electrodes were rinsed first in toluene and then in acetone, allowed to dry, and then mounted on a threaded brass rod enclosed in a glass tube. Tri-

fluoroethylene resin (Teflon®) compression gaskets were used to seal the electrode to the glass tube. A saturated calomel reference electrode, connected by a potassium chloride (KCl) saturated salt bridge and Luggin probe, was brought to within 1 mm of the electrode surface. Two platinum auxiliary electrodes (2.5 cm by 2.5 cm) sealed to glass tubing were used to complete the polarizing current circuit. The polarization cells were placed in a Janke and Kunkel "Ikameg-9" nine-place stirrer/heater bath at $60 \pm 2^\circ\text{C}$.

Before the test electrodes were mounted in the polarization cells, the specimens were filmed and rinsed using the same procedure and inhibitor concentrations as for the film persistency wheel tests. The "run" step in this method consisted of performing time-based linear polarization measurements to determine the instantaneous corrosion rate from the measured corrosion current. The electrodes were polarized ± 20 mv from their free corrosion potential using both a Floyd Bell Associates, Inc., AIS Potentiostat, Model V-2LR-D, and an ECO Potentiostat, Model 553, with a Model 567 function generator. The ECO potentiostat was controlled by a Hewlett Packard Model 86 desk-top computer.

Field Measurements

Corrosion Monitoring Loop—Corrosion monitoring devices were located in a wellhead loop which was mounted on a conventional rod-pumped well (Figs. 1 and 2). This particular well was chosen because it was representative of the major production method and because it had a history of frequent downhole corrosion failures.

The loop contained the following monitoring devices:

- corrosion coupons (AISI 1020 mild steel, sand tumbled finish) in normal, elbow, and water leg positions.
- spool piece (AISI 1020, 15 cm outside diameter by 0.32 cm thickness by 30.5 cm in length).
- electrical resistance probes (Rohrbach 2000 Series Wire Loop—40 mils (0.102 cm), Rohrbach 2000 Series Tube Loop—8 mils (0.020 cm), and a Rohrbach Model 2171 flush mounted—8 mils (0.020 cm). These electrical resistance probes were connected to a Rohrbach Model 4200 Corrosion Measurement System.
- linear polarization probes: Petrolite Model M-540E Flush mounted probe and Petrolite Model M-535 3-finger probe. These probes were connected to a Petrolite Model M-3010 Corrosion Rate instrument for continuous readings or to a Petrolite Model M-4100 Potentiodyne Analyzer for anodic polarization scans.

Tracer Studies

The batch-circulation well treatment efficiency was measured by monitoring the returning concentration of three components injected simultaneously

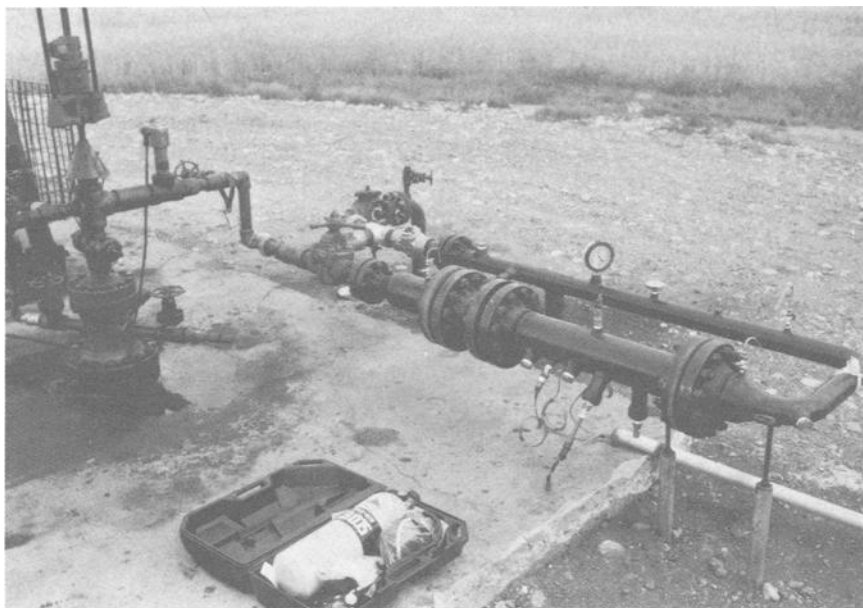


FIG. 1—*Corrosion monitoring loop.*

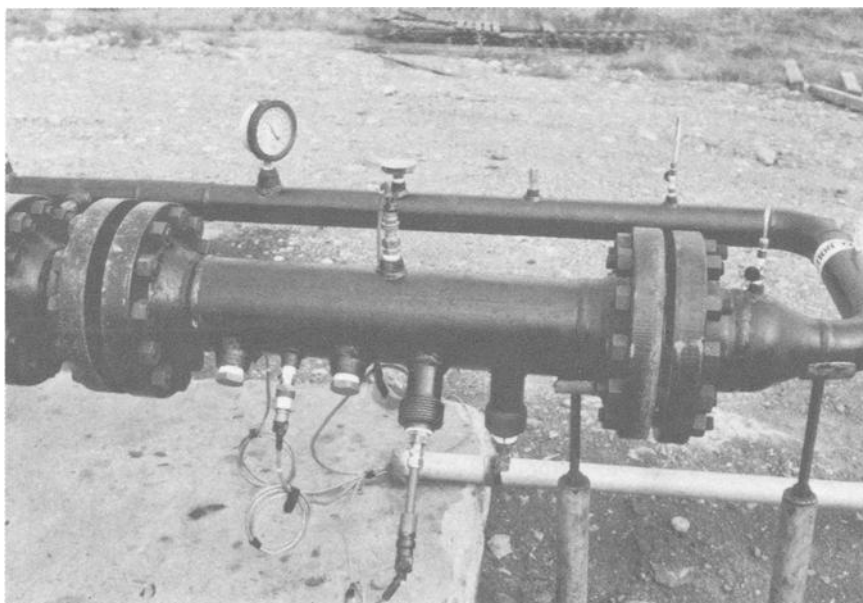


FIG. 2—*Closeup of probe section.*

into the casing/tubing annulus of the well. Ammonium thiocyanate (NH_4SCN) was measured colorimetrically after the addition of ferric chloride to produce the blood-red complex, $\text{Fe}(\text{SCN})_3$. Tritiated water was measured in a Beckman LS 9000 Scintillation Counter after separation by distillation in a Dean and Stark condenser. Residual inhibitor concentrations were measured using fourier transform infrared spectrophotometry (FTIR) in a Nicolet Analytical Instruments Model 170 SX after extracting into methylene chloride, evaporating to dryness and final dilution with carbon tetrachloride.

Results and Discussion

Inhibitor Concentration

The percent protection results of the four inhibitors, at the 24-h exposure period in the film persistency wheel test, are shown in Fig. 3. Each inhibitor exhibited increased protection with increased filming concentration, although the increase was more dramatic for an inhibitor that had the potential for high protection (Inhibitor A) than for an inhibitor that never achieved adequate protection levels (Inhibitor C).

Figure 4 shows the percent protection results for the 72-h exposure period. Generally, the percent protection decreased when compared to the 24-h period, with the 500-ppm filming concentration showing the greatest decrease.

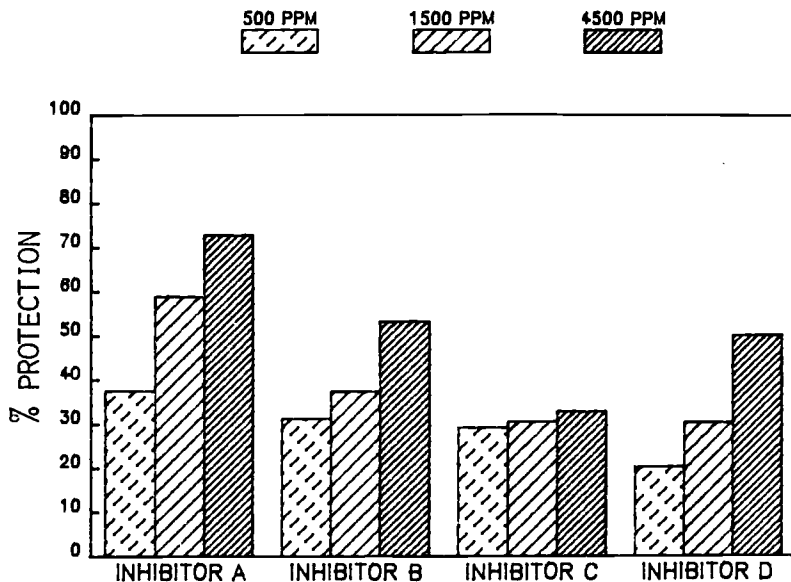


FIG. 3—Film persistency wheel tests (24-h exposure).

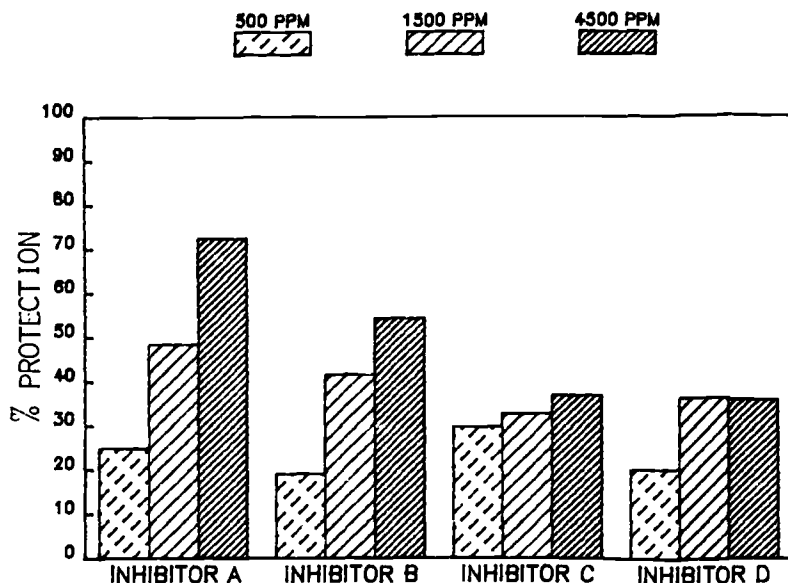


FIG. 4—Film persistency wheel tests (72-h exposure).

The percent protection results from the linear polarization measurements are shown, in Figs. 5 and 6 for the 24-h and 72-h periods, respectively. Since linear polarization measures the instantaneous corrosion rate, the percent protection values for each period must be calculated from the corrosion current integrated with respect to time. The weight loss is then compared to the same integral for a blank electrode that has seen the "film," "rinse," and "run" steps without inhibitor additions. Thus the following equation was used to calculate weight loss for percent protection:

$$W = \frac{(MW}{nF)} \frac{(\beta_a \beta_c)}{2.3(\beta_a + \beta_c)\Delta V} \int_{T_0}^{T_1} I_{\text{meas}} dt$$

where

- W = weight loss, g
- MW = molecular weight of corroding metal, g/mole,
- n = number of electrons in half-cell reaction,
- F = Faraday's constant, C/equivalent,
- β_a = anodic Tafel slope, V/decade,
- β_c = cathodic Tafel slope, V/decade,
- ΔV = applied polarization potential, V,
- I_{meas} = measured anodic current, A,
- T_0 = initial time, s, and
- T_1 = final time (for 24- or 72-h integration), s.

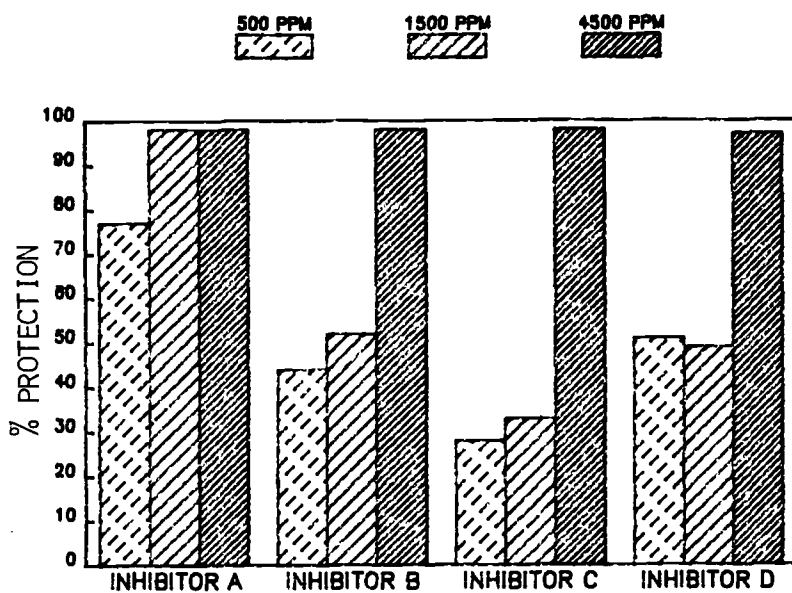


FIG. 5—Linear polarization measurements (24-h results).

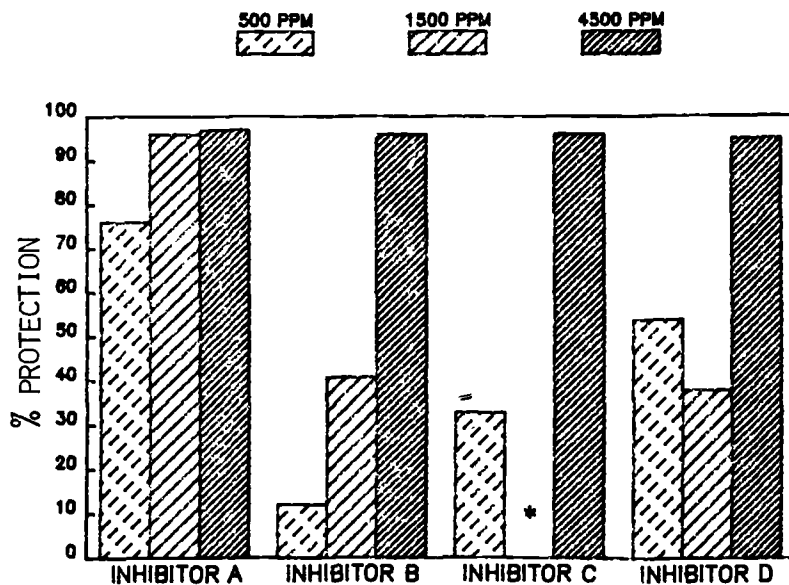


FIG. 6—Linear polarization measurements (72-h results).

The linear polarization results paralleled the wheel test results, although the percent protection results usually were higher for the linear polarization measurements. Both techniques showed increased protection for increased inhibitor filming concentration, and both techniques showed that Inhibitor A provided the best overall protection. Subsequent ranking of Inhibitors B, C, and D was sensitive to both filming concentration and exposure period. Generally, these three inhibitors were closely ranked. (Asterisk for Inhibitor C, 1500 ppm and 72 h, indicates invalid data due to oxygen contamination).

Film Life

The decrease in corrosion protection with time gives an indication of the effective film life for each inhibitor. This is an important parameter when batch-treating production wells, since the treatment frequency as well as the proper dosage level must be optimized to achieve adequate corrosion protection. Linear polarization directly measures the continuous corrosion rate data. This information also could be obtained from weight-loss measurements by removing coupons at timed intervals, but a large number of test specimens would be required to avoid changing the conditions of exposure when the coupons were removed for cleaning and weighing.

Figures 7, 8, and 9 show the comparison between the continuous corrosion rate data obtained by linear polarization and the results from two exposure periods in the film persistency wheel tests. The results are compared for the 500, 1500, and 4500-ppm filming concentrations respectively. Within experimental accuracy, both techniques yielded similar film persistency trends.

Corrosion Measurements in the Field

Linear Polarization Probes—Corrosion measurements using both the flush and 3-finger type linear polarization probes proved difficult due to oil fouling, even though the produced fluid had a water content of approximately 97% and the probes were located at the 8 o'clock and 6 o'clock positions, respectively, in the wellhead loop. When freshly cleaned, the probes responded for a period of one or two days, thereafter indicating near zero corrosion rates.

Potentiodynamic polarization scans were performed using the Petrolite methods and instrumentation to measure the extent of pitting corrosion since the produced fluids in this well contained approximately 64 000 ppm chlorides, an anion commonly associated with pitting. Both the flush and three-finger probes were used, when freshly cleaned and after long equilibration periods. The scans did not exhibit a positive hysteresis intersecting the original cathodic scan, a condition that has been reported to be an indication of active pitting [1,2]. Furthermore, these results did not correspond to actual corrosion coupon pit rates of 10 to 12 mpy (0.25 to 0.31 mm/year), nor to frequent pit-initiated corrosion fatigue in that well's carbon steel sucker rod string.

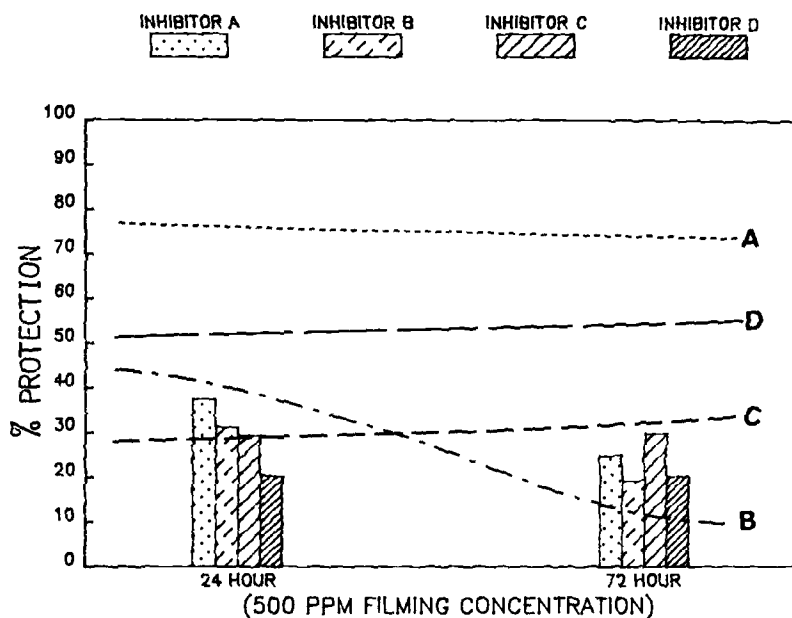


FIG. 7—Film persistency wheel tests versus linear polarization measurements.

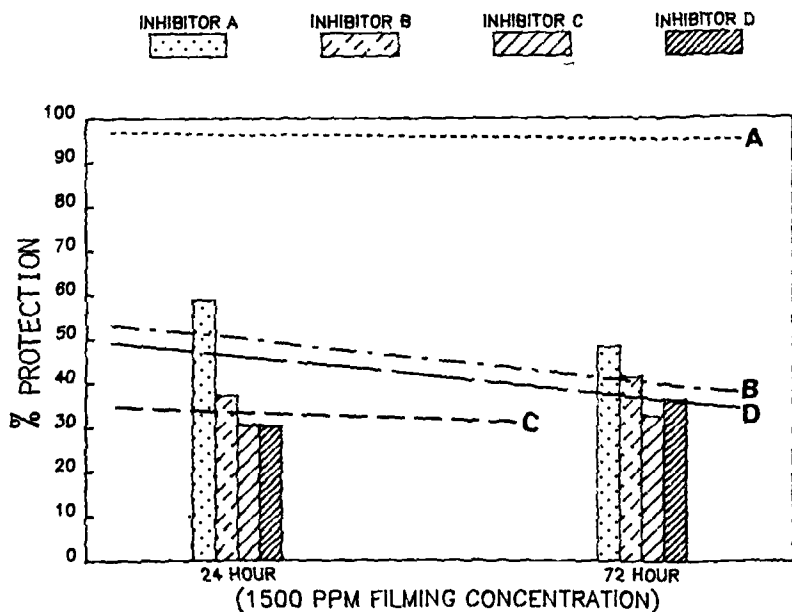


FIG. 8—Film persistency wheel tests versus linear polarization measurements.

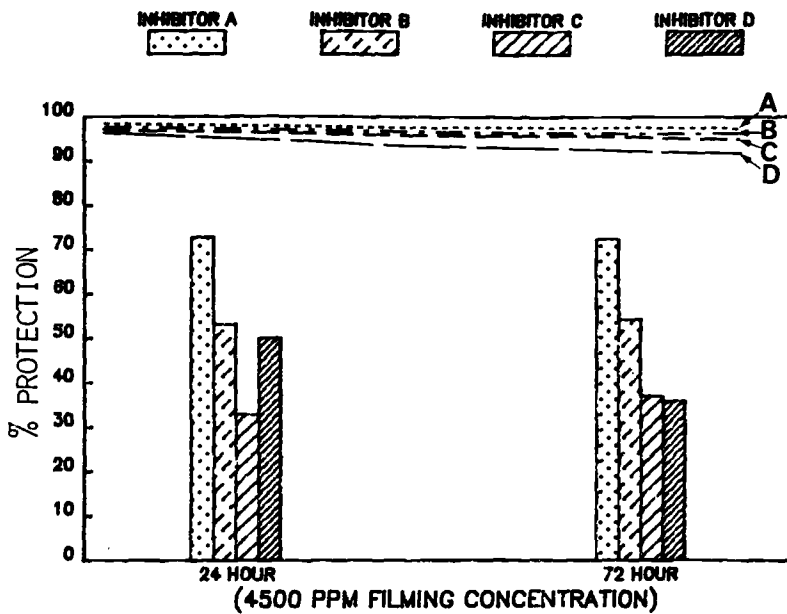


FIG. 9—Film persistency wheel tests versus linear polarization measurements.

Electrical Resistance Probes—The metal loss data from the wire, tube loop, and flush strip electrical resistance probes, for the six-month period February to July 1983, were compared to the corrosion coupon results (Table 1). Measurements from the flush strip probe, located at the 6 o'clock position, best correlated to the rate of the coupon positioned at the pipe bottom. The commonly higher corrosion rate at this position also was evident between the 5 and 7 o'clock positions on the spool piece. The wire and tube loop elements, protruding into the fluid flow at either the 4 or 8 o'clock positions, are in agreement with the coupon results located in a similar position.

TABLE 1—Corrosion coupon results.

Monitoring Method	Corrosion Rate	
	mpy	m Mpa
Corrosion coupon (normal position)	0.69	0.018
Corrosion coupon (elbow)	0.73	0.019
Corrosion coupon (pipe bottom)	2.34	0.059
Spool piece	1.01	0.026
Wire loop probe	0.58	0.015
Tube loop probe	0.64	0.016
Flush strip probe	2.51	0.064

Although the long-term metal-loss data shows good correlation, there are periods when the probes indicate "metal gain." These negative readings could be caused by temperature fluctuations uncompensated by the probe, or by conductive deposits such as iron sulfide affecting the measured resistance in the sensing element.

The present and long-term corrosion rates calculated by the Model 4200 Corrosion Measurement System did not correlate well to the indicated metal loss on the probes, as illustrated in Fig. 10. The present rate exhibited wide fluctuations, from zero to over 1000 mpy (25 mm/year), and anomalies such as increase in corrosion rate when the metal loss was negative (for example, June 3 to 4), and a decrease in corrosion rate when metal loss was positive (for example, June 16 to 17). Similar anomalies were evident between the long-term rate and metal loss, although this rate showed better correspondence with the metal loss data. This type of response can exist when the general corrosion rate is low compared to the measurement span of the probe elements [3].

Tracer Studies

The results of the wellhead tracer studies are given, in Figs. 11 and 12, for the two-hour and four-hour circulation times, respectively. Application guidelines recommend that an inhibitor concentration of at least 1000 ppm be in contact with the production tubing for at least one hour in order to achieve effective filming, and thus adequate corrosion protection. Figure 11 shows that this filming concentration was not achieved with two hours of circulation

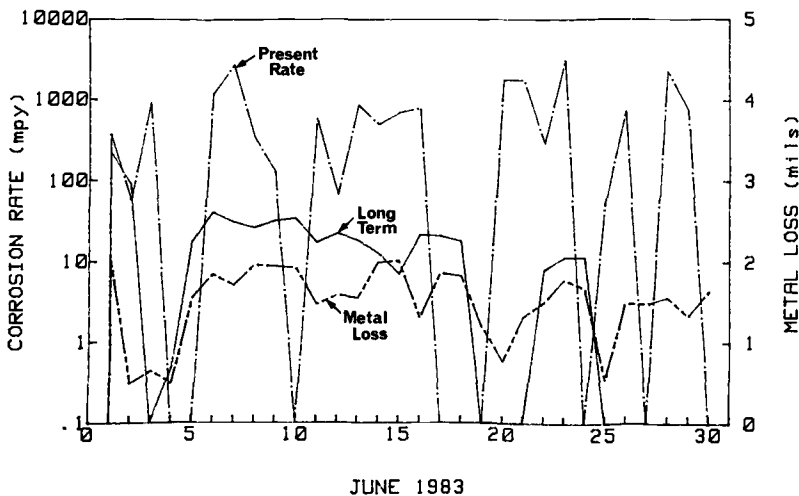


FIG. 10—ER flush strip probe data.

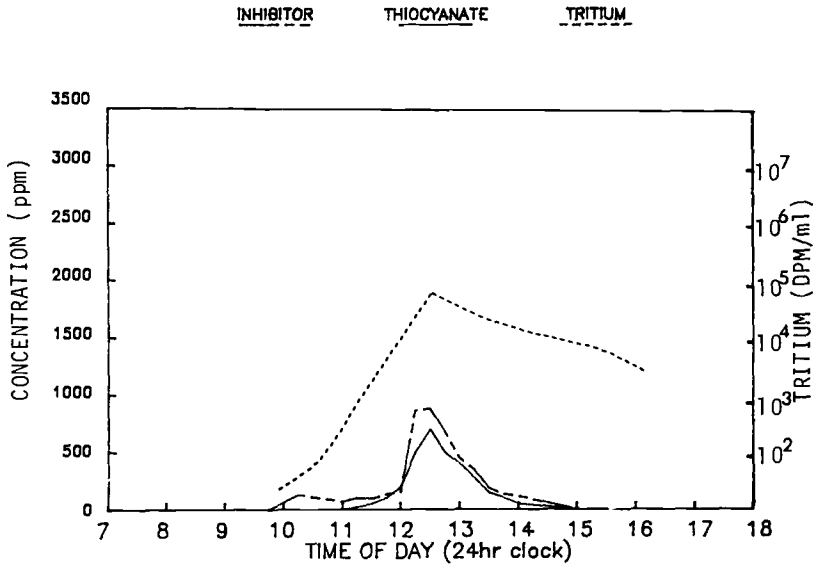


FIG. 11—Wellhead tracer tests (2-h circulation).

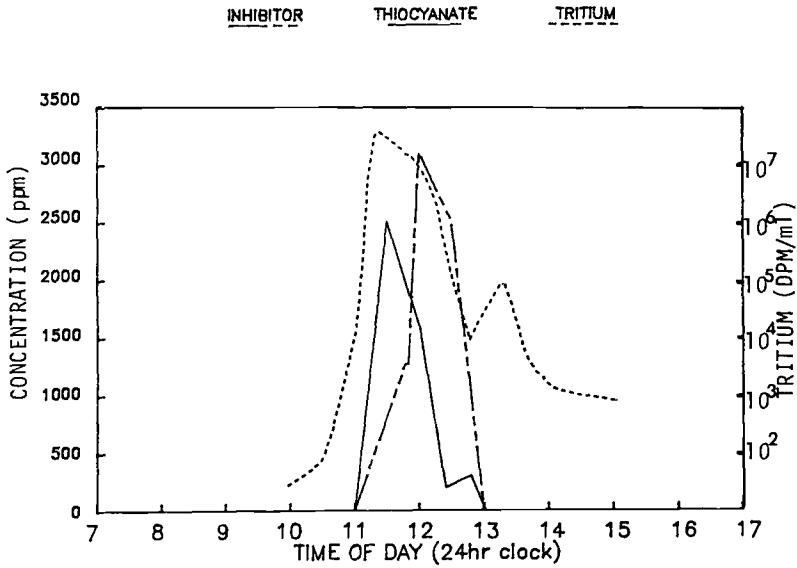


FIG. 12—Wellhead tracer tests (3-h circulation).

after batch treatment, whereas Figure 12 shows that for the same inhibitor/thiocyanate/tritium injection volumes, the filming concentration and contact time criteria were met. The difference in returning inhibitor concentrations for these two circulation times were also reflected in the ammonium thiocyanate and tritium concentration levels.

Although the main objective of the tracer study was to optimize the inhibition program on the test well, the results were also used to derive an empirical relationship to determine circulation times on other rod-pumped wells. Continuing tracer studies will refine the empirical equation so that it may be applied to high production electrical submersibly pumped wells.

Conclusions

Film persistency wheel tests and electrochemical measurements (conducted in the laboratory) produced similar inhibitor ranking, although the percent protection values for the latter technique were generally higher. Time-based linear polarization measurements had the advantage of readily providing information on the effective film life of an inhibitor, but wheel tests would be a more efficient method for ranking a large number of inhibitors.

Long-term corrosion measurements run in the field using linear polarization probes were not possible due to oil fouling of the electrodes. Short-term measurements could be made using freshly cleaned electrodes, but interpretation of results associated with inhibitor treatments was difficult since the decrease in the corrosion rate could have been due to either the presence of inhibitor or the progressive oil fouling. Pitting rate measurements by anodic polarization did not correlate to coupon measurements or the common failure cause of the well components.

Long-term metal loss data from electrical resistance probes located in the field flow loop correlated to weight-loss coupon measurements; however, the calculated corrosion rates were not in good agreement with the metal loss data.

The wellhead tracer studies showed that circulation time was the controlling factor in effectively treating wells with high annular fluid levels.

APPENDIX

Test Procedure Employed for Corrosion Inhibitor Evaluation for Batch Application in Oil Wells

General

1. The dynamic wheel test procedure was used. The "wheel" rotated the test containers end for end at a rotation speed of approximately 25 rpm.
2. The "wheel" was enclosed in such a manner that the desired test temperature was maintained within $\pm 2^\circ\text{C}$, that is, $60^\circ\text{C} \pm 2^\circ\text{C}$.

Coupons

1. Coupons were sheared from low carbon steel. Typical coupon dimensions were 16.5 by 0.95 by 0.084 cm ($6\frac{1}{2}$ by $\frac{3}{8}$ by $\frac{1}{30}$ in.).
2. All coupons for the test program were from the same batch of material.
3. All coupons were screened using $\times 10$ magnification. Coupons exhibiting surface anomalies were discarded.
4. For identification and subsequent examination, each coupon had a small identifying number stamped on it.
5. The coupons were sand tumbled (72 h) to remove surface contamination, solvent degreased and acetone rinsed. The weight of dried coupons was recorded to 0.1 mg.

Test Fluids

1. The test fluid consisted of uncontaminated (previously uninhibited) produced brine and crude oil transported from Redwater in five-gallon dense polyethylene containers.
2. Samples were separated into oil and water fractions and stored in inert containers. For subsequent use in the test procedure, the oil and water phases were purged with carbon dioxide a minimum of six hours.

Inhibitors

1. All inhibitors were evaluated using commercially available "as sold" strengths. The samples submitted were repackaged and coded as A, B, C, or D, with no other identifying features.
2. Test concentrations were set at 500 ppm, 1500 ppm, and 4500 ppm.

Test Procedure

1. The test bottles were initially purged with CO_2 to remove oxygen prior to filling.
2. The test fluids were syphoned from their respective containers to the test bottles after receiving a six-hour CO_2 purge.
3. The final H_2S concentration of the fluids was 450 ppm.
4. No oxygen scavenger was added to the test solutions.

Filming Step

5. The proper amount of inhibitor was dispensed into the test bottle using a micro-pipette with a suitable delivery volume. Each inhibitor to be tested was run in six bottles, triplicates for each of the 24-h and 72-h test.
6. The brine solution was then added to the bottle followed by the crude oil fraction. The ratio to be used throughout this test procedure was 93% aqueous phase, 7% hydrocarbon phase. The bottles were filled to 90% of their capacity.
7. The coupon was then added to the bottle, the CO_2 purging gas tube was removed, and the cork or cap was placed on top.
8. The bottles were mounted on the wheel and rotated at approximately 25 rpm and 60°C for one hour. When the containers were removed, observations were recorded concerning any emulsion characteristics.

Rinse Step

9. The coupons were removed from the filming bottles and placed in new bottles containing the appropriate volumes of CO_2 -saturated oil in the same 93/7 ratio of

water to hydrocarbon. These bottles were then mounted on the wheel and rotated at ≈ 25 rpm and 60°C for one hour.

Run Step

10. After the one-hour rinse, the coupons were transferred to new bottles containing the same brine and oil mixture as described in the film and rinse steps. The bottles were placed on the wheel and rotated at ≈ 25 rpm and 60°C .

11. After 24 h, three bottles were removed for each inhibitor concentration tested, as well as six blanks. Any contaminated bottles or other anomalies (that is, leaks) were noted and recorded. The coupons were removed, cleaned and weighed as described in the section following.

After 72 h, for each inhibitor concentration the remaining three bottles and another six blanks were removed. The bottle fluids were not changed during the interim between the 24-h and 72-h test times. Again, any anomalies were recorded. The coupons were treated in the same fashion as the 24-h coupons.

Coupon Cleaning and Analysis

1. The coupons were cleaned in 15% inhibited HCl for 15 to 30 seconds. Cleaned, nonexposed coupons were also subjected to the same procedure to assess the weight loss due to cleaning alone. The weight loss due to cleaning alone was found to be 1.0 mg.

2. Coupons were rinsed in water and rubbed lightly with 4/0 steel wool to remove tenacious deposits. Steel wool cleaning was followed by a water rinse, acetone rinse and drying.

3. Coupon weights were recorded to 0.1 mg.

4. Coupons were examined under $\times 10$ magnification to assess the type of attack.

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Ronald A. Yeske¹

Electrochemical Techniques for Monitoring Corrosion Rates in Simulated Kraft White Liquors

REFERENCE: Yeske, R. A., "Electrochemical Techniques for Monitoring Corrosion Rates in Simulated Kraft White Liquors," *Corrosion Monitoring in Industrial Plants Using Nondestructive Testing and Electrochemical Methods, ASTM STP 908*, G. C. Moran and P. Labine, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 266-288.

ABSTRACT: Corrosion severely damages carbon steel equipment exposed to alkaline sulfide liquors during kraft pulping operations. Studies have been conducted to determine whether linear polarization or electrical resistance methods could be used to monitor corrosion rates in kraft white liquors. Corrosion rates determined by these two methods have been compared with actual corrosion rates determined by weight loss. Linear polarization and electrical resistance methods both were found to provide accurate assessments of instantaneous corrosion rates, although errors in linear polarization results were observed when carbon steel was at passive potentials and liquor oxidation was possible. Empirical calibration of the linear polarization method is necessary for quantitative prediction of corrosion rates in kraft white liquors.

KEY WORDS: corrosion, pulping liquors, linear polarization, corrosion rate measurement, alkaline sulfide, carbon steel, resistance

Pulping and papermaking industries utilize chemical environments notorious for their ability to cause corrosion and corrosion-assisted cracking of construction materials. Corrosion damage is particularly troublesome in certain process streams associated with the kraft pulping process for delignification of wood prior to papermaking. Plain carbon steels are the usual materials of construction in kraft pulp mills, and the alkaline sulfide process liquors are responsible for serious corrosion problems with these steels.

The kraft pulping process involves the separation of useful cellulose from

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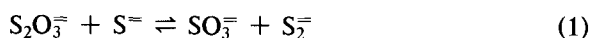
other constituents of wood by digestion, a cooking process wherein wood chips are exposed to hot alkaline sulfide solutions. The lignin that normally binds wood fibers is dissolved in the digestion process. The cellulose is retained for papermaking, while the spent cooking liquor containing dissolved organic species and residual inorganics is concentrated and then burned in recovery boilers. The inorganic constituents of the spent liquor fuel, mostly sodium carbonate and sodium sulfide, are recovered at the bottom of the recovery boiler for use in subsequent digestions. These recovered salts are dissolved in water, and the carbonate is converted to caustic by contact with slaked lime to replenish the alkaline sulfide cooking liquor for subsequent digestion. The product of this chemical recovery process is known as white liquor.

White liquor concentrations vary from mill to mill but will typically include 70 to 140 g/L of sodium hydroxide (NaOH), 20 to 50 g/L of sodium sulfide (Na₂S), and 10 to 60 g/L of sodium carbonate (Na₂CO₃) as major constituents. In addition, white liquors will contain minor constituents, consisting of a few grams per litre of sodium sulfate (Na₂SO₄), sodium sulfite (Na₂SO₃), sodium thiosulfate (Na₂S₂O₃), sodium chloride (NaCl), and sodium polysulfide (Na₂S_x) [1-2]. The temperature of white liquor is usually maintained at 85 to 95°C.

Plain carbon steels are the most common materials of construction for storage tanks, clarifiers, piping and other components in contact with white liquor. The use of 18Cr-8Ni stainless steels is becoming more common in response to high levels of attack of carbon steel in contact with the white liquor. Materials selection between carbon steel and stainless steel is dominated by the higher cost of the stainless versus the cost of occasional replacement of carbon steel.

Corrosion damage to carbon steel equipment exposed to the alkaline sulfide liquor is common. This damage is particularly troublesome at the liquid level line in storage tanks and clarifiers. Corrosion also occurs in the carbon steel pressure vessels used in the digestion process, but many of these vessels have now been overlaid with stainless steel to prevent further deterioration.

There have been numerous studies of the corrosivity of white liquor (and of mixtures of white liquor and spent liquor) toward carbon steel, with most of these studies focused on the corrosion behavior of digester steels. Ahlers [3] and Tromans [4], among others, have shown that small amounts of polysulfides present in liquors can affect corrosion rates. At low concentrations, polysulfide promotes corrosion because of its oxidizing character, whereas passivation with corrosion protection is observed when the polysulfide concentration is high—greater than 2 g/L excess sulfur. Thiosulfates present in white liquor also affect the rate of dissolution, but the mechanism is not clear. Haegland and Roald [5] have shown that if sulfites are also present, a small concentration of polysulfide is maintained in the liquor via the reaction



Based on this observation, the thiosulfate effect could be attributed to the maintenance of a stable concentration of oxidizing species. On the other hand, Wensley and Charlton [6] have shown that thiosulfate increases the peak current density required for passivation, with a corresponding increase in the probability that carbon steel will remain active in the liquor rather than spontaneously passivate. This observation differs from the expected effect accompanying an increased level of oxidant, so the effects of thiosulfate on corrosion are not only related to additions of an oxidizing species.

Since minor constituents of white liquors affect the corrosion behavior of carbon steel, it is not surprising that large variations in corrosivity can occur in actual kraft white liquors. Wensley and Charlton [7], for example, have used weight loss measurements to show that the average corrosion rate over two-week exposures in a single white liquor clarifier varied by more than a factor of twenty over an 18-month period. The lowest corrosion rate was approximately 2 mil per year (mpy), which is acceptable, but the 42-mpy rate of loss of the clarifier wall during periods of high corrosivity would be unacceptable. Presumably, the observed changes in corrosivity are a consequence of changes with time in liquor composition at that mill.

It would be useful to have a means of monitoring the corrosion rate to detect periods of high corrosivity. During those periods when corrosion is high, the species responsible for accelerated corrosion could be identified by grab sampling and chemical analysis. Once those periods are identified, process engineers could examine the recovery process to identify and eliminate practices that produce the corrosion accelerants in the white liquor. Likely sources of corrosion accelerants are incomplete reduction of sulfoxo compounds in the recovery boiler and excessive oxidation of the liquor by unwarranted contact with the atmosphere, both of which could be eliminated without jeopardizing pulping operations.

The unique brew of chemicals present in kraft white liquor may confound the usual techniques available for on-line corrosion monitoring. For example, the sulfurous species in white liquor are electroactive in the vicinity of the rest potential of steel, and redox reactions involving these species could invalidate the linear polarization measurements. Moreover, some of the sulfide deposits that form during corrosion are known to be conductive under some circumstances, which could have effects on both linear polarization and electrical resistance methods for corrosion rate monitoring. The absence of clearly defined Tafel slopes and the problems associated with large polarizations from the rest potential preclude the use of the Tafel slope extrapolation approach.

The objective of this investigation was to determine if the linear polarization or electrical resistance methods could be used to obtain accurate, on-line measurements of the corrosion rate of carbon steel in kraft white liquor. The accuracy of each of these indirect methods was established by continuous measurement of corrosion rate using one or the other of the indirect methods at the same time that weight loss coupons were being exposed. At the conclu-

sion of an exposure, the integrated corrosion rate from the indirect methods was compared with the actual corrosion rate determined by weight loss. Tests were conducted in several simulated white liquors at a single temperature of 90°C. Supplementary electrochemical tests were conducted to gain insight into the corrosion process. Electrical resistance measurements were also made continuously over a period of two weeks, with simultaneous exposure of weight loss coupons in the same liquor, to assess the accuracy of this method.

Experimental Procedure

Linear polarization (LP) measurements were made using two types of linear polarization instrumentation. Most LP measurements were made using a ten-channel Petrolite Model 1010 corrosion rate instrument, but occasional LP measurements were made using a PAR 350 Corrosion Instrument. The Petrolite Instrument was programmed to impose alternate +10 and -10 mV polarizations of 15-min duration on each of eight electrodes. Measurements of the open circuit potential of each electrode were made before each polarization. The current required to maintain the ± 10 mV polarization was captured by the instrument at the end of the 15-min cycle and converted into an electrical signal proportional to the corrosion rate in mils per year. For the coupon size selected, the instrument assumes a value of β equal to 83.3 mV, where β is given by

$$\beta = \frac{\beta_a \beta_c}{\beta_a + \beta_c} \quad (2)$$

and β_a and β_c are the anodic and cathodic Tafel constants, respectively. Also assumed is a value of Z equal to 2 in the overall corrosion rate equation

$$\text{Corrosion rate} = \left(\frac{1}{2.3 F} \right) \left(\frac{\beta}{Z} \right) \left(\frac{\text{Molecular weight}}{\text{Density}} \right) \left(\frac{i}{\Delta E} \right) \quad (3)$$

Alternative values of (β/Z) can be accommodated by multiplying the apparent mpy reading by an appropriate calibration factor.

The raw corrosion rate data and the rest potential data were stored on a floppy disk after processing by an Apple IIe microcomputer equipped with an ISAAC 91A Interface. Data were acquired, stored, plotted, and printed automatically. The average corrosion rate was determined for the LP measurements by a numerical integration of the corrosion rate versus time curve using a Simpson's Rule routine. The corrosion rate data are generally presented at this average corrosion rate taken over the period of the exposure.

Electrical resistance measurements of the corrosion rate of carbon steel in simulated liquors were made using a Rohrbach Model 4000 Corrosometer with wire-element sensing probes rated at 40 mpy. The carbon steel wire in

the probe was an AISI 1020 carbon steel. The Corrosometer provided a continuous digital indication of the normalized loss of wire cross section due to corrosion. This digital output was converted to an average corrosion rate by calculating the loss of wire thickness divided by the total exposure time.

Weight loss exposures were conducted at the same time (and in the same chamber) as the LP and ER measurements described above. The coupons were cylinders of AISI 1018 carbon steel with an exposed area of 9 cm^2 , with a surface which was ground to a 120-grit furnish before exposure. The heavy black films formed on these coupons were removed before weighing by brief immersion in an inhibited Clarke's solution; in some cases, mild abrasion was necessary to remove stubborn deposits prior to acid cleaning.

The coupons and electrodes were exposed simultaneously in 100 mL Teflon® chambers containing the simulated liquors. Each specimen was mounted on a threaded rod that penetrated the Teflon® chamber lid, with sealing provided by hypalon gaskets. The solutions were prepared from Fisher, reagent-grade chemicals dissolved in deionized water under a pre-purified nitrogen sparge. The specimens were mounted and the chambers closed in a nitrogen atmosphere to create a small nitrogen plenum above the liquors. In spite of these precautions, some faint straw color was evident in many of the solutions as a result of Na_2S_x formation. Other sulfoxy anions were also present in small concentrations after liquor preparation. The liquors in the chambers were stagnant and heated to 90°C with a hot water bath.

Potential measurements were facilitated by the use of a silver/silver sulfide (SSS) reference electrode. This electrode has been found [8] to produce a reasonably stable potential in white liquors that is slightly dependent on the sulfide concentration, but is independent of the concentration of the other species typically encountered in white liquor. Depending on the $\text{S}^{=}$ concentration, the rest potential ranges from -865 mVSCE at $6\text{ g/L Na}_2\text{S}$ to -905 mVSCE at $42\text{ g/L Na}_2\text{S}$. The SSS electrode is attractive because it is directly immersible in hot alkaline sulfide liquor, whereas most reference electrodes employing silver and mercury electrodes would be poisoned by this exposure. Although stable SSS potentials had previously been observed and reported [8], frequent calibrations of SSS potential were made versus a calomel electrode protected by a double salt bridge with sodium hydroxide (NaOH) and potassium chloride (KCl) electrolytes. The calomel electrode was maintained at room temperature, and no corrections were made for thermal or liquid junction potentials. Potentials are reported versus the SSS potential, as well as the saturated calomel electrode (SCE) potential.

Results

Corrosion Characteristics

In liquors containing only NaOH and Na_2S , the corrosion rate of carbon steel was relatively insensitive to the concentrations of NaOH and Na_2S in the

simulated liquor over the range likely to be encountered in service [8]. Weight loss measurements on specimens exposed for two, four, six, or eight weeks demonstrated the trends. In liquors containing either NaOH or Na₂S alone, the corrosion rate was negligible. Solutions containing 60 to 140 g/L NaOH and 10 to 40 g/L Na₂S exhibited active corrosion during an initial two week exposure, at rates of 2 to 6 mpy. In solutions with only 10 to 20 g/L Na₂S or only 60 g/L NaOH, the corrosion rate fell to very low levels thereafter. In solutions with higher concentrations of NaOH or Na₂S, the initial corrosion rate of 4 to 6 mpy was maintained indefinitely.

Changes in open circuit potential accompanying exposures to NaOH/Na₂S liquors followed the expected trends. Coupons that remained active throughout the eight-week exposure exhibited a rest potential in the vicinity of -240 mVSSS (~ -1.1 VSCE). When the corrosion rate was initially high but fell dramatically during the exposure, the open-circuit potential began at ~ -240 mVSSS but increased to a steady-state value of +100 mVSSS (~ -0.8 VSCE) during the exposure. In a few cases, an intermediate potential of approximately -100 mVSSS (~ -1.0 VSCE) was observed, coinciding with a reduced corrosion rate of ~ 2 mpy.

Thus, the corrosion behavior of carbon steel in binary NaOH/Na₂S liquors was either active at a corrosion rate of ~ 4 to 6 mpy or active-passive with a negligible corrosion rate following spontaneous passivation. The changes in rest potential of carbon steel during corrosion in these liquors follow the expected trends.

Additions of either sodium thiosulfate, Na₂S₂O₃, or elemental sulfur (forming polysulfide, Na₂S_x) to a reference white liquor containing 100 g/L NaOH and 33 g/L Na₂S had a large effect on the corrosion rate. The corrosion rate increased from 6 mpy in the undoped reference liquor to 28 mpy in liquor containing 25 g/L Na₂S₂O₃ (Fig. 1). An addition of only 2.5 g/L Na₂S₂O₃ increased the corrosion rate to nearly 20 mpy. Additions of elemental sulfur to the reference liquor also increased the average corrosion rate of carbon steel up to a certain concentration. As shown in Fig. 2, additions of 0.5 and 2.5 g/L S^o increased the average corrosion rate, whereas 5 and 10 g/L S^o induced rapid passivation with virtual cessation of corrosion in five of six specimens. In the sixth specimen exposed in the 5 g/L S^o solution, passivation was apparently delayed and the average corrosion rate was higher.

The open-circuit potentials of carbon steel in liquors doped with Na₂S₂O₃ and Na₂S_x reflected the apparent corrosion behavior. Coupons exposed to liquors containing 0, 2.5, or 5 g/L Na₂S₂O₃ exhibited the previously observed active potential—approximately -240 mVSSS (-1.1 VSCE). Specimens exposed to liquors containing 25 g/L Na₂S₂O₃ exhibited an initial potential of -240 mVSSS, but the potential gradually increased to a rest potential of -100 mVSSS (-1.0 VSCE) over a period of 18 days.

Polysulfide additions also affected the rest potential. When 0.5 g/L S^o was added to the chamber, the rest potential remained at -240 mVSSS (-1.1 VSCE) throughout the exposure, but complete consumption of the Na₂S_x was

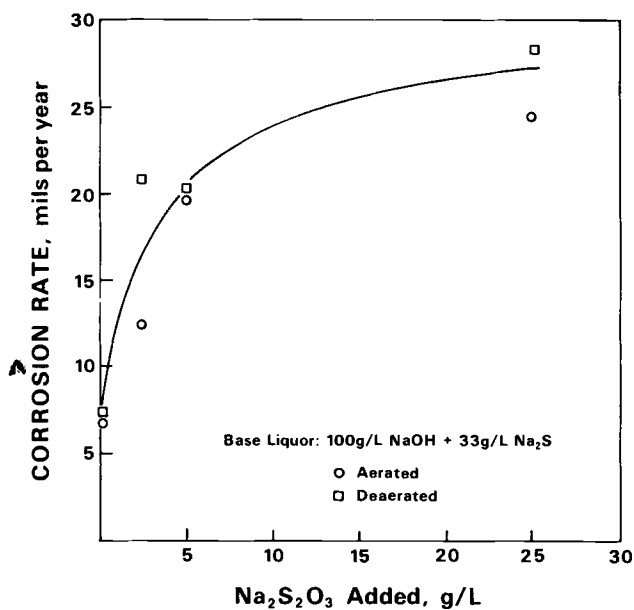


FIG. 1—Effect of added Na₂S₂O₃ on average corrosion rate of carbon steel exposed to a simulated liquor containing 100 g/L NaOH and 33 g/L Na₂S.

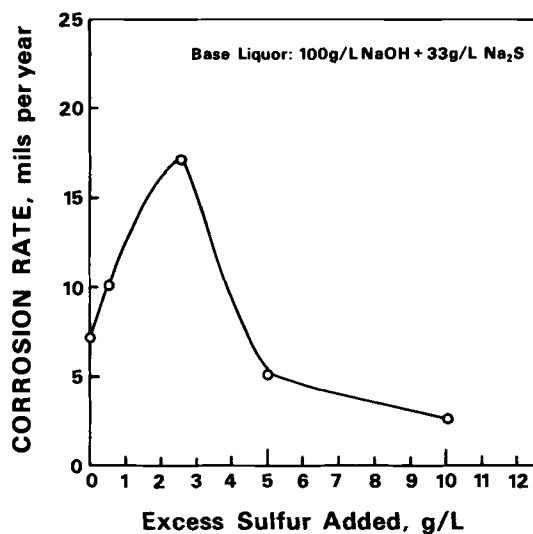


FIG. 2—Effect of added sulfur on average corrosion rate of carbon steel exposed to simulated liquor.

likely in this case. For tests in a solution containing 2 g/L S^0 , the open-circuit potential decreased from -80 mVSSS (-985 mVSCE) to -140 mVSSS (~ -1035 mVSCE) over the 400-h exposure. Concentrations of 5 or 10 g/L excess sulfur resulted in rapid establishment of a stable rest potential of approximately $+100$ mVSSS (-795 mVSCE).

Thus, in liquors containing Na_2S_x or $Na_2S_2O_3$, passivation with cessation of corrosion is observed when the rest potential is about $+100$ mVSS or above, and active corrosion results in a rest potential of about -240 mVSSS. For high concentrations of $Na_2S_2O_3$ and intermediate concentrations of Na_2S_x , active corrosion occurred at an accelerated rate at potentials between -240 mVSSS and -100 mVSSS.

Following exposure, the composition of the surface films was determined by X-ray diffraction and found to depend on the composition of the liquor and the corrosion behavior exhibited by the steel. In binary NaOH/ Na_2S solutions and most of the solutions containing small amounts of $Na_2S_2O_3$ or Na_2S_x , the coupons were covered with a thick black film composed largely of iron (II) sulfides. In solutions containing large amounts of $Na_2S_2O_3$, specimens were covered with a thick green-black film that occasionally spalled from the coupon in sheets. This film was identified by X-ray diffraction as $NaFeS_2$, a compound not listed in many X-ray powder pattern files but identified by Taylor and Shoesmith [9]. Specimens passivated by additions of Na_2S_x exhibited a thin black film with metallic luster; in some cases, this film was very thin, and the underlying shiny metal surface was visible.

Linear Polarization

Linear polarization studies were conducted simultaneously with several of the weight loss measurements described above. Raw data from the LP instrument were integrated over time to determine an average corrosion rate over the period of exposure. This average corrosion rate was then compared with the actual corrosion rate in the same liquors as determined by weight loss measurement. Differences between the LP and weight loss measurement of average corrosion rate were accommodated by adjusting the (β/Z) parameter in Eq 3 to bring the LP results into agreement with the actual corrosion rate. This critical value of (β/Z) , labeled $(\beta/Z)^*$, was determined for exposures in liquors that produced active, active-passive, and passive behavior.

Imposition of a ± 10 mV polarization on the test electrode resulted in a large instantaneous current that rapidly decayed to a steady-state value, as shown in Fig. 3. The shape of the transient was similar for anodic and cathodic polarizations. A similar transient was observed during -20 mV step polarizations imposed with the PAR 350 instrument.

The instantaneous measurement of average corrosion rates by the LP method generally agreed qualitatively with the results of the weight-loss exposures described above. In some of the NaOH/ Na_2S solutions presumed to

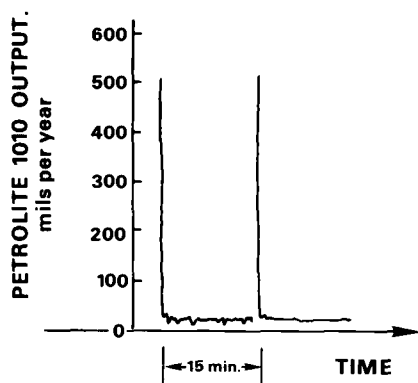


FIG. 3—Current required to maintain 10-mV polarization as a function of elapsed time.

contain trace quantities of polysulfide oxidant, the initial corrosion rate was higher—up to 20 times as high—as the steady-state corrosion rate established later (Fig. 4). Presumably, the high corrosion rate occurs on the film-free specimens until the polysulfide is consumed; thereafter, the corrosion occurs under the influence of the hydrogen evolution reaction. Liquors producing either high or low rates of active dissolution also resulted in LP measurements of corrosion rate that were high and low, respectively. In tests where a surface film apparently delaminated during the exposure, the instantaneous corrosion rate measured by LP methods exhibited several peaks in dissolution rate that may be attributed to the disruption of this film.

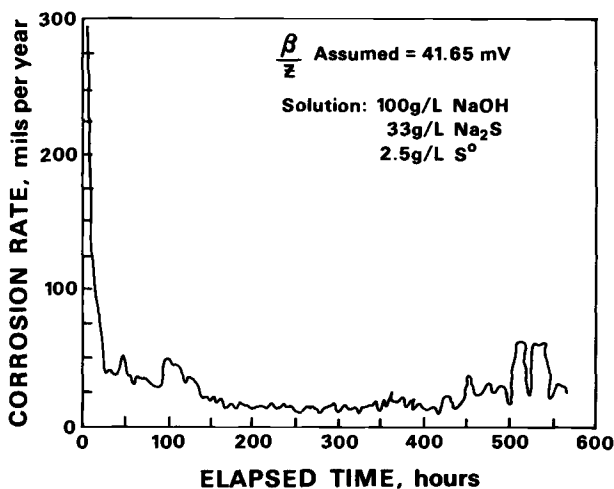


FIG. 4—Example of high initial corrosion rates at the start of an exposure to simulated liquors.

Finally, as shown in Fig. 5, additions of corrosion promoters to a liquor in mid-test resulted in an abrupt, transient increase in corrosion rate followed by a higher steady-state corrosion rate that was subsequently verified by weight-loss measurements. Thus, with some exceptions discussed below, the corrosion rate determined instantaneously by LP methods follows the expected trends for corrosion in white liquor.

However, the quantitative agreement between the average corrosion rates determined by LP measurements and weight loss was not as good. The corrosion rates measured by the LP method using the (β/Z) values inherent in the instrument were generally higher than the actual rates measured by weight loss. The corrosion rates measured by anodic polarization were higher than those determined with a cathodic step potential, and were consequently in greater error. The instantaneous corrosion rates determined by anodic and cathodic LP measurements are compared in Fig. 6 with the average corrosion rate determined by weight loss measurement. The liquor in this case was the reference liquor containing 100 g/L NaOH and 33 g/L Na₂S. Obviously, the raw corrosion rates taken directly from the LP device—without adjusting the value of (β/Z) —are considerably higher than the actual rate determined by weight loss.

The actual corrosion rates observed in several simulated liquors are shown in Table 1, together with the average corrosion rates derived from integration of anodic and cathodic LP rates measured in these liquors. A critical value of (β/Z) will bring the mean of the anodic and cathodic corrosion rates shown in Table 1 into agreement with the average corrosion rate determined by weight

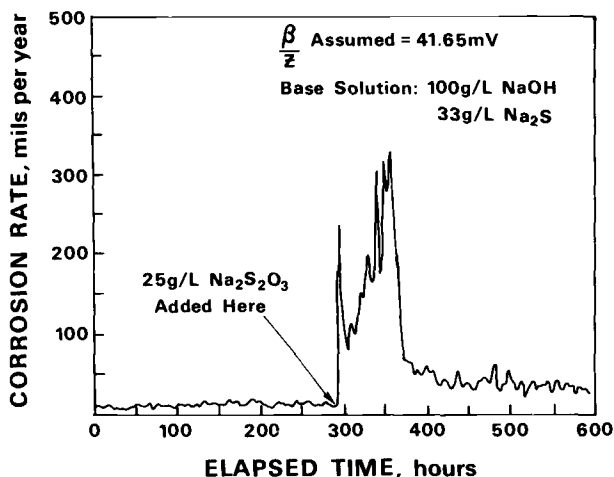


FIG. 5—Example of an instantaneous increase in corrosion rate measured by linear polarization at the time of addition of 25 g/L Na₂S₂O₃.

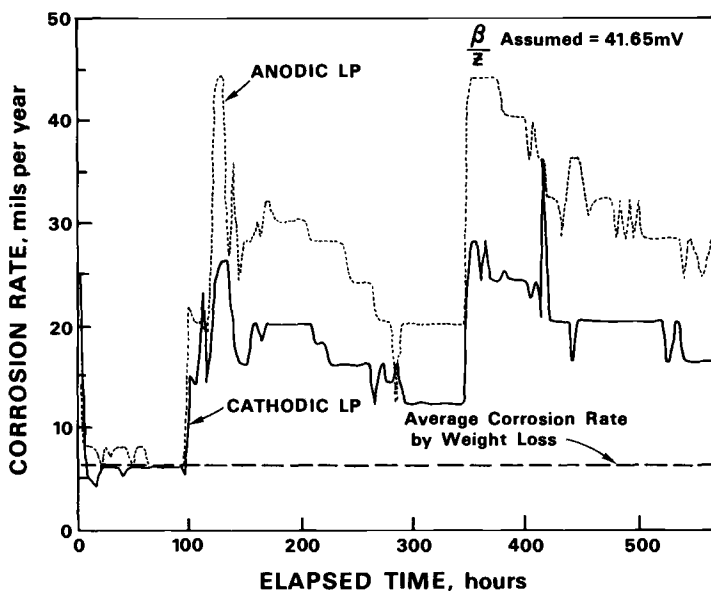


FIG. 6—Comparison of average corrosion rate (weight loss) with corrosion rates determined by linear polarization (uncorrected for β and Z).

loss. These critical values of $(\beta/Z)^*$ are also tabulated in Table 1. The (β/Z) value inherent in the LP instrument is $(\beta/Z) = 41.65$ mV, but the data in Table 1 indicate that an empirical (β/Z) value of approximately 18 mV gives much better agreement with the actual corrosion rate data in most of the simulated liquors. The (β/Z) value inherent in the LP device is apparently too large by a factor of about 2.3. This correction factor does not arise from a failure to accommodate the factor of 2.3 involved in conversion from natural to common logarithms in Eq 3.

The empirical correction factor required to bring the LP results into agreement with the actual weight loss results is approximately the same for a variety of simulated liquors. A $(\beta/Z)^*$ value of 18 mV is acceptable for several binary NaOH/Na₂S solutions, as well as solutions doped with Na₂S₂O₃ or low concentrations of Na₂S_x. Generally speaking, the LP measurement with (β/Z) adjusted to 18 mV will give accurate results when the steel is actively corroding and the open circuit potential is below -100 mVSSS (~ -995 mVSCC).

The empirical adjustment of (β/Z) is not appropriate for solutions containing enough polysulfide to achieve spontaneous passivation. As shown in Table 1, the values of $(\beta/Z)^*$ appropriate for these solutions are in the range 3 to 10 mV, but these values of $(\beta/Z)^*$ would be difficult to justify on the basis of known kinetics of corrosion reactions. The anomalous $(\beta/Z)^*$ values represent high rates of corrosion measured by LP methods in polysulfide-doped

TABLE 1—Comparison of actual and predicted corrosion rates in simulated white liquor.

Environment				Total Exposure Time, h	Actual Corrosion Rate (avg), mpy	Avg LP Rate (Anodic and Cathodic), mpy	$(\beta/Z)^*$, mV
NaOH, g/L	Na ₂ S, g/L	Na ₂ S ₂ O ₃ , g/L	S ^o , g/L				
BINARY LIQUORS							
60	20	...	...	508	4.2	11.5	15.8
60	33	...	...	508	4.4	12.4	14.6
60	40	...	...	508	4.0	12.1	13.6
80	33	...	...	508	5.9	15.7	16.1
100	15	...	...	520	4.0	12.9	15.0
100	20	...	...	520	4.4	12.6	15.9
100	25	...	...	520	4.9	14.1	15.0
100	30	...	...	520	4.8	15.9	13.4
100	33	...	...	508	5.3	16.1	14.3
100	33	...	...	568	7.0	20.5	14.2
100	33 ^a	...	...	472	7.0	21.0	13.9
100	35	...	...	520	4.2	15.0	11.7
100	40	...	...	520	4.4	14.9	12.9
100	45	...	...	520	4.4	13.0	14.6
100	50	...	...	520	4.4	14.0	13.5
120	33	...	...	508	5.4	17.5	13.6
140	33	...	...	508	5.0	16.6	13.2
140	40	...	...	508	5.0	17.6	12.6
THIOSULFATE ADDITIONS							
100	33	2.5 ^a	...	472	12.0	29.5	16.9
100	33	2.5	...	568	20.0	45.5	18.3
100	33	5.0 ^a	...	472	18.0	43.0	17.4
100	33	5.0	...	568	18.0	43.0	17.4
100	33	25.0 ^a	...	472	25.0	59.5	17.5
100	33	25.0	...	568	28.0	70.5	16.5
SULFUR ADDITIONS (POLYSULFIDE)							
100	33	...	0.5	568	10.0	20.5	20.3
100	33	...	2.5	568	17.0	29.5	24.0
100	33	...	5.0	568	5.0	21.5	9.7
100	33	...	10.0	568	2.5	36.0	2.9

^aAir-saturated solutions at start of testing.

solutions, whereas the electrodes are actually passive and corroding at a very low rate. This anomaly in the LP measurements of the corrosion rate appears to occur only with passive steel electrodes, that is, electrodes with rest potentials in the vicinity of +100 mVSSS (~ -0.8 VSCE).

Attempts to rationalize the critical $(\beta/Z)^*$ of 18 mV in terms of β_a , β_c , and Z determined by independent electrochemical measurements met with some success. Anodic and cathodic polarization curves usually exhibited some limited Tafel behavior soon after the plain carbon steel was immersed in white

liquor. A representative pair of polarization curves is shown in Fig. 7. The linear range is short for anodic polarization because of the onset of film formation and oxidation of species in the liquor, but a rough estimate of a Tafel constant is generally possible. The extent of Tafel behavior in the cathodic polarization is greater. Considerable noise is encountered at the open circuit potential because the curves are generated as soon as the electrode achieves a relatively constant potential. Table 2 shows the β_a and β_c values for tests in several simulated liquors. The average anodic Tafel slope measured was 49 mV and the average cathodic Tafel slope was 118 mV, giving an average β value of 35 mV. If the charge transfer is a two electron event, Z equals 2 and the independently determined (β/Z) value would be 17.5 mV—in excellent agreement with the empirical value of $(\beta/Z)^* \cong 18$ mV. Degeneration in the Tafel behavior occurs as the electrodes become film covered, so a similar approach on filmed electrodes is not possible.

Electrical Resistance Method

The electrical resistance (ER) method was used with success in monitoring the corrosion rate of carbon steel exposed to white liquor in a few tests of limited duration. As shown in Table 3, the average corrosion rate during a 13-day exposure was virtually identical for the results of ER testing and the si-

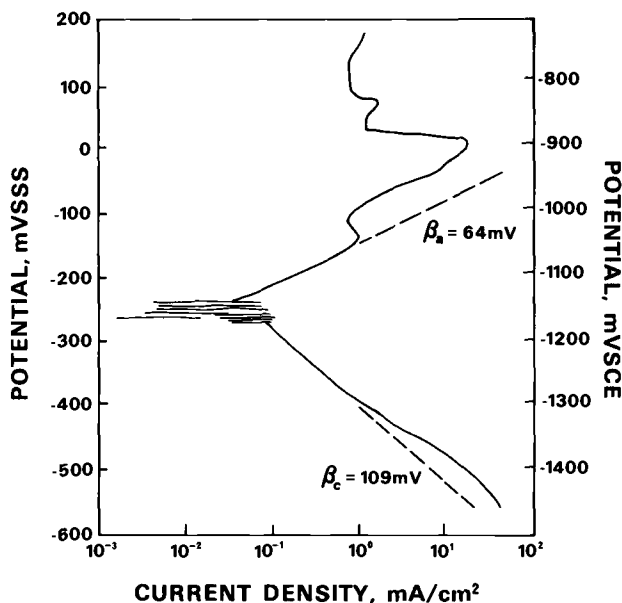


FIG. 7—Polarization curves for carbon steel exposed to a simulated white liquor, showing Tafel behavior soon after immersion.

