

On-Site Corrosion Inhibitor Detection for Improved Corrosion Management

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ABSTRACT

Corrosion inhibitors are widely used across the oil and gas industry to protect valuable infrastructure and manage corrosion issues. It is critical these chemicals are applied at a suitable dose: too much chemical can cause emulsion problems and increase OPEX, while too little chemical can leave a system at risk. The detection of corrosion inhibitor micelles can be used to identify the optimum dose. Micelles are nanoscale aggregates and identifying them in complex oilfield fluids, which often consist of multiple phases, is extremely challenging. The first-generation micelle detection technology we developed used complex instrumentation which required highly trained personnel and a lab environment to conduct testing. The technology has since undergone significant development and now consists of a small, rugged instrument, easy-to-use method and the ability to be deployed on-site (i.e. beside a sample point on a pipe). Advances have also been made in data processing and software has been built which gives immediate results. This sophisticated technology package has allowed us to deploy a new corrosion management strategy in areas of the US onshore pipeline network, whereby an initial audit of a system is conducted to identify any sites of overdosing or underdosing. The corrosion inhibitor injection rates are adjusted accordingly, until dosing is detected to be optimal, and then regular (usually monthly or quarterly) monitoring is implemented. The concentration of chemical required to protect a system can change for a wide variety of reasons, such as increased solids production or

change in fluid composition, therefore regular monitoring is essential. Data will be presented on the use of this method in the field.

Key words: Corrosion inhibitor, micelles, CMC, on-site, testing, new technology, automation, user friendly

INTRODUCTION

Corrosion inhibitors are widely used as a primary control mechanism in the oil and gas industry but need to be applied under optimal dosage regimes. Application of too little inhibitor can lead to increased corrosion risk and possible infrastructure failure, whereas too much chemical can lead to physical separation issues such as emulsions and increased operational expenditure. These chemicals work predominantly using surfactant molecules to form a protective, reversible physisorption film on the pipeline wall.¹

Conventional testing of water soluble corrosion inhibitor in production brine is carried out using a colorimetric residual test, such as methyl orange, or by using an expensive separative process combined with spectroscopic determination of component molecules (GC-MS, LC-MS etc.).² Both methods suffer in the time difference between sample collection and analysis, during which material changes to corrosion inhibitor composition and bulk fluid chemistry can alter dramatically providing misleading results. Additionally, traditional residual methodology, derived from kits designed to be applied to clean water systems, are prone to wide ranging positive interference from chemicals found in oil and gas systems.³ Although both chemical residual and separative technologies are widely used across oil and gas systems to monitor concentration levels, neither technique provides information on whether the chemical is being dosed at the *optimal* level, providing corrosion protection while minimizing emulsification issues and chemical spend.

Management of system protection, using corrosion inhibitors, can largely be broken down into the three highlighted areas detailed in Table 1.

Table 1
Corrosion management toolbox

Technique	Example	Effect
Operational efficiency of chemical injection	Maintenance of chemical skid	Assurance of accurate chemical delivery
Physical corrosion symptoms	Coupons, iron counts	Determination of metal loss and corrosion products
Residual amine quantification	Methyl orange, LC-MS	Determination of excess amine components within fluids

Of the techniques highlighted, operational efficiency of pumps and integrity of valves, is largely an engineering challenge. Determination of the symptoms of corrosion is an inorganic analysis and material chemistry practice, while amine quantification is an organic chemistry technique. Although chemical monitoring of water from the asset is a routine procedure, the data attained provides a snapshot of the system only at the time of analysis, not of collection. Exposure of test water to elevated oxygen environments and light can lead to precipitation of solids in test samples, this in turn can lead to new binding sites for filming amine analytes and a loss of accuracy in subsequent quantification. On reaching the analytical lab, clean-up practices such as filtration can lead to further loss of surfactant from the sample, potentially further decreasing the accuracy.

On-site techniques for analysis of corrosion inhibitors in production waters potentially provides operators with a faster, reliable means of assessing the available dosage of chemical in a sample, without the requirement for delaying tests during transfer to specialist laboratories.

Micelles and Optimal Dose

Table 1 details the current methodologies available to an operator in assessing the delivery and efficacy of a selected corrosion inhibitor to a production or transmission pipeline. Combined, the results of these checks and analyses can help indicate whether the chemical is operating at an effective dosage. However, as indicated previously, sample age, treatment and degradation can lead to anomalous results which in turn provide an inaccurate, or incomplete, snapshot of treatment at a sample point.

