STEM-Corrosion™

Paper Number: 2020-01

Position Paper

Need for Laboratory Evaluation of Corrosion Inhibitors using Standard Test Methods (STM)

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The global corrosion inhibitors market is anticipated to reach about USD 10 billion in 2027; oil and gas industry is the predominant user of corrosion inhibitors[1].

Corrosion inhibitor is a chemical substance or combination of substances that, when present in the proper concentration and forms in the environment, reduces the corrosion rate[2]. The extent it reduces the corrosion rate depends on transportability, efficiency, availability, and secondary inhibitor properties (TEAS)[3]:

- Transportability: Measure of ability of corrosion inhibitors to get transported from the injection point or application location to the surface undergoing corrosion. The transportation may occur through water-phase, oil-phase, gas or vapor-phase [vapor-phase corrosion (VPC) inhibitor and top of the line (TLC) inhibitor], and solid-phase [underdeposit corrosion (UDC) inhibitor]
- Efficiency: Measure of ability of corrosion inhibitor to reduce the corrosion rate by adsorbing onto the metal surface
- Availability: Measure of logistics in place to replenish the inhibitor tank
- Secondary inhibitor properties: Measure of interactions of corrosion inhibitor with other chemicals and materials. These interactions may influence the efficiency and persistency of the inhibitors on the surface. Secondary inhibitor properties may include: water/oil partitioning, solubility, emulsification tendency, foam tendency, thermal stability, toxicity, compatibility with other additives (e.g., drag reducing agencies, biocides, and scale inhibitors) and compatibility with other materials (e.g., stainless steel and non-metallics).

Commercial corrosion inhibitor packages contain active molecule (that adsorbs onto the surface undergoing corrosion) as well as other chemicals that enhance transportability and secondary inhibitor properties. The efficiency of active molecule - either alone or in the inhibitor-package - is central to the success of controlling internal corrosion using corrosion inhibitors. The efficiency is primarily determined in the laboratory methodologies.

For reliability and economic reasons, oil and gas industry must report efficiency of corrosion inhibitors in reference to Standard Test Methods (STM) and must collectively develop STM to evaluate other properties of corrosion inhibitors.

Standard Test Methods are developed by standards-making organizations (such as ASTM International) based on interlaboratory tests (in which a minimum of six laboratories must participate). The interlaboratory tests are used to develop "repeatability" and "reproducibility" statements (also known as "Precision and Bias" Statements).

- Repeatability is the variation in the results from same operator carrying out the same test following same procedure
- Reproducibility is the variation in the results from multiple operators carrying out the same test following same procedure.

Of the 5,500+ STM published by ASTM International, there is only one for corrosion inhibitor evaluation, i.e., ASTM G202. Oil and gas industry must use ASTM G202 for reporting inhibitor efficiency and must collectively develop additional STM on other properties of corrosion inhibitors.

Myth, Fact, and Move Forward #1

Myth #1

Current situation (Covid-19 and low oil price) is not good either for evaluating corrosion inhibitors using STM or for developing additional STM.

Fact #1

It is true that we are cognizant of the situation caused by Covid-19. As responsible persons, we need to maintain the social distance and be safe. At the same time, we should also realize that the Covid-19 and low oil price will have huge and immediate impact on internal corrosion control strategies due to:

- Loss of personnel
- Less funding to conduct test
- Temptation to use inferior and cheap chemicals without testing.

If failure happens due to any one of them, it will expose the fault line in the oil and gas industry's current approach with respect to the evaluation of corrosion inhibitors and will place the industry in a very vulnerable position. How? All other corrosion control strategies are evaluated and selected based on "quantitative" criteria or on STM. For example[3]:

- Materials for sour service are qualified and selected based on NACE MR0175/ISO 15156
- External pipeline coatings are qualified and selected based on 13 ASTM STM (or derivatives of them as developed by NACE, CSA, and ISO)

- Cathodic protection (CP) is applied based on well-established quantitative criteria, e.g., -850 mV (on or off) vs copper-copper sulfate electrode.