TABLE 2—Composition of measured anodic and cathodic Tafel slopes in simulated white liquors (short immersion times).

NaOH, g/L	Na ₂ S, g/L	β_a , mV	β_c , mV	β , mV	($\beta/2$), mV
60	15	53	98	34.4	17.2
60	20	56	94	35.1	17.6
60	25	58	101	36.8	18.4
60	30	53	98	34.4	17.2
60	35	56	101	36.0	18.0
60	40	53	117	36.5	18.3
80	25	48	109	36.0	18.0
80	40	64	109	40.3	20.1
100	15	56	105	36.5	18.3
100	20	56	110	37.1	18.6
100	25	50	150	37.5	18.8
100	30	46	130	34.0	17.0
100	35	28	84	21.0	10.5
120	10	34	98	25.0	12.5
120	25	48	235	39.0	19.5
140	10	34	134	27.0	13.5
140	15	68	105	41.0	20.5
140	20	31	144	25.5	12.8

TABLE 3—Comparison of actual corrosion rates with rates determined by ER methods.

Environment	ER Corrosion Rate, mpy	Weight Loss Corrosion Rate, mpy
100 g/L NaOH, 33 g/L Na ₂ S	14.2	14.4, 13.6, 14.6
As above, +25 g/L Na ₂ S ₂ O ₃	40.6	41, 41, 40
As above, +10 g/L S ^o	3.4	5.8

multaneous weight loss exposure. The agreement between the actual corrosion rate and the ER measurement of that rate is acceptable in the three liquors producing corrosion rates ranging from 5 to 40 mpy. It is noteworthy that the ER method accurately monitored a low corrosion rate in a high polysulfide liquor, whereas problems with interpretation were encountered with the linear polarization methods used in high polysulfide liquors.

As shown in Fig. 8, the corrosion rate was more or less constant over the period of the exposure, as was also observed during the linear polarization measurements. Unusual resistance changes were evident at the start of the three tests, as shown in Fig. 8. In two of the three cases, the resistance decreased during the first 24 h of exposure. While this anomaly may be attributed to the precipitation of a conductive deposit on the wire, another credible explanation is a failure to achieve full temperature equilibrium at the temperature-compensating element during the earliest resistance measurements.

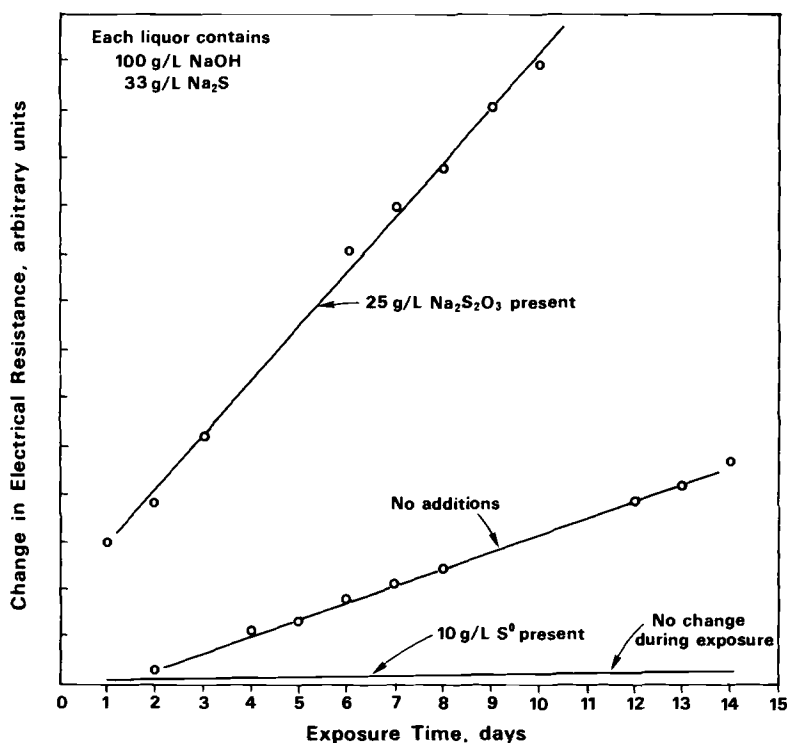


FIG. 8—Corrosion rate versus time determined by differentiation of the resistance-versus-time curve for ER monitoring.

Corrosion Products

Limited X-ray diffraction studies were conducted on the corrosion products formed during exposure of the weight loss coupons to carbon steel in an attempt to understand whether two electrons or three electrons are created by each dissolution event.

The principal corrosion product in the binary NaOH/Na₂S liquors was Mackinawite, an iron-rich form of ferrous sulfide (FeS). This deposit is consistent with a two-electron dissolution event such as the formation of ferrous ions, Fe⁺⁺, or dihypoferrite ions, HFeO₂⁻, and subsequent precipitation of the sulfide. In solutions containing a high concentration of Na₂S₂O₃, the corrosion product has been analyzed as sodium iron sulfide (NaFeS₂) [9]. In this case, the oxidation state of the iron is probably +3, but the fraction of dissolved iron oxidized to this valence state is not clear because all the dissolved iron did not precipitate as a corrosion product. In some cases, sulfur precipitates have been detected at isolated pores in the FeS corrosion products. Changes in the nature of the deposit after withdrawal from the solution were

also observed, with the deposit initially having a gray, metallic luster, but changing into a black friable deposit as drying took place. These changes were not associated with a chemical reaction involving species in the atmosphere, since a similar transformation occurred in dry nitrogen gas. The change in character of the film with time could be associated with loss of water of hydration. Further work appears to be necessary to rationalize an independent verification of the value of Z in Eq 3.

Discussion

Average corrosion rates in simulated white liquors of 5 to 40 mpy are in the range encountered in earlier studies of white liquor corrosivity in laboratory and field studies. Wensley and Charlton [7] found that the corrosion rates in actual white liquors containing little polysulfide but 7 to 8 g/L $\text{Na}_2\text{S}_2\text{O}_3$ were about 20 mpy, which agrees well with the present results for high-thiosulfate liquors as shown in Fig. 1. The deleterious effects of $\text{Na}_2\text{S}_2\text{O}_3$ and low levels of polysulfide agree with the results of early studies involving mixtures of white and spent liquors [10–15]. Passivation induced by high levels of polysulfide in mixtures of white and spent liquors has been reported by several investigators [8,13,14].

The observed absence of a significant effect on active corrosion rates caused by variations in NaOH and Na_2S concentration in white liquor devoid of oxidants (for example, polysulfide) has not been reported earlier. Uusitalo [12], Mueller [13], and Wensley and Charlton [6] have shown that the peak current density required for the active-passive transition in white liquors is raised as the NaOH or Na_2S concentrations increase, and these species may therefore affect the likelihood of spontaneous passivation. In the absence of oxidizing species, spontaneous passivation will be impossible, and the net effect of variation in caustic and sulfide in the liquor should be small, as is observed.

The current test results demonstrate the corrosion rate variations attributed to inadvertent additions of polysulfide oxidants to the liquor. In three separate tests in liquors containing 100 g/L NaOH and 33 g/L Na_2S , the actual corrosion rates measured by weight losses were 3.4, 7, and 14 mpy. This fourfold variation in corrosion rates under nominally identical conditions is thought to be a result of differences in polysulfide concentration in the three liquors, although the polysulfide levels were not actually determined during the testing. The best grades of commercially available sodium sulfide contain various levels of polysulfide, as is evident from the intensity of yellow color in the Na_2S crystals, and this polysulfide enters the solution with the sulfides added to the liquor. The higher level of Na_2S_x would be expected to support higher levels of corrosion. Tests on multiple coupons exposed to a single liquor have shown that the standard deviation in corrosion rate was only 1.3 mpy for 24 specimens corroding at an average rate of 3.4 mpy. The effect of

inadvertent polysulfide additions could be avoided by preparing alkaline sulfide solutions from prepurified H_2S gas bubbled through the caustic solution. This precaution was considered unnecessary in the present study since the LP, ER, and weight-loss comparisons were made simultaneously in the same liquor; this approach removes variable Na_2S_x content as a source of error in the evaluation of on-line monitoring methods.

The corrosion behavior of steel exposed to alkaline sulfide media is apparently controlled by the available cathodic reactions on the steel surface, with the added complexity of an active/passive transition and a superimposed redox reaction. The corrosion characteristics are summarized in the schematic Evans diagram shown in Fig. 9.

In the absence of polysulfide or other oxidants in the white liquor, hydrogen evolution is the only cathodic reaction available to support dissolution. Since the half-cell potentials for metal oxidation and hydrogen evolution are close, the corrosion current at the mixed potential of the corroding steel surface will be small—equivalent to the 3 to 6 mpy observed in long-term tests in $\text{NaOH}/\text{Na}_2\text{S}$ solutions where any oxidant has been consumed. In simulated liquors containing significant levels of NaOH and Na_2S , the peak current density for an active-passive transition will not be achieved by the limited reduction currents associated with hydrogen evolution. Consequently, carbon

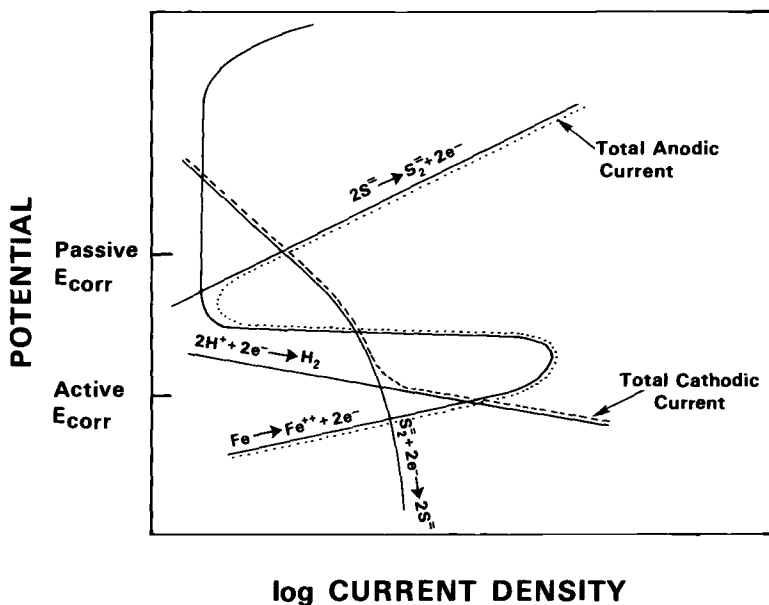


FIG. 9—Corrosion behavior of steel exposed to alkaline sulfide media, as represented by a schematic Evans diagram.

steel exposed to alkaline sulfide liquors devoid of oxidizing species will remain active, but the corrosion rate will be modest. The situation is analogous to the slow dissolution of iron in neutral, deaerated waters.

When polysulfides are present, they provide an alternative reduction reaction that can support higher levels of dissolution, or at sufficiently high concentrations, promote spontaneous passivation of the carbon steel. The two successive reduction reactions are clearly evident on an inert gold electrode immersed in a simulated liquor, as shown in Fig. 10. As the potential is lowered from the redox potential ($\sim +100$ mVSSS), a diffusion-limited reaction is the first reduction process encountered. With further depression of the potential, a second reduction appears at a potential of ~ -250 mVSSS. This second reduction process is also observed in pure caustic solutions at similar potentials and is therefore unrelated to sulfur chemistry. Since the potential for the onset of the second reduction is close to the redox potential observed when molecular hydrogen has been evolved on gold surfaces, the second reduction is attributed to hydrogen evolution by Eq 2. The first reduction is

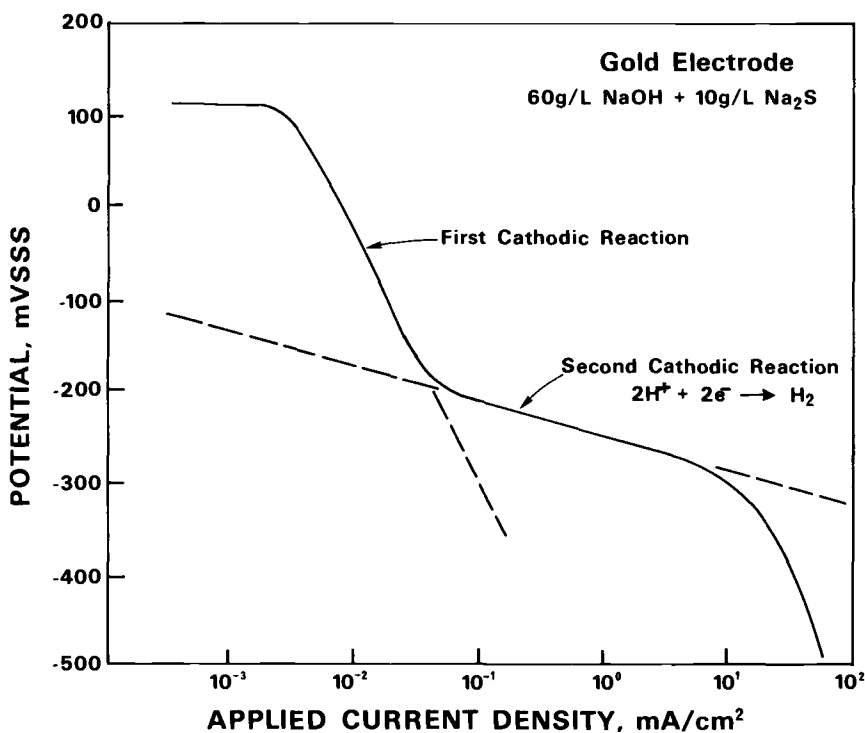
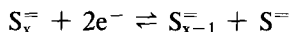


FIG. 10—Sequential reduction processes evident on a gold electrode cathodically polarized in an alkaline sulfide solution.

attributed to reduction of an oxidant—either S_x^- in alkaline sulfide solutions or dissolved oxygen in pure caustic.

When a small amount of polysulfide is present, the corrosion rate is increased, but the cathodic current limitations will preclude a transition to the passive state. When higher levels of S_x^- are available, spontaneous passivation is possible. Once passivated, the carbon steel will act as an inert host for the same redox reactions that establish the redox potential on gold. As a result, the rest potential of passivated carbon steel is quite close to the redox potential of a gold electrode in these same liquors—approximately +100 mVSSS. This redox potential may be established by



but other redox reactions are possible.

Intermediate potentials near -100 mVSS are puzzling; they do not appear as simple mixed potentials involving dissolution and a coupled cathodic reaction because the corrosion rate is reduced even though the potential is more noble than active potentials of -240 mVSSS. Incomplete formation of a film could be responsible for these intermediate rest potentials.

With the role of polysulfide in the above scenario is clear, the origins of the large effect of thiosulfate as a corrosion accelerant remain unclear. Thiosulfates may indeed stabilize a certain concentration of S_x^- as suggested by Roald [10], but deliberate additions of polysulfide in excess of amounts anticipated from the dissociation reaction have a smaller effect on corrosion rate than the $S_2O_3^{2-}$ addition. It is interesting to note, however, that the nature of the corrosion product film is altered by the presence of a high concentration of thiosulfates. Perhaps the $NaFeS_2$ film is a less effective barrier to corrosion in white liquors than the more common FeS film that develops in the absence of thiosulfate.

Corrosion Monitoring

The results of the LP measurements of corrosion rate of carbon steel exposed to white liquor are easily understood in light of the corrosion processes described above. The LP method appears to be responsive to changes in the active corrosion rate, even though a (β/Z) correction is required for accurate corrosion rate prediction. As long as the corrosion process remains active, linear polarization provides a good estimate of the actual corrosion rate, provided the output of the LP instrument is modified to account for the actual (β/Z) values.

The empirically derived value of $(\beta/Z)^*$ that provides the best agreement with the average corrosion rate in all tests is ~18 mV. Although this $(\beta/Z)^*$ value can be rationalized in terms of independent anodic and cathodic Tafel slope measurements and oxidation state assessments based on corrosion

product analysis, the link between the empirical $(\beta/Z)^*$ value and the independent verification is tenuous. There is evidence from deposit analysis that both two- or three-electron events can occur, depending on the composition of the test liquor. The value of Z required for agreement between the empirical $(\beta/Z)^*$ and the actual corrosion rate is two, and this value does not appear to change depending on the likelihood of NaFeS_2 formation. Similarly, the measured Tafel slopes for specimens immersed in white liquor combine to give a (β/Z) value that agrees with the empirical value of $(\beta/Z)^* \approx 18$. However, the Tafel slopes must be determined with electrodes recently immersed in the white liquor; if the anodic and cathodic polarizations are delayed, the Tafelian behavior deteriorates as the deposited film thickens with increasing exposure time. Admittedly, the large-scale polarizations required to determine Tafel slopes are more likely to be affected by the presence of heavy films, and the Tafel behavior on film-free electrodes may indeed be representative of the corrosion processes on heavily filmed electrodes not subjected to large polarizations. However, it is difficult to reconcile the apparent agreement between dissolution kinetics on filmed and film-free electrodes.

The discrepancy between the actual corrosion rate on passivated steel surfaces and the rate determined by LP methods is certainly caused by liquor oxidation effects. Tromans [3] has shown that carbon steel in the passive range is covered with a protective oxide film that forms under the heavy sulfide deposits. This oxide film apparently impedes further dissolution while serving as an efficient electron transfer medium for oxidation of liquor species—presumably sulfides—on the electrode surface.

The evidence that liquor oxidation occurs at potentials in the vicinity of +100 mVSSS is convincing. First, the redox potential of noble metals resides at more or less the same potential as passivated iron, and the only oxidation reaction possible on gold involves redox reactions involving liquor species. Second, redox reactions involving polysulfide can be followed by the generation or removal of the characteristic yellow color of the polysulfide anions; this color can be created or extinguished by polarizing passivated steel electrodes several millivolts above or below the rest potential, respectively. Finally, Shoesmith et al [16] have shown by X-ray analysis and cyclic voltammetry that sulfide can be oxidized to elemental sulfur at potentials in the vicinity of the passive rest potential, as a precursor to formation of the polysulfide anion. Apparently, passive steel acts as a host for redox reactions, and the oxidation of liquor species masquerades as metal dissolution during linear polarization measurements at passive potentials.

Liquor oxidation does not appear to affect the accuracy of linear polarization at potentials where the carbon steel is actively corroding. Extrapolation of the Tafel slope for liquor oxidation on gold, for example, suggests that the current contributed by oxidation of liquor species at -240 mVSSS would be less than one $\mu\text{A}/\text{cm}^2$. Assuming gold is a more effective charge transfer surface than heavily filmed carbon steel at -240 mVSSS, this current density

limit on gold would be an upper bound to the corresponding current due to liquor oxidation on steel. This liquor oxidation would contribute less than 1 mpy to the apparent corrosion rate at active potentials of ~ -240 mVSS. Extrapolation of the linear portions of the anodic polarization curve in the passive range for steel suggests that the rate of liquor oxidation on steel is at or below the rate observed on the noble metal electrode. Consequently, the effect of liquor oxidation on apparent corrosion rates at active potentials is negligible, as is observed (Fig. 11).

Errors in the linear polarization method due to liquor oxidation effects are conservative; that is, the actual corrosion rate is below the estimated corrosion rate. Detection of circumstances where liquor oxidation can contribute to errors in LP measurement is simple, since significant errors arise from liquor oxidation only when the rest potential of the steel approaches +100 mVSS. The potential of steel electrodes versus the silver/silver sulfide reference electrode is easily determined with the three-electrode LP configuration, of course, and the linear polarization instrument used in this study could be programmed to provide frequent indications of rest potential during corrosion rate measurements. This potential measurement provided early warning when effects of liquor oxidation were likely to be significant.

The electrical resistance method of corrosion rate measurement also pro-

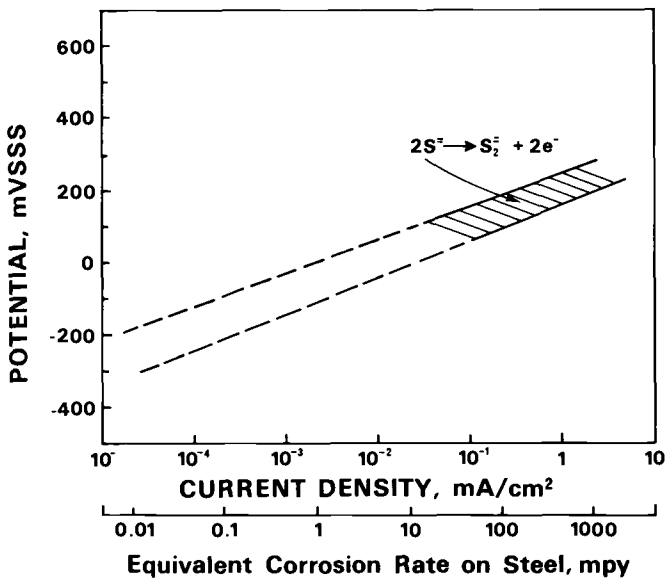


FIG. 11—Estimation of current (and equivalent corrosion rate of iron) resulting from oxidation of liquor species, based on extrapolation of Tafel behavior observed at high potentials.

vided accurate predictions of corrosion rate in a few simulated white liquors, including a liquor where oxidation affects the accuracy of the linear polarization method. In particular, artifacts in the ER method were not detected as a consequence of deposition of conductive films on the wire element. However, testing of the electrical resistance method was not as extensive in duration or scope as the evaluation of the linear polarization method, and the effects of fluctuating temperature, in particular, were not examined.

Thus, LP and ER methods both appear suitable for corrosion rate monitoring in white liquors, and each method has its advantages. The LP method provides a more rapid response (assuming reasonable lifetimes of ER probe elements), is immune to artifacts caused by temperature fluctuation, and also provides some indication of the electrochemical conditions accompanying the corrosion process. The electrical resistance technique will be advantageous where continuous immersion does not occur as, for example, at the liquid level line. Furthermore, the ER method does not require significant calibration or interpretation or both, particularly in liquors where oxidizing species are present. The output of the LP method is an actual corrosion rate, whereas the output of the ER method is an accumulated penetration that must be differentiated in time to determine a rate.

Conclusions

The following four conclusions result from this investigation:

1. Corrosion rates in simulated white liquors depend in a complex way on the concentration of major and minor species in the liquor. Thiosulfates and low levels of polysulfides accelerate the corrosion of carbon steel.
2. Linear polarization tests provide a good qualitative indication of corrosion rates in stagnant white liquor. Quantitative assessments of corrosion rate by linear polarization require empirical calibration of terms in the corrosion equation involving the Tafel constants and oxidation number.
3. Liquor oxidation will cause excessive corrosion rates to be measured by LP methods on carbon steel that is in passive condition. Liquor oxidation does not affect the LP measurement when steel is actively corroding.
4. Limited testing indicates that electrical resistance method is an accurate technique for monitoring corrosion rates of carbon steel exposed to simulated white liquor.

Acknowledgments

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Trouble-shooting Industrial Corrosion Problems with Electrochemical Testing Techniques

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ABSTRACT: Two case histories illustrate the use of simple electrochemical testing techniques for trouble-shooting corrosion problems in the chemical process industry. Simple electrochemical techniques that are within the capability of the non-electrochemical specialist are seen to be powerful tools for problem-solving. The measurement and interpretation of corrosion potentials, galvanic currents, and polarization curves, in particular, are presented. How these techniques are used by the production-support corrosion engineer and the researcher is seen to differ, because of their differing objectives and constraints. Accordingly, their work must be judged by different criteria.

KEY WORDS: electrochemistry, troubleshooting, polarization, case history, practical applications, galvanic corrosion, pitting, electrochemical potential, stainless steels, weld corrosion, localized corrosion, testing, corrosion testing

Electrochemical corrosion testing techniques have been used for many years by corrosion researchers. The use of these techniques in a production-support corrosion engineering function, however, remains uncommon. For the purpose of this paper, the author defines "production-support corrosion engineering" as activity carried out for the primary purpose of solving a specific corrosion-related problem that is connected with a manufacturing or related function. Typically, such activity centers on one specific question or problem at a time, time itself is of the essence, and the test results lead directly to some corrective action. Corrective action on a problem must often be taken within a certain time, and if the answer is not ready within that time, someone else's best guess prevails.

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Why electrochemical techniques are not widely used in the production-support function is a matter for speculation. It may be that many of the people performing this function have no training or background in the field of electrochemistry. Perhaps, with practically no mention in the literature of the use of electrochemical techniques in their job function, they presume that the techniques are not suitable for that application, or even that no one else is using them in that way. It may also be that many production-support corrosion engineers are intimidated by the apparent complexity of the techniques, and believe that they could not effectively use such complicated tools.

In fact, the techniques are not too complicated for use in the production-support function. Neither are they unsuited for that use because of inaccuracy or ambiguity. In fact, some features of these techniques, such as their speed and sensitivity, make them especially suited for production-support work. Engineers should not perform electrochemical testing on a cookbook basis, with no understanding of the meaning and limitation of the data. However, the typical production-support corrosion engineer who is willing to invest some time learning about the techniques is certainly capable of using these techniques to great advantage.

The following references provide a beginning for those who wish to do additional reading. Many basic concepts of electrochemistry in corrosion and how they relate to electrochemical testing can be found in Fontana and Greene [1] and in Chapter 3 of the NACE Basic Corrosion Course [2]. Greene [3] discusses experimental technique and equipment in detail. Additional guidance for electrochemical testing can be found in Shrier [4], Bond [5], Pleskov and Filimovskii [6], and Pickering [7]. Valuable information is also available from the following ASTM Standard Recommended Practices: Conventions Applicable to Electrochemical Measurements in Corrosion Testing (G 3), Conducting Potentiodynamic Polarization Resistance Measurements (G 59), and Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion (G 61). Numerous reviews of electrochemical techniques have been published [8–12], many of them with discussions of their uses and available instrumentation. The use of electrochemical techniques for many specific applications has also been treated in the literature. Topics include galvanic corrosion [13], alloy selection [14], application to aluminum alloys [15], detection of sensitization [16–18], measurement of pitting rates [19], and even coating evaluation [20]. Specific electrochemical test techniques and examples of their application to specific problems can also be found in the literature [21, 22, 25, 26].

The following case histories illustrate how even simple electrochemical corrosion testing techniques can be used effectively in the production-support job function. The discussion after the case histories considers how the use of these techniques and the approach to testing is fundamentally different for the researcher and the production-support corrosion engineer.

Case History No. 1: Rapid Pitting Failure of a Stainless Steel Tank***Background***

A used S30400 stainless steel (304 SS) tank was put in service to hold activated carbon for an absorber unit. A process stream containing approximately 5% sodium chloride (NaCl) and a small amount of dissolved organic was pumped through the tank. The process stream was approximately 20°C, and had a pH ranging between three and four. The tank was steamed out about once per week to remove the organics absorbed by the carbon.

One month after startup, the tank failed by pitting. As shown in Fig. 1, the tank had multiple pits scattered over the entire surface. There was no apparent corrosion outside of the pits. A 304 SS pump elsewhere in the same system showed no pitting attack. Production personnel speculated that the failure could have been caused by any of the following:

1. The tank, being used equipment, had pitted in previous service and was already in such poor condition that very little additional corrosion resulted in

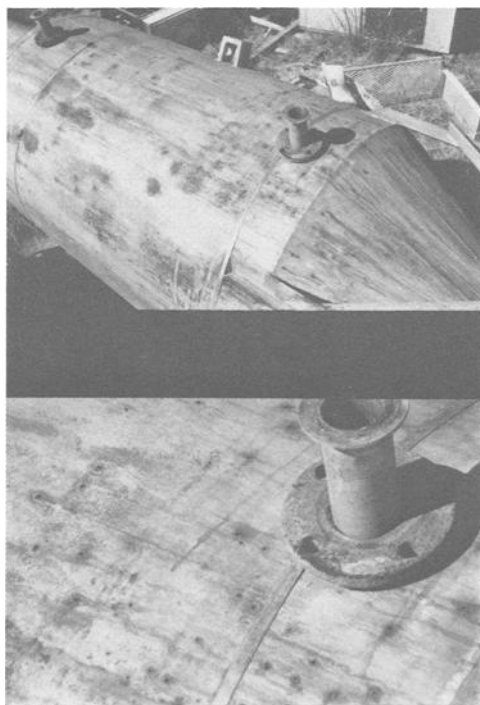


FIG. 1—AISI 304 stainless steel tank which failed by pitting after one month of service.

failure. This view was favored by plant personnel, and is supported by the very short service time and the fact that the pump had not corroded.

2. High temperatures during the steam cycle plus chlorides from the process stream caused pitting. This view explains why the pump did not pit (it was not steamed), but not how failure could have occurred in only one month.

3. Chlorides from the process stream and the galvanic effect of the carbon caused pitting, with sufficiently high penetration rates to cause failure after one month.

A test program was begun to determine why the tank had failed, and to guide us in deciding how to replace it.

Experimental Procedure

A series of electrochemical tests was planned to determine if the galvanic effect of the carbon could have caused pitting failure in only one month. A simple approach was planned which involves making a polarization (E -log i) curve for 304 SS in the appropriate solution, identifying the breakdown potential, and assuming that it is a reasonable approximation of the pitting potential. If the corrosion potential of the carbon/304 SS couple is more positive than the breakdown potential, then pitting under those conditions is highly likely.

Actual process solutions are often preferred for troubleshooting, but a synthetic solution was used in this case because it allowed us to avoid the logistical problems of shipping samples from a remote plant site. The synthetic process stream was 5% NaCl, made from reagent NaCl and distilled deionized water. The pH was adjusted to 4.0, as measured with a pH electrode. Chloride ion interference with the pH measurement was ignored here, as it was when the actual process stream pH was tested.

Activated carbon granules were used as an electrode in some tests. Containing the small granules (approximately 50 mesh) of activated carbon so that they could act as an electrode presented a problem. It was quickly and easily solved by a trip to the local discount store to buy nylon hose (knee-high, shear toe). Electrical contact was made with a pure carbon rod of the type used in arc lamps. The activated carbon granules raised the alkalinity of the water in which they were immersed to about pH 9. Prior to use in the pH 4.0 test solution, therefore, they were soaked in water adjusted to pH 4.0 until the pH remained stable at 4.0, which usually required about 24 h.

The following was done in preparation for all tests: The test solutions were boiled to remove dissolved oxygen, then cooled with an argon sparge; the 304 SS electrodes were abraded immediately prior to testing with 180-grit silicon carbide abrasive cloth, wiped clean with a paper towel, then rinsed with acetone. Polarization curves were done with an Aardvark V-2LR potentiostat and Model Scan-3 potential scanning unit. Galvanic currents were measured with an Aardvark Model PEC-AM zero resistance ammeter.

Results

Figure 2 shows the polarization curve for 304 SS in the synthetic process stream. The rapid increase in current density at $+50 \text{ mV}_{\text{Ag}/\text{AgCl}}$ results from the breakdown of the passive film, and is related to the pitting phenomenon. The potential at which the current density increases as in Fig. 2 is called the breakdown potential.

Corrosion potentials of 304 SS and activated carbon in the synthetic process solution were measured, and are shown in Table 1. Some scatter was observed in repeated measurements of different electrodes taken at different times, which is reflected in the table. The more positive potentials of the carbon show that, as expected, carbon is the more noble (that is, galvanically protected) member of the couple, and that 304 SS should corrode faster as the result of galvanic contact. The large potential difference, approximately 425 to 500 mV, indicates that the galvanic effect will be large.

Because the galvanic couple in the failed tank was between 304 SS and activated carbon, we wished to conduct the galvanic corrosion tests with activated carbon. Determining the surface area of activated carbon, however, presents a difficult problem. Upon considering the goal of this work, how-

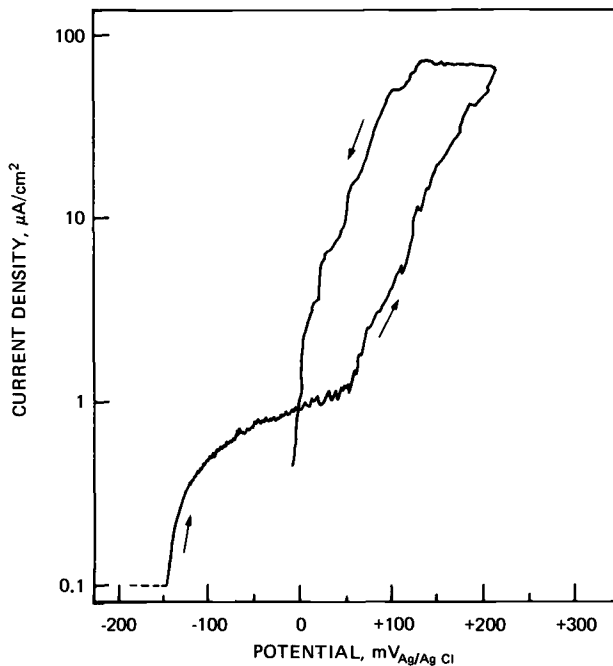


FIG. 2—Polarization curve for AISI 304 stainless steel in a synthetic process stream of Case History No. 1.

TABLE 1—Corrosion potential in the deaerated, 5% NaCl, pH 4 synthetic process stream.

Material	Potential, mV _{Ag/AgCl}
S30400 (304) stainless steel	−200 to −180
Activated Carbon	+290 to +298

ever, it becomes clear that we may handle the area-ratio parameter as a volume/area measurement instead, if we use the same type and size of activated carbon that was used in the failed process vessel. This is true because we are not concerned about true area ratios, only about area ratios relative to that which existed in the process vessel. We can express the area-ratio parameter in the process vessel as a ratio of volume of activated carbon to area of 304 SS. This value in the failed vessel was calculated to be approximately 30 cm³ of activated carbon per cm² of 304 SS. This same parameter of (volume/area) is used in the data from the galvanic tests with activated carbon.

For volume/area ratios of 0.6 to 28 cm³/cm², the potential of the activated carbon/304 SS couple varied from +180 to +290 mV_{Ag/AgCl}, and the galvanic current ranged from 42 to 624 μA/cm² of 304 SS area. The test series was stopped at a ratio of 28 cm³/cm² because a runner developed in the stocking which spilled the granules. The highest galvanic current density, 624 μA/cm² of 304 SS area, was measured at this (volume/area) ratio, which is very close to the ratio that existed in the failed vessel.

Discussion

Because the potential of carbon (especially activated carbon) is so much more positive than the breakdown potential of 304 SS, it is likely that a galvanic couple of the two would result in pitting of the 304 SS. Whether that actually occurs depends upon the area ratio of the carbon to the 304 SS. This is true because the potential of the galvanic couple depends upon the area ratio, and it is the potential of the couple (not of the carbon alone) which determines whether pitting will occur.

The results of the activated carbon/304 SS galvanic corrosion tests indicate that little carbon is required to cause 304 SS to exceed the breakdown potential. At a V/A ratio of only 0.6 cm³/cm², the couple potential is already highly positive. The actual V/A ratio which existed in the process vessel was approximately 30 cm³/cm². At a V/A ratio of 28 cm³/cm² (as close as we came to process conditions in our lab tests), the galvanic current density was 624 μA/cm² of stainless steel. Extrapolated to the process vessel, one calculates a galvanic current of 58 amps between the vessel wall and the activated carbon.

Galvanic current is *not* always approximately equal to the total corrosion current on the corroding member of a galvanic couple, because some signifi-

cant cathodic reaction could conceivably be occurring on the anode. In the case being considered here, however, the potential of the 304 SS is shifted sufficiently far positive when coupled to carbon that the cathodic reaction on the 304 SS is negligible, and the measured galvanic current can be considered a good approximation of the corrosion current. Using an approximate conversion from current density to mm/year of $1 \mu\text{A}/\text{cm}^2 = 0.010 \text{ mm}/\text{yr}$ for 304 SS, one calculates a corrosion rate of 6.35 mm/year (250 mpy), assuming that the corrosion is uniform.

The laboratory data and the failed vessel itself, however, show that the corrosion is not uniform, but pitting. Nearly all the corrosion current, therefore, is concentrated at the pits. Inspections of the failed process vessel and the 304 SS electrodes used in the lab tests show that a conservative estimate of the area covered by pits is that it is less than 10% of the total surface area. This makes the estimated effective penetration rate at the pits 63.5 mm/year (2.5 in. per year). At that rate, the 4.78-mm (0.188 in.) walls of the process vessel would begin leaking after only 27 days. The author is compelled to note that 27 days is much closer to the one-month service time than one can reasonably expect to get in this sort of work.

Based on this data, it was concluded that the vessel failure resulted from severe pitting corrosion induced by the combined effects of chlorides in the 5% NaCl process stream and the galvanic action of the activated carbon. It was also concluded that damage to the vessel from previous service was not a factor. High temperatures from the weekly steaming may have accelerated attack for a short time, but the weekly steaming does not have to be invoked as a cause of failure.

Case History No. 2: Premature Failure of a Steel Pipeline by Weld Corrosion

Background

After only three years of service, a 5.6-km-long ($3\frac{1}{2}$ mile) pipeline began experiencing a rash of leaks. The pipe was 10 cm (4 in.) in diameter, schedule 40 (6 mm thick), and met ASTM Standard Specification for Pipe, Steel, Black and Hot-Dipped, Zinc-Coated Welded and Seamless (A 53-78). Sections of the pipe were field-welded together with AWS E6010 weld electrodes. The pipe transports a slurry of small inorganic particles in a 20% NaCl brine at approximately 55°C. The slurry is not intentionally aerated, but contains dissolved air from the slurring process.

Sections of the pipe removed for inspection had the appearance shown in Fig. 3. The circumferential field welds between sections of pipe were found to be badly corroded. The pipe itself was also corroded, but not as much as the welds. Metallurgical cross sections confirmed the attack to be predominantly of the weld deposits, and not of the base metal or heat-affected zone (HAZ).

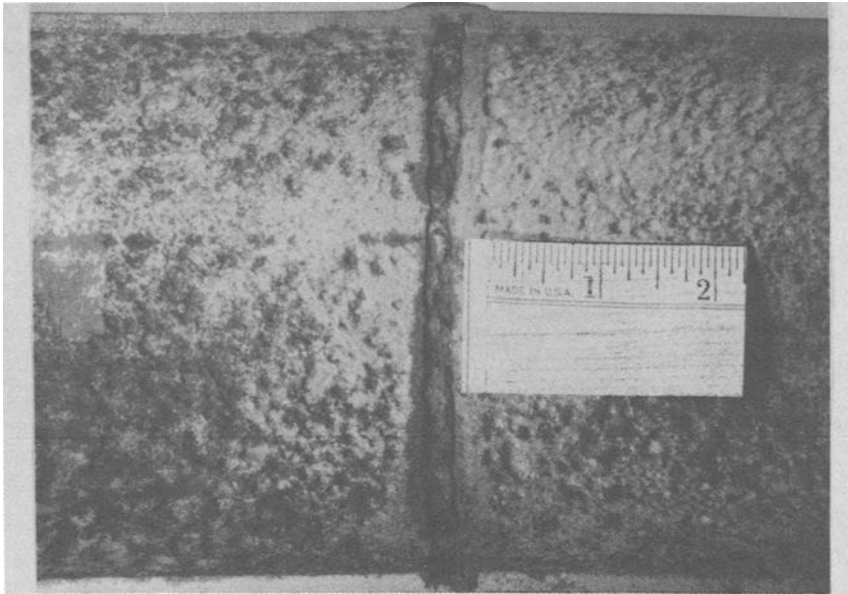


FIG. 3—Steel pipeline which failed after only three years of service.

The suddenness, severity, and frequency of leaks made repair or replacement of the pipeline an immediate problem. Production personnel needed to know the following as soon as possible:

1. Why did the pipeline fail?
2. How should it be repaired or replaced?

A series of laboratory tests were begun to answer their need. Electrochemical test techniques were chosen for their speed and ease of use. In-process coupons were prepared and installed concurrently with the electrochemical tests to provide confirmation (or denial) of the conclusions drawn from the laboratory tests.

Testing began with galvanic tests of the weld metal and pipe base metal, because the appearance of the pipe in Fig. 3 suggests that the weld metal had corroded preferentially to the pipe wall. Additional tests were planned based on the results of previous tests. In this manner, the entire test program described in this case history was eventually executed. As testing progressed, the following questions were posed, then answered with test data:

1. Is E6010 weld actually anodic to the pipe wall (that is, does it corrode preferentially)?
2. Is the galvanic effect sufficiently large to account for failure of 6-mm-thick (schedule 40) pipe after only three years?

Answers to these questions formed the basis for deciding whether to repair or replace the pipeline, and how to do so.

Experimental Procedure

A specimen of the slurry was obtained from the production plant for testing, and most of the solids were removed to facilitate testing. The solids are essentially inert under these conditions and do not participate in the corrosion process. The test solution was then subjected to the conditions specified for the tests. Unless otherwise specified, solution conditions were aerated, 55°C, and agitated with a stir-bar.

Test electrodes of E6010 weld deposit and A 53 pipe wall were cut directly from specimens of the failed pipeline, taking care not to include any HAZ or base metal in the E6010 specimen. Test electrodes of other weld materials, listed in Table 2, were made later by depositing the indicated weld material on a steel plate. The test electrode was then machined from the deposit, again taking care not to include any HAZ or base metal in the electrode.

Potential and galvanic current measurements were made with Aardvark

TABLE 2—Weld materials used in the investigation in
Case History No. 2.

Weld Designation	Characteristics ^a												
E6010	minimum 60-ksi ^b tensile strength; plain carbon steel; no chemical requirements												
E7016	minimum 70-ksi tensile strength; very low alloy content: Chemical Composition, max %												
	<table><tr><td>Si</td><td>Mn</td><td>Ni</td><td>Cr</td><td>Mo</td><td>V</td></tr><tr><td>0.90</td><td>1.25</td><td>0.3</td><td>0.2</td><td>0.3</td><td>0.08</td></tr></table> Mn + Ni + Cr + Mo + V = 1.5% maximum	Si	Mn	Ni	Cr	Mo	V	0.90	1.25	0.3	0.2	0.3	0.08
Si	Mn	Ni	Cr	Mo	V								
0.90	1.25	0.3	0.2	0.3	0.08								
E7010-G	minimum 70-ksi tensile strength; slightly higher alloy content: Chemical Composition, min %												
	<table><tr><td>Mn</td><td>Si</td><td>Ni</td><td>Cr</td><td>Mo</td><td>V</td></tr><tr><td>1.00</td><td>0.8</td><td>0.50</td><td>0.30</td><td>0.20</td><td>0.10</td></tr></table> indicated minimum of <i>only one</i> of the above elements is required	Mn	Si	Ni	Cr	Mo	V	1.00	0.8	0.50	0.30	0.20	0.10
Mn	Si	Ni	Cr	Mo	V								
1.00	0.8	0.50	0.30	0.20	0.10								
E8018-C2	minimum 80-ksi tensile strength; 3.00 to 3.75% Ni required												
INCO 182	alloy 600-type composition												
M1G 18	metal inert gas welding wire, with approximately 0.5% molybdenum												

^aFrom *Introductory Welding Metallurgy*, Appendix B, American Welding Society, 1968.

^b1 ksi = 6.894 MPa.

Models PEC-VM and PEC-AM meters, respectively. Degree of agitation was determined by the speed of revolution of a magnetic stir-bar, yielding a relative measure of velocity or agitation.

Results

Shown in Fig. 4 are the corrosion potentials of the six weld materials in Table 2, relative to the corrosion potential of an A 53 pipe specimen in the test solution. E6010 weld material is seen to be 30 mV anodic to A 53 pipe, while E7016 weld is near the potential of A 53 pipe. The other four weld materials are cathodic to A 53 pipe material by 10 to 60 mV.

Each weld material was galvanically coupled to A 53 pipe material with a zero-resistance ammeter, yielding the galvanic currents in Fig. 5. Only the E6010 weld was consistently anodic (that is, corroded preferentially) to the pipe, although the E7016 weld was sometimes anodic.

The effects of several variables on the galvanic current between A 53 pipe and E6010 weld were then evaluated. The effect of area ratio on galvanic current was evaluated by sliding long specimens of pipe in and out of the test solution through cut rubber stoppers. The results are shown in Fig. 6. Gal-

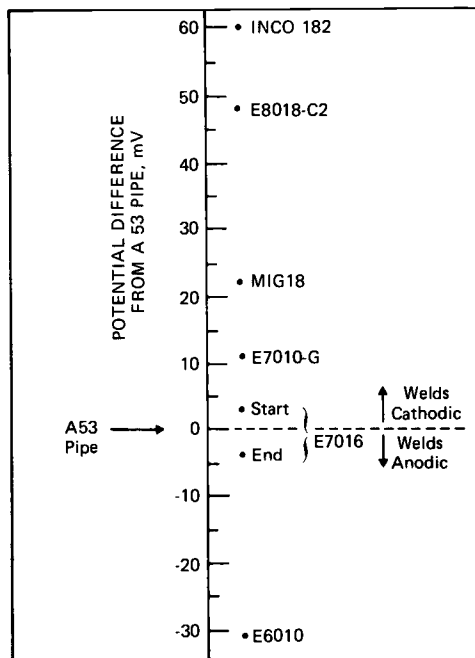


FIG. 4—Electrochemical corrosion potentials of six weld materials relative to A 53 steel pipe, in the process stream of Case History No. 2.

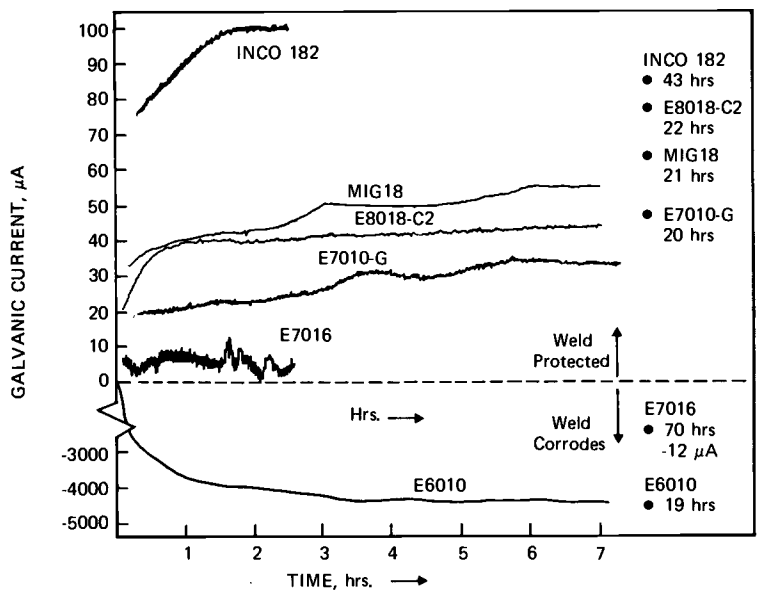


FIG. 5—Galvanic currents of six weld materials coupled to A 53 steel pipe, in the process stream of Case History No. 2.

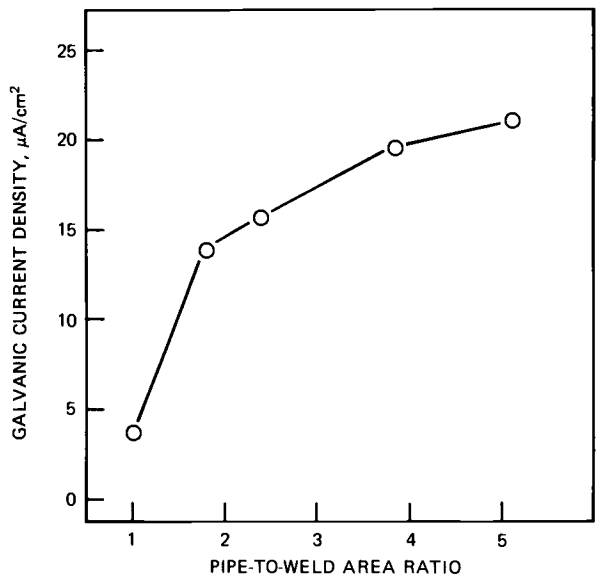


FIG. 6—Effect of pipe-to-weld area ratio on galvanic current density, for A 53 steel pipe and E6010 weld deposit, Case History No. 2.

vanic current increases steadily with increasing pipe-to-weld area ratio. The effect of agitation on galvanic current is presented in Fig. 7. This test, conducted at 50°C, shows a fairly strong dependence of galvanic current on agitation, and so also presumably on velocity. The actual velocity achieved in this test was not determined quantitatively, but was certainly well below the velocity in the failed slurry pipeline.

Discussion

The results in Fig. 4 support the contention that the E6010 welds in the pipeline corroded preferentially to the A 53 pipe, because E6010 is 30 mV negative to the A 53. This was further confirmed by the galvanic current data in Fig. 5, which show a stable galvanic current of approximately 4300 μA , in a direction indicating corrosion of the E6010. In the heat of the moment, unfortunately, the area of the E6010 electrode was not recorded, so that the data could not be converted to corrosion rates. These data, however, were sufficient to establish that E6010 does corrode preferentially to A 53 pipe in the slurry solution.

The question at that point became, "Could E6010 welds have galvanically

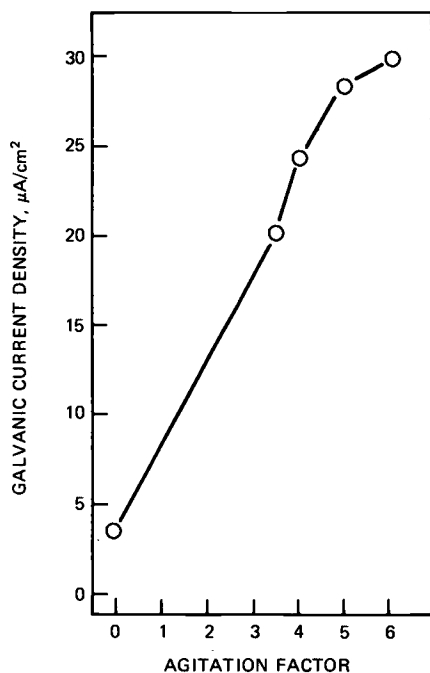


FIG. 7—Effect of agitation on the galvanic current density between A 53 steel pipe and E6010 weld deposit, Case History No. 2.

corroded fast enough to account for failure after only three years?" Thickness measurements of pipe specimens cut from the line indicated a corrosion rate of about 0.76 mm/year (30 mpy) for the pipe base metal. That rate can also be presumed to apply to non-galvanic corrosion of the weld material. Galvanic effects can be considered additive to that rate. Over three years one would expect to have lost 2.28 mm (0.090 in.) by nongalvanic corrosion. Because schedule 40 pipe is approximately 6.02 mm (0.237 in.) in thickness, the galvanic contribution must be 3.74 mm (0.147 in.) over three years, or approximately 1.25 mm/year (49 mpy). If one assumes that the galvanic current approximates the galvanic contribution to the overall corrosion rate, and that the average iron valence is 2.5 in the corrosion product, then one calculates that a galvanic current density of about $122 \mu\text{A}/\text{cm}^2$ is required if the pipeline failure is to be explained as the result of galvanic weld corrosion.

The data in Fig. 6 show that galvanic current increases as the pipe-to-weld area ratio increases. We find a current density of $21 \mu\text{A}/\text{cm}^2$ at a pipe-to-weld area ratio of 5 to 1. The actual area ratio in the four-inch pipeline is approximately 64 to 1, assuming that the root pass is 6.4 mm (0.25 in.) wide, and that the galvanic current is transmitted two pipe diameters down the line. The effect of agitation on galvanic current is strong, as shown in Fig. 7. The fastest agitation achieved in these lab tests with a stir-bar does not nearly approach the velocities in the pipeline.

The largest galvanic current density measured in the laboratory tests was approximately $30 \mu\text{A}/\text{cm}^2$, for an area ratio of 6.4 to 1 and stir-bar agitation. It was judged reasonable that this current density could be increased by four times to $120 \mu\text{A}/\text{cm}^2$ by changing to conditions existing in the pipeline. This involves greatly increased velocity and turbulence, and a pipe-to-weld area ratio that is increased by a factor of ten. The actual increase in galvanic current density is probably greater than four times, but a factor of four is sufficient to answer the question posed earlier. It was concluded that the E6010 welds did, by high probability, galvanically corrode fast enough to account for failure of the pipeline after only three years.

The question remaining at that point was how to repair or replace the pipeline. The answer to that question is found in Figs. 4 and 5. The ideal weld material should be slightly, but reliably, cathodic to the pipe wall. We would rely on the large pipe-to-weld area ratio to eliminate any significant galvanic corrosion of the pipe wall. Based on this criterion, E7010-G weld material was chosen for the weld on the new pipeline. (The old pipeline was determined to be beyond repair). E7016 weld material was usually, but not reliably, cathodic to the pipe wall, and was considered to be a poorer risk than E7010-G.

The suitability of E7010-G weld was further evaluated by monitoring its galvanic behavior as a function of factors which might change as the result of unexpected shutdowns or upsets. In particular, the effect of changes in temperature and aeration were evaluated. It was found that as temperature decreases to 22°C , the galvanic current decreases, but the weld remains stead-

fastly cathodic (that is, protected). As the temperature increases to 70°C, the current was found to increase as well, but it was judged that the favorable area ratio between the pipe and weld will mitigate any corrosion damage to the pipe. The effect of deaeration was similarly evaluated. Deaerating the test solution caused the galvanic current to reduce to very low levels, but not to change polarity. It was concluded that E7010-G weld is unlikely to be adversely affected by such upsets in the process. As a result of these conclusions, replacement pipe and E7010-G weld electrodes were ordered and preparations for replacing the pipeline were made.

A section of pipe containing the welds in Table 2 had been installed in the pipeline shortly after the laboratory tests had begun. The welds were placed two feet apart to reduce galvanic effects between them. Just prior to actually beginning the pipeline replacement, this test pipe was removed and examined. Although the test pipe had only been in several weeks, the results confirmed the conclusions of the laboratory testing. Replacement using E7010-G weld electrodes proceeded. The new pipeline is now starting on its seventh year with no failures.

Discussion

As mentioned at the beginning of this paper, the use of electrochemical techniques for production-support corrosion engineering differs in many ways from the use of these techniques for research. The case histories described above illustrate many of the differences. Specific differences and hints for using electrochemical techniques for production-support work are presented here with illustrations drawn from the case histories above.

Neither the electrochemical test techniques nor the instrumentation need to be complex to be useful. The high-impedance voltmeter and zero-resistance ammeter (ZRA) are simple instruments, relatively inexpensive, and easy to use. Yet they provide very powerful information. A ZRA and high-impedance voltmeter provided all the data necessary to determine the cause of the pipeline failure in Case No. 2, and determined the correct weld electrode to use as well. Instrumentation to generate polarization curves is more complex, but its operation is certainly not beyond the ability of the average engineer. The concepts involved in using the curves are basically simple: The passivation, breakdown, and protection potentials are approximate benchmarks against which one places corrosion potentials to gain information as to what type and degree of corrosion is to be expected. While one needs to have an understanding of electrochemical principles to guide him, the Stern-Geary equation does not have to be derived to use these techniques effectively.

A production-support corrosion engineer should be prepared to innovate in order to obtain good data that is relevant to the problem. An example from Case No. 2 is quickly and easily getting various pipe-to-weld area ratios by sliding long specimens of pipe in and out of a test solution through stoppers.

It is not sophisticated, but it is easy and effective. Using the volume of activated carbon as an effective measurement of electrode surface area is not what one normally finds in research work or journal articles, but in Case No. 1 it relates perfectly to the plant problem.

Information based on probability is often sufficient for action in production-support work. To strive for conclusive certainty in this activity is sometimes appropriate, but other times merely results in lost time and frustration. In Case No. 2, for example, the galvanic effect between the weld and pipe wall was probably large enough to explain the failure after only three years. To prove it conclusively for the actual pipe, weld, and process stream would be an exhausting ordeal. By the time it was accomplished, production personnel would have already been compelled to take action on the problem, even if it was the wrong action! Conclusions need to be rigorously supported in research work, but in production-support work conclusions are often appropriately based on probability and judgement.

Production-support corrosion engineers should not feel compelled to totally plan a test program before starting. It is often more effective to determine future test conditions and types of tests as one goes along, based on information as it is generated. In Case No. 1 for example, it was clear after seeing the large positive potential of the activated carbon/304 SS galvanic couple, that scratch tests (for pitting corrosion) would be unnecessary. In cases where the measured potentials are close to the breakdown potential, however, potentiostatic or scratch tests would be advisable. The entire direction of an investigation is often properly determined by the results of tests made along the way.

Because this activity involves working with a wide variety of materials and environments, which one may not be familiar with, it is important to be aware of what one is doing, and to be alert for the unexpected. The way activated carbon alkalinized the test solution in Case No. 1 was a subtle occurrence, but its effect was important. Even when it alkalinized only the solution in the nylon hose, the potential was shifted negative by over 200 mV, and the galvanic current was greatly reduced. Had that problem not been recognized, the conclusions would have been quite different. Computerized equipment and automatic test procedures are no substitute for alertness and understanding of the system. Subtle factors can have large effects, so it is important to be alert to what is happening in the tests.

It is often wise to conduct tests with solutions and specimens from the production area, rather than in solutions made from reagents. This helps to account for many unknown factors that may affect corrosion behavior and be part of the problem. An artificial slurry liquor could have been used in Case No. 2, but it was felt that using the actual slurry liquor would provide the best data for determining the correct weld electrode with which to repair the pipeline. There is always the danger, of course, that one's test specimen from the plant may be different in some obscure but important way from the material

that caused the problem. Accordingly, it is important to characterize the material as best one can if one suspects that there may be important differences. This can be a difficult part of the job, and is another reason why being alert, as discussed above, is so important.

Using specimens from the plant usually means that one's work will not be reproducible by workers in other laboratories, because they do not have access to identical materials. However, reproducibility of test results by other laboratories, which is so important in scientific research, is generally not important in the production-support function. Production-support testing and data must be of good quality, but it is not necessary to structure the tests such that other laboratories can reproduce them. Since the work normally applies only to a specific problem, outside laboratories rarely hear about the tests, and even more rarely wish to reproduce them.

Conclusions

Electrochemical techniques are powerful tools and can be used very effectively for production-support corrosion engineering. Relatively simple techniques can yield powerful information, even for those who are not specialists in electrochemistry. It is important to recognize that different standards must be applied to electrochemical testing done for production-support, and that done for research. This is because the goals, objectives, and constraints on each type of worker are entirely different. Because of these differences, the production-support corrosion engineer must approach electrochemical testing differently than a researcher would. Innovations and shortcuts that are properly frowned upon in scientific research may be the very things that make a production-support corrosion engineer particularly effective. Production-support corrosion engineers and corrosion researchers are all corrosion specialists, and electrochemical corrosion testing techniques are tools that, though used differently by each, are valuable to both.

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DISCUSSION

C. Ronchetti¹ and R. Rizzi¹ (written discussion)—We agree that the use of simple electrochemical measurements can lead to the solution of serious corrosion problems, but this is generally possible in the presence of a more or less clamorous design error only available upon data supplied by an "a posteriori" detection.

The more sophisticated methodologies for on-line corrosion control are useful on correctly designed and realized plants. These measurements help to check, during a correct management, the corrosion situations not easily eliminable or expected (cooling water pollutions, increasing condenser leakages, resin exhaustion, etc.), and they also contribute to increase the reliability and availability of the plants.

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E. L. Liening (author's closure)—I support the use of more sophisticated methods for corrosion monitoring and investigation in plants, whether the plants are correctly designed or not. The effective use of simple electrochemical techniques, however, is not limited only to cases of poor design or equipment failure. I have not attempted here to explore the entire range of simple techniques, or the variety of ways in which they can be used. However, they can be advantageously applied to a wide range of circumstances, including upsets and subtle changes in plant operation.

Paul Labine,¹ W. Norman,¹ D. King,¹ and J. Minalga¹

Techniques for the Evaluation of Cooling Water Corrosion and Scale Inhibitors in the Laboratory and at the Industrial Plant Site

REFERENCE: Labine, P., Norman, W., King, D., and Minalga, J., "Techniques for the Evaluation of Cooling Water Corrosion and Scale Inhibitors in the Laboratory and at the Industrial Plant Site," *Corrosion Monitoring in Industrial Plants Using Nondestructive Testing and Electrochemical Methods*, ASTM STP 908, G. C. Moran and P. Labine, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 307-313.

ABSTRACT: Polyphosphate based chemical treatment programs were evaluated in experimental cooling towers using linear polarization and potentiodynamic polarization techniques to monitor uniform corrosion and pitting corrosion rates. Correlations between laboratory and field corrosion rates are quite good. Relative heat transfer data indicate that two synthetic polymers are more effective than five phosphonates in minimizing calcium phosphate deposition.

KEY WORDS: corrosion, polarization, calcium phosphates, pitting corrosion

Linear polarization techniques have been used extensively for years for monitoring the effectiveness of various corrosion inhibitors for cooling water applications in the laboratory and in the field [1-11]. Although the general corrosion rates obtained from these linear polarization studies are quite useful, the measurement of pitting corrosion rates is even more important since most corrosion failures are caused by high pitting rates [2]. For this reason, pitting corrosion rates should be determined routinely. A technique that modifies conventional potentiodynamic scanning techniques has been used extensively by its developer R. Martin and his co-workers since 1978 to monitor pitting corrosion rates in the laboratory and in the field [1-8]. The pitting corrosion rates obtained by this technique correlate quite well with those obtained by microscopic examination of coupons from the same system [2].

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Minimizing the mild steel or admiralty general corrosion rates will usually minimize the pitting corrosion rates. Occasionally, extremely high pitting corrosion rates are measured even though the measured general corrosion rates are quite low. For example, two years ago, several potential corrosion inhibitors provided low mild steel general corrosion rates that were below 0.075 mm/year, but these corrosion inhibitors provided high mild steel pitting corrosion rates in excess of 2.5 mm/year [7,8].

Probes and electrodes used for linear polarization and potentiodynamic polarization studies were installed in corrosion test racks in corrosion test loops or experimental cooling towers, which were used for the evaluation of cooling water corrosion inhibitors. The corrosion racks, probes, and electrodes were identical to those used in the field [2], and the corrosion rates obtained in these units correlated quite well with those obtained in the field [5,6].

The effectiveness of various corrosion inhibitors is very dependent on pH, calcium levels, total alkalinities, and somewhat dependent on the temperature of the water and total dissolved solid levels [5]. The numerical values of these parameters can be converted to appropriate factors, which can be used to calculate the pH of saturation for calcium carbonate for natural waters. Ryznar developed an index that compared the measured pH to the calculated pH of saturation and qualitatively predicted the corrosivity of the water [12]. Recently, a modified Ryznar index was developed which compares the calculated pH of saturation to an equilibrium pH obtained from a total alkalinity versus pH chart [13]. Although this stability index is claimed to be the best predictor of scaling or corrosion conditions by its originator, the Ryznar index was found to be adequate to explain the results of our evaluations of a blend of a phosphonate, a low molecular weight polyacrylic acid, and a copper corrosion inhibitor in the Ryznar stability index range of 3.1 to 5.7 [5]. As predicted, the mild steel uniform corrosion and pitting corrosion rates increase as the Ryznar index increases [5].

Before 1980, nonchromate programs could not provide both corrosion and fouling control simultaneously as effectively as zinc chromate programs [10,11]. Since 1980, a few chemical treatment programs consisting of polyphosphate, calcium phosphate dispersant, and usually phosphonate and copper corrosion inhibitor have been found to provide corrosion and deposit control similar to zinc chromate programs [6,14,15]. Pitting corrosion rates were also comparable to those obtained with zinc chromate treatment programs [6].

The best calcium phosphate dispersants that were discovered during 1983 and were identified as Polymers A and B in a previous paper [6] were found to be superior to several phosphonates that will be reported in this technical paper.

The acrylate copolymer evaluated previously [6] is still one of the poorest calcium phosphate dispersants and provides poor uniform corrosion and pitting corrosion protection.

Experimental Procedure

The polyphosphate based chemical treatment programs discussed in this paper were evaluated by experimental cooling tower tests. Descriptions of the experimental procedures and system characteristics are presented below:

The values for the blowdown rate and system volume for these experimental cooling towers are 0.727 L/h and 40.0 L, respectively. The cooling water recirculates over the surfaces of 1018 mild steel electrodes, admiralty brass electrodes, heated 1018 mild steel tubes, heated admiralty brass tubes, heated stainless steel tubes, and a mild steel fouling monitor at a linear flow rate of 0.91 to 1.52 m/s (3 to 5 ft/s). Each experimental cooling tower is equipped with a corrosion test rack, deposit monitors, and a pH controller. A conductivity controller is used to control the blowdown and the syringe pumps that are used for chemical feed. The fouling monitor consists of a heated metal tube equipped with a thermocouple that measures the instantaneous skin temperature. The heat transfer rate can be controlled by a potentiometer.

Initially, 40 L of synthetic water is added to the tower basin. The pH of the basin is adjusted to the desired initial pH and the initial slug dosage of product is added to the basin. The basin water is then recirculated through the corrosion test rack, fouling monitor, the deposit monitors, and the cooling tower. The deposit monitor tubes can be preweighed in order to allow the determination of deposit weights and corrosion rates on the heat transfer surfaces by a procedure previously described [7,8]. However, fouling factor data and relative heat transfer rate data are considered to be more indicative of fouling control than relative deposit weight values. The chemical feed rate is proportional to the blowdown losses from the system.

During the experimental cooling tower tests, biocides are either slug fed or fed continuously. For instance, sodium hypochlorite solution may be fed continuously to simulate continuous chlorination. Bacterial activity is monitored by standard plate count techniques or by the use of microbiological test strips.

General corrosion rates are determined twice each day by linear polarization methods. Before terminating a test, the pitting rates are measured by potentiodynamic methods described previously [1,2]. Although previous laboratory work [1,2] utilized a silver-silver chloride (Ag-AgCl) electrode as a reference electrode, the reference electrode used in this paper is the probe body that is identical to the technique used for the determination of uniform corrosion and pitting corrosion rates in the field. The auxiliary electrode, the cathode, and the anode are essentially American Iron and Steel Institute (AISI) 1018 mild steel electrodes, which are degreased with xylene, rinsed with acetone, and sandblasted with Meramec Warrior WB-15 sand followed by rinsing with acetone. Admiralty brass electrodes were prepared for use by the same technique. The geometric surface areas of the mild steel and admiralty electrodes were 9 and 15 cm², respectively [2]. A typical industrial electrode holder is shown elsewhere [2], and typical potentiodynamic polarization curves are shown in previous technical papers [1-4].

