Comparison of the Corrosion Protection Effectiveness of Vapor Corrosion Inhibitor and Nitrogen Blanketing System

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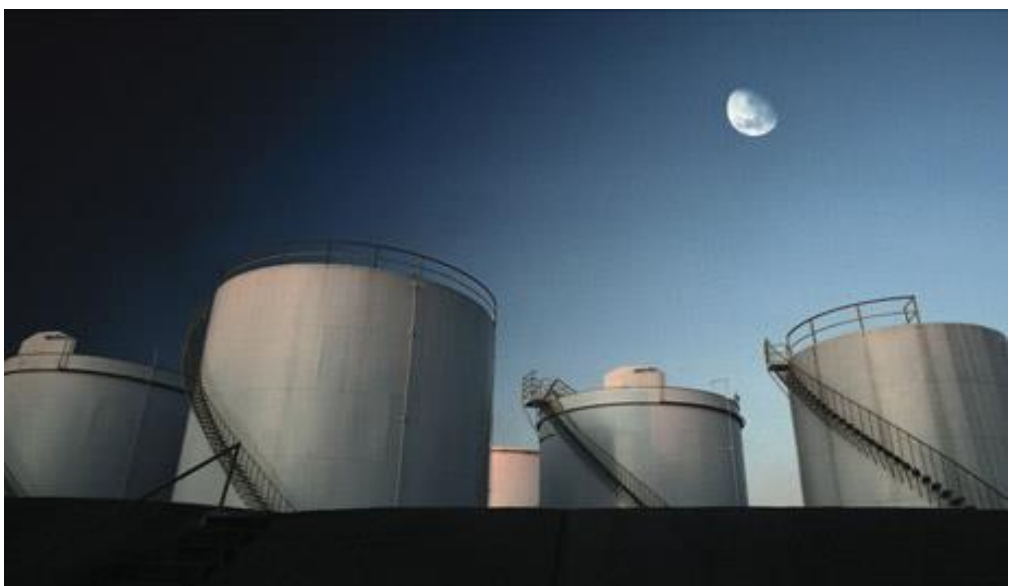

CORROSION 2015
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Steel storage tanks

- Steel storage tanks are used throughout the world in power generation, municipal water, biodiesel, mining, waste, oil and gas.
- Their prevalence is not surprising considering the variety of storage tank contents: grain, water, oil, chemicals, and fuel.
- Storage tanks, however, are susceptible to corrosion when exposed to moisture or an aggressive environment.

Overview

- Soil-side corrosion of the bottom plates of above ground crude oil storage tanks is a major corrosion challenge in the oil and gas industry, especially when these tanks are constructed on oiled-sand pads.
- Severe corrosion has been identified on tank bottoms at a crude oil tank farm in the Middle East. Corrosion led to the costly replacement of bottom plates.
- The soil-side surfaces of the bottom plates were designed to be protected by a shallow anode impressed current cathodic protection (CP) system.
- The oily sand layer and air gaps under the bottom plates reduced CP effectiveness and resulted in severe corrosion.

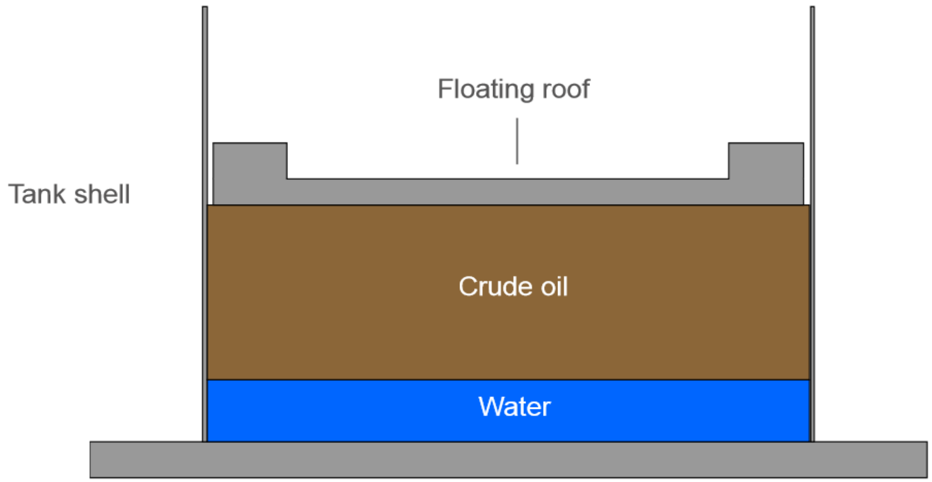
Oil Chemistry Concerns

Heavy fuel oils or crude oil once were assumed to be non-corrosive.

