Pitting Corrosion on the un-protected tank bottom

Influence of Particle Size of Vapor Corrosion Inhibitor V_pCI 309 and V_pCI 309 DPM Powders on their Inhibiting Effectiveness for Above Ground Tank Bottoms

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March 2016

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Summary

The protection effectiveness of commercially available vapor corrosion inhibitors powders (V$_p$CI 309 and V$_p$CI 309 DPM) with different particle size was evaluated. Conventional powder size of VpCI 309 and nano-particle powder inhibiting of V$_p$CI 309 DPM effectiveness was compared using the vapor-inhibiting ability (VIA) NACE TM 208. Optical microscopy post VIA corrosion tests revealed that the particle size of inhibitor powder has a significant influence on the degree of protection. The VCI 309 DPM nano-particle inhibitor showed a corrosion rating grade 4 and more than 41% decrease on the corrosion rate compared with the inhibitor with coarse particle size VCI 309. Surface coverage also showed improvement mainly due to increase of effective surface area and the partial pressure of vapor inhibitors as powder particle size decreased. Adsorption energy was roughly -16,740 J/mol for VCI 309 DPM nano-particle size inhibitor, while, adsorption energy is roughly -13,660 J/mol for the coarse-particle size VCI 309 inhibitor, indicative of a stronger physical adsorption to the metal surface for (nano) VCI 309 DPM than the coarse inhibitor, leading to better corrosion protection. Laser Doppler Velocimetry (LDV) or Laser Doppler Anemometry (LDA) measurement using the Doppler shift in a laser beam to measure the flow velocity showed a velocity of 6-7 ft/sec for VCI 309 DPM and uniform flow. VCI 309 (coarse) had a lower velocity of 3-4 ft/sec and non-uniform flow.

Key words: corrosion inhibitor, vapor corrosion inhibitor, nanoparticles, localized corrosion, adhesion model, Laser Doppler Velocimetry

INTRODUCTION

Corrosion inhibitors can adsorb to a metal surface, protecting it from the environment by forming a non-reactive, hydrophobic layer that prevents corrosion. To be effective, an inhibitor will interact with the anodic or cathodic sites to slow oxidation and reduction reactions. Vapor Phase Corrosion Inhibitors (VCIs) rely on vapor pressure for transport of active inhibitor compounds. VCIs form a bond with the metal surface and create a barrier layer to minimize corrosive ions on the surface. VCIs can be used alone or can be incorporated into packaging materials, oils, chemicals and coatings. Some applications have been demonstrated for long term (2 years or more) storage of LNG gas piping in Abu Dhabi, power and desalination plant boiler tubes, also in Abu Dhabi, and gas pipe flanges in Wales [1]. Other applications include above ground storage tanks with underside corrosion between the tank bottom plate and its concrete foundation.

The mechanism of the NANO-VCIs involves the transport of the inhibitor to the metal surface and the inhibitor interaction with the metal substrate to form a protective film.

When added to a liquid coating, the inhibitors react with water and dissociates. After application, as the liquid coating cures, the charged inhibitors migrate and adsorb onto the bare metal surface; adsorption occurs as a result of electrostatic forces between the electric charge of the metal and the ionic charges of the inhibitor molecules. Once attached to the metal, the tails of the inhibiting molecules produce a highly hydrophobic film that repels water and other corrosive species, which in turn reduces corrosion [2]. A good level of corrosion protection can be obtained with an inhibitor that forms a passive micro-hydrophobic layer on the metal surface using micron sized powder particles. However, as a result of the larger particle size, gaps may exist between the particles that are deposited on to the metal surface. This lack of coverage provides an opening for corrosive species to attack the unprotected surface [Figure 1].

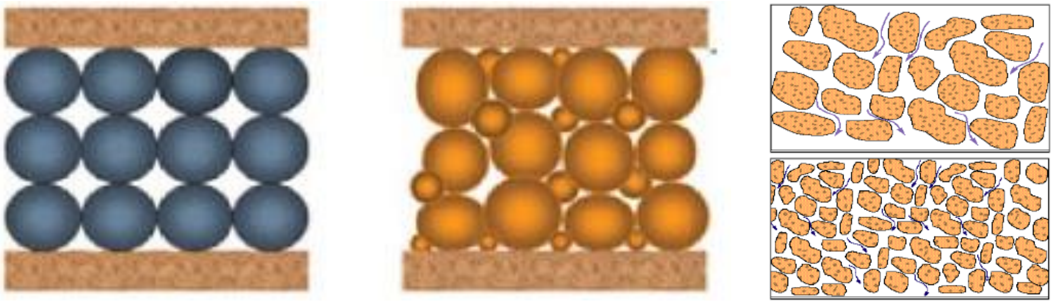


Figure 1: particle size variation can lead to ingress of corrosive species that may attack the surface of the metal.

Particle size influences many properties and is a valuable indicator of performance. This is true for powders, suspensions, emulsions and aerosols. The size and shape of powders influences flow and compaction properties. Larger, more spherical particles will typically flow more easily than smaller particles that tend to agglomerate [3]. Smaller particles dissolve more quickly and lead to higher suspension viscosities than larger ones. In the case of a vapor phase corrosion inhibitors, size also matters. Figure 2 shows a comparison of particles, contaminants and agglomeration of small particles, all of which can influence the effectiveness of corrosion protection. Nanotechnology deals with structures that are 100 nanometers (nm) or smaller and involves developing materials or devices within that size range. To improve corrosion performance nano-sized powders are incorporated into vapor corrosion inhibitors. Particle deposition is the spontaneous attachment of particles to surfaces. The particles in question are normally colloidal particles, while the surfaces involved may be planar, curved, or may represent particles much larger in size than the depositing ones. Depositing particles may form a monolayer which inhibits further particle deposition or may facilitate further particle deposition depending on the dynamics.

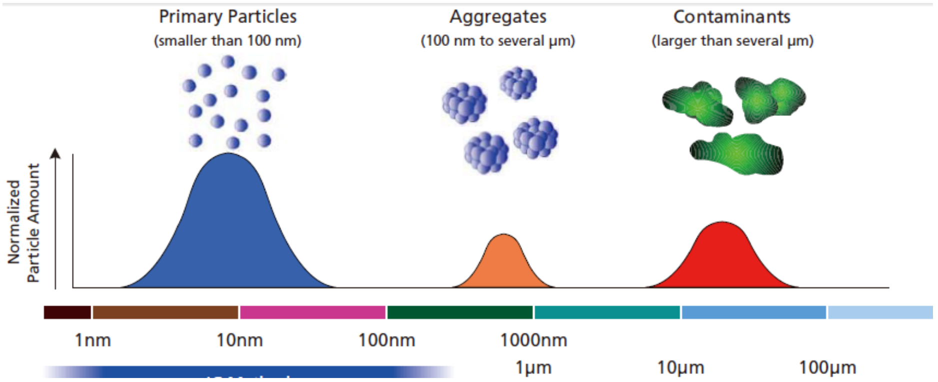


Figure 2: Relative size for particles, aggregates and corrosive species.

