

Review of Volatile Corrosion Inhibitors Evaluation Methods and Development of Testing Protocols

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ABSTRACT

Top of the Line Corrosion (TLC) is now known to be the main mode of failure in incidents associated with a number of wet gas pipelines operated all over the world. TLC is nevertheless a relatively recent phenomenon in a sense that its existence was only acknowledged about 10 to 15 years ago. Several research activities have been carried out since then to identify the main corrosion mechanisms and to propose appropriate mitigation techniques. Among them, the use of volatile corrosion inhibitors (VCI) seems very promising. However, the industry now suffers from a lack of consistency in the TLC inhibition evaluation methods. This paper presents a comprehensive and critical review of the different experimental setups proposed in the literature for the evaluation of VCI performances, highlighting benefits and drawbacks of each method. Building on this valuable experience, an effort is then made to propose a state of the art testing protocol for the determination of corrosion inhibition efficiency and persistency of VCI for TLC applications.

Key words: Top of the line corrosion, volatile corrosion inhibitor, laboratory methodology

INTRODUCTION

Only properly acknowledged about fifteen years ago, Top of the Line Corrosion (TLC) is now a common feature in every corrosion management plan developed for wet gas lines, at the same level as CO₂/H₂S corrosion, Microbiologically Induced Corrosion (MIC), Under-Deposit Corrosion (UDC) and so on. TLC is a form of acid corrosion which occurs due to the condensation of water vapor on the cooled internal

surface of pipelines. Depending on the production conditions (especially fluid temperature, flow regime, Water Condensation Rate (WCR), CO₂/H₂S content, organic acid concentration), it can lead to severe metal loss, localized corrosion and rapid pipeline failures [1-3]. Management of TLC requires its own set of mitigation measures. Fortunately, much progress has been made on the understanding of the mechanisms, mostly through laboratory experimentation [4-7] and sharing of field experience [8-11]. Several modeling tools, with varied levels of complexity and validity, have been developed to predict TLC rates in field environments [12-17]. These modeling tools are commonly used to estimate WCR and TLC rates at the pipeline design stage or for failure analysis. In addition, In-Line Inspection (ILI) tools are also routinely used to confirm the extent of metal loss [18]. Once the severity of the TLC threat is determined, typical mitigation measures involve the use of Corrosion Resistant Alloys (CRA) on some sections of the line [19], efforts to decrease the WCR by adding thermal insulation [20], increased pipeline wall thickness for higher corrosion allowance [21] and chemical inhibition [22]. This paper focuses on this last aspect, especially as it relates to Volatile Corrosion Inhibition (VCI).

The development and successful application of VCI in field environments is of considerable importance. As for its more standard Bottom of Line (BOL) corrosion inhibitor counterpart, it is seen as an economical and practical mitigation method. However, many challenges remain regarding VCI applications. The formulation of effective VCIs is problematic as standard imidazoline or quat-type inhibitor molecules are not volatile due to their large molecular weights. Finding the correct balance between volatility (which often means relatively small molecules) and inhibition efficiency is complex. Determining the optimal functional group that will determine the adsorption mechanism and the right length of the alkyl tail is also difficult. Recent efforts have been published in this area [23, 24, 25] but many issues still remain regarding partitioning of the VCI in water and oil, injection method, effectiveness and longevity of the VCI once in the pipe and so on.

MOTIVATION AND OBJECTIVES

The first step in selecting an inhibitor for field application often goes through a careful laboratory determination of its efficiency. As the interest regarding VCI has grown considerably over the last few years, a number of testing and research institutions have proposed several methodologies and experimental setups to evaluate VCI efficiency. Although these testing methodologies hold many similarities, they can also differ considerably, generating results that are not consistent and often not directly comparable. There is consequently a need in the industry to develop a set of unified recommended test practices for the investigation of VCI efficiency.

The objective of this work is twofold:

- Critically review existing literature on VCI evaluation methods and standards and assess their applicability for mitigation of TLC in wet gas pipelines,
- Propose a comprehensive testing methodology to evaluate VCIs properties for TLC applications.

LITERATURE REVIEW

Standards

VCI or VpCI (vapor phase corrosion inhibitor) are common terms used to qualify chemical products used to mitigate corrosion of equipment parts exposed to the vapor phase. These terms appear in two standards published by NACE and ASTM:

- ASTM D5534: Standard test method for vapor phase rust-preventing characteristics of hydraulic fluids.[26]
- NACE TM 208-2008: Standard test method - Laboratory Test to Evaluate the Vapor-Inhibiting Ability of VCI Materials for Temporary Protection of Ferrous Metal Surfaces.[27]

These two standards propose relatively similar set-ups where a steel specimen is exposed to an aerated water-saturated gaseous environment (Figure 1 and Figure 2). The systems consist of a glass cell equipped with a specially made lid. Some brine is injected at the bottom of the cell which can be heated to the required temperature. An aluminum or stainless steel rod is mounted through the lid and serves as specimen holder and cooling system. The specimen is cylindrical and mounted around the rod. Water is circulated through the inside of the rod to provide external cooling. However, condensation rate is neither measured nor controlled. There is also no method to measure the temperature of the specimen. The environment inside the cell is atmospheric air and there are no specific guidelines on how way to control the gas phase composition, although this could be easily addressed. Specimen post analysis is limited to visual observation of rust “spots” on the surface. These standards are clearly not intended to simulate the corrosive environments encountered in gas pipelines and are more adapted for corrosion issues encountered in atmospheric applications.

