

CORROSION INHIBITOR SCREENING USING RAPID RESPONSE CORROSION MONITORING

Timothy H. Bieri
BP Exploration (Alaska), Inc.
CIC Group
900 East Benson Blvd.
Anchorage, AK 99519

David Horsup, Ph.D.
Nalco Company – Energy Services Division
7705 Highway 90-A
Sugar Land, TX 77478

Melvyn Reading
Rohrback Cosasco Systems, Inc.
11841 E Smith Avenue
Santa Fe Springs, CA 90670

Richard C. Woollam
BP America, Inc.
501 Westlake Park Blvd.
WL 18.118
Houston, TX 77079

ABSTRACT

The continuous improvement process for corrosion inhibitor development requires an active program of testing new and/or novel chemistries. The original process for field testing prospective corrosion inhibitors required 36 days for each different product and utilized standard electrical resistance probe monitoring to determine inhibitor performance. The new process utilizes enhanced electrical resistance monitoring that allows the same testing to occur in four days, while providing higher quality data. The net benefits of the new process include shortened test times, increased number of inhibitors evaluated, reduced test inhibitor volume and an increase in data quality and quantity. These benefits together, have increased the probability of identifying corrosion inhibitors that offer significant cost-performance improvements.

Keywords: corrosion inhibitor, enhanced electrical resistance, corrosion monitoring

INTRODUCTION

Background

Control of corrosion in oil and gas production pipelines is frequently achieved through the use of corrosion resistant alloys. These, however, add significantly to capital costs and alternative corrosion prevention strategies are often considered. In many cases the most cost-effective option is the use of low carbon steel with a corrosion inhibition program.

The significant increase in the global demand for oil and gas has driven the industry to pursue production from fields previously uncharted. These may be located in deep water (3,000 - 6,000') or even ultra deep water (6,000 - 10,000'), and many of these are situated in environmentally sensitive

regions. Associated with these challenging environments are extremely aggressive corrosive conditions caused by elevated temperatures and pressures, challenging water chemistries and often high shear conditions. It is, therefore, imperative that a corrosion inhibition program is capable of providing effective corrosion control under the most aggressive conditions.

CORROSION INHIBITOR DEVELOPMENT

In order to address some of the extremely challenging conditions experienced at Prudhoe Bay, Alaska, an extensive inhibitor synthesis effort has been undertaken to identify novel corrosion inhibitor actives that exhibit a step-change in performance over conventional chemistries. Annually, it is not unusual to have synthesized several hundred new potential corrosion inhibitor molecules in a quest for more cost-effective formulations. In order to assess the performance of such a large number of potential corrosion inhibitors, a fast, reproducible laboratory test is required. This is achieved through the use of a wheel test^{1,2}. This weight-loss technique is run under the standard conditions described in Table 1.

Table 1 - Standard Conditions

Variable	Value
Temperature	176 °F (80 C)
Pressure	14 psi (96 kPa) CO ₂
Oil	LVT 200 deodorized kerosene
Water	Synthetic Prudhoe Bay
Water : Oil ratio	90:10
Agitation	26 RPM
Coupon metallurgy	1018 carbon steel, sand-blasted
Inhibitor dosage	0, 5, 10, 25, 50 ppm
Duration	24 hours

Each new molecule is evaluated in triplicate over a range of dosage and the performance is compared to that of a reference corrosion inhibitor. An example of the performance profiles obtained for different corrosion inhibitor molecules is given in Figure 1.

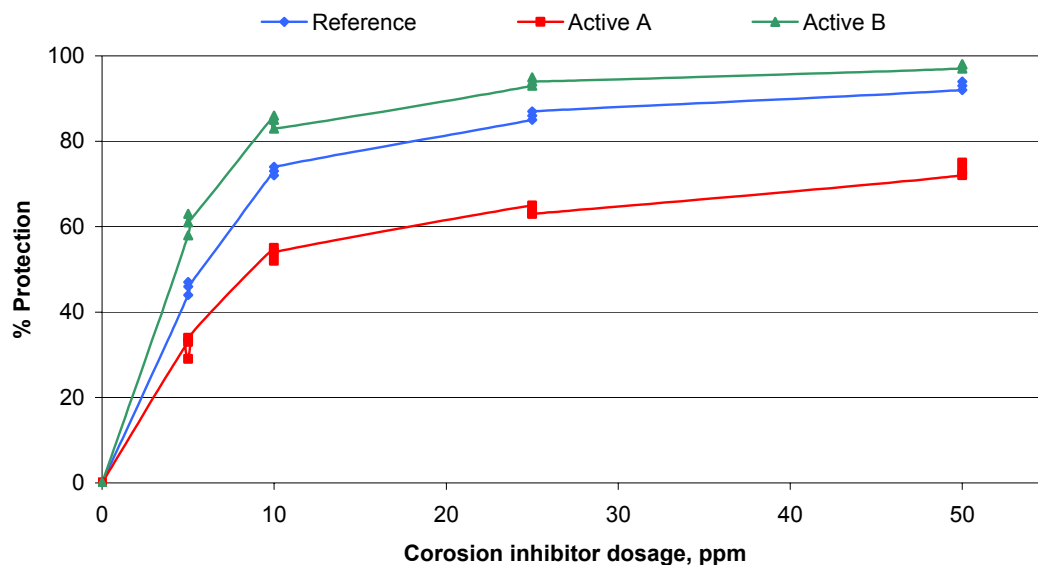


Figure 1 - Corrosion Inhibitor Performance Profile

Only those new actives that exhibit a cost-performance equivalent, or superior, to that of the reference material are promoted for further evaluation (e.g. Active B).