Discussion of Results

Phosphonates vary considerably in their ability to disperse calcium phosphate and to maintain reasonable heat transfer rates. In a previous paper [6], general testing procedures were outlined for the evaluation of various calcium phosphate dispersants in a blend of a polyphosphate, calcium phosphate dispersant, a phosphonate, and a copper corrosion inhibitor. In this study, the initial phosphonate level was 5.0 mg/L as phosphate (PO_4) and the maintenance phosphonate level was 3.3 mg/L as PO_4 . These phosphonate levels were maintained in addition to the phosphonate levels already provided by the other phosphonate used in the product.

Details of the typical water composition are shown in Table 1. The new experimental data presented in Table 2 indicate that Polymers A and B can

TABLE 1—Composition of recirculating corrosion water.

Components	Water A
pH	7.0
Calcium as CaCO_3 , mg/L	450
Magnesium as CaCO_3 , mg/L	300
M alkalinity as CaCO_3 , mg/L	40
Chloride as Cl, mg/L	300
Sulfate as SO_4 , mg/L	1000
Silica as SiO_2 , mg/L	75
Total dissolved solids, mg/L	2024
Conductivity, $\mu\text{S}/\text{cm}$	3200
Ryznar index	7.9
Langelier index	-0.44
Water temperature, $^{\circ}\text{C}$	38

TABLE 2—Heat transfer rate control provided by blends containing polyphosphate + dispersant + HEDPA phosphonate + azole.

Rank	Polymer Description	Relative Heat Transfer Rate Data or %Uc Data During the First 6 Days	
		Low (e)	Average (e)
1	Polymer A	93	96
2	Polymer B	91	96
3	Phosphonate A	79	87
4	Phosphonate B	74	89
5	Phosphonate C	73	87
6	Phosphonate D	73	83
7	Phosphonate E	69	86
8	Acrylate copolymer ($M_w \sim 13\,700$)	62	71

NOTE: (a) Orthophosphate level as $\text{PO}_4 = 8\text{ mg/L}$. (b) Initial calcium phosphate dispersant level was 5 mg/L. Maintenance level was 3 mg/L. (c) Test length was 6 days. (d) M_w = weight average molecular weight obtained by size exclusion chromatography. (e) Error = $\pm 5\%$; initial value = 100%.

help maintain higher %*Uc* values (instantaneous overall heat transfer coefficient divided by the initial overall heat transfer coefficient times 100%) than all of the phosphonates reported in this paper. The acrylate copolymer, which has a weight average molecular weight of approximately 13 700, is still one of the poorest dispersants evaluated so far [6]. The difference in performance between Phosphonate A and Phosphonate E may not be significant in view of the expected error in %*Uc* of ± 5 for the low and average %*Uc* values.

The mild steel uniform corrosion rates presented in Table 3 indicate that only the acrylate copolymer provides higher uniform corrosion rates after six days. All of the other uniform corrosion rates are comparable to the 0.05 mm/year (2.0 mpy) or less corrosion rates obtained with zinc chromate treatments.

The mild steel pitting corrosion rates presented in Table 4 are generally comparable to the 1 mm/year (40 mpy) or less pitting corrosion rates obtained with zinc chromate treatments. Only Phosphonate E and the acrylate copolymer increased the mild steel pitting corrosion rates to unacceptable levels.

TABLE 3—Uniform corrosion rate on unheated mild steel probes during the first 6 days.^a

Polymer Description	Corrosion Rate, mm/year (mpy)			
	High		Low	
Polymer A	0.14	(5.4)	0.028	(1.1)
Polymer B	0.16	(6.3)	0.028	(1.1)
Phosphonate A	0.07	(2.8)	0.018	(0.7)
Phosphonate B	0.10	(4.1)	0.020	(0.8)
Phosphonate C	0.11	(4.2)	0.018	(0.7)
Phosphonate D	0.13	(5.1)	0.035	(1.4)
Phosphonate E	0.10	(4.1)	0.018	(0.7)
Acrylate copolymer ($M_w \sim 13\ 700$)	0.18	(7.1)	0.140	(5.4)

^aFor conditions see Table 2.

TABLE 4—Pitting corrosion rate on unheated mild steel probes after 6 days.^a

Polymer Description	Pitting Corrosion mm/year (mpy)
Polymer A	0.15 (6)
Polymer B	0.25 (10)
Phosphonate A	0.93 (37)
Phosphonate B	0.45 (18)
Phosphonate C	0.08 (3)
Phosphonate D	0.45 (18)
Phosphonate E	3.75 (150)
Acrylate copolymer ($M_w \sim 13\ 700$)	2.10 (84)

^aFor conditions see Table 2.

The admiralty uniform corrosion rates presented in Table 5 are acceptable for Polymer A, Phosphonates A, B, and D, and the acrylate copolymer. Additional copper corrosion inhibitor should be added to any formulations containing Polymer B and Phosphonates C and E.

The admiralty pitting corrosion rates presented in Table 6 indicate that most of the formulations containing these calcium phosphate dispersants provide adequate admiralty pitting corrosion rates below 0.125 mm/year (5.0 mpy).

In some cases, blends of dispersants will provide synergistic assistance in maintaining high heat transfer rates. A blend of dispersants was very successful in maintaining at least 80% of the initial heat transfer rate when the heat flux on the fouling monitor was 14 000 BTU/h ft² in a side stream test loop at a Gulf Coast gas plant where a flow rate of 0.9 to 1.5 m/s (3 to 5 ft/s) was maintained. The cooling water system consisted of a three cell induced draft cross flow cooling tower having a recirculation rate of 7400 gpm and a cooling

TABLE 5—Uniform corrosion rate on unheated admiralty probes during the first 6 days.^a

Polymer Description	Corrosion Rate mm/ylar (mpy)	
	High	Low
Polymer A	0.005 (0.2)	0.003 (0.1)
Polymer B	0.080 (3.1)	0.02 (0.9)
Phosphonate A	0.015 (0.6)	0.005 (0.2)
Phosphonate B	0.015 (0.6)	0.005 (0.2)
Phosphonate C	0.020 (0.8)	0.010 (0.4)
Phosphonate D	0.028 (1.1)	0.005 (0.2)
Phosphonate E	0.030 (1.2)	0.018 (0.7)
Acrylate copolymer ($M_w \sim 13\ 700$)	0.015 (0.60)	0.005 (0.2)

^aFor conditions see Table 2.

TABLE 6—Pitting corrosion rate on unheated admiralty probes after 6 days.^a

Polymer Description	Pitting Corrosion, mm/ylar (mpy)
Polymer A	0.005 (0.2)
Polymer B	0.025 (1.0)
Phosphonate A	0.113 (4.5)
Phosphonate B	0.088 (3.5)
Phosphonate C	0.105 (4.2)
Phosphonate D	0.125 (5.0)
Phosphonate E	0.025 (1.0)
Acrylate copolymer ($M_w \sim 13\ 700$)	0.05 (2)

^aFor conditions see Table 2.

water return temperature of 29 to 38°C (85 to 100°F). Both mild steel and admiralty metallurgy are present in the cooling water system. Skin temperatures ranged from 35 to 40°C (95 to 104°F).

In addition to obtaining excellent fouling control, mild steel corrosion rates of less than 0.025 mm/year (1.0 mpy) and admiralty corrosion rates of less than 0.0075 mm/year (0.3 mpy) were observed in this field trial. Even better results are expected with Polymer A or Polymer B.

Summary

1. The back scan technique used in this paper to determine the mild steel and admiralty pitting corrosion rates is a modification of the potentiodynamic scanning techniques and has been used extensively since 1978.

2. Polymers A and B provide excellent maintenance of heat transfer rates and minimize mild steel and admiralty uniform corrosion and pitting rates. Both polymers are more effective than Phosphonates A, B, C, D, or E and the acrylate copolymer.

3. Mild steel and admiralty corrosion rates and pitting corrosion rates, obtained with treatment systems incorporating most of the calcium phosphate dispersants, were comparable to those obtained with zinc chromate treatment programs. In some cases, high levels of copper corrosion inhibitor might be needed in order to minimize admiralty uniform and pitting corrosion rates.

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On-Line Monitoring of the True Corrosion Rate in Problems Related to Power Plants

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ABSTRACT: The know-how gained during corrosion studies performed for several years has enabled the authors' company to design and construct various probes for the measurements of the true corrosion rate in industrial plants. In some cases, for instance, the monitoring of steam condensers and of different circuits in thermal plants has been in operation for some years, now showing good reliability and usefulness.

Further developments have been made for use of the probes even under difficult working conditions, and the experimental results carried out on pilot loops propose such probes as a tool for a wider corrosion rate monitoring of different structural materials in different operating conditions.

KEY WORDS: corrosion probes, linear polarization resistance, corrosion rate, monitoring, on-line, instrumentation, corrosion, galvanic corrosion, coupling current, chemical treatment, steam condenser material, conventional and nuclear power plant, coolant, water

On-line monitoring of chemical and physico-chemical parameters is an on-going CISE program to upgrade the water chemistry in power plants. This program is expected to have benefits in the areas of system corrosion, material-coolant interaction, and corrosion product transport to get improved system operation. Of particular interest in these studies is the improvement of the analytical systems, which must supply exact information on different phenomena. Consequently, particular attention has been directed toward the development of extremely reliable on-line instruments that must provide continuous and highly accurate measurements.

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In order to provide adequate water impurity monitoring, ENEL (Italian Electricity Board) has committed a research program to CISE for the development of an analytical system, the instrumentation of which is commercially available. The main objective of this program is to provide a field test of an analytical system capable of detecting, recording, and working out the most common physico-chemical parameters and ionic impurities in the ppb range of concentrations. The system is designed for on-line sampling of power plant steam-producing water.

The measurements obtained with this instrumentation, however, are only indirect information on material corrosion, whereas the direct measurements of the corrosion rate give straight information on the anomalous behavior of the structural material [1].

Moreover, the need for continuous monitoring of corrosion rate prevents its evaluation through the specimen weight losses. Therefore, CISE has designed and constructed measurements cells allowing the direct evaluation of the corrosion rate [2-4] to be carried out by the electrochemical method of the linear polarization resistance [5].

This paper describes the performance of such cells and the results obtained from their applications in different fields of water chemistry in power plants.

Design Problems of Corrosion Probes

Systems capable of supplying the corrosion rate have been developed in recent years. Such systems make use of different methodologies and consist of a probe inserted in the plant component and of an instrument for conversion of the probe signal into corrosion rate.

It turns out that the corrosion rate measurements depend on probe and instrument performances. In both cases, good understanding of the phenomenon (as far as materials and chemistry are concerned) and good knowledge of the operating conditions of the plant are essential for the design.

The systems currently available on the market are unable to carry out reliable measurements either in high-purity water or in high-temperature and high-pressure conditions. These systems usually supply information on the environment aggressiveness and on its trend; only in simple cases do they supply the true value of corrosion rate.

Various approaches were explored at CISE to meet the required qualifications. The understanding of the corrosion phenomenon and of related parameters was gained during long-term research activities on both corrosion of different materials and chemistry of power plants [6-11].

The compliance with the hydraulic conditions on the electrode surfaces, often impossible using the current three-rod probe, is obtained using tubular electrodes, where feasible and necessary.

The problem of high resistivity is overcome by means of convenient development of commercial corrosimeters and by computer-aided design of the

probes, thanks to the availability of finite element computer models that permit in-depth understanding of potential fields and current vectors inside the probes [12-14]. Figure 1 shows a typical example. The same computer model permits one to assess the potential behavior of an electrode surface as a function of electrode length (Fig. 2), water conductivity (Fig. 3), and corrosion rate (Fig. 4), while holding the other parameters constant.

After defining the probe design parameters it is then possible to assess the behavior of the two values, which are basic for the consistency of the results, that is, measured and true polarization resistance ratio and maximum and measured potential ratio, as a function of the water conductivity and corrosion rate (Fig. 5).

Finally, a set of calibration curves, capable of supplying the true corrosion rate from the measured polarization resistance value, are plotted as functions of water conductivity under operating conditions (Fig. 6). The electric problems, such as streaming potentials and noises related to high water resistivity, are solved by a convenient geometry of the probe and by proper electronic adjustment at the corrosimeter inlet [11].

The most important improvement in the probe design is the use of five tubular electrodes electrically connected, as shown in Fig. 7. This almost eliminates the contributions related to streaming potentials and noises. Temperature and pressure problems are solved by using suitable insulator and gasket materials [6-8]. This approach is fundamental in overcoming the major limitations of the classic three-finger corrosion probes in the aim of obtaining "true" values of the rate of the generalized corrosion.

Further progress is expected in this field, allowing good results under increasingly complex geometric and environmental conditions to be obtained.

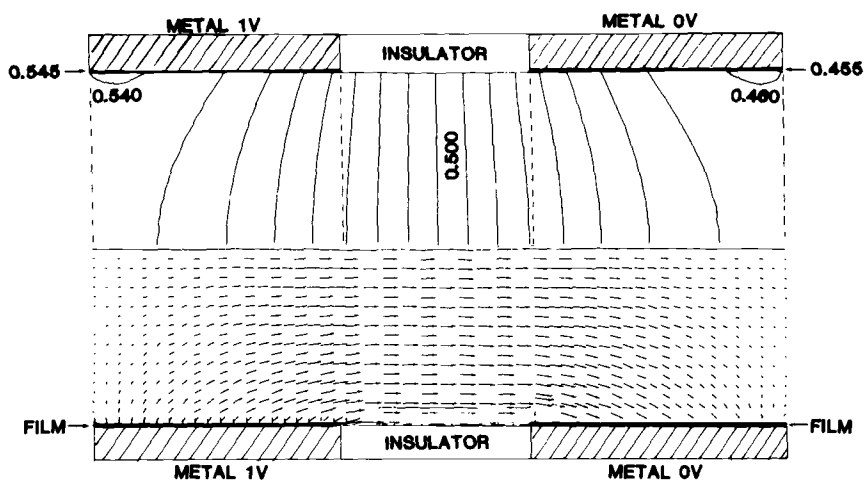


FIG. 1—Equipotential lines and current vectors for a metal with high corrosion rate.

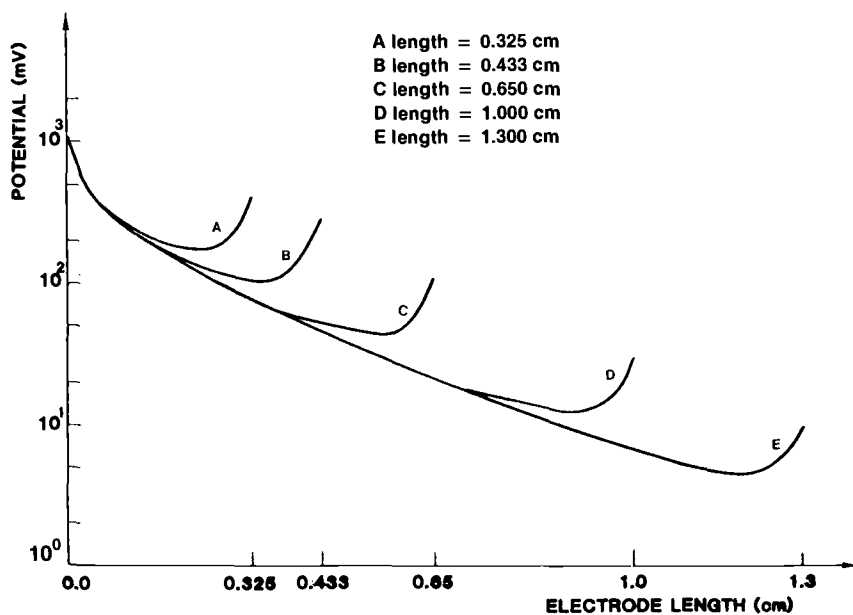
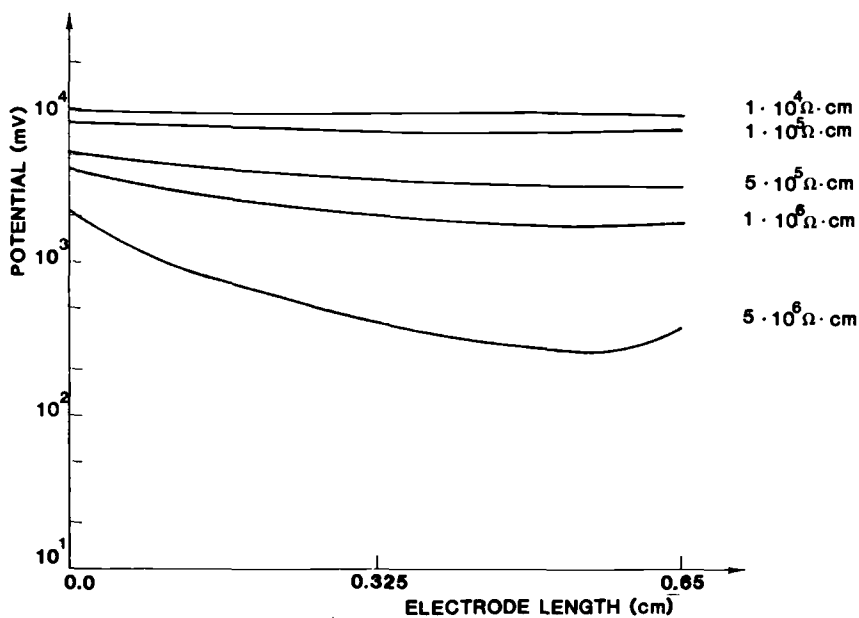


FIG. 2—Working electrode potential as a function of its length.

FIG. 3—Working electrode potential for several water resistivities ($k\Omega \cdot \text{cm}$) with the same corrosion rate (0.1 mdd).

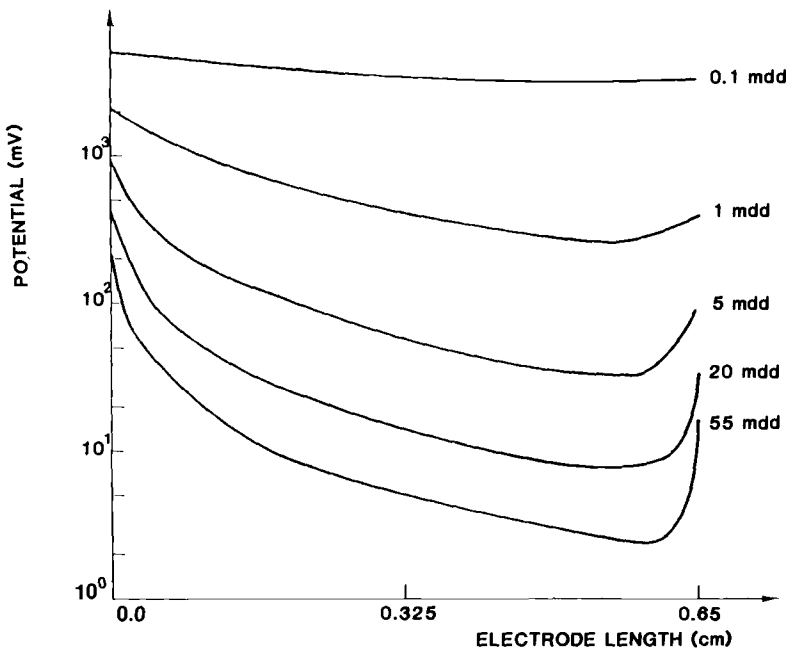


FIG. 4—Working electrode potential for several corrosion rate (mdd) with the same water resistivity ($5 \cdot 10^2 \text{ k}\Omega \cdot \text{cm}$).

Applications

Two of the different corrosion probe applications studied at CISE will be described in detail: the former, on steam condenser tubes, has been exploited for some years in power plants; the latter has been developed for use in arduous environmental conditions (high-water purity, high temperature, and high pressure). Other experimental applications will also be discussed.

Steam Condensers

In order to minimize the corrosion rate in copper-nickel and aluminum-brass tubes, used in seawater-cooled condensers, it is necessary to provide a good initial oxidation of the tubes [12,13]. Good cleaning of tubes before the first start-up and proper start-up procedures (for example, circulation of good quality water) usually produce a suitable protective film. During plant operations, the resistance of the protective oxide film depends on the water quality; few pollutants can in fact dissolve the film, thus greatly increasing the corrosion rate of the copper alloy tubes.

In both start-up and operation conditions, proper treatments (for example, ferrous sulphate addition and Taproge cleaning) are usually adopted to im-

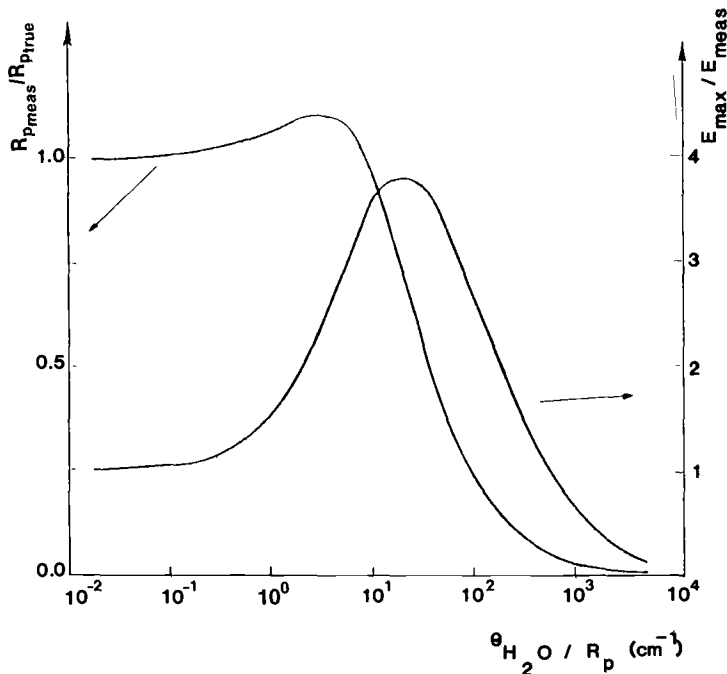


FIG. 5—Measured and true polarization resistance ratio, and maximum and measured potential ratio, as a function of the water conductivity and corrosion rate ratio.

prove the oxide film protectiveness and reduce the corrosion rate. The optimization of the treatments would be greatly improved by real-time checks on their efficiency.

To this purpose, on-line corrosion measurements cannot be carried out using the commercial three-finger probes because of the impossibility of simulating the effects of water and Taprogge ball velocities on them. To overcome such difficulties, "ad hoc" corrosion probes were designed and constructed; they were installed on the tube sheet at the tube outlets and constitute ideal extensions of the same tubes (Fig. 8) [11,15,16]. The probes were previously set up in a pilot plant and successively used in 160-MW power plant condensers.

The good agreement between measured corrosion rates and weight losses is shown in Fig. 9.

In addition to the water aggressiveness the CISE probes are also capable of detecting the actual corrosion conditions of the tube. Figure 10 compares the corrosion rates obtained by a probe set in an unconstricted tube and in a tube accidentally plugged. In the first case, the abrasive effect of the carborundum balls is evident as well as the successive good oxidation during the treatment with ferrous salts. In the second case, the anomalous condition of the tube is

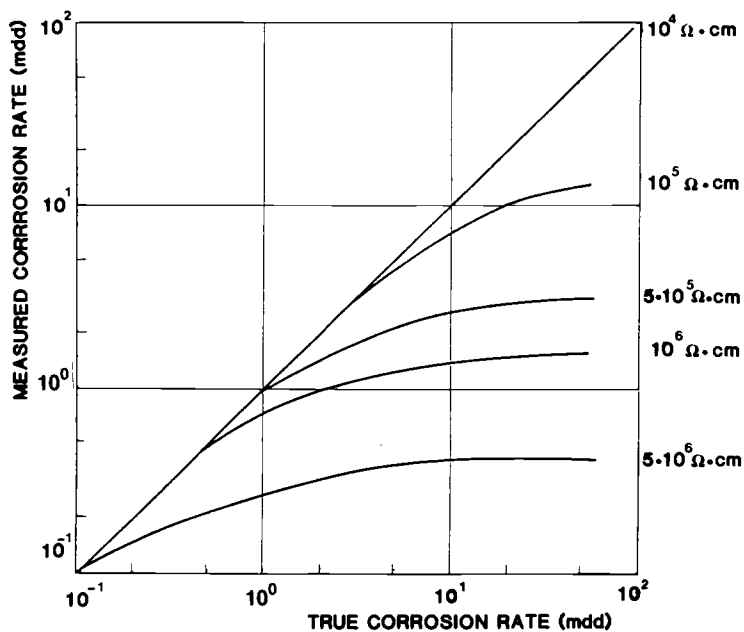


FIG. 6—Relation between the measured corrosion rate and the true corrosion rate for different water conductivity (electrode length 0.65 cm).

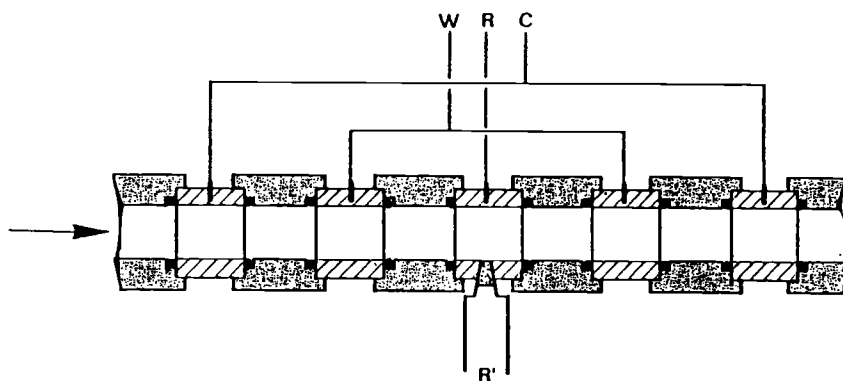


FIG. 7—Schematic view of the CISE high-temperature probe.

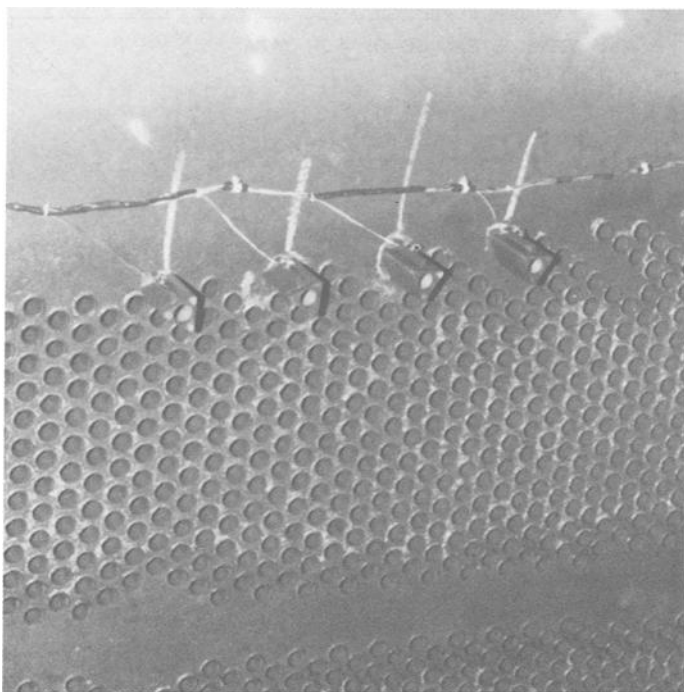


FIG. 8—CISE probe for condenser in operating conditions.

shown. As a matter of fact, the corrosion rate at start-up is lower, probably because of the presence of a soft passivation of the tube, whereas in the successive steps the corrosion rate rapidly increases, demonstrating the effect of poor hydrodynamic and oxidation conditions. During the first year of probe applications it was pointed out that the corrosion problems were ascribable to inadequate initial oxidation of the tubes. The optimization of mechanical cleaning and ferrous salt treatments supplied a satisfactory reduction in the corrosion rate and total weight loss.

Figure 11 reports two different water treatments in the case of 70-30 copper-nickel: it is evident that the latter treatment reduces the oxidation times by half, and therefore the metal thinning diminishes from 35 to 10 μm during the first 50 days.

The recent use of titanium and stainless steel as condenser tube material has led to galvanic corrosion problems in the tube sheet, usually made of less noble material.

In the frame of corrosion studies on condenser materials performed at CISE, corrosion probes were set up, capable of detecting the galvanic current behavior between two materials, while maintaining the typical hydrodynamic conditions of a condenser tube.

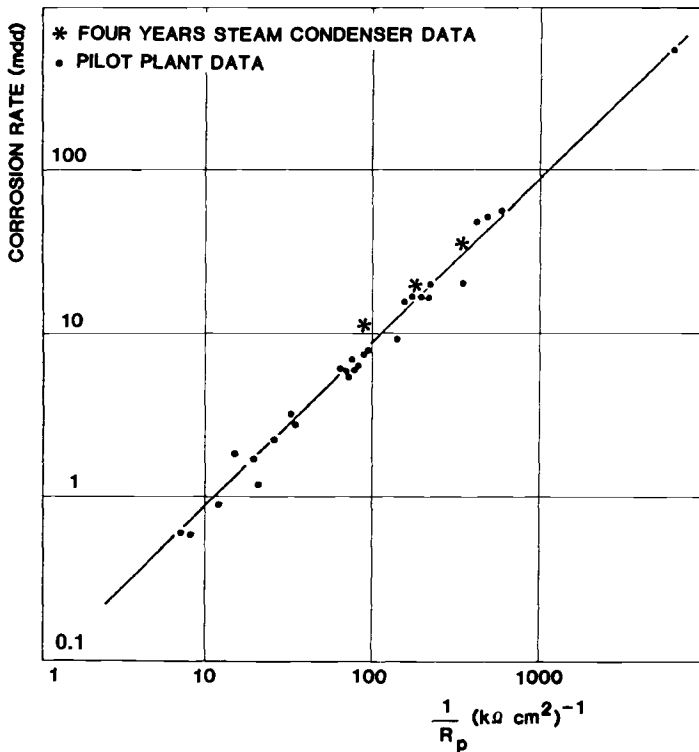


FIG. 9—Relation between aluminum-brass corrosion rates obtained by weight loss and by linear polarization resistance.

The probe, placed on the tube sheet at the outlet of a condenser tube, is made of shaped plastic so that it does not interfere with the water flow-rates in the tube and in the bordering ones; the probes house two tubular electrodes of the material under study.

Some characteristic behavior of coupling current, carried out in a condenser of an ENEL power plant (160 MW, fossil fuel), are shown in Figs. 12 and 13, where the effects of different chemical treatments and the material behaviors in stagnant water (first period) are easily noticed. As an example, Table 1 compares the corrosion rates relevant to Muntz metal calculated from coupling current integrals and from final weight losses. The agreement among different results is excellent because generalized corrosion is very low even if it is not measured by the experimental device.

At present five steam condensers, installed in three thermal power plants, with electric power between 160 MW and 320 MW, are being monitored using these probes. The first have been operating for six years. Since 1979 about

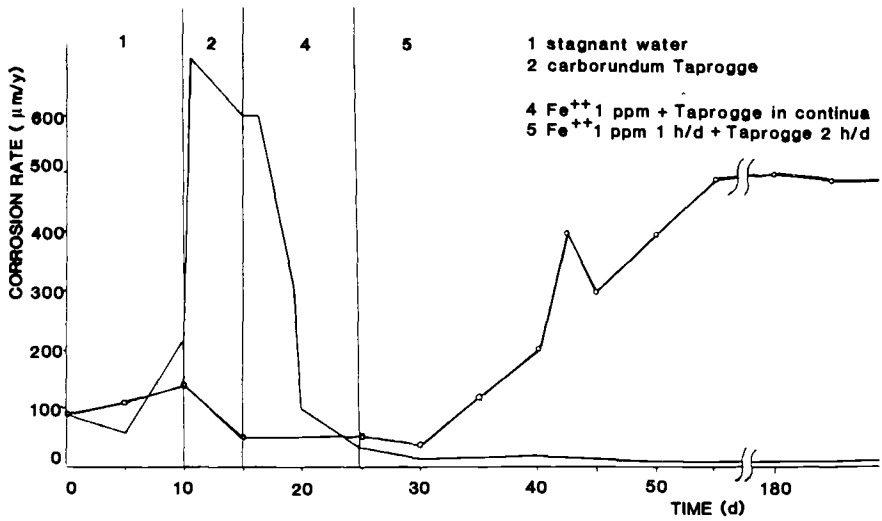


FIG. 10—Different corrosion rates obtained by a copper-nickel 70-30 probe set in a free tube and in a tube accidentally plugged by a Taprogge ball.

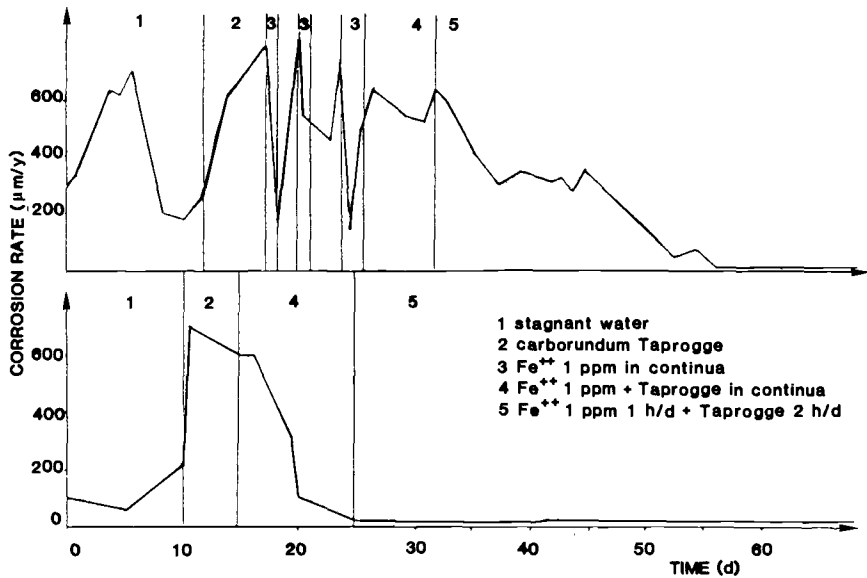


FIG. 11—Corrosion rates obtained by a copper-nickel 70-30 probe in two different start-up treatments.

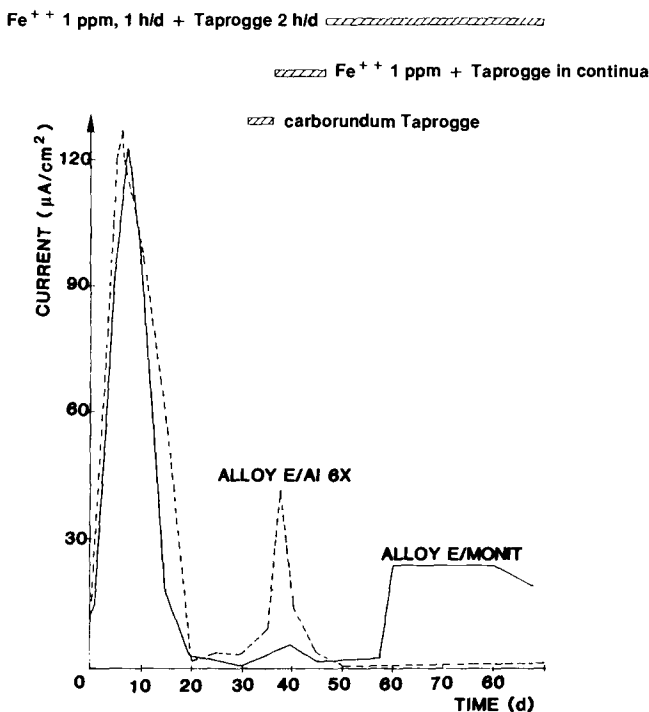


FIG. 12—Coupling currents carried out in a power plant condenser between tube sheet (Alloy E) and tube (Al 6X, Monit) material.

70 probes have been installed, and the first of them are still successfully operating.

High-Purity Water in High-Temperature and High-Pressure Conditions

Until now, the use of the CISE probes for the measurement of corrosion parameters in very pure water has been carried out only on experimental loops working in high temperature and pressure conditions (Fig. 14) [6-9], but the application on power plants is being planned. At CISE such experimental loops are used in the physico-chemical conditions typical of steam-water loops of nuclear and conventional power plants. It is thus possible to assess and characterize the corrosion of different materials, carbon and low-alloy steels in particular, and to deepen the understanding of the effect of the most significant chemical and physico-chemical parameters. Information on the good behavior of structural materials and on water aggressiveness was already obtained by corrosion potential measurements (Fig. 15).

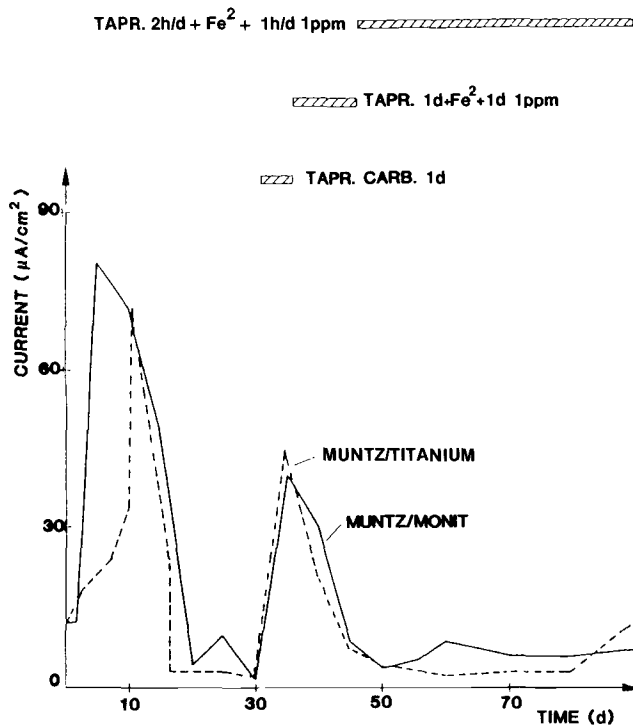


FIG. 13—Coupling currents between tube sheet (Muntz metal) and tube (titanium, Monit) material carried out in a power plant condenser.

TABLE 1—Muntz metal corrosion rate comparison.

	Corrosion Rate, $\mu\text{m}/\text{year}$	
	Weight	Couple Current
Muntz/Al 6×	293	217
Muntz/titanium	664	586
Muntz/Monit	84	82

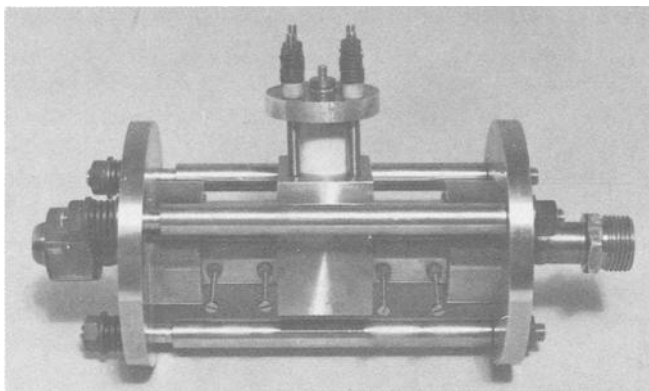


FIG. 14—High-temperature and high-pressure test section for corrosion rate measurement.

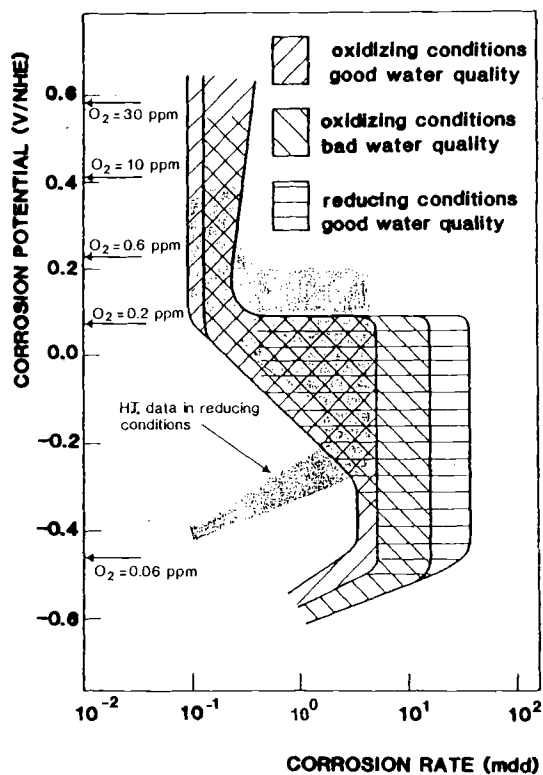


FIG. 15—Corrosion rate of the carbon steel as a function of corrosion potential in different operating conditions.

Much more important turned out to be the possibility of direct measurement of the corrosion rate of the materials in different parts of the loop. As an example Fig. 16 shows the behavior of the corrosion rate measured during a corrosion run of carbon steel in basic reducing conditions at high temperature. The figure clearly shows the initial transient due to the steel oxidation process and the further decrease of the corrosion rate one month after a chemical improvement.

The monitoring system proved that it can promptly detect the possible difficulties in the passivation process and the effect of water purity change (Fig. 17).

Corrosion rate measurements in oxidizing conditions prove that carbon and low-alloy steels comply with the corrosion law

$$\Delta W = k_1 t_1^n + k_2 t_2$$

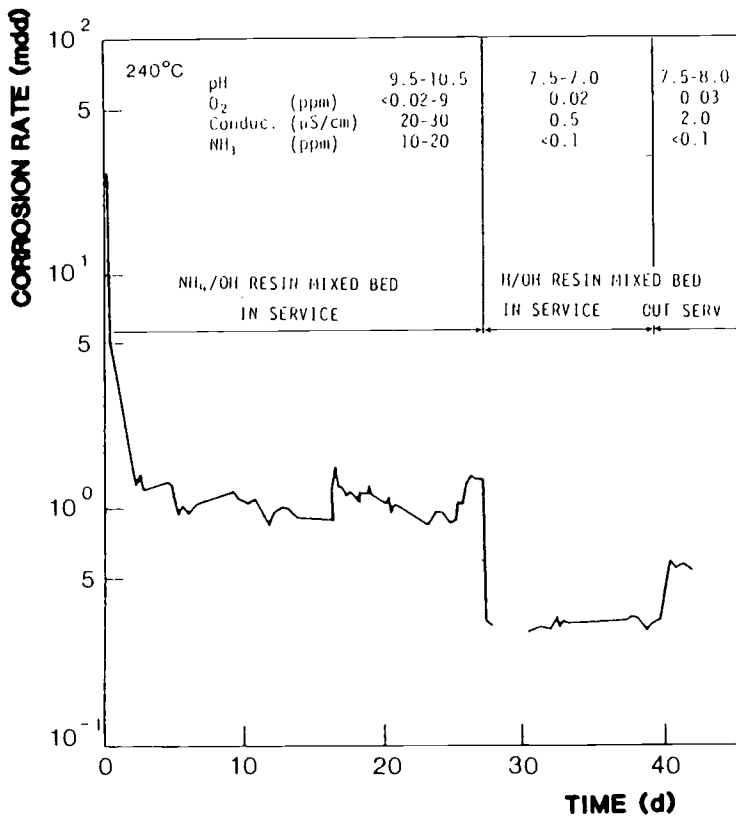


FIG. 16—Corrosion rate of the carbon steel during a corrosion run.

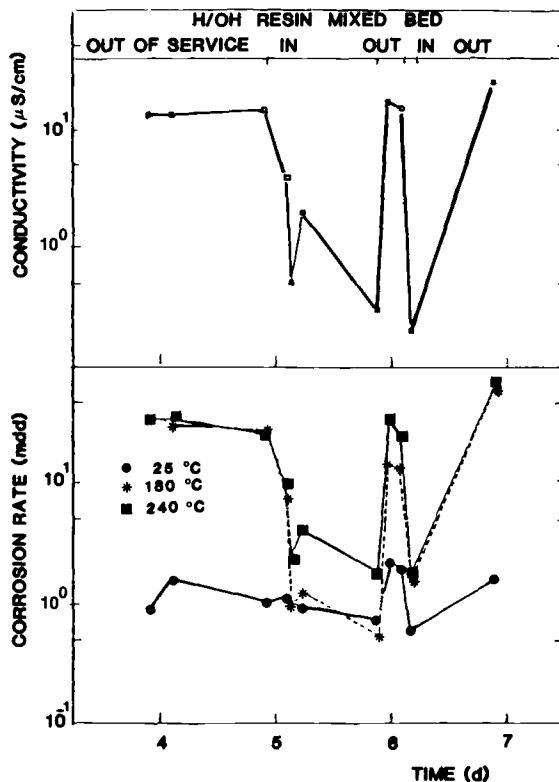


FIG. 17—Corrosion rate transient during a corrosion tests as a function of the water conductivity.

During t_1 time an oxide layer grows, whose protective characteristic controls the corrosion rate during t_2 time.

The tests demonstrate that the most important parameter is the water quality (cationic condition $< 0.5 \mu\text{S/cm}$), even if high oxygen concentration can partially balance the bad water quality, and that a protective oxide, grown in a good chemical conditions, can endure significant water quality worsening for a few days [9]. The most interesting results, relevant to the corrosion rate of carbon steel measured in different operating conditions, are compared in Fig. 18 with the literature data. Taking into account the relative experimental simplicity of the performed electrochemical measurements, the agreement can be considered good.

Different from the results presented by other authors [17], those obtained at CISE (Figs. 19 and 20) show that a first passivation step, followed by a nearly constant corrosion step, is also present in reducing conditions. A be-

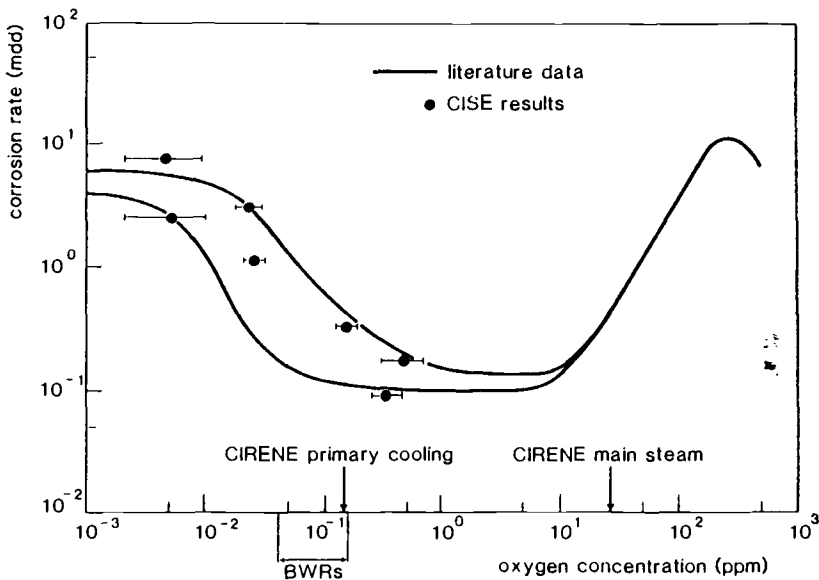


FIG. 18—Corrosion rate of the carbon steel in oxidizing conditions compared with literature data.

havior in agreement with the literature data was obtained for bad water quality (ammonia plus 5 to 10 $\mu\text{S}/\text{cm}$ of cationic conductivity) and for low oxygen concentration (<0.01 ppm); however, this should simply mean a longer passivation time, a high corrosion rate which means a lower error in the weight loss measurements.

Finally, analyses of the corrosion tests show that significant results are obtained from a few short corrosion runs, in comparison with those published by other authors, which require several different duration tests to obtain the corrosion rates from the weight losses.

Other Applications

On the basis of the theoretical and experimental data relevant to the applications previously mentioned, probes for the monitoring of other systems were developed: cooling circuits both in the presence and in absence of corrosion inhibitors or other additives to reduce water aggressiveness; acid cleaning of circuits; decontamination processes; etc.

Corrosion Control in Cooling Systems—Corrosion phenomena in cooling systems of thermal plants depend on local physical conditions (flow-rate, pressure, temperature, etc.) and water quality [16].

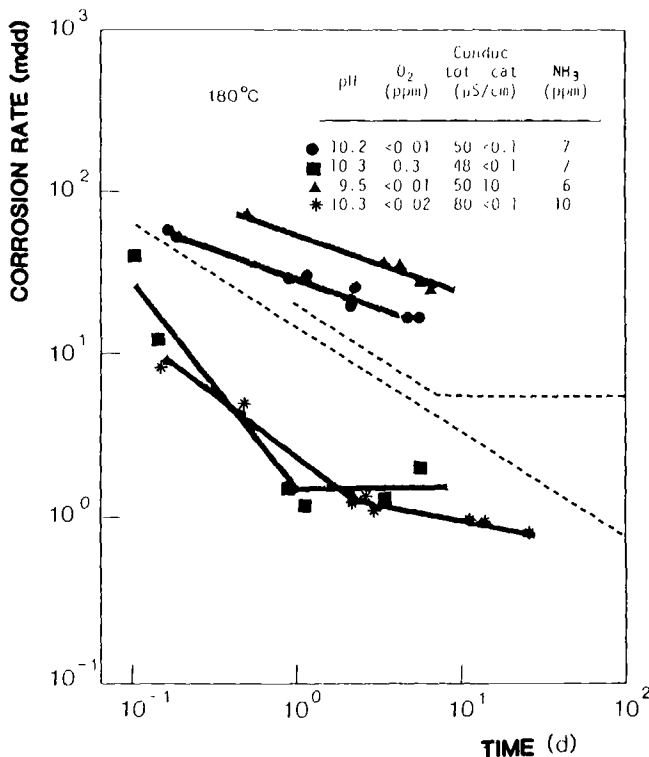


FIG. 19—Corrosion rate of the carbon steel at 180°C in reducing conditions compared with literature data (dotted lines).

For cooling system loops, a chemical water treatment is performed in order to control scale formations, corrosion processes, and biological fouling. Such loops are usually realized by nonprotected mild steel pipes, which rely on anti-corrosive treatment for their preservation.

The need for correlating water corrosiveness with chemical treatment procedure requires an automatic control of water treatment in order to timely detect possible wrong treatments, check the expected corrosion rate, compare the effectiveness of the different corrosion inhibitors, and optimize their dosage (Fig. 21).

In recent years CISE was asked to collaborate on the correct application of the linear polarization resistance method for corrosion rate measurements in cooling system loops. During different tests the carbon steel behavior was studied as a function of various parameters such as conductivity, pH, presence of chemical impurities, and addition of inhibitor, chelant, and complexing agents. Figure 22 shows the good correlation obtained between integrated

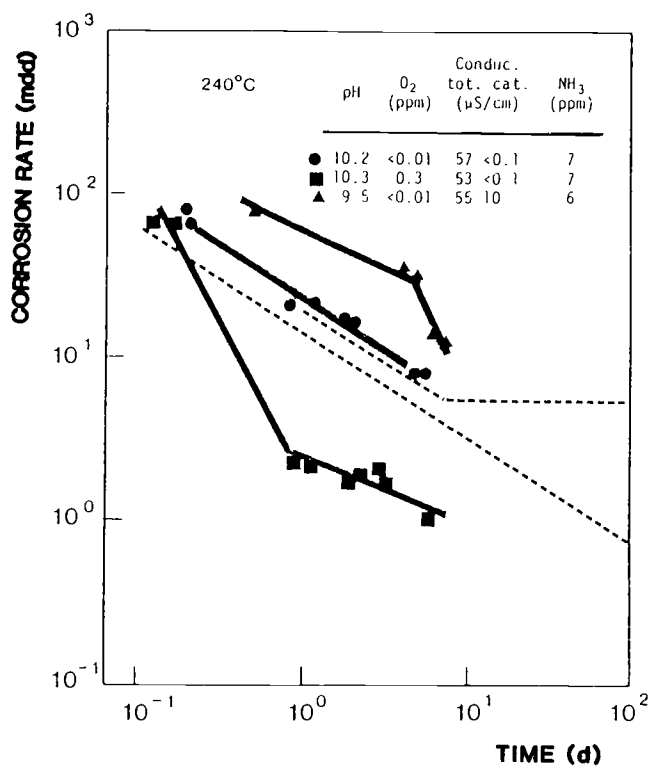


FIG. 20—Corrosion rate of the carbon steel at 240°C in reducing conditions compared with literature data (dotted lines).

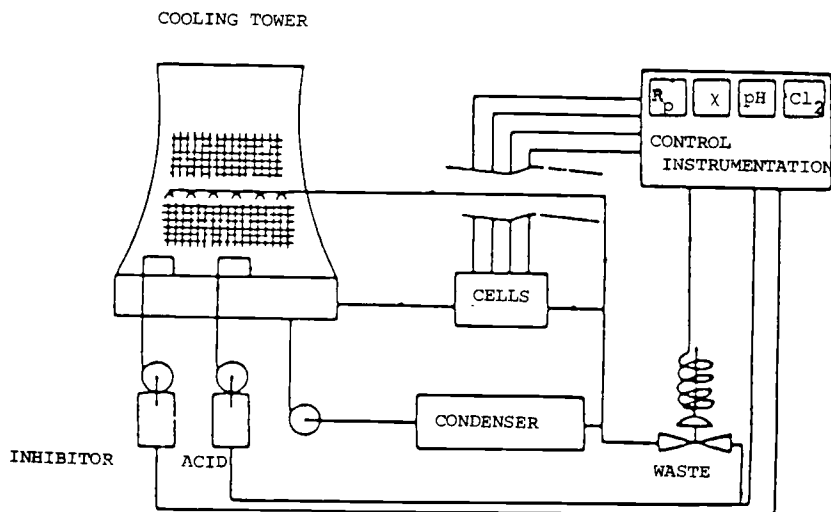


FIG. 21—Plan for the automatic control of cooling water treatment in tower loop.

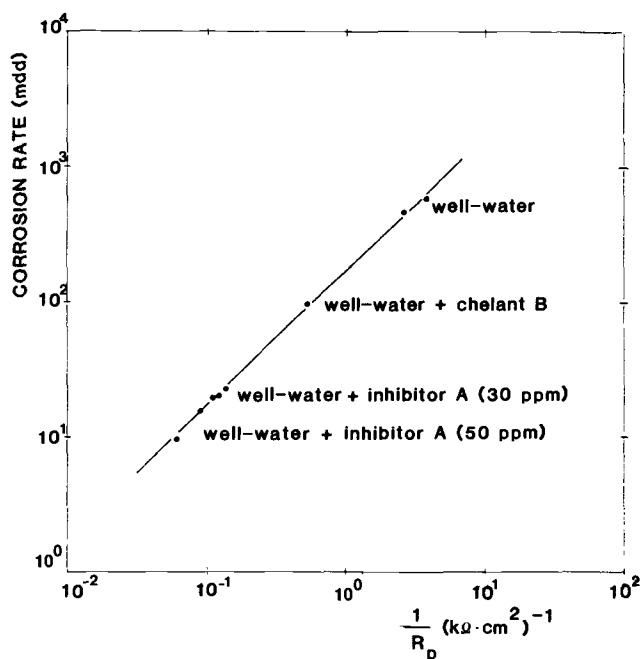


FIG. 22—Correlation between integrated and weighted corrosion rates for well-water with different inhibitor agents.

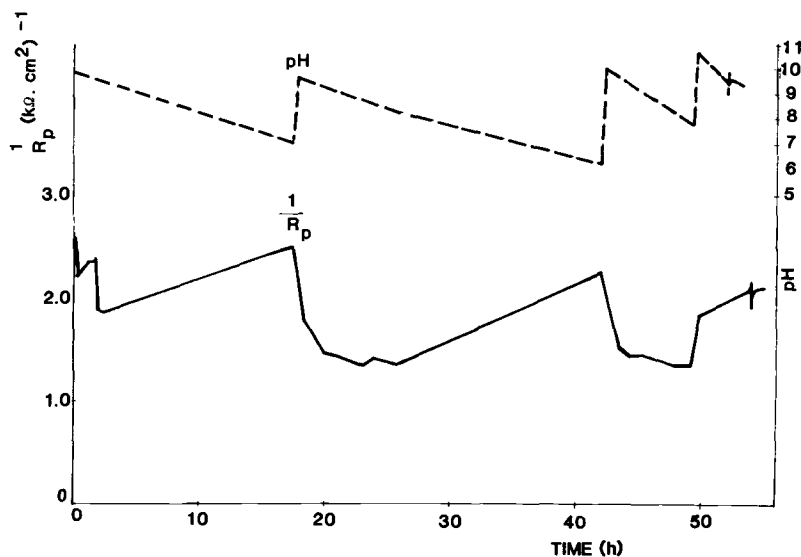


FIG. 23—Corrosion rate and pH behaviors during a corrosion test in well water containing chelant agent.

and weighted corrosion rates for well-water with different inhibitor and chelant agents.

In addition, measurement probes proved to be capable of following the corrosion rate behavior due to worsening of water chemical conditions. Figure 23 shows the corrosion rate increases corresponding to the pH decreases which move the water from a scaling to a corrosive condition also related to the particular added chelant.

Decontamination Processes—One of the main research activities of the CISE Material Department is the reactor system decontamination for dose-rate control on out-of-reactor surfaces and for decommissioning purposes [18–22].

The reagents, both soft and hard acid solutions, were tested on an “ad hoc” experimental loop in dynamic conditions, simulating a real *in situ* procedure of the decontamination process. Probes providing the direct evaluation of the dissolution/corrosion rate were used (Fig. 24).

The latest results, already presented in part at other conferences, show the usefulness of electrochemical measurements for monitoring the decontamination process, with the aim of providing a selective oxide dissolution. In fact, the linear polarization resistance can be a good signal of the radioactivity re-

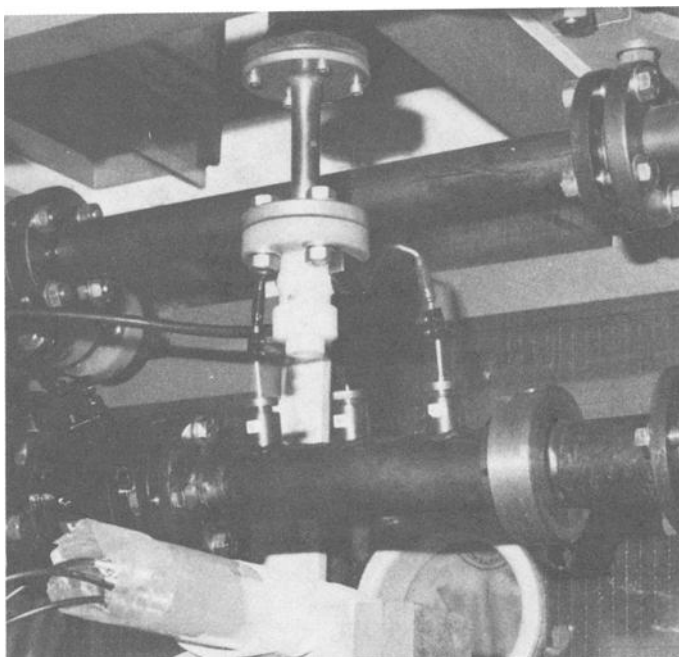


FIG. 24—Electrochemical test section on DECO loop for decontamination rate measurements.

moval. This is clearly shown by the example reported in Fig. 25, where the radioactivity behavior of a 5.08-cm (2 in.) steel tube is reported together with the linear polarization resistance obtained in a decontamination run. During the first step, when $1/R_p$ is low because of the presence of a compact oxide layer, the radioactivity progressively decreases; however, during the second step the corrosion rate becomes equal to that of the steel, while at the same time radioactivity falls to background values.

The corrosion rates measured by the probes are correlated with those obtained from the specimen weight losses (Fig. 26). The position of the experimental points in the middle of the figure between steel and oxide curves appears most significant. In fact, the dissolution mechanism takes place following the oxide reduction process and metal corrosion. In this case, the dissolution rate evaluation is, at least, inaccurate, owing to the difficult evaluation of the partial contribution of the two dissolution processes.

In decontamination processes, in addition to the corrosion rate value, the CISE probes are capable of detecting the actual dissolution/corrosion condi-

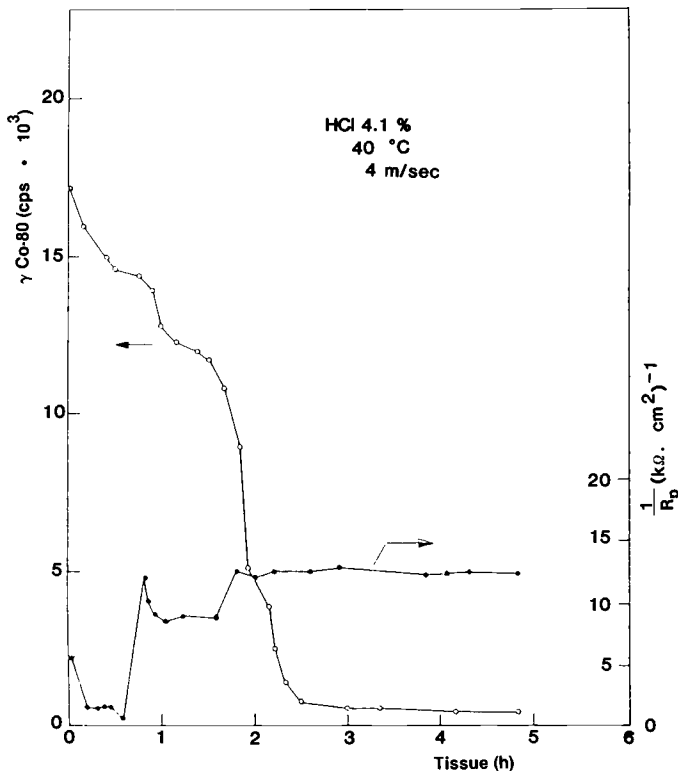


FIG. 25—Radioactivity and linear polarization resistance during 5.08-cm (2-in.) primary tube decontamination on DECO loop.

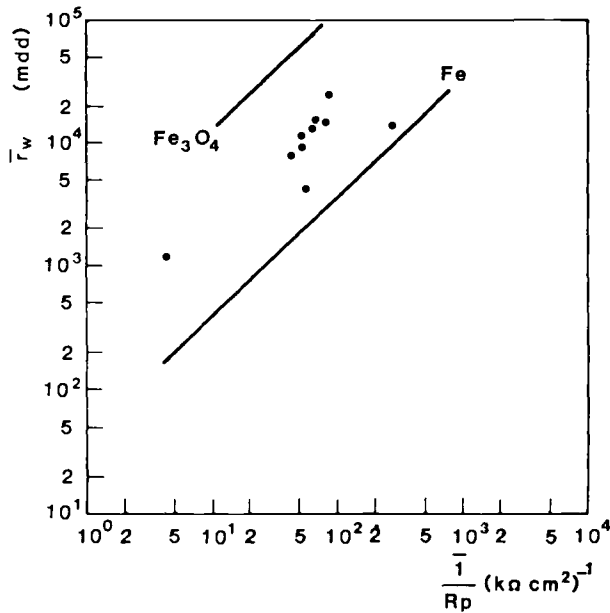


FIG. 26—Comparison at 90°C between linear polarization resistances and corrosion rates obtained by weight losses of oxidized carbon steel specimens. Fe and Fe₃O₄ straight lines are relevant to integrated corrosion rates obtained using the average Stern and Geary constants for non-oxidized carbon steel and magnetite electrodes.

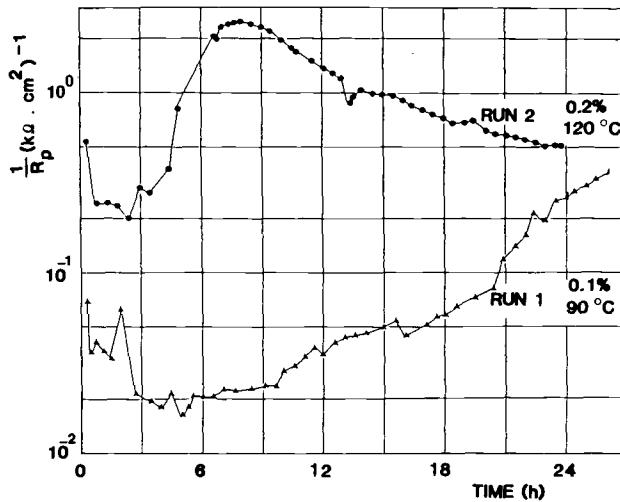


FIG. 27—Corrosion behaviours of a 5.08-cm (2 in.) stainless steel tube obtained using a commercial soft decontamination procedure in two different operating conditions.

tions. Figure 27 shows the behavior of a 5.08-cm (2-in.) stainless steel tube, obtained using a commercial soft decontamination procedure in two different operating conditions. The tube is a part of the primary circuit of an ENEL nuclear power plant (150 MW). The results are in good agreement with the obtained decontamination factors, and reflect the on-line radioactivity behavior.

Finally, Fig. 28 shows the effect of different amounts of the corrosion inhibitor (Rodine 31A), and Fig. 29 shows the effect of the solution flow rate in the decontamination tests performed on 5.08-cm (2-in.) carbon steel tubes removed from the in-pile CART loop after CIRENE nuclear fuel tests.

Conclusions

The studies performed at CISE Laboratories using complex experimental loops and thanks to the know-how acquired on power plants show that a proper use of the patented probes permits to measure the true corrosion rate of the monitored systems.

This is particularly important for:

- knowledge of the trend of different corrosion processes;
- check of the protective oxide resistance to pollutant aggressiveness;
- dosage of chemicals additions; and
- knowledge of metal weight losses.