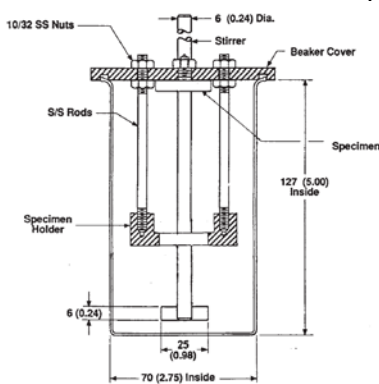


Figure 1: ASTM D5534 – Rusting test apparatus
(reproduced from [26] – © ASTM International 2005)

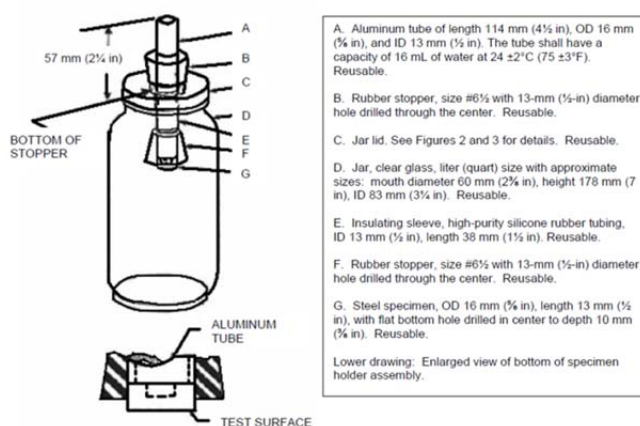


Figure 2: NACE TM 208-2008 – Test apparatus
(reproduced from [27] – © NACE International 2008)

Outside of these standards, several experimental setups have been proposed to study corrosion in dewing conditions, for applications as diverse as packaging or storage of radioactive wastes.

Test setups developed for industries other than oil and gas

The addition of VCI to boost Controlled Humidity Protection (CHP) system used for storage application in atmospheric conditions gave encouraging results [28]. In this study, carbon steel specimens and Electrical Resistance (ER) probes (Figure 3) were exposed to aerated conditions with controlled relative humidity, typically less than 40%, over a six months period. The test setup is shown in Figure 4. The corrosion rate could be monitored in-situ and post analysis of the specimens involved Scanning

Electron Microscopy (SEM) analysis and mass loss measurements. Measurement of condensation rate was not relevant here since the corrosion mechanism was more dependent on the presence of hygroscopic corrosion products or scales on the metal surface. Consequently, the specimens themselves were not externally cooled.



Figure 3: Electrical resistance (left) and weight loss (right) specimens proposed by Bavarian *et al.* (reproduced from [28] – © NACE International 2016)

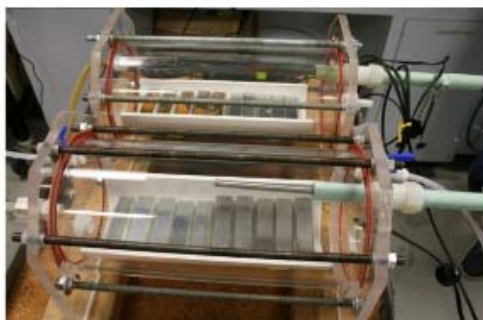


Figure 4: Test chambers for controlled humidity evaluation of steel samples proposed by Bavarian *et al.* (reproduced from [28] – © NACE International 2016)

The management of radioactive wastes, which are stored for long periods of time in holding tanks, raises also a number of critical corrosion issues related to containment needs. The use of VCI (ammonia in this case) has also been investigated for this application, leading to the development of dedicated testing apparatus aimed at approximating vapor phase corrosion [29, 30]. In one of these setups, the aerated vapor phase was sparged through the bottom of columns (15 cm internal diameter) containing an aqueous solution at rest and equipped with several ring-shaped specimen holders installed above the liquid level (Figure 5). Small disk steel specimens were mounted in this holder, facing the inside of the column. While some specimens were only exposed to the vapor phase, some holders were periodically immersed in the bottom aqueous solution. Heat loss through the column was enough to generate water vapor condensation on the steel specimens. Post analysis was limited to visual inspection of the specimens.



Figure 5: Transparent glass column vapor space corrosion test apparatus proposed by Fuentes *et al.* (reproduced from [29] – © NACE International 2015)

Test setups dedicated to application in oil and gas industry

A comprehensive review of the experimental setups developed for the study of TLC has already been presented by the author in 2015 [31]. This section presents a brief summary of some of these systems that have been used for the study of volatile corrosion inhibition. New setups introduced more recently are also presented.

Olsen [32] and Pots [33], were among the first researchers to propose experimental setups dedicated to TLC. While VCIs were not identified as a viable technique at that time, these setups hold useful concepts that still appear in more recent systems. One of the most innovative features was the external cooling of the steel specimens and attempts to control the condensation rate, as shown in Figure 6.

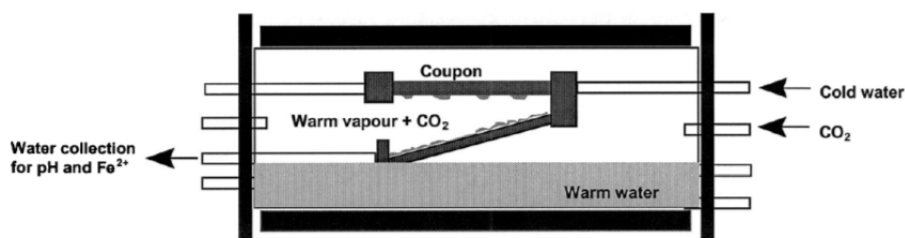


Figure 6: TLC experimental device involving a cooled steel tube proposed by Pots *et al.* (reproduced from [33] – © NACE International 2000)

It took about ten years for the use of VCIs, as a legitimate TLC mitigation technique, to become a topic of research. In 2010, Gunaltun *et al.* [34] published a comprehensive study, evaluating the efficiency of VCIs using different innovative experimental setups. One of the systems was an experimental glass cell design dedicated to TLC with real time vapor phase corrosion measurement via Electrical Resistance (ER) probe (Figure 7). The probe was flushed mounted to the top lid of the cell, and externally cooled, to simulate corrosion at the 12 O'clock position of a pipeline. At that time, it was thought that the low conductivity of the condensed water would pose solution resistance issues that would prevent the use of Linear Polarization Resistance (LPR) probes. The ER technique seemed more appropriate since it did not require a good electrolyte. This said, several issues still remained since the sensing element of the ER probe needed to be always fully wetted to acquire meaningful data. In addition, the use, in parallel, of regular weight loss specimens was still required for validation of the ER corrosion rates and for the investigation of localized corrosion. Although this system was used for VCI efficiency evaluation, a main drawback of the design was that the condensed water could not be collected. An in-house heat transfer model was used to predict the temperature of the specimens and the consequent WCR, which could not be measured directly. Similar setups were later used by other authors to investigate VCI efficiency [35]. Pojtanabuntoeng [36] improved the experimental setup by using of a thermoelectric “Peltier” device to cool the specimens. This enabled a much better control of the temperature of the corroding samples and of the local condensation rate.