Therefore, if an incidence happens, it is relatively easy to establish "what went wrong", e.g., CP application did not meet the criteria. Thus, the industry has established procedures to generate "quantitative" data that enable them "speak in one voice" with respect to materials, coating, and CP performance.

On the other hand, the industry does not follow any STM to quality and select corrosion inhibitors. Therefore, if an incidence happens, there is no way the industry can demonstrate that the corrosion inhibitor was appropriately evaluated and selected, i.e., the industry will speak in different voices.
Those who faced the media and public will attest that it would be challenging to talk to them even with defendable data[4-7]. If the industry has to face them without defendable data, the interaction with neither be pleasant nor be reflection of our professionalism.

Yes, it is challenging to address this issue now, but it would be a nightmare to address it under the watchful and scrutinizing eyes of regulators, stakeholders, media and public.

Move forward #1

- Start qualifying and selecting corrosion inhibitors using ASTM G202. At present ASTM G202 is the only STM available for evaluating corrosion inhibitors (Even in Covid-19 and low oil price situations, the industry does test corrosion inhibitors, and a portion of funds may be used to test them using STM)
- Collaborate and coordinate development of STM to evaluate other properties of corrosion inhibitors.

Myth, Fact, and Move Forward #2

Myth #2

Our operational conditions are unique. To simulate field conditions in the laboratory we use several correlations. Therefore, STM are not useful for us.

Fact #2

Laboratory methodologies can never quantitatively simulate field conditions. At best, they may only qualitatively simulate field conditions for the following three reasons:

1. Field conditions are dynamic in nature. To quantify field conditions compositions (materials, oil, water, gas, and solid), temperature, and pressure (including partial pressures of acid gases such as CO_2 and H_2S) and flow <u>as well as their variations over time</u> must be understood. Compositions, temperature and pressure can be directly measured, i.e., they are direct variables, and flow can't be directly measured, i.e., it is an indirect variable. To account for the effect of flow, pressure drop is measured and from that wall shear stress is calculated.

   From the proceeding discussions it is obvious that we neither could map all field conditions nor such an approach is economically feasible from the perspective of using them for inhibitor evaluation in the laboratory. For this reason, one field operating condition is assumed for simulation in the laboratory.

2. To simulate field conditions in the laboratory both direct and indirect variables must be considered. Simulation of direct variables is relatively easy, i.e., keep values exact the same as in the field. However, simulation of indirect variable is difficult. Field wall shear stress (measured through the pressure drop caused mostly by non-corrosive oil and gas phases) is often used to establish laboratory wall shear stress caused by corrosive water-phase, i.e., flow effects of non-corrosive phases are used to simulate flow effects of corrosive phase which diminishes the ability of laboratory methodologies to simulate field flow conditions.

   Further, more than 30 equations, Computational fluid dynamic (CFD) models, and logics are available to calculate wall shear stress in various methodologies. There is no consensus as to what is the correct equation. The equations can vary by 2 to 3 orders of magnitude[8]. Consequently, any laboratory test conditions can be correlated to any field conditions by using an equation that provides such a correlation. Besides, the original equation developers have clearly established procedures to ensure that the equations are valid for an experimental setup and have established boundaries of applications. These limitations and boundaries are often ignored.

3. Even in a simple "dip and drip" type of laboratory methodologies, more than 20 factors can influence corrosion. If any of the factors are not considered, it will lead to variation in the test result[9]. The variation will further increase if effects flow, pressure, and multiphases are simulated. If the technician is not educated and trained on the importance of these factors, addition deviations in the results will occur. Standard Test Methods are primarily developed to determine the influence of them in a given laboratory methodology. Only when a STM is published, the ability of technicians, laboratories, and apparatus be ascertained by comparing their test data with the data published in STM (Such practice is used as second nature in other fields, e.g., medical field).

Dynamic nature of the field, qualitative nature of equations correlating laboratory-field conditions, and absence of STM for inhibitor evaluation (or non-use of the only one STM) have resulted in generation of plethora of data individually by corrosion inhibitor suppliers, end-users and third-party laboratories. These data are neither comparable nor agreed by other players. Other corrosion control professionals (e.g., those who control corrosion by coatings) have resolved this issue long ago by anchoring the evaluation only to STM. It is time for corrosion professionals dealing with corrosion inhibitor recognize the importance of STM.