One of the greatest challenges faced by chemical service companies is to be able to conduct laboratory tests that provide the same relative order of product performance that is observed in the field. Typically, a corrosion inhibitor has to effectively treat a pipeline system that may be operated over a range of conditions, e.g. various flow regimes, oil-water ratios, differences in the nature of the pipeline surface etc. For these reasons it is not possible to develop a single test that simulates field conditions in the laboratory. In order to assess the performance of an inhibitor for field use, it is therefore necessary to perform a series of laboratory tests, each of which evaluates a specific performance attribute for an inhibitor. A typical example of the process is shown in Figure 2. This is depicted as a continuous process since knowledge gained at each stage in the development cycle provides molecular structure-activity information that is used in the synthesis of future corrosion inhibitor actives.



Figure 2 - Corrosion Inhibitor Development Process

The performance of the product is then evaluated under static conditions in the bubble test. This investigates how effective the product is at partitioning from an oil phase into brine, a key requirement for inhibition in low flow, and dead-leg locations. Effective formulations are then progressed to the next round of testing.

Inhibition under high shear conditions is a critical requirement for the Prudhoe Bay asset. In order to assess this, two techniques are used. The first, jet impingement, can investigate an inhibitor's performance at shear stresses up to 1,500 Pa^{3,4}. This technique can be operated in a once-through configuration to investigate the persistency of the inhibitor film on the metal surface. This simulates the condition when the injection of the inhibitor is interrupted, and can provide an indication of how long the inhibitor film remains protective. The second high shear technique is the flow loop⁵. This is a long-term test that can evaluate inhibitor performance at various shear stresses depending upon the probe configurations and fluid velocity.

Since corrosion inhibitors are surface active agents, they have a tendency to promote emulsification and foaming⁶. These so called 'secondary properties' of an inhibitor formulation are best evaluated in the field in 'bottle tests'. At this stage, the compatibility of the new formulation with materials encountered in the injection system and the performance compatibility with other production chemicals is also investigated.

Field Testing

Formulations that successfully pass all these performance hurdles are subsequently manufactured in the pilot plant and evaluated in the field in a short-term test. This field evaluation requires approximately 36 days (Figure 3) and performance is determined using standard electrical resistance probes. The products that exhibit a cost-performance superior to the incumbent formulation are subsequently commercialized and expanded to a facility-wide test.

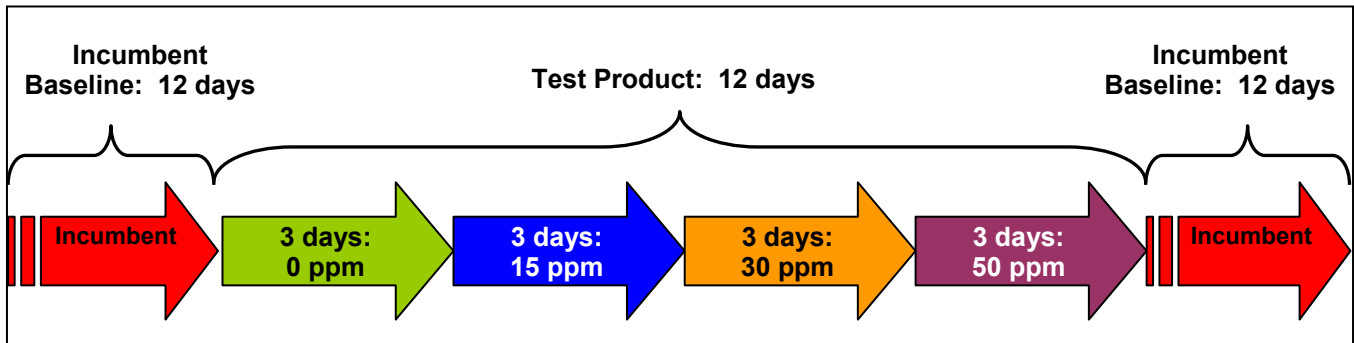


Figure 3 - Standard Test Duration

This detailed process is designed to qualify an inhibitor formulation for field application. Unfortunately, due to the extensive nature of the process, it takes a significant amount of time to promote a new inhibitor from the lab to field-wide application. Typically, each year only 8-10 new formulations would make it through the laboratory qualification process and get evaluated in the field. With the hundreds of potential new inhibitor actives that are being developed, this significantly increases the time to market for a potential step-change formulation.

ENHANCED ELECTRICAL RESISTANCE CORROSION MONITORING:

In order to reduce the time required for field testing and increase the data available for performance evaluation, a more sensitive corrosion rate monitoring technique needed to be utilized. After reviewing available technologies, enhanced electrical resistance monitoring was selected.

The electrical resistance monitoring technique is well suited to the on-line monitoring of corrosion in mixed phase, and predominantly non-conducting environments. A sensing element of known, and regular, geometry manufactured in the alloy of construction of the pipe, or vessel, of interest, is inserted into the process. The increase of the electrical resistance of the sensor is measured, as its cross-section is reduced by corrosion. This translates into a metal thickness loss and, by reference to time, into a corrosion rate. The basis of the technique can be seen in Figure 4.