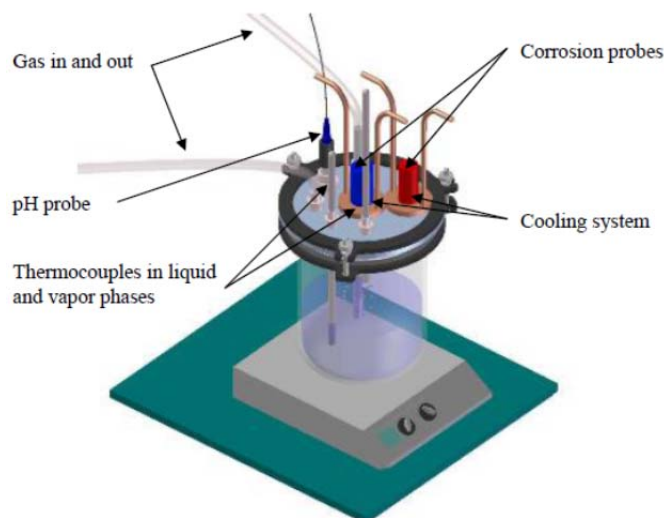


Figure 7: Experimental setup using Electrical Resistance (ER) probe proposed by Gunaltun *et al.* (reproduced from [34] – © NACE International 2010)

Another setup proposed in this study [34] consisted of two main parts: a glass cell reactor generating the water vapor and an externally cooled condensation cell, where electrochemical measurements were made using an externally cooled LPR probe. The water vapor was circulated through the system which was also equipped with a condensed water collection port and condensed water pH measurement capabilities. The only drawback of this rather comprehensive system was that dynamics of droplet condensation was not reproduced accurately since the electrodes were facing up instead of down.

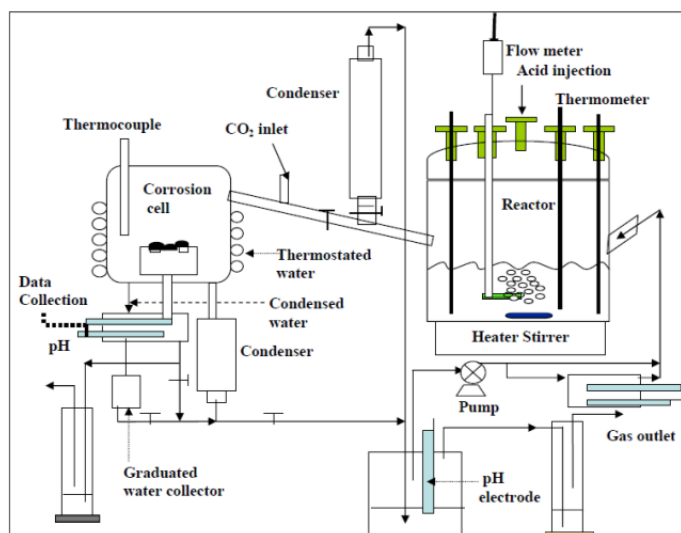


Figure 8: Volatile inhibitor testing equipment proposed by Gunaltun *et al.* (reproduced from [34] – © NACE International 2010)

In 2012, Jovancicevic [37] investigated the use of a Quartz Crystal Microbalance (QCM) to measure the mass of adsorbed VCI film in the vapor phase. This technique is worth mentioning here since it has the potential of monitoring both the corrosion rate (if an electrochemical QCM is used) and the inhibitor adsorption process. However, it also presents many challenges especially related to the relationship between the change of frequency of the quartz crystal substrate and the actual mass adsorbed since the inhibitor films are typically not rigid.

In 2012, Cough [38] and Oehler [39] developed an experimental glass cell setup in which the vapor phase corrosion rate was recorded using an LPR probe. The innovation here was that the corrosion

probe was made of three carbon steel pins which were externally cooled. The vapor phase condensing on the pins was collected in a cup located below the probe. The pins were used both as weight loss specimens and as working and counter electrodes for LPR measurements. Since LPR readings could not be taken while the probe was held in the vapor phase (the thin layer of electrolyte could not bridge the pins), it was periodically lowered and fully immersed in the condensed water cup where LPR readings could be taken. Issues with high solution resistance were probably encountered by the authors but were not discussed. In addition, the use of vertical pins could not properly simulate the mechanism of condensed water droplet/film formation, as it is expected to occur in a pipeline. This, in turn, could mask the effects of controlling parameters and alter the occurrence of localized corrosion.

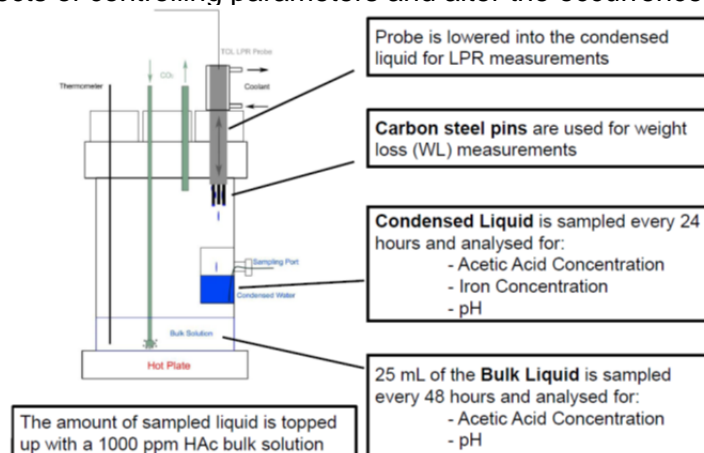


Figure 9: Cooled finger probe concept proposed by Oelher *et al.*
(reproduced from [39] – © NACE International 2012)

In 2012, Jenkins [40] proposed another similar setup to study VCI efficiency. The main innovation was with the use of a hollow carbon steel tube as a corrosion specimen. Refrigerated glycol is circulated on the inside of the tube while the outside is exposed to the corrosion vapor environment. The tube was then later used as a weight loss specimen. The setup also included a condensed water collection cup that was used for condensation water chemistry and rate measurements (Figure 10). The same setup was again used in 2017 in a study published by the same authors [41]. They stressed the importance of performing baseline corrosion inhibition evaluation in the brine (equivalent to bottom of the line corrosion). They also used liquid chromatography–mass spectroscopy (LC-MS) to determine the inhibitor composition and concentration in the condensed water phase as it was not assumed that the same inhibitor components would be present in the vapor phase and in the brine.