As determined in this research, the vapor phase inhibitors adsorbed to the metal surface by physiosorption. Irving Langmuir developed an adsorption isotherm that models gases adsorbed to solid surfaces [4]. It is a semi-empirical isotherm with a kinetic basis and was derived based on statistical thermodynamics. It is the most common isotherm equation to use due to its simplicity and its ability to fit a variety of adsorption data. It is based on four assumptions:

1. All of the adsorption sites are equivalent and each site can only accommodate one molecule.
2. The surface is energetically homogeneous and adsorbed molecules do not interact.
3. There are no phase transitions.
4. At the maximum adsorption, only a monolayer is formed. Adsorption only occurs on localized sites on the surface, not with other adsorbates.

Some of the criteria assumed in Langmuir’s model do not fit with the observations from this investigation. There are always imperfections on the surface, adsorbed molecules are not necessarily inert, and the mechanism is clearly not the same for the first molecules to adsorb to a surface as for the last molecules. Another condition has to do with the thickness of particle deposition, and more likely, molecules will adsorb to the initial monolayer. Despite its shortcomings, the Langmuir isotherm has many applications in surface kinetics. For the BET model (an isotherm developed by Stephen **B**runauer, Paul **E**mmett, and Edward **T**eller), given that the four assumptions made to fit the Langmuir isotherm model are, in general, not realistic, it is assumed that the molecules may form multilayers. However, BET theory ignores inhomogeneity of the surface and lateral adsorbate-adsorbate interactions [5].

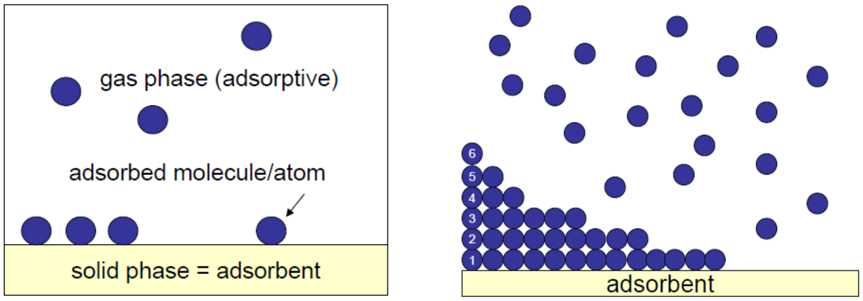
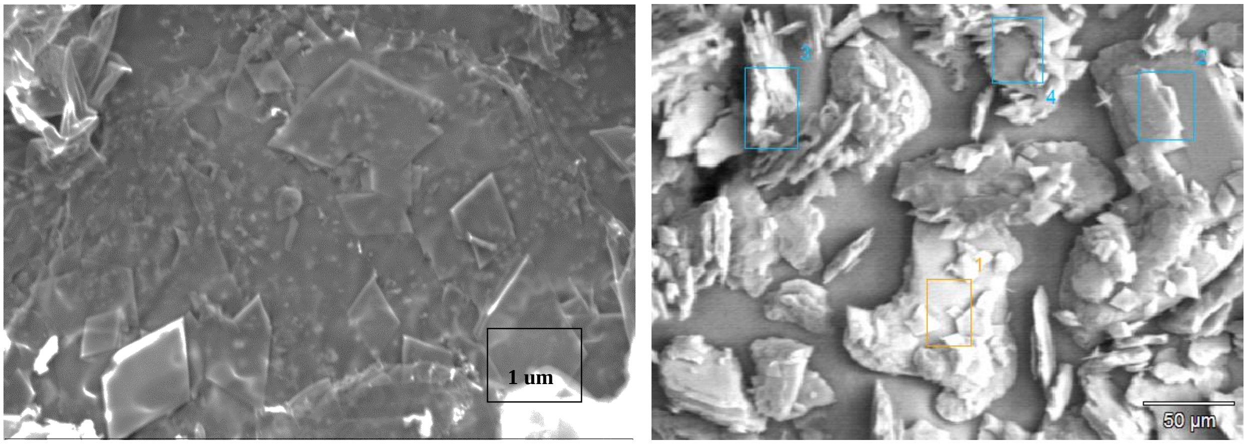


Figure 3: Atomic models for possible types of surface coverage, monolayer or multiple particle deposition on the metal [5].

EXPERIMENTAL PROCEDURE

Corrosion behavior of carbon steel (UNS G10180) samples were studied in two different vapor corrosion inhibitors with coarse particle size (~150 um, V_pCI 309 refer to as VCI-A-C) and vapor corrosion inhibitors with nanoparticle size (~500 nm, V_pCI 309 DPM refer to as VCI-A-N) using the NACE TM 208-2008 Standard Test Method. [6]. Figure 4 shows SEM micrographs of these inhibitors, demonstrating the difference of the particle size for these two inhibitors.



VCI 309 DPM size particle

VCI 309 Coarse particle

Figure 4: SEM micrographs shows particle size and distributions for VCI 309 and VCI 309 DPM.

This laboratory test method evaluates the vapor-inhibiting ability (VIA) of various forms of VCI materials for temporary corrosion protection of ferrous metal surfaces. The VIA corrosion test method provides for standard conditions in a test jar of water-saturated, warm air without the presence of accelerating contaminants. The combination of (1) vapor transport across a gap containing air, water vapor and VCI, and (2) corrosion protection are evaluated in this test method. The VIA tests consist of four steps of sample conditioning or saturation for 20 hours at 22 °C, cooling cycle at 2°C, pre-warming at 50°C, followed by three hours at 22 °C for specimen conditioning. After the last three hour conditioning period, the steel samples were inspected for visible water condensation. Following verification of water condensation on each sample, visual examination of the surface was done and microscopic observation was conducted to determine the corrosion rating for each sample. The corrosion criteria for rating steel specimens consist of grade 0 through grade 4 (Figure 5). To have a valid test, the control sample must have grade 0; samples with no inhibitor received worst grade. The control samples consistently rated a grade 0 for all VIA tests, therefore, validating the test method. Relative humidity and the temperature of each test jar were monitored by (Sensirion) sensors and data logging software. Figure 6 shows relative humidity and the temperature changes during these tests.