- STM provides an anchoring point, i.e., it removes the uncertainty caused by laboratory methodology. Therefore, it helps to understand how field conditions may affect corrosion rate and helps to narrow down the equations that can be used to qualitatively correlate laboratory and field conditions. Thus, the use of STM reduces the variables from three (variation in field conditions, variation in the laboratory and field correlation; and variation in the laboratory methodology) to 2 (laboratory-field correlation and field conditions) or probably to 1 (field conditions). This will in turn decrease the number of tests and consequently cost of laboratory testing.

Move forward #2

- Test corrosion inhibitors using ASTM G202 and based on the comparison of corrosion rate and type (general or pitting corrosion) in the STM and field conditions, establish laboratory-field correlation.

Myth, Fact, and Move Forward #3

Myth #3

I do several tests on my own. My laboratory has tons of equipment and data. I can conduct my own tests and can defend my data.

Fact #3

Even with tons of data, by a single person or single company can only make "repeatability" statements. Continuation on this path only creates confusion, debate, and chaotic noise as well as more and more tests. Only collective leadership and collaborative approach will result in consensus STM that will provide clarity, consensus, and synchronized voice as well as less tests; i.e., instead inhibitor supplier, end-user and third-party laboratories performing tests with their own procedures, only one test needs to be carried out - using one common procedure provided in STM.

Move forward #3

- Participate in the consensus development of STM based on individual laboratory data and experience. This approach will produce data that will not only defend individual companies but also the whole industry. This approach will reduce the cost of laboratory inhibitor evaluation because only one-set of tests need to be performed (rather than the current approach of doing 3 tests). The results from the single test set should be within "repeatability" and "reproducibility" statements in STM – no matter if the test is conducted in inhibitor supplier laboratory, end-user laboratory or third-party laboratory

Myth, Fact, and Move Forward #4

Myth #4

The only STM is ASTM G202 and is on rotating cage. Rotating cage is not reliable

Fact #4

"First they ignore you, then they laugh at you, then they fight you, then you win" Mahatma Gandhi. The quote is so true for rotating cage.

A very reputed and unbiased government laboratory (with financial support from oil and gas companies and access to three sour production pipelines) ranked 13 laboratory methodologies in terms of their ability to simulate field operating conditions. Based on 64 comparisons using both general and pitting corrosion rates and using 6 corrosion inhibitors (3 continuous and 3 batch), they ranked rotating cage to be the top-ranked methodology. They also found that this is the most compact laboratory methodology for simulating heterogeneous flow conditions of the field and consequently for simulating localized corrosion conditions. Every inhibitor that controlled general and localized corrosion rates in rotating cage also controlled them in the field; and the inhibitor that could not control general and localized corrosion rates in rotating cage could not control them in the field[10].

Rotating cage is the only laboratory methodology that passed the rigorous ASTM interlaboratory testing that preceded the publication of ASTM G202[11]. It should be noted that the interlaboratory tests were conducted using geometry of rotating cage, sample size, number of coupons, rotation speed, and solution volume. If any one of them is changed by the user, then that will invalidate the test result obtained by the user, i.e., the user can't claim that they meet ASTM G202 test conditions.

Move forward #4

- Rank corrosion inhibitors based on ASTM G202 to establish a common benchmark
- Collaborate to develop additional STM on laboratory methodologies for evaluating other properties.

Myth, Fact, and Move Forward #5

Myth #5

I am dealing with different types of corrosion mechanisms such as UDC, TLC, and VPC. ASTM G202 does not help me.

Fact #5

It is important that STM are developed for evaluation of UDC, TLC, and VPC inhibitors. The laboratory developing new and special laboratory methodologies should publish "repeatability" statement. In the absence of it, the qualification of the special laboratory methodologies can't be independently verified and STM on them can't be developed.