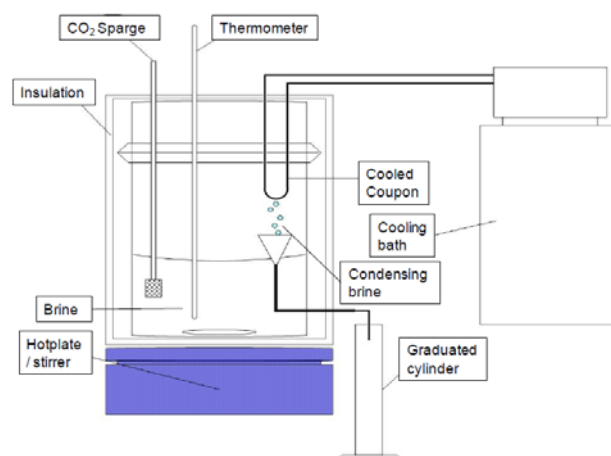


Figure 10: Schematic of TLC test cell proposed by Jenkins *et al.*
(reproduced from [40] – © NACE International 2012)

In 2015, further advanced versions of a VCI testing glass cell setup (Figure 11) were proposed by Yaakob. [42]. They involved most of the innovations proposed by other researchers that have become standards of TLC testing: collection of the condensed water for pH and Fe^{2+} concentration measurements, precise control and direct measurement of condensation rate. In addition, the externally cooled carbon steel specimens were flushed to the top lid, exposing a horizontal surface to the vapor phase. This is thought to better represent the phenomena of dropwise condensation observed in field applications. This particular setup was used extensively to study sweet/sour TLC and was even applied to investigate black powder formation, with a perfected use of thermoelectric coolers [43, 44].

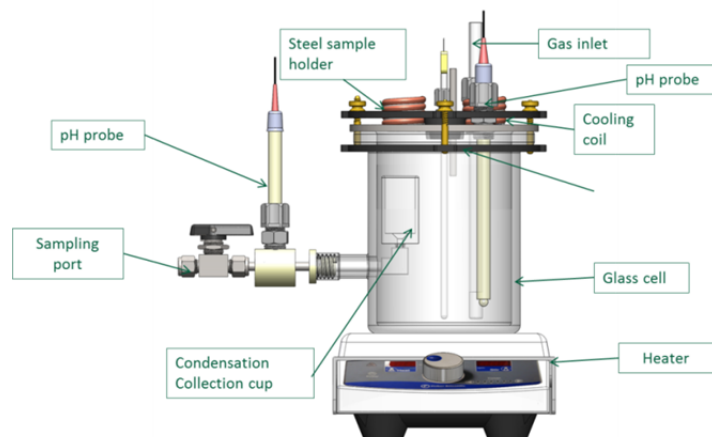


Figure 11: Experimental TLC setup using condensed water collection cup, as proposed by Yaakob *et al.* (reproduced from [42] – © NACE International 2015)

Belarbi extensively used the above setup to investigate the efficiency of model compounds (amines and thiols) as VCIs [23, 24, 25]. The author also adapted the setup for VCI persistency studies in which the brine containing the inhibitor was replenished by non-inhibited brine, while monitoring the corrosion occurring on the carbon steel specimens exposed to the vapor phase. The only drawback in this study was that the TLC rate was monitored exclusively using weight loss specimens. The use of ER or LPR probe could have permitted to monitor continuously the corrosion rate.

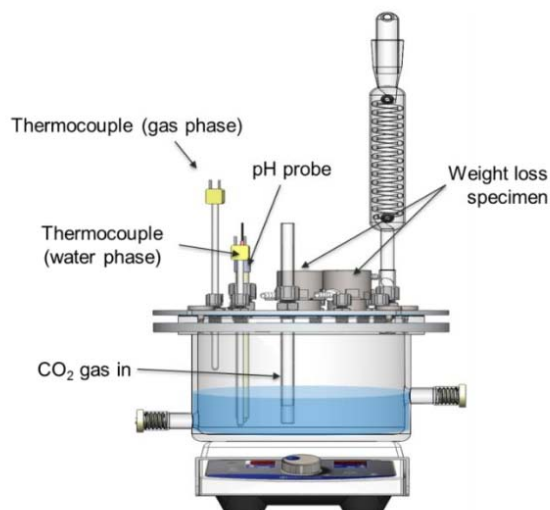


Figure 12: Experimental setup for evaluating efficacy and persistency of VCI candidates for TLC, as proposed by Belarbi *et al.* (reproduced from [25] – © NACE International 2018)

The most recent development in term of small scale TLC setup was proposed by Islam [45, 46]. In addition to the standard condensed water collection cup, the cell was equipped with a linear

polarization resistance (LPR) probe (Figure 13, left), flushed to the top lid and externally cooled. The authors' LPR probe design minimized issues related to solution resistance by decreasing the separation distance between the counter and the working electrode. The cell was also equipped with probes monitoring the liquid, vapor and sensing element temperatures (Figure 13, right).