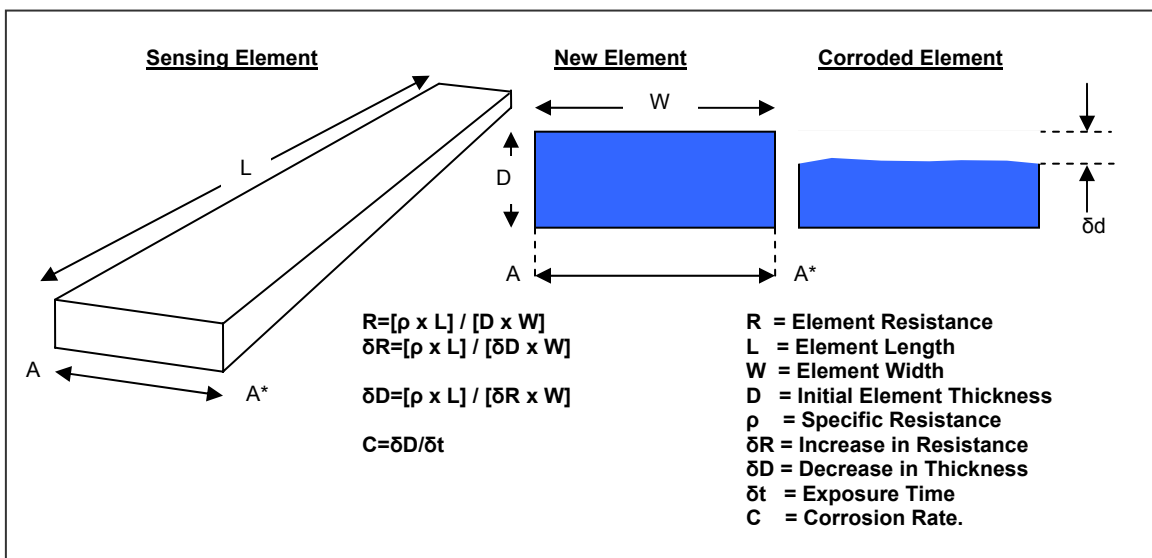


Figure 4 - Basic Principle of Electrical Resistance Monitoring

In order to avoid interference from the impact of temperature on resistance, practical measurements are made as a resistance ratio between a freely corroding sensing element, and a non-corroding reference element as illustrated in Figure 5.

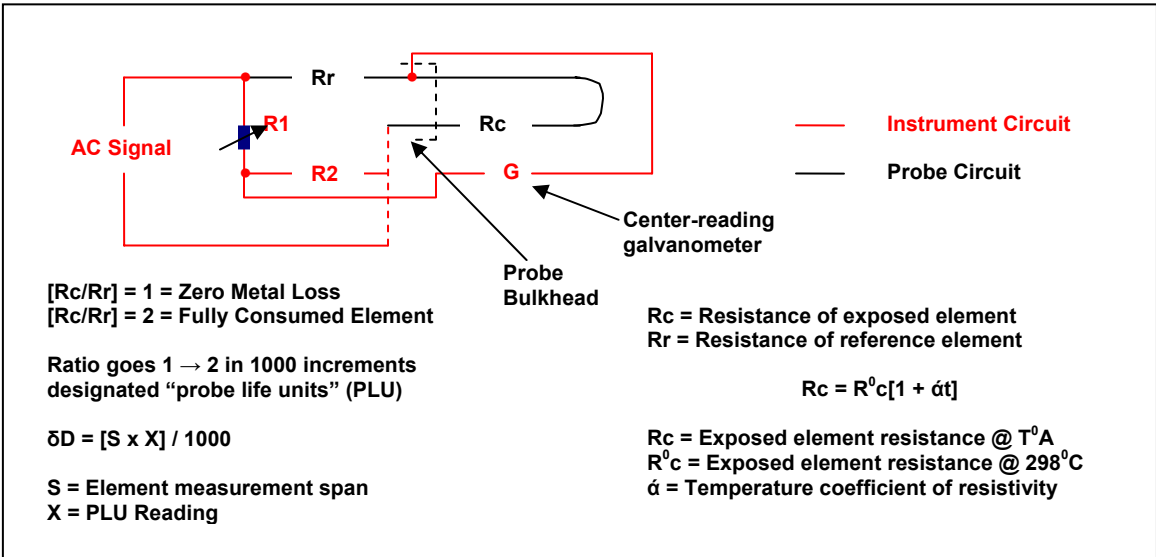


Figure 5 - Principle of Temperature Compensation

The resistance of both the reference element and the corroding element are equally affected by temperature. Consequently, any change in the resistance ratio is attributable to metal loss from the corroding element.

The time required to measure a given change in corrosion rate is a function of the smallest change in metal thickness that can be measured by the technique, and is given by:

$$T = \frac{S \cdot N \cdot 365}{(I_r \cdot C)} \tag{1}$$

Where:

- T = Time required for a measurable change in element thickness (response time), days
- S = Element measurement thickness (measurement span), mils
- N = Noise factors, uncertainty in measure value
- I_r = Instrument resolution
- C = Prevailing corrosion rate, mpy

So, the response time can be decreased by decreasing the element measurement span. However, in practical environments, the mechanical integrity of sensors cannot be ensured with element thicknesses of less than approximately 5 mils. Elements of this thickness are commonly in use and, further improvement in response time by producing yet thinner elements is unlikely, and impractical.

In principle, increases in instrument resolution could be used to improve response time. However resolution cannot be considered in isolation. Increases in instrument resolution will produce no

significant reduction in response time, unless corresponding reductions in noise factors are simultaneously achieved.

Under present circumstances, the largest single noise source results from readings taken at times when the corroding element and reference elements are not at the same temperature, such as may happen just after a process temperature change. The magnitude of such noise is difficult to estimate, since it is a function of frequency, and extent, of system temperature changes, and is also a function of specific sensor design. However, a modest temperature difference of 1°C, with a carbon steel sensor ($\alpha \approx 0.004 \text{ } ^\circ\text{C}^{-1}$), produces an uncertainty of 1:250, at the conventional resolution of 1:1000. It is not uncommon, using conventional instrument/sensor design to see a noise band of 1:250, superimposed on the 1:1000 instrument resolution. Consequently without reducing the inherent noise sources in the system design, increases in instrument resolution would do little to improve response time.

The response times for a 5 mil (13 mm) element, at various corrosion rates, is shown in Figure 6. Within the range of most commonly experienced corrosion rates (1-30 mpy) response times will range from 6-175 hours, even with a probe span as small as 5 mils (13 mm). These numbers are somewhat optimistic, in the sense that several data points are required to establish a slope, and hence a rate, with reasonable accuracy and, even with the inclusion of a noise factor allowance of 1:250, these estimates should be doubled to give practical response times ranging from 12-350 hours.