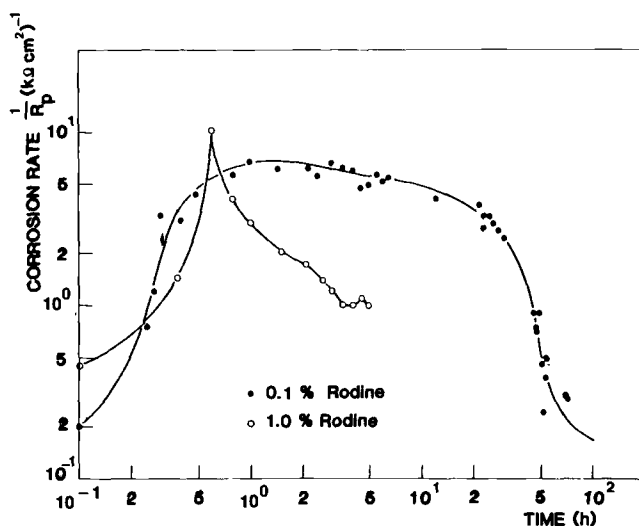


FIG. 28—Linear polarization resistance relevant to 5.08-cm (2 in.) carbon steel tube in acid solution containing different inhibitor concentrations at 90°C.

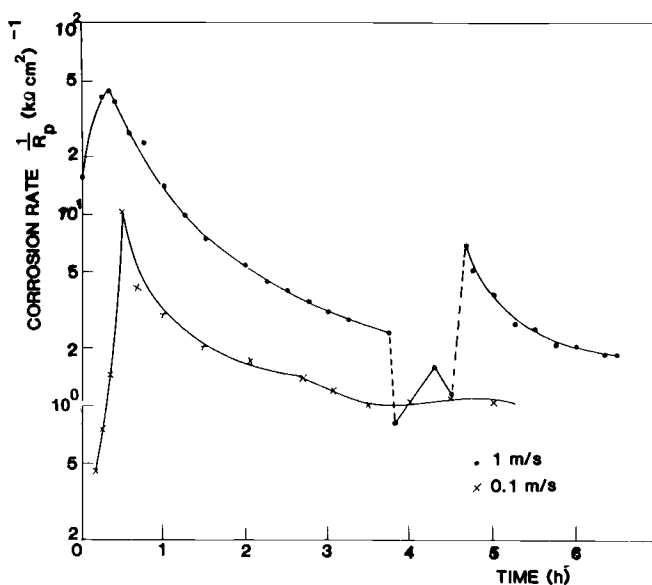


FIG. 29—Effect of the flow-rate increase on the linear polarization resistance in carbon steel decontamination.

The performed studies also show that the corrosion rate measurements are true when:

- the measurement probes are made up of the same materials and operate in the same thermohydraulic and chemical conditions as the part of the plant under monitoring;
- a wide experimental understanding of the corrosion phenomena involved is available; and
- there is enough information on the electrochemical processes and on the sources of possible electric noises or difficulties in the detection of the small utilized signals.

Following the development of different research programs, supported by ENEL and ENEA, in the frame of which it was possible to improve the electrochemical cell characteristics for linear polarization resistance measurement, such probes can be proposed as reliable and useful tools for corrosion rate monitoring of different structural materials in different operating conditions.

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Waterside Corrosion Control During Operation of Drum-Type Utility Boilers

REFERENCE: Gabrielli, F. and Mohn, N. C., "Waterside Corrosion Control During Operation of Drum-Type Utility Boilers," *Corrosion Monitoring in Industrial Plants Using Nondestructive Testing and Electrochemical Methods, ASTM STP 908*, G. C. Moran and P. Labine, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 339-357.

ABSTRACT: The water and steam side surfaces of a high pressure fossil fuel boiler are subject to a variety of potential corrosion problems. Construction materials include copper alloys, carbon steels, ferritic alloys, and austenitic stainless steels. Assessing the degree of corrosion of components is important to allow planning for maintenance during scheduled outages and to avoid unscheduled downtime. Corrosion control programs recommended by Combustion Engineering, Inc. (CE) include two areas of corrosion monitoring. First, on-line monitoring of the water and steam side environment is used to evaluate the duration and degree of exposure to corrodents, and to provide feedback information to assist in minimizing corrosion. In addition, both nondestructive testing and destructive testing during unit outages is used to assess corrosion damage. Typical operational corrosion problems in a high pressure (1241 kPa [>1800 psi]) fossil fuel utility boiler are detailed and recommended corrective measures are presented.

KEY WORDS: corrosion control, hydrogen damage, caustic damage, corrosion cracking, corrosion pitting, chemistry monitoring, water purity limits, steam purity limits, inspection, nondestructive testing

The selection of construction materials for a thermal electric power plant is based on the optimum relationship between cost and reliability. Design decisions must be based on a review of the entire boiler turbine cycle, recognizing the interactive problems which may occur with individual components. The design engineer may have a tendency to specify materials with more emphasis

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on mechanical properties than corrosion susceptibility thus affecting the ultimate cost. Conversely, the corrosion engineer may select much more costly and corrosion-resistant materials which cannot be justified financially on the basis of the benefits realized. Therefore, a balance must be achieved between those items affecting capital costs and operating costs. A key factor which can be manipulated to achieve this balance is the water and steam chemical environment.

Minimizing corrosion-related problems by controlling water chemistry has been a challenging and successful experience over the long history of steam power plants. As new steam generator designs were developed and marketed, innovative water treatment developments were required to assure reliable service. Today, however, corrosion-related problems are still the predominant cause of pressure parts failures and, thus, loss of availability.

Constant awareness of the water and steam chemical conditions in the power cycle, as well as swift action in the event of chemical upsets, are a major deterrent to these corrosion problems and failures.

Power Cycle

Regardless of operating pressure, all modern power cycles require water of relatively high purity. Fortunately, makeup water of excellent quality can be produced at reasonable cost by either evaporation or ion-exchange. Impurity concentrations are normally expressed in terms of parts per billion (ppb) rather than parts per million (ppm).

Keeping the water pure after it enters the cycle is a major problem. Corrosion within the feedwater system results in metal oxide release, which in turn will deposit contaminants and promote problems in other areas of the cycle. Undesired contamination of the feedwater is also caused by condenser leakage salts. The total steam generation cycle, as well as particular problems which may occur during operation of individual system components, must be considered in both the selection of materials and the specification of water treatment control.

A brief review of a boiler/preboiler cycle is presented in the following section. We have chosen to describe the 16 536 kPa (2400 psig) cycle since it is one of the most common in utility service (Fig. 1).

The 2400-psig Cycle

As illustrated in Fig. 1, most 16 536 kPa (2400 psig) turbines are designed for steam pressures of 17 363 kPa (2520 psia). To allow for pressure drop through the superheater and main steam line, a boiler drum pressure of 18 948 to 19 637 kPa (2750 to 2850 psia) is required. The characteristic tendency of salts to remain within the boilerwater facilitates drum blowdown. Since drum-type boilers can produce steam of acceptable quality in spite of condenser leakage, condensate demineralization is not normally required.

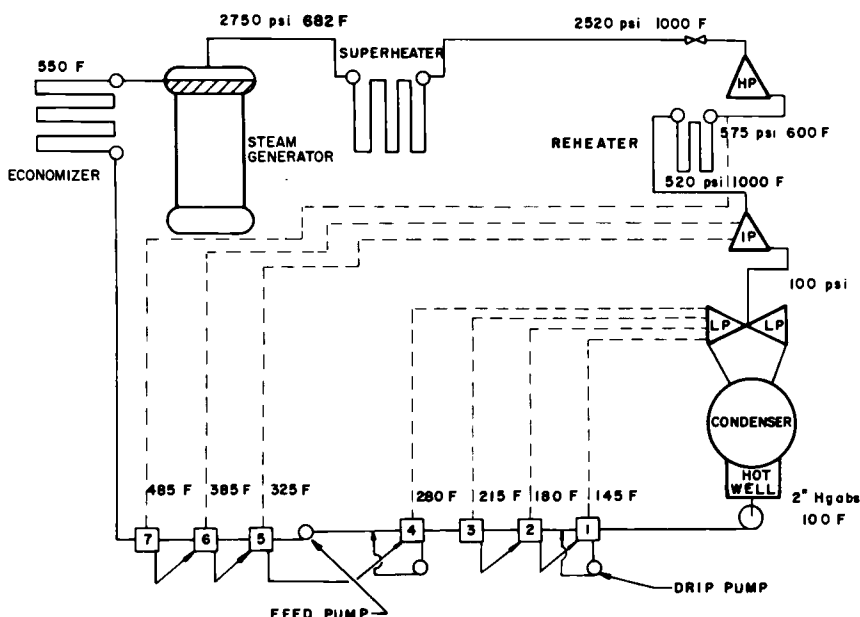


FIG. 1—Typical subcritical power cycle. Heat rate: predicted minimum = 7650 Btu/Kwhr; typical annual = 9000 to 9500 Btu/Kwhr. Conversion: 1 kPa = 6.89 psi; 1 kg/cm² = 28.96 in Hg; °C = 5/9 (°F - 32); 1 kcal/kwhr = 0.2520 Btu/kwhr.

Inleakage salts may increase corrosion within the boiler, however, and boiler-turbine cycle operation must be guided by the magnitude of such leakage. The capability to utilize an alkaline additive such as phosphate within the boilerwater assists in minimizing corrosion during operation with condenser leakage. Specific methods of realizing optimum internal chemistry during operation are presented in later sections.

Preboiler System Design

Minimizing cycle corrosion becomes more difficult as the utility boiler-turbine cycle increases in operating pressure. To obtain the maximum efficiency from a high-pressure unit, it is necessary to elevate feedwater temperatures to near saturation before entering the boiler. As pressure is increased, the boiling temperature increases while the heat of vaporization decreases. Thus, a proportionately greater amount of energy must be absorbed in the preboiler system, which requires a greater surface area. Since feedwater heaters are the primary source of metallic oxide boiler deposits, the amount of deposition may be expected to increase as cycle operating pressure is increased.

Also, many utilities have been faced with the necessity of operating older, high pressure boilers as cyclic units instead of as originally designed base-loaded units. From a corrosion standpoint [1,2], a greater potential problem

exists for cyclic units. Probability of air ingress in the preboiler system is higher when the unit is subjected to low-load operation, frequent startups, and load swings characteristic of cyclic service. Even with the best water treatment, high pressure cyclic boilers will accumulate more internal deposits than an equivalent base-loaded boiler.

Table 1 presents the materials of construction most commonly used in the utility cycle. Copper alloys are employed as tubing material in feedwater heaters and condensers of many power stations. Carbon and stainless steel-tubed feedwater heaters are also being extensively utilized in subcritical plants. Although ferritic and copper alloys behave differently under operating or standby conditions, both are subject to corrosion, and the corrosion products released will subsequently deposit within the boiler itself.

Corrosion

Waterside corrosion problems in utility boilers are generally associated with one or more of the following environments:

1. low pH
2. high pH
3. dissolved oxygen

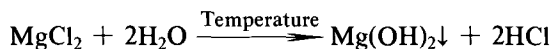
Low pH environments may be the result of the direct introduction of acids to the feedwater due to improper demineralizer regeneration or contamination by chemical cleaning solvents. However, the most frequent source of acids is leakage of cooling waters containing acid-forming salts, such as magne-

TABLE 1—*Materials of construction in power plant cycles.*

Steam generator	2400 psig
pressure parts	CS
tubing	CS
Superheater-reheater	
tubing	CS, C-1/2 Mo, 1 ¹ / ₄ Cr-1/0 Mo, 2 ¹ / ₄ Cr-1 Mo, 9 Cr-1 Mo, 18-8 SS
Condenser	
shell	CS
tubing	brass, CS, SS, Cu-Ni, titanium
Low-pressure heaters	
shell	CS
tubing	brass, CS, SS, Cu-Ni
High-pressure heaters	
shell	CS
tubing	CS, Cu-Ni, SS, monel

NOTE: Conversion: 1 kPa = 6.89 psi.

sium chloride. Under high temperature boilerwater conditions, these salts undergo chemical reactions forming scales and acids.



The predominant corrosion mechanisms associated with acidic boilerwater conditions include hydrogen damage and pitting-type corrosion. Hydrogen damage results in brittle-type failures due to microstructural damage to the tube metal (Fig. 2). Pitting-type corrosion has often been found as crack-like penetrations which, upon close examination, are revealed as a series of pits lined up to form cracks (Figs. 3 and 4).

High pH corrosion is generally associated with caustic (sodium hydroxide) in the boilerwater. Corrosion mechanisms include caustic embrittlement, a form of stress corrosion cracking which may affect highly stressed areas such as rolled tube ends, and caustic "gouging." "Gouging" is a term for a localized corrosion of tube metal which results in an irregular wastage (Fig. 5).

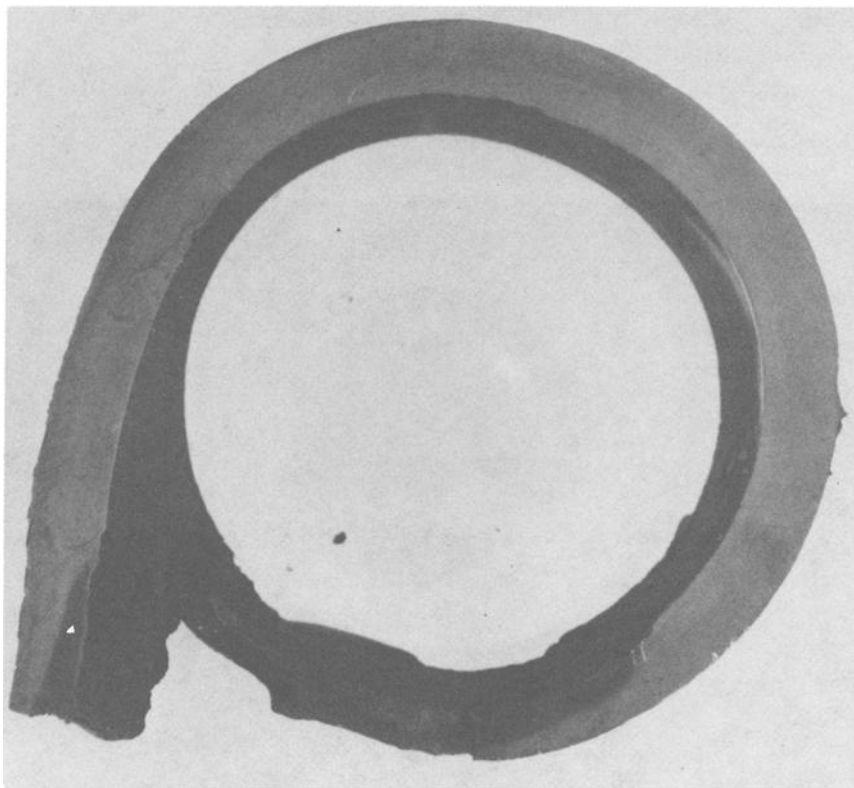


FIG. 2—*Brittle corrosion failure hydrogen damage.*

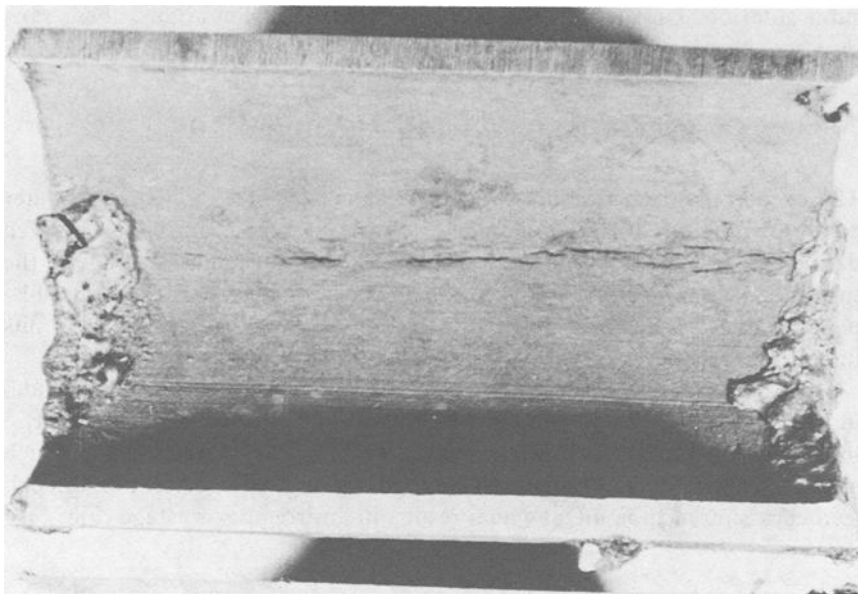


FIG. 3—*Crack-like corrosion of penetration on internal surface of waterwall tube.*

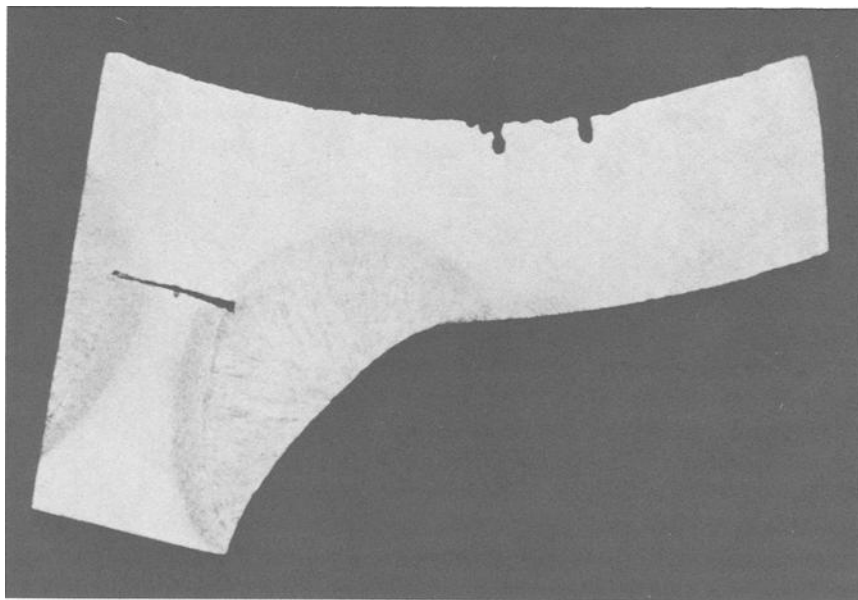


FIG. 4—*Sectional view across crack-like penetration shown in Fig. 3.*

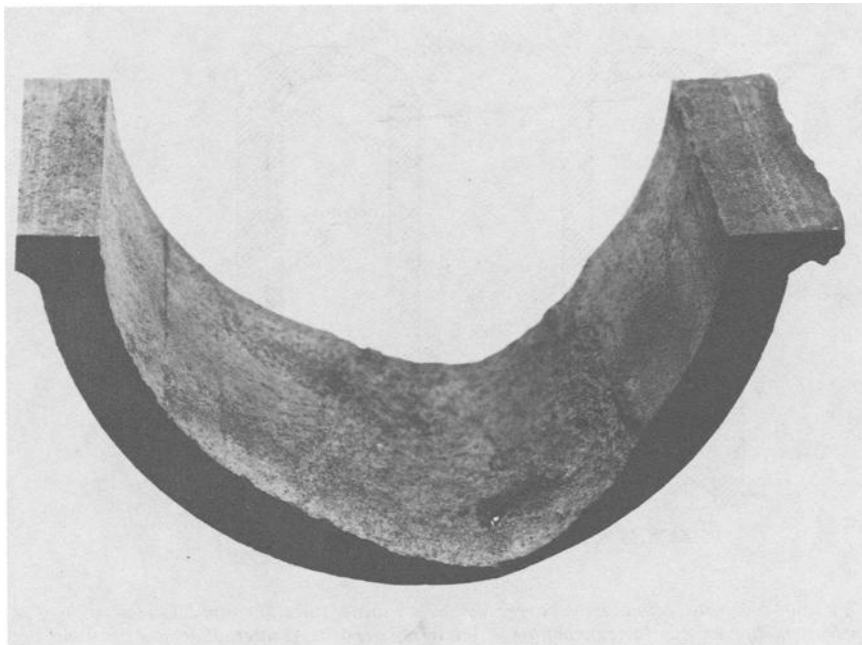


FIG. 5—Caustic "gouging" in tube metal.

Both caustic gouging and hydrogen damage are accelerated by the presence of internal deposits on heat transfer surfaces. These deposits provide the concentrating mechanism for low levels of alkaline or acid contaminants in the bulk fluid. As Fig. 6 illustrates, internal deposits act as insulators, increasing the tube wall temperatures. This temperature increase results in higher concentrations of chemical beneath the deposit than present in the bulk fluid. Thus, the pH beneath a deposit will undergo far more dramatic fluctuations than the bulk fluid if contamination by an acid or alkali occurs.

Other forms of pH-related corrosion, including pitting attack and corrosion fatigue, do not require a concentrating mechanism, but are rather associated with areas of residual or operational stress.

In contrast to low and high pH corrosion which occurs during operation, oxygen corrosion can occur in a boiler whenever metal surfaces are exposed to both moisture and oxygen; this may include shutdown, startup, and normal operation. Oxygen corrosion during shutdown can result in failures due to localized pitting associated with a differential oxygen concentration cell. In addition, exposure of economizer and boiler surfaces to dissolved oxygen during startups and operation can lead to both corrosion fatigue (Fig. 7) and stress-related pitting corrosion. Both dissolved oxygen and low pH environments are believed to produce similar crack-like pitting corrosion (Fig. 3).

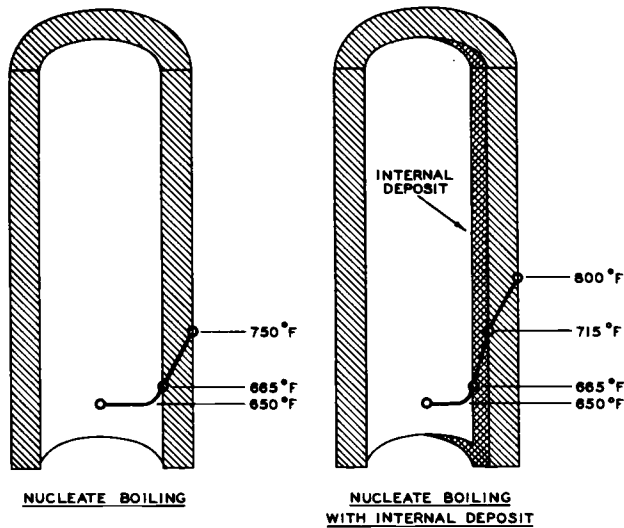


FIG. 6—Nucleate boiling: Even at very high heat-transfer rates, the film ΔT is low, as long as nucleate boiling exists. Nucleate boiling with internal deposit: As internal deposit develops, the bulk-to-surface ΔT increases. This not only increases the concentration level which can potentially be reached, but the deposit also retards diffusion which promotes stability of the high-concentration gradient. (Conversion: $^{\circ}C = 5/9 (^{\circ}F - 32)$.)

Water Chemistry

The water treatment program in a power plant cycle must consider the interactions and specific requirements of various systems. Cycle chemistry control must, for example, be equally compatible with the boiler, turbine, and preboiler systems. It must provide an environment conducive to the maintenance of stable, protective oxide films on the various materials of construction, as well as to react with possible contaminants entering the system.

Feedwater Chemical Control

The boiler acts as a concentrating device during operation. Soluble feedwater impurities, when entering the boiler, become concentrated in the water since the steam leaving the boiler drum does not carry off any appreciable amount. Additionally, the feedwater is used for spraying into the superheater/reheater to control steam temperatures. These features of the cycle must be taken into account when utilizing treatment chemicals to protect the equipment against general corrosion. It is the industry practice to utilize volatile, neutralizing amines such as ammonia, morpholine, and cyclohexylamine to control pH conditions throughout the cycle. This treatment includes the use of hydrazine as a reducing agent in the event of oxygen infiltration.

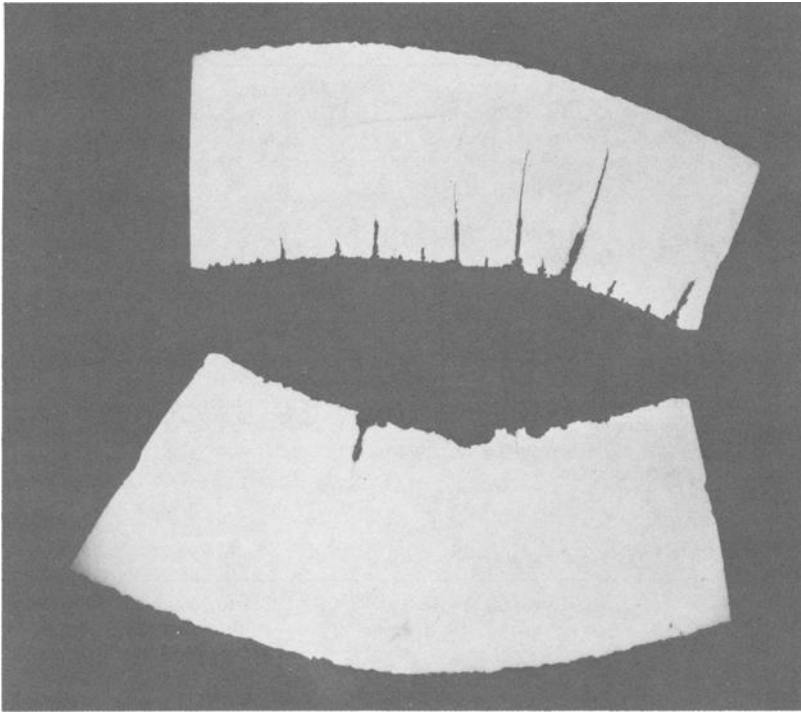


FIG. 7—Corrosion fatigue caused by dissolved oxygen during startups and operation.

It should also be emphasized that preboiler corrosion products are the major contributor to deposit formation on the internal surfaces of boiler tubes. During operation, boiler blowdown is not effective in reducing suspended oxides, as these are readily captured and retained on the heat transfer surfaces. These considerations are the basis for the recommended feedwater quality values presented in Table 2.

Boilerwater Chemistry

As stated previously, the boiler acts as a concentrating device during operation. Soluble impurity levels are controlled by boiler blowdown operations, and the required blowdown rates are dependent on both boilerwater and feedwater impurity concentrations. The basic CE recommendations for boilerwater quality are given in Table 3. These values are consistent with recently published boilerwater quality and steam purity guidelines by the American Boiler Manufacturers Association (Table 4) [4]. As indicated, phosphate chemical additives are recommended for corrosion control of boiler components. Although a volatile additive such as ammonia may be selected for normal opera-

TABLE 2—*Feedwater limits for high pressure drum-type boilers.*

Parameter	Maximum Concentration, ppb
Total solids	50
Sodium	see note
Total iron	10
Total copper	10
Total silica	20
Oxygen	5
Hydrazine	10–20 (residual)

NOTE: Sodium values in the feedwater, as well as its frequency of analysis, to be consistent with steam purity recommendations for specific units [3]. Also, pH should be maintained between 8.8 and 9.2 in a copper-alloy system; between 9.2 and 9.4 in a copper-free system.

TABLE 3—*Recommended boilerwater limits—drum-type boilers.*

	1001 to 1800 psig	1801 to 2350 psig	2351 to 2600 psig	2601 to 2900 psig
Total solids, ppm	<100	<50	<25	<15
Phosphate ^a , ppm	5 to 20	5 to 10	5 to 10	2 to 6
pH ^a	9.1 to 10.1	9.1 to 9.8	9.1 to 9.8	9.1 to 9.6
Silica	controlled on basis of silica in boilerwater and pressure relationship to maintain less than 20 ppb in steam leaving the drum			

^aPhosphate and pH control in accordance with coordinated phosphate treatment to maintain a sodium-to-phosphate molar ratio ≤ 2.6 .

Conversion: 1 kPa = 6.89 psi.

tion by the plant operator, it must be replaced by phosphate treatment in the event of condenser leakage. This change is required because pH adjustment with ammonia produces a weakly ionized, essentially unbuffered solution. Such volatile treatment in a boilerwater environment does not have enough buffering ability to maintain pH control under conditions of salt leakage.

Tables 5, 6, 7, and 8 illustrate a philosophy of operation with respect to the level of contamination entering the cycle. The recommendations and guidelines in these tables represent a method of operation which will result in long-term steam generator integrity and cleanliness. Certain deviations from normal chemistry specifications may occur on occasion during plant life, with little or no effect on component integrity. These deviations are designated as abnormal conditions. Other deviations which might occur may result in extensive corrosion problems. The serious nature of such deviations requires immediate action, and this is noted where applicable.

TABLE 4— *Watertube boilers: recommended boiler water limits and associated steam purity at steady-state full-load operation.*

DRUM-TYPE BOILERS				
Drum Pressure, psig	Range of Total Dissolved Solids ^a Boiler Water, ppm (max)	Range of Total Alkalinity ^b Boiler Water, ppm	Suspended Solids Boiler Water, ppm (max)	Range of Total Dissolved Solids ^{b,d} Steam, ppm (max expected value)
0 to 300	700 to 3500	140 to 700	15	0.2 to 1.0
301 to 450	600 to 3000	120 to 600	10	0.2 to 1.0
451 to 600	500 to 2500	100 to 500	8	0.2 to 1.0
601 to 750	200 to 1000	40 to 200	3	0.1 to 0.5
751 to 900	150 to 750	30 to 150	2	0.1 to 0.5
901 to 1000	125 to 625	25 to 125	1	0.1 to 0.5
1001 to 1800	100		1	0.10
1801 to 2350	50		N/A	0.10
2351 to 2600	25		N/A	0.05
2601 to 2900	15		N/A	0.05
ONCE-THROUGH BOILERS				
1400 and Above	0.05	N/A	N/A	0.05

^aActual values within the range reflect the TDS in the feed water. Higher values are for high solids, lower values are for low solids in the feed water.

^bActual values within the range are directly proportional to the actual value of TDS of boiler water. Higher values are for the high solids, lower values are for low solids in the boiler water.

^cDictated by boiler water treatment.

^dThese values are exclusive of silica.

Source: American Boiler Manufacturers Association (ABMA) [4].

Conversion: 1 kPa = 6.89 psi.

Analytical and Monitoring Methods

The implementation of control methods to minimize corrosion products release as well as the detection of contaminant inleakage requires a continuous and vigorous analytical program. All automatic analytical instrumentation should be maintained in an operational and calibrated status.

If chemical auto analyzers are not operational, greater emphasis must then be placed on laboratory analyses. Table 9 provides guidelines for an analytical schedule in the event of continuous instrumentation failure. Of particular importance within the cycle is a condenser leak detection system; leakage instrumentation should be installed such that if the condenser has segmented compartments, each compartment can be analyzed for leakage individually. All devices should generally employ a sodium analyzer for maximum sensitivity or cation conductivity, or both. Should condenser leak detection systems be out of service, it is recommended that manual readings be taken at the condensate discharge pump at least three times daily.

TABLE 5—Criteria for operation of drum-type boilers (1001 to 1800 psig).

Hotwell Conditions		Operational Limitations	Control Limits		Boilerwater Control
Solids	ppm		Phosphate-pH ^a	Volatile	
Total Solids (recommended)	<0.05	none	TS <100 ppm pH 9.1–10.1 PO ₄ 5–20 ppm	TS <2 ppm pH 8.5–9.0	normal
Total Solids (acceptable)	<0.5	volatile treatment not suitable	TS <100 ppm pH 9.1–10.1 PO ₄ 5–20 ppm		if on volatile treatment, change to coordinated phosphate pH control.
Total Solids (abnormal)	0.5–2.0	limited operations. Schedule inspection and repair of condenser as soon as system load requirements permit.	TS <200 ppm pH 9.1–10.4 PO ₄ 5–40 ppm		immediately start chemical injection pumps to maintain excess phosphate and pH conditions. Do not continue to operate unit if pH cannot be maintained above 8.0 or the total solids below 200 ppm. Increase blow-down to limit total dissolved solids concentration. Avoid use of desuperheating spraywater by (1) permitting reheat temperatures to fall or (2) reducing load.
Total Solids (excessive)	>2.0	emergency operation. 1. Immediately reduce load as necessary to permit isolation of damaged condenser. 2. Prepare for orderly shutdown of the unit if hotwell concentration cannot be quickly reduced below 2 ppm.	TS <200 ppm pH 9.1–10.4 PO ₄ 5–40 ppm		see above. Prepare to establish chemical conditions for wet layup of boiler unit and auxiliary equipment during condenser repair.

Conversion: 1 kPa = 6.89 psi.

^aMaintain sodium/phosphate ratio ≤2.6.

TABLE 6—Criteria for operation of drum-type boilers (1801 to 2350 psig).

Hotwell Conditions		Operational Limitations	Control Limits		
Solids	ppm		Phosphate-pH ^a	Volatile	Boilerwater Control
Total Solids (recommended)	<0.05	none	TS < 50 ppm pH 9.1–9.8 PO ₄ 5–10 ppm	TS < 2 ppm pH 8.5–9.0	normal
Total Solids (acceptable)	<0.5	volatile treatment not suitable	TS < 50 ppm pH 9.1–9.8 PO ₄ 5–10 ppm		If on volatile treatment, change to coordinated phosphate pH control.
Total Solids (abnormal)	0.5–2.0	limited operations. Schedule inspection and repair of condenser as soon as system load requirements permit.	TS < 100 ppm pH 9.1–10.1 PO ₄ 5–20 ppm		Immediately start chemical injection pumps to maintain excess phosphate and pH conditions. Do not continue to operate unit if pH cannot be maintained above 8.0 or the total solids below 100 ppm. Increase blow-down to limit total dissolved solids concentration. Avoid use of desuperheating spraywater by (1) permitting reheat temperatures to fall or (2) reducing load.
Total Solids (excessive)	>2.0	emergency operation. 1. Immediately reduce load as necessary to permit isolation of damaged condenser. 2. Prepare for orderly shutdown of the unit if hotwell concentration cannot be quickly reduced below 2 ppm.	TS < 100 ppm pH 9.1–10.1 PO ₄ 5–20 ppm		See above. Prepare to establish chemical conditions for wet layup of boiler unit and auxiliary equipment during condenser repair.

Conversion: 1 kPa = 6.89 psi.

^aMaintain sodium/phosphate ratio ≤ 2.6.

TABLE 7—Criteria for operation of drum-type boilers (2351 to 2600 psig).

Hotwell Conditions		Operational Limitations	Control Limits		Boilerwater Control
Solids	ppm		Phosphate-pH ^a	Volatile	
Total Solids (recommended)	<0.05	none	TS <25 ppm pH 9.1-9.8 PO ₄ 5-10 ppm	TS <2 ppm pH 8.5-9.0	normal
Total Solids (acceptable)	<0.25	volatile treatment not suitable	TS <25 ppm pH 9.1-9.8 PO ₄ 5-10 ppm		If on volatile treatment, change to coordinated phosphate pH control.
Total Solids (abnormal)	0.25-1.0	limited operations. Schedule inspection and repair of condenser as soon as system load requirements permit.	TS <50 ppm pH 9.1-10.1 PO ₄ 5-20 ppm		Immediately start chemical injection pumps to maintain excess phosphate and pH conditions. Do not continue to operate unit if pH cannot be maintained above 8.0 or the total solids below 50 ppm. Increase blow-down to limit total dissolved solids concentration. Avoid use of desuperheating spraywater by (1) permitting reheat temperatures to fall or (2) reducing load.
Total Solids (excessive)	>1.0	emergency operation. 1. Immediately reduce load as necessary to permit isolation of damaged condenser. 2. Prepare for orderly shutdown of the unit if hotwell concentration cannot be quickly reduced below 1 ppm.	TS <50 ppm pH 9.1-10.1 PO ₄ 5-20 ppm		See above. Prepare to establish chemical conditions for wet layup of boiler unit and auxiliary equipment during condenser repair.

Conversion: 1 kPa = 6.89 psi.

^aMaintain sodium/phosphate ratio ≤ 2.6 .

TABLE 8—Criteria for operation of drum-type boilers (2601 to 2900 psig).

Hotwell Conditions		Operational Limitations	Control Limits		
Solids	ppm		Phosphate-pH ^a	Volatile	Boilerwater Control
Total Solids (recommended)	<0.05	none	TS <15 ppm pH 9.1-9.6 PO ₄ 2-6 ppm	TS <2 ppm pH 8.5-9.0	normal
Total Solids (acceptable)	<0.1	volatile treatment not suitable	TS <15 ppm pH 9.1-9.6 PO ₄ 2-6 ppm		If on volatile treatment, change to coordinated phosphate pH control.
Total Solids (abnormal)	0.1-1.0	limited operations. Schedule inspection and repair of condenser as soon as system load requirements permit.	TS <50 ppm pH 9.1-10.1 PO ₄ 5-20 ppm		Immediately start chemical injection pumps to maintain excess phosphate and pH conditions. Do not continue to operate unit if pH cannot be maintained above 8.0 or the total solids below 50 ppm. Increase blow-down to limit total dissolved solids concentration. Avoid use of desuperheating spraywater by (1) permitting reheat temperatures to fall or (2) reducing load.
Total Solids (excessive)	>1.0	emergency operation. 1. Immediately reduce load as necessary to permit isolation of damaged condenser. 2. Prepare for orderly shutdown of the unit if hotwell concentration cannot be quickly reduced below 1 ppm.	TS <50 ppm pH 9.1-10.1 PO ₄ 5-20 ppm		See above. Prepare to establish chemical conditions for wet layup of boiler unit and auxiliary equipment during condenser repair.

Conversion: 1 kPa = 6.89 psi.

^aMaintain sodium/phosphate ratio ≤2.6.

TABLE 9—*Frequency of water analysis for high-pressure drum-type units.^a*

FEEDWATER PARAMETERS	
pH	twice/shift
Oxygen (O ₂)	twice/shift
Hydrazine (N ₂ H ₄)	twice shift
Silica (SiO ₂)	once/shift
Copper (Cu)	twice weekly
Total iron (Fe)	twice weekly
BOILERWATER PARAMETERS	
pH	twice/shift
Phosphate (PO ₄)	twice/shift
Total solids	twice/shift
Silica (SiO ₂)	once/shift

^aTake all measurements at the high pressure feedwater heater outlet or at the economizer inlet except where noted. Oxygen can be measured at the deaerator outlet. Also, should condenser leak detection equipment be out of service, take cation conductivity (or sodium) readings manually at the condensate pump discharge three times per shift.

Most corrosion-related failures can be prevented if contamination ingress into the system, especially in the condensate area, is detected and if countermeasures are implemented. In the absence of contamination, chemistry in the cycle is fairly static and does not require constant control, since almost all of the steam is returned as condensate (makeup water requirements are generally less than 5%). However, because of the high temperature and pressures in the system (boiler and turbine), constant surveillance of feedwater and boilerwater quality is imperative, as these components are extremely sensitive to even very small amounts of contaminants.

As implied by the information in Tables 5 through 9, the current methodology is to monitor and control those parameters which identify potential corrosive situations and aid in preventing corrosion attack. Other constituents such as iron oxide, copper, and silica are measured principally to determine system cleanliness, performance of pH and oxygen control measures, and the need to chemically clean the boiler. For cyclic operation, it is even more critical to maintain a monitoring program to assess the generation and transport of oxides in the system.

As noted, we have not specifically required or recommended the measurement of constituents such as hydrogen, which may be indications of ongoing corrosion attack. There are a number of physical and chemical activities in the cycle (hydrazine decomposition, product oxide film formation, etc.) which affect the hydrogen concentration. It is therefore difficult to assess whether the hydrogen concentration level is indicative of an immediate corrosion problem. The development of techniques or equipment for the direct measurement of corrosion is encouraged, however. There are cases, for exam-

ple, of corrosion fatigue or stress-assisted corrosion where the measurement of typical water chemistry parameters is not necessarily indicative of slow corrosion processes over the long term.

Inspection

In addition to monitoring and controlling the water and steam environment, periodic outage inspections can provide valuable data on the unit condition. Both destructive and nondestructive testing methods are used to evaluate the integrity of boiler components.

Evaluation of tube samples from the high heat flux areas of the waterwalls are often used to determine the rate of deposition in these circuits in order to schedule chemical cleanings. In addition, because hydrogen damage and caustic gouging are generally localized beneath areas of heavy deposit, an examination of the tube surface, visually or microstructurally, or both, of samples removed for deposit measurements can provide an indication of corrosion affecting these surfaces. During longer-term inspections such as would be undertaken during "life extension" studies, a broader program of tube sampling may be undertaken. Using unit failure history, combined with water chemistry logs, areas of the boiler can be selected for further examination. For example, a history of cyclic operation, combined with high dissolved oxygen levels during startup, would highlight the need to examine the economizer for internal corrosion.

Non-destructive testing methods (NDT) are of value in performing examinations of large sections of boiler components. Areas with indications of major distress can then be further examined by selective destructive tests. The primary inspection techniques used for utility boilers are ultrasonics, radiography, dye penetrant, and magnetic particle testing. Each technique has advantages and limitations in terms of the surface to be examined, the type of corrosion which has occurred, the location, and of course cost and time requirements. Table 10 [5] compares these nondestructive testing methods.

The use of nondestructive techniques for locating corrosion which results in general wall thinning, such as caustic gouging, is fairly straightforward. However, the detection of non-uniform corrosion, including pitting attack, corrosion fatigue, and hydrogen damage, requires experienced NDT technicians and incorporates a degree of "art" along with the science.

Summary

This paper has presented an overview of water treatment practices which provide a protective environment in the power cycle. The following conclusions are noted:

1. Corrosion is a major factor in loss of availability.
2. Corrosion can be minimized by effective control of water chemistry.

TABLE 10—*Nondestructive testing methods* [5].

	Liquid Penetrant Testing	Magnetic Particle Testing	Radiographic Testing	Ultrasonic Testing
Definition	Uses a penetrating liquid to seep into a surface imperfection, thus providing a visible indication.	Uses electrical current to create a magnetic field in a specimen while magnetic particles indicate where the field is broken by an imperfection.	Uses electro-magnetic rays (X-rays and Gamma rays) to penetrate material, recording on film imperfections in the material.	Uses ultrasound to penetrate material, indicating imperfections on an oscilloscope screen.
Uses	Used on metal, glass, ceramics to locate surface imperfections. Simple to use and does not require elaborate equipment.	Used on metal that can be magnetized (Ferromagnetic) to detect surface or subsurface imperfections. Simple to use. Equipment is portable for field testing.	Used on any metal stock or articles as well as a variety of other materials to detect (and record on film) surface or subsurface imperfections. Film provides a permanent record of the discontinuities.	Used on metal, ceramics, plastics, etc., to detect surface and subsurface imperfections. When automated, permanent records are available. Also measures material thickness.
Limitations	Does not detect imperfections beneath the surface of a specimen.	Cannot be used on metal that cannot be magnetized. Requires electrical power.	High initial cost. Requires electrical power source. Potential radiation hazard to personnel.	Moderately high initial cost. Interpretation of test results requires highly trained personnel.

3. A properly designed monitoring and analytical program is essential to control water chemistry, and thus to the success of maintaining high availability.

4. Availability can be improved by utilizing proper inspection techniques to locate damaged tubing.

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DISCUSSION

C. Ronchetti¹ and R. Rizzi¹ (written discussion)—The old question between the U.S. and European schools on the corrosion behavior of carbon steel in the presence of oxygen cannot be easily solved by traditional methods of corrosion evaluation, which utilize the specimen weight loss. In fact, during the short experimental period, the measurement integrates the high initial Δw together with the small contribution related to the constant corrosion phase (2nd step). The use of the probe set up and patented by CISE permits us to determine the two partial contributions, and to measure both oxidation times and steady corrosion rates of new or oxidized specimens. It also permits us to test the oxide film resistance to the deterioration of water quality (see results reported in our paper, "On-Line Monitoring of the True Corrosion Rate in Problems Related to Power Plants," in this volume).

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Corrosion Rate of Cast Iron and Copper Pipe by Drinkable Water

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ABSTRACT: The corrosion rates of cast iron and copper in drinkable water distribution systems are compared in this investigation. Sixty-one solutions were prepared, of varying concentrations in Cl^- , NO_3^- , SO_4^{2-} , and with differences in alkalinity, pH, and Langelier index.

Cut from actual pipe, 2070 specimens 4 cm by 3 cm by 0.1 cm (1035 cast iron and 1035 copper) were immersed in the solutions for 3, 6, 9, 12, or 15 days, and their corrosion was determined by weight loss. For both metals, corrosion was more rapid during the first three days.

The cast iron corrosion product contained between 35% and 55% iron. X-ray diffraction revealed the presence of goethite, lepidocrocite, and after three days of immersion, amorphous magnetite.

For the same experimental conditions, the copper corrosion rate was significantly smaller than that of ductile cast iron.

The corrosion rate of copper was not found to be affected by the composition of the water. In this investigation, no correlation was found between the Langelier index and the corrosion rate for copper or cast iron. This was true for both negative and positive Langelier index.

KEY WORDS: corrosion, drinkable water, water pipe

Corrosion, “a destruction of metal by chemical or electrochemical reactions with its environment,” is well-exemplified by many systems involving metal plus water. Water pipe corrosion costs alone were evaluated to reach some \$700 million in the United States in 1975 [1]. Moreover, corrosion produces a rusty red water that stains and has a poor taste. The impact of such

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water on public health has not yet been completely evaluated [2], but the presence of heavy metals such as copper, iron, chromium, cobalt, and zinc [3] has been correlated with an increase of cardio-vascular disease. If these consequences on public health could be verified, water pipe corrosion would have important social implications, and the resulting costs to our economy would be much higher than currently evaluated.

Present remedies for the problem of corrosion of pipe for drinkable water could be improved with a better understanding of the interaction between the metal pipe and the water. This investigation is an effort to improve our knowledge of the effect of the chemical composition of the water on the cast iron and copper pipes used by the City of Laval (Québec).

Experimental Procedure

A basic synthetic water was prepared with a chemical composition simulating the composition of the water distributed by the City of Laval (Table 1). It had a pH_5 of about 8.9 and a measured pH of 7.5 to 7.8. The Langelier index varied between -1.1 and -1.4 . It is an aggressive water.

The basic synthetic water was then used to prepare two series of solutions. A first series of 34 solutions was produced to study the ionic effect on the corrosion rate. The concentrations of sulfates (SO_4^{2-}), chlorides (Cl^-), nitrates (NO_3^-), and the alkalinity were varied as shown in Table 2. All these solutions had a negative Langelier index.

A second series of 27 solutions were prepared with compositions of mixed ions. They were adjusted to obtain solutions with positive Langelier indices (Tables 3 to 5).

The chemical compositions of ductile cast iron and copper are given in Ta-

TABLE 1—*Chemical composition of basic water.*

Parameters	Concentration
Temperature	19.9°C
Free CO_2	2.5 mg/L
Total hardness ($CaCO_3$)	48.6 mg/L
Alkalinity ($CaCO_3$)	19.4 mg/L
pH	7.8
Fluorides (F^-)	0.2 mg/L
Dissolved oxygen	9.8 mg/L
Sulfates (SO_4^{2-})	16.8 mg/L
Phosphates (PO_4^{3-})	0.02 mg/L
Nitrates (NO_3^-)	5.3 mg/L
Chlorides (Cl^-)	5.1 mg/L
Calcium (Ca^{2+})	16.0 mg/L
Magnesium (Mg^{2+})	2.1 mg/L
Sodium (Na^+)	3.0 mg/L
Potassium (K^+)	0.8 mg/L

TABLE 2—Anion concentrations in synthetic water utilized.

Solution	Sulfates (mg/L)-SO ₄ ²⁻	Chlorides (mg/L)-Cl ⁻	Nitrates (mg/L)-NO ₃ ⁻	Alkalinity (mg/L)-CaCO ₃
1	0.0	0.0	0.57	10
2	10.0	11.5	7.10	86
3	18.0	22.5	15.60	80
4	46.0	50.0	28.90	126
5	96.0	100.0	57.60	178
6	255.0	190.0	84.60	234
7	330.0	230.0	110.00	282
8	470.0	490.0	174.00	364
9	...	...	343.00	376

TABLE 3—Initial composition of synthetic water (calcocarbonic equilibrium)^a [(Cl⁻) = 13.5 mg/L; (NO₃⁻) = 19.0 mg/L].

Parameter	Solution Number								
	1	2	3	4	5	6	7	8	9
Temperature (°C)	28.0	28.0	28.0	28.0	28.0	29.0	28.0	28.0	27.5
O ₂	7.50	7.40	7.40	7.40	7.30	7.20	7.30	7.30	7.40
Free CO ₂ ^b	0.56	0.30	3.56	5.39	3.84	5.43	8.06	5.46	8.89
NO ₃ ⁻	19.51	18.51	19.51	17.64	17.90	19.50	17.55	18.36	18.94
pH	8.06	8.74	7.87	7.74	7.85	7.77	7.62	7.91	7.64
Alkalinity ^b	32	82	132	148	136	160	168	222	194
SO ₄ ²⁻	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0
Cl ⁻	13.5	13.0	13.5	13.5	13.5	13.5	13.5	13.5	13.0
Na ⁺	11.5	11.2	10.5	10.4	10.1	10.1	10.2	10.2	10.2
K ⁺	1.5	1.4	1.3	1.2	1.3	1.3	1.3	1.3	1.3
Ca ²⁺	20.0	39.5	64.5	76.0	94.0	110.0	100.0	123.0	137.0
Mg ²⁺	1.4	1.5	1.5	1.5	1.7	1.7	1.8	1.9	1.9
Mn ²⁺	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cu ²⁺	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Fe ²⁺	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

^aThe values in this table are expressed in mg/L.^bValue expressed in mg/L of CaCO₃.

ble 6. Samples 4 cm by 3 cm by 0.1 cm were cut from these metals, and their surfaces were prepared by a method analogous to that used by Larson and King [4]. A schematic view of the experimental system is presented in Fig. 1. The basic water was prepared in a 2000-L plastic (PVC) container from distilled water and pure reagent grade chemicals. The solution was then transferred to nine smaller 200-L containers where its composition was adjusted to the various desired concentrations.

From the 200-L containers, solutions were pumped into the 4-litre corrosion cells (16 cm in diameter and 20 cm high). A constant flow rate of 4 cm³/min was maintained. Each cell initially contained 15 specimens of ductile cast

TABLE 4—Initial composition of synthetic water (calcocarbonic equilibrium)^a [(Cl⁻) = 157.0 mg/L; (NO₃⁻) = 199.0 mg/L].

Parameter	Solution Number								
	1	2	3	4	5	6	7	8	9
Temperature (°C)	30.0	30.0	30.0	30.0	29.0	30.5	31.0	31.0	30.0
O ₂	7.30	7.30	7.40	7.15	6.90	5.80	7.00	6.50	7.20
Free CO ₂ ^b	24.28	21.41	23.12	42.56	160.00	417.65	45.44	180.38	40.41
NO ₃ ⁻	199.0	195.0	197.0	199.0	199.0	197.0	199.0	193.0	199.0
pH	6.87	7.24	7.31	7.07	6.29	6.26	7.25	6.55	7.33
Alkalinity ^b	90.0	186.0	236.0	250.0	156.0	380.0	404.0	320.0	432.0
SO ₄ ²⁻	53.0	50.0	52.0	60.0	60.0	60.0	50.0	50.0	50.0
Cl ⁻	157.0	157.0	157.0	157.0	157.0	157.0	157.0	157.0	157.0
Na ⁺	150.0	150.0	155.0	150.0	155.0	150.0	150.0	150.0	150.0
K ⁺	1.2	1.2	1.3	1.3	1.3	1.3	1.3	1.3	1.3
Ca ²⁺	48.4	93.0	118.0	106.0	82.0	155.0	164.0	160.0	186.0
Mg ²⁺	8.7	8.9	9.0	9.1	8.7	9.8	10.5	9.1	9.7
Mn ²⁺	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cu ²⁺	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Fe ²⁺	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

^aThe values in this table are expressed in mg/L.^bValue expressed in mg/L of CaCO₃.TABLE 5—Initial composition of synthetic water (calcocarbonic equilibrium)^a [(Cl⁻) = 56.0 mg/L; (NO₃⁻) = 87.0 mg/L].

Parameter	Solution Number								
	1	2	3	4	5	6	7	8	9
Temperature (°C)	25	26.0	26.0	25.5	27.0	26.0	27.0	27.0	27.0
O ₂	8.30	8.10	8.00	8.00	7.80	8.00	7.80	7.90	7.50
Free CO ₂ ^b	1.46	3.22	11.13	15.10	14.66	14.81	26.16	37.19	56.55
NO ₃ ⁻	87.22	87.22	91.67	87.22	91.67	87.22	87.22	83.22	87.22
pH	8.08	7.88	7.49	7.44	7.55	7.40	7.26	7.36	7.01
Alkalinity ^b	88	122	172	208	260	186	238	426	494
SO ₄ ²⁻	21.0	20.5	22.5	23.0	22.5	21.0	21.0	22.5	21.0
Cl ⁻	56.0	58.0	56.0	58.0	50.0	58.0	58.0	58.0	58.0
Na ⁺	55.0	48.6	48.4	52.0	48.4	50.0	50.0	50.0	48.0
K ⁺	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Ca ²⁺	41.0	54.0	82.5	99.0	106.0	145.0	184.0	107.0	164.0
Mg ²⁺	2.1	2.1	2.2	2.6	2.4	2.6	2.8	2.8	2.8
Mn ²⁺	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cu ²⁺	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Fe ²⁺	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

^aThe values in this table are expressed in mg/L.^bValue expressed in mg/L of CaCO₃.

TABLE 6—*Chemical composition of copper and ductile iron.*

Chemical Element	Material	
	Copper, %	Ductile iron, %
Cu	98.8	0.12
Fe	0.002	93.11
Ni	0.003	0.14
Pb	0.004	0.01
Zn	0.003	0.01
Mn	...	0.60
Cr	...	0.15
Mo	...	0.05
Mg	...	0.02
C	...	3.39
Si	...	2.33
P	...	0.02
S	...	0.01

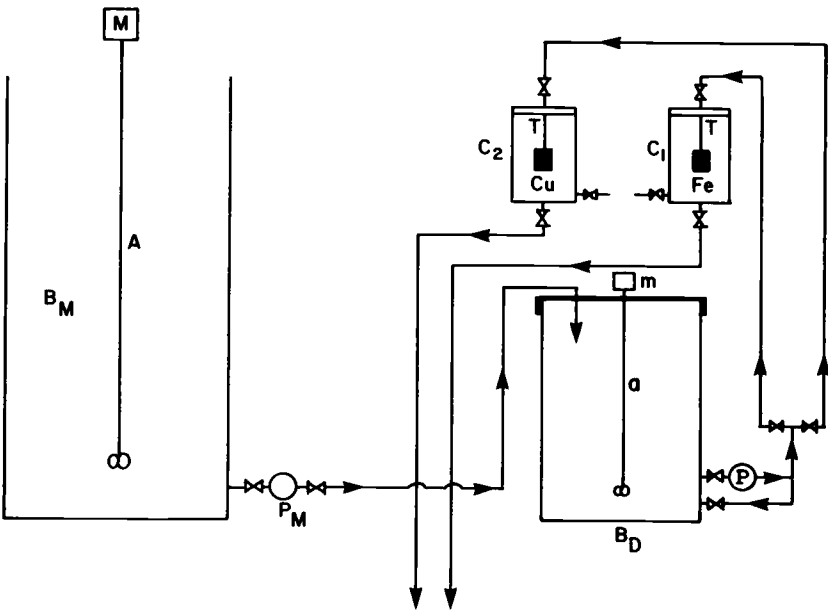


FIG. 1—*Schematic representation of experimental equipment.*

iron or 15 specimens of copper. Three samples of each metal were removed for study after 3, 6, 9, 12, or 15 days of immersion. A total of 69 solutions and 15 specimens per solution resulted in an investigation of 1035 specimens of each metal.

Specimens were weighed before immersion. After immersion they were dried at 105°C for 24 h and weighed with their dry deposits. The deposit was then carefully removed and the specimens weighed again. Some noncorroded specimens were submitted to the same treatment as blanks, and their weight loss was subtracted from that observed on corroded specimens.

The average corrosion rate was then computed by dividing the weight by the number of immersion days. An average was taken of the three specimens withdrawn from the solution at the same time. Chemical analyses of the water were frequently conducted to control its chemical composition.

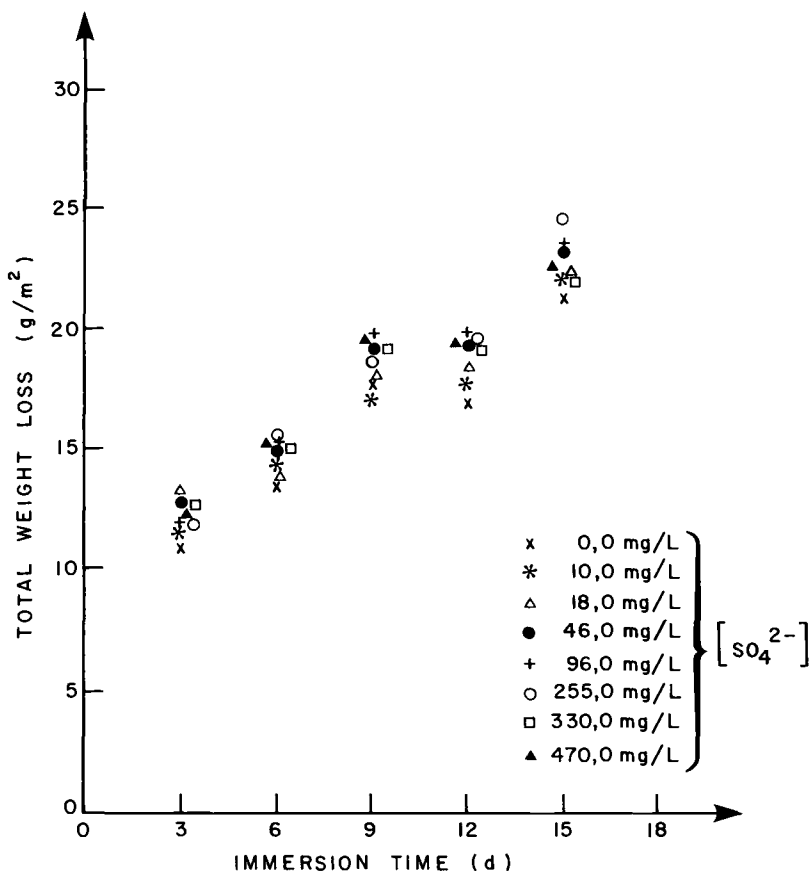


FIG. 2—Cumulative weight loss versus immersion time and sulfate concentration.

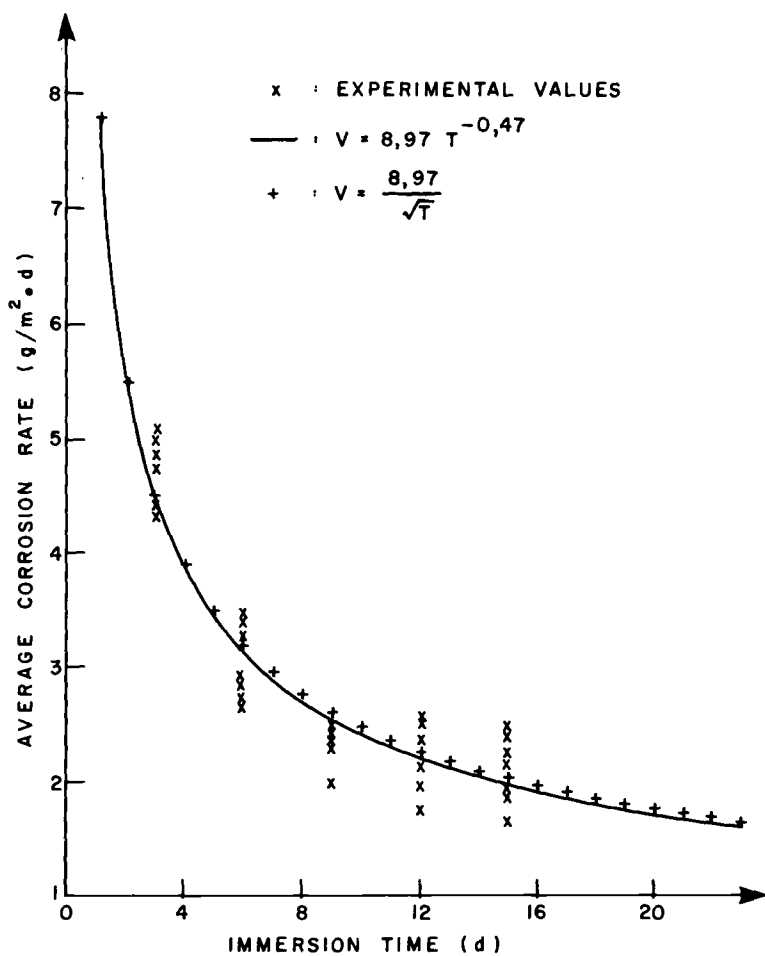


FIG. 3—Average corrosion rate as a function of immersion time and in the presence of chlorides and nitrates. (Cl^-) = 157 mg/L; (NO_3^-) = 199.0 mg/L.

TABLE 7—Values of the constants K_1 and K_2 and explication coefficient R^2 .

Variable	Constant		
	K_1	K_2	R^2
$(\text{Cl}^-) = 0.0 @ 360.0 \text{ mg/L}$	5.90	0.54	0.90
$(\text{SO}_4^{2-}) = 0.0 @ 470.0 \text{ mg/L}$	4.74	0.40	0.88
$(\text{NO}_3^-) = 0.0 @ 343 \text{ mg/L}$	5.42	0.45	0.77
$(\text{AlK}) = 10.0 @ 376 \text{ mg/L}$ from CaCO_3	6.33	0.57	0.91
$(\text{Cl}^-) = 13.5 \text{ mg/L}$	7.78	0.51	0.86
$(\text{NO}_3^-) = 19.5 \text{ mg/L}$	10.37	0.53	0.93
$(\text{Cl}^-) = 56.0 \text{ mg/L}$	8.97	0.47	0.68
$(\text{NO}_3^-) = 87.0 \text{ mg/L}$			
$(\text{Cl}^-) = 157.0 \text{ mg/L}$			
$(\text{NO}_3^-) = 199.0 \text{ mg/L}$			

Results and Discussion

The cumulative weight loss for cast iron is given in Fig. 2 as a function of time and for various concentrations of sulfate ions. These results are typical, and similar to those obtained for Cl^- , NO_3^- , and alkalinity.

A fast corrosion rate was observed during the three first days; during that period cast iron specimens lost 45% of the total weight loss over 15 days. After three days the corrosion rate became constant, as can be seen from a linear increase in weight loss as a function of time (Fig. 2). This behavior was previously observed by Stumm [5] and by Amilcar [6].

Figure 3 gives the average corrosion rate (computed by dividing total weight loss by the duration of immersion) as a function of time. Each point expresses the weight loss divided by the number of immersion days. A decreasing rate can be observed with the passage of time. These results were typical for all ions. In all cases, the results can be represented by the following best-fit equation:

$$V = k_1 t^{-k_2} \quad (1)$$

where

V = the average corrosion rate $\text{g/m}^2 \cdot \text{d}$,

t = the immersion time (hours),

k_1 = constant, and

k_2 = constant.

The values obtained for k_1 and k_2 are given in Table 7. It can be seen that k_1 varies between 4.74 and 10.37. Its value becomes larger for the more complex solutions of the second series.

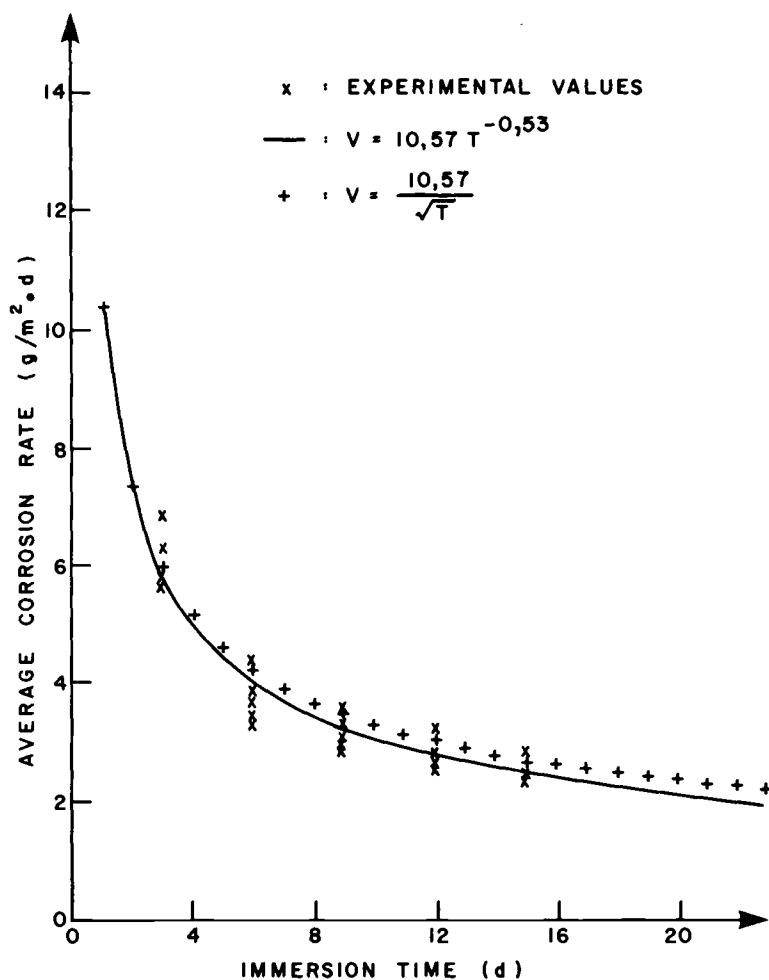


FIG. 4—Average corrosion rate as a function of immersion time and in the presence of chlorides and nitrates: $(Cl^-) = 56.0 \text{ mg/L}$; $(NO_3^-) = 87.0 \text{ mg/L}$.