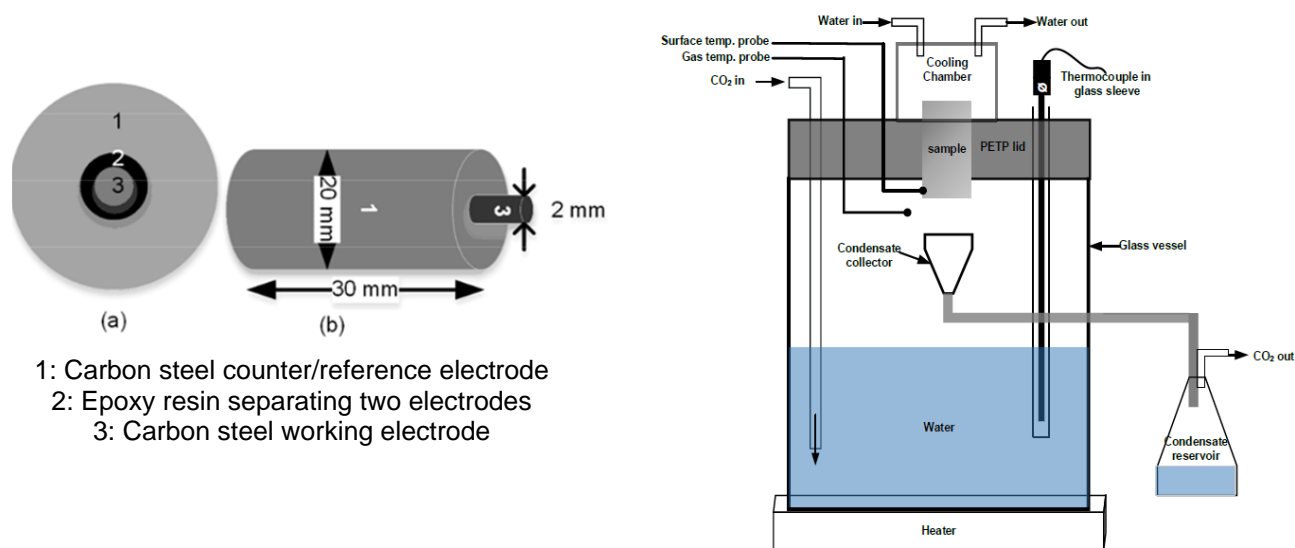


Figure 13: LPR probe (left) and Schematic of TLC setup (right), as proposed by Islam *et al.* (reproduced from [46] – © Corrosion Science 2016)

Other experimental setups have also been developed involving high pressure [39, 47, 48, 49] and flowing systems [50, 51, 52]. Some of them have also been used directly for VCI efficiency evaluation in conditions more representative of the field environments [34, 39]. One of the main challenges in these systems, especially as it relates to autoclave testing, is the accurate control and measurement of condensation rates. They also infer substantially greater capital and operating costs than small scale glass cells. It is not the purpose of this paper to review these types of setup but a review of the challenges in operating procedures will be the topic of future publication.

PROPOSED METHODOLOGY

A comprehensive VCI testing methodology is proposed here, building up on the experience and lessons learned over the years.

The proposed experimental setup is a combination of the apparatus initially presented by Islam [45, 46], Belarbi [25] and Yaakob [42]. It consists of a glass cell (4L or 6L) that is equipped with a set of features designed for top of the line corrosion studies. Figure 14 shows different views of such a setup. The main characteristics of this systems are described below.

- The glass cell must be placed on top of a hot plate to allow for the heating of the bottom solution
- The glass cell should be thermally insulated to better control the fluid and gas temperatures
- A stainless-steel lid equipped with at least two corrosion probe ports (for weight loss, ER or LPR probes), gas inlet and outlet, pH probe port (pH probe has to be long enough to reach the bulk liquid phase), gas and bulk liquid phase temperature probes
- A condenser on the outlet vapor line to prevent depletion of the aqueous phase and of the inhibitor
- A heated pre-bubbler (not shown in the figures) to make sure that the inlet vapor phase enters the cell at the right temperature and humidity level
- A post-bubbler (not shown in the figures) to check that the glass cell holds a positive pressure and to limit oxygen ingress

- A condensed water collection cup (with a volume of around 40mL), connected to a liquid-outlet line for determination of the condensed water chemistry (pH, $[\text{Fe}^{2+}]$, inhibitor concentration) and for measurement of water condensation rate
- A liquid-in/out port on the side of the glass cell to enable replenishment of the liquid phase in case persistency study is warranted