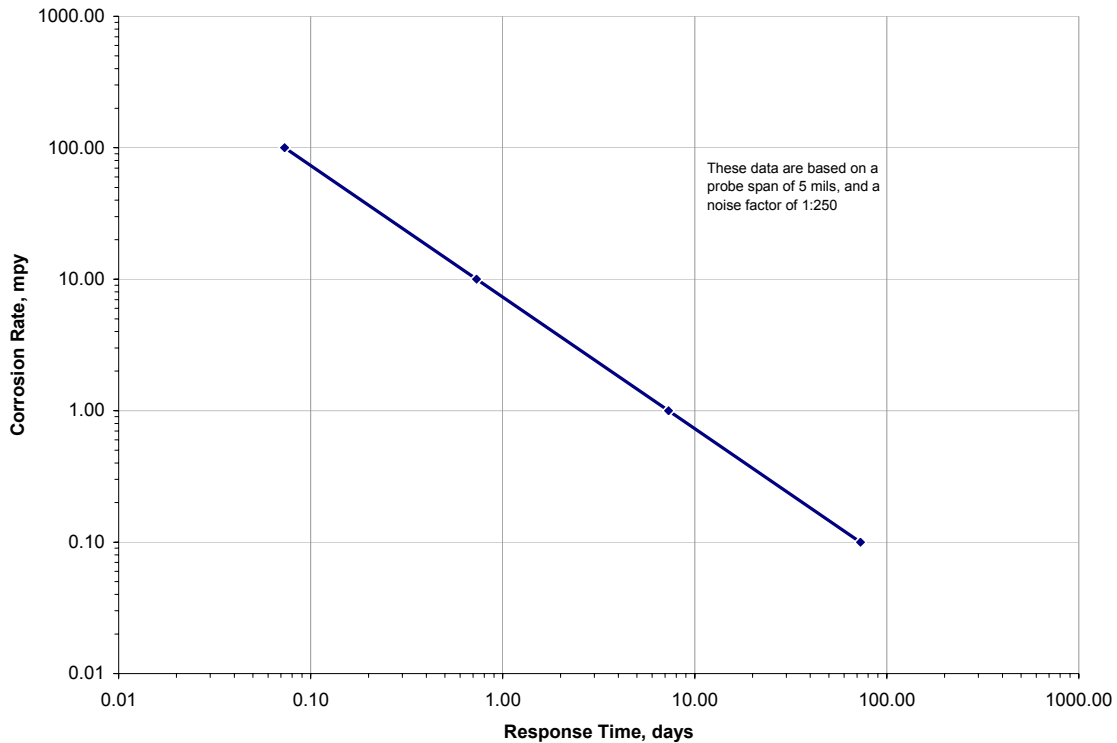


Figure 6 - Response Time vs. Corrosion Rate

A further practical consideration is probe life, in that although it is possible to measure 30 mpy in approximately 12 hours, using a probe span of 5 mils, the probe life would be approximately 60 days, before probe replacement would be required. This is considered to be too short a life and, many operators would use a thicker element span (c. 10 mil). In this way the probe life would be increased, at the expense of reducing the response time to 24 hours.

As a result of these various trade offs, and the unpredictable level of noise, the response times for electrical resistance probes in current use varies from ½ - 1 day at the higher end of the normal corrosion rate ranges, to 5-10 days at the lower end of the typical corrosion rate ranges.

These response times are adequate for establishing trends in corrosion behavior in systems that change slowly, and for fine tuning of corrosion mitigation measures. However, close correlation of operational events with changes in corrosion rates is difficult with response times of this order. Generally, by the time an increased corrosion rate has registered, several operational changes may have taken place since the culpable event, making corrosion behavior diagnostics a less than precise activity.

The slow response of electrical resistance probes is also a shortcoming in the trials used to initially establish effective corrosion mitigation programs. This is particularly true when selecting an inhibition program, where several different formulations may need to be evaluated, at a variety of different dose rates. Such inhibitor trials may take 30-60 days, or longer, to complete using conventional electrical resistance monitoring technology.

In order to decrease response times for electrical resistance technology, design audits have been conducted to reduce noise sources, and take advantage of increases in instrument resolution. The key aspects of design that have been considered in system noise suppression are:

Isothermal Probe Design:

As discussed above, the most significant noise source results from readings that are taken when the corroding, and reference, elements are at different temperatures. This will, typically contribute 1:250 parts of noise, in thermally unstable systems.

In order to minimize these effects, only probe designs where the reference element is located in extremely close proximity to the corroding element, offer the opportunity for low noise levels. Further, the residual space between the reference, and the corroding, element needs to be filled with material that has very high electrical insulating properties, combined with a high degree of thermal conductivity. Such designs minimize both the duration, and size, of any thermal gradients, that may develop during system temperature changes.

Based on these criteria, only cylindrical, and flush, elements designs can be considered, since wire, and thin walled tube, designs cannot be constructed with the necessary proximity of reference, and corroding elements, as illustrated in Figure 7.