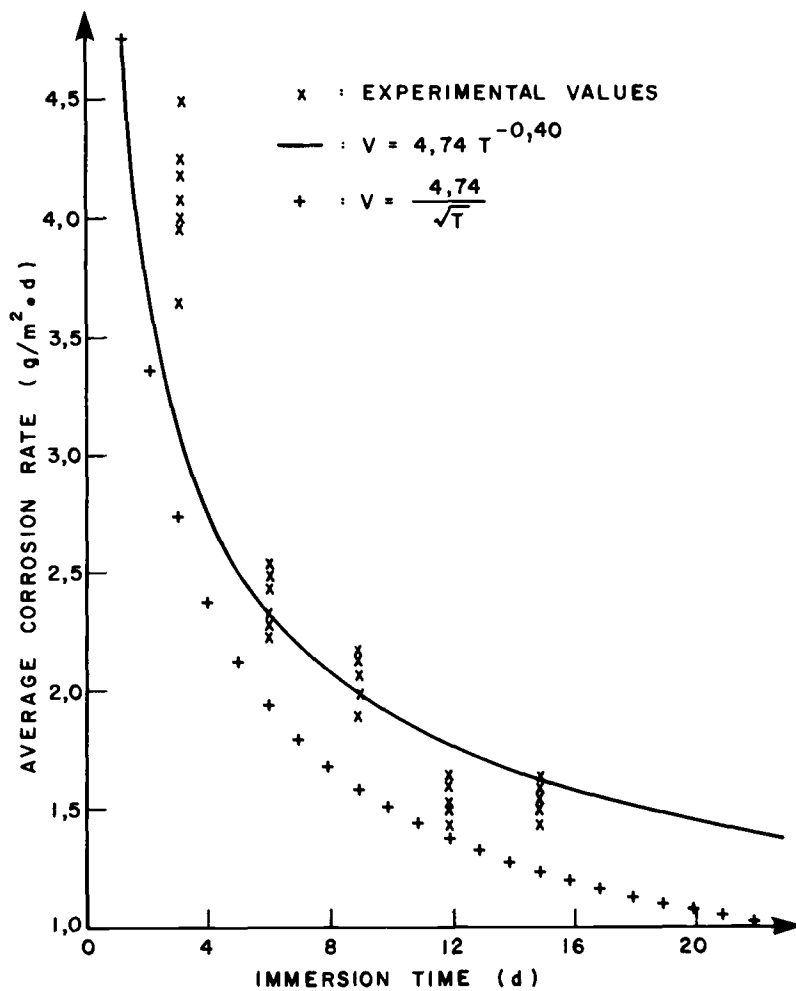


FIG. 5—Average corrosion rate as a function of immersion time and in the presence of sulfates.

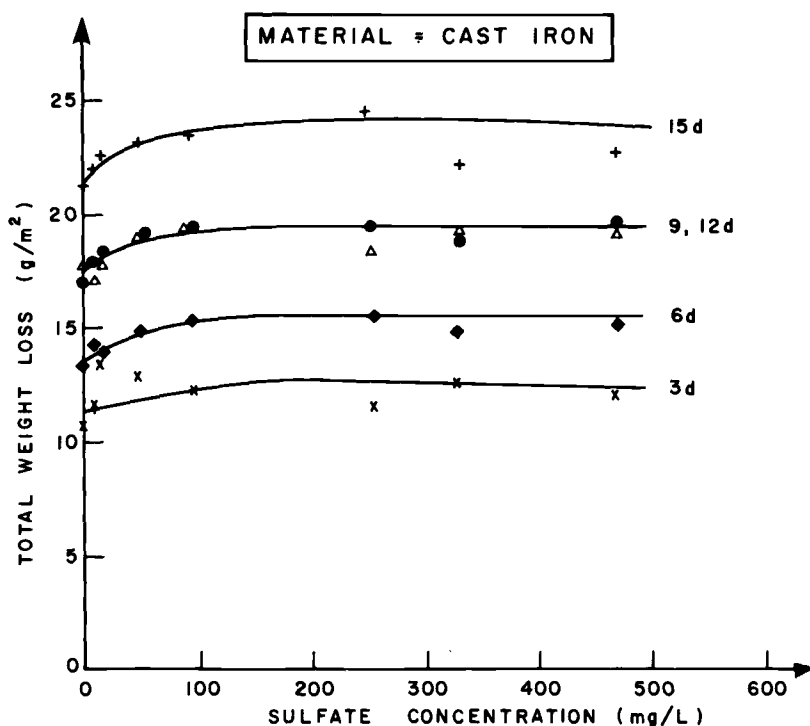


FIG. 6—Cumulative weight loss as a function of sulfate concentration and immersion time.

The value of k_2 appears to be nearly 0.5 for all solutions except when the $\text{SO}_4^{=}$ ions were dominant in the first series of solutions. Figure 3 also compares the actual data of the average corrosion as a function of time, represented by $\times$, with the values computed with the equation and using a value of $k_2 = 0.5$. The line represents the result obtained when $k_2 = 0.47$. All three sets of points are well represented by the same curve.

Figure 4 was obtained in the case of a complex mixed ion solution of Cl^- and NO_3^- . It was quite typical of all the results obtained for the second series of solutions. In mixed complex solutions the value of $k_2 = 0.5$ was good for computing the average corrosion rate of cast iron.

The same value of $k_2 = 0.5$ was also found to be good for the solutions of the first series containing primarily Cl^- and NO_3^- . For the solutions in which the alkalinity was the dominant composition factor, the value of $k_2 = 0.57$ was measured. In this case, the use of $k_2 = 0.5$ in the computations provided corrosion rate values about 15% higher than those obtained experimentally.

It was, however, the solutions containing primarily sulfate, which is a bi-valent ion, that gave the most different values for k_2 . In this case $k_2 = 0.4$, and the use of $k_2 = 0.5$ in the computations gave corrosion rate values nearly

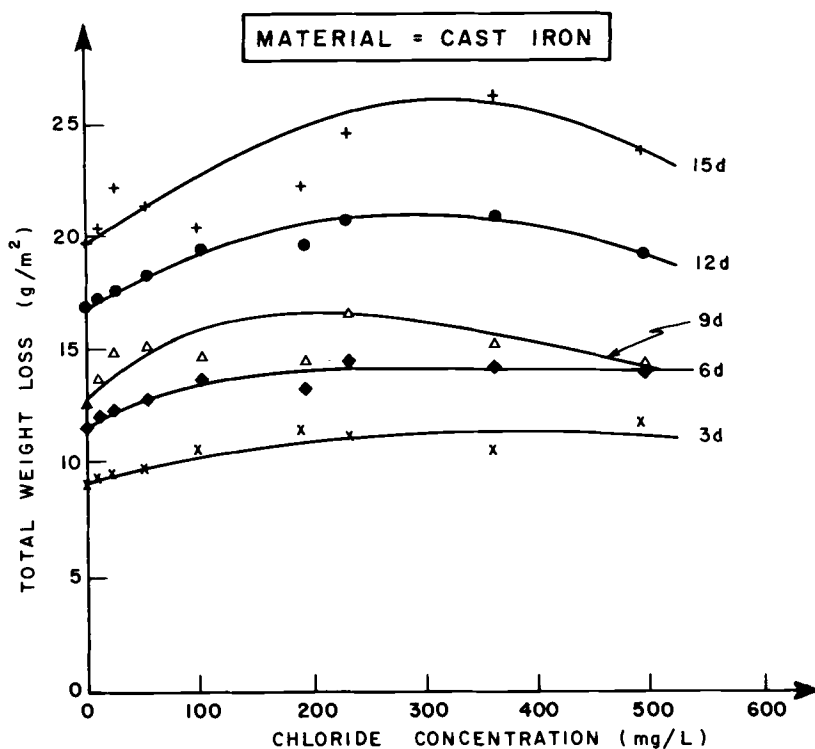


FIG. 7—Cumulative weight loss as a function of chloride concentration and immersion time.

25% lower than the measured values. This is shown in Fig. 5, using the same symbol as in Fig. 3.

Figure 6 shows the cumulative loss of iron (g/m^2) as a function of the sulfate concentration. It is characterized by an initial increase in the corrosion rate with increasing concentration up to 200 mg/L sulfate.

A similar effect was observed with nitrate salts. Increasing concentrations up to 150 mg/L accelerate corrosion, but higher nitrate content had little effect on corrosion rate. In the case of chloride, a concentration of 300 mg/L produces a maximum in the corrosion rate (Fig. 7). On the other hand, the alkalinity content, up to 500 mg/L, did not show any effect on the corrosion rate (Fig. 8).

Another interesting result is the absence of correlation between the corrosion rate and the value of the Langelier index. As can be seen from the typical Fig. 9, a large dispersion in corrosion rates was observed for both positive and negative Langelier indices. Solutions with positive Langelier index produce precipitation, but no protective deposit on the metal.

Corrosion products were, however, produced on the metal surface and

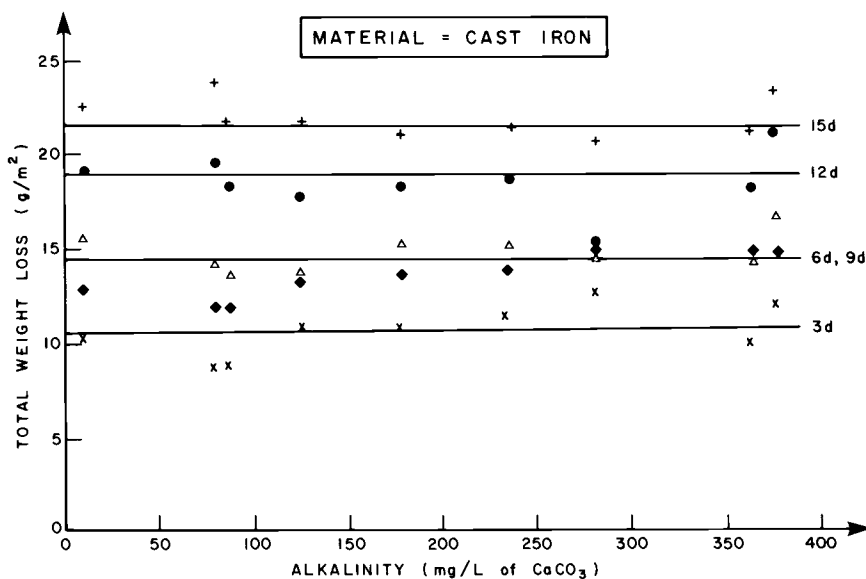


FIG. 8—Cumulative weight loss as a function of water alkalinity and immersion time.

could be responsible for the decrease in corrosion rate observed after three days immersion. The weights of these deposits were determined, and their values are shown in Fig. 10 in g/m^2 after 15 days immersion and for all anion concentrations. It can be seen that NO_3^- produced the heaviest deposits, with $30 \text{ g}/\text{m}^2$, and that sulfate solutions produced deposits of only $15 \text{ g}/\text{m}^2$. It should be noted, however, that after three days immersion, both NO_3^- and SO_4^- solutions produced deposits of about $15 \text{ g}/\text{m}^2$.

The red color characteristic of alumina (Fe_2O_3) was common on cast iron surfaces, particularly when the pH was low. The films that resulted from the cast iron corrosion were analyzed. They contained from 30% to 55% iron compounds, with 97% as ferric iron and only 3% as ferrous iron. Goethite, lepidocrocite, and $\gamma\text{Fe}_2\text{O}_3$ were found. $\gamma\text{Fe}_2\text{O}_3$ becomes the stable species after three days. Some calcite and aragonite were also present. It should be mentioned that no siderite iron carbonate (FeCO_3) and magnetite ferrosferic oxide (Fe_3O_4) were found.

The results obtained with the 1035 specimens of copper were similar to those for iron, but the corrosion rates were much smaller. For alkaline solutions, for instance, the weight loss was only $1 \text{ g}/\text{m}^2$, compared with $12 \text{ g}/\text{m}^2$ after three days for ductile cast iron.

In that case, however, an increase in alkalinity from $10 \text{ mg}/\text{L}$ to $376 \text{ mg}/\text{L}$ produced a decrease in the corrosion rate from $2 \text{ g}/\text{m}^2$ to $1.1 \text{ g}/\text{m}^2$, although this did not have any effect on cast iron. An increase of pH was in general favorable to the corrosion resistance of copper.

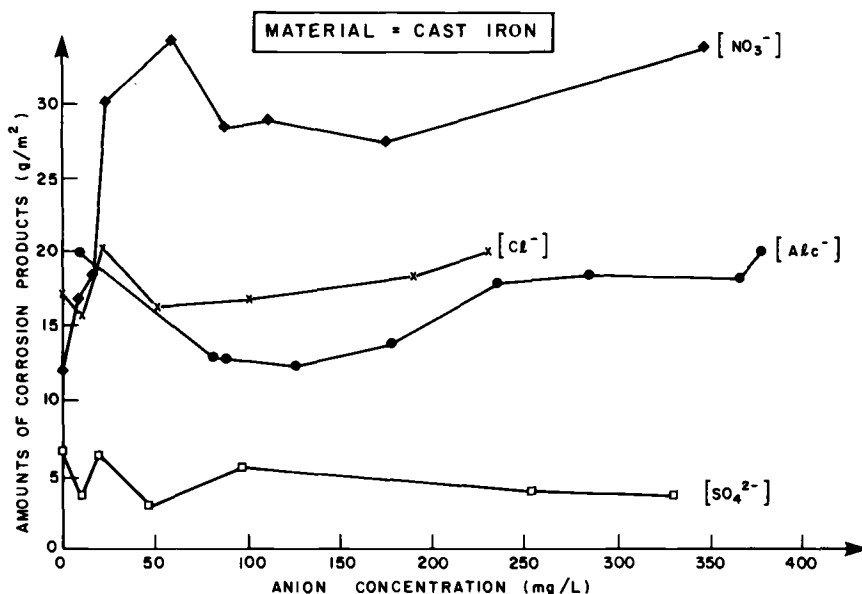


FIG. 10—Amount of corrosion products observed after 15 days immersion time as a function of anion concentration.

Conclusions

1. Ductile cast iron corroded faster during the initial period of three days. The corrosion product formed during that time later slowed down the corrosion rate.
2. A steady rate of corrosion of ductile cast iron was observed after three days.
3. The average corrosion rate of ductile cast iron can be represented as a function of time by the relation

$$V = k_1 t^{-k_2} \quad (1)$$

4. The values of k_2 for cast iron were about 0.5 in most cases, except for sulfate solutions, where they were only 0.4.
5. pH variations between 6.3 and 8.3 did not have an effect on the corrosion rate with 15 days or less of immersion.
6. No correlation, positive or negative, could be found between the corrosion rate of either metal and the Langelier index.
7. The corrosion of copper was very small in all solutions studied. The nature and concentration of the anions had no significant effect on the corrosion rate.

8. X-ray analysis of the films formed revealed an oxide film of CuO and Cu₂O on the immersed specimens of copper.

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Computer-Controlled AC Impedance Measurements for the Determination of Water Penetration of Anticorrosion Coatings

REFERENCE: Kellner, J. D., "Computer-Controlled AC Impedance Measurements for the Determination of Water Penetration of Anticorrosion Coatings," *Corrosion Monitoring in Industrial Plants Using Nondestructive Testing and Electrochemical Methods*, ASTM STP 908, G. C. Moran and P. Labine, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 374-385.

ABSTRACT: A computer-controlled system is described for the measurement of the AC impedance spectrum of coated pipe samples in the laboratory. The extent of water penetration into various coatings were compared.

Bode plots were made of the coated pipes until water penetration became excessive. Then Nyquist plots were used to demonstrate the mechanism of water penetration. The data showed that water incorporation into these thick pipeline coatings is into pores and defects rather than a uniform general penetration.

Thus, it is contrary to the observed mechanism of water penetration to calculate a penetrated thickness as recommended in the ASTM Test Method for Water Penetration into Pipeline Coatings (G 9).

KEY WORDS: AC impedance, polyethylene, coal tar, fusion bonded epoxy, extruded polyethylene, water penetration, pipeline coatings, computer control, capacitance

AC impedance techniques have been used in corrosion research, corrosion monitoring, and for the elucidation of reaction mechanisms. The advantages of using these methods and an excellent review of the pertinent literature have been given by Mansfeld [1], who also gave a detailed account of the analysis of the raw data. The analysis gives information on the capacitances and resistances that are present in the equivalent circuit representation of the test sample. Leidheiser [2] has summarized the application of AC measuring tech-

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niques to the determination of the water penetration in thin organic coatings such as paint. In this paper, the AC measuring technique is applied to pipeline coatings, and an attempt is made to interpret the results on the basis of the mechanism of water penetration into these thick coatings.

In the case of a 50.8-mm (2 in.) pipe specimen, coated with an insulating layer and immersed in an electrolyte solution, the simplest equivalent circuit consists of a very small capacitance, of the order of a thousand picofarads, and a large resistance, of the order of megohms in parallel. The capacitance occurs because of the charge separation between the electrolyte and the steel surface. The value of the capacitance depends on the thickness of the insulation separating the electrolyte and the steel surface, and on the dielectric constant of the insulating medium.

This property is the basis of the very sensitive test used in the laboratory evaluation of pipeline coatings, ASTM Test Method for Water Penetration into Pipeline Coatings (G 9). In this test, the penetration of water into the insulating coating is detected by the change in capacitance that occurs during the test. As water is absorbed or otherwise incorporated into the coating, the capacitance changes because of the large dielectric constant of water and the small dielectric constant of the organic coating. The interpretation of the rise in the capacitance is the fact that water, having a larger dielectric constant, causes the increase in direct proportion to its absorption into the coating.

The ASTM test is normally carried out using a capacitance bridge that determines the capacitance at a frequency of 1000 Hz. Both the capacitance and the dissipation factor are reported. The dissipation factor can be obtained either from the bridge or by a separate measurement of the resistance of the specimen. The value of the dissipation factor is indicative of the magnitude of a resistance in parallel with the capacitor. The dissipation factor D is given by

$$D = 1/\omega RC \quad (1)$$

where

ω = frequency in radians,

R = resistance, and

C = capacitance.

Since the dissipation factor is dependent on both the resistance and the capacitance, its interpretation is difficult. Moreover, if the resistance is too small, the bridge is difficult to balance and is not accurate. Also, if more than one RC circuit exists, it cannot be detected by this method. Thus, no information is obtained relating to the mechanism of water penetration. Rather, the water is assumed to penetrate to some average distance given by the increase in capacitance.

This paper describes the application of AC impedance techniques to the determination of the water penetration into insulating pipeline coatings.

Some of the ideas developed by workers [2] using paint films are applied to thick pipeline coatings in order to elucidate the mechanism of water penetration into these coatings.

The measurement of the impedance of the test sample allows the determination of the change in capacitance as well as the simultaneous change of resistance with no interference between the two. If the incorporation of water into the coating results in the formation of more than one capacitance-resistance combination, then the AC technique may be useful in the modeling of the equivalent circuit, and perhaps, the mechanism of water incorporation. In addition, the use of a laboratory desktop computer, the Hewlett Packard 9836C, is described for the control, acquisition, and the analysis of the data obtained.

Three general types of coatings were studied: polyethylene, coal tar enamel, and fusion bonded epoxy. The configuration of sample used, 50.8-mm-diameter (2-in.) pipe, was chosen to ensure the availability of suitable coatings and to mimic as closely as possible field conditions. The immersed surface area is about 645 cm^2 (100 in.^2) and the approximate thicknesses for the three coatings were 0.127 cm (50 mils), 0.254 cm (100 mils), and 0.030 cm (12 mils). These dimensions, due to the dielectric constants of about 2.3, 8, and 4, respectively, give rise to capacitances of about 1000, 1100, and 7000 pF, respectively, and to resistances from 1 to $10^3 \text{ M}\Omega$. Capacitances of this magnitude are easily determined from a Bode plot of the log frequency versus log impedance.

This same measurement yields the resistance in the circuit, and both the capacitance and the resistance can be followed independently with time. Using this technique, it may be possible to differentiate between water invasion at a single point in the coating at the site of a flaw, and water invasion throughout the coating. This is because the failure of the coating at a single point causes the entry of electrolyte, and this lowers the resistance considerably. This situation makes it difficult to measure the capacitance using a bridge. If water invades the coating more generally, an increase in capacitance occurs due to the increased dielectric constant of water, without appreciably changing the resistance. The AC measurement is an ideal technique to use to follow this behavior because additional circuit elements created by advancing water can be detected.

Experimental Procedure

Specimen Preparation

The test specimens were prepared as required in ASTM G 9. Specimens were 0.61-m-long (24 in.), 50.8-mm (2-in.) diameter pipe coated with various pipeline coatings such as coal tar enamel, fusion bonded epoxy, and polyethylene, both extruded and in tape form. The specimens were bought commer-

cially from a pipe coater. The bottom ends only of the pipe specimens were sealed with epoxy cement and covered with polyethylene caps. Connections were made with stainless steel bolts. All other requirements for the test procedure were followed as in ASTM G 9.

Impedance Data

The test specimens were removed from the -6 V power supply before measurement. Shielded cable was used to connect a potentiostat (Solartron 1186) to the pipe specimens. The AC impedance was determined using a Solartron 1250 Transfer Function Analyzer and Hewlett Packard 9836C computer. The data were plotted on a 9872 plotter or formatted and printed for hard copy. A schematic diagram of the electrical connections is shown in Fig. 1. Frequency scans from 65 kHz to 0.2 Hz were used, with ten steps for each decade of sweep. Sweeps were always in direction of decreasing frequency. The data were plotted in the form of a Bode plot, log impedance versus log frequency. A computer program was written to determine the best fit of the straight-line portions of the curves. Then the lines were extrapolated by the computer program and the values for resistances and capacitances in the circuit were calculated automatically.

This technique is suitable only if the resistance in parallel with the capacitance is very high. In this case the slope of the descending portions of the curves are equal to -1 . This was always the case unless the specimen had failed in some way and the resistance greatly decreased. In this case, the Nyquist plot was used to determine the circuit components present. A computer

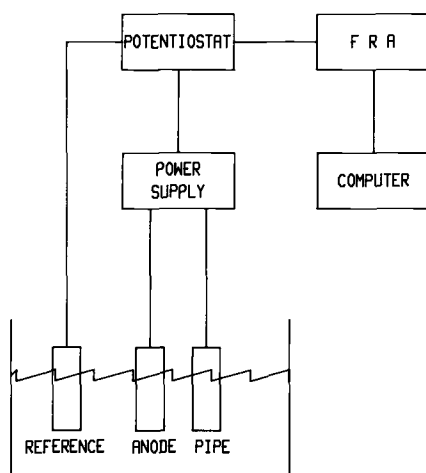


FIG. 1—Schematic diagram of impedance measurement experimental setup.

program to fit the best circles was used to determine the equation for the circle and the radius, and frequency at which the imaginary component was a maximum was used to calculate the resistances and capacitances. In the cases for which two semicircles were obtained, each was plotted separately to determine the individual circuit elements or to determine if a Warburg impedance [3] was the cause of the second feature.

Rather than use mercury to determine the dielectric constant, the coating thickness was measured and used to calculate the initial dielectric constant. In view of other uncertainties in the measurement, this does not introduce any untoward inaccuracy.

Results and Discussion

The dielectric constants, calculated from a measurement of the thickness of the coating are shown in Tables 1 and 2. The dielectric constant, K , for the insulating medium in a cylindrical capacitor is given by [4],

$$K = \frac{C \ln(D'/D)}{2\pi \epsilon L}$$

where

D' = diameter of coated pipe,

D = diameter of bare pipe,

TABLE 1—Calculation of dielectric constant for Set 1.

Specimen	D' , cm	D , cm	L , cm	Capacitance, pF	Dielectric Constant
PE tape-1	6.29	6.03	35.6	1486	3.1
FBEC	6.09	6.03	35.6	7814	4.0
Coal tar	6.67	6.03	35.6	1704	8.8
Ext PE-1	6.29	6.03	35.6	1706	3.6
Ext PE-2	6.32	6.03	35.6	1172	2.8
PE tape-2	6.29	6.03	35.6	1236	2.6

TABLE 2—Calculation of dielectric constant for Set 2.

Specimen	D' , cm	D , cm	L , cm	Capacitance, pF	Dielectric Constant
PE tape	6.29	6.03	38.1	1405	2.7
FBEC	6.09	6.03	38.1	6012	4.2
Coal tar	6.67	6.03	38.1	1749	8.4
Ext PE-1	6.29	6.03	38.1	1382	2.7
Ext PE-2	6.32	6.03	38.1	1553	3.5

ϵ = permittivity of a vacuum, $8.85 \times 10^{-12} \text{C}^2/\text{Nm}^2$,
 L = length of cylinder, and
 C = capacitance in Farads.

In all cases, the dielectric constant calculated from the thickness measurement was close to the value expected [5]. In any event, the increase in capacitance or dissipation factor is the determining factor in assessing the coating, and therefore the initial dielectric constant need not be known more accurately by using mercury.

The capacitance is calculated from the Bode plots of log frequency versus log impedance. Figure 2 shows the Bode plots for each specimen in the second set of data, taken on the first day. The impedance spectrum shown is from 20 kHz to 0.63 Hz. Each of the specimens shows the same high-frequency behavior, a slope of -1 until, at lower frequencies, the slope becomes close to zero, and the impedance is independent of frequency. The computer is easily programmed to determine the slope of each section of the curve, using linear regression, and from an extrapolation to a log w of 1, both the capacitance and

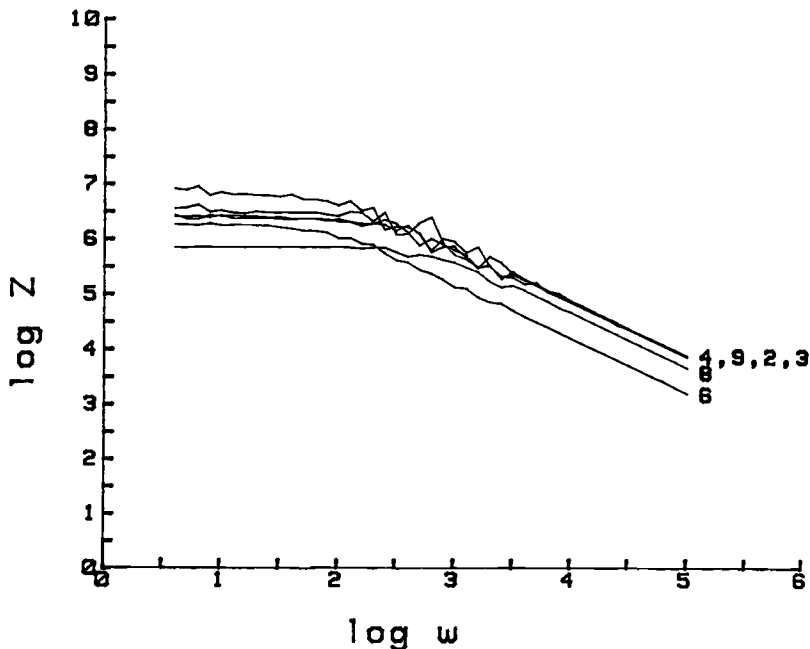


FIG. 2—Bode plots for pipeline coatings, first day: 2,3-Ext. PE; 8,4-PE tape; 6-FBEC; and 9-coal tar.

the resistance is calculated. In their respective frequency regions, the capacitance is given by

$$C = \frac{1}{Z}$$

and the resistance is the impedance, $R = Z$. Figure 3 shows the same specimens for the second day with a frequency range of 65 kHz to 0.41 Hz. All of the specimens show slight decreases in resistance except for the coal tar specimen, which showed a large decrease. The capacitance values obtained from the Bode plots when the resistances were high enough, and the resistance values were used to calculate the dissipation factor at 1 kHz according to Eq 1. The dissipation factors for each set of data are in Tables 3 and 4. These data show some specimens that have failed after a short time in test. The capacitance values for the 14 days of testing for Data Set 1 are plotted versus time in Fig. 4. The values for the coal tar specimen clearly show that a large increase in capacitance has occurred and the values for fusion bonded epoxy coating (FBEC) have increased also. The other specimens show small increases. The data for the second set of specimens show similar behavior and are illustrated in Fig. 5. Again, the coal tar and the FBEC specimens show an increase in capacitance.

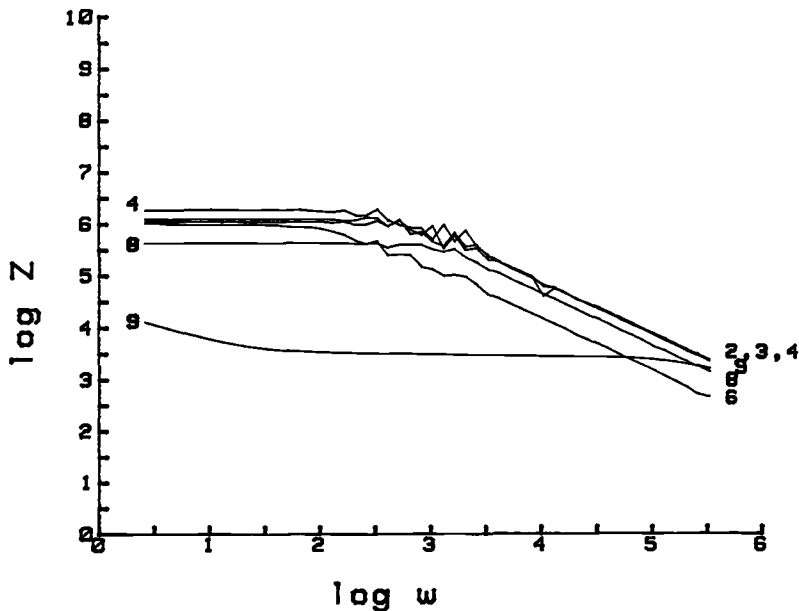


FIG. 3—Bode plots for pipeline coatings, second day: 2,3-Ext. PE; 8,4-PE tape; 6-FBEC; and 9-coal tar.

TABLE 3—Dissipation factor—Set 1.

	Days				
	1	2	3	6	14
Specimen					
PE tape-1	0.003	0.002	...	...	0.036
PE tape-2	0.004	0.004	...	0.003	...
FBEC	0.001	0.001	...	...	0.0003
Coal tar	0.003	0.003	0.060	9.5	...
Ext PE-1	0.002	0.002	...	...	0.004
Ext PE-2	0.003	0.003	...	0.006	80.0

TABLE 4—Dissipation factor—Set 2.

	Days				
	1	2	4	6	11
Specimen					
PE tape	0.0006	0.0060	0.055	0.041	0.054
FBEC	0.0017	0.0015	0.0032	0.015	0.120
Coal tar	0.0043	20.0	26.0	...	...
Ext PE-1	0.0029	0.0086	0.055	0.042	0.066
Ext PE-2	0.0035	0.010	0.052	0.038	0.058

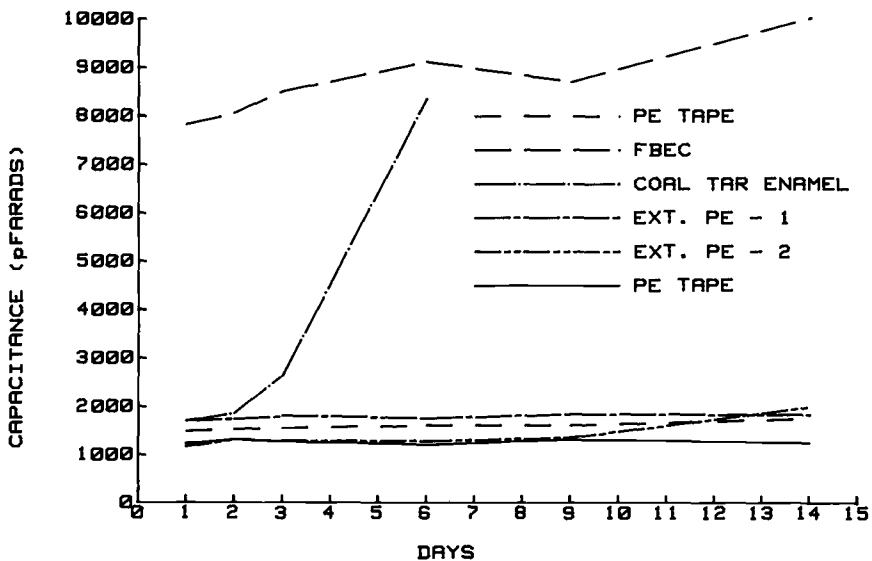


FIG. 4—Capacitance increase with time—Data Set 1.

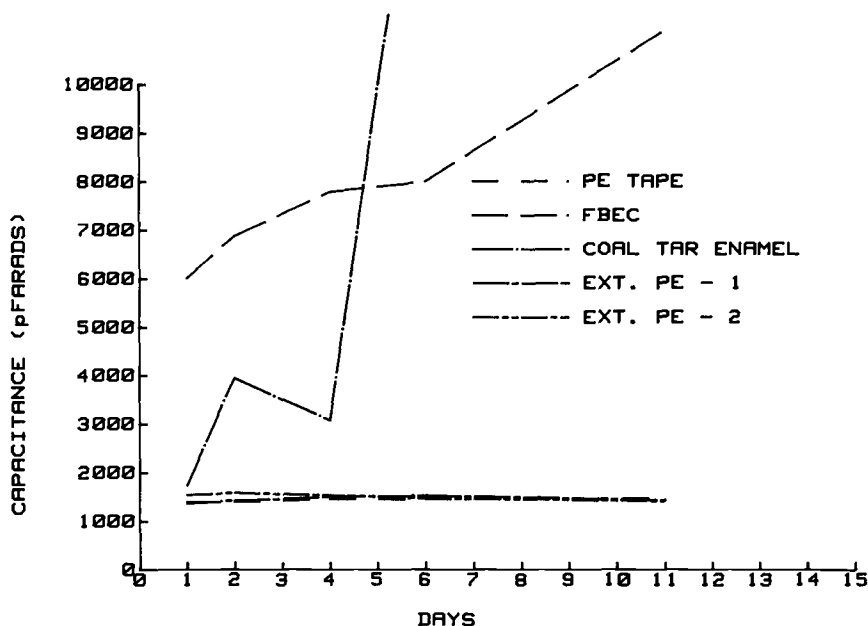


FIG. 5—Capacitance increase with time—Data Set 2.

If the procedure in ASTM G 9 is followed, the penetrated thickness is now calculated from the increase in capacitance. The specimen becomes two concentric cylinders, each with its own capacitance and resistance in parallel with it. The inner cylinder contains the unpenetrated coating and the outer one the water penetrated layer. According to this model, water would penetrate uniformly throughout the coating and advance toward the metal/coating interface. The penetrated thickness can be calculated using the equation of Brasher and Kingsbury [6] which gives the position of that advance. The penetrated thickness, t_p is given by

$$t_p = t_0 - D/2(\text{EXP}(N*K*L/C) - 1)$$

where t_0 is the initial thickness and N is a proportionality constant. In order to compare the results with the two models described, the penetrated thicknesses were calculated and are listed in Tables 5 and 6.

At this point, although the information obtained from the a-c impedance measurement is amenable to computer control, analysis, and storage, it is not much different from that obtained from an impedance bridge. However, when a specimen has apparently failed due to excess water absorption, as evidenced by the fact that the dissipation factor has increased past the value of 1, or the capacitance has shown a large increase, or the penetrated thick-

TABLE 5—*Penetrated thickness—Set 1, mm.*

	Days						Final %
	1	2	3	6	9	14	
Specimen							
PE tape-1	0	0.076	0.102	0.127	0.152	0.229	18
PE tape-2	0	0.102	0.076	0.000	0.102	0.051	4
FBEC	0	0.025	0.051	0.076	0.051	0.102	25
Coal tar	0	0.457	1.30	2.64	...	...	81
Ext PE-1	0	0.076	0.102	0.076	0.152	0.127	10
Ext PE-2	0	0.203	0.178	0.178	0.254	0.635	44

TABLE 6—*Penetrated thickness—Set 2, mm.*

	Days					Final %
	1	2	4	6	11	
Specimen						
PE tape	0	0.076	0.025	0.025	0.127	10
FBEC	0	0.076	0.102	0.127	0.203	46
Coal tar	0	1.91	1.52	2.92	...	90
EXT PE-1	0	0.076	0.152	0	0	0
EXT PE-2	0	0.076	0.025	0.152	0.102	8

ness has increased to more than 50% of the initial thickness, an impedance spectrum can be used to determine the mode of failure. For example, in the case of the coal tar specimen in the first set of data, the Bode plot indicates two features where there was only one at first. This can be seen more clearly in a Nyquist plot in which the imaginary component is plotted versus the real component. The second wave in the Bode plot can be seen as an additional semicircle or start of one in the Nyquist plot. This second feature shown in Fig. 6, can be interpreted as either a capacitor and resistor in series with the first, or a Warburg impedance caused by the diffusion of corrosion products in pores and defects that have appeared in the coating. The model equivalent circuits that represent these cases have been given by Mansfeld [7]. It is apparent that the initial slope of the low frequency feature in Fig. 6 is close to 45° , and this has been shown [8] to be indicative of diffusion processes occurring in pores. The low frequency limit, extrapolated to the real axis, is related to the value of the diffusion coefficients of the reacting species and the reaction rates. It is apparent that the equation of Brasher and Kingsbury [6] cannot be used as it is in ASTM G 9 to calculate a penetrated thickness, t_p .

This has been found to be the case for certain paint systems by Padgett and Moreland [9], who observed similar Warburg "tails" on Nyquist plots of water penetrated paint films.

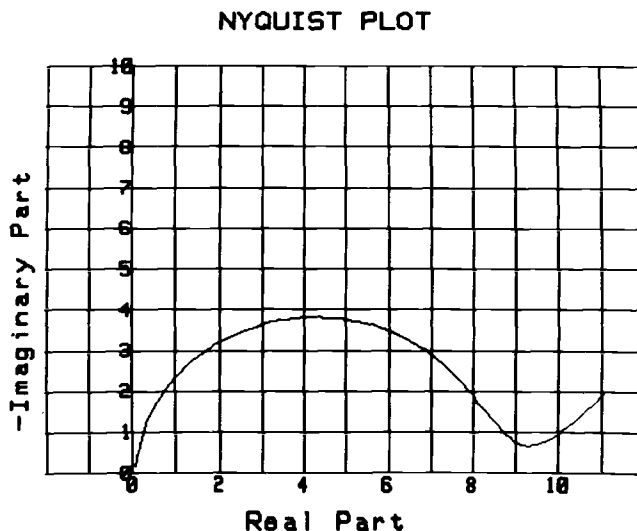


FIG. 6—Nyquist plot for coal tar enamel specimen that exhibited excessive water penetration.

Conclusions

The specimens run in this study have shown that when water penetration was excessive, the mode of failure was always pore penetration. No evidence was found for the gradual, uniform invasion of water into these pipeline coatings that would allow the Brasher and Kingsbury equations to be used for the calculation of a penetrated thickness. Rather, the test is indicative of the invasion of defects or pores with electrolyte. Since the pores or defects that are detected may be a result of application or indeed of specimen preparation, the information obtained does not seem as useful for the comparison of pipeline coatings as it is for the ranking of thin paint films.

The effectiveness of pipeline coatings does not depend on the relatively small amount of water in the vapor form that can be incorporated into a coating. Yet this is precisely what is causing the increase in capacitance in coatings that have not failed, but that have been immersed in electrolyte at large negative potentials for long periods of time. The important parameter for the evaluation of pipeline coatings is the measurement of liquid water that enters a defect and is available for a corrosion reaction on pipe areas that are cathodically shielded.

Although these defects may be detected by the water penetration test when the AC technique is used, they can also be found by other means. For example, after a period of immersion under electrical stress, the resistance of the specimens can be measured. This coating behavior is potentially important, since the defects that are undetectable before the immersion and electrical

stress may appear some time after the coating is in service, and greatly increase the current requirements for cathodic protection.

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Dependence of Stress Corrosion Cracking of Parent, Heat-Affected Zone, and Weld Metal of HSLA Line-Pipe Steel on Potential

REFERENCE: Hoey, G. R., Ramsingh, R. R., and Bowker, J. T., “Dependence of Stress Corrosion Cracking of Parent, Heat-Affected Zone, and Weld Metal of HSLA Line-Pipe Steel on Potential,” *Corrosion Monitoring in Industrial Plants Using Nondestructive Testing and Electrochemical Methods*, ASTM STP 908, G. C. Moran and P. Labine, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 386–403.

ABSTRACT: Potentiostatically controlled slow-strain-rate tension tests ($\sim 10^{-6}\text{s}^{-1}$) were conducted on the parent steel, simulated heat-affected zone, and weld metal specimens obtained from a sample of Canadian grades 483 and 414 high-strength low-alloy (HSLA) line pipe. All stress corrosion cracking (SCC) tests were conducted in $0.5\text{ mmol/cm}^3\text{ Na}_2\text{CO}_3 + 1.0\text{ mmol/cm}^3\text{ NaHCO}_3$ solutions at 75°C in a stressed-electrode cell. Percentage reduction in area and apparent secondary cracking velocity were used as measures of SCC susceptibility. The potentials at which cracking occurred were correlated with fast and slow scan anodic potentiodynamic polarization curves in the same environment.

Secondary cracks occurred along the gage length normal to the stress in a narrow potential range with crack growth rate reaching a maximum in the range from -700 mV to -650 mV versus saturated-calomel electrode. This maximum in the crack depth versus potential curves occurred near the primary passive potential. Scanning electron microscopy provided unambiguous evidence for the presence or absence of SCC in the parent steel, HAZ and weld metal samples in a $\text{CO}_3^{2-}/\text{HCO}_3^{-1}$ environment.

The results support a mixed dissolution-hydrogen embrittlement model for SCC of HSLA line-pipe steel.

KEY WORDS: stress corrosion cracking (SCC), carbonates, potential, pipeline steel, strain rate, polarization curves, crack velocity, metallography, fractography, hydrogen stress cracking (HSC), slow-strain rate technique (SSRT), saturated calomel electrode scale (SCE)

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Stress corrosion can play an important role in the degradation of gas transmission pipelines. Forms which have been identified are: sulphide stress cracking (SSC) attributed to the action of wet hydrogen sulphide on the internal surfaces of pipes; stress corrosion cracking (SCC) of external surfaces of buried pipelines under cathodic protection; and hydrogen stress cracking (HSC) at hard spots on external surfaces of buried pipelines under cathodic protection. The present work concerns the laboratory investigation of SCC of line-pipe steel using the slow-strain rate technique (SSRT).

Stress corrosion cracking from an external environment has been recognized since 1965 as a cause of failure in buried gas transmission pipelines [1]. The failures consist of multiple cracks that are branched, intergranular, and normal to the hoop stress of the pipe. Iron carbonate and magnetite have been identified on the surface of such cracks. Fessler listed and described the important variables in SCC of pipelines [1]. These variables are chemical environment, potential, condition of the coating, stress, condition of the steel, and temperature.

Field studies conducted on failed transmission pipelines have indicated that chemical environment is probably the principal cause of most failures. In most cases, slightly alkaline water solutions containing primarily sodium carbonate (Na_2CO_3) and sodium bicarbonate (NaHCO_3) were found in the cracks. It is believed that Na_2CO_3 and NaHCO_3 were formed when carbon dioxide (CO_2) from the soil reacted with hydroxide (OH^-) ions produced at the pipe surface by the action of cathodic protection current.

Laboratory investigations of SCC of line-pipe steel have been conducted by the slow strain rate test (SSRT) first developed by Parkins [2]. The presence of SCC can be determined by visual examination, optical metallography, and scanning electron microscopy. Influence of certain variables can be studied on similar materials, but the SSRT has not gained general acceptance for comparing materials of widely different compositions and strengths. Slow strain rate testing is a very severe, rapid, go-no-go test of material-environment interactions [3].

In previous work at the Physical Metallurgy Research Laboratories, Revie and Ramsingh studied SCC of parent metal specimens of four samples of Grade 483 line-pipe steels [4]. Their objective was to establish the critical potential ranges over which SCC occurs in four line-pipe steels that were candidates for construction of the Alaska Highway Pipeline in Canada. The four steels were low-carbon, manganese, molybdenum, niobium steels. Slow strain rate testing was carried out under potentiostatic control in solutions of $0.5 \text{ mmol/cm}^3 \text{ Na}_2\text{CO}_3 + 1.0 \text{ mmol/cm}^3 \text{ NaHCO}_3$ at a pH of 9.5. They tested each steel in the range -550 to -800 mV versus SCE at 40°C . The following conclusions were drawn from their work: intergranular SCC occurred during slow strain rate tests of four high strength low-alloy (HSLA) grade 483 line-pipe steels at potentials 50 to 150 mV noble to the primary passive potential; secondary transgranular cracking occurred at primary passive potentials; and

an electrochemical dissolution model for SCC was suggested for high-strength steels.

In this study, the SCC propensity of weld metal, coarse-grained heat-affected zone and parent metal tension specimens of one sample of each of Canadian grades 414 and 483 line-pipe steels is compared by the SSRT. Weld metal and heat-affected zone (HAZ) are potential locations for initiation and propagation of SCC of pipelines.

Experimental Procedures

Materials

Parent and weld metal specimens were obtained from one sample pipe of each of grade 414 and grade 483 line pipes of Canadian manufacture. Table 1 provides chemical composition and mechanical properties of the pipes. Grade 414 (508 by 8.74 mm) and Grade 483 (1219 by 13.7 mm) were controlled-rolled submerged-arc welded pipe with longitudinal and spiral mill welds, respectively. Specimens were cut perpendicular to the mill welds, that is, perpendicular to the plate-rolling direction.

The Gleeble 1500, a weld thermal simulator, was used to simulate the coarse-grained HAZ in specimens. The rapidly changing HAZ microstructure of a real weld with distance from the fusion line prevents the determination of mechanical properties. The Gleeble, however, which operates by resistance heating, is capable of cycling a large enough volume of material so that an

TABLE 1—Steel compositions (weight %) and properties.

Element	Grade 414		Grade 483	
	Parent	Weld	Parent	Weld
carbon	0.110	0.085	0.080	0.075
manganese	1.350	1.100	1.980	1.340
silicon	0.240	0.500	0.290	0.600
aluminum	0.026	0.015	0.017	0.010
sulfur	0.002	0.005	0.005	0.008
phosphorus	0.009	0.007	0.011	0.012
niobium	0.028	0.015	0.045	0.025
molybdenum	0.002	0.170	0.240	0.310
copper	0.012	0.060	0.053	0.105
chromium	0.050	0.060	0.097	0.080
nickel	0.005	0.090	0.033	0.035
Yield strength, MPa	479	...	613	...
Ultimate tension strength, MPa	560	...	724	...
%RA	63.3	...	50.0	...
%EL	31.5	...	22.0	...

evaluation of mechanical properties can take place. Parent metal specimens were thermally cycled to a peak temperature of 1350°C and control quenched with an argon gas stream to give a cooling time from 800°C to 500°C (Δt) of 30s. These conditions simulate a weld heat input which is typical of that used in the welding of line-pipe steels.

Tension specimens of weld, HAZ, and parent metal nominally had a gage length of 9.53 mm and diameter of 2.54 mm, except weld metal tension specimens of Grade 414 steel, which had a shorter gage length of 6.35 mm.

Cylindrical specimens with an exposed area of 5.70 cm² were used for potentiodynamic polarization studies.

SCC Tests

The trifluoroethylene resin (Teflon) cell and tensile specimen used in the SCC tests are illustrated in Fig. 1. The assembly fitted into a dynamic strain tension testing machine of standard design. A constant nominal strain rate of $2 \times 10^{-6} \text{ s}^{-1}$ was employed. A load cell and recorder were used to obtain load-time curves during the tests.

All tests were conducted in deaerated 0.5 mmol/cm³ Na₂CO₃ + 1.0 mmol/cm³ NaHCO₃ solutions at 75°C. A proprietary "stop-off" lacquer, "Microshield," was used to coat the whole specimen except for the gage length. The potential of the gage length was controlled by a Wenking poten-

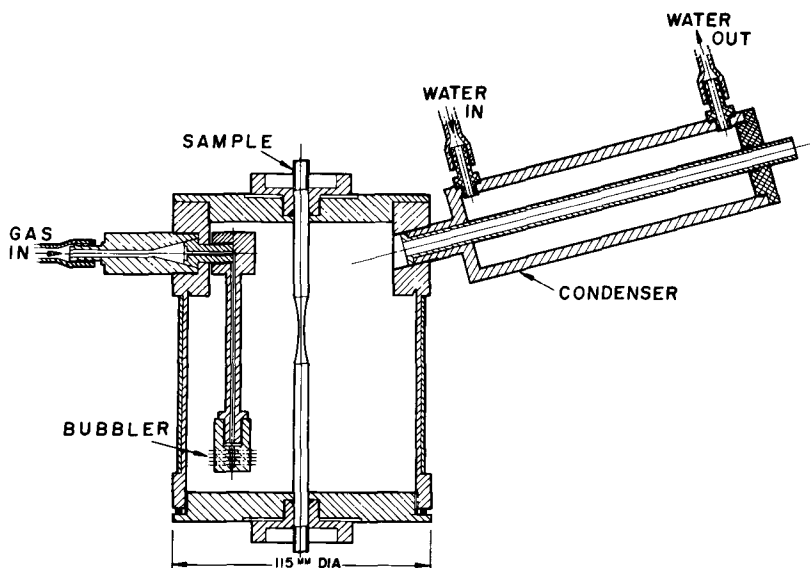


FIG. 1—Electrochemical cell for SCC tests.

tiostat. A Luggin probe (not shown in Fig. 1) was contained in the cell with its tip 2 mm from the specimen. Potentials are given on the saturated calomel electrode scale (SCE). SCC was studied in the potential range from -900 mV to -500 mV versus SCE. Crevice corrosion was not significant in the SCC tests.

After fracture, the specimen was washed in water, then in methanol, and dried. The percentage reduction in area was determined for each specimen as a measure of SCC susceptibility. Secondary crack depth and morphology were determined by optical metallography and fracture mode by scanning electron microscopy.

Potentiodynamic Scan

Potentiodynamic anodic polarization curves were determined for cylindrical weld, HAZ, and parent metal specimens of grade 414 and grade 483 line-pipe in $\text{CO}_3^{2-}/\text{HCO}_3^{-1}$ solutions at 75°C , deaerated with nitrogen. The Teflon polarization cell has been described by Revie [5]. An Aardvark potentiostat and voltage scanning unit were used to determine the curves at potential sweep rates of 1.67×10^{-2} and 3.33×10^{-4} Vs^{-1} . Methods used for specimen preparation and polarization techniques have been described [4].

Results

Coarse-Grained HAZ Simulation

The parent metal of both steels had a directional "partially acicular ferrite" microstructure. For the simulated HAZ material, a constant microstructure was produced over a length of ~ 20 mm, twice the gage length of tension specimens machined following simulation. In both steels the structure consisted of coarse bainite with a prior austenite grain size of 150 to 200 μm . This compares with ~ 100 μm in the coarse-grained heat-affected zone (CGHAZ) of a mill weld in grade 483 steel that had undergone the same thermal cycle given above (*Materials* section) [6]. The SCC behavior might be different as well. This lack of agreement in grain size has been explained by Dolby and Widgery as being the result of the temperature gradient that exists in a mill weld preventing the grains from reaching their equilibrium value for a given peak temperature [7]. Despite this problem, the Gleeble 1500 simulator provides a useful technique for the study of weld heat-affected zones. For example, it has been used successfully in the improvement of submerged-arc weld HAZ toughness of Titanium-bearing line-pipe steels [8,9].

A comparison of CGHAZ structures of grades 414 and 483 revealed coarser bainitic ferrite grains and the presence of pro-eutectoid ferrite in Grade 414. This difference can be explained in terms of the presence of molybdenum in

Grade 483, which is known to cause a substantial decrease in bainite transformation temperature over a large range of cooling rates.

Corrosion Morphology

Corrosion morphologies were determined by optical metallography for the parent metal, HAZ, and weld metal specimens for both steels at all test potentials. Typical of SSRT, secondary cracks were formed along the gage length [2,3,4]. At the test temperature of 75°C, secondary cracks were predominantly intergranular in nature in the parent metal specimens, whereas Revie and Ramsingh reported both intergranular and transgranular cracks at 40°C for four grade 483 steels in the same environment [4]. Because all other experimental conditions were identical, an increase of temperature appears to promote intergranular cracking in parent metal specimens.

Selected photomicrographs are presented to illustrate corrosion morphologies of the gage length of fractured specimens. Crack depth was found to increase with proximity to the fracture, which is classified as intermediate susceptibility to SCC (Fig. 2). By comparison, a corrosion morphology with cracks of equal depth along the gage length indicates a higher susceptibility, and cracks appearing only in the necked-down region indicate a lower susceptibility [10]. In specimens of intermediate susceptibility, crack initiation and

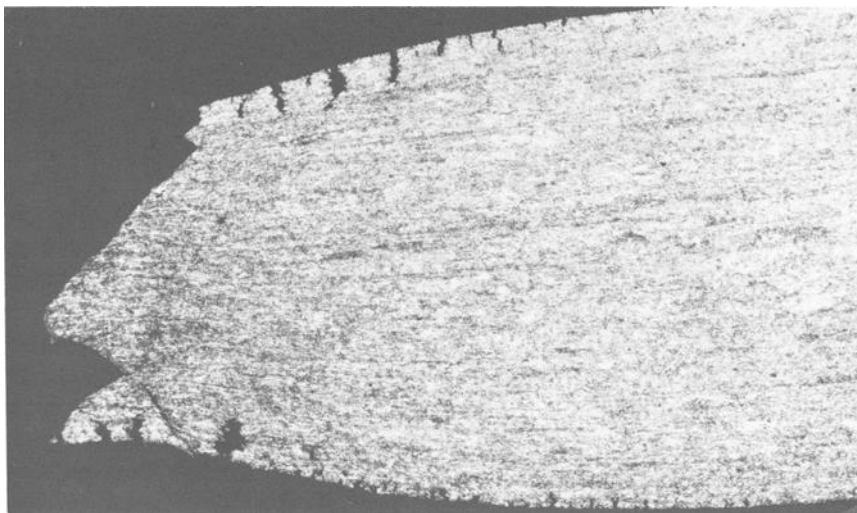


FIG. 2—Photomicrograph of Grade 483 parent metal specimen fractured in $\text{CO}_3^{2-}/\text{HCO}_3^{-}$ at -600 mV versus SCE ($\times 50$).

propagation occurs before maximum load, whereas in specimens of greater susceptibility, cracks occur only during necking.

A wide range of corrosive deterioration was found on metallographic examination. At low potentials, pitting occurred in the necked-down region, for example, at -850 mV for Grade 483 weld metal specimen, and a decrease of potential to -900 mV eliminated pitting and secondary cracks. The corrosion potential was -870 mV at 75°C . Figure 3 shows a long crack at the bottom of a pit on a specimen of parent metal fractured at -650 mV. Secondary cracks without pitting were also observed. Thus, although pits act as stress risers, they do not appear to be essential for SCC to occur in this environment.

Fractography

Prior to examination by SEM, corrosion products on the fracture surface were removed with an inhibited hydrochloric acid solution. SEM was only

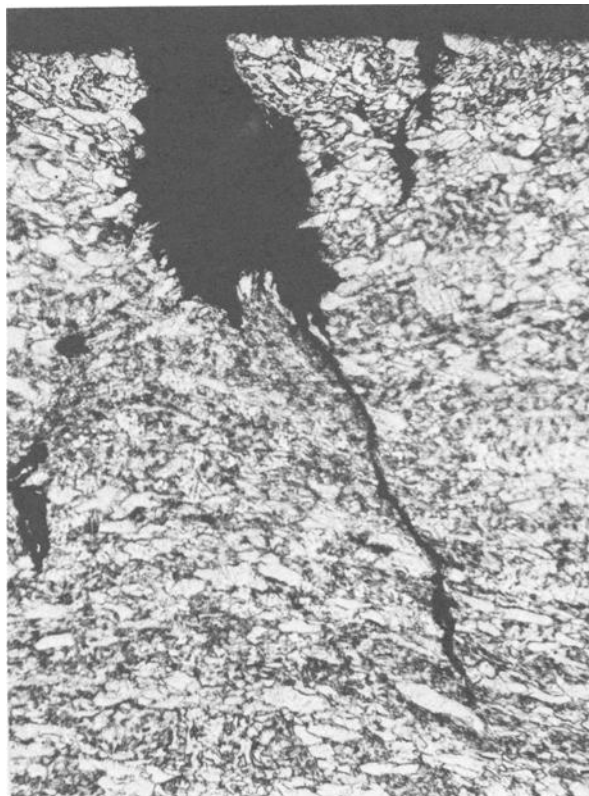


FIG. 3—Photomicrograph of Grade 483 parent metal specimen fractured in $\text{CO}_3^{-2}/\text{HCO}_3^{-1}$ at -650 mV versus SCE ($\times 400$).

performed on specimens fractured in the region of potentials of high susceptibility to dissolution SCC, that is, -650 to -700 mV. Figure 4 shows the fracture surface, secondary cracks, and necking of grade 483 weld metal tension specimen fractured in a $\text{CO}_3^{2-}/\text{HCO}_3^{-1}$ environment at -700 mV (reduction in area is 34%). Over 90% of the fracture surface exhibited failure by a ductile-dimple mode. A region which shows both ductile dimple and quasi-cleavage fracture modes is shown in Fig. 5 which indicates transgranular cracking. The weld specimens fractured in air failed entirely in a ductile-dimple manner with no evidence of any cleavage facets.

Secondary cracks along the gage length and fracture morphology are shown in Fig. 6 for grade 483 HAZ specimen strained to failure in a $\text{CO}_3^{2-}/\text{HCO}_3^{-1}$ environment at -650 mV. The intergranular nature of SCC is shown where a secondary crack emerges at the fracture surface. The fracture was brittle with a reduction in area (RA) of 18.4%. A large intergranular crack on the circumference is shown in Fig. 7. Scanning electron microscopy indicated that SCC susceptibility was greater for HAZ than for weld metal and that both secondary cracking and fracture surface cleavage are indicative of failure by SCC in this specific environment.

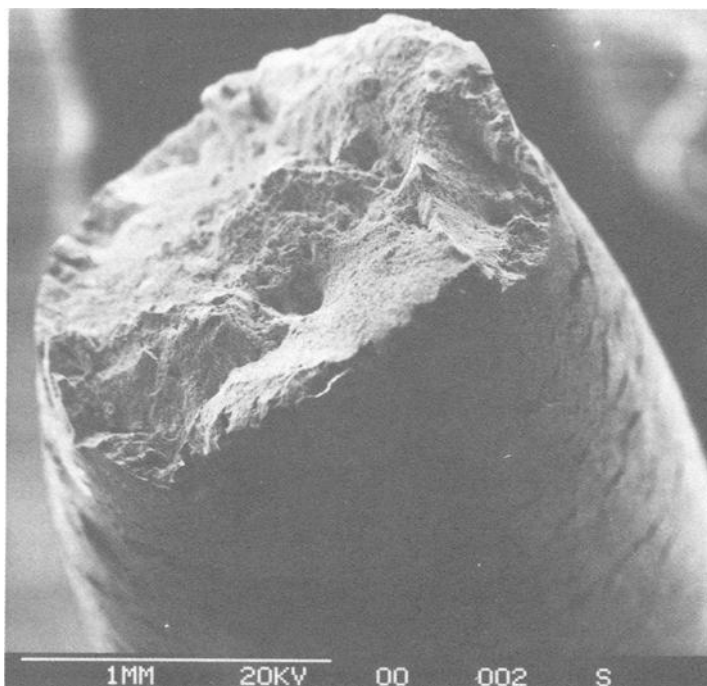


FIG. 4—SEM micrograph of fracture surface of Grade 483 weld metal specimen fractured in $\text{CO}_3^{2-}/\text{HCO}_3^{-1}$ at -700 mV versus SCE ($\times 340$).

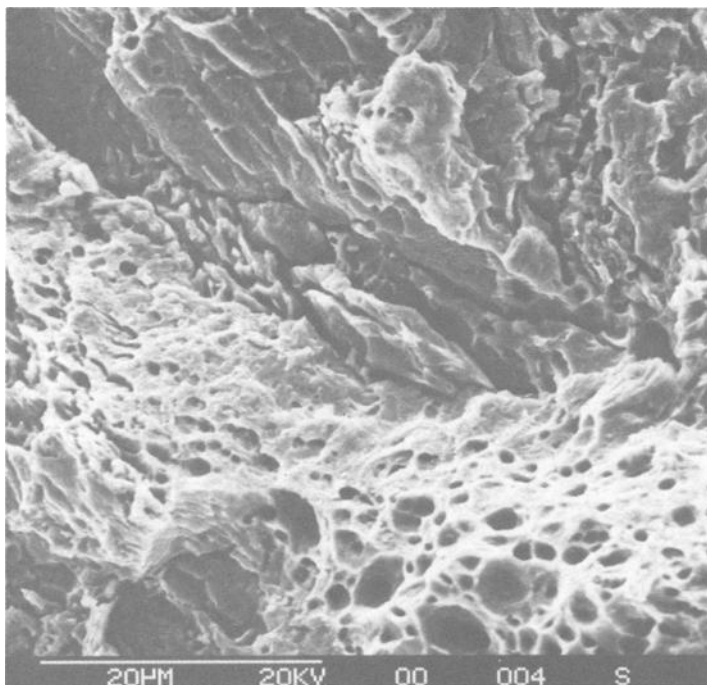


FIG. 5—SEM micrograph of fracture surface of Grade 483 weld metal specimen fractured in $\text{CO}_3^{-2}/\text{HCO}_3^{-1}$ at -700 mV versus SCE ($\times 1690$).

SCC Susceptibility Parameter

Percent reduction in area (%RA) is the mechanical property generally used to compare SCC susceptibility in SSRT of steels. In Eqs 1 and 2, the relative change in reduction of area in noncorrosive and corrosive environments is used as a criterion of SCC susceptibility.

$$\Delta RA = RA_a - RA_s \quad (1)$$

$$I_{SCC} = \Delta RA / RA_a \quad (2)$$

where

RA_a = % reduction of area in air,

RA_s = % reduction of area in $\text{CO}_3^{-2}/\text{HCO}_3^{-1}$ environment, and

I_{SCC} = SCC susceptibility parameter.

Percentage reduction in area versus potential data are presented in Figs. 8, 9, and 10 for parent, HAZ, and weld metal specimens in a $\text{CO}_3^{-2}/\text{HCO}_3^{-1}$

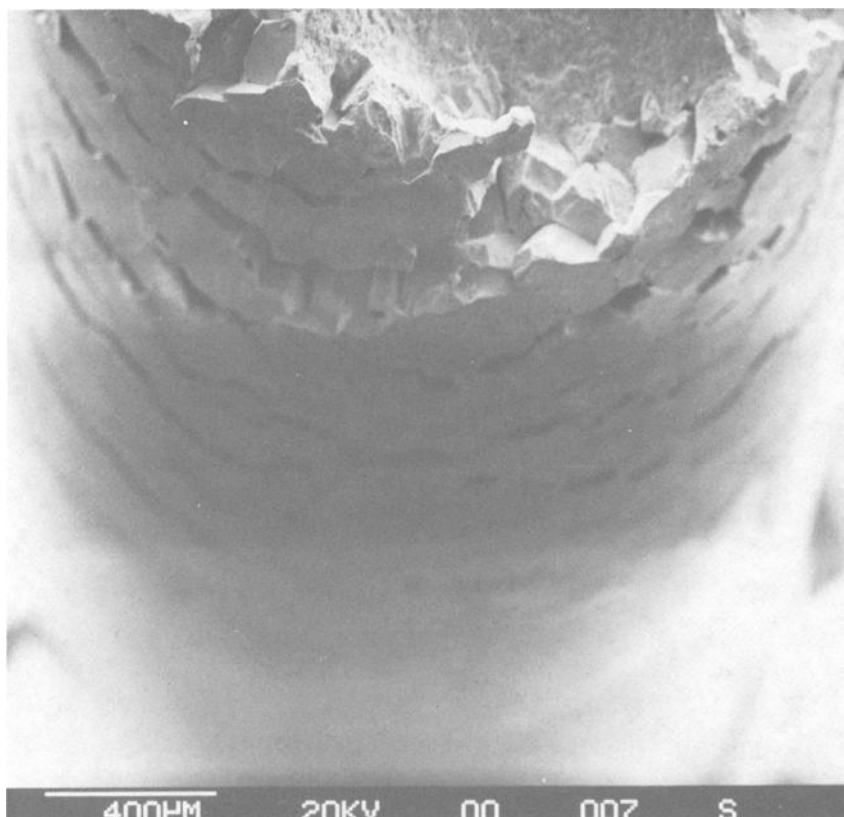


FIG. 6—SEM micrograph of Grade 483 HAZ specimen fractured in $\text{CO}_3^{2-}/\text{HCO}_3^{-1}$ at -650 mV versus SCE ($\times 44$).

environment at 75°C . Minima are observed for parent and HAZ specimens at -650 mV, whereas the curves for weld metal do not have well-defined minima. Data are compared in Table 2 for I at -650 mV for parent steel, HAZ, and weld metal specimens. The data show that Grade 483 linepipe steel is more susceptible to SCC than Grade 414 and weld metal specimens are less susceptible than HAZ or parent metal specimens. The susceptibility of HAZ equals parent for 483 but for 414 parent is halfway between HAZ and weld.