Samples were visually inspected and their surface conditions were documented after VIA tests were completed. Photography, optical microscopy and SEM/EDAX analysis were conducted using a JEOL JSM-6480LV and Thermo System Seven detector.

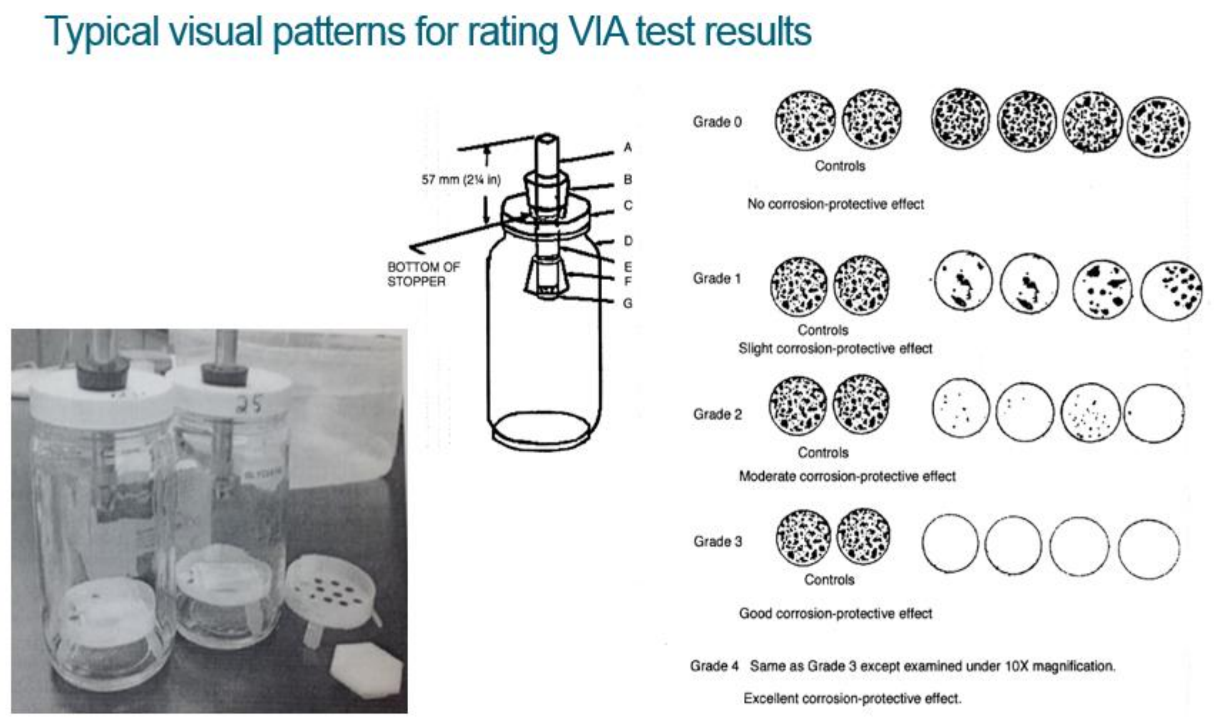


Figure 5: Test setup and rating criteria for the NACE TM 208-2008 Standard Test Method.

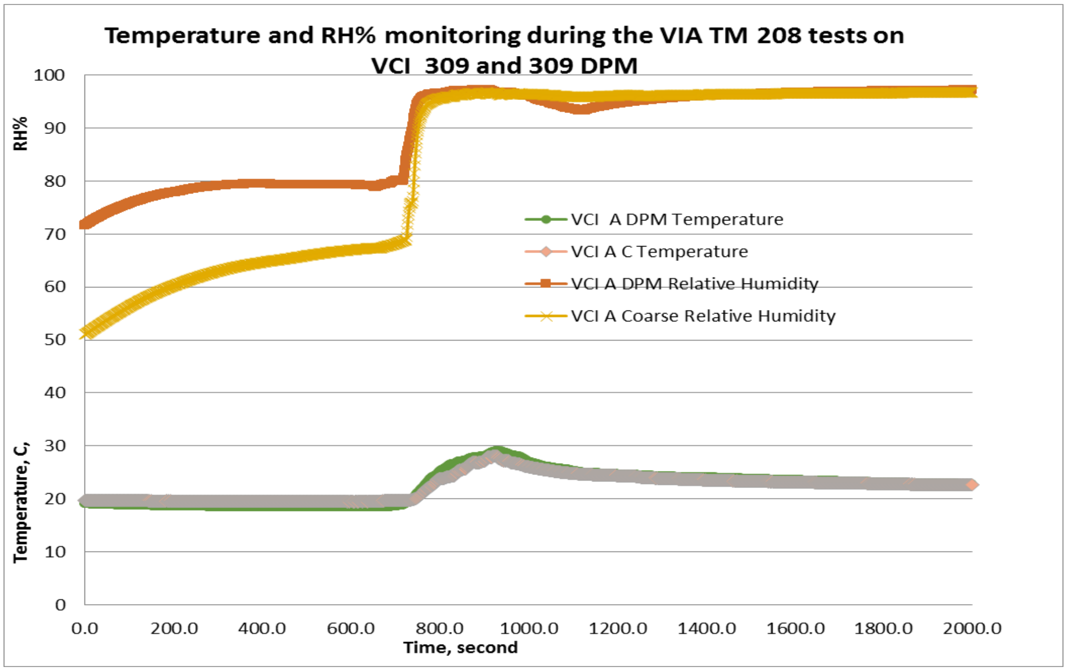


Figure 6: Monitoring temperature and RH% during TM 208 tests.

Electrochemical polarization standards for corrosion rate and resistance polarization (Rp/CR) measurements using Gamry Rp/CR techniques were also used to evaluate the behavior of this inhibitor on the steel samples in 200 ppm chloride solution and to compare overall corrosion behavior of these different particle size corrosion inhibitors. These electrochemical tests were conducted using Gamry PC4/750 Potentiostat/Galvanostat/ZRA instrumentation and DC105 corrosion test software. Samples were polished (1.0 um), placed in a flat cell and tested in deionized water solutions containing 200 ppm Cl^- and 1.0% VCI inhibitor.