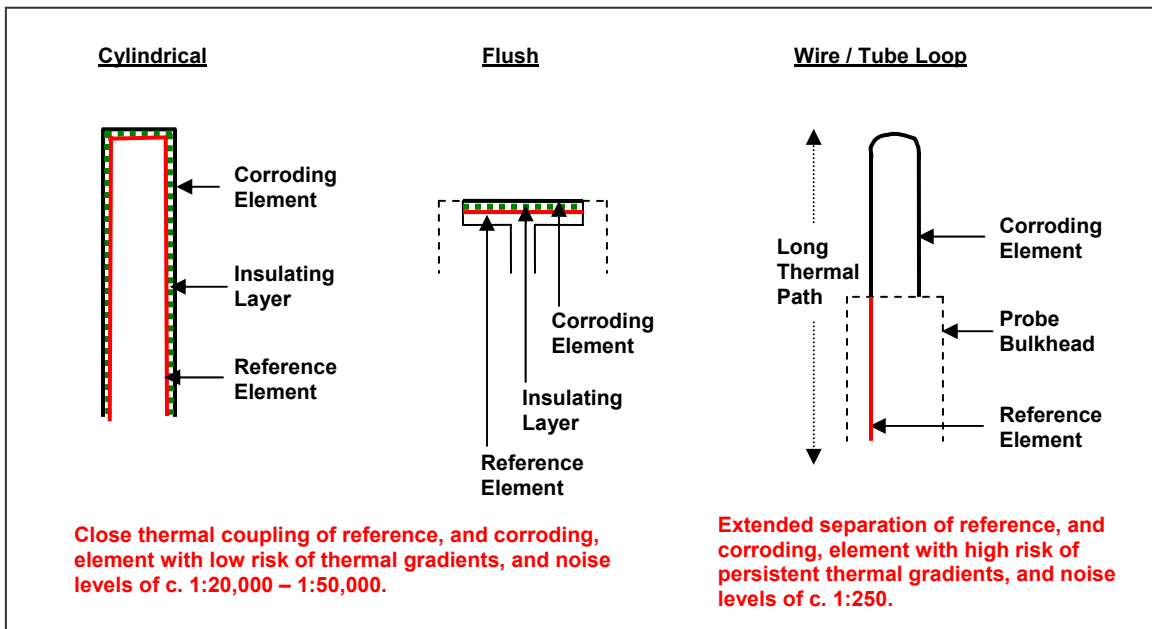


Figure 7 - Sensing Element Design

By restricting element designs to cylindrical or flush geometries, the separation distance between the reference and corroding elements can be greatly reduced. Further, by carefully selecting the insulation material between the reference and corroding elements, the heat conduction can be maximized, while maintaining electrical isolation. Enhanced performance electrical resistance probe designs are now available that can take advantage instrument resolutions as high as 1:262,144.

Minimal Signal Dissipation:

Traditional sensing elements have an absolute electrical resistance in the order of 1-5 milliohms, and the excitation current used to measure this resistance is in the order of 50mA. Current levels are limited by the need to conform to regulations for intrinsically safe operation. As a consequence, conventional electrical resistance measurements, are attempting to measure voltage changes in the order of 0.00025 mV. The situation is made two orders of magnitude worse, when attempting a resolution of 1:262,144. Since signal is dissipated in direct portion to the distance between the excitation source and the sensing element, it is critical that this distance be as short as possible for enhanced electrical resistance measurements. This involves direct coupling of the measuring instrument to the probe, and keeping probe lengths as short as practically possible, as is illustrated in Figure 8.



Figure 8 – Direct Coupling of Transmitter and Sensor

The measuring device is directly coupled to the probe by a short adapter, with positive engagement at both the probe and the instrument end. This ensures maximum signal retention, and limits the extent of required amplification, and extraneous noise generation. As a corollary to this aspect of design, the conventional connectors that are used in electrical resistance measurements, while adequate for most purposes, will generate sufficient noise to impact an enhanced measurement, and gold plated connections are required for coupling of the probe to the instrument.

Minimal Instrument Temperature Drift

Temperature drift in instrument reading, unlike the noise created by thermal gradients in the probe, is usually of a systematic nature, creating a 24 hour, sinusoidal wave on data. This effect is illustrated in Figure 9. While this is seldom a serious problem with conventional electrical resistance, it can be limiting in the case of enhanced electrical resistance measurements, where rate determinations need to be established in much less than a 24 hour period. The cause of this type of systematic noise is simply the net sum of individual component drift, with temperature.

In consequence of this phenomenon, instrumentation for enhanced electrical resistance monitoring requires a much more stringent design of heat sinks, and component spacing, to minimize temperature changes in the instrument. In addition it requires some degree of individual component matching, such that individual component responses to temperature tend to cancel each other.

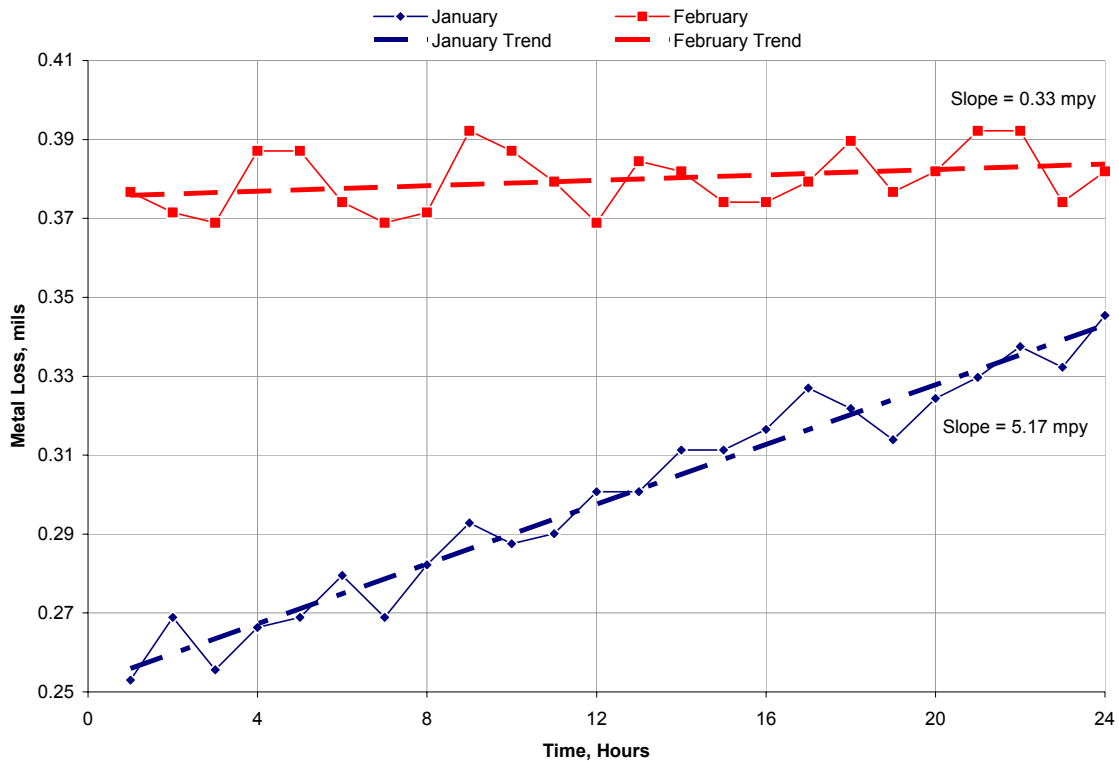


Figure 9 - Instrument Temperature Drift (Diurnal Cycling)

By making these various design changes in the basic construction of instruments, sensors, and their arrangements in systems it is now possible to reduce system noise in electrical resistance measurements, to the point at which it is possible to take real advantage of 18 bit (1:262,144) digital instrument resolution.