Kinetics of Secondary Crack Growth

Secondary cracks were observed in the potential range from -500 mV to -900 mV and the length of the longest crack on the gage length reached a maximum at potentials in the range from -650 mV to -700 mV. The maximum in the crack depth versus potential curves occurred near the primary

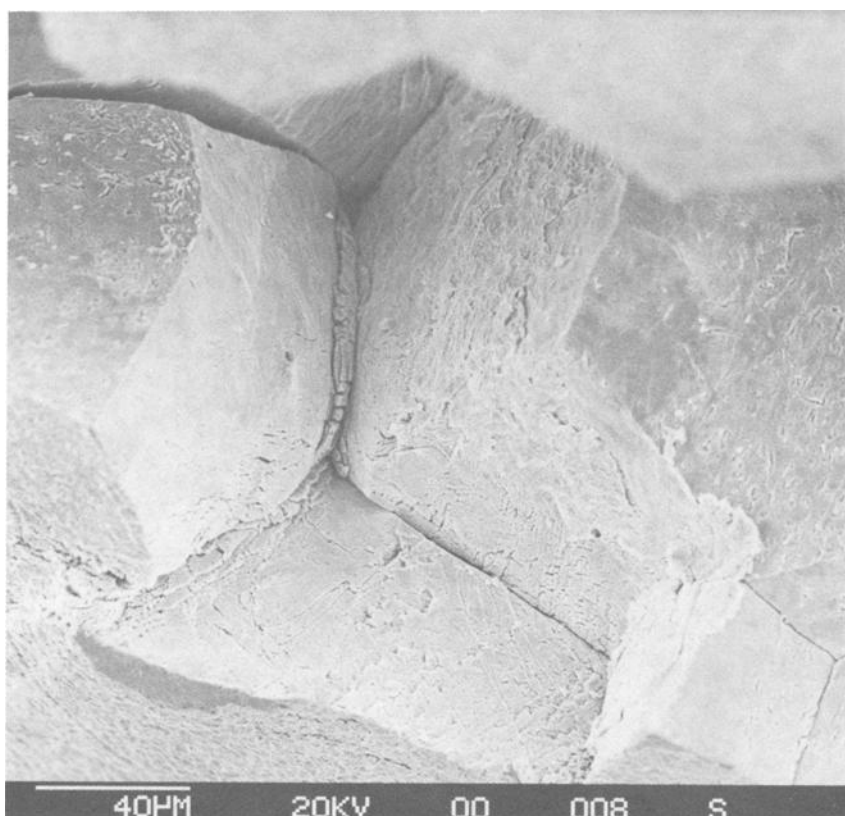


FIG. 7—SEM micrograph of Grade 483 HAZ specimen fractured in $\text{CO}_3^{-2}/\text{HCO}_3^{-1}$ at -650 mV versus SCE ($\times 410$).

passive potential for each of the six types of tension specimens. Typical maximum crack depth versus potential curves are presented in Fig. 11 for HAZ specimens. Because the crack initiation time is unknown, it is not possible to obtain crack growth rate accurately, but a kinetic parameter may be defined as

$$da/dt = d_m/t_f \quad (3)$$

where

d_m = maximum crack depth,
 t_f = time to failure in a $\text{CO}_3^{-2}/\text{HCO}_3^{-1}$ environment at 75°C , and
 da/dt = crack growth rate parameter.

Secondary crack growth rate data are presented in Table 3. Based on da/dt , Grade 483 steel has a higher susceptibility to SCC than Grade 414. In

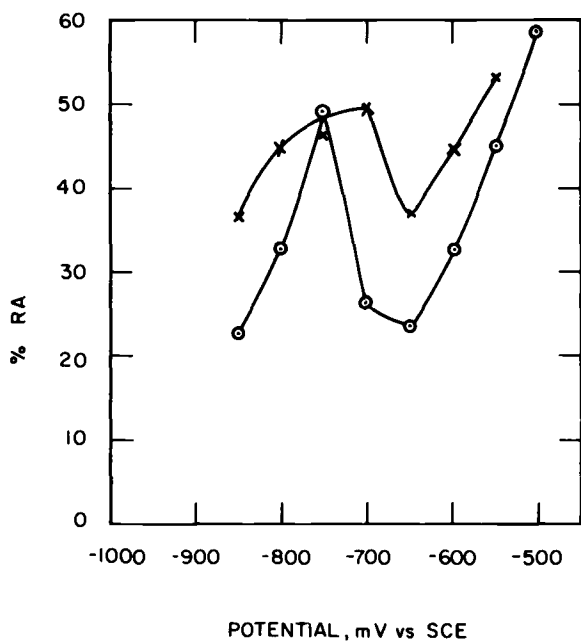


FIG. 8—Percent reduction-of-area versus potential for parent metal specimens: 0 Grade 483; X Grade 414.

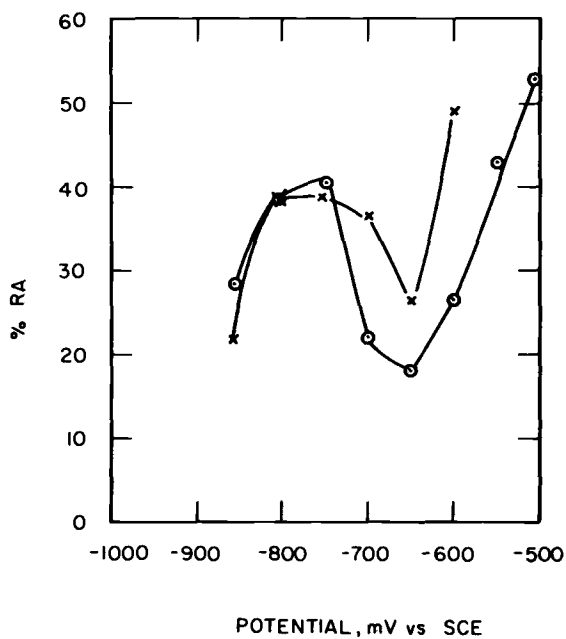


FIG. 9—Percent reduction-of-area versus potential for HAZ specimens: 0 Grade 483; X Grade 414.

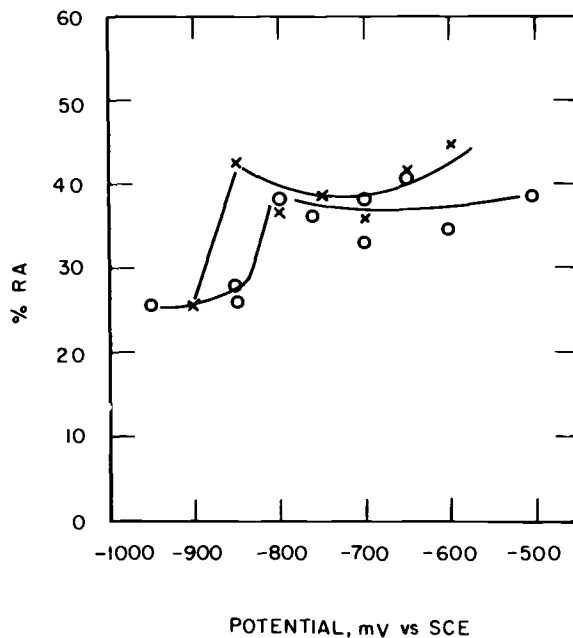


FIG. 10—Percent reduction-of-area versus potential for weld metal specimens: 0 Grade 483; X Grade 414.

TABLE 2—Stress corrosion cracking susceptibility at -650 mV versus SCE.

Material		I_{SCC}
Grade 414	Parent	0.39
	HAZ	0.54
	weld	0.28
Grade 483	Parent	0.63
	HAZ	0.66
	weld	0.22

a previous study, parent metal grade 483 tension specimens had a value of $da/dt = 1.0 \times 10^{-6}$ mm/s at 40°C [11]. Thus, an increase of temperature from 40°C to 75°C caused a threefold increase in the crack growth rate parameter.

Improvements to the slow-strain-rate technique would be advantageous so that da/dt may be determined accurately. For example, crack initiation data could be obtained by the development and use of a stressed-electrode cell for in-situ microscopy of tension specimens [11].

Newman et al, in their study of SCC by the slow-strain-rate technique of

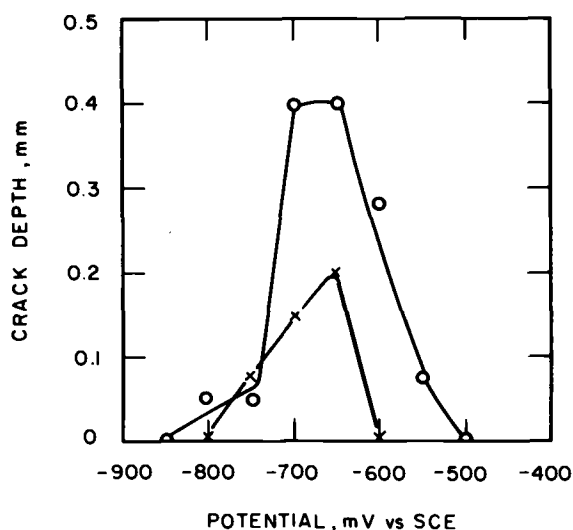


FIG. 11—Maximum crack growth versus potential for HAZ specimens: O Grade 483; X Grade 414.

TABLE 3—Secondary crack growth rate.

Material	Crack depth, mm	Time, h	da/dt , mm/s	V , mm/s
Grade 414 parent	0.19	30.6	1.7×10^{-6}	2.6×10^{-6}
	0.20	26.6	2.1	3.8
	0.25	49.8	1.4	3.3
Grade 483 parent	0.26	24.4	3.0×10^{-6}	3.4×10^{-6}
	0.40	18.9	5.9	4.2
	0.25	28.0	2.5	2.0

sensitized Type 304 stainless steel in thiosulfate solutions, established apparent crack velocities by taking the longest crack and the time from the yield point to failure [12].

Crack Tip Dissolution Kinetics

Electrochemical data were generated for the six test materials to aid in interpretation of SCC test results. Typical anodic potentiodynamic polarization curves are presented in Fig. 12 for grade 414 steel. All six materials showed similar behavior. Parkins has postulated that the current density value obtained at the primary passivation potential in the fast scan represents the corrosion rate of unfiled metal at the crack tip, and the slow scan current density at the passive potential represents the corrosion rate of filmed metal on

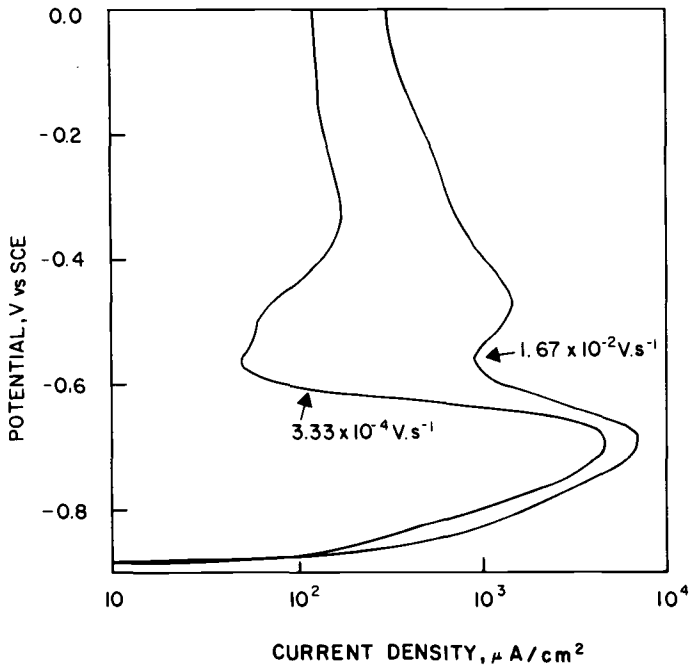


FIG. 12—Potentiodynamic polarization curves for parent metal specimen of Grade 414 steel.

the crack wall [13]. The peak value of the anodic current density at the nose of the anodic polarization curve prior to passivation was assumed to be the maximum crack-tip velocity. The primary passive current density obtained from the potentiodynamic curves was used to calculate theoretical crack tip velocities from the following equation developed from Faraday's Laws:

$$v = \frac{i_a M}{z F \rho} \quad (4)$$

where

- i_a = primary passivation current density,
- M = molecular weight,
- z = valence,
- F = Faraday,
- ρ = steel density, and
- v = theoretical crack tip velocity.

Theoretical crack tip velocity data are presented in Table 3 for parent metal, HAZ, and weld metal specimens of Grades 414 and 483 steels. For the steels tested, anodic potentiodynamic polarization curves gave the apparent

cracking velocity to within a factor of three and the potential for maximum crack growth to within 25 mV.

Mechanism of Cracking

An electrochemical dissolution model for SCC has been proposed by previous investigators [14,15]. In this model, the tip of the advancing crack, which is anodic to the rest of the specimen, is consumed in the corrodent by the dissolution of steel. A decrease in pH may be produced at the crack tip by hydrolysis of metal ions. The change in pH caused by the hydrolysis is related to solution composition and deposition of oxides and hydrogen. Hydrogen may recombine to form hydrogen gas or dissolve at the cathode walls and diffuse to stress zones. Hydrogen recombination poisons, if present on the crack wall, could accelerate absorption into the metal lattice. Thus, hydrogen embrittlement may also contribute to SCC failures.

This model is supported empirically by the data presented in this paper. Maximum SCC susceptibility as defined by percentage reduction in area occurred at potentials which were near the primary passive potential indicating an anodic dissolution mechanism. Secondary cracking occurred only in a narrow range of potentials with maximum crack velocity occurring near the primary passive potential, again indicating an anodic dissolution mechanism. However, the hydrogen embrittlement mechanism may also have been operative. A maximum was observed at lower potentials in the %RA versus potential curves and at -850 mV the %RA indicates some hydrogen embrittlement. Steel deterioration at the lower potentials is probably due to a hydrogen embrittlement mechanism, whereas dissolution SCC appears to be dominant at -650 mV.

Research is needed to measure crack tip pH experimentally so that the potential for hydrogen evolution can be calculated. Singbeil and Tromans have differentiated between the two mechanisms by measuring crack tip pH of double cantilever beam samples in their studies of caustic cracking of mild steel at 92°C [16,17]. The evidence for hydrogen embrittlement in this study is tentative and additional research is needed at the lower potentials where it has been assumed to occur.

Conclusions

The following conclusions may be drawn from the study of SCC of parent, HAZ, and weld metal tension specimens of Grades 414 and 483 line-pipe steels in $\text{CO}_3^{2-}/\text{HCO}_3^{-1}$ solutions at 75°C using the slow strain rate techniques.

1. Grade 483 steel had a higher SCC susceptibility than Grade 414. Weld metal specimens were less susceptible than HAZ or parent metal specimens.

Susceptibility of HAZ equaled parent for Grade 483 but for Grade 414 parent was halfway between HAZ and weld.

2. Maximum susceptibility occurred at potentials near the primary passive potential in the potential range from -650 mV to -700 mV versus SCE.

3. Apparent maximum crack propagation rates were of the order of 10^{-6} mm/s.

4. The study suggests a mixed anodic dissolution-hydrogen embrittlement mechanism for SCC in the $\text{CO}_3^{2-}/\text{HCO}_3^{-1}$ environment.

Acknowledgments

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Corrosion of Carbon Steel in Concentrated NaOH Solutions: Influence of LiOH Additions

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ABSTRACT: The present study aims at determining quantitatively the influence of lithium hydroxide (LiOH) as an inhibitor on the corrosion behavior of carbon steel in a 33-weight percent sodium hydroxide (NaOH) solution at temperatures < 110°C. This work is conducted as a prelude to further high temperature studies dealing with stress corrosion. Potentiodynamic methods are used in determining the influence of LiOH additions. Cyclic voltammograms indicate gradual variation in the intensities corresponding to certain peaks, depending on the presence or absence of LiOH and on the temperature of the solution. An improvement in corrosion behavior is indicated when LiOH is present at a concentration of 20 g/L. Apparent activation energies are calculated and certain ideas are put forward in order to explain the behavior of carbon steel in NaOH containing LiOH.

KEY WORDS: carbon steel corrosion, sodium hydroxide, lithium hydroxide, voltammogram, apparent activation energy

High-temperature behavior of carbon steel in hydroxide solutions is of industrial interest in view of the wide-ranging application of hydroxide solutions in alumina extraction, water electrolysis, heat transport in nuclear power stations, and in alkaline battery systems. A majority of these industries need sodium hydroxide (NaOH) or potassium hydroxide (KOH) whereas some of them use lithium hydroxide (LiOH) for their applications.

It has been indicated [1-4] that the corrosion behavior of mild steel in

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LiOH is different from that observed in other alkali hydroxides at temperatures of 200 to 300°C. Anodic polarization of mild steel in LiOH solutions at 300°C shows lower critical currents when compared to those obtained in equivalent solutions of sodium or potassium hydroxide [5,6]. Moreover, Jones and Humphries show results indicating that stress corrosion susceptibility of low-carbon mild steel is significantly lower in boiling LiOH solutions than in equivalent NaOH solutions [6]. Lithium hydroxide appears to be beneficial in combatting pitting corrosion as well [7,8]. Additions of small amounts of LiOH to alkaline secondary battery electrolyte (concentrated KOH) are considered to be beneficial in improving battery performance [9]. A knowledge of the corrosion of battery container materials in the presence of LiOH therefore becomes necessary. It is hence logical that a study be undertaken to quantitatively determine the influence of LiOH on the corrosion behavior of carbon steel in concentrated NaOH solutions at different temperatures ($< 110^{\circ}\text{C}$). This study is intended to pave the way for further corrosion studies and for slow-strain-rate stress corrosion tests at higher temperatures. Using LiOH as an additive to NaOH can be foreseen in different industrial applications, depending on how successful these tests are.

Experimental Procedure

The experiments were carried out in a two-compartment trifluoroethylene resin cell. The reference electrode (saturated calomel electrode) compartment and the main cell were connected by trifluoroethylene resin capillary tube filled with the electrolyte used. The auxiliary electrode was a coiled platinum wire installed in the main cell. Potentiodynamic tests were conducted using the "Electrochemistry system model 370" (E.G. & G. PARC, NJ) equipped with a Model 175 universal programmer and a Model RE0074 X-Y recorder. Temperature was controlled using a thermostatic bath (Julabo Model 12, Juchheim Labortechnik KG, West Germany). Solutions were prepared using American Chemical Society (ACS) certified NaOH and LiOH and demineralized water of resistivity > 1 megohm/cm. All solutions were purged with nitrogen prior to and during experiments in order to diminish the quantity of dissolved oxygen and to prevent entry of carbon dioxide from the surrounding atmosphere.

Steel specimens (of typical analysis shown in Table 1) were machined to rods 9 mm in diameter. The circular sections of the specimens were polished successively with emery paper #100 to #600, followed by polishing with $1\text{-}\mu\text{m}$ diamond paste, washing with methanol in an ultrasonic bath, washing with tap water, and polishing with $0.3\text{-}\mu\text{m}$ alumina. The surfaces were cleaned by rinsing successively with tap water, acetone, and demineralized water. The polished working electrode specimen was then transferred to the main cell filled with the desired solution and maintained at the required temperature.

TABLE 1—Chemical composition of steel specimens (weight %).

Steel	C	Mn	P	S	Si	Cu	Ni	Cr	Mo	Sr
A516	0.24	1.15	0.008	0.007	0.25	0.044	0.025	0.033	0.004	0.002
A285	0.19	0.71	0.020	0.026	0.01	0.007	0.004	0.033	0.002	0.002

The electrode was immediately activated by holding it at -1.45 V/saturated calomel electrode (SCE) for five minutes.

The cyclovoltammetric studies were conducted at scan rates ranging from 1 to 1000 mV/s in order to determine the optimal rate to be used in further studies. At faster rates (1000 mV/s), the peaks are not well-defined, whereas at rates such as 1 mV/s, the experimentation takes more time. A good majority of the results considered in this presentation deal with those obtained at a scan rate of 10 mV/s in 33% NaOH solutions. Some results obtained using other scan rates and other solutions are briefly dealt with. Where necessary, LiOH was added to a concentration of 20 g/L.

Results

Cyclic voltammograms obtained in 33% NaOH solutions using steel specimens (A285 or A516) as working electrodes are shown in Figs. 1 and 2. At

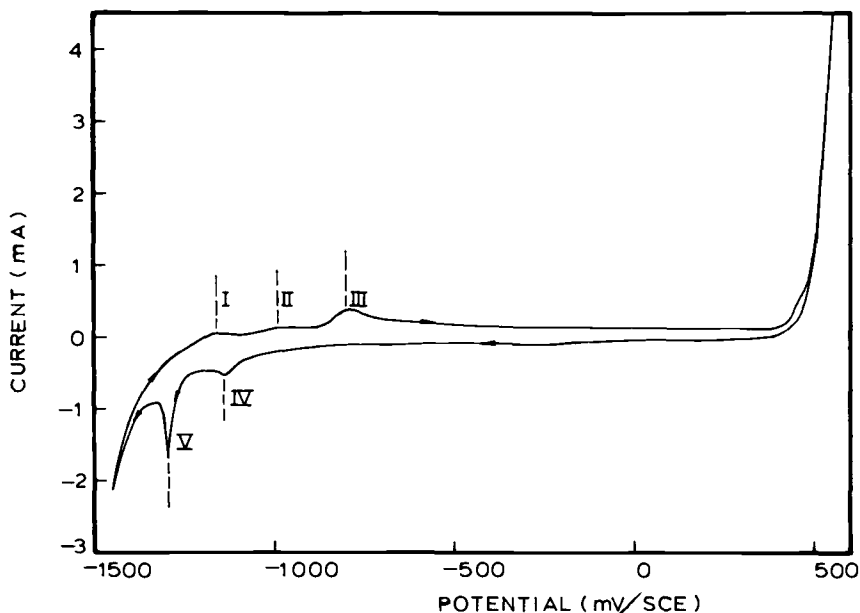


FIG. 1—Cyclic voltammograms obtained in 33% NaOH using carbon steel A285 specimens; temperature 20°C, scan rate 10 mV/s.

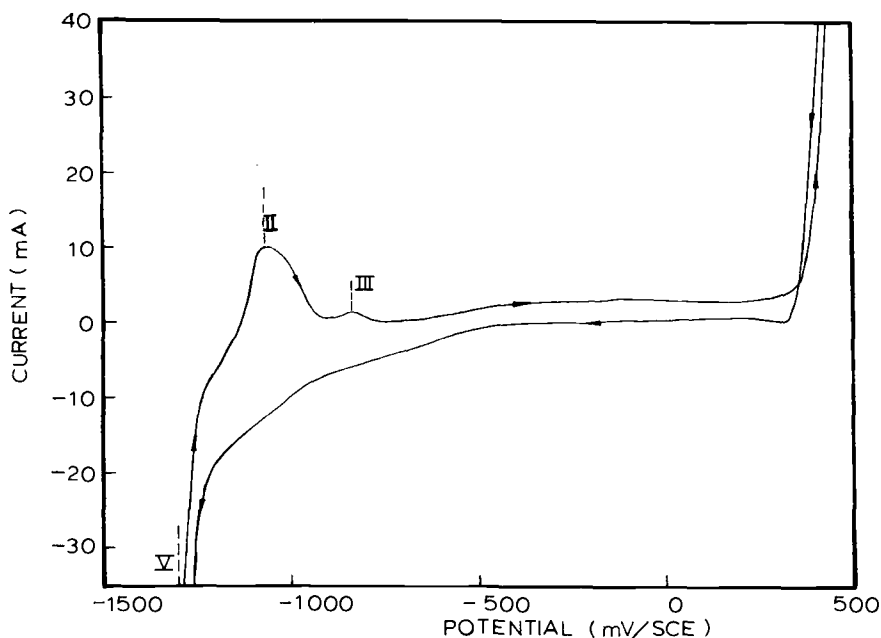


FIG. 2—Cyclic voltammograms obtained in 33% NaOH using carbon steel A285 specimens; temperature 85°C, scan rate 10 mV/s.

20°C, five main peaks are observed in the stabilized pattern, as in Fig. 1. Approximately 30 cycles are required to obtain a stable profile. At 85°C, Peaks I and IV practically disappear and only a few cycles are required to obtain stable conditions. Intensities (corrected for residual reactions) corresponding to Peaks II and V systematically increase with temperature. There are shifts in the peak potentials as a function of temperature, but these shifts are not very pronounced for the range of temperatures considered here. As a general rule, the difference in potential between conjugate peaks decreases as the temperature is increased.

Figures 3 and 4 show cyclic voltammograms obtained in 33% solutions containing 1.5% LiOH (20 g LiOH per litre of 33% NaOH solution at room temperature) under conditions similar to those used for experiments in 33% NaOH. Peak III increases in intensity and Peak IV nearly disappears with increasing temperature; Peak V is invariably present at all temperatures. During the cycling process at 85°C in 33% NaOH containing 1.5% LiOH, it was observed that the potential corresponding to Peak III shifted from approximately -0.60 V/SCE to a stable value at -0.82 V/SCE. Such a shift was not observed in the absence of LiOH. The stabilized peak potentials are nearly the same as those observed in 33% NaOH in this temperature range, but the peak current intensities are lower.

The variation of current intensities of Peak V as a function of temperature

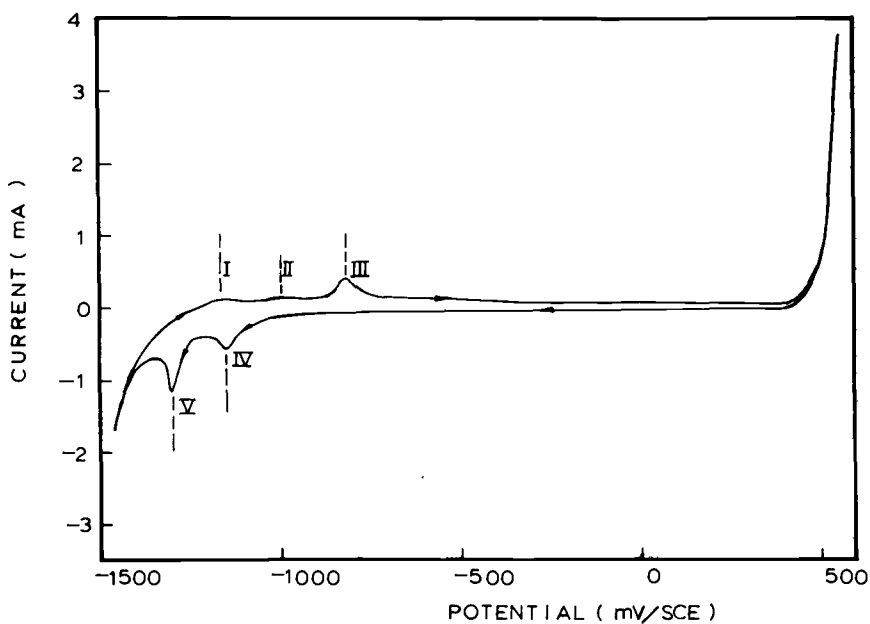


FIG. 3—Cyclic voltammograms obtained in 33% NaOH containing 1.5% LiOH using carbon steel A285 specimens; temperature 20°C, scan rate 10 mV/s.

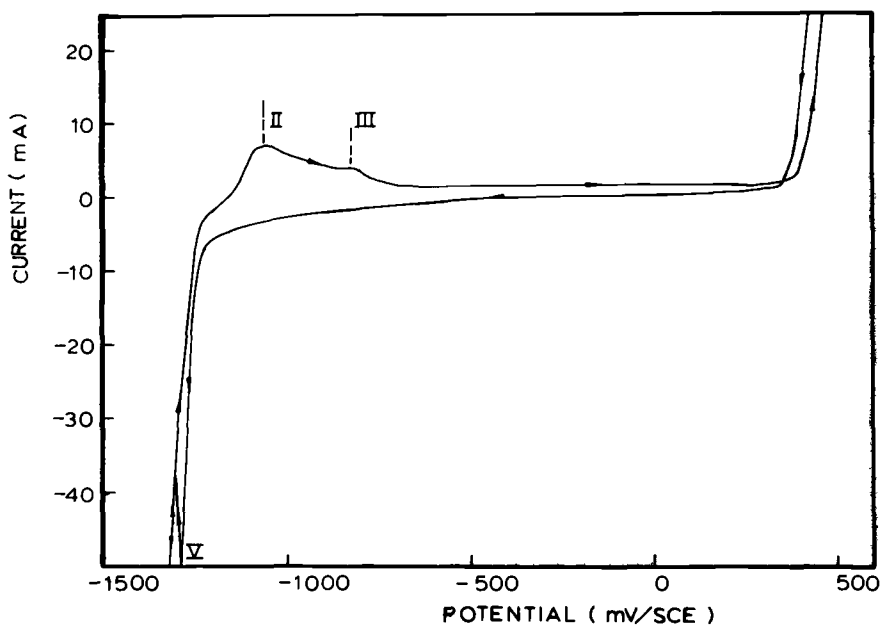


FIG. 4—Cyclic voltammograms obtained in 33% NaOH containing 1.5% LiOH using carbon steel A285 specimens; temperature 85°C, scan rate 10 mV/s.

is presented in Table 2 for 33% NaOH solutions and 33% NaOH solutions containing 1.5% LiOH. Peak V appears in all plots and is easily identified.

Table 3 shows the variation of peak potentials for Peaks I and V in 33% NaOH solutions and in saturated LiOH solutions at 20°C, at different scan rates. It is noted that the peak potentials are marginally more active in 33% NaOH, but the difference in potential between these two conjugate reactions stays nearly the same in both solutions. It is found that there is a linear relationship between peak potential and logarithm of scan rate. In Table 4, it is shown that the potential of Peak V does not change appreciably in different solutions of NaOH in the presence or in the absence of LiOH.

TABLE 2—*Current intensities of Peak V in 33% NaOH: influence of temperature and LiOH.*

33% NaOH Containing No LiOH		33% NaOH Containing 1.5% LiOH	
Temperature, K	Current, mA	Temperature, K	Current, mA
295	0.90	291	0.70
312	2.05	312	1.85
330	9.00	330	2.50
346	40.00	348	9.00
356	45.00	358	25.00

TABLE 3—*Variation of peak potentials for Peaks I and V in 33% NaOH and in saturated LiOH solutions at 20°C.*

Scan Rate, mV/S	33% NaOH		Saturated LiOH	
	Peak I V/SCE	Peak V V/SCE	Peak I V/SCE	Peak V V/SCE
1000	−1.10	−1.33	...	...
100	−1.12	−1.40	−1.08	−1.33
10	−1.17	−1.31	−1.13	−1.27
1	−1.19	−1.27	−1.15	−1.24

TABLE 4—*Potentials of Peak V in solutions of varying NaOH concentration at 20°C.*

NaOH Concentration, weight %	Potential of Peak V, V/SCE	
	Solution Containing No LiOH	Solution Containing 1.5% LiOH
4	−1.22	−1.22
15	−1.25	−1.26
33	−1.29	−1.30

Discussion

The initial reaction of iron with both NaOH and LiOH solutions is probably the formation of insoluble magnetite (Fe_3O_4) and soluble dihypoferrite (HFeO_2^-) [10]. Subsequent reaction involved in NaOH is the oxidation of Fe_3O_4 to form haematite (Fe_2O_3) [11,12]. In LiOH solutions, Fe_3O_4 is formed but the formation of Fe_2O_3 was not observed [1]. Instead, compounds such as LiFeO_2 and LiFe_5O_8 are formed depending on the concentration and temperature of the solution.

Higher concentrations of LiOH appear to favor the formation of LiFeO_2 . It has been indicated in the literature that the lithium compounds formed cause blocking of the pores of the outer layer of solid Fe_3O_4 , giving lower anodic activity at both low and high temperatures [1,3,8]. Bloom, Krulfeld, and Fraser [3] have identified low- and high-temperature forms of LiFeO_2 and LiFe_5O_8 by X-ray diffraction analysis of mild steel specimens attacked by LiOH solutions. This is in contrast to the formation of Fe_3O_4 in NaOH and KOH solutions.

Macdonald and Owen [2] obtained cyclic voltammograms of iron in 1 M LiOH at 22°C and at 200°C. By reversing the sweep after each anodic peak, it was shown that both Peaks I and II result in a single conjugate, Peak V. In addition, they observed that Peaks III and IV correspond to conjugate reactions. A mechanism was proposed indicating the formation of Fe_2O_3 or $\text{Fe}(\text{OH})_3$ at ambient temperatures, and the formation of LiFeO_2 at higher temperatures.

In the series of experiments conducted in the present work, it has been shown that there is a gradual diminution in the current corresponding to Peak V in the presence of LiOH (Table 2). Given the fact that Peak V is the conjugate of Peaks I and II, a decrease in the intensity of Peak V corresponds to a decrease in the intensities of Peaks I and II, barring any other parasitic effects. The decrease in the intensities of Peaks I and II perhaps indicates the formation of lithium-containing compounds. The evolution of potential of Peak I in lithium-containing solutions might also support this hypothesis, indicating different reaction mechanisms in the presence of LiOH.

Apparent activation energy of the conjugate of the corrosion reaction was calculated using the variation of current intensities of Peak V as a function of temperature for 33% NaOH solutions in the presence or in the absence of LiOH; this is shown in Table 5. There is a gradual increase in the apparent activation energy in solutions of NaOH as the concentration of NaOH is increased from 4% to 33%. This perhaps suggests increasing energy barriers to the reduction reactions involved. In solutions containing added LiOH, the apparent activation energy calculated is likely to be that of the reaction where the lithium-containing compounds play a part. The results indicate a trend of decreased energy barriers for this reaction, with increasing concentration of NaOH, all solutions simultaneously containing LiOH. In 33% NaOH the apparent activation energy has a value of 61 ± 5 kJ per mole in the absence of

TABLE 5—Variation of apparent activation energy.

NaOH Concentration, weight %	Apparent Activation Energy, kJ/mol	
	Solution Containing No LiOH	Solution Containing 1.5% LiOH
4	50 ± 3	64 ± 14
15	54 ± 7	46 ± 7
33	61 ± 5	42 ± 7

LiOH and a value of 42 ± 7 kJ per mole in the presence of LiOH. The results in effect, seem to indicate that the formation of lithium compounds is favored in NaOH solutions containing LiOH at high concentrations of NaOH. Efforts are being made to identify the reaction products to confirm the hypothesis proposed. Studies in the temperature range of 110 to 250°C are presently being conducted in NaOH/LiOH solutions. It is expected that similar conclusions would hold in those situations as well.

Conclusion

Cyclic voltammetric studies of carbon steels conducted in concentrated sodium hydroxide solutions containing lithium hydroxide show a certain degree of inhibition of the corrosion reaction in the temperature range 20 to 85°C. The inhibitive action is expected to be more pronounced at still higher temperatures. If stress corrosion tests prove to be favorable under such conditions, the use of lithium hydroxide as an additive to sodium hydroxide can be foreseen in different industrial applications.

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A Review of Microbiological and Electrochemical Techniques in the Study of Corrosion Induced by Sulfate-Reducing Bacteria

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ABSTRACT: Methods of measuring and evaluating the presence and distribution of sulfate-reducing bacteria are discussed. The microbiological methods are based on cell-counting (enumeration) techniques, microscopic examination, determination of bacterial activity, and immunological detection. Several experimental approaches to these methods are outlined with emphasis on their suitability and limitations in studies of sulfate-reducing bacteria associated with corrosion problems.

Electrochemical methods employed in laboratory studies of corrosion induced by sulfate-reducing bacteria are reviewed, with emphasis on the advantages and limitations of current techniques, such as determination of open circuit potentials, anodic and cathodic polarization curves, polarization resistance measurements, and determination of critical potentials for pitting. The applicability of microbiological and electrochemical techniques to field studies is briefly discussed.

KEY WORDS: sulfate-reducing bacteria, microbiological corrosion, enumeration of bacteria, microcalorimetry, fluorescent antibody, radioisotope techniques, microscopic techniques, localized corrosion, pitting potential, polarization methods, polarization resistance measurements

There are numerous examples of microbiological corrosion problems resulting from the bacteria reduction of sulfate in various industrial installations [1-4]. The purpose of this paper is to review various methods for detection, counting (enumeration), and activity measurements of sulfate-reducing

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bacteria for use in the examination of corrosion failure cases. Many of the applications have been developed in sediment studies in aquatic environments, and little emphasis has been placed on applications for studying corrosion problems of microbiological origin in industrial installations. While sulfate-reducing bacteria are ubiquitous in anaerobic environments [5,6] and of particular interest in sediments because of their interactions with methanogens and key role in the anaerobic breakdown of organic carbon [7,8], they also constitute a major consortium in corroded metal structures in chemical, petrochemical, and paper and pulp industries as well as in other industrial constructions. Their importance is exemplified in many case histories of corrosion failures typically associated with the formation of sulfides and the presence of sulfate-reducing bacteria [9-11].

In the anaerobic corrosion of metals, many other bacteria in addition to sulfate-reducers are present; these include various heterotrophic microorganisms that reduce nitrate to either ammonium ion or nitrogen gas, and those capable of degrading organic carbon compounds fermentatively. Nitrate-reducing sulfur-oxidizers and hydrogen-oxidizers represent other examples of facultatively anaerobic organisms which do not require organic carbon compounds for growth. The microbiological emphasis in corrosion failure examination cases has been on determining particularly the presence of sulfate-reducing bacteria; these determinations have been exclusively qualitative. Published case histories have been typically descriptive and give little insight to the microbiological complexity and activities in the anaerobic corrosion resulting in failures.

Recent new descriptions of sulfate-reducing bacteria [12-14] indicate that they have different ecological and physiological requirements which are not readily resolved by current microbiological methods used in corrosion studies. The quantitative associations of sulfate-reducing bacteria with industrial corrosion problems have not been addressed, and it is doubtful whether such associations can be uniformly established or indexed; qualitative demonstrations of the presence of sulfate-reducing bacteria have yielded little useful information in this respect. While the recent developments in microbiological methods have not been fully explored in studies of industrial corrosion failures, electrochemical methods have been developed in bench studies which have provided valuable information on the cathodic and anodic behavior of metallic materials in the presence of sulfate-reducing bacteria. These methods are also summarized in the present paper, with a notation that some may be useful for monitoring purposes and as early indicators of microbial corrosion problems.

Microbiological Methods

Viable Counting and Enumeration

In many instances it is important to be able to determine the number of viable or living bacteria per unit (volume or weight) of sample material. Vari-

ous culture media for sulfate-reducing bacteria have been described [12,13,15-17], and they can be used for enumeration purposes. A major problem associated with the viable counting of sulfate-reducing bacteria arises from the fact that many types exist which differ in their nutrient requirements. Previous efforts to enumerate sulfate-reducers associated with corrosion studies have been largely limited to using lactate as the growth substrate. During the past ten years several new descriptions of sulfate-reducers have been published (See Refs 12-24, for example), and the range of carbon compounds capable of supporting the growth of sulfate-reducers has now expanded to include more complex carbon compounds. There are no uniform media that would support the growth of all sulfate-reducing bacteria. The recoveries and efficiencies of the viable counting procedures have not been determined, and little effort has been made to compare and standardize various enumeration media for sulfate-reducing bacteria.

Sulfate-reducing bacteria have been isolated and characterized from freshwater, marine, and thermally altered environments, and these bacteria have unique growth requirements with respect to salinity and temperature. Current enumeration techniques are usually specific to a few species depending on the medium formulation and have been used with either liquid media [based on a serial dilution technique which yields a most-probable-number (MPN) estimate of bacterial density] or solidified media (usually agar-based) designed for colony counting. Because sulfate-reducing bacteria are typically obligately anaerobic, the enumeration techniques are based on media incubation under anaerobic conditions. In many cases it takes several days before the growth of bacteria can be observed. For the MPN technique, several weeks are required for the completion of the incubation.

The long incubation time is a major disadvantage of the viable counting techniques. The selectivity of the enumeration is based on the composition of the medium and the incubation conditions (for example, an elevated temperature of about 55°C for the thermophilic sulfate-reducers). In most media the resulting growth is associated with the formation of black iron sulfides, which facilitates the differentiation from other anaerobes that often are present in the sample material and are able to grow in the medium. The formation of sulfide from inorganic sulfate is invariably a good indicator of bacterial sulfate reduction because the reductive reaction does not occur in sterile culture media. Some sulfate-reducing bacteria can grow fermentatively in the absence of sulfate, but if sulfate is added, sulfide production is resumed.

In enumeration procedures the sample manipulation before enumeration may influence the counting efficiency. Exposure to air (oxygen) immediately inactivates the bacterial sulfate reduction, but there is very little information to evaluate the reversible nature of this inhibition [25]. Sulfate-reducing bacteria have been isolated from bulk aerobic aquatic environments [26], but it is not established whether they are dormant or, as shown in studies of aerobic sediments [27], associated with anaerobic microcosms of particulate material under such conditions. For enumeration purposes, the samples should be

processed without delay because a prolonged storage even under anaerobic conditions is likely to result in changes of bacterial numbers.

In standard enumeration procedures, the lower limit of detection, depending on the technique, is about 1 to 5 bacteria/mL sample. Methods have been developed for concentrating bacteria by either centrifugation or filtration prior to enumeration, but these have not been tested specifically for sulfate-reducing bacteria.

The adherence of sulfate-reducing bacteria on exposed metal surfaces may be important in the initial enhancement of corrosion [28], but its significance needs to be evaluated in future work. This initial attachment of bacterial cells should be distinguished from the establishment of occlusions and differential aeration cells, typically associated also with biofouling problems, which are recognized to be important factors in deposit attack [11]. Both phenomena complicate the viable counting procedures which are better suited for the quantitative enumeration of free-swimming bacteria.

There is some doubt about the quantitative relationship between sulfate-reducing bacteria and aggressiveness of the environment [29], based on a demonstration that corrosion of mild steel by *Desulfovibrio vulgaris* was enhanced in the presence of another bacterium; the latter organism (*Vibrio* sp.) was not a sulfate-reducer and it did not influence the corrosion in the absence of *D. vulgaris*. The significance of this observation cannot be evaluated because other microorganisms and their interactions with sulfate-reducing bacteria have not been characterized in bench and field studies of microbiological corrosion.

Microscopic Detection

Microscopic detection methods, recently reappraised [30] and tested [31] for practical applications, are of limited use in studies of sulfate-reducing bacteria. There are several different morphological types of sulfate-reducing bacteria, including rod-shaped and filamentous forms, none of which are unique to this particular group of microorganisms. The turbidity of the sample material interferes with microscopic observations, and this is a major drawback in corrosion-related studies because of the presence of insoluble corrosion products. However, if a microscopic examination reveals bacterial cells in corrosion products, the presence of sulfate-reducing bacteria should be suspected and confirmed by other methods. The lower limit of detection with $\times 1000$ magnification is about 10^5 bacteria/mL sample if samples are not preconcentrated for example by centrifugation. The contrast can be improved with either phase contrast or Nomarski interference contrast microscopy. Fluorochromes (for example, acridine orange) requiring a fluorescent microscope have also been used to improve the differentiation of microbial cells from other particulate material.

Scanning electron microscopy (SEM) increases the level of resolution, but

the sample preparation is time-consuming because of the chemical fixation, dehydration, drying; and coating before sample examination. Energy-dispersive X-ray Spectrometry (EDS) is useful in mapping elemental distribution of the sample material but has little relationship to bacterial distribution. Moreover, in the past EDS has been extremely difficult to use as a quantitative method, and its applications have been typically limited to qualitative characterizations of surfaces of corrosion specimens (See Refs 32 and 33, for example). In many cases it is also difficult to discern bacterial cells in corrosion products such as iron sulfides, which tend to physically mask bacteria embedded in the deposits. This is illustrated in Fig. 1, which shows that sulfate-reducing bacteria are increasingly embedded in and covered by anaerobic corrosion products.

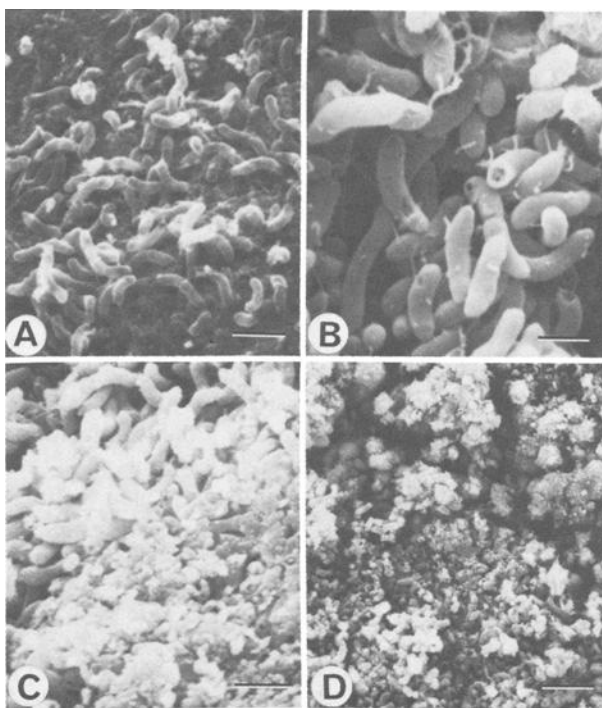


FIG. 1—Scanning electron micrographs of *Desulfovibrio desulfuricans* incubated for four days in a liquid medium. Bacteria adhered on the surface of cast iron immersed in the culture. (a) and (b) Cell aggregation; the cells are relatively free of external precipitates, and strands and flagella are discernible. Marker bars: (a) 2 μm (b) 1 μm . (c) Bacteria are partially covered by corrosion precipitates, marker bar 2 μm . (d) Bacteria are completely embedded in corrosion products, marker bar 5 μm .

Immunological Detection

The fluorescence antibody (FA) detection technique has many diverse analytical applications because antibodies can be raised against virtually any kind of microorganisms. Smith [34] developed an indirect FA technique specifically for sulfate-reducing bacteria. Several species of *Desulfovibrio* and *Desulfotomaculum* were tested as sources of antigens and for cross-reactivity in the assay. A polyvalent antiserum preparation, obtained by mixing all test antisera, was reported to be successful for the detection of *Desulfovibrio* spp. and *Desulfotomaculum* spp. While the FA technique is applicable in principle to detecting sulfate-reducing bacteria associated with corrosion problems in field and failure cases, it has not been extensively tested for this purpose. In a recent report on this application, it was suggested that antisera raised against wild strains of sulfate-reducing bacteria isolated from field samples, rather than those produced against established laboratory cultures, may increase the sensitivity and eliminate some problems of cross-reactivity [35]. However, because sulfate-reducing bacteria are associated with anaerobic corrosion problems, the antisera raised against these bacteria should also be tested against other microorganisms that typically live in similar environments (for example, *Clostridium* spp.).

The FA techniques developed for various microorganisms are subject to cross-reactivity with nontarget organisms in sample materials. This problem has been demonstrated with many different FA applications. Therefore, the use of the FA technique should be accompanied with confirmation of FA positive samples by cultural methods where possible.

The FA technique does not differentiate between living and dead cells because the reactive antigen components are typically cell surface antigens. However, there are vital stain techniques available that can be used in combination with fluorescent antibodies. An example is the reduction of 2-(*p*-iodophenyl)-3-(*p*-nitrophenyl)-5-phenyl-tetrazolium chloride (INT) as a result of electron transport activity [36]. In the reduced form INT forms an insoluble dark red complex which can be readily observed in cells under microscopic examination. The technique can be combined with FA methodology (FAINT) and it has found many different applications in environmental studies. The application of the FAINT method for the detection of sulfate-reducing bacteria has not been reported and it needs to be firmly established whether INT gives a positive reaction in an anaerobic electron transport system. The main advantage of FAINT is that it differentiates between actively respiring and inactive cells; it does not, however, alleviate the problem of cross-reactivity.

The cross-reactivity problem can be partially alleviated by using high dilutions of the antisera that still react with the target organisms. It is not known, however, how environmental isolates of various sulfate-reducing bacteria react with antisera raised using pure cultures of sulfate-reducers as sources of antigens. The cell surface antigenic properties may alter during culture manipulation; for example, extracellular materials may be removed from cell

surface upon washing of bacterial suspensions. Polyvalent antisera are likely to be more suitable for the detection of sulfate-reducers, in comparison to using isolated cell components (for example, lipo-polysaccharides) as antigens for antiserum production. The increased specificity of antibody preparation obtained by using purified cell components eliminates cross-reactivity with nontarget organisms, but is probably counterproductive for detection of sulfate-reducers in corrosion samples because of the broad spectrum of sulfate-reducers that may be present in the sample material.

For practical purposes, an epifluorescence microscope with oil immersion objective and total magnification of about $\times 1000$ is required for optical resolution of fluorescent bacterial cells. With this limitation, the lower level of detection is about 10^4 to 10^5 cells/mL sample. Samples can be concentrated by either centrifugation or filtration, but both procedures also increase the turbidity and aggregation in the sample material, both of which will interfere with the microscopic examination.

The level of detection of the FA technique can be improved by resorting to enzymic methods coupled with the antibody reaction. In this technique, an enzyme is adsorbed on the antibody which is then reacted with the sample antigen (target organism in this case). After removing the excess nonreacted components from the sample mixture, a substrate for the enzyme is added and the reaction is determined by standard procedures such as colorimetry. With appropriate standards, the enzyme-linked immunosorbent assay (ELISA) can be standardized and used as a measure of the initial amount of antigen material present in the sample. The ELISA method represents a 10- to 100-fold increase in the level of detection when compared with the FA technique, but the cross-reactivity and specificity problems may remain the same. The ELISA may also be sensitive to interference by toxic components in the sample material (for example, sulfide or metal ions) because it is based on an enzymic reaction. Some applications of the ELISA and other enzymic immunoassay techniques were recently reviewed [37]; their application to the detection of sulfate-reducing bacteria warrants research because, if successful, it may result in the development of rapid, automated methods suitable for multiple testing.

Highly specific antibodies can be obtained via the monoclonal antibody technology for use as analytical probes for sulfate-reducing bacteria, but their extreme specificity negates their broad-spectrum applications. At the present time no published information is available on the use of either ELISA or monoclonal antibodies developed for sulfate-reducing bacteria, although interest has been expressed by the National Association of Corrosion Engineers (NACE) Unit Committee T-3J in exploring ELISA for analytical applications.

Detection by Impedance Measurement

Growth of microorganisms is always associated with fluxes of nutrients, metabolites, and end-products to and from the medium. These processes in-

fluence the electrolytic composition of the sample material because of changes in concentrations of ionic compounds. The ionic composition of the solution including conductivity is therefore affected in bacterial cultures, and electrical impedance techniques can be used as measures of growth.

It should be noted that this technique is mainly related to the conductivity of the solution and not to the interfacial impedance because inert electrodes and high frequency of the AC signal excitation are used. Moreover, the capacitive component of the impedance may be affected by the adsorption of metabolites and bacteria on the electrodes. Any change that influences the conductivity will affect this method and therefore the technique is not highly specific.

The method has been used for measuring bacterial sulfate reduction in pure cultures and sediment samples. A good correlation was found between impedance changes and biological activity measurements of sulfate-reducing bacteria [38]. The method is based on a continuous monitoring of the impedance ratio between the sample and a sterile reference. A change in the impedance ratio is indicative of microbial activity, and the time from the beginning of the assay to the observed change of the ratio is related to the initial number of active bacteria present. The specificity of the assay is based on using a selective medium which, in this case, favored the growth of sulfate-reducing microorganisms. Current instrumentation has the capacity of simultaneous monitoring of several hundred samples. Typical detection times can be as short as two to three hours, depending on the initial density of the bacteria present. The method has not been tested in microbiological corrosion studies with laboratory or field installation failure samples.

Microcalorimetric Detection

Metabolic changes brought about by microorganisms involve loss of energy as heat which can be sensitively measured by microcalorimetric methods. This methodology has found use in the characterization of growth patterns of sulfate-reducing bacteria [39]. Microcalorimetry has been used to evaluate the effects of antislime agents in paper industry [40], but its application to test sulfate-reducing bacteria in corrosion-related studies has not been reported. The method yields results within a few hours, but the instrument has a limited capacity because only one test per run can be performed.

Radioisotope Techniques

Bacterial sulfate reduction in anaerobic sediments has been extensively studied using radioisotope techniques. The method is based on spiking the sample material with ^{35}S -sulfate followed by incubation and measurement of either the loss of radioactive sulfate or production of radioactive sulfide. Several experimental procedures have been developed for tube and flask assays [41–46]. The radioactive sulfide can be separated from the residual sulfate by

purging with nitrogen, volatilization with hydrochloric acid, or trapping with zinc acetate. The radioisotope method has been used in laboratory evaluation studies of inhibitors of sulfate-reducing bacteria [43-45], and it offers the advantage of multiple testing within a few hours. The technique seems to be useful for determining the activity of sulfate-reducing bacteria in association with metal electrodes [47], an application which may find some use in laboratory evaluation of corrosion caused by sulfate-reducing bacteria. The technique is specific for sulfate-reducing anaerobes and extremely sensitive by virtue of the specific activity of the labelled sulfate. A requirement associated with this method for routine industrial laboratory use is the assignment of laboratory space and associated disposal of radioactive waste material in compliance with the Nuclear Regulatory Commission (NRC) regulations. In addition, isotope techniques currently are objectionable to the industry because of reluctance to adopt radioisotope handling techniques.

Chemical Methods

Determination of Sulfide

The detection of sulfide ion in the sample material is a common method used as an indicator of bacterial sulfate reduction. However, this method may not have a quantitative association with either the numbers or activities of sulfate-reducing bacteria in field situations and can only be used for qualitative evaluation. The premise of biogenic sulfide production is also the basis of the ASTM Test Methods for Sulfate-Reducing Bacteria in Water and Water-Formed Deposits (D 993). An analytical problem is associated with the sulfide ion measurement in that sulfide precipitates metal ions and sulfides form first on surface films [2,48], which ensure to cover the metal surface with a massive precipitate if sufficient sulfate is present for bacterial activity. This may result in a false negative result by sulfide ion measurement. Sulfide ion is not stable in the presence of oxygen, and sulfide analysis in oxygen-containing process waters may yield negative results even when anaerobic microbiological corrosion is occurring on interior surfaces of installation structures.

Determination of Cellular Components Unique to Sulfate-Reducing Bacteria

In general, many biomass measurements are based on the chemical determination of cellular constituents such as ATP, DNA, or components of the cell wall. However, these components are not specific to sulfate-reducing bacteria, but are rather uniformly present in various microorganisms. Some sulfate-reducers contain a fluorescent compound, desulfoviridin, which can be analyzed by its spectral and fluorescent properties (see, for example, Refs 49 and 50), but this compound has only been detected in species of the genus

Desulfovibrio. Thus, the compound has very little analytical application as a detection technique for sulfate-reducing bacteria, particularly as the detection of the fluorescence reaction is difficult in samples of high particulate material content as is the case for corrosion products.

Another approach is the determination of cellular lipid profiles [51] as fingerprint analysis of microbial composition and biomass, but this methodology, which involves gas-liquid chromatography and mass spectrometry and is sensitive at 10^{-10} to 10^{-12} molar range, has not been evaluated specifically for sulfate-reducing bacteria and corrosion products. It seems that many sulfate-reducers also have characteristic fatty acids that may serve diagnostic purposes [52,53]. However, the analysis of lipid and fatty acid profiles is relatively sophisticated, expensive, and time-consuming. The profiles are known to change as a result of changes in growth conditions and will not readily avail themselves for routine detection and speciation of sulfate-reducing bacteria in field samples.

Electrochemical Techniques

In metal corrosion induced by sulfate-reducing bacteria, the basic principles of electrochemical corrosion are valid and have been applied to explain the acceleration of the metal dissolution process observed at times in neutral aqueous environments under anaerobic conditions. Therefore, various electrochemical methods have been employed in the laboratory over the last 30 years to study corrosion influenced by sulfate-reducing bacteria. In this review, we discuss the advantages and limitations of these methods and assess their applicability to field studies.

Open Circuit Potential Measurements

Hadley [54] and later on Wanklyn and Spruit [55] were among the first authors to measure open circuit potentials as a function of time for steel specimens immersed in a culture of sulfate-reducing bacteria. Although similar curves were obtained in both studies (Fig. 2), different interpretations were suggested. Hadley [54] indicated that the initial potential decay was due to cathodic depolarization of the steel electrode, whereas Wanklyn and Spruit [55] claimed that it was associated with an enhanced anodic process, as predictable in terms of mixed potential theory by using Evans' diagrams. Later on, Horvath [56] carried out similar measurements, as plotted in Fig. 2, but he measured also the redox potential of the medium by using a Pt electrode. It is clearly seen that the redox potential decreased from 0.2 V_{SHE} to approximately -0.15 V_{SHE} (Fig. 2); this was associated with an increase in bacteria counts and thus with generation of hydrogen sulfide (H₂S). This species is probably responsible for both the low redox potential and the acceleration of the corrosion process. After the initial drop, the corrosion potential increased

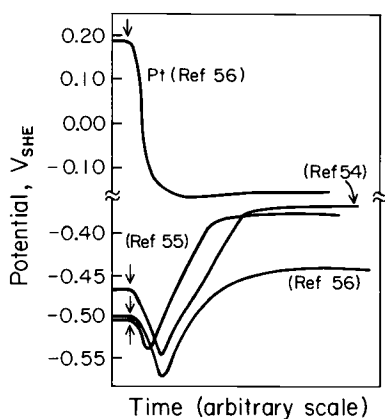


FIG. 2—Open-circuit potential for steel electrodes and redox potential measured on platinum electrodes in culture solution inoculated (arrow) with sulfate-reducing bacteria. An arbitrary time scale is indicated because different time courses were employed in the referenced experiments.

and reached a steady-state value, probably because of the formation of a semi-protective film of iron sulfide [56,57].

These results are presented to illustrate initial attempts of applying electrochemical methods for studying corrosion induced by sulfate-reducing bacteria. The limitations are also obvious; without monitoring other variables it seems rather difficult to obtain data that could be unambiguously interpreted.

However, a plot of potential as a function of time could be useful to detect the initiation of an accelerated attack due to sulfate-reducing bacteria. As demonstrated in some instances of crevice corrosion [58] and stress corrosion cracking [59], a potential decay due to the activation of the electrode can give some rough indication of the initiation of a localized corrosion process.

Galvanostatic and Potentiostatic Polarization Methods

Horvath and Solti [60] as well as Booth and Tiller [61] carried out galvanostatic polarization studies in order to obtain anodic and cathodic polarization curves for mild steel electrodes in culture media inoculated with various species of sulfate-reducing bacteria. Figure 3 summarizes the polarization curves obtained by Booth and Tiller [61] in the presence of *Desulfovibrio desulfuricans*, a hydrogenase-positive species, and *Desulfotomaculum orientis*, a hydrogenase-negative species. Only *D. desulfuricans* caused a marked decrease in cathodic polarization (Fig. 3a) after two days, which was revealed as a significant increase in the current density at a given cathodic overpotential. No such effect was observed for the hydrogenase-negative species (Fig. 3c). The anodic process was inhibited in both cases (Fig. 3b and 3d).

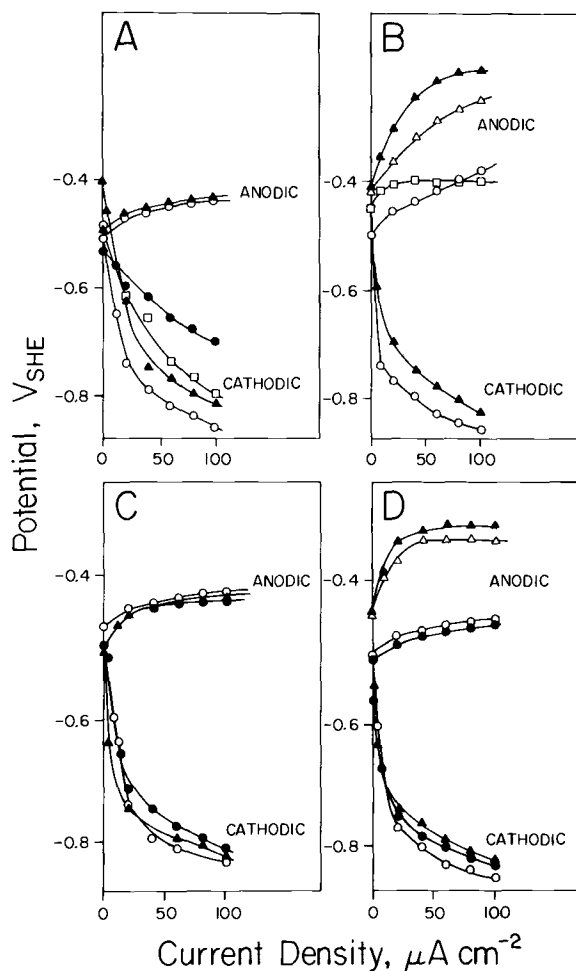


FIG. 3—Anodic and cathodic polarization curves for mild steel at 30°C. (a) Anode compartment sterile; cathode compartment inoculated with *Desulfovibrio desulfuricans*. (b) Anode compartment inoculated with *D. desulfuricans*; cathode compartment sterile. (c) Anode compartment sterile; cathode compartment inoculated with *Desulfotomaculum orientis*. (d) Anode compartment inoculated with *Dt. orientis*; cathode compartment sterile: ○, initially; ●, after 2 days' inoculation; □, after 3 days' inoculation; △, after 7 days' inoculation; ▲, after 10 days' inoculation [61].

At that time, these results were interpreted as a confirmation of the so-called "cathodic depolarization theory" proposed by von Wolzogen Kühr and van der Klugt [62]. From an experimental point of view, these studies [60,61] represent initial attempts to apply external polarization to an electrode in order to identify the basic mechanisms of corrosion induced by sulfate-reducing bacteria. Other authors have measured cathodic polarization curves for mild

steel in sterile medium containing either suspensions of iron sulfide [63] or dissolved hydrogen sulfide [64], in order to demonstrate that cathodic depolarization can be enhanced by iron sulfide or by hydrogen sulfide. The latter is the result of the reduction of sulfate by the bacteria, whereas iron sulfide is produced either as a surface film or as a precipitate, depending on the concentration of ferrous ions in the medium. If the concentration of ferrous ions is relatively large, the sulfide generated by bacterial action will tend to react with the iron cations in the solution phase, and no semiprotective surface film can be formed. In the latter case, the corrosion rate was found to be significantly accelerated [65].

Booth and Tiller [66] employed potentiostatic methods in order to correlate current density versus time curves for mild steel at various applied potentials within the cathodic range with the hydrogenase activity of the sulfate-reducing bacteria, expressed in terms of the hydrogen absorption coefficient ($-Q_{H_2}^B$). The tests were performed in a medium containing benzyl viologen as the electron acceptor instead of sulfate, to avoid the complications associated with the generation of sulfide. More recently, potentiostatic polarization has been employed [67-68] to establish current densities required for cathodic protection of steels in anaerobic mud samples containing sulfate-reducing bacteria in order to simulate conditions in marine sediments. While these types of measurements have been carried out in laboratory experiments to identify mechanisms of microbiological corrosion in relatively well defined culture media, no experience exists for similar measurements in the field. Therefore, the comparison and evaluation of the polarization behavior for a given material in the presence and absence of sulfate-reducing bacteria is not possible.

Determination of Pitting Potentials

As we have discussed previously [11], sulfate-reducing bacteria can lead to very localized forms of corrosion attack depending mainly on the passive properties of the alloy involved. One of the prevailing forms is pitting corrosion; therefore, different electrochemical methods commonly employed to determine characteristic pitting potentials [69] can be extremely useful to define the tendency of a given alloy/environment system to pitting corrosion in the field. Although no information exists in the literature regarding field studies, it has been shown in laboratory studies [70] that the presence of sulfate-reducing bacteria decreases the pitting potential of mild steel in deaerated artificial seawater. This is clearly illustrated in Fig. 4, which shows the effect of bacteria and sulfide on potentiostatic polarization curves obtained by increasing the potential in steps after a constant current was attained. It was concluded [70] that the decrease in the pitting potential was associated with the total concentration of sulfide generated by the sulfate-reducing bacteria. This method, or more specifically those methods based in consecutive forward and

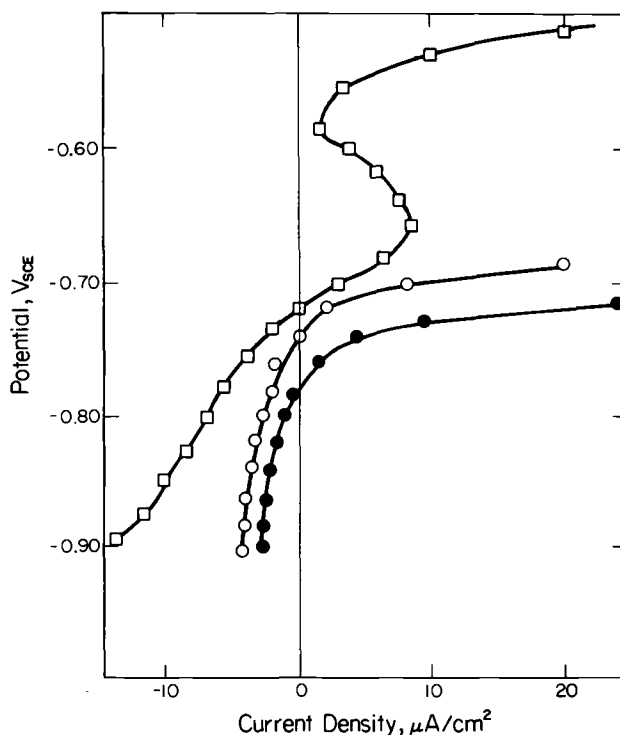


FIG. 4—Potentiostatic polarization curves for AISI 1020 steel in anaerobic artificial seawater (pH 8) (□); in artificial seawater contaminated by sulfate-reducing bacteria (total sulfide 10^{-3} M, pH 7.8, redox potential -510 mV) (○); and in artificial seawater with the addition of 10^{-3} M Na_2S (pH 8.0) (●) [70].

reverse potential scans, have been applied to studies of localized corrosion in the field [71]. Microbiological analysis should be useful in evaluating such field applications when microbiological corrosion problems are suspected.

It has been suggested that corrosion rates due to pitting corrosion can be monitored in the field by potentiodynamic polarization [71,72]. However, more data are needed to establish that the correlation postulated between the electrochemical measurement and the rate of pit penetration is valid. The analysis of the polarization data may be extremely dependent on the choice of the cathodic Tafel coefficient that in neutral environments is usually not very well defined.

Polarization Resistance Measurements

Linear polarization methods have been employed in the laboratory [48,73] to measure corrosion rates of mild steel in different media inoculated with

sulfate-reducing bacteria. However, corrosion rates were given in units of the reciprocal of polarization resistance [48], indicating that no attempt was made to determine the values of the Tafel coefficients required to calculate corrosion rates in units of penetration as a function of time or that the determination was too cumbersome. The authors [48] showed a linear plot of weight loss versus integral value of the reciprocal of the polarization resistance $\int (1/R_p) dt$, which indicates that proportionality exists between corrosion rate and the reciprocal of the polarization resistance. Note that the authors indicated that in the presence of a sulfide film it was difficult to obtain stable values of the current under potentiostatic conditions. These observations imply relatively large errors in the determination of the polarization resistance.