This turned out not to be the case, particularly when these products were contaminated with water and acids.

Presently there more than ~440 different types of crude oil chemistry.

Past experience has shown that bottoms of storage tanks, and first one to two meters of vertical walls are most heavily attacked when the cargo is sour crude oil, heavy fuels contaminated with water.

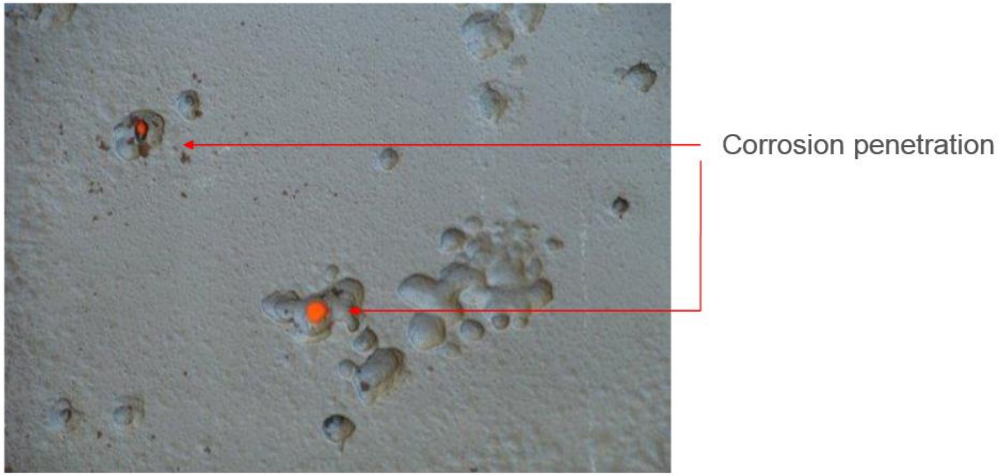


The main types of corrosion seen in originally uncoated tanks are:

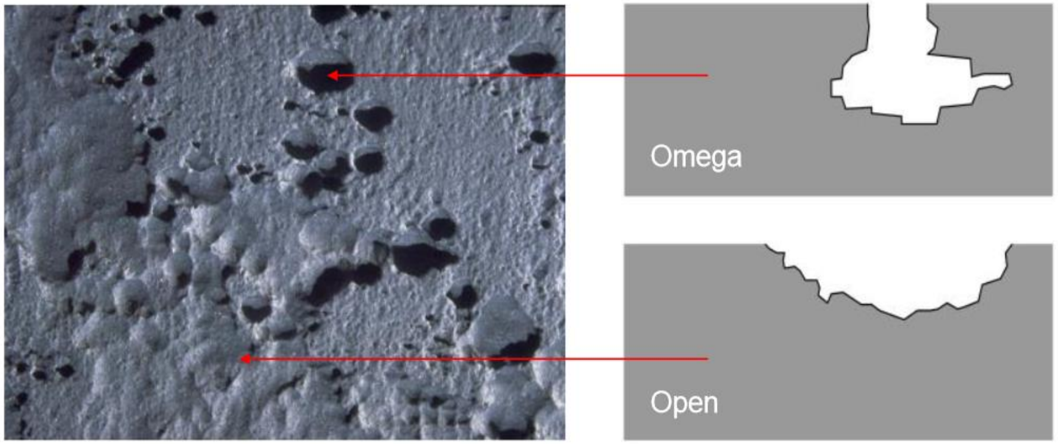
- Concentration cell corrosion
- Galvanic cell corrosion
- Sulfate reducing bacteria (SRB)
- Under deposit corrosion

Generally more than one form of corrosion attacks can be identified in any corroded tank