Laser Doppler Velocimetry (LDV) or Laser Doppler Anemometry (LDA) is the technique of using the Doppler shift in a laser beam to measure the velocity in a flow, or the linear or vibratory motion of particles. The measurement with LDA is absolute and linear with velocity and requires no pre-calibration. Flow pattern and particle velocity measurements were conducted for the V_pCI309 and V_pCI309 DPM using Laser Doppler Anemometry (LDA). A square chamber of 6 ft (180 cm) long was used and 0.5 grams of each VCI particles were injected into chamber using a 20 psi dry air. LDA measurements was initiated after 15 seconds of spraying to maintain a continuous flow.

RESULTS

Electrochemical polarization test results for the polarization resistance and corrosion rate measurements are shown in Figures 7-8. Both corrosion rate and polarization resistance data showed that VCI 309 DPM nano particles have a 41% lower corrosion rate compared with the coarse particle size.

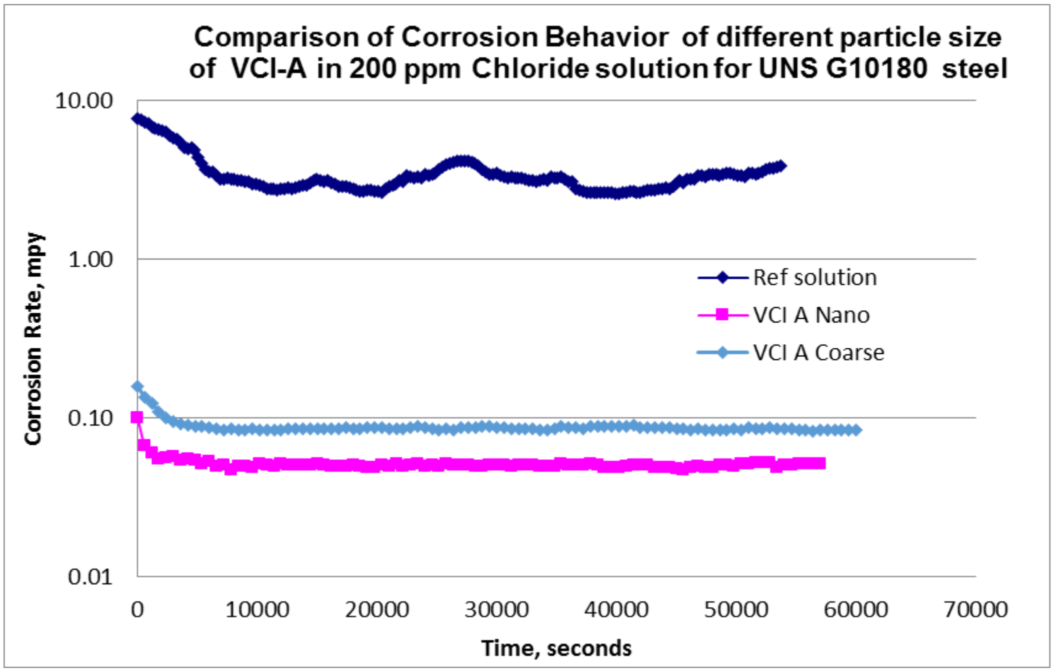


Figure 7: Comparison of corrosion behavior of different particle size for VCI 309 and VCI 309 DPM in 200 ppm chloride solution for UNS G10180 steel.

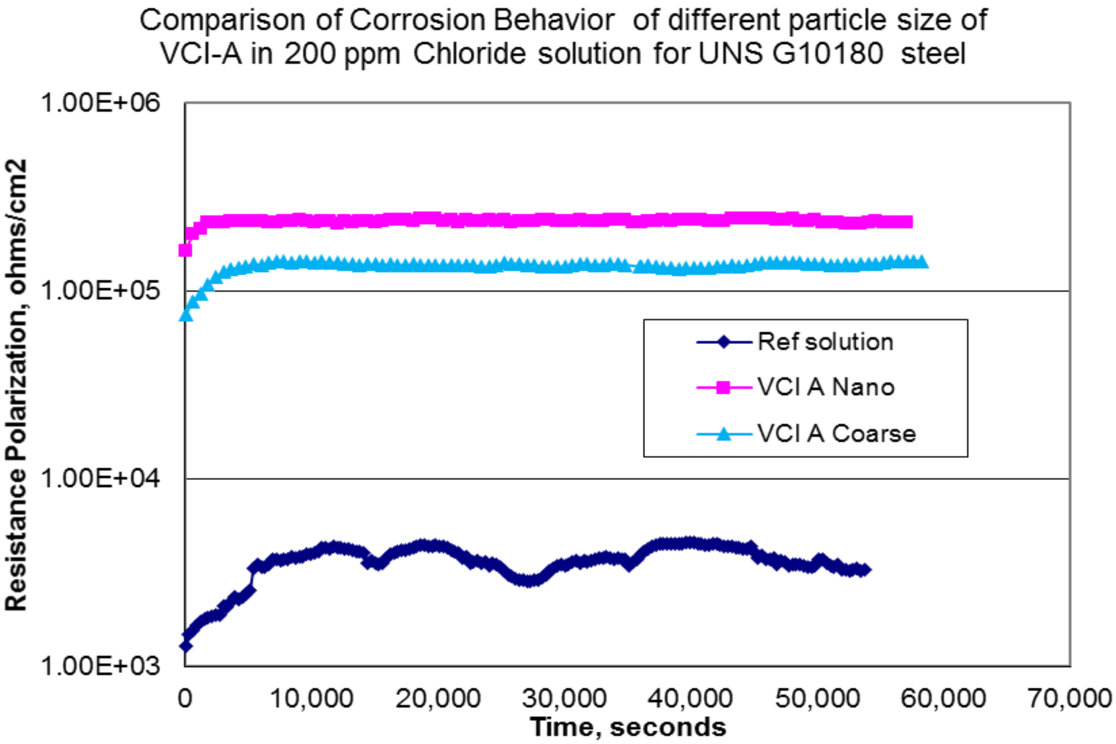
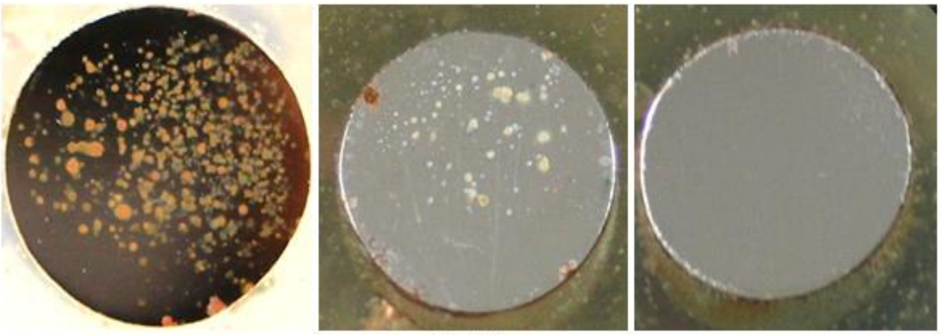
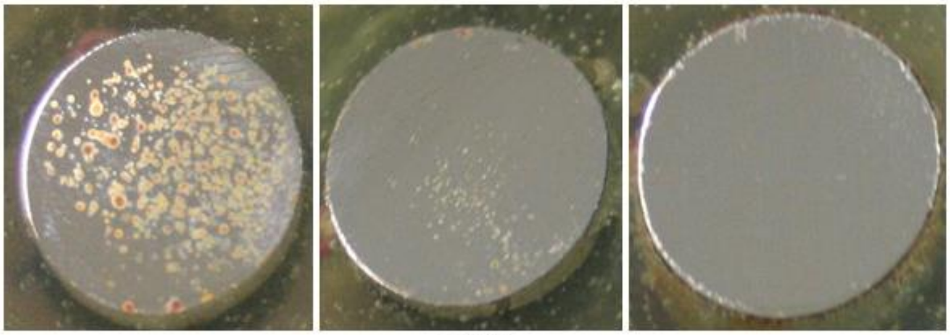