To illustrate the results reported, Fig. 5 shows the variation of potential and corrosion rate for the mild steel electrode as a function of time and the simultaneous increase in the viable counts of bacteria, the rate of formation of H_2S , and its concentration. Note also that the first cell refers to an electrochemical cell which contains the bacterial culture (*Desulfovibrio* in a nutrient medium), whereas the second cell contains artificial seawater with dissolved H_2S produced by the bacteria in the first cell and carried to the second one by a stream of nitrogen gas. It can be seen that H_2S began to be generated with the initiation of logarithmic growth phase of the bacteria and that the peak of H_2S formation rate corresponds to a peak in the bacterial population. The concentration of H_2S in the second cell followed the formation rate of H_2S . The variation of the corrosion potential is similar to that presented in Fig. 2. The minimum is reached when the formation rate and the concentration of H_2S attained a maximum, but in the first cell the potential increase after the decay in the formation rate of H_2S is more attenuated than in the second cell; this was interpreted as due to the formation of a less protective sulfide film. The corrosion rate showed a corresponding variation, with a maximum at the time at which the generation rate of H_2S reached a maximum, and a decrease when a semiprotective film of iron sulfide was formed. The authors [48] suggested that the corrosion rate in the first cell was systematically lower than that in the second cell, with the exception of the initial period after inoculation, because organic degradation products (which were not characterized) of the culture medium had an inhibiting effect which competed with the accelerating effect of H_2S .

It is out of the scope of this review to discuss the implications of the previous results and additional information regarding the effect of H_2S concentration of the corrosion rate and the film formation process on the mechanism of anaerobic corrosion enhanced by sulfate-reducing bacteria. However, results as shown in Fig. 5 illustrate the complexity of the phenomena involved and the problems that can be expected in the monitoring of corrosion rates when changing concentrations of the active species may affect redox potentials, corrosion potentials, and the corrosion rates as determined by several

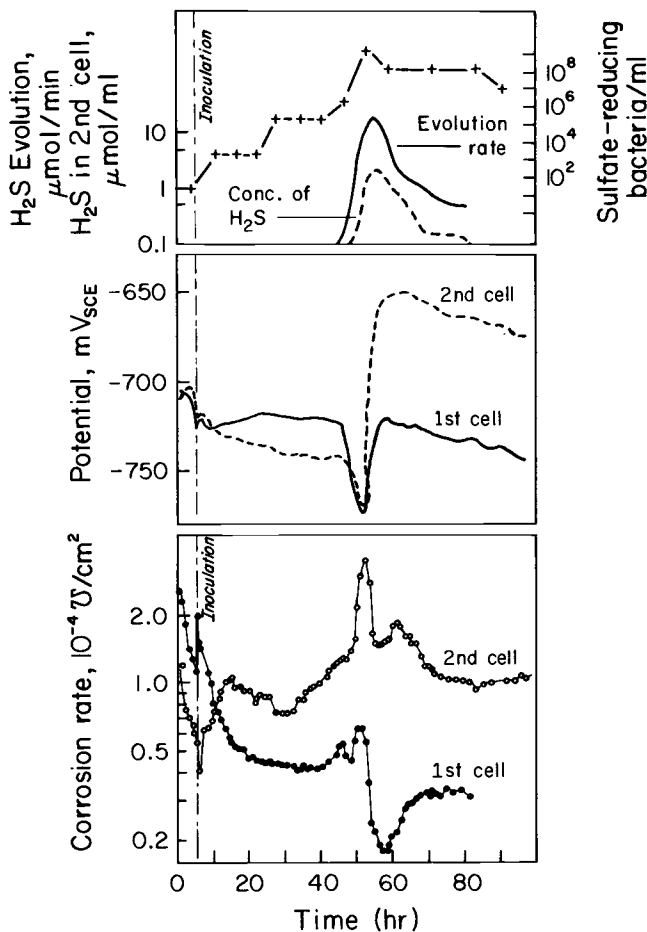


FIG. 5—Evolution rate and concentration of H_2S , number of bacteria, potential, and corrosion rate as a function of time for mild steel specimens exposed to artificial seawater culture medium containing sulfate-reducing bacteria (first cell) and H_2S generated by the bacteria (second cell) [48].

parallel processes: anodic dissolution, film formation, and cathodic reactions.

During recent years, AC impedance techniques have become used extensively for measuring the polarization resistance of a corroding interface. Problems of accuracy and reproducibility, frequently found when stationary methods are applied, led to an increasing use of nonstationary methods, in particular AC impedance [74, 75]. With the instrumentation now available, measurements can be carried out over a wide range of frequencies (10^{-3} to 10^3 Hz). It is easy then to separate the interfacial impedance from the resistance of the solution, but measurements could be extremely time-consuming at low

frequencies. However, as discussed by Haruyama and Tsuru [76], by appropriate choice of two frequencies (0.01 Hz and 10 kHz), it is possible to build an automatic AC corrosion monitor based in a two-electrode cell configuration. The instrument gives corrosion rate regardless of the morphological development of the corrosive attack (uniform or localized). Nevertheless, the authors emphasized that the initiation of pitting corrosion can be easily detected by a sharp increase in the corrosion current. The application of this type of instrumentation to the study of corrosion induced by sulfate-reducing bacteria should be encouraged as a first step to the possible in-line monitoring in the field.

Concluding Remarks

Studies with other aquatic bacteria have shown that microorganisms may be stressed in their environment because of starvation and adverse physico-chemical conditions including low doses of biocides in industrial waters. As a result, microorganisms may be rendered nonrecoverable by culture methods, but they may be recovered by resuscitation techniques which usually involve nutrient-rich nonselective incubation conditions; or they may lapse into a nonrecoverable stage with respect to growth media but maintain viability and activity which can still be detected by microscopic and radiolabeling techniques. This problem also applies to the microbiological examination of corrosion problems in industrial installations. The lack of growth of sulfate-reducers in culture media cannot be unambiguously evaluated for corrosion samples without resorting to other methods of analysis such as resuscitation techniques, which have not been developed for sulfate-reducers, and activity measurements. Routine monitoring and early detection are very important in attempts to control microbiological corrosion problems in industrial installations. It should also be emphasized that sampling may bias bacterial detection and enumeration as well as biocide testing in industrial systems. In view of the close association of sulfate-reducing bacteria with corrosion deposits and metal surfaces, a meaningful approach involves the direct sampling of surfaces and deposits or testing with coupons or other immersed devices. Variation due to stagnation and configuration of the system should be accommodated in microbiological surveillance. Microorganisms in water samples taken from contaminated systems do not adequately represent those associated with surfaces and corrosion deposits. Biocide testing with laboratory cultures may lead to erroneous conclusions when extrapolated to industrial systems because the attached microorganisms are better protected from the antimicrobial effects. Empirically, however, most examinations have been post mortem analyses of corrosion failure cases. The examples mentioned in this paper indicate that there are a large number of potential methods available for detecting sulfate-reducing bacteria, but little effort has been made to apply and standardize them for use in industrial situations.

An additional problem is the lack of fundamental and interdisciplinary studies on localized corrosion of stainless steel, high nickel alloys, and other corrosion resistant materials in the presence of sulfate-reducing bacteria. This makes it extremely difficult to evaluate appropriate techniques to detect and follow the development of the more common forms of localized corrosion, such as pitting and crevice corrosion. Systematic areas of study include further development and testing of electrochemical methods to determine breakdown of passive films and measurement of corrosion rates in bacteria inoculated environments.

Several practical problems are envisaged for field applications of electrochemical methods. One of the more difficult problems that should be confronted is the appropriate location of the working electrode. In many cases it will be difficult to predict the specific location in which bacteria will colonize, and therefore electrochemical measurements may not be able to detect any eventual increase in the corrosion rate if the electrodes are not properly located. This is a common situation in corrosion monitoring, but it is even more complicated in microbiologically induced corrosion.

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Harmonic Impedance Spectroscopy for the Determination of Corrosion Rates in Cathodically Protected Systems

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ABSTRACT: The nonlinear current-voltage response which is characteristic of a corroding metal/electrolyte interface prohibits the use of corrosion resistance measurements in conjunction with the Stern-Geary relationship, to provide an in situ determination of corrosion rates, at potentials removed from the free corrosion potential.

In this paper we describe the development of a technique for the electrochemical measurement of the anodic corrosion current ("corrosion rate") under conditions of an applied cathodic protection potential. Our effort has been directed towards a simplified theoretical treatment of the harmonic current response at frequencies of $1f$, $2f$, $3f$, $4f$. . . to a 20 to 50-mV AC voltage perturbation at frequency f .

Experimental verification of the theoretical treatment was obtained by comparing the results of harmonic analysis with those obtained by mass loss determinations for copper: nickel alloy specimens of varying geometries, in oxygenated synthetic ocean water, at various levels of applied cathodic polarization.

KEY WORDS: AC impedance, cathodic protection (CP), waterbox corrosion, seawater corrosion

Corrosion problems in the waterbox regions of a condenser can often be mitigated by installing cathodic protection (CP) systems in those regions. However, cathodic protection current (or potential) requirements may change with time because of changes in the corrosivity of the environment. For in-

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stance, pollution of the cooling water with sulfide can substantially increase the CP current needed to maintain copper alloy condenser components at a safe potential. In the latter case, not only do the current requirements increase at a fixed CP potential when sulfide pollution occurs, but also the potential must be depressed to even more negative values to achieve the same level of protection as obtained in unpolluted waters. Thus, no matter whether the CP system is under current control or under potential control, the corrosion rate of copper alloy condenser components would increase if the water became polluted with sulfides.

The damage resulting from a malfunctioning or inadequate CP system may be detected during one of the infrequent inspection periods or when failure of a component occurs and leakage of the cooling water into the steam condensate causes significant increases in condensate conductivity. In either case, the detection of the high corrosion rates would normally occur after substantial damage had already taken place. Clearly, there is a need for a method of monitoring the efficacy of the CP system during its operation. In the following discussion, we introduce the concept of using an in-situ electrochemical technique to monitor the corrosion rate of the "protected" structure. By measuring this corrosion rate, the CP current or potential can be adjusted at frequent intervals to ensure adequate low corrosion rates while avoiding power wastage because of over-protection.

Analysis of the response of an electrode to small amplitude (< 10 mV) sinusoidal voltage perturbations forms the basis of the well established technique known as a-c impedance spectroscopy [1-3]. In studies of corrosion, a small amplitude perturbation is imposed about the free corrosion potential, and the impedance ($\tilde{Z} = \tilde{V}/\tilde{I}$, where $\sim$ denotes a complex variable, V is voltage, and I is current) is extrapolated to a real value at low frequency to define a "corrosion resistance," R_{corr} , that is, characteristic of a particular electrode/electrolyte combination [4-5]. The Stern-Geary relationship [4] may be used to calculate the corrosion current, I_{corr} , as follows:

$$I_{\text{corr}} = \vec{\beta}_a \tilde{\beta}_c / 2.303 R_{\text{corr}} (\vec{\beta}_a + \tilde{\beta}_c) \quad (1)$$

where $\vec{\beta}_a$ and $\tilde{\beta}_c$ are the Tafel coefficients for anodic and cathodic partial reactions, respectively.

The derivation leading to Eq 1 assumes that the corroding electrode responds linearly to the imposed electrical perturbation [4-6]; that is, doubling the perturbing voltage amplitude results in a doubled current response (but an unchanged impedance). Since physical variables in all physically realizable systems must have a finite first derivative,³ it is always possible to achieve linear conditions by applying a perturbation of limitingly small amplitude.

The nonlinearity of the current/voltage relationship, in corroding systems,

³Any discontinuity in a variable plotted against time requires the application of an infinite force.

prohibits the use of conventional AC impedance spectroscopy either at DC potentials more than a few millivolts from the free corrosion potential, or using other than a limitingly small perturbation. The reason is that the electrical perturbation, which is imposed on the system at a frequency of f , in a nonlinear system results in a response at $2f$, $3f$, $4f$, etc., in addition to a DC component [6-11]. Neither the fundamental response (f_0) nor the total power response ($\sum_{h=0}^{\infty} h f$)⁴ can be analyzed to determine uniquely the corrosion resistance.

The origin of the harmonic response is shown schematically in Figs. 1 to 3 for an input voltage sinewave at frequency f , superimposed on a current/voltage curve of the form,

$$I = I_{fc} \{ \exp[\beta_a(V - V_{fc})] - \exp[-\beta_c(V - V_{fc})] \} \quad (2)$$

where I_{fc} is the free corrosion current flux, defined at the free corrosion potential (V_{fc}) as

$$I_{fc} = I_a = -I_c; \quad \text{at } V_{fc} \quad (3)$$

Figure 1 shows a perturbing voltage sinusoid reflected about the DC current voltage response curve at V_{fc} and at some positive bias. In the linear re-

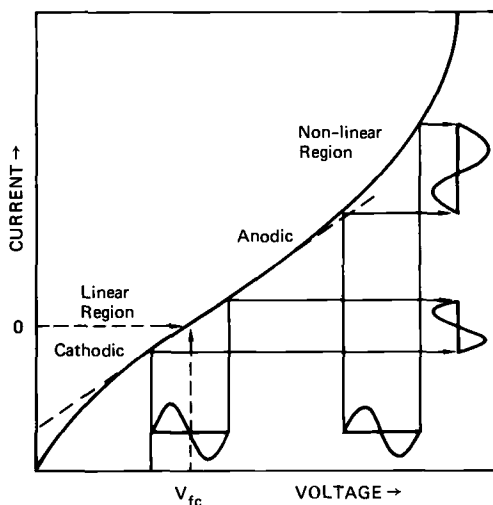


FIG. 1—Source of harmonic response: Reflection of input sinewave on nonlinear current/voltage curve.

⁴Pre-subscripts are used throughout the text to denote the harmonic number.

gion this reflection results in an undisturbed current response, with V/I being a constant (equal to the DC corrosion resistance).

The expected response is shown in the time-domain, schematically, in Fig. 2. The output is generally shifted in phase with regard to the input, due to reactive terms associated with diffusional and capacitive processes. The extent of the distortion in the nonlinear region can be quantified by performing a Fourier series analysis. As indicated in Fig. 3, when a sinusoidal perturbation of moderate amplitude is applied to a corroding electrode the response will consist of a component of the same frequency (generally shifted in phase with respect to the input), as well as terms at integral multiples of the input frequency (the harmonics). Unless the input excitation is symmetric about V_{fc} , then the output also will show a DC offset that we term the zeroth harmonic. These harmonic response terms contain information sufficient to completely specify the current/voltage curve, in principle, at any DC voltage, and thus to monitor the instantaneous corrosion rate even in the presence of an applied cathodic polarization. The purpose of this communication is to describe the limits of practical application of the concept.

Theoretical Analysis

The analysis of the harmonic response of a system to a sinusoidal current or voltage perturbation has received periodic attention in the electrochemical

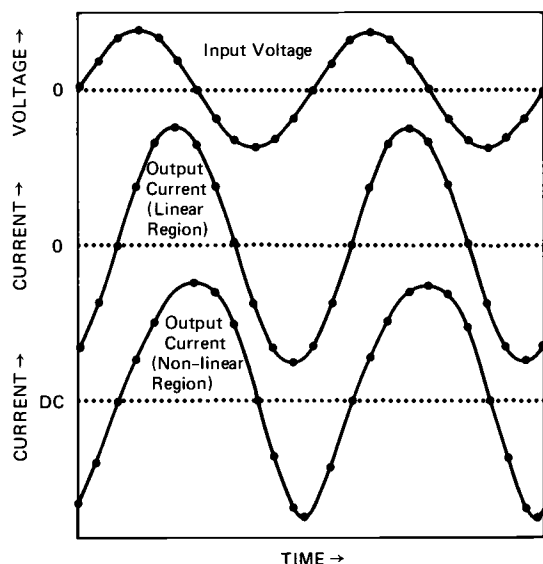


FIG. 2—Source of harmonic response: Time-domain representation of input and output waveforms.

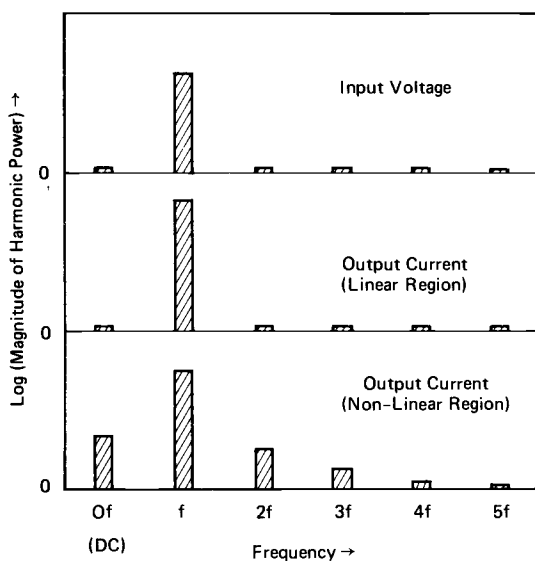


FIG. 3—Source of harmonic response: Frequency-domain representation of input and output waveforms.

literature since the pioneering work of Warburg [12] and Kruger [13]. This effect has been studied as Faradaic rectification [14–19] and Faradaic distortion [22], and the results of this form of analysis have been applied to the development of AC polarography [7]. More recently, Bertocci [9–10] and others [11] have investigated the effect of large amplitude perturbations in increasing the corrosion rates of electrical conduit materials.

The theoretical treatment presented here⁵ is similar in form to that described by Bertocci [9–10], by us previously [6], and by workers in Hungary [23–25], India [26–28], and England [29–31].

We are interested in the current response of an electrode to a voltage perturbation of the form

$$V = V_0 + v \sin(\omega t) \quad (4)$$

⁵These theoretical treatments all suffer from a major deficiency. The nonlinear term of interest in corrosion (the electron transfer process) is contained within a circuit comprising other linear (electrolyte resistance) and nonlinear (double layer capacitance and diffusional impedance) terms. Since the voltage dropped across nonlinear circuit elements cannot be considered to linearly superimpose, we cannot use the equivalent circuit method to isolate the impedance terms of interest. Properly, one must solve for the system as a whole, including diffusional and double layer terms, and identify the harmonic components associated with the Faradaic process of interest. We have solved this problem, but the resulting equations are cumbersome. This will be reported subsequently.

Substituting Eq 2 into Eq 4

$$I = I_{fc} \{ \exp[\vec{\beta}_a(\eta + v \sin(\omega t))] - \exp[-\vec{\beta}_c(\eta + v \sin(\omega t))] \} \quad (5)$$

where

$$\eta = V_0 - V_{fc} \quad (6)$$

One can make the substitution [10,32]

$$\begin{aligned} \exp[z \sin(x)] = J_0(z) + 2 \sum_{k=0}^{\infty} (-1)^k J_{2k+1}(z) \sin[(2k+1)x] \\ + 2 \sum_{k=1}^{\infty} (-1)^k J_{2k}(z) \cos[kx] \end{aligned} \quad (7)$$

where $J_n(z)$ is a modified Bessel function of order n . The value of $J_n(z)$ can be calculated by means of the expression

$$J_n(z) = (z/2)^n \sum_{k=0}^{\infty} [(z/2)^{2k}/k!(n+k)!] \quad (8)$$

The first term in Eq 7 represents the expected DC response (or Faradaic rectification component) attributable to an AC perturbation. The second term gives the odd order harmonic response, and the last term gives the even harmonics. In the limit as $v \rightarrow 0$, all response functions except the fundamental disappear, and for $\eta = 0$ we obtain the familiar expression for the Stern-Geary relationship [4]

$$\frac{dI_{fc}}{dV} = \frac{1}{R_c} = \frac{2.303 I_{fc}(\vec{\beta}_a + \vec{\beta}_c)}{\vec{\beta}_a \vec{\beta}_c} \quad (9)$$

Under all other conditions the Faradaic current must be represented by a Fourier Series of harmonic responses, as indicated by Eqs 6 to 8.

Substituting Eqs 7 and 8 into Eq 6, we obtained an equation of the form

$$\begin{aligned} I/I_{fc} = \{ \exp[\vec{\beta}_a \eta] \} \{ {}_0C^+ + {}_1C^+ + {}_2C^+ + {}_3C^+ + \dots \} \\ - \{ \exp[\vec{\beta}_c \eta] \} \{ {}_0C^- + {}_1C^- + {}_2C^- + {}_3C^- + \dots \} \end{aligned} \quad (10)$$

Where the harmonic series of constants, $C^\pm$, are $\exp[\pm v \sin(\omega t)]$ evaluated according to Eq 7.

Figures 4 to 8 demonstrate the influence of various corrosion parameters on the expected harmonic response, calculated from Eq 10. Figures 4 and 5 show

the effect of the AC amplitude (ν) on the magnitude of the response at large overvoltages. In Fig. 4 the absolute response is shown, while in Fig. 5 the responses are normalized by that at the first harmonic. Clearly, the application of perturbation levels as low as 50 mV can result in significant powers of the harmonic response at $0f$, $2f$, and $3f$.

The effect of DC potential and Tafel coefficient on the harmonic response is shown in Figs. 6 to 8. The power of the current response normalized by the free corrosion current (I_{fc}), shown on a log/linear scale, parallels that of the DC current response with constant ratio between the harmonics. For the symmetric case, shown in Fig. 4, the minimum in harmonic response occurs at the free corrosion potential. However, as the ratio of the reverse cathodic to forward anodic Tafel coefficients is increased, the potential at which the response is a minimum for each harmonic, is also increased. This phenomenon is shown more clearly in Fig. 8, and has been suggested as the basis for a corrosion monitor [31].

In order to monitor the corrosion rate of an electrode under an applied cathodic bias, it is necessary to measure the component of interest, the anodic current density, in the presence of significant interference. In applying the harmonic method, one of the major sources of interference is the presence of an uncompensated electrolyte resistance, R_u , between the reference and working electrodes. The methods by which this is eliminated are discussed in the following section. Having removed the effects of R_u , the next two major

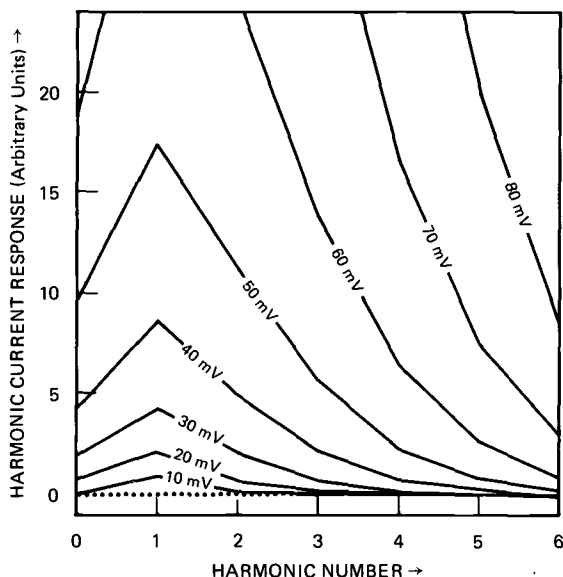


FIG. 4—Effect of AC amplitude on magnitude of harmonic response for a two-electron process: absolute response.

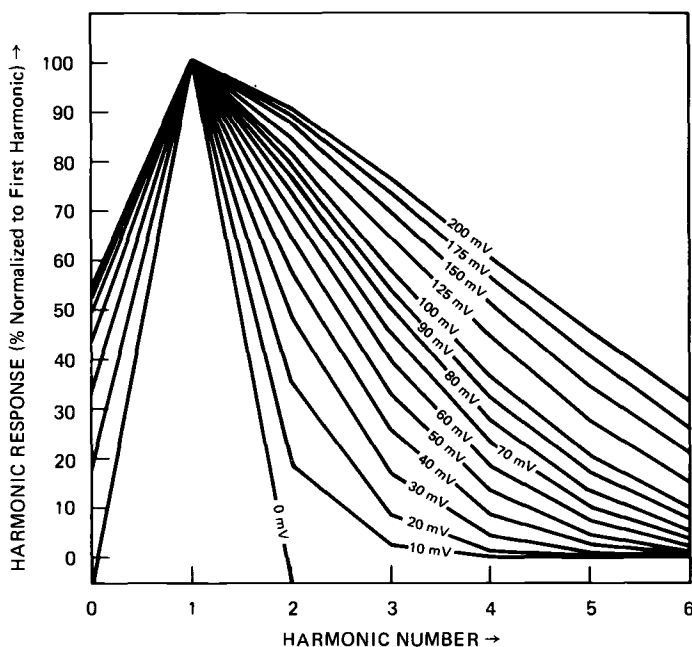


FIG. 5—Effect of AC amplitude on magnitude of harmonic response for a two-electron process: normalized response.

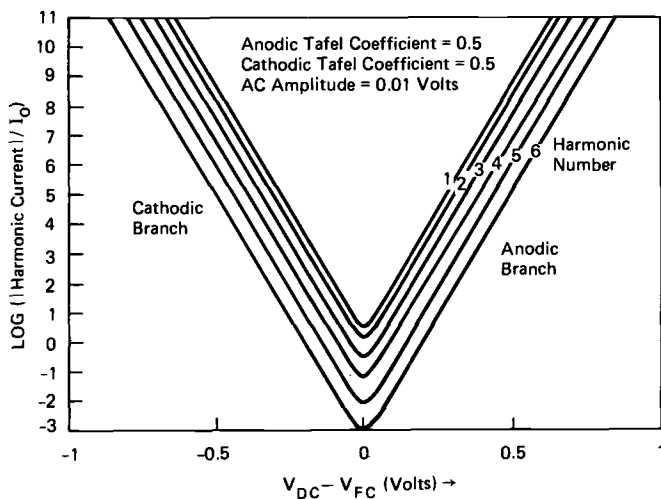


FIG. 6—Effect of DC applied potential on harmonic current response, as influenced by the Tafel coefficients: symmetric.

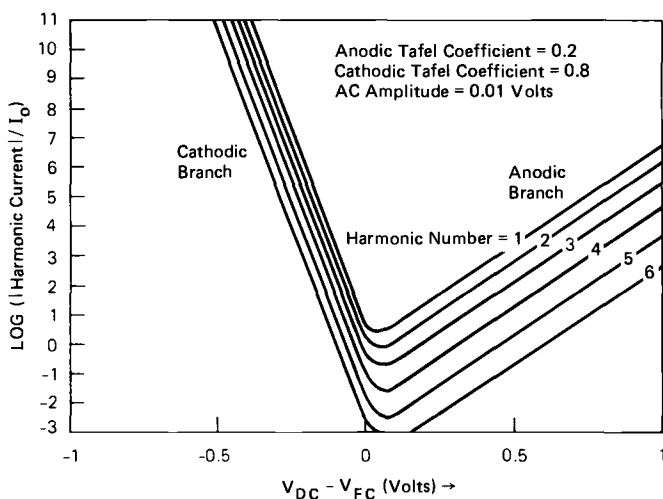


FIG. 7—Effect of DC applied potential on harmonic current response, as influenced by the Tafel coefficients: asymmetric 0.2/0.8.

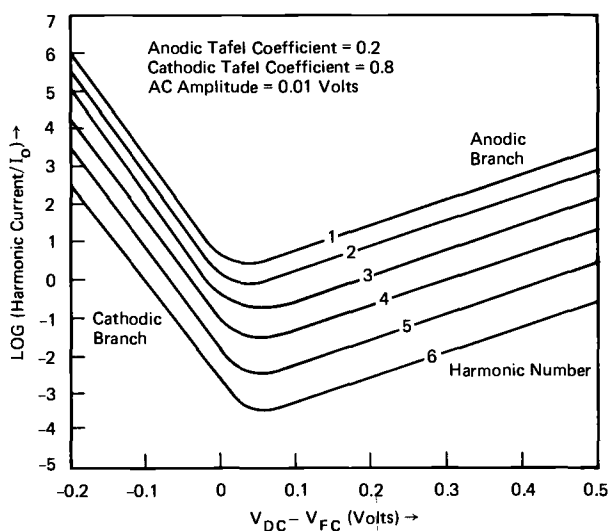


FIG. 8—Effect of DC applied potential on harmonic response for asymmetric corrosion process.

sources of interference are the presence of a large cathodic current, and the effects of diffusion. These are shown schematically in Figs. 9 and 10.

The only current that is observable externally is that due to the net reaction, indicated by the solid line in Figs. 9 and 10. This is composed of the sum of the forward anodic process and the reverse cathodic process, indicated by

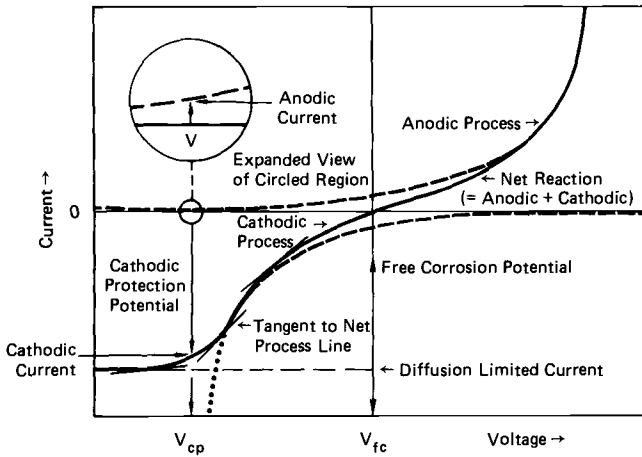


FIG. 9—Linear representation of anodic and cathodic processes at corroding electrode.

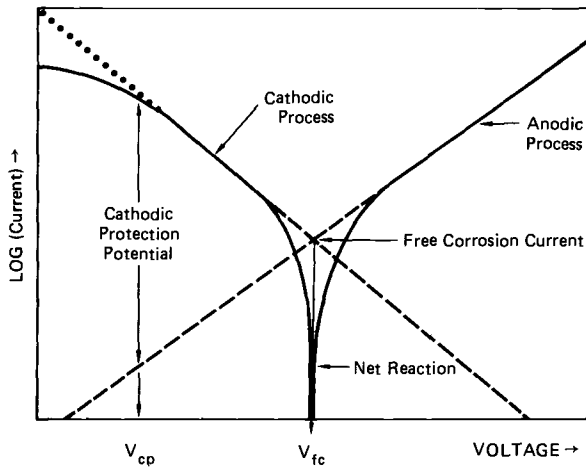


FIG. 10—Log/linear representation of anodic and cathodic processes at corroding electrode.

dashed lines. In the cathodic direction the reaction deviates from the exponential Tafel form (indicated by the dotted line) due to diffusion limitation.

In order to present data in the form required by Eq 10, the effects of diffusion limitation must be removed. This requires that a separate determination of the diffusional parameters be made. At large protection overvoltages, the following interference sources may become very large.

- When the reverse cathodic process is operating almost completely under diffusion control the measured current is considerably less than that predicted by Eq 5.

- The current in which we are interested, the forward anodic current shown expanded in Fig. 9, may be a very small fraction of the net current response.

Figure 11 shows in a very simplified form the equivalent circuit for a corroding electrode. By measuring the (first harmonic) impedance response as a function of frequency, we can separate explicitly the terms due to uncompensated resistance and due to diffusion [1-3]. The real component of the impedance terms that remain we can associate with the charge transfer (or corrosion) resistance, R_c , where

$$R_c/\nu = I = I_{fc} \{ \exp[\vec{\beta}_a(\eta + \nu \sin(\omega t))] - \exp[-\vec{\beta}_c(\eta + \nu \sin(\omega t))] \} \quad (11)$$

Experimental Procedures

Four alloy types have been examined; 90:10 copper nickel (CuNi) alloy, 70:30 CuNi alloy, 1018 carbon steel, and commercially pure titanium. Results will be described here only for the CuNi alloys. The electrolyte used in all tests was a synthetic ocean water (without the addition of heavy metals), prepared according to the ASTM Specification for Substitute Ocean Water (D 1141), using analytical grade reagents without further purification. The electrolyte was maintained in equilibrium with the atmosphere by sparging with air. Fresh electrolyte was used for each new experiment.

Experiments were performed to measure the zeroeth, first, second, and third harmonic response at various cathodic protection potentials, as a function of frequency in the range $0.05 \leq f \leq 20\,000$ Hz. The experimental setup is shown in Fig. 12. Briefly, under the control of the microcomputer, the frequency response analyzer (FRA) supplies a combined AC/DC output to the potentiostat via a signal-conditioning interface that was designed and constructed at SRI. Details may be found in Refs 8 and 33. The potentiostat closely maintains the computer-set DC voltage between the working (speci-

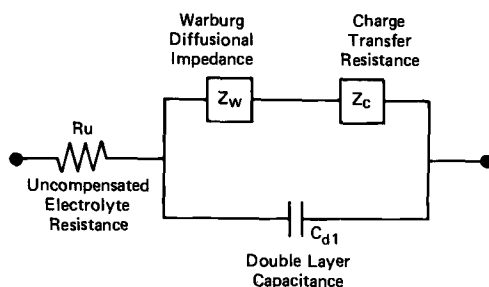


FIG. 11—Simplified equivalent circuit for corroding electrolyte.

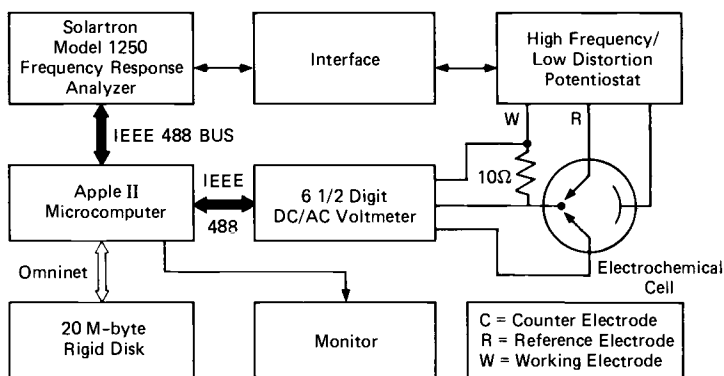


FIG. 12—Harmonic response measurement circuit.

men) and reference electrodes, while the AC is supplied with attenuation and phase shift (due to the limited bandwidth of this device) which increase with increasing frequency. The interface unit simultaneously provides the FRA with the AC voltage measured between the working and reference electrodes and the AC voltage across a resistor which is in series with the counter electrode (proportional to current).

The digital multimeter is used to perform several tasks. Before each frequency scan the multimeter is set (by the microcomputer) to the resistance range and is used to calibrate the series, current-measuring, resistance. During the frequency scan the multimeter operates as a dc voltmeter to monitor the net DC current. At the end of the frequency scan the multimeter is used to measure the zero'th harmonic response at three frequencies: 60, 600, and 6000 Hz.

The higher harmonic components of the AC voltages supplied to the FRA are measured by a pulse rate multiplication technique described in Ref 6.

The objective of this work was to measure corrosion rates from V_{fc} to approximately -700 mV versus a saturated calomel electrode (SCE). The intention was to determine the limits of applicability of the harmonic methods under a wide range of conditions of electrolyte flow rate, DC potential, and specimen geometry. The accuracy of the corrosion rate determinations using the harmonic analysis method was verified by comparison with mass loss measurements.

Three different specimen geometries were studied: a rotating cylinder electrode, a surface probe, and a circular flag specimen multicell. The rotating cylinder shown in Fig. 13 was used in initial studies of the effect of electrolyte convection; the geometry shown allows a uniform primary current density and a constant Reynolds number to be maintained over the electrode surface [34].

The scanning electrode configuration shown in Fig. 14 was intended to demonstrate the harmonic-analysis corrosion-monitoring concept for use un-

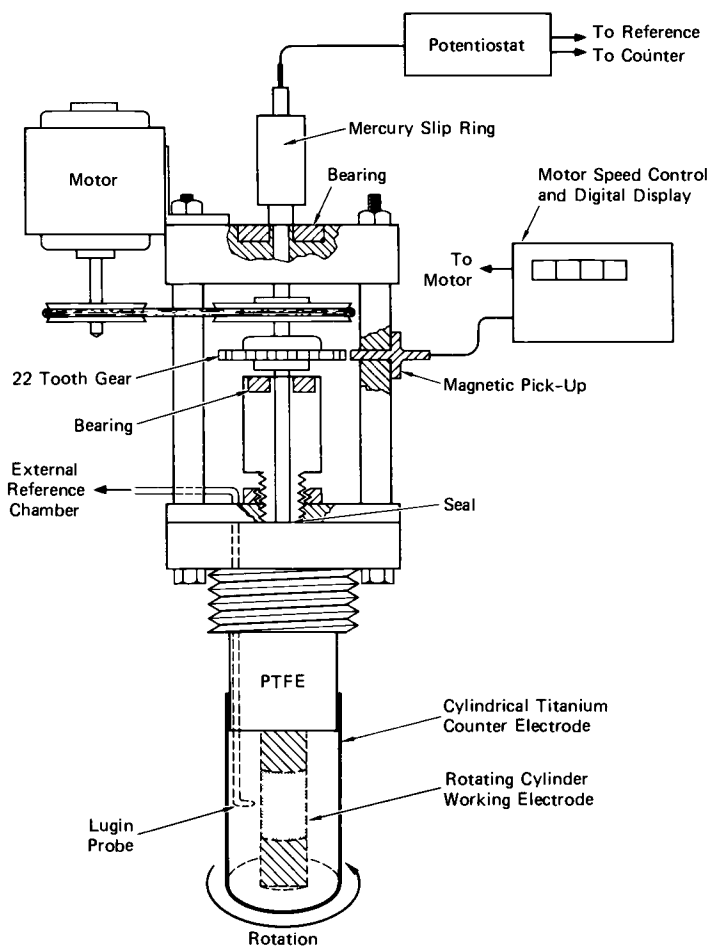


FIG. 13—Rotating cylinder electrode, motor control, and slip ring assembly.

der plant conditions. Since it is not practical to impose a sinusoidal voltage perturbation on the cathodic protection circuit itself, this perturbation must be imposed with respect to a counter electrode associated with the corrosion-monitor probe. The probe shown in Fig. 14 comprises a helical counter electrode in a separate chamber, a reference electrode connected via a Lugin probe to near the probe tip, and a pseudo-reference electrode, with respect to which the AC response is measured.

Figures 15 and 16 show details of the flow multi-cell and the circular flag specimen holders used for simultaneous mass loss and harmonic measurements. Up to six specimens can be held simultaneously under potentiostatic control, with respect to a single reference electrode/Lugin probe that can be

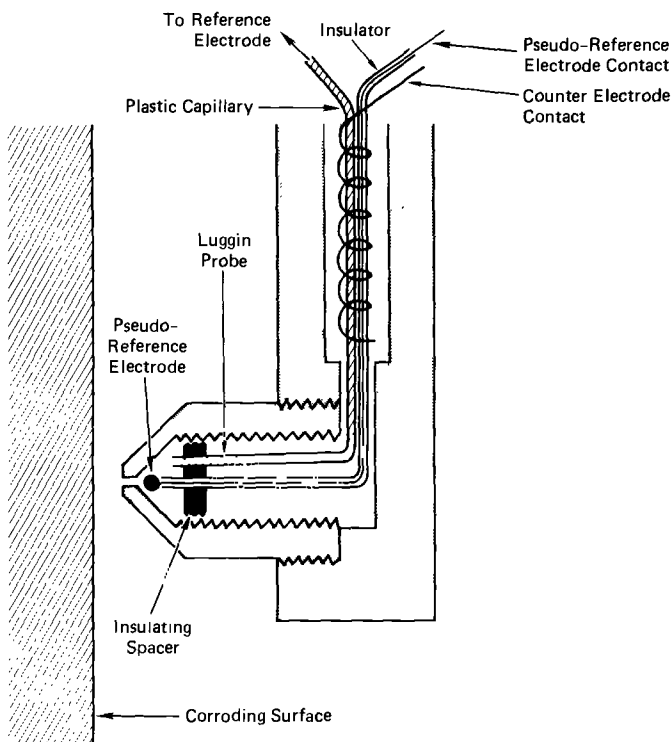


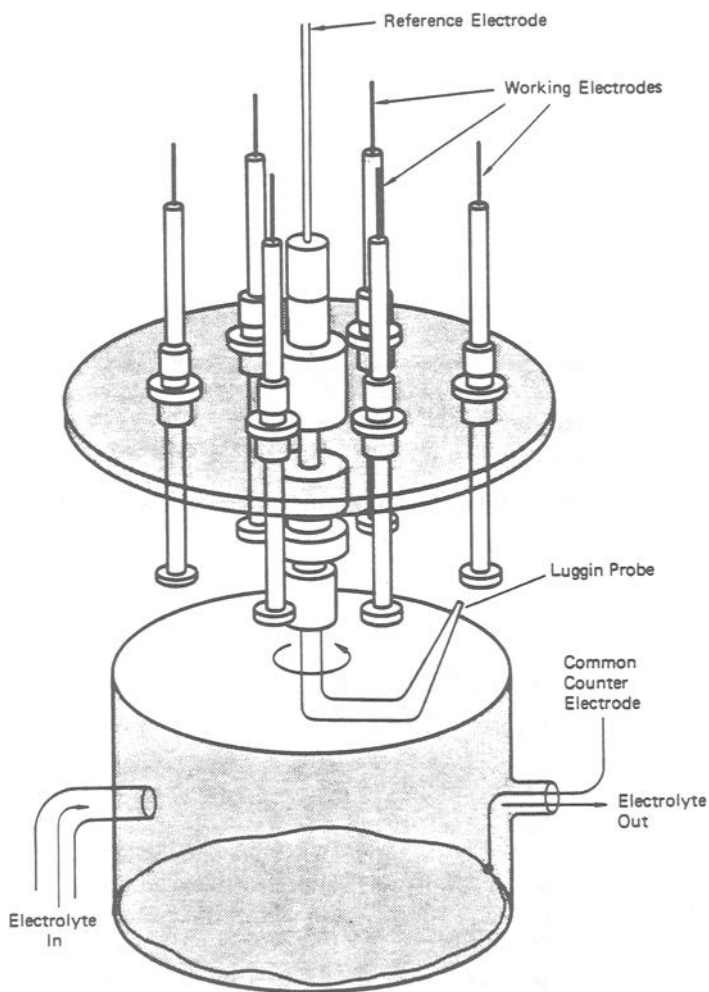
FIG. 14—Scanning surface probe for harmonic current studies.

rotated to be immediately adjacent to the bottom surface of each working electrode. Each specimen was masked so that only the downward-facing surface was exposed to the electrolyte. All six surfaces were situated in a single plane parallel to that of the common counter electrode. Each specimen was connected via individual $10\ \Omega$ resistors to ground. In this way, by rotating the Luggin probe assembly and by reconnecting the current-monitoring electrode, any one of the specimens could be examined using AC impedance or harmonic analysis techniques or both.

Electrolyte was recirculated via a large external reservoir with an effective velocity of approximately $10\ \text{cm s}^{-1}$ with respect to exposed surfaces of the circular flag specimens.

Data Reduction

Experiments were performed under microcomputer control with the resultant data recorded on a rigid disk for subsequent numerical analysis. The



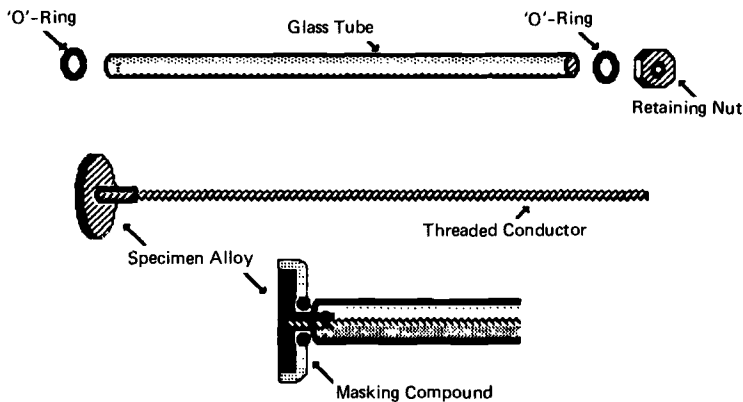


FIG. 16—Schematic diagram of circular flag specimens.

data reduction procedures will not be described here in detail, but the successive steps of the collection/analysis process basically were as follows:

1. Establish DC potential, AC amplitude, minimum and maximum frequencies, and initiation time of the experiment.
2. Instruct the FRA to measure the harmonic components of the input voltage and output current at $1f$, $2f$, and $3f$, at 39 logarithmically spaced frequencies between the established minimum and maximum.
3. Instruct the digital multimeter to measure the $0f$ response at 60, 600, and 6000 Hz.
4. Save results to rigid disk; if more data are required then loop to beginning.
5. Subtract the components of the harmonic current response that are due to harmonic distortion of the input voltage waveform.
6. Calculate on admittance (Y) for each of the terms $0I/1V$, $1I/1V$, $2I/1V$, $3I/1V$, and extract terms due to the series measurement resistance.
7. Transform the first harmonic reduced admittance terms to the impedance (Z) plane and fit the high frequency data to the form expected for a series/parallel RC circuit, to calculate the residual series uncompensated (R_u) electrolyte resistance and the double layer capacitance (C_{dl}).
8. Remove the terms in $2Z$ and $3Z$ due to R_u .
9. Remove the terms in $1Z$ due to R_u , C_{dl} , and the Warburg diffusional impedance (Z_w).
10. Retransform data to the admittance plane and calculate frequency independent values for the ratios: $0Y/1Y$, $2Y/1Y$, $3Y/1Y$.

The admittance ratios, thus determined, are used to evaluate the desired

corrosion parameters. Equation 10 can be expressed in the appropriate form by noting that

$$\frac{nY}{mY} = \frac{nI}{1V} \cdot \frac{1V}{mI} = \frac{nI}{mI} = \frac{nI}{I_{fc}} \cdot \frac{I_{fc}}{mI} \quad (12)$$

Thus

$$\frac{0Y}{1Y} = \frac{\{\exp[\vec{\beta}_a\eta]\}\{0C^+\} - \{\exp[-\vec{\beta}_c\eta]\}\{0C^-\}}{\{\exp[\vec{\beta}_a\eta]\}\{1C^+\} - \{\exp[-\vec{\beta}_c\eta]\}\{1C^-\}} \quad (13)$$

$$\frac{2Y}{1Y} = \frac{\{\exp[\vec{\beta}_a\eta]\}\{2C^+\} - \{\exp[-\vec{\beta}_c\eta]\}\{2C^-\}}{\{\exp[\vec{\beta}_a\eta]\}\{1C^+\} - \{\exp[-\vec{\beta}_c\eta]\}\{1C^-\}} \quad (14)$$

$$\frac{3Y}{1Y} = \frac{\{\exp[\vec{\beta}_a\eta]\}\{3C^+\} - \{\exp[-\vec{\beta}_c\eta]\}\{3C^-\}}{\{\exp[\vec{\beta}_a\eta]\}\{1C^+\} - \{\exp[-\vec{\beta}_c\eta]\}\{1C^-\}} \quad (15)$$

The constants ${}_hC^\pm$ are known from Eq 9; the unknown parameters η , $\vec{\beta}_a$, $\vec{\beta}_c$ are calculated from the best fit of the measured admittance ratios to this system of equations.

All steps in this data reduction procedure were performed with a micro-computer using programs developed at SRI.

Results

Figures 17 to 21 show the results of an experiment performed on a 90:10 CuNi alloy circular flag specimens, intended to examine the effects of protection potential on the harmonic current response. Figures 17 and 18 show a complex admittance plot, covering the full range of fundamental frequencies used, with results at different applied DC biases overlayed. Figure 18 shows low frequency data on an increased scale. The responses at -235 , -260 ($\approx V_{fc}$) and -300 mV can be clearly distinguished, but the data at -397 , -473 , and -623 mV overlap. Thus, at potentials more than 140 mV from the free corrosion potential, there is very little resolution in the fundamental response until other cathodic processes (hydrogen evolution) begin to occur at -774 mV.

This lack of discrimination in the potential range of interest does not extend to the second and third harmonic responses. Figures 19 to 21 show the same data presented in Figs. 17 and 18 plotted as the magnitude of the admittance versus frequency and DC bias. The fundamental response at -397 , -473 , and -623 , shown in Fig. 19, are very similar. However, the higher harmonic responses, shown in Figs. 20 and 21, display a high degree of differentiation between the applied cathodic protection levels.

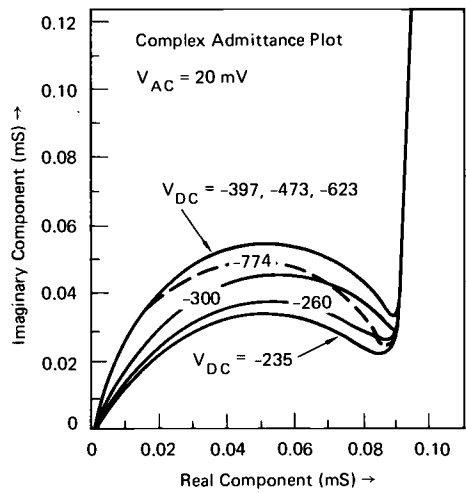


FIG. 17—Effect of applied DC voltage on the admittance of 90:10 CuNi alloy specimens, all frequencies (1 to 11 kHz).

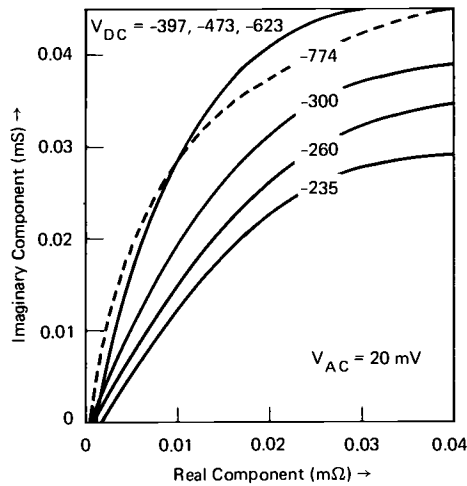


FIG. 18—Effect of applied DC voltage on the admittance of 90:10 CuNi alloy specimens, low frequency data.

The data shown in Figs. 19 to 21 were analyzed using the procedure outlined in the previous section to determine the admittance ratios and corrosion parameters for 90:10 CuNi alloy, as a function of cathodic bias. The results of this analysis are summarized in Table 1; the last column presents the calculated corrosion rates in mils per year. Unfortunately, the fitting procedure

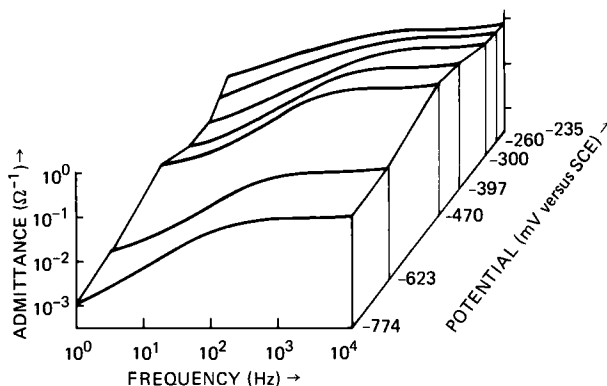


FIG. 19—Harmonic admittance magnitude response of 90:10 CuNi alloy specimens, as a function of frequency and cathodic protection potential, first harmonic.

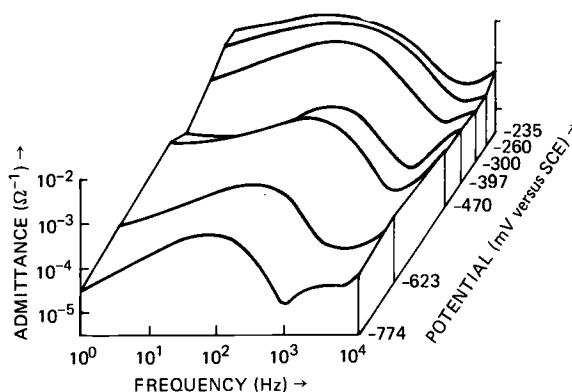


FIG. 20—Harmonic admittance magnitude response of 90:10 CuNi alloy specimens, as a function of frequency and cathodic protection potential, second harmonic.

employed does not allow a sensitivity analysis of the results, and the errors are not known. It is probable that the determinations at -473 and -623 mV are significantly in error, and no meaningful solution could be obtained at -774 mV. Nevertheless, the calculated corrosion rates trend in the right direction.

In order to provide an experimental verification of the results of our harmonic analysis, a number of long-term corrosion tests were performed in which harmonic analysis results were compared with those of mass loss determinations. Tables 2 and 3 summarize some of the results obtained in our laboratory and data obtained from the literature covering a range of environmental conditions [35–37] for various CuNi alloys.

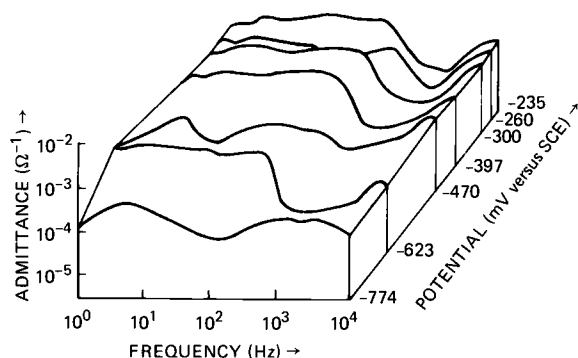


FIG. 21—Harmonic admittance magnitude response of 90:10 CuNi alloy specimens, as a function of frequency and cathodic protection potential, third harmonic (smoothed data).

TABLE 1—Initial^a corrosion rates determined from the harmonic admittance ratios measured for 90:10 CuNi alloy in synthetic ocean water.

V_{oc}/V	I/mA	$_2Y/_1Y$	$_3Y/_1Y$	I_a/mA	I_c/mA	k/mpy
-235	+0.210	2.62×10^{-3}	3.45×10^{-4}	2.1×10^{-1}	...	6.7×10^0
-260	+0.016	3.75×10^{-3}	2.46×10^{-4}	2.9×10^{-2}	1.3×10^{-2}	9.3×10^{-1}
-300	+0.116	2.11×10^{-3}	8.59×10^{-5}	3.4×10^{-3}	1.2×10^{-1}	1.1×10^{-2}
-397	-0.443	7.59×10^{-4}	3.51×10^{-5}	1.9×10^{-4}	4.4×10^{-1}	6.1×10^{-3}
-473	-0.613	1.49×10^{-3}	7.20×10^{-4}	5.0×10^{-5}	6.1×10^{-1}	1.6×10^{-3}
-623	-1.033	8.32×10^{-4}	3.43×10^{-4}	1.4×10^{-6}	1.0×10^0	4.5×10^{-5}
-774	-1.469	2.60×10^{-3}	1.89×10^{-4}	...	1.5×10^0	...

^aExperiments performed on specimens exposed for between 48 and 56 h.

At the free corrosion potential (Table 2) data are reported in the range 0.31 to 1.43 mpy for 90:10 alloy and 0.08 to 1.66 mpy for 70:30 alloy. It has been previously noted [35] that the corrosion rate of CuNi alloys decreases rapidly with time even up to 120 h from the initiation of the test. The corrosion rate of these alloys also increases somewhat with increasing water velocity [35–36]. These two effects can be used to explain the data tabulated in Table 2.

The results of long-term mass loss tests of CuNi alloys under cathodic bias are presented in Table 3. The data in the last column showing the corrosion rate calculated from mass loss, must be treated with great care for two reasons. First, the experiments at -300 and -400 mV versus SCE were performed with a 50 mV imposed sinusoidal perturbation. Since the free corrosion potential of these alloys is around -265 mV versus SCE, the imposed sinusoid may result in an anomalously large corrosion rate. Second, at all potentials more negative than -300 mV the coupons exhibited mass gain rather than a mass loss. For all weight loss determinations the product buildup on the surfaces was removed by repeated dipping in 0.1 M HCl. In

TABLE 2—Mass loss determination of the corrosion rate of copper nickel alloys in seawater: free corrosion potential.

Source of Data	Electrode			Electrolyte			Potential		Time of Exposure, days	Measured Mass Loss, mg	Measured Corrosion Rate, mpy
	Type	Geometry ^a	Area, cm ²	Type	[O ₂], ppm	Velocity, cm s ⁻¹	AC, mV	DC, mV versus SCE			
Ref 3	90:10	A	11.04	sea ^b	26.3	1620	0	V _{fc} ^b	8.17	3.18	0.57
	70:30	A	11.04	sea	26.3	1620	0	V _{fc}	8.17	9.33	1.66
	90:10	A	11.04	sea	6.60	1620	0	V _{fc}	7.88	7.78	1.43
	70:30	A	11.04	sea	6.60	1620	0	V _{fc}	7.88	4.45	0.82
Ref 33	90:10	B	31.35	sea	5 → 9	2000	0	V _{fc}	90	c	1.18
	70:30	B	31.35	sea	5 → 9	2000	0	V _{fc}	90	c	0.95
Ref 34	100:0 ^d	B	c	sea	AS ^b	0	0	V _{fc}	530	c	0.55
	90:10	B	c	sea	AS	0	0	V _{fc}	530	c	0.31
	70:30	B	c	sea	AS	0	0	V _{fc}	530	c	0.08
	100:0	B	c	sea	AS	500	0	V _{fc}	530	c	0.57
	90:10	B	c	sea	AS	500	0	V _{fc}	530	c	0.33
	70:30	B	c	sea	AS	500	0	V _{fc}	530	c	0.08
	90:10	C	7.85	SOW ^b	AS	0	20	V _{fc}	6.9	3.4 ± 0.2	1.01 ± 0.06
	70:30	C	7.85	SOW	AS	0	20	V _{fc}	7.4	2.1 ± 0.2	0.58 ± 0.06
This work	90:10	C	7.85	SOW	AS	62.8	20	V _{fc}	8.2	4.5 ± 0.2	1.12 ± 0.06
	70:30	C	7.85	SOW	AS	62.8	20	V _{fc}	5.1	1.6 ± 0.2	0.64 ± 0.06

^aElectrode type: A = inside surface of tube (Ref 32); B = single flat rectangular surface (Refs 33, 34); C = outside surface of rotating cylinder (this work).^bSOW = ASTM Standard D 1141-75 synthetic ocean water; sea = natural seawater; AS = air saturated. V_{fc} = free corrosion potential.^cNot reported.^dPure copper.

TABLE 3—Mass loss determination of the corrosion rate of copper nickel alloys in seawater: applied cathodic polarization.

Experiment ^a No.	Electrode		Electrolyte			Potential		Time Exposure, days	Measured Mass Loss, mg	Calculated Corrosion Rate, mpy
	Type	Geometry ^b cm ²	Area, cm ²	Type	[O ₂], ppm	Velocity, cm s ⁻¹	AC, mV			
D1/1	90:10	D	4.94	SOW ^c	AS ^c	~3	0	-641	0.03	3.6×10^{-3}
D1/2	70:30	D	4.79	SOW	AS	~3	0	-641	0.01	1.2×10^{-3}
D2/1	90:10	D	4.80	SOW	AS	~3	0	-550	0.02	2.2×10^{-3}
D2/2	70:30	D	5.05	SOW	AS	~3	0	-550	0.02	2.1×10^{-3}
E2/CR1	90:10	E	3.06	SOW	AS	10	50	-400	...	...
E2/CR2	90:10	E	3.06	SOW	AS	10	50	-400	9.63	<0.41
E2/CR3	90:10	E	3.06	SOW	AS	10	50	-400	4.44	<1.18
E2/CR4	90:10	E	3.06	SOW	AS	10	50	-400	4.47	<0.21
E2/CU1	70:30	E	3.06	SOW	AS	10	50	-400	3.30	<0.22
E2/CU2	70:30	E	3.06	SOW	AS	10	50	-400	4.47	<0.21
E3/2	90:10	E	3.05	SOW	AS	~10	50	-300	3.81	1.36
E3/5	90:10	E	3.04	SOW	AS	~10	50	-300	3.85	1.38
E3/7	90:10	E	3.04	SOW	AS	~10	50	-300	...	...
E3/1	70:30	E	3.05	SOW	AS	~10	50	-300	1.7	0.61
E3/4	70:30	E	3.03	SOW	AS	~10	50	-300	1.4	0.50
E3/6	70:30	E	3.01	SOW	AS	~10	50	-300	1.0	0.36

some instances the final mass still was greater than the initial, and the possibility exists that material remained on the surface that was insoluble in 0.1 M hydrochloric acid (HCl), either electro-deposited from the synthetic ocean water or due to incomplete removal of the masking compound. Accordingly, the results presented for -400 mV represent the total mass lost due to dipping in HCl, and thus represent a probable upper limit on the corrosion rate.

Conclusions

The results in Tables 1, 2, and 3 pertaining to 90:10 CuNi alloy have been summarized in Table 4, and are plotted in Fig. 22 in order to compare the

TABLE 4—Comparison of corrosion rates estimated from mass loss data, and harmonic current analysis, for 90:10 CuNi alloy.

Measurement Type	Specimen Type	Potential, mV versus SCG	Corrosion Rate	Time, days
Mass loss	D	-641	$3.6 \times 10^{-3} \pm 100\%$	27
Harmonic	E	-623	4.5×10^{-5}	<1
Mass loss	D	-550	$2.2 \times 10^{-3} \pm 100\%$	30
Harmonic	E	-473	1.6×10^{-3}	<1
Mass loss	E	-400	$< 4.1 \times 10^{-1}$	122
Harmonic	E	-397	6.1×10^{-3}	<1
Mass loss	E	-300	< 1.38	44
Harmonic	E	-300	1.1×10^{-2}	
Mass loss	C	V_{fc}	< 1.18	8.2
Harmonic	E	V_{fc}	0.9	<1

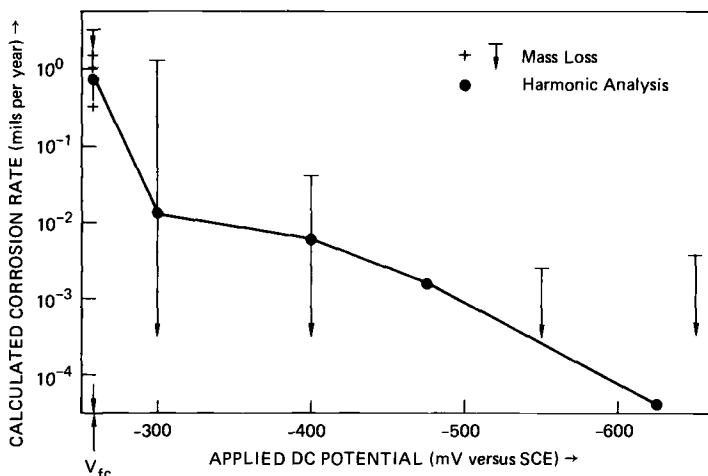


FIG. 22—Comparison of corrosion rate of 90:10 CuNi alloy specimens calculated using mass loss and harmonic analysis methods, using data from Table 4.

TABLE 5—Comparison of corrosion rates calculated from mass loss data and harmonic current analysis data for 90:10 CuNi alloy.

DC Potential, mV versus SCE	Velocity, cm s ⁻¹	Test Period, days	Corrosion Rate, mpy	
			Mass Loss Data	Harmonic Data
~ -260 (V_{fc})	0	7	1.01 ± 0.06	0.93
~ -260 (V_{fc})	~ 10	< 1		
~ -260 (V_{fc})	62.8	7	1.12 ± 0.06	
-300	~ 10	44	1.37 ± 0.01	1.1 × 10 ⁻² 6.1 × 10 ⁻³
-300	~ 10	< 1		
-397	~ 10	< 1		
-400	10	20	< 1.18	
-400	10	112	< 0.21	
-400	10	122	< 0.41	1.6 × 10 ⁻³
-473	~ 10	< 1		
-550	~ 3	30	2.2 × 10 ⁻³ (± 2.2 × 10 ⁻³)	
-623	~ 10	< 1		4.5 × 10 ⁻³
-641	~ 3	27	3.6 × 10 ⁻³ (± 2.4 × 10 ⁻³)	

results of mass loss determinations and harmonic analysis. Within the precision and scatter of the mass loss results shown, there is adequate agreement between the two techniques. Considering, particularly, the fact that the harmonic results shown were obtained at short times, where the corrosion rate is expected to be a maximum [35], these tend to be lower than the mass loss results (Table 5). However, due to experimental difficulties, the mass loss determinations represent a probable upper limit, with the lower limit being effectively zero, at large protection overvoltages. Under these conditions, it is likely that the harmonic method yields results of greater accuracy than does mass loss.

For the system described, 90:10 CuNi alloy in seawater, the harmonic method is sensitive to corrosion rates on the order of 0.001 mpy. Operation as a continuous or intermittent monitor is likely to be highly effective in detecting the presence of low levels of oxidizing species, or failures in the control electronics of a cathodically protected structure. When used to provide positive feedback, a monitor of the type described could minimize power consumption in the protection system, and minimize the possibility of overprotection leading to hydrogen embrittlement, while maintaining the corrosion rate at acceptably low levels.

Acknowledgment

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Electrochemical Noise as an Indicator of Anaerobic Corrosion

REFERENCE: Iverson, W. P. and Heverly, L. F., "Electrochemical Noise as an Indicator of Anaerobic Corrosion," *Corrosion Monitoring in Industrial Plants Using Nondestructive Testing and Electrochemical Methods*, ASTM STP 908, G. C. Moran and P. Labine, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 459-471.

ABSTRACT: Anaerobic (bacterial) corrosion is an important cause of failures of underground structures such as pipelines. Pipeline failures could be prevented if better methods for determining the presence and location of areas of bacterial corrosion existed. A technique was developed which permits the detection and recording of rapid potential fluctuations (noise) produced in a corroding metal. It is believed that this noise is mainly caused by the breaking of protective films on the metal surface. Anaerobic bacterial corrosion also produces a type of noise, probably due to the breaking of iron sulfide films.

Preliminary evidence indicates that detection and production of this noise on pipelines may offer promise in locating areas of microbial corrosion as well as other types of corrosion. Differences in the type of noise signal could enable differentiation between biological and nonbiological corrosion. Continuing studies should verify or reject these premises.