CORROSION AND PITTING OF BOTTOM PLATE



Pitting Types



Basic of steel Corrosion: Anodic and Cathodic Reactions

Anodic reactions

$3Fe + 4H_2O \rightarrow Fe_3O_4 + 8H^+ + 8e^-$

$2Fe + 3H_2O \rightarrow Fe_2O_3 + 6H^+ + 6e^-$

$Fe + 2H_2O \rightarrow HFeO_2^- + 3H^+ + 2e^-$

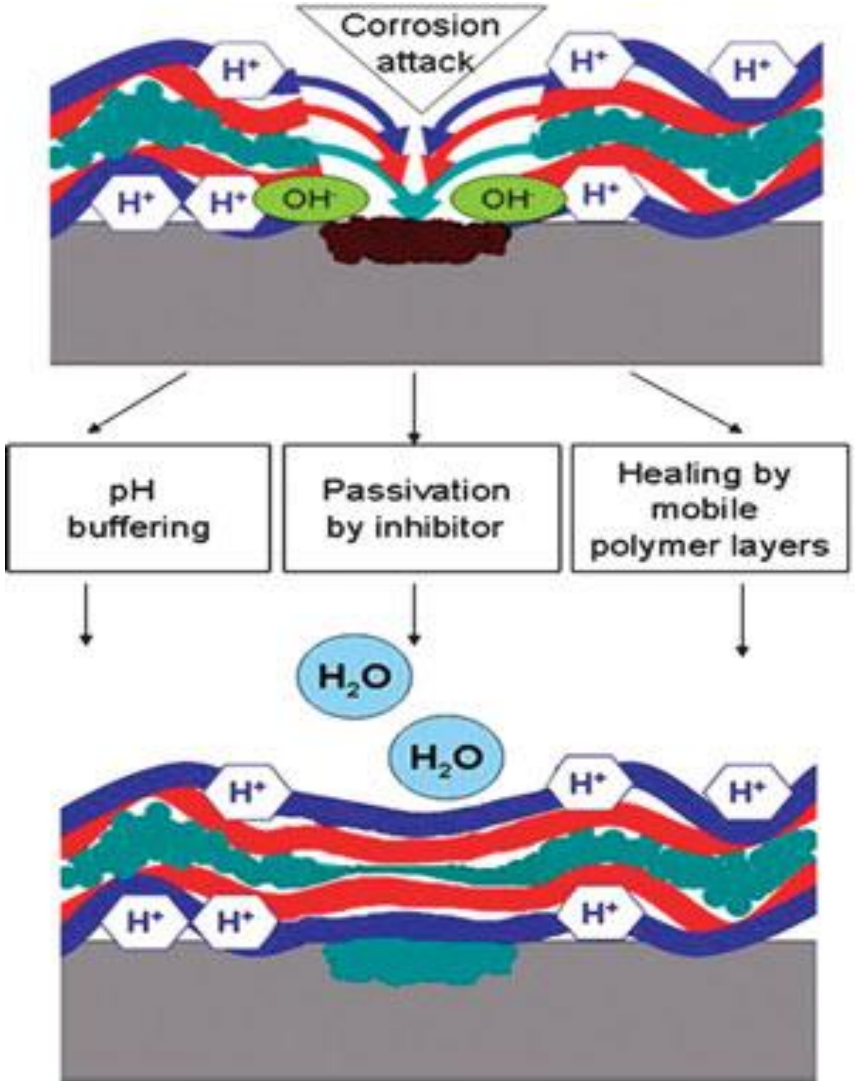
$Fe \rightarrow Fe^{++} + 2e^-$

Cathodic reactions

$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$

or

$2H^+ + 2e^- \rightarrow H_2$


Corrosion attack
H+
OH-
pH buffering
Passivation by inhibitor
Healing by mobile polymer layers
H2O


Project Objective

- Corrosion behavior of steel samples used for storage tanks and cross casing pipe applications were investigated using two different protection mechanisms:
  - **Vapor corrosion inhibitor**
  - **Nitrogen blanketing system**
- To demonstrate which technique provides more protection in corrosive environments, especially where there are restricted geometries such as crevices, threads, notches and under-deposits.

Procedure

- The corrosion behavior of steel probes was studied in two different conditions.
- Two ER and LPR probes were placed in an environment that contained 200 ppm chloride solution + 10% corrosion inhibitor.
- Two additional ER and LPR steel probes were placed in a different environment that included 200 ppm chloride solution (no inhibitor) and a nitrogen blanketing system at 10 psi applied pressure.
- In each case, one probe was immersed in solution and the other was suspended above the solution. The corrosion rate of the steel samples was monitored for more than five months (~4,000 hours) using linear polarization resistance (LPR) and electrical resistance (ER) probe techniques.