Figure 8: Comparison of polarization resistance for different particle size of VCI 309 and VCI 309 DPM in 200 ppm chloride solution for UNS G10180 steel.

The VIA visual observations are shown in Figure 9. The corrosion rating per TM-208 indicated that the control sample had Grade 0, while VCI-A coarse (309) rating was Grade 2, and VCI-A nano (309 DPM) rating was Grade 4. Optical micrographs of the surface condition of samples after VIA tests is shown in Figure 10. Figure 11 shows SEM micrographs of the steel sample after VIA tests. The high resolution SEM images show a significant improvement for VCI 309 DPM with no sign of any pitting corrosion. The black dots on the VCI-309 and 309 DPM nano samples are mainly alloy inclusions. The VCI-A nano 309 DPM tested samples showed superior corrosion protection during VIA tests.



Test#1



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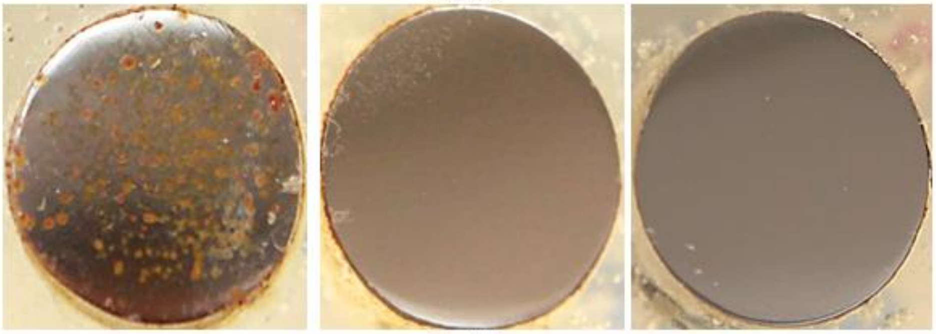


Test#3

Control: Grade 0 VCI-A Course: Grade 2 VCI-A Nano: Grade 4

Figure 9: Photographs of steel samples after VIA tests and their corrosion rating; shows superior performance for VCI 309 DPM exposed samples.

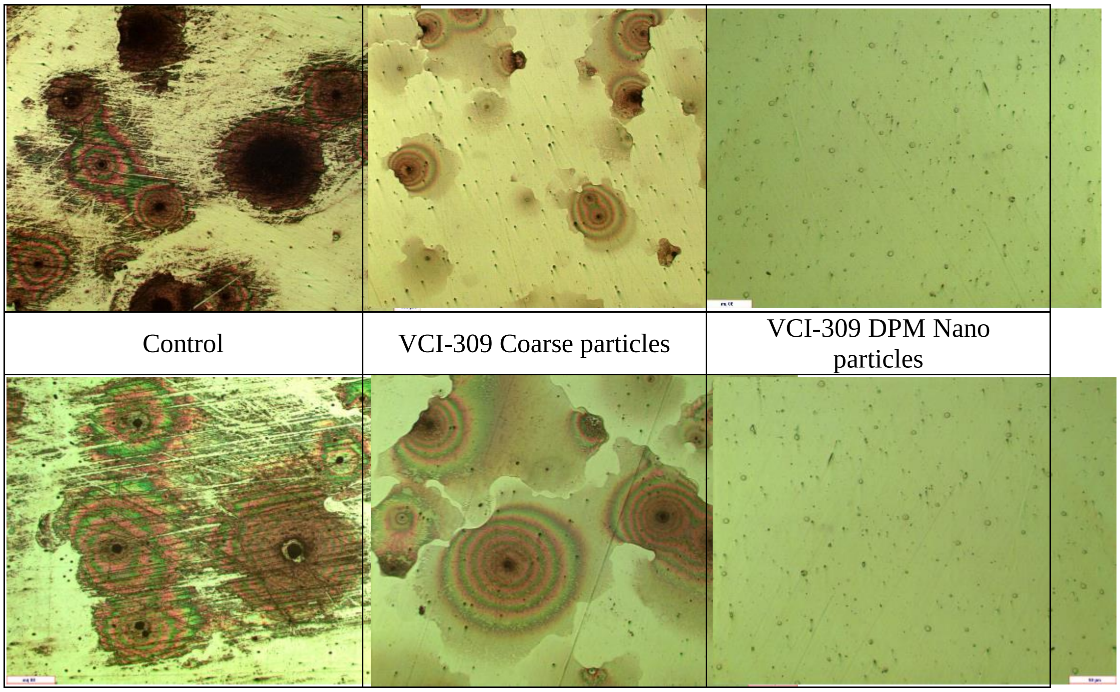
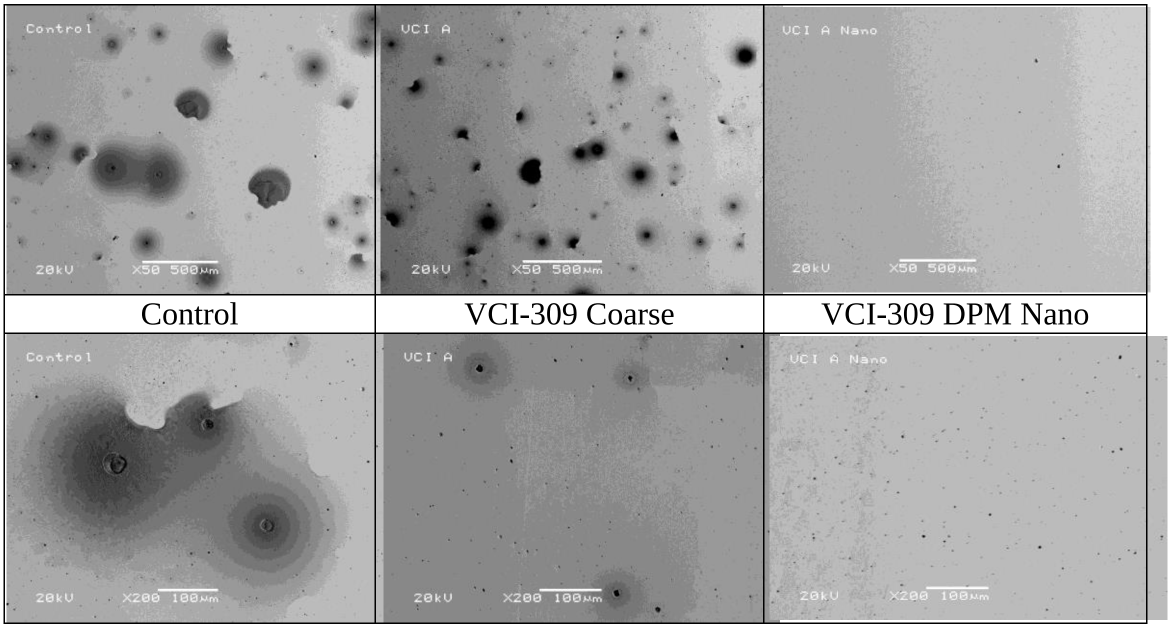