KEY WORDS: anaerobic corrosion, bacterial corrosion, *Desulfovibrio*, electrochemical noise, cathodic depolarization, iron phosphide, corrosive metabolite, iron sulfide, cathodic protection

It has been estimated by the National Bureau of Standards (NBS)/Battelle study that in 1975 the national cost of corrosion of pipelines alone was 158 million dollars [1]. For many years, the exterior corrosion of underground pipelines by anaerobic sulfate-reducing bacteria has been recognized as an important cause of this corrosion [2]. Although there are no recent published estimates of pipeline corrosion failures due to bacterial causes in the U.S., Booth [3] estimated (1964) that at least 50% of failures in Great Britain were due to bacterial corrosion. It is highly probable that there could be as many if not more reportable cases of bacterial corrosion failures of pipelines in the

¹Microbiologist and guest worker, respectively, National Bureau of Standards, Room A329, Building 223, Washington, DC 20234.

U.S. were it not for the fact that bacterial corrosion failures are not recognized or detected by many pipeline operators. Some even do not admit that this type of corrosion exists.

At the present time, there are no available techniques which can accurately determine the location on the exterior surface of underground steel pipelines where sulfate-reducing bacteria are actively causing corrosion. Location of these areas and the ability to determine the effectiveness of cathodic protection measures would provide a major cost savings and reduce the danger to human life.

Preliminary results obtained at the NBS laboratory indicate the existence of random fluctuations of the corrosion potential, hereinafter called "electrochemical noise," that appears to be peculiarly characteristic of steel corrosion caused by anaerobic sulfate-reducing bacteria. It is the object of our work at NBS to develop a new nondestructive field procedure based upon the detection and analysis of this "noise," for locating, with a high degree of resolution, these areas of biological corrosion on the outside of in-service pipelines.

Anaerobic Corrosion

The severe anaerobic corrosion of underground pipelines at soil pH levels near neutrality was associated with the presence of hydrogen sulfide in the soil by von Wolzogen Kühr [2] as early as 1923. Hydrogen sulfide was previously ascribed by Beijerinck [4] in 1895 to the process of sulfate reduction to hydrogen sulfide carried out by the anaerobic bacterium (now called *Desulfovibrio desulfuricans*).

Cathodic Depolarization Theory

Based on the work of Stephenson and Stickland [5], which demonstrated that this organism (*D. desulfuricans*) can utilize hydrogen gas in the reduction of sulfate to hydrogen sulfide, von Wolzogen Kühr and van der Vlugt [6] proposed a theory, the so-called "Cathodic Depolarization" Theory, to account for this anaerobic corrosion of iron. This theory was based on the removal of hydrogen from the iron surface and its utilization for the reduction of sulfate to hydrogen sulfide (Fig. 1). Hydrogen removal by the bacteria due to an enzyme, hydrogenase, shown in Step IV, causes iron to ionize (corrode) to ferrous ions. The ferrous ions then react with sulfide ions and hydroxyl ions, as indicated by Steps V and VI, respectively.

Evidence for and against this theory has accumulated and has been well-reviewed over the last several years [7-10]. A few facts were established. First, no direct correlation between hydrogenase activity and corrosion rate was found using semicontinuous and continuous cultures [11,12]. Second, the addition of ferrous ions to the culture was found to result in the stimulation of corrosion rates [13]. It is believed that ferrous ions reacted with the sulfide

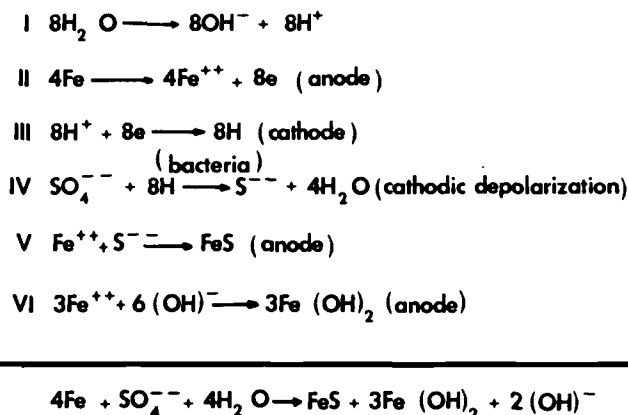


FIG. 1—Cathodic depolarization theory of von Wolzogen Kühr and van der Vlugt.

ions in solution to form bulk iron sulfide, and so prevented the establishment of a partially protective film of iron sulfide on the surface of the iron. Mara and Williams [14] postulated that the bulk iron sulfide was involved, acting as a cathode and absorbing cathodic hydrogen as an ionized interstitial species in proportion to the cationic defects in the iron sulfide. Earlier, King and Miller [15] suggested that the bacteria on the surface of the ferrous sulfide continually "regenerated" or depolarized the iron sulfide by removal of atomic hydrogen by their hydrogenase activity. An additional possibility suggested by Miller [10] was that the bacteria, as a result of their motility, caused fresh iron sulfide surfaces to be brought constantly into contact with the steel surface, thus insuring prolonged, continuous contact and corrosion in bacterial cultures in contrast to the decrease in corrosion rate observed with chemically prepared bulk iron sulfide.

In addition to these proposed mechanisms, Costello [16] postulated that the depolarizing activity of sulfate-reducing bacteria was due to the cathodic activity of the dissolved hydrogen sulfide produced by these organisms.

Corrosive Metabolite Theory

In contrast to the cathodic depolarization theory, Iverson [8,17] has proposed a theory that anaerobic corrosion is caused by the production of a highly corrosive metabolite by the sulfate-reducing bacteria. This theory is based on a number of observations and results obtained over the last several years employing two hydrogenase-positive strains of *Desulfovibrio desulfuricans*, an American Petroleum Institute (API) strain and a marine strain isolated from an iron piling at Dam Neck, Virginia.

The following evidence was presented in support of the theory:

1. In a culture of sulfate-reducing bacteria containing iron (mild steel) and without added ferrous ions, very little corrosion occurs. Usually the corrosion is inhibited by the formation of a protective film of iron sulfide. The corrosion rate greatly increases only when the film breaks [11,18].

2. In a model used to demonstrate bacterial cathodic depolarization, no cathodic depolarization of iron could be observed if sulfate ions were present as an electron acceptor [19].

3. The main corrosion product of the anaerobic corrosion of iron was found to be a complex of iron phosphides, Fe_2P and Fe_3P , rather than iron sulfide as determined by chemical analysis, X-ray diffraction, and Mössbauer studies [19].

4. Extensive corrosion of bulk iron ($115.2 \text{ g/m}^2 \cdot \text{d}$; maximum rate) was obtained from a culture of sulfate-reducing bacteria from which both the bacterial cells and the free sulfide ions were removed (by the addition of ferrous ions and subsequent removal of the ferrous sulfide). Thus, extensive corrosion rates, similar to those found in the field, could be obtained without bacterial cells, sulfide ions, and iron sulfate [17].

The presence of bacterial cells in contact with iron was considered an essential part of the cathodic depolarization theory. As the sulfide ions were removed, no iron sulfide could be formed. Iron sulfide was considered to be an essential part of the later modifications to the cathodic depolarization theory proposed by Mara and Williams [14], King and Miller [15], and Miller [10], as previously mentioned. These findings could explain the stimulation of corrosion by the addition of ferrous ions to the culture medium containing iron, as noted above.

5. The anaerobic corrosion of iron resulting in iron phosphide formation was found to be due to a volatile, water-soluble phosphorus compound [20]. Based upon these observations, it was suggested by Iverson [21] that in the anaerobic corrosion process, by sulfate-reducing bacteria, corrosion may be initially inhibited by the action of the bacterially produced hydrogen sulfide on the surface of iron to form a protective film of iron sulfide. As these films are somewhat unstable [10] and break down, the highly corrosive phosphorus compound, also produced by the bacteria, could come in contact with the iron surface to initiate the corrosion process. The corrosion rate has been observed to be very rapid after the breakdown of the sulfide film [11,18]. The corrosion process, therefore, could consist of filmmaking, breaking, and corrosion. However, laboratory studies indicate that the iron sulfide film is unable to reform after breakdown of the original film [10].

Electrochemical Noise

In 1968 Iverson [21], using the circuit shown in Fig. 2, reported on the electrochemical noise associated with the corrosion process. This simple cir-

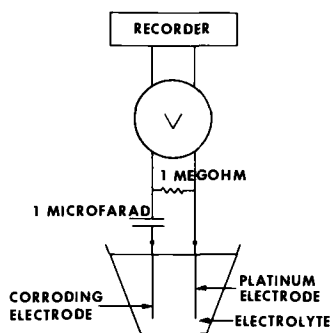


FIG. 2—Corrosion cell and circuit for detecting potential variations in corroding metals and alloys.

cuit consisted of a corroding electrode connected in series with a capacitor and a resistor which was connected to a noncorroding platinum electrode. The potential changes in the corroding electrode were measured across the resistor with a microvoltmeter and a recorder.

Recorder tracings of these transient potential changes or “noise” with time are indicated in Fig. 3. Figure 3a is the tracing obtained when a second platinum electrode was substituted for the corroding electrode. Essentially, no potential transients were observed. The left portion of the tracings in Fig. 3b were obtained from an iron (1010 steel) electrode in a 0.1% sodium chloride (NaCl) solution. At Time I, indicated by the arrow, both electrodes (iron and platinum) were placed in 0.1% NaCl solution containing a corrosion inhibitor (NaNO_2). An immediate cessation of electrochemical noise was noted. Upon transfer to 0.1% NaCl solution without an inhibitor (at Time II), initiation of the electrochemical noise was observed.

This noise has been further investigated by Bertocci [22–24], Bertocci and Kruger [25], Blanc et al [26], Epelboin et al [27], Hladky and Dawson [28], and Okamoto et al [29]. A paper entitled “An Application of Electrochemical Noise Techniques to the Corrosion of Reinforced Steel in Concrete Structures” was presented at the 1984 National Meeting of the National Association of Corrosion Engineers held in April 1984 [30].

According to Bertocci [22], “the measurement and analysis of the fluctuations in current and potential (electrochemical noise) appears to hold promise as a useful tool for the detection of localized corrosion [22]. . . . With a more modern and complex instrumentation there is reason to believe that the method can be quite powerful and susceptible of application outside the laboratory for the monitoring of corrosion on underground cables and pipes, metallic structures and in chemical plants.”

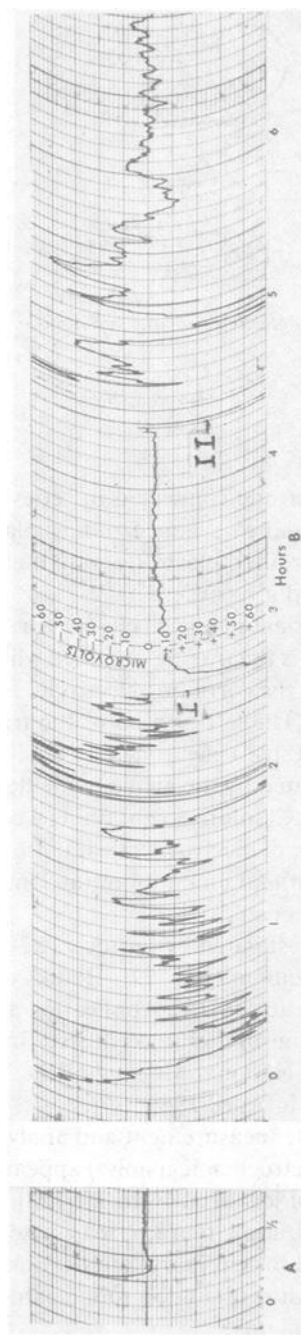


FIG. 3.—Recorder trace of noise waveforms. Chart speed 76.2 mm/h (3 in./h). A. Completely immersed platinum electrode (1 by 4.5 cm) in 0.1% NaCl solution; conductivity, 0.22 mhos; platinum electrode 1 cm from completely immersed auxiliary electrode, 25°C. B. Partially immersed (5.5 cm) 1010 steel electrode (1.3 by 18 cm) corroding in 0.1% NaCl solution; electrode 1 cm from completely immersed auxiliary electrode, 25°C. Time I, electrodes transferred to fresh 0.1% NaCl solution plus 1% NaNO_2 ; Time II, electrodes transferred to fresh 0.1% NaCl solution.

Electrochemical Noise and Anaerobic Corrosion

Laboratory Studies

A brief study was made by Iverson [31] of the electrochemical noise from a 1020 steel electrode in a trypticase sea-water culture of a sulfate-reducing bacterium (marine strain), using the circuit depicted in Fig. 2.

Unique potential fluctuations were obtained (Fig. 4*b*). These fluctuations differ from the fluctuations shown in Fig. 3*b* in that they all appear to be on one side of a baseline. When ferrous ions, which prevent iron sulfide film formation, were added to the culture, no potential fluctuations were noted (Fig. 4*a*). In this technique, the absence of potential fluctuations appears to indicate either generalized corrosion or the absence of corrosion.

It appears from these very preliminary observations that iron sulfide film formation and breakdown, previously discussed, could be responsible for these unusual wave forms. A somewhat analogous situation was found in the process of passive film breakdown and healing which are of fundamental importance in the understanding of the initiation and development of localized corrosion. For example, Bertocci and Kruger [25] associated passive film breakdown-repair events with the generation of considerable electrochemical noise.

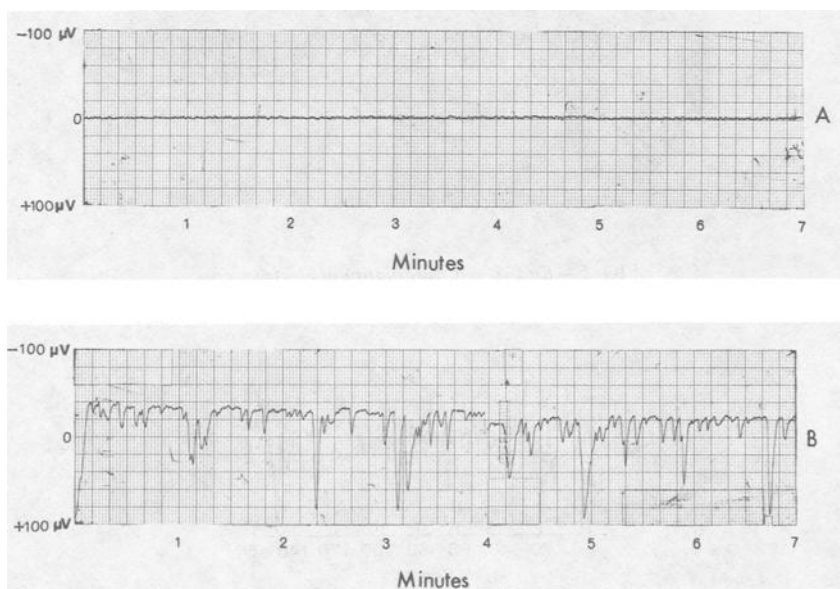


FIG. 4—A. Absence of noise waveforms from steel electrode (1020) in trypticase-seawater culture of *Desulfovibrio desulfuricans* with added ferrous ions. B. Noise waveforms without added ferrous ions (17-day-old culture).

Preliminary Field Studies

As part of a continuing study in the field, a section of abandoned pipeline 486.4 m long (1600 ft) was made available in West Virginia. This pipeline section has both coated and uncoated portions, and a capability for cathodic protection. This section also passes through soil in which pipes have previously undergone verifiable anaerobic corrosion.

The same circuit as shown in Fig. 2 was used in a preliminary study to determine if electrochemical noise could be detected from this pipeline. The pipelines served as the corroding electrode and connections were made to it at four locations. The platinum reference electrode consisted of a plastic tube with two platinum tip electrodes mounted in one end (Fig. 5). Lead wire from these two platinum tips were exposed at the other end of the tube.

The electropotential fluctuations obtained with the platinum electrode pressed in the soil surface above one of the pipe connections are indicated in Fig. 6. Electropotential fluctuations were also found when the platinum electrode was placed in the vicinity of the other three pipe connections, but they

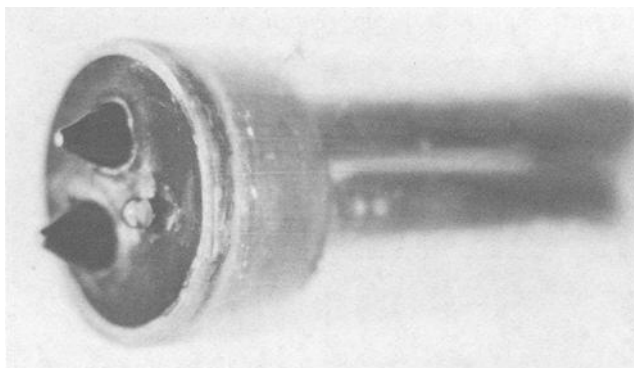


FIG. 5—End view of two platinum electrodes.

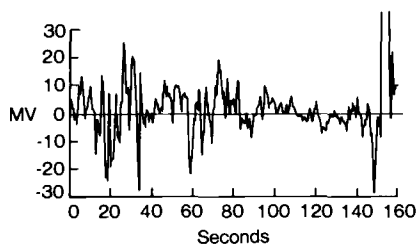


FIG. 6—Noise waveforms obtained with platinum electrodes on soil over a pipe connection (bare pipe). Pipe exposed to air the previous day [pipe-to-soil potential (psp) -0.55 V; Cu-Cu SO_4 ref]. Amplitude decreased with time (anerobic condition).

were of lesser amplitude. These wave forms cross the zero baseline and were probably due to an oxide film breakdown since the pipe had been exposed to the atmosphere the day previously. In this respect they are similar to the fluctuations shown in the left portion of the chart in Fig. 3b, which were obtained from a wet iron electrode that had been exposed to the air. The potential range, from the latter, however, is in microvolts while the range from the pipe is in millivolts.

In moving the platinum reference electrode on the soil above the pipe at intervals east and west of one pipe connection, two areas of possible anaerobic corrosion, based on the electropotential fluctuations, were located. The fluctuations for one of these areas are shown in Fig. 7. The recorder tracings 7.62 m (25 ft) on either side of this area, showed little noise, as indicated in Figs. 8 and 9. Electropotential fluctuations for the second area of possible microbial corrosion are indicated in Fig. 10. Fluctuations from an area 7.62 m (25 ft) closer to the pipe connection indicate very small noise amplitudes (Fig. 11). If these areas of possible anaerobic corrosion on the pipeline, as suggested by

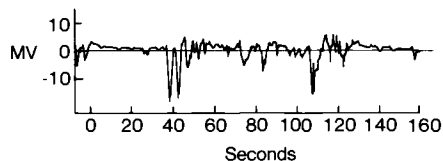


FIG. 7—Noise waveforms with probe over pipe 28.35 m (93 ft) west of pipe connection (bare pipe) (psp -0.43 V; Cu-Cu SO_4 ref).

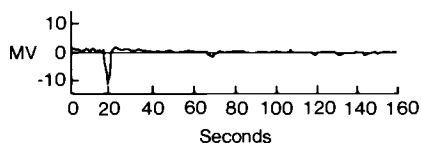


FIG. 8—Relative absence of waveforms with probe 7.62 m (25 ft) west of position indicated in Fig. 7 (bare pipe) (psp -0.58 V; Cu-Cu SO_4 ref).

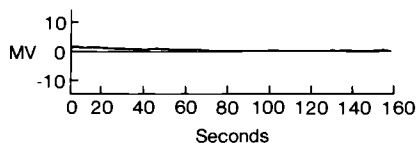


FIG. 9—Absence of waveforms with probe 7.62 m (25 ft) east of position indicated in Fig. 7 (bare pipe) (psp -0.46 V; Cu-Cu SO_4 ref).

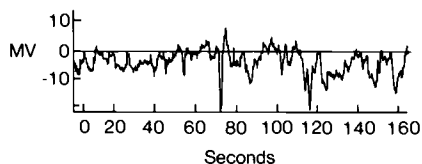


FIG. 10—Noise waveforms with probe 25.0 m (82 ft) east of pipe connection (coated pipe) (psp -1.93 V; Cu-Cu SO_4 ref).

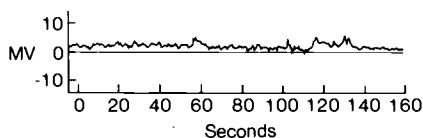


FIG. 11—Noise waveforms with probe 7.62 m (25 ft) west of position indicated in Fig. 10 (coated pipe) (psp -2.10 V; Cu-Cu SO_4 ref).

similarity of their electropotential fluctuations to Fig. 4b, were relatively small in size, the results indicate the possibility for determining fairly closely their location along the pipeline. Time did not permit obtaining electropotential fluctuations at closer intervals, which could provide a higher resolution picture of the underground pipeline condition.

On a second visit to the pipeline site, an area of possible microbial corrosion on a coated section of the pipe was located, using the above technique, and excavated. Upon physical examination, an area of anaerobic bacterial activity was noted around the pipe as evidenced by the strong smell of hydrogen sulfide and soil characteristics. Unfortunately, only one side of the pipe could be excavated because a guy wire for a pole was anchored close to the other side. No obvious corrosion pits on the exposed side of the pipe were located. Time did not permit a thorough examination of the pipe, however, because the trench was filling with water.

Discussion and Conclusions

From these very preliminary observations, it appears that electrochemical noise may be detected as a result of anaerobic corrosion processes. In laboratory studies, the electropotential fluctuations also appeared to be on one side of a baseline. It is of interest that these unique, one-sided electropotential fluctuations have also been detected in an aluminum-borate buffer system containing sodium chloride [32], above the pitting potential, suggesting spontaneous breakdown of the passive film.

As no fluctuations (waveforms) were detected in the laboratory when ferrous ions were added to the solution, preventing iron sulfide film formation, it is suggested that the one-sided electropotential fluctuations were due to sul-

fide film breakdown. Further investigation will be necessary to resolve this matter. Fluctuations of a similar one-sided type were also observed from the pipeline, but of a greater potential suggesting a possible similar mechanism, film formation, and breakdown. Although no fluctuations were noted in the presence of added ferrous ions where corrosion is extensive, this is an abnormal condition which might not be expected under field conditions.

It was of considerable significance that the detection of these electropotential fluctuations was related to the position of the platinum electrode with reference to distances along the pipeline. This finding indicated that the source of the noise along the pipe could be located with reference to specific areas. Considerable work remains to relate the "noisy" areas along the pipe, as indicated by the position of the platinum electrode, to areas of anaerobic corrosion. As controls, areas on the pipe which are noise-free must also be examined and found free of active corrosion.

It would be desirable to substitute the copper-copper sulfate half cell for the platinum electrode. Results so far using the half cell have not been conclusive. Further analysis of the noise fluctuations, including Fourier analysis, would be desirable to detect additional unique characteristics.

If this nondestructive technique proves feasible for the detection and location of anaerobic corrosion along pipelines, cathodic protection could then be employed at these areas. Further monitoring, using the noise technique, could be used to verify the continued effectiveness of this cathodic protection. For cathodic protection to be effective in cases of anaerobic corrosion, a pipe-to-soil potential of -0.950 V has been found to be necessary. This value is based on laboratory as well as field studies [33-35].

If nonbiological pipeline corrosion can be characterized by noise waveforms similar to those observed in Fig. 3*b* and Fig. 6, in contrast to the one-sided electropotential fluctuations observed in anaerobic biological corrosion, it may also be possible to distinguish between the two forms of corrosion, based on these characteristic fluctuations.

Acknowledgments

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Design Considerations for Occluded Cell Corrosion Monitoring

REFERENCE: Silverman, D. C. and Krisher, A. S., "Design Considerations for Occluded Cell Corrosion Monitoring," *Corrosion Monitoring in Industrial Plants Using Nondestructive Testing and Electrochemical Methods*, ASTM STP 908, G. C. Moran and P. Labine, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 472-491.

ABSTRACT: Occluded cell corrosion is a major contributor to unexpected and premature failures. A reliable, on-line instrument to monitor for occluded cell corrosion would generate benefits of a decreased frequency of failures and a more reliable estimation of service life. This paper reviews the thermodynamic and kinetic bases for such a practical monitor to show that the concept is sound. Crevice dimensions, cathode-to-anode area ratio, and defined hydrodynamics—parameters important in the in-plant monitor—are defined in this discussion. Finally, a conceptual model of a proposed in-plant monitor is presented. The dimensions and geometry are derived from the discussion of the theory.

KEY WORDS: crevice corrosion, thermodynamics, electrochemistry, occluded cell corrosion, metals, cathode, anode

Nomenclature

- A* Area, m²
- α Equiv/mole
- B* Coefficient of area ratio, Eq 7, V
- C* Concentration, mole/m³
- F* Faraday constant, C/equiv
- k* Mass transfer coefficient, m/s
- r* Reaction rate, mole/m²-s
- R* Gas constant, J/mole-K
- T* Temperature, K
- V* Voltage, volts

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Subscripts

a Activation
cath Cathode
MT Mass transfer

Introduction

Occluded cell corrosion is a major contributor to unexpected and premature failure of structural materials including steel, stainless steels, nickel alloys containing chromium, and titanium [1-3]. Data to allow for a precise quantitative estimation of its impact are not available, but from the fragmentary information available, at least 15 to 20% of premature failures in the chemical process industries are caused by occluded cell corrosion [1-4].

The corrosion engineer has two basic options. The first option is to avoid the alloy-environment combinations which are known to cause occluded cell corrosion. Unfortunately, such a practice would eliminate the use of carbon steel in aerated water, stainless steels in chloride-containing aqueous solutions, and a number of other alloy-environment combinations which are routinely and economically used.

The second option is to ignore potential crevice corrosion problems and to install materials which appear to have adequate resistance to general corrosion. Such an approach will lead to premature failure in some (but not all) cases. Premature failure is reflected in increased maintenance cost and unscheduled down-time.

A reliable on-line instrument to monitor for occluded cell corrosion would generate substantial benefits. Such a monitor would allow for safe use of materials in systems where there is some risk of crevice corrosion. Data from the monitor would allow plant operators to modify process conditions so as to reduce the risk or to schedule down-time for repairs. The rate of propagation could be monitored, allowing for a reliable estimation of remaining service life.

The purpose of this paper is not to cover all aspects of crevice corrosion fundamentals because numerous, wide-ranging reviews of crevice corrosion are available [1-4]. Rather, the purpose is to discuss those concepts that insure that the occluded cell monitor designed with separated anode and cathode is theoretically justified. The paper discusses the design criteria that should be fulfilled and presents a device concept.

Fundamental Basis for the Occluded Cell Monitor

The place to begin such a discussion is to describe briefly the thermodynamic, kinetic, and geometric factors that are known to affect crevice corrosion. These factors are shown in Fig. 1, adapted from Oldfield and Sutton [5].

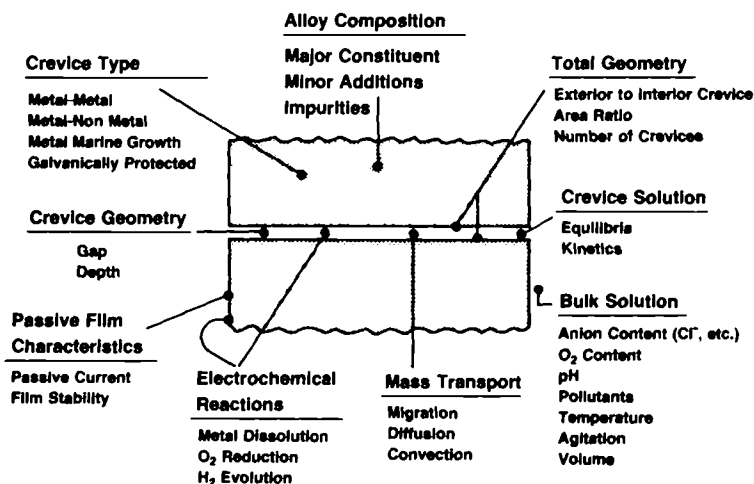


FIG. 1—Factors affecting crevice corrosion [5].

In terms of an in-situ occluded cell monitor, two general types of factors can be differentiated. First are factors that will be taken into account automatically by the very fact that the occluded cell monitor is in situ using the alloy or alloys of interest in the solution of interest. That is, they are environment- or alloy-dependent. Second are the factors that impinge on the design of the crevice assembly and on the concept of the separated anode and cathode. These are the factors that insure that the crevice assembly does model reality. The following discussion of the second group is divided into the two areas of thermodynamics and kinetics.

Thermodynamics

Localized corrosion is a rate process. The final state of such a process cannot be in violation of thermodynamics. For example, the final steady state concentration of any component cannot be greater than that concentration predicted by the reaction equilibrium constant. Thus, if all possible solid and ionic species can be guessed, then all of the reactions between them can be written. In principle, these concentrations could be compared to measured concentrations to determine if the reaction model is in violation of thermodynamics.

Unfortunately, this approach has not been applied to crevice corrosion except in a few isolated cases for several reasons. All possible solid species on the surface of an alloy are not known. Activity coefficients can be estimated accurately for only a relatively few combinations of inorganic ions [6]. Less rigorous methods are available for near-saturation conditions, but again, the

number of components having known properties are limited [7]. Computer programs written to make these involved calculations are only now becoming available [8]. At present, the thermodynamic basis for the occluded cell monitor must be discussed in terms of less rigorous calculations and simpler models.

Some of the earliest discussions of the thermodynamic basis for the occluded cell being of a different concentration than the environment are those of Pourbaix. He showed that EMF-pH diagrams could be used to assess the possible equilibrium states in the occluded cell [9,10]. Pourbaix showed that thermodynamic estimates of pH and potential for a number of single metal systems agree at least qualitatively with measurements in artificial crevices. Unfortunately, no account was taken of activity coefficients. Thus, only in those applications in which the ions are at dilute concentrations and activity coefficients are not far removed from unity, for example, copper, was quantitative agreement achieved. The important point is the fact that the concept of the occluded cell solution being of higher ionic strength and of lower pH than the external environment is consistent with thermodynamics. This observation means that a real crevice might be modeled by an appropriately designed cavity that can restrict mass transport to create these conditions.

The calculations for iron were refined by McCafferty [11], who combined activity coefficient estimates with free energies of formation to calculate the expected ionic concentrations and equilibrium potentials in an occluded cell of iron. He assumed several models. The solids considered were iron (Fe) $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, and the solid oxides or hydroxides Fe_3O_4 , $\text{FeOOH}/\text{Fe}_2\text{O}_3$, or $\text{Fe}(\text{OH})_2$. A diagram using the revised data reported recently [12] and including $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and a chloride ion activity of 10 is shown in Fig. 2 for the pH and potential region of interest in crevice corrosion [11]. The free energies of formation used are shown in Table 1. The only major difference from the analysis of McCafferty is the presence of solid $\text{Fe}(\text{OH})_2$ as a stable species

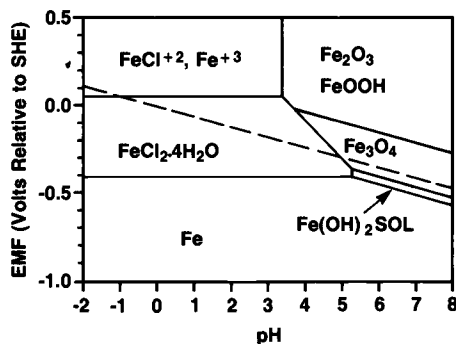


FIG. 2—EMF-pH diagram of iron-chloride system at 298 K. Activity of $\text{Cl}^- = 10$.

TABLE 1—Free energies of formation of iron species considered in Fig. 1.

Species	ΔG , J/mole
Fe	0
Fe^{+2}	-9.22×10^4
$\text{Fe}(\text{OH})_2$ SOL	-4.93×10^5
Fe_3O_4	-1.02×10^6
Fe_2O_3	-7.42×10^5
FeOOH	-4.90×10^5
$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	-1.28×10^6

[12]. The pH and potentials for the various equilibrium models [11] are similar to the values calculated by McCafferty.

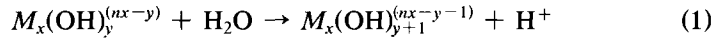
The conclusion from this calculation is the fact that the decrease in pH to $5(\pm 0.5)$ as measured in occluded cell arrangements for iron can be accounted for by the equilibrium between Fe^{+2} and the solids $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ or $\text{Fe}(\text{OH})_2$. The hydrolysis reaction of Fe^{+2} to FeOH^+ does not have to be invoked to account for the decrease in pH. Indeed, the decrease in pH being explainable completely by thermodynamics suggests an equilibrium limitation on the iron crevice corrosion propagation rate.

Few thermodynamic studies comparable to that of McCafferty have been made for the localized attack of alloys. One recent study is that of Taylor and Caramihas [13], who created an artificial crevice of Inconel 600 and took in-situ potential and pH measurements at elevated temperatures. They showed that crevice conditions measured at elevated temperatures and pressures agree with thermodynamic predictions arising from the limited data available. These conditions differ from the external environment. One finding has particular impact on in-situ measurements. Both the experiments and theoretical results suggest that the ionic behavior can be strongly dependent on the conditions under which the measurement is made. Once the crevice was removed from the autoclave and allowed to cool, the internal environment changed. This point is a graphic illustration of the need to do crevice corrosion monitoring in-situ and not rely totally on laboratory simulations.

Unfortunately, this type of combined theoretical and experimental study of crevice conditions has not been pursued for alloys in general. The thermodynamic calculations require a rather complex computer program similar to those now appearing [8] to account for all reactions, activities, and the charge balance. Often, the form of and thermodynamic data for some of the solid and ionic species, as for example the "polymeric" iron hydroxides or forms of iron oxyhydroxides [14,15,16], are either not known or are known only approximately. The forms of mixed metallic oxides that might exist are often not known. However, the following discussion shows that even with the above uncertainty, thermodynamics may be used to shed light on the mechanism

that creates the occluded cell. The understanding can aid in development of an approximate monitor.

The general hydrolysis reaction can be written as



The equilibrium constant can be written in terms of activity

$$K = \frac{[a_{M_x}(\text{OH})_{y+1}^{(nx-y-1)}][a_{\text{H}^+}]}{[a_{M_x}(\text{OH})_y^{(nx-y)}][a_{\text{H}_2\text{O}}]} \quad (2)$$

Taking negative logarithms results in

$$-\log_{10} K = \log_{10} \frac{[a_{M_x}(\text{OH})_y^{(nx-y)}][a_{\text{H}_2\text{O}}]}{[a_{M_x}(\text{OH})_{y+1}^{(nx-y-1)}]} - \log_{10}(a_{\text{H}^+}) \quad (3)$$

Except in those instances in which water is tightly bound to the solid, the activity of water even in saturated solutions tends to be no lower than about 0.4 [17,18]. Therefore, assuming $a_{\text{H}_2\text{O}} = 1$ and the activities of the two metallic species are equal, the pK of the hydrolysis reaction equals the pH of the solution. Table 2 shows a representative sampling of pK values for a number of hydrolysis reactions that might occur in crevices of iron-nickel-chromium alloys. A compendium of such constants is available [16]. A comparison of the measured pH to the pK values gives an indication of which hydrolysis reactions could be important.

Bogar and Fujii created artificial crevices of various iron-chromium alloys as well as 304 stainless steel [19]. They showed that the final pH depended on chromium content. The final pH dropped from about 4.7 to 2 as chromium composition increased. They attributed this pH dependence to the chromium

TABLE 2—*pK values of various commonly occurring hydrolysis reactions [16].*

Metal Ions	pK
$\text{Fe}^{+2}/\text{FeOH}^+$	9.5
$\text{Fe}^{+2}/\text{Fe}(\text{OH})_2$ (solid)	12.85
$\text{Fe}^{+3}/\text{Fe}(\text{OH})^{+2}$	2.19
$\text{Fe}(\text{OH})^{+2}/\text{Fe}(\text{OH})_2^+$	5.67
$\text{Fe}^{+3}/\text{FeOOH}$ (solid)	2.5
$\text{Ni}^{+2}/\text{NiOH}^+$	9.86
$\text{NiOH}^+/\text{Ni}(\text{OH})_2$ (dissolved)	10.8
$\text{Cr}^{+3}/\text{Cr}(\text{OH})^{+2}$	4.0
$\text{CrOH}^{+2}/\text{Cr}(\text{OH})_2^+$	9.7
$\text{Cr}(\text{OH})_2^+/\text{Cr}(\text{OH})_3$ (dissolved)	18.0

hydrolysis reaction becoming important. As shown in Table 2, the pK of the chromium hydrolysis reaction agrees with their analysis. As suggested by Suzuki et al [20], the effect of the activity coefficients would be to raise the hydrogen ion activity and lower the measured pH relative to that calculated by assuming ideality. Indeed, these workers found comparably lowered pH values in their synthetic crevices.

In addition, Suzuki et al discovered that activation of pure chromium and molybdenum yielded pH values similar to those found with 304ss and 316ss. These results are in substantial agreement with those of Lukomski and Bohnenkamp who also showed the similarity between the final pH in crevices of chromium and crevices of iron-chromium steels [21]. This similarity suggests that high concentrations of Cr(III) and possibly Mo(VI) in the crevice are the components that can lead to the low pH environment by a combination of their effect on activity coefficients, their hydrolysis constants, and any solid phases that are formed.

This discussion shows that the concept of the synthetic occluded cell with the lowered pH is consistent with the few thermodynamic calculations available. Thermodynamics supports the idea that the anode and cathode can be separated physically and the crevice can still initiate and propagate by an occluded cell mechanism. Thermodynamic results are not a function of path; they are only a function of the initial and final states. Thus, the thermodynamic constraints are independent of how the crevice is formed. Occluded cell corrosion resulting when the anode and cathode are physically attached can, in principle, be the same as that resulting when there is physical separation of the anode and cathode with completion of the electrical circuit by an external measuring device only. Thus, an occluded cell monitor using a separated anode and cathode connected through an "inert" measuring device should be able to simulate reality.

Factors Affecting Rate Processes in Occluded Cell Monitors

There are a number of models of both the initiation and propagation of crevices [3,22]. The starting point of this discussion of factors affecting the kinetic phenomena is with the acceptance of the fact that because of the physics of the processes of initiation and propagation, conditions within the occluded cell are altered from the bulk environment. The goal of the discussion is to describe the known physics in terms of criteria pertinent to designing an occluded cell monitor. By fulfilling these criteria, the monitor would be able to predict the propensity for a given alloy to undergo localized corrosion.

The main variables controllable by the monitor are the method of measurement and the crevice geometry. This latter variable, in turn, controls mass transport and can influence the crevice solution. Thus, the variables that must be considered are the gap depth, gap width, cathode-to-anode area ratio, number of crevices, and method of measurement. The numerical value given to each variable is set so that the crevice solution and kinetics model reality.

Gap Dimensions

Rosenfeld and Marshakov examined a number of the physical phenomena important to the crevice corrosion of iron, aluminum, and iron-chromium stainless steel [23, 24]. These workers systematically examined the variables of gap width, effect of connection between internal anode and external cathode, need for oxygen, effect of agitation, and potential response with time. These variables are important in appropriate design of an occluded cell monitor.

The width of the crevice plays a major role in the ability of the crevice to corrode. If the width is too small, a large internal resistance can be established, possibly because of solid corrosion product. Such resistance can decrease the amount of current for a given potential difference between internal anode and external cathode. If the width is too large, the differential aeration cell can be destroyed because oxygen will have easier access to the anode, decreasing the difference between its potential and that of the external cathode surface. Hence, an optimum crevice width exists.

The optimum width is most likely dependent on the external flow field, alloy, environment, and the length of the crevice. One particular finding of Rosenfeld and Marshakov supports the hypothesis of the effect of external flow field. Crevice widths of 0.005 to 0.025 cm seemed to offer more resistance to current in the absence of agitation than did wider clearances. This finding implies that when the crevice becomes too narrow, the resistance caused by solid product may become large enough to "shut down" the crevice. Widths greater than 0.05 cm seemed to result in less aggravation by agitation than did widths narrower than this dimension. The explanation given is that the narrower crevice hindered the diffusion of oxygen to a greater degree than the wider crevice [23]. The practical importance of this finding is the fact that the crevice width will most likely have to be known, adjustable, and measured with a micrometer. The adjustment is most likely a function of the alloy, the environment and possibly the flow conditions. Indeed, McCafferty has suggested that the critical crevice width beyond which width has no effect on retarding oxygen flow is approximately the external oxygen mass transfer boundary layer thickness, which is flow dependent [25].

That the relationship could be one of depth-to-width ratio, and not just of width, has been shown by the experimental studies of Beck for flow in a rectangular cavity [26] coupled with the more theoretical work of Pan and Acrivos [27], Antonini et al [28], and Ozawa [29]. The theoretical work covered laminar flow conditions while the experimental work covered both laminar and turbulent flow conditions. The prediction from these studies are shown in Figure 3. The ratio of the Sherwood number, defined as

$$\frac{(\text{mass transfer coefficient})(\text{width})}{(\text{diffusion coefficient})}$$

at the base of a cavity relative to the Sherwood number at the cavity surface decreases with an increasing quotient of depth divided by width in direction of

flow. Reynolds and Sherwood numbers are based on cavity width for large cavities. For small cavities, for example, crevices, the appropriate dimension for the Reynolds and Sherwood numbers is unclear.

The importance of Fig. 3 is as follows. The Sherwood number ratio shown could be used to estimate the rate of oxygen mass transport through the crevice to the base. The wider the crevice, the deeper is the point at which oxygen is depleted. Once this point reaches the base of the crevice, the crevice should become "oxidized" and the occluded cell corrosion should cease [5]. Note that in turbulent flow the ratio decreases very gradually, suggesting the need for a very large depth-to-width ratio. Turbulent flow is normally encountered in chemical process equipment.

The decrease in the Sherwood number ratio with increasing Reynolds number does not mean that the Sherwood number actually decreases. As the Reynolds number increases, the Sherwood number (mass transfer coefficient) at the cavity base does not increase as rapidly as the Sherwood number (mass transfer coefficient) at the surface. The difference becomes greater, the greater the depth-to-width ratio.

The mechanism of crevice corrosion would most likely involve differential aeration, for example, depletion of oxygen in the crevice [30]. Thus, for crevice corrosion to exist, the point of oxygen depletion must occur in front of the crevice base. Judging from the gradual slope of the turbulent flow curve in Fig. 3, a required ratio of between 10 and 100 may not be unreasonable for turbulent conditions. The need to be able to adjust the depth-to-width ratio

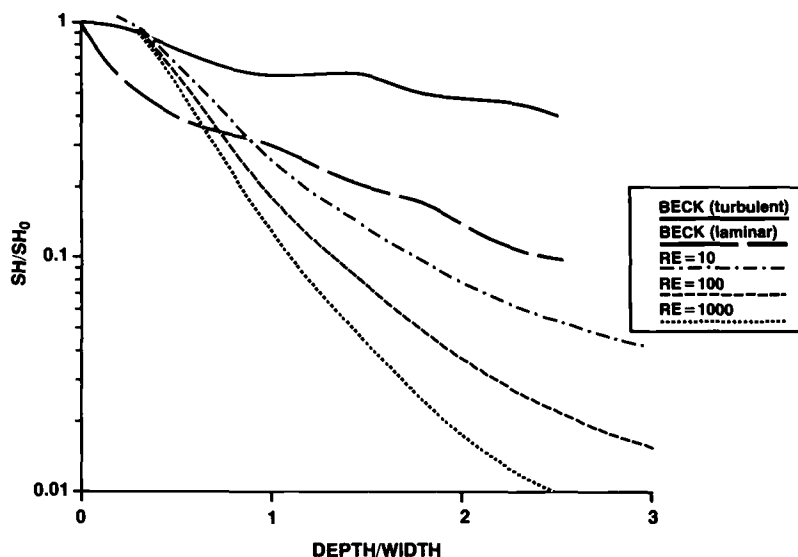


FIG. 3—Relationship between Sherwood number at base of crevice and Sherwood number at surface [26,28].

even in the absence of external flow is supported by the combined experimental and theoretical work of Alkire et al [31].

The main point of this discussion is the fact that the crevice used in an occluded cell monitor should have adjustable and reproducible depths and widths with the ratio of depth-to-width being much greater than one. Using the 0.03- to 0.05-cm width derived from the Rosenfeld and Marshakov data to be a breakpoint below which oxygen depletion is found results in a crevice depth of about 0.5 to 2.5 cm for carbon steel. Further work is required to define the appropriate width and depth-to-width ratio for other alloys.

Anode-Cathode Potential Difference—IR Drop Consideration

Current is carried by ions within a crevice. The narrowness of the crevice combined with the possibility of solid product decreasing the cross-sectional area still further, can create voltage drops within the crevice. As suggested by the results of Karlberg and Wranglen [32], Rosenfeld and Marshakov [23,24], and McCafferty [11,25], the final voltage difference between internal anode surface and external cathode surface could be in the range of 50 to 150 mV with a drift to 8 to 10 mV after several days. These results suggest that very small potential differences can support crevice corrosion.

Though the potentials developed between anode and cathode can be small, current densities could be rather large, depending on the resistances established by the alloy and environment. The best measuring device would be a zero resistance ammeter which will maintain zero voltage drop through the external circuit between the anode and cathode. The circuit could contain a battery, or preferably an operational amplifier [2,34,35] or potentiostat [36].

Cathode-to-Anode Area Ratio

The ratio of the areas of the cathode (external surface) and anode (crevice) for a differential aeration cell can have a profound effect on the rate of propagation of crevice attack. In terms of the differential aeration model of crevice corrosion, the area ratio should affect the time to initiation after the cathodic oxygen reduction rate within the crevice falls to zero and the external cathodic reaction begins to drive any anodic dissolution reactions. Assuming that the propagation reaction is limited by the rate of oxygen diffusion to the cathode, the effect of area ratio on crevice corrosion can be depicted as shown in Fig. 4 [1]. As the cathode area increases, the cathodic current increases. The point of intersection of the anodic and cathodic curves moves to higher currents. The corrosion current increases. Since the anodic current is created by active corrosion, the crevice solution potential increases and the polarization of the crevice increases.

As an example of the effect of area ratio on anode potential, assume that the material is carbon steel and the cathode is the wall of a pipe for which the

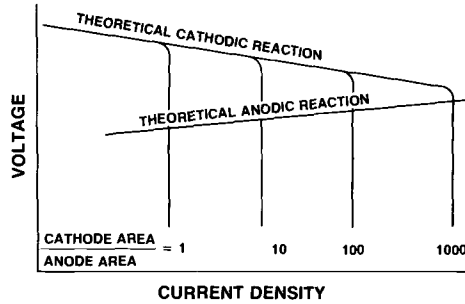


FIG. 4—Effect of cathode-to-anode surface area ratio on limiting cathodic current.

mass transfer coefficient can be calculated from the Reynolds number. The rate expression can be taken from Turnbull and Thomas [37], who note that over a broad pH range the rate seems to be independent of hydrogen ion concentration. No dependence on chloride ion concentration is assumed to be present. The equation is

$$r = k_a(A_{\text{anode}})\exp\left(\frac{\alpha FV}{RT}\right) \quad (4)$$

The cathodic reaction is mass transfer limited and can be written as

$$r = k_{\text{MT}}A_{\text{cath}}(C_{\text{bulk}}^{\text{O}_2} - C_{\text{surf}}^{\text{O}_2}) \quad (5)$$

Assuming that

$$C_{\text{surf}}^{\text{O}_2} = 0$$

and that the mass transfer coefficient can be calculated from the Harriott and Hamilton [38] relationship

$$\text{Sh} = 0.0096 \text{ Re}^{0.913} \text{Sc}^{0.346} \quad (6)$$

the point of intersection of Eqs 4 and 5 can be calculated as a function of area ratio and Reynolds number. Equations 4 and 5 can be equated to give the corrosion potential as a function of the cathode to anode area ratio. The relationship has the form

$$V = (B)\ln\left(\frac{A_{\text{cath}}}{A_{\text{anode}}}\right) - V^\circ \quad (7)$$

In Eq 7, V° is the potential at equal areas of the cathode and anode. It will be a function of all of the other variables in Eqs 4 and 5, so it is not a constant.

The maximum crevice corrosion rate can be estimated by substituting this potential into Eq 4. Table 3 shows the properties used to calculate B and V° . For this calculation, a Schmidt number of 1000 is assumed to represent water. Figure 5 shows the effect of Reynolds number and of increasing cathode-to-anode area ratio on corrosion potential.

The corrosion potential becomes more positive with increasing Reynolds number in agreement with the fact that the rate of mass transfer of oxygen increases with flow rate (Reynolds number) [39]. More importantly, as the cathode-to-anode area ratio increases, the corrosion potential also increases in agreement with Fig. 4. As shown by Mansfeld [40], this dependence is a monotonically increasing function of cathode-to-anode area ratio as long as

TABLE 3—Physical properties for Eqs 4, 5, and 6.

Property	Value
Rate constant (k), A/m ²	2×10^{11}
Tafel parameter (α), equiv/mole	1
Temperature (T), K	298
Kinematic viscosity (ν), m ² /s	1×10^{-6}
Diffusion coefficient (D), m ² /s	2×10^{-9}

CORROSION POTENTIAL DEPENDENCE ON FLOW AND GEOMETRY

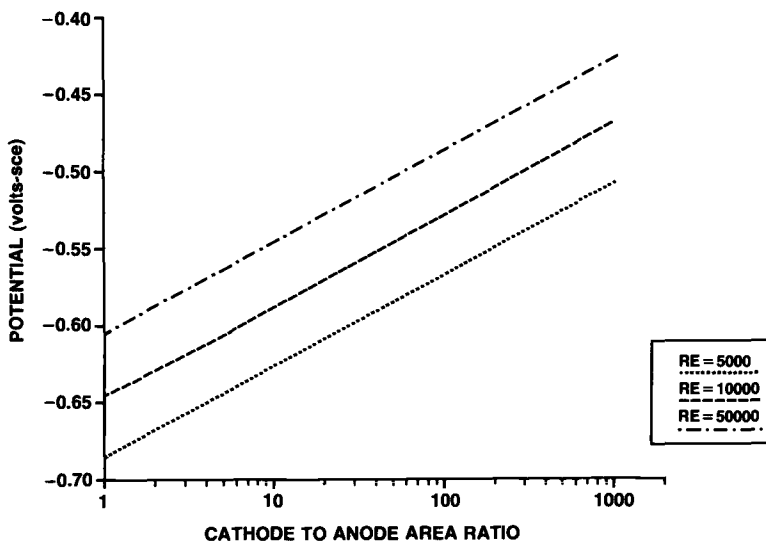


FIG. 5—Estimated corrosion potential of iron in a crevice as a function of cathode-to-anode surface area ratio and Reynolds number.

Eq 4 is obeyed. If a precipitate forms, for example, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ [5] or $\text{Fe}(\text{OH})_2$ [23], the corrosion rate may become limited by the rate of diffusion of material out of the crevice. Equation 4 no longer governs the anodic reaction. This behavior would explain the current peak that occurs shortly after coupling anode to cathode [33,41].

The area ratio most likely must be greater than one [41]. Whether a 10 to 1 or 100 to 1 ratio is appropriate cannot be stated at present. The ratio may even depend on the alloy and environment. Mathematical modeling efforts will shed light on this subject. One point that can be made is that the cathode should be mounted so as to create defined hydrodynamics. One way is to orient it parallel to the flow stream so that a flat plate is created. In this way, knowledge of the flow rate leads to knowledge of the rate of oxygen mass transfer. Then a relationship could, in principle, be derived between flow rate and crevice attack in the environment.

Mathematical Modeling of Crevices

One aspect of the overall design not yet discussed is the fact that if the occluded cell monitor can be designed so the results can be interfaced with a mathematical model, the usefulness of the monitor can be greatly enhanced. Such coupling could aid in making the monitor a predictive tool with respect to the given alloy and environment.

Several workers have created very simple models of crevice attack or pitting in the limit of no external flow [31,42-44]. One of the more successful attempts to model the initiation and propagation of crevice corrosion is that of Oldfield and Sutton [5]. This model has been used in conjunction with various experimental inputs to quantify the initiation and propagation stages of crevice corrosion of iron-nickel-chromium-molybdenum alloys in seawater [45,46]. This work is one of the few attempts to combine a mathematical model with experimentation to predict all phases of the crevice corrosion mechanism. In addition, Bernhardsson et al have attempted to build a somewhat more fundamental model for iron-nickel-chromium-molybdenum alloys in seawater [47]. Turnbull and coworkers have taken an even more fundamental approach and have attempted to use the complete, coupled, non-linear, fundamental reaction, migration and diffusion equations to predict the steady state profiles in an iron crack under stress [48,49]. Because the equations are fundamental, the work is applicable to crevices.

Geometry of the crevice monitor should be chosen with an eye toward possible use with a mathematical model. The easiest coordinate systems upon which to build a model are Cartesian and cylindrical coordinates. Thus the shape of the crevice should be a rectangular parallelepiped, a right circular cylinder, or a disk. The shape should be dictated by ease of fabrication.

Alternative Devices

Laboratory Monitors

A large assortment of artificial crevice geometries has been reported [3,4]. Two types of laboratory devices have appeared. The first type of device is the double cell in which separate electrodes are placed in each compartment. A frit placed between compartments is used to restrict mass transport. This type of device has been used by Verink [50]. Although it allows for introduction of measuring electrodes and removal of solution, this type of device is far too cumbersome for in-plant use.

The second type of device is the artificial crevice constructed so as to create restricted mass transport by close proximity of the walls of the crevice. Many geometries have been reported. Only those that provide guidance for an in-plant monitor are discussed here. As mentioned previously, McCafferty used an artificial crevice with an adjustable crevice width [25]. The adjustment is one of crevice width, not depth, because one side of the crevice, not the end or base, is movable. Most of the laboratory devices reported have this same characteristic. For example, Bates [51] used a rubber stopper with wick to complete the circuit as one side of a crevice. The specimen formed the opposite side. Lizlovs created an adjustable crevice width by attaching the working electrode to a bolt which would move the working electrode close to a copper counter-electrode [52].

Similar types of arrangements were used by Ulanovskii [53,54]. Hebert and Alkire [55] made one major modification. They used the fine focus micrometer on a microscope lens mount to adjust the distance between a working electrode and the bottom surface of a plexiglass cylinder. The anode was disk-shaped. In this way, a reproducible yet adjustable crevice width was achieved. The importance of this technique is the fact that by being able to reproduce dimensions, the experimenters could tie their results to a mathematical model.

Several other unique modifications of laboratory crevices have been reported and should be mentioned. Suzuki et al have proposed use of an anionic selective membrane [56,57] to cover the alloy being tested. The objective is to accelerate the accumulation of cations arising from the anodic reaction while allowing for the passage of chloride ions through the membrane. In addition, the membrane could, in principle, help to circumvent the velocity effects shown in Fig. 3. However, there are drawbacks to the technique. One anion selective membrane may not show comparable selectivity to different anions. For example, Vicentini et al examined the crevice attack of titanium in sulfuric acid [58]. If the need arose to monitor for this type of corrosion in the plant, the anion selective membrane would have to be selective to SO_4^{-2} ions. Often the appropriate anion is not known. Until there is more experience with

the membrane technique, a deep, narrow crevice would still be more appropriate for a general in-plant monitor than an alloy plate covered with an anion selective membrane.

One capability that all laboratory crevices have is an ability to measure potential as well as current. McCafferty [25] demonstrated that a bare chloridized silver wire could be used as a pseudo-reference electrode. The solution could be extracted and then the potential could be measured relative to a silver chloride reference electrode contacting 4M or saturated KCl. The point is that providing for measurement of both the external and internal corrosion potentials could greatly enhance the capabilities of the monitor. The measurement of a potential difference would serve as an additional check for crevice corrosion.

In-Plant Monitors

Construction and testing of an in-plant corrosion monitor for crevice corrosion has begun only recently. In a recent patent, Isaacs and Weeks [59] show a device that is claimed to be capable of monitoring the corrosion of surfaces of a crevice. The device seems to be of limited usefulness for a general purpose in-plant monitor.

The geometry is specific to steam generators. There is no guarantee that the conical shape is applicable to process streams. As no predictive model is available, the relationship between this and other geometries is unclear. Finally, the conical shape has a depth-to-width ratio that varies with distance. In this design, care must be taken that fluid flow does not flush the crevice contents.

Another recently reported crevice monitor is that discussed by Diegle [60]. The device was designed to incorporate real-time measurement of corrosion rate, an ability to accelerate initiation, capability of monitoring corrosion potential, and ruggedness. The ultimate design had a separate container for the reference electrode, which was connected to the crevice cell through a bridge arrangement. The results were promising in terms of duplicating a separate "standard" crevice immersed in the same environment. However, there are several serious drawbacks to this design.

The use of an external compartment for the reference electrode is unwieldy. Since the ability to measure potential is desirable, use of an internal reference electrode or a chloridized silver wire seems to be more appropriate. Unfortunately, most high-temperature/high-pressure reference electrodes are experimental [61]. The ones that are available commercially have about a 125°C, 150-psig limit ($\sim 10^6$ Pa) [62, 63]. Therefore, the concept of using a silver chloride (or sulfide) wire would be a viable alternative, and such an electrode is easy to make. It is a stable electrode [64]. Its use would require one extra external measurement of the potential between the wire and a real reference electrode in a sample of the solution at the temperature of the process. Since the potential of an Ag/AgCl reference electrode is relatively insensitive to

pressure to several hundred atmospheres [61], the measurement can be made at atmospheric pressure as long as the temperature is not above the fluid boiling point.

The formation of the crevice by pressing the alloy against polytetrafluoroethylene (PTFE) [60] cannot give reproducible dimensions. Knowledge of the crevice width is very important, and a large depth-to-width ratio must be achievable. However, there is no way to determine the crevice width in the Diegle design [60]. Thus, there is no way to compare results with a mathematical model and to make predictions about other crevice geometries.

The annular geometry is not necessarily inappropriate as demonstrated by Hebert and Alkire [43]. No information was given about the cathode-to-anode area ratio. From the diagram given, if it is drawn to scale, the cathode-to-anode area ratio is about 8 to 1 when account is taken of all exposed surfaces. As discussed previously, this ratio may be adequate for the monitor. A slightly larger ratio might be more appropriate.

Conceptual Design of Improved Monitor

The improved occluded cell monitor should build on that reported by Diegle [60]. The main improvements are better defined crevice dimensions of appropriate depth-to-width ratio, an appropriately oriented cathode, an in-situ reference electrode, most likely a silver chloride (or sulfide) wire, and a more compact device. The entire assembly should be able to fit through a blind flange for incorporation in a chemical process. The concept is shown in Fig. 6.

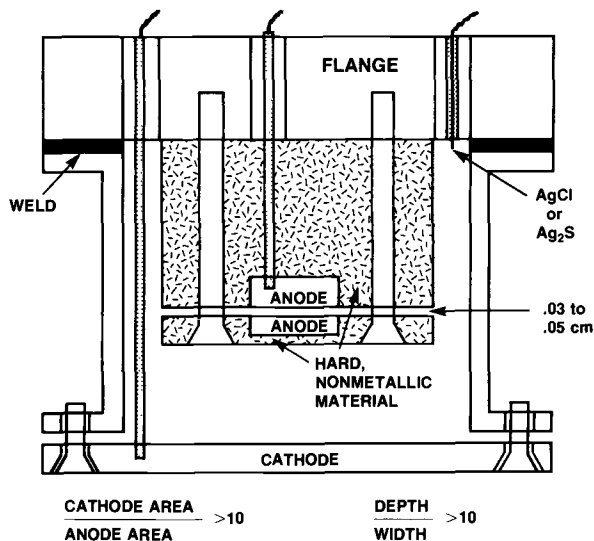


FIG. 6—Concept of in-plant occluded cell corrosion monitor.

To fulfill the need for a known, narrow width of less than about 0.05cm, the setting must be made with a micrometer or against a thin, nonmetallic material of known thickness. There are two ways for this setting to be made. The crevice width could be set and locked in place prior to immersion. Or, the crevice width could be set once the monitor is in place. The latter procedure offers the most versatility, especially in those cases in which the optimum crevice width is unknown. However, design and construction would be formidable. Thus, the first method is probably the most feasible. Once the width setting is made, the crevice would be secured. Such a reproducible system would allow comparison to be made between alloys and predictions to be made of the effect of tightness.

In order to utilize models, the geometry should be simple. A disk like that reported by Hebert and Alkire [55], a right circular cylinder as shown by Alkire et al [31], or a rectangular parallelepiped are the optimum geometries. The disk would most likely be the easiest geometry to machine. The positioning of one disk close to another and against a nonmetallic spacer would probably offer the least complex method of insuring a constant average crevice width. Note that imperfections in the surface finish could cause point-to-point variations in width. The crevice itself could be "dead ended" on one side. Also, the anode could be placed in the neck of a nozzle so that it is out of the flow stream.

A silver chloride (or sulfide) wire could be mounted so as to contact the bulk fluid for the measurement of potential. Note that measurement of potential is not necessarily essential for the monitor. A silver chloride wire might even be placed within the crevice as a microelectrode to measure chloride concentration if chloride is the expected anion [65]. The voltage response of the wire in the bulk solution could be measured against a silver/silver chloride (Ag/AgCl) reference electrode in a separate, external experiment so that all potentials are placed on a conventional scale. One possible shortcoming is that the voltage response could vary somewhat if the process is subject to wide swings in temperature, pH, or ionic concentration. Another drawback of the silver chloride wire is its possible brittleness [64]. Precautions would have to be taken that it is screened appropriately from high fluid velocities or particulates in the process stream. The cathode can be oriented so it acts like a flat plate, the hydrodynamics of which are well-known.

The design in Fig. 6 incorporates the changes discussed here. The design is not meant to be a final working model, but is meant to show how the improvements might appear. A disk-shaped crevice has been chosen for simplicity. The entire crevice assembly can be bolted into a flange with the crevice being formed by narrow, removable spacers of appropriate thickness. The entire assembly can be mounted so that the cathode can lie in the free stream. Obviously, experimentation with the design will be necessary, especially of the mounting of the anode within the nonmetallic insulating spacer to prevent unwanted additional crevices.

Conclusions

1. The concept of a practical, useful on-line monitor for occluded cell corrosion is soundly supported by thermodynamics and kinetics.
2. Thermodynamic arguments for iron suggest that equilibria between solid phases and Fe^{+2} and activity coefficients can account for the depressed pH found in crevices of iron.
3. Among the variables that are important to the monitoring system are crevice dimensions, cathode-to-anode area ratio, and defined hydrodynamics on the cathode.
4. A practical occluded cell corrosion monitor should have provision to allow these critical variables to be changed so that the monitor can be optimized for a specific application. A conceptual model has been presented here.

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Summary of Electrochemical Methods

An excellent overview of electrochemical methods of monitoring corrosion is presented in the paper written by Dean, which covers topics such as polarization resistance, stress corrosion cracking, localized corrosion, polarization diagrams, hydrogen probes, AC impedance, and occluded cell corrosion. The importance of employing redundancy in corrosion monitoring is emphasized. For example, time average devices such as polarization resistance and electrical resistance devices can be used to supplement instantaneous corrosion rate measuring devices to assure the reliability of these instantaneous measurements.

More specific techniques for monitoring corrosion, such as hydrogen monitoring and electrical resistance methods, are presented in the papers written by Yamakawa and Cooper. Yamakawa claims that his new hydrogen probe, in which a thin nickel layer was deposited at the extraction side, improves the detection limits for hydrogen monitoring. Cooper summarizes the uses of electrical resistance and electrochemical methods of monitoring corrosion. The major advantage of electrical resistance probes over electrochemical probes is that electrical resistance probes can be used to monitor corrosion in fluids having very low conductivity such as refinery process fluids, oil production fluids, and boiler condensate. The major disadvantage in the use of electrical resistance probes is that corrosion rate information is not as easily obtained. The first three papers should be read in detail before proceeding to the next series of papers.

Specific applications of the use of electrochemical techniques (such as linear polarization and potentiodynamic polarization) for monitoring corrosion and corrosion inhibition are presented in the second grouping of technical papers. Cameron discusses the optimization of oil production corrosion inhibitor programs using electrochemical techniques. Monitoring corrosion in pulp and paper applications in Kraft white liquors is discussed by Yeske in his paper. Labine presents methods of monitoring corrosion inhibitor performance in cooling water applications using linear and potentiodynamic polarization techniques. It should be emphasized the potentiodynamic polarization techniques are especially useful in measuring pitting corrosion rates in oil field, pulp and paper, and cooling water applications. Equipment lifetime may be reduced to one-tenth or less of the time predicted by the general or uniform corrosion rate caused by high pitting corrosion rates.

Liening presents several case histories in which simple electrochemical techniques have provided adequate data to suggest options for temporarily solving emergency corrosion problems until more permanent solutions can be implemented.

Although the use of electrochemical techniques in monitoring corrosion in utility boilers is quite limited because of the low conductivity of the water and the high temperatures, Ronchetti discusses electrochemical techniques for monitoring corrosion in steam condensers and circuits in power plants. Gabrieli and Mohn have taken a different approach and discuss the use of metallurgical techniques and visual examinations of tube samples, from the high heat flux areas of the waterwalls of utility boilers, for hydrogen damage and caustic gouging. Piron's paper illustrates that simple coupon techniques can be used to study the corrosion of cast iron and copper pipe in potable water applications.

Laboratory methods used to minimize field problems are discussed in the third series of papers. Kellner discusses the use of computer controlled AC impedance measurements for the determination of water penetration of anti-corrosion coatings. Hoey and coworkers present the use of potentiostatically controlled slow strain rate tension tests to study the potential dependence of stress corrosion cracking of high-strength low-alloy (HSLA) line pipe steel. Vijayan and coworkers studied the influence of lithium hydroxide additions on the corrosion of carbon steel A516 in concentrated sodium hydroxide solutions using potentiodynamic and potentiostatic polarization techniques. Tuovinen and Cragolino discuss the use of microbiological and electrochemical techniques in the study of corrosion induced by sulfate reducing bacteria. The location of the electrodes may be crucial in detecting microbiologically induced corrosion in the laboratory. Although McKubre and Syrett have used harmonic impedance spectroscopy to monitor the corrosion of cathodically protected cupronickel alloys in the laboratory, further refinements of the techniques are required to optimize the instrument's sensitivity. In addition, the technique of using electrochemical noise in detecting anaerobic corrosion, discussed by Iverson, will also require more improvements.

In the future, in-plant monitoring of occluded cell corrosion should be possible based on the paper written by Silverman and Krisher. A conceptual model of this proposed occluded cell corrosion monitor is presented in their paper. The importance of crevice dimensions, cathode to anode ratios and hydrodynamics at the cathode are discussed by the authors. When this monitor becomes commercially available, premature and unexpected equipment failures caused by occluded cell corrosion should be minimized.

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