Prior literature has shown the benefit of aiming to inject corrosion inhibitor at, or slightly above, a level known as Critical Micelle Concentration (CMC) to optimize dose.^{4,5} Micelles are formed when a specific concentration of surfactant molecules, the filming component of corrosion of inhibitors, are present in the bulk water of a sample, this concentration varies with chemical formulation and water chemistry. The theory maintains that, at the point micelles can be observed in a system, that all surfaces within the system have adsorbed a full coverage of chemical, and that spare chemical is available in the bulk fluid to replace bound chemical lost by desorption or shear.⁶ Where micelles are absent, gaps are left in the surface film where corrosion events can then occur. Conversely, where an excess of micelles is present in a sample, potential chemical overdose issues may be apparent (Figure 1).

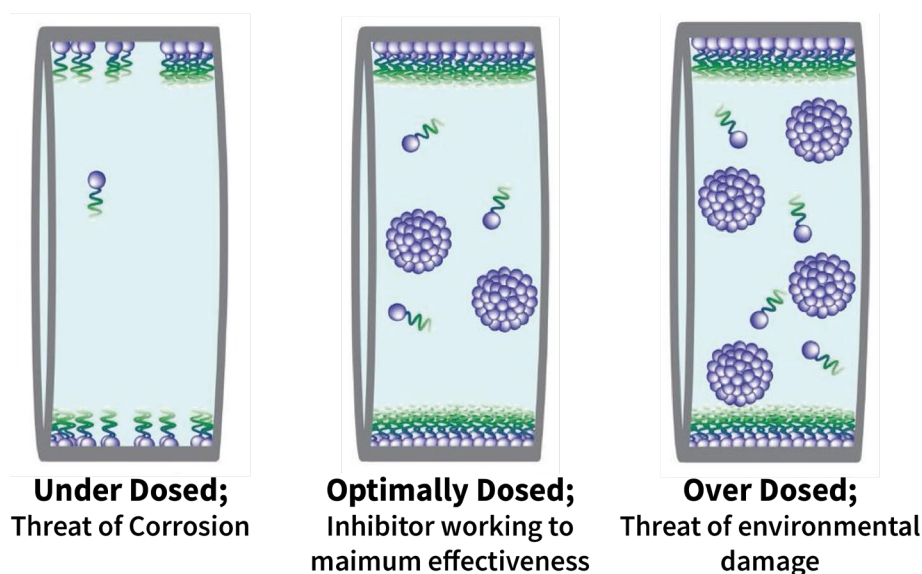


Figure 1: Micelle formation and relationship to optimal corrosion inhibitor dose

Development of Kits, Mobile Laboratory and Point of Collection Testing

Instrumentation and user deployable kits have been developed which allow operators to quickly assess the micelle signal present in a collected water sample. The instrumentation has been developed to be robust and deployable to a range of physical environments, including offshore use.^{7,8} Evolution of the instrument and kits has been guided by cycles of deployment and user feedback and has led to an evolution of the format to allow it to be operational from a mobile laboratory. This has allowed the system to be taken directly to sampling points, and for the analysis to be run at point of sampling, reducing time available for the degradation of sample through oxidative mechanisms.

Data Processing & Reporting

The complexity of importing, reading and processing the multipart micelle data originating from multiphase systems is a challenge that must be overcome if fast, on-site analysis of production water is to become a routine measurement at point of collection.

Steps have been taken to automate the processing of proprietary data sets in a way that protects core IP but allows the user straightforward access to their data. Simple data importation and processing steps have been built into a simple graphical user interface (GUI) that is currently undergoing field testing. Methods of software distribution and visualization are currently undergoing investigation to determine the optimal mechanism for placing a complete analysis package in the hand of production technicians.

EXPERIMENTAL PROCEDURE

Mobile Laboratory Set-Up and Data Acquisition

A general set-up procedure for mobile lab micelle analysis would be as follows:

A Windows 10 Lenovo Yoga laptop (8 GB RAM) running custom-built acquisition software was connected to a first-generation analyzer by USB-A—USB-A cable. The analyzer was tested for acquisition consistency using the internal QC standard provided in the reagent kit box.

The instrument, centrifuge and laptop were run from the tailgate of a Toyota Tacoma truck and powered directly from the battery of the vehicle using an Ampeak 1000W inverter. The centrifuge used in the studies was a Medifuge (ThermoFisher) operating at 120 V and 60 Hz. The centrifuge fitted with a fixed angle rotor containing space for eight individual 15 mL centrifuge tubes.

Data was recorded according to the naming structure indicated in Table 2. This naming structure is required to permit importation of the data into software for automated processing.

Equipment was generally left *in situ* during transit but only connected to power supply while stationary.

Table 2
Naming structure of micelle analysis data

File Naming Structure	Key
DDMMYY_hhmm_xy	D = day of sample
	M = month of sample
	Y = year of sample
Example Data Set	h = hour of sample (24 h clock)
260819_1530_1a	m = minute of sample
to	x = vial number (1 to 5)
260819_1530_5b	y = vial replicate (a or b)