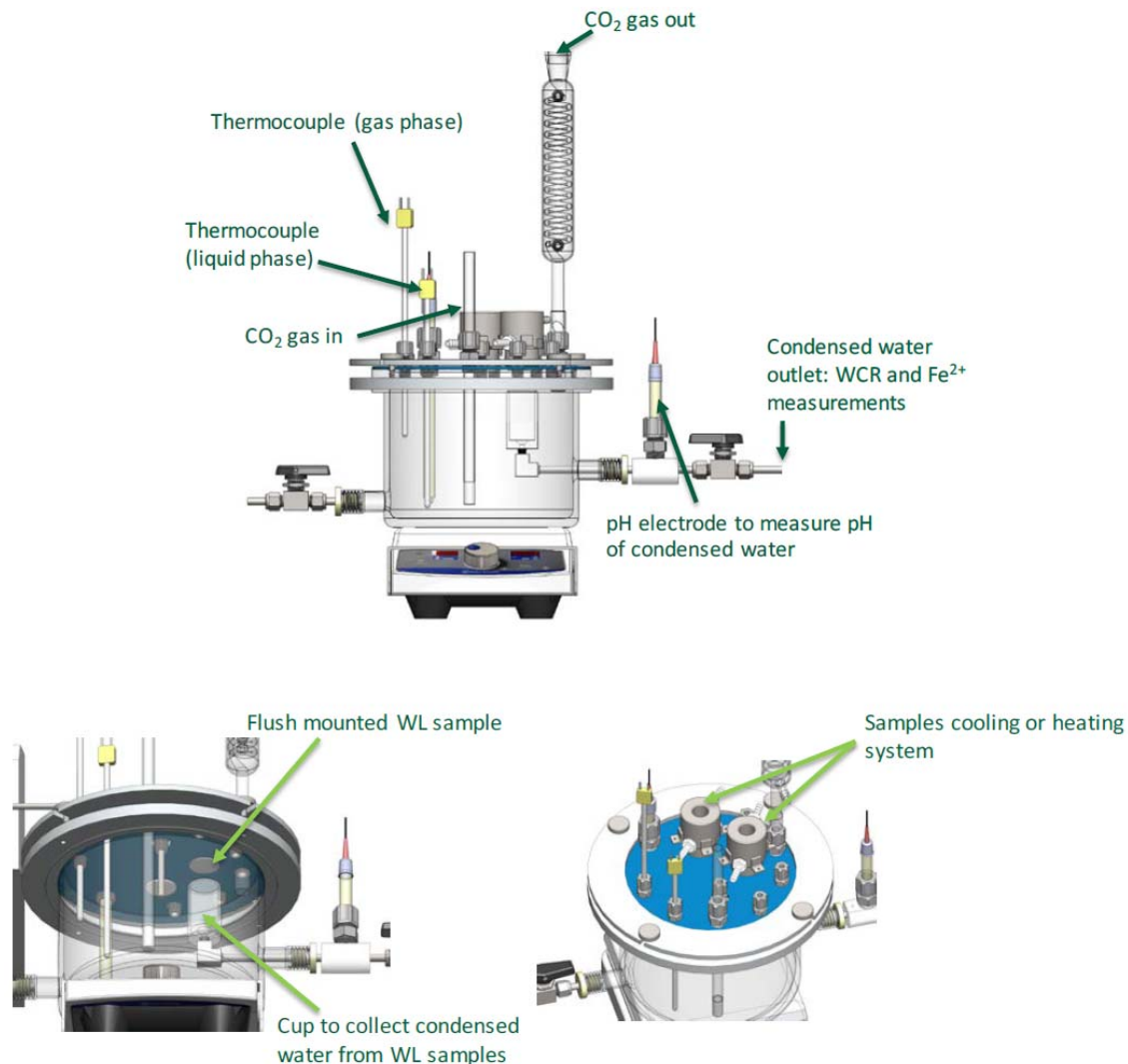


Figure 14: Proposed TLC experimental setup for VCI studies

External cooling on the corrosion probes is also essential and can be achieved following different methodologies:

- For WL probes, a thermoelectric cooler can be connected to the back of the specimen holder (using the appropriate heat transfer glue). This enables precise control of the sample temperature and can even be used to cycle period of heating and cooling.
- For ER or LPR probes (and also for WL probes), a concentric heat exchanger can be mounted on the circular probe body and refrigerator water or glycol can be circulated to cool the specimen. Figure 2 shows a picture of a WL specimen and how it is mounted in the cooling/heating system.

The WL samples should be fabricated from the pipeline steel of interest in a cylindrical shape, with a diameter of at least 3 cm and 1cm height. The faces of the specimen not exposed to the vapor phase should be covered with electrically insulating coating.



Figure 15: (a) picture of a carbon steel WL sample, (b) WL sample mounted in the cooling/heating system.

The proposed experimental procedure is extracted mostly for laboratory experience obtained on VCIs evaluation and published by Belarbi [23-25,44]. It is summarized as follows:

1. 2.5 L of solution are placed in the glass cell and purged with CO_2 (or a mixture of $\text{CO}_2/\text{H}_2\text{S}$) for at least 4 hours, until the O_2 concentration in the outlet gas is measured below 40ppb (via the use of an O_2 sensor). The gas mixture is bubbled throughout the test duration. The bubbler is either directly inserted into the liquid phase or located as close as possible to the liquid/gas interphase in case issues with foaming arise. The WCR will not be significantly affected either way.
2. A WL sample is ground with sand paper to a 600-grit finish, rinsed with DI water and isopropanol and dried in cold air.
3. The WL sample is weighed using an analytical balance with a 0.1 mg readability.
4. The WL/ER/LPR probes are placed in the heating/cooling system and flush-mounted on the lid of the glass cell. The test must be completed in a vent hood and appropriate measures must be taken to avoid exposure to the toxic conditions (H_2S , organic inhibitors, hydrocarbons...).
5. Gas and steel temperature are monitored during the experiment.
6. The appropriate corrosion inhibitor concentration is injected directly in the liquid phase, avoiding any oxygen ingress.
7. The duration of the test depends on the experimental objective. For evaluation of the VCI efficiency on bare steel, 1 or 2 days of exposure is enough if a “black or white” answer is required. Although an accurate corrosion rate will be difficult to obtain due to the low measured mass loss, the surface of the specimen can be investigated for sign of corrosion (corrosion products, surface roughness). However, longer term tests (at least 7 days long) are necessary to distinguish the performances of different VCIs. In addition, if the investigation of the effect of corrosion products (FeS , FeCO_3 ...) is of interest or if information about persistency or localized corrosion is sought, then longer term tests are also required (at least 7 days long).
8. The condensed water is collected as often as possible, typically two times per day depending on the condensation rate.
9. The pH of the condensed water is measured in-situ, while collecting the water.
10. The volume of the collected water is measured to calculate the water condensation rate. In addition, the iron concentration is determined with spectrophotometry by adding a complexing agent to the condensed diluted solution.
11. At the end of the experiments the WL sample is rinsed with isopropanol and dried with nitrogen.
12. The surface characterization of the WL specimens is performed using SEM, EDS and XRD analysis before removal of corrosion product.
13. The weight loss corrosion rate is calculated after the removal of corrosion products with Clarke solution [53].
14. In order to check if there is general or localized corrosion, profilometry analysis is performed after removal of corrosion product layer.

Post analysis of the WL specimens could involve SEM/EDS for surface feature morphology and chemical composition. However, EDS or even X-ray diffraction can only give limited information about

the properties of the inhibitor films as the films are either amorphous or/and too thin. X-Ray Photoelectron Spectroscopy (XPS) can be used to determine whether the inhibitor film is physisorbed or chemisorbed.

Cross section analysis of the WL specimen can also be helpful to look for localized corrosion although profilometry is preferred.

In term of analysis of the condensed water, LC-MS or UV-VIS spectroscopy can be used to characterize the inhibitor composition and concentration [41,54,55]. Using the same method, the concentration of the VCI in the bulk liquid phase should also be measured to confirm there was no depletion during the test.

CONCLUSIONS

The multitude of studies and experimental setups proposed over the years to investigate the efficiency of VCIs has considerably improved the quality and validity of the results. However, it has also added some level of confusion regarding the appropriate methodology to follow. Considering that available standards related to vapor phase corrosion inhibition (ASTM D5534 [26] and NACE TM208 [27]) are not applicable to gas pipelines, it has become quite relevant for the industry to unify all the proposed methodologies and to develop best practices.

This work proposes a methodology for evaluation of VCI performances, based on a review of the most successful experimental setups published in the literature. It is centered around:

- the use of a glass cell experimental setup reproducing representative condensation pattern,
- a tight control of WCR, steel and vapor phase temperatures,
- the use of effective corrosion measurement techniques (WL, ER, LPR),
- the implementation of an appropriate testing methodology and,
- the use of post analysis techniques aimed at acquiring useful information about the adsorbed VCI layer characteristics.