Control | VCI-309 Coarse particles | VCI-309 DPM Nano particles

Figure 10: Optical micrographs of steel samples after VIA tests; superior performance is seen for VCI-309 and 309 DPM nano exposed samples.



Control | VCI-309 Coarse | VCI-309 DPM Nano

Figure 11: SEM micrographs of steel sample after VIA tests. Superior performance for VCI-A nano exposed samples. The black dots on the VCI-309 and 309 DPM nano samples are mainly alloy inclusions.

Inhibitor Adsorption Mechanism

The adsorption isotherm relationship between surface coverage and temperature for both VCI-309 coarse and VCI-A nano 309 DPM inhibitors on the surface of steel is shown in Figure 12. Adsorption energy was roughly -16,740 J/mol for the nanoparticle size inhibitor, while, adsorption energy was roughly -13,660 J/mol for the coarse-particle size inhibitor. This energy range is indicative of a strong physical adsorption to the metal surface. However, it can be seen that interaction of VCI-A nano with the steel surface is higher than the coarse inhibitor, leading to better corrosion protection. The size effect of this inhibitor appears to be more pronounced at higher temperature than the room temperature. XPS depth profiling analysis showed ~ 60-80 nm of adsorbed inhibitor on the exposed samples, indicating that multilayer Brunauer Emmett Teller Model (BET Model) is more realistic adsorption model than the monolayer Langmuir model for this case. But for the adhesion energy calculation between inhibitor molecules and metal surface, it is appropriate to use the monolayer Langmuir model.

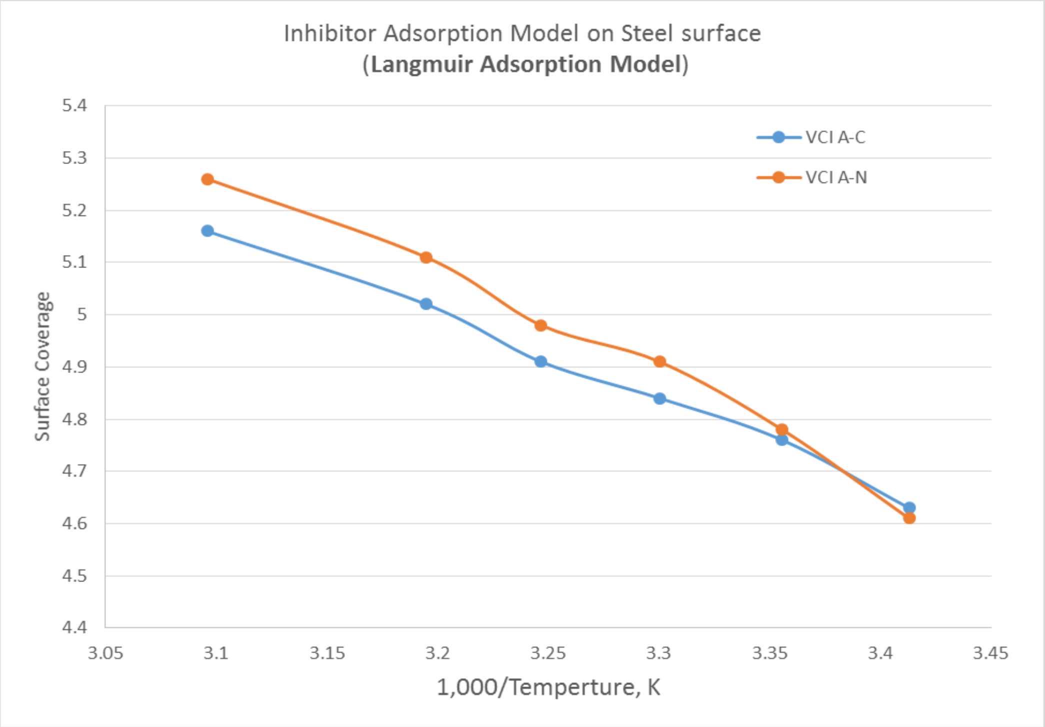


Figure 12: The adsorption isotherm relationship between surface coverage and temperature for VCI inhibitor on the surface of steel. Adsorption energy was roughly -16,740 J/mol for the nanoparticle size inhibitor, while, adsorption energy was roughly -13,660 J/mol for the coarse-particle size inhibitor.