Noise related to electrical resistance changes caused by varying element stress (e.g. varying system flow rates, and pressures), and hydrogen uptake, remain a problem. However, they are of a much lower magnitude than the noise sources present in conventional electrical resistance measurement systems. Equally, all of the noise related to temperature gradient gradients in the sensing element, have not been suppressed. This means that the full advantage of 18 bit resolution has yet to be realized. However, the current level of improvement has cut response times by a factor of 20-50, depending on detailed system characteristics, and this permits the electrical resistance technique to approach a real time monitoring basis. Figure 10 and Table 2 show the results of a comparison between standard ER and enhanced ER monitor methods.

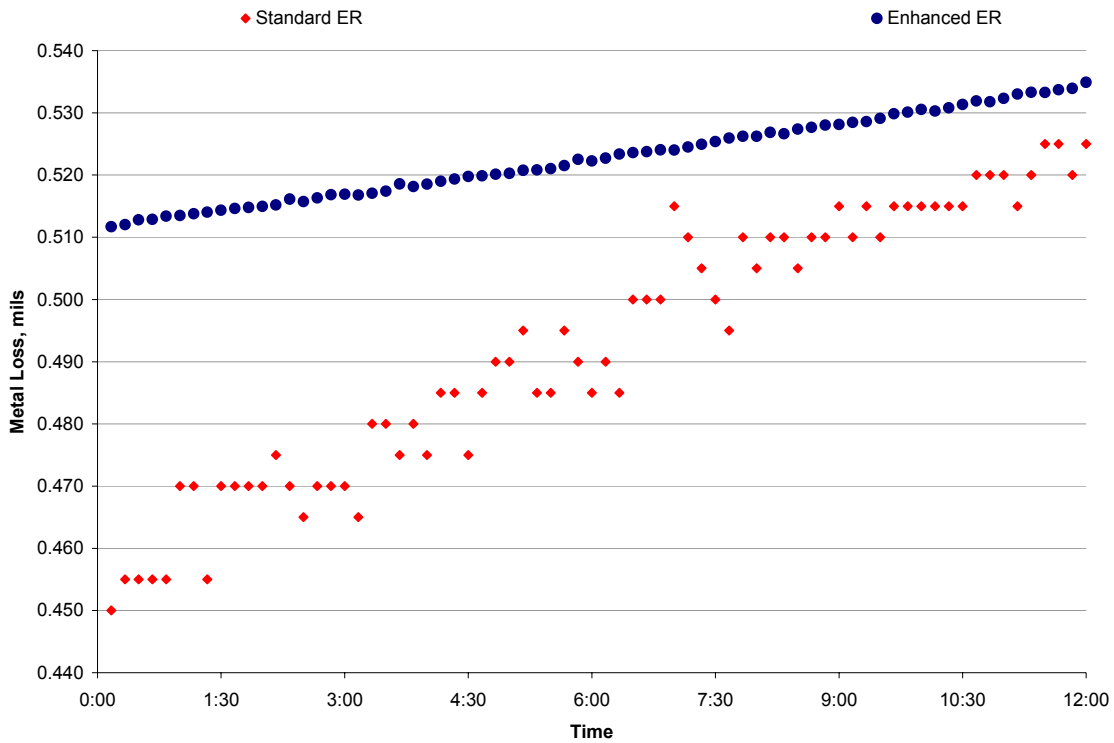


Figure 10 - Metal loss data for Standard and Enhanced ER monitoring

Table 2 - Data comparison between Standard and Enhanced ER monitoring

	Standard ER	Enhanced ER
Duration	12 hr	12 hr
Sample Size	73	73
Corrosion Rate	51.8 mpy	16.7 mpy
95% CI	±3.05 mpy	±0.19 mpy
Standard Error	42 x10 ⁻⁴	2.62 x10 ⁻⁴

The results show ~16 fold less variability using the enhanced ER method as compared to the standard ER method. Rapid screening of various corrosion mitigation regimens is now a realistic goal, and correlations between corrosion events and process changes can be made within limits of ± 1 hour.

WELL LINE CORROSION INHIBITOR TESTING

The field inhibitor testing protocol using standard ER probes required 12 days to complete an incumbent baseline, 12 days to complete the test using the candidate chemical, followed by another incumbent baseline test, for a total of 36 days. Since this is a test using an operating well, many of the tests suffered interruption or changes in the production fluid characteristics that would influence the results and complicate the data analysis. The data collected from the standard ER probes typically resulted in limited data at the lower concentrations, which is where there was the greatest interest.

To address the challenges of the standard testing process, a field evaluation technique has been developed which utilizes enhanced electrical resistance probes⁷ to rapidly screen candidates. This technique has reduced the time to evaluate new formulations from 36 days to 4 days (Figure 11).