REFERENCES

1. Y. Gunaltun, "Design of multiphase offshore pipelines with high risk of sweet top of the line corrosion", in: *Proc. Corrosion*, Orlando, FL, 2013, paper. 2290.
2. S. Smith, M. Joosten, "Corrosion of carbon steel by H₂S in CO₂ containing environments", In: *Proc. Corrosion*, Houston, TX, 2006, paper. 6115.
3. Y. Gunaltun, D. Supriyataman and A. Jumakludin, "Top of the line corrosion in multiphase gas line. A case history", In: *Proc. Corrosion*, Houston, TX, 1999, paper. 36.
4. M. Singer, D. Hinkson, Z. Zhang, H. Wang, and S. Nesic, "CO₂ Top-of-the-Line Corrosion in Presence of Acetic Acid: A Parametric Study", *Corrosion*, vol. 69, no. 7, 2013.
5. M. Singer, "Study of the Localized Nature of Top of the Line Corrosion in Sweet Environment", *Corrosion*, vol. 73, no. 8, 2017.
6. D. Hinkson, Z. Zhang, M. Singer, S. Nesic, "Chemical composition and corrosiveness of the condensate in top-of-the-line corrosion", *Corrosion*, vol. 66, no. 4, 2010.
7. R. Nyborg, A. Dugstad and T. Martin, "Top of line corrosion with high CO₂ and traces of H₂S", In: *Proc. Corrosion*, Atlanta, GA, 2009, paper. 9283.

8. M. Edwards and B. Cramer, "Top of the line corrosion – Diagnostic, root cause analysis and treatment", In: *Proc. Corrosion*, Houston, TX, 2000, paper. 72.
9. N.N. Bich, K.E. Szklarz, "Crossfield Corrosion Experience", In: *Proc. Corrosion*, Saint Louis, IL, 1988, paper. 196.
10. D.F. Ho-Chung-Qui, A.I. Williamson and P. Eng, "Corrosion experiences and inhibition practices in wet sour gathering systems", In: *Proc. Corrosion*, San Francisco, CA, 1987, paper. 46.
11. Y. Gunaltun, S. Punpruk, M. Thammachart, T. Pornthep, "Worst-case TLC: Cold spot corrosion", In: *Proc. Corrosion*, San Antonio, TX, 2010, paper. 10097.
12. Z. Zhang, D. Hinkson, M. Singer, H. Wang, S. Nesic, "A mechanistic model for Top of the line corrosion", *Corrosion*, vol. 63, no. 11, 2007.
13. C. DeWaard, U. Lotz, D.E. Milliams, Predictive model for CO₂ corrosion engineering in wet natural wet gas pipelines, *Corrosion*, vol. 47, no. 12, 1991.
14. U. Kaewpradap, M. Singer, S. Nesic, S. Punpruk, "Comparison of Model Predictions and Field Data – the Case of Top of the Line Corrosion", *Corrosion*, vol. 73, no. 8, 2017.
15. G. Svenningsen, R. Nyborg, Modeling of Top of the line corrosion with organic acid and glycol, In: *Proc. Corrosion*, San Antonio, TX, 2014, Paper. 4057.
16. F. Vitse, Y. Gunaltun, D. Larrey de Torreben, P. Duchet-Suchaux, Mechanistic model for the prediction of top-of-the-line corrosion risk, In: *Proc. Corrosion*, Houston, TX, 2003, Paper. 3633.
17. S.L. Asher, W. Sun, R.A. Ojifinni, S. Ling, C. Li, J.L. Pacheco, J.L. Nelson, Top of the line corrosion modeling in wet gas pipelines, In: *Proc. 18th International Corrosion Congress*, Perth, Australia, 2011, Paper. 303.
18. M. Thammachart, Y. Gunaltun and S. Punpruk, "The use of inspection results for the evaluation of batch treatment efficiency and the remaining life of the pipelines subjected to top of line corrosion", In: *Proc. Corrosion*, New Orleans, LA, 2008, paper. 8471.
19. B.F.M. Pots, T. Bos, R. Henkes, "Evaluation of CRA requirements to control top of line corrosion at warm gas pipeline tie-in", In: *Proc. 3rd TOL Corrosion conference*, Bangkok, 2012.
20. Y. Gunaltun and D. Larrey, "Correlation of cases of top of the line corrosion with calculated water condensation rates", In: *Proc. Corrosion*, Houston, TX, 2000, paper. 71.
21. Y. Gunaltun, "Design of multiphase offshore pipelines with high risk of sweet top of the line corrosion", In: *Proc. Corrosion*, Orlando, FL, 2013, paper 2290.
22. S. Punpruk, M. Thammachart, Y. Gunaltun, "Field testing of volatile corrosion inhibitors and batch treatment efficiency by cooled probe", In: *Proc. Corrosion*, San Antonio, TX, 2010, paper. 10096.
23. Z. Belarbi, T.N. Vu, F. Farel, D. Young, M. Singer, S. Nesic, "Thiols as volatile corrosion inhibitors for top-of-the-line corrosion", *Corrosion*, vol. 73, no. 7, 2017.
24. Z. Belarbi, F. Farel, M. Singer and S. Nesic, "Role of Amines in the Mitigation of CO₂ Top of the Line Corrosion", *Corrosion*, vol. 72, No. 10, 2016.