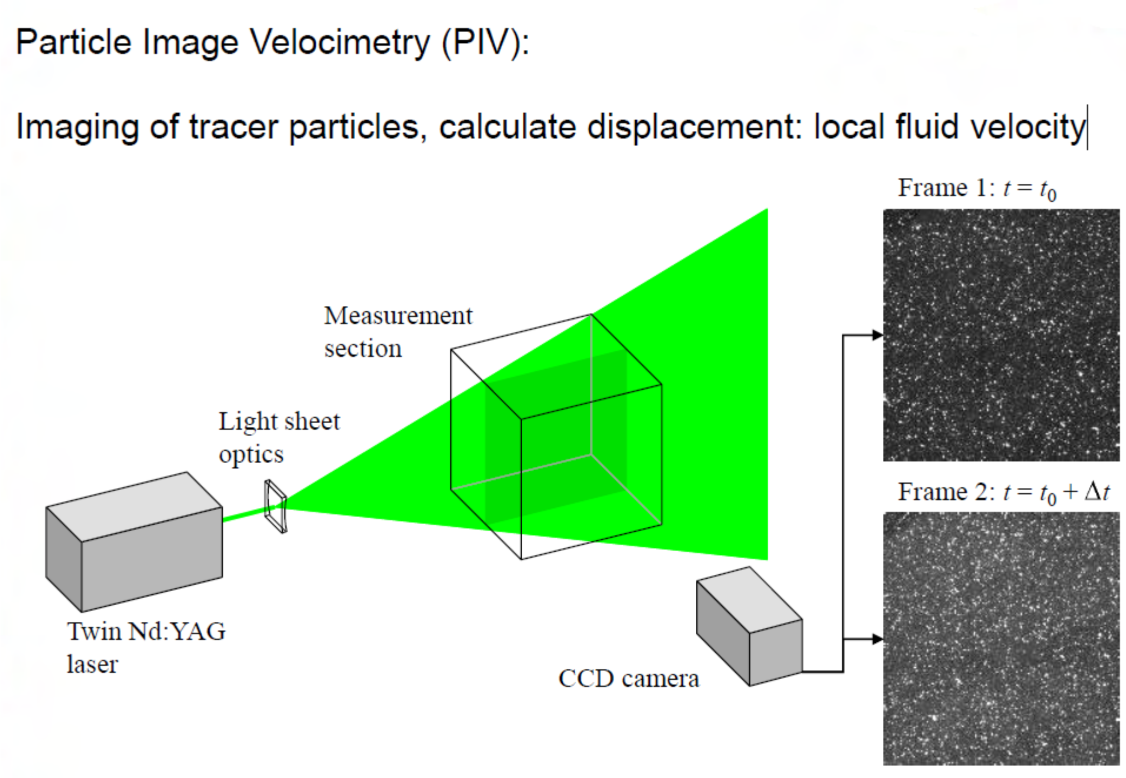
Comparison of flow rate and velocity for VCI 309 and VCI 309 DPM

Almost all industrial flows are turbulent. All naturally occurring flows on earth, in oceans, and atmosphere are turbulent. Turbulent motion is 3D, vortical, and diffusive governing

Navier-Stokes equation (Eqn 1) are very hard (or impossible) to solve. It requires numerous simplification and assumptions that interfere with the outcomes.

(Eqn 1)
$$\rho \frac{Du_i}{Dt} = \frac{\partial \tau_{ij}}{\partial X_j} + \rho f_i - \frac{\partial p}{\partial X_j}$$

Therefore, measurements are easier using Particle Image Velocimetry (PIV, Figure 13), Laser Doppler Velocimetry (LDV) or Laser Doppler Anemometry (LDA) as seen in Figure 14.



Particle Image Velocimetry (PIV):

Imaging of tracer particles, calculate displacement: local fluid velocity

Figure 13: Particle Image Velocimetry (PIV)

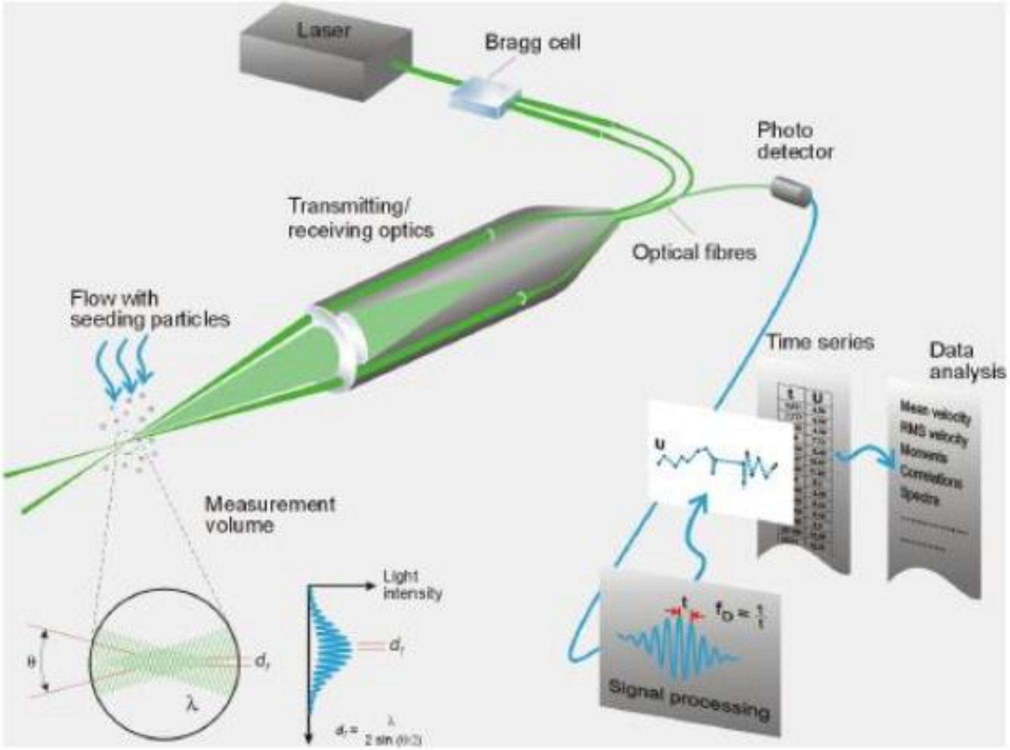


Figure 14: Laser Doppler Velocimetry (LDV) and Laser Doppler Anemometry (LDA)