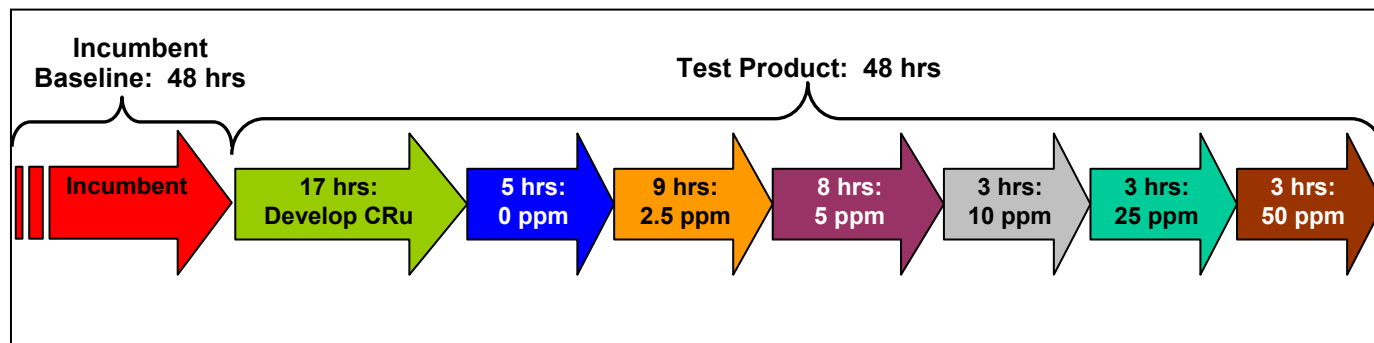


Figure 11 - Rapid Screen Test Duration

The shortened duration results in a higher percentage of tests completed without interruption or changes in production fluid characteristics. The short duration also eliminates the need for an incumbent baseline test at the conclusion of a single test chemical trial. Since the test duration has been shortened, several candidate inhibitors can be tested in series over the course of several weeks and periodic incumbent baseline tests are included prior to, during and following a series of tests.

Typical data collected from the standard method is shown in Figure 12. The slope of the metal loss data provides the corrosion rate. Essentially, there is the uninhibited portion followed by essentially complete inhibition at the first concentration of 15 ppm.

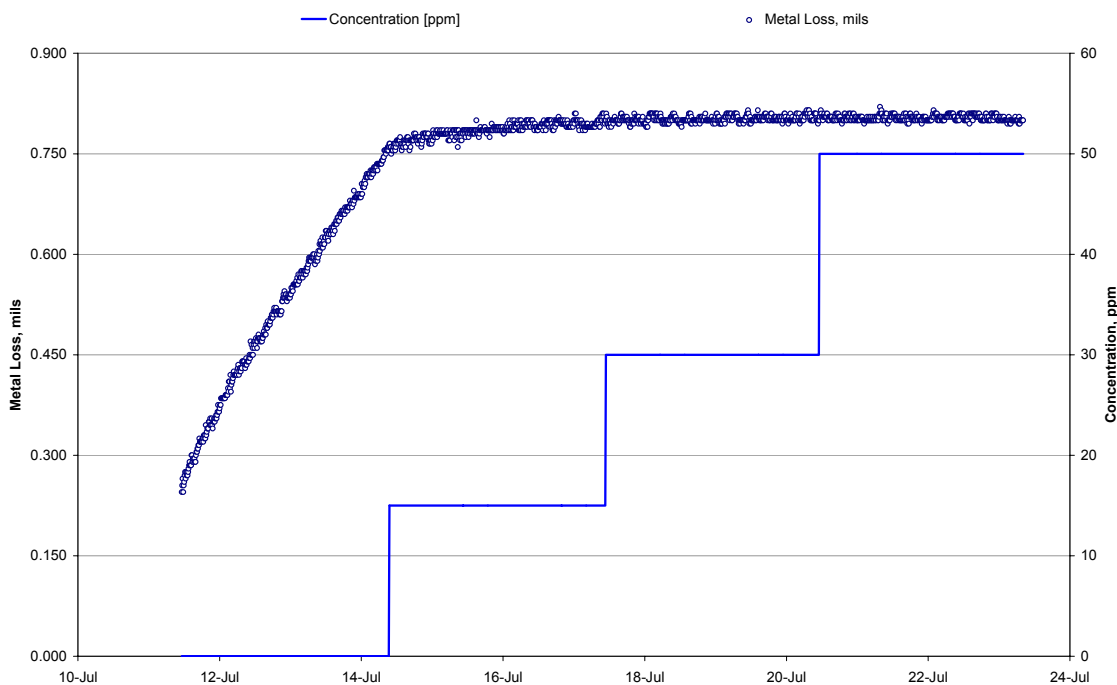


Figure 12 - Metal Loss data for standard test method using standard ER monitoring

Typical data collected from the rapid screen method is shown in Figure 13. Again, the slope of the metal loss data provides the corrosion rate data. There are several inflection points, or changes in metal loss data, visible. Given the higher resolution monitoring data, the number of test concentrations was increased from three to five. This allows a better analysis of the data, especially at the lower concentrations, leading to an improved understanding of the inhibitor performance over a range of concentrations.