25. Z. Belarbi, F. Farel, D. Young, M. Singer, and S. Nesic, "Effect of Operating Parameters on the Inhibition Efficacy of Decanethiol", In: *Proc. Corrosion*, Phoenix, AZ, 2018, paper. 10823.
26. ASTM D5534: Standard Test Method for Vapor Phase Rust-Preventing Characteristics of Hydraulic Fluids. *ASTM International*, 2014.
27. NACE Standard TM0208-2008, Laboratory Test to Evaluate the Vapor-Inhibiting Ability of Volatile Corrosion Inhibitor Materials for Temporary Protection of Ferrous Metal Surfaces. *NACE International*, 2008.
28. B. Bavarian, L. Reiner, Y. Ikder, B. Miksic, "Improving the controlled humidity systems by addition of VpCI", In: *Proc. Corrosion*, Vancouver, Canada, 2016, paper. 7100.
29. R. Fuentes, B. Wiersma, "Laboratory simulation of vapor space corrosion in radioactive waste storage tank", In: *Proc. Corrosion*, Houston, TX, 2015, paper. 5572.
30. J. Gray, et al, "Laboratory testing to simulate vapor space corrosion in radioactive waste storage tanks", In: *Proc. Corrosion*, San Antonio, TX, 2014, paper. 3969
31. M. Singer, M. Achour, C. Li, A. Jenkins, S. Hernandez, "Top of the line corrosion – Part 1: Review of the mechanism and laboratory experience", In: *Proc. Corrosion*, San Antonio, TX, 2014, paper. 4055.
32. S. Olsen, A. Dugstad, "Corrosion under dewing conditions", In: *Proc. Corrosion*, Houston, TX, 1991, paper. 472.
33. B.F.M. Pots, E.L.J.A. Hendriksen, "CO₂ corrosion under scaling conditions – The special case of top-of-the-line corrosion in wet gas pipelines", In: *Proc. Corrosion*, Houston, TX, 2000, paper. 31.
34. Y. Gunaltun, T.E. Pou, M. Singer, C. Duret, S. Espitalier, "Laboratory testing of volatile corrosion inhibitors", In: *Proc. Corrosion*, San Antonio, TX, 2010, paper. 10095.
35. M. Shen, A. Furman, R. Kharshan, T. Whited, "Development of corrosion inhibitors for prevention of TLC", In: *Proc. Corrosion*, Orlando, FL, 2013, paper. 2509.
36. T. Pojtanabuntoeng, M. Singer, S. Nesic, "Water/Hydrocarbon co-condensation and the influence on top-of-the-line corrosion", In: *Proc. Corrosion*, Houston, TX, 2011, paper. 11330.
37. V. Jovancicevic, S. Ramachandran, K. Cattanch, I. Ahmed, "TLC control by volatile corrosion inhibitors in sweet gas systems", In: *Proc. 3rd TOL Corrosion conference*, Bangkok, 2012.
38. M. Cough, I. Salim, R. Saberon, M.H. Asraf., "Design and development of inhibitors for TOL corrosion control", In: *Proc. 3rd TOL Corrosion conference*, Bangkok, 2012.
39. M.C. Oehler, S.I. Bailey, R. Gubner, M. Cough, "Testing of generic VCI compounds in different TLC laboratory test methods", In: *Proc. Corrosion*, Salt Lake City, UT, 2012, paper. 1483.
40. A. Jenkins, I. Gilbert, "Development of a top of the line corrosion inhibitor and a top of the line corrosion test method", In: *Proc. Corrosion*, Salt Lake City, UT, 2012, paper. 1275.
41. A. Jenkins, I. Gilbert, A. Kamaruzaman, A. Lone, "Top-of-Line Corrosion Inhibition and Proposal of an Inhibition Mechanism", In: *Proc. Corrosion*, Phoenix, AZ, 2018, paper. 11117.
42. N. Yaakob, Localized TLC in marginally sour environments, PhD dissertation, Ohio University, 2015.

43. M. Colahan, D. Young, M. Singer, and R. P. Nogueira, "Black powder formation by dewing and hygroscopic corrosion processes", *Journal of Natural Gas Science and Engineering*, vol. 56, 2018.
44. Z. Belarbi, B. George, N. Moradighadi, D. Young, S. Nesic, M. Singer, and R. P. Nogueira, "Volatile Corrosion Inhibitor for Prevention of Black Powder in Sales Gas Pipelines", In: *Proc. Corrosion*, Phoenix, AZ, 2018, paper. 10962.
45. M. Islam, T. Pojtanabuntoeng, R. Gubner, "Study of the top-of-the-line corrosion using a novel electrochemical probe", *Corrosion*, vol. 74, no. 5, 2018.
46. M. Islam, T. Pojtanabuntoeng, R. Gubner, "Condensation corrosion of carbon steel at low to moderate surface temperature and iron carbonate precipitation kinetics", *Corrosion Science*, vol. 111, 2016.
47. M. Singer, "Top of the line corrosion in sour environments – Study of the controlling parameters", In: *Proc. International Corrosion Congress*, Perth, 2011, paper. 80.
48. L. Zhang, J. Yang, M. Lu, "Effect of pressure on wet H₂S/CO₂ corrosion of pipeline steel", In: *Proc. Corrosion*, Atlanta, GA, 2009, paper. 9565.
49. H. Qin, L. Xu, W. Chang, M. Lu, L. Zhang, "Top of the line corrosion under low temperature and high condensation rate conditions", In: *Proc. Corrosion*, Houston, TX, 2011, paper. 11328.
50. F. Vitse, Y. Gunaltun, D. Larrey de Torreben and P. Duchet-Suchaux, "Mechanistic model for the prediction of top-of-the-line corrosion risk", In: *Proc. Corrosion*, Houston, TX, 2003, paper. 3633.
51. T. Andersen, A.M.K. Halvorsen, A. Valle and G. Kojen, "The influence of condensation rate and acetic acid concentration on TOL corrosion in multiphase pipelines", In: *Proc. Corrosion*, Nashville, TN, 2007, paper. 7312.
52. R. Nyborg, A. Dugstad and T. Martin, "Top of line corrosion with high CO₂ and traces of H₂S", In: *Proc. Corrosion*, Atlanta, GA, 2009, paper. 9283.
53. ASTM G1: Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens, *ASTM International*, 2017.
54. Y. Ding, B. Brown, D. Young, M. Singer, "Effectiveness of an imidazoline-type inhibitor against CO₂ corrosion of mild steel at elevated temperatures (120°C-150°C)", In: *Proc. Corrosion*, Phoenix, AZ, 2018, paper. 11622.
55. J. Anthony, R. Harrington, C. Durnell, J. Sanders, D. Gerritsen, G. de vries, H. Sonke, "Lessons learned from residual corrosion inhibitor measurements by LC-MS in a mature north sea gas/condensate/MEG production system", In: *Proc. Society of Petroleum Engineer*, Aberdeen, Scotland, paper. 190902.