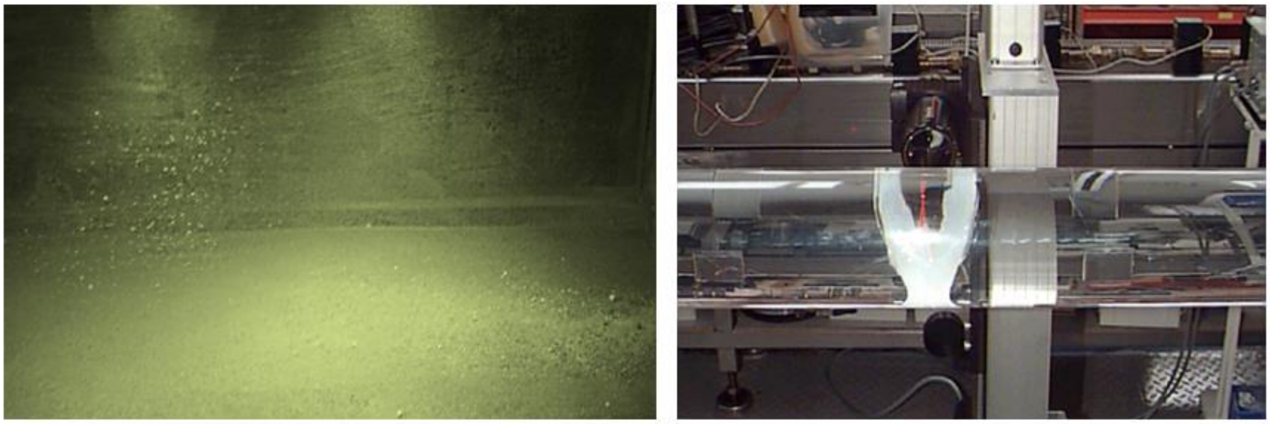
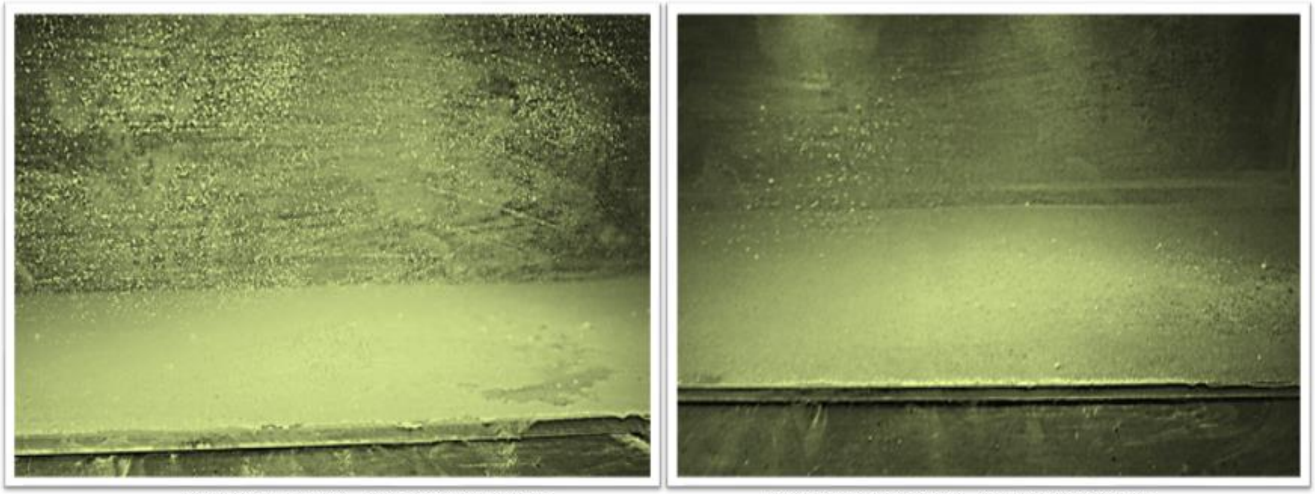


Figure 15: Setup used for the Laser Doppler velocimetry (LDV) measurements.



VCI 309 DPM , 20 psi flow rate

Coarse VCI 309, 20 psi flow rate

Figure 16: Shows the flow of VCI 309 and VCI 309 DPM during Laser Doppler Velocimetry (LDV) measurements.

Laser Doppler Velocimetry (LDV) or Laser Doppler Anemometry (LDA) is the technique of using the Doppler shift in a laser beam to measure the velocity in a flow, or the linear or vibratory motion of particles. The measurement with LDA is absolute and linear with velocity and requires no pre-calibration. Laser Doppler Anemometry (LDA) is a high resolution, single point technique for velocity measurements in turbulent flows. LDA works based on a seed flow with small tracer particles illuminating the flow with one or more coherent, polarized laser beams to form a MV (measurement volume). The system receives scattered light from particles passing through the MV that interfere. Measurement of the resultant light intensity frequency is related to particle velocity. Figure 15 shows a typical setup that is used for flow and velocity measurements. Laser Doppler Anemometry (LDA) measurement using the Doppler measurements showed that V_pCI 309 DPM had a velocity of 6-7 ft/sec and uniform flow. While V_pCI 309 coarse had a velocity of 3-4 ft/sec and non-uniform flow.

CONCLUSIONS

The effectiveness of commercially available vapor corrosion inhibitors powders with different particle size was evaluated. Conventional powder size and nano-particle powder inhibiting effectiveness was compared. Optical microscopy post VIA corrosion tests revealed that the particle size of inhibitor powder has a significant influence on the degree of protection. The nano-particle V_pCI 309 DPM inhibitor showed a corrosion rating grade 4 and more than 41% decrease on the corrosion rate. Surface coverage also showed improvement due to increase of effective surface area and the partial pressure of vapor inhibitors as powder particle size decreased. Adsorption energy was roughly -16,740 J/mol for nano-particle size V_pCI 309 DPM inhibitor, while, adsorption energy was roughly -13,660 J/mol for the coarse-particle size inhibitor, indicative of a strong physical adsorption to the metal surface for both inhibitors. However, V_pCI 309

DPM nano showed a stronger interaction with steel surface than the coarse inhibitor, leading to better corrosion protection.

Laser Doppler Velocimetry (LDV) or Laser Doppler Anemometry (LDA) measurement using the Doppler measurements showed that VCI 309 DPM had a velocity of 5-7 ft/sec and uniform flow. While VCI 309 coarse had a velocity of 3-4 ft/sec and non-uniform flow.

In summary, these investigation showed that the nano-particle powder inhibitor such as VCI 309 DPM provides better corrosion protection, and higher flow ability and velocity that provide more effectiveness in field applications such as the bottom of the above ground tanks.

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