Until STM are developed for UDC, TLC or VPC inhibitors, comparison of efficiencies of inhibitor in ASTM G202 and in special laboratory methodologies will provide information if they indeed simulate different mechanisms. If the efficiency of inhibitors in special laboratory methodology is:

1. higher than in ASTM G202, then the merit of the laboratory methodology should be further evaluated for two reasons:
    a. Corrosion rate in the absence of corrosion inhibitors is low, i.e., the laboratory methodology is not simulating worst case scenario
    b. The laboratory methodology does not adequately simulate the transport of active molecule through various phases (during transportation through various phases some active molecule will be lost and this will obviously decrease inhibitor efficiency)
2. similar both in ASTM G202 and in the special laboratory methodology, then the results should be used with caution
3. lower than in ASTM G202, then the special laboratory methodology may be accepted.

Move Forward #5

Develop STM on laboratory methodologies for evaluating UDC, TLC, and VPC inhibitors. Until they are developed, use ASTM G202 as a qualitative screening tool to evaluate the merit of non-standard laboratory methodologies.

Summary

1. Oil and gas industry must report efficiency of corrosion inhibitors in reference to ASTM G202 (the only STM available at present) and must collectively develop STM to evaluate other properties of corrosion inhibitors
2. Use of STM will increase the reliability of test results and decrease cost of laboratory corrosion testing
3. If industry does not report efficiency of corrosion inhibitors in reference to STM and if it does not develop STM on their own, the industry may be forced to do them under the watchful and scrutinizing eyes of regulators, stakeholders, media, and public.

References

1. Corrosion Inhibitors Market Size, Share, and Trends Analysis Report by Product (Organic, Inorganic), by Type (Water-based, Oil-based), by End Use, by Region, and Segment Forecasts, 2020-2027, May 2020, https://www.researchandmarkets.com/reports/3765905/corrosion-inhibitors-market-size-share-and?utm_source=MC&utm_medium=Email&utm_code=mzr9496gl&utm_ss=43&utm_campaign=1402153+-+Corrosion+Inhibitors+Market+(2020+-+2027)&utm_exec=adke277mtd
2. NACE/ASTM G193, Standard Terminology and Acronyms Relating to Corrosion
3. S. Papavinasam, R. Venkatesan, and S. Mudiam, "Quantitative Evaluation of Corrosion Inhibitors in the Laboratory: The First Step for Successful Application of Inhibitors in the Oil and Gas Industry", CORROSION 2019, Paper # 12878, NACE International, Houston, TX, USA (2019)
4. Senate of Canada, Issue 36 – Evidence "Bulk Transportation of Hydrocarbon Products in Canada", February 5, 2013
5. Bill Hedges Interview, in Run to Failure, A. Lustgarten, W.W. Norton and Company, NY, ISBN: 978-0-393-08162-6 (2012)
6. "Science Trumps Fiction on Oil Sands Corrosion Claims" ExxonMobil Perspectives, Nov. 29, 2012, http://www.exxonmobilperspectives.com/2012/11/29/science-trumps-fiction-on-oil-sands-corrosion-claims-2/ "…According to lead researcher Sankara Papavinasam, quoted in *The Globe and Mail*, "We did not see any difference whatsoever" between crude oil from oil sands and other crudes…".
7. TRB Special Report 311: Effects of Diluted Bitumen on Crude Oil Transmission Pipelines, National Research Council, Washington DC, ISBN: 978-0-309-28675-6, 2013
8. D. Silverman, "The Rotating Cylinder Electrode for Examining Velocity-Sensitive Corrosion – A review", Corrosion 60 (11), 2004, P. 1003.
9. ASTM G31, "Standard Practice for Laboratory Immersion Corrosion Testing of Metals"
10. S. Papavinasam, M. Attard, R.W. Revie, A. Demoz, and K. Michaelian, Comparison of Laboratory Methodologies to Evaluate Corrosion Inhibitors for Oil and Gas Pipelines, Corrosion, 59 (10), p. 897 (2003).
11. ASTM Research Report G01-1025, Interlaboratory Study to Establish Precision Statements for ASTM G202-12 Standard Test Method Using Atmospheric Pressure Rotating Cage, November 2012.