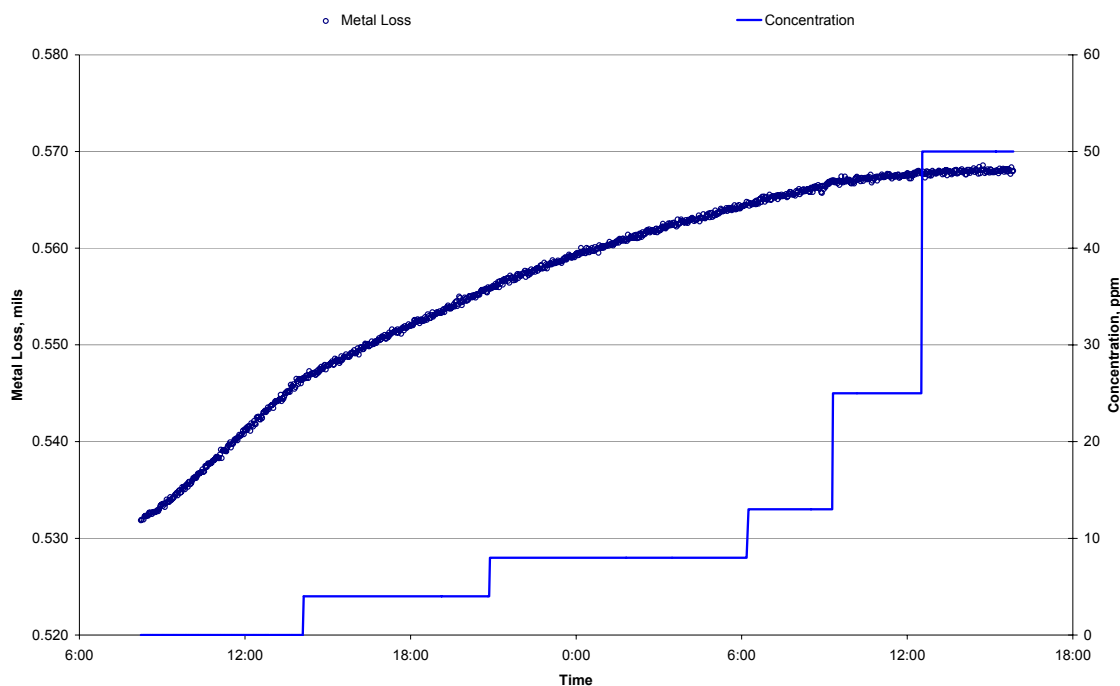


Figure 13 - Metal loss data for rapid screen method using enhanced ER monitoring

Benefits

As a result of the rapid screen process, the number of new formulations that can be evaluated has been increased significantly. As a result of the increased field testing capability and capacity, the laboratory development process has been modified to reduce the time to field testing hence increasing the number of test products for field trial. Following the identification of the most effective new corrosion inhibitor molecules from the wheel test, the actives are formulated and the partitioning performance of the product evaluated in the bubble test. Final low temperature stability formulation work, however, is not performed at this stage. At this point the most effective formulations are then selected for field evaluation.

Since the rapid screen test is conducted over a much shorter period of time, only 5 gallons of product is required for the complete field evaluation. This contrasts with ~100 gallons that is required using the standard evaluation protocol. The use of smaller quantities of test chemicals has numerous benefits including:

- The product can be blended in the laboratory rather than in the pilot plant.
- Significant reduction in field deployment costs.
- Shipping options for chemicals
- Smaller volumes of test chemicals reducing handling and waste management issues

- The test well is uninhibited for less time (17 hours vs. 72 hours), which equates to lower corrosion risk.
- Reduced time per test results in an increase of the number of candidates tested. During 2004, more than 50 products were tested.
- Reduced time per test increases the likelihood that a test will be completed without interruption or changes in the well production characteristics, which might change the corrosion rate,

Additionally, since the majority of the evaluation is performed in the field, this eliminates the discrepancies often encountered between field and lab results. This, combined with the larger number of products evaluated each year, significantly increases the probability of successfully developing the next generation of high-performance corrosion inhibitor products.

Those products that exhibit a cost-performance superior to that of the incumbent corrosion inhibitor are subsequently winterized and then the remainder of the laboratory development process in Figure 2 is completed. The products then progress to a larger-scale field evaluation. By establishing the field performance of the new formulations early in the development cycle, little time is expended on developing formulations that ultimately do not meet field performance specifications.

Table 3 - Summary Comparison of Standard and Rapid Screen Processes

	Standard Process	Rapid Screen Process
Test duration	36 days	4 days
Test chemical volume	75 gallons (284 liters)	5 gallons (19 liters)
Corrosion rate monitoring	3-standard ER probes	1-enhanced ER probe
Data frequency	10 minute interval, low sensitivity	2 minute interval, high sensitivity
Data results	Analysis at near full protection	Analysis of entire curve
Number of concentrations	3 different concentrations	5 different concentrations
% of tests completed without interruption	30%	93%

CONCLUSIONS

The existing process of corrosion inhibitor continuous improvement involves a series of laboratory steps to identify promising candidates. Once a candidate is identified, it is tested in the field over the course of a couple of weeks. A new testing protocol was developed to speed the time of inhibitor development with the hopes of finding the next generation corrosion inhibitor.

The new process identifies promising candidates early in the research cycle and sends a small quantity to the field for a rapid screening test. The new protocol shortens the over all development cycle and increases the number of candidate evaluations by almost a factor of 10. The new development cycle utilizes enhanced electrical resistance measurements to provide better quality data, which enables the researcher to analyze the entire performance curve over shorter test duration. By establishing the field performance of the new formulations early in the development cycle, little time is expended on developing formulations that ultimately do not meet field performance specifications, and more of the development effort can be focused products with a demonstrable field performance improvement.

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REFERENCES

1 Papavinasam, S, Revie, R.; Attard, M.; Demoz, A.; Michaelian, K. "Comparison of Laboratory Methodologies to Evaluate Corrosion Inhibitors for Oil and Gas Pipelines." NACE International CORROSION 2003, 59

2 Papavinasam, S.; Revie, W.; Bartos, M. "Testing Methods and Standards for Oilfield Corrosion Inhibitors." NACE International CORROSION 2004, Paper 04424.

3 A. Demoz, T., Dabros, K., Michaelian, Papavinasam, S., Revie, W. "A New Impinging Jet Device for Corrosion Studies." NACE International CORROSION 2003, Paper 03322

4 "State of the Art Report on Controlled Flow Laboratory Corrosion Tests." NACE International Technical Committee Report 5A195, December, 1995.

5 Fu, B., Strickland, B. "Corrosion Study in Dynamic High Velocity Flow Application Based on New Flow Loop Data." NACE International CORROSION 1993, Paper 93117.

6 Moon, T., Horsup, D. "Relating Corrosion Inhibitor Surface Active Properties to Field Performance Requirements." NACE International CORROSION 2002, Paper 02298.

7 Denzine, A., Reading, M. "An Improved, Rapid Corrosion Rate Measurement Technique for All Process Environments." Materials Performance, January, 1998: 35.