Advantages of the Vapor Phase Corrosion Inhibitors

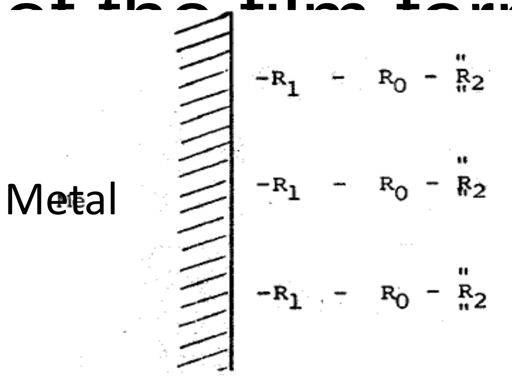
- Easy Application
- Product Versatility,
- Bio-friendly, organic chemistry, free of hazardous amines, nitrites and phosphate ester.
- Non-flammable, biodegradable with no hazardous decomposition by-products.

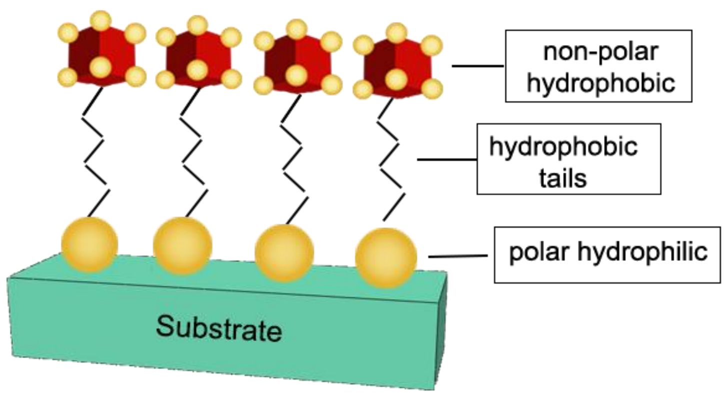
VCI Mechanism

- The vapor phase corrosion inhibitors are water-based and ideal for equipment with complex geometries such as boilers, heat recovery steam generators and pressure vessels.
- VCI forms a solution in water and when applied by spraying or dipping, will protect ferrous and nonferrous metals, including castings, tubular parts, finished parts, gears, pumps, housings, structural steel, sintered metals, bars and roll stock.
- VCI has excellent wetting properties and forms a clear, dry, hydrophobic film of roughly 0.25 mils thick (6.35 micron) on the surface that is stable up to 350°F (176°C).
- Adsorption of the inhibitor on to the metal surface provides a protective inhibitor layer. As well, the vapor phase action protects surfaces that have not been directly coated and are difficult to reach.
- This type of corrosion inhibitor is useful when oil, grease or other adherent films are not practical.
- The protective vapor expands within the enclosed space until the equilibrium determined by its partial pressure is reached; the higher the vapor pressure, the sooner saturation is achieved.

Adsorption of VCI to Surface

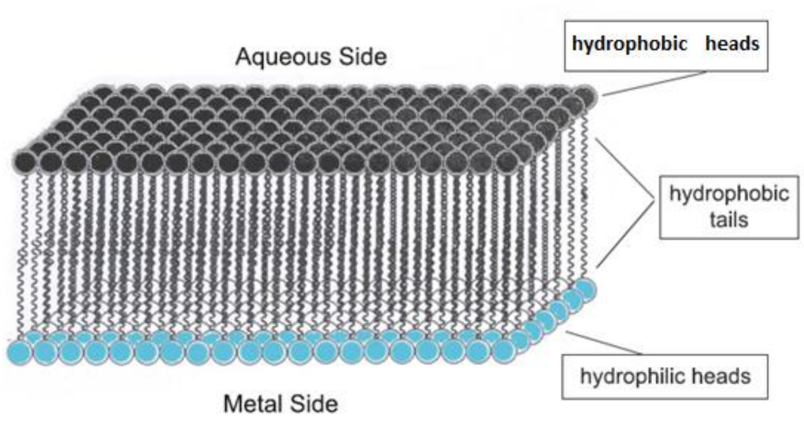
- The functional group R1 linked to the nucleus R_o of the inhibitor molecule is responsible for adsorption in a given environment. The functional group R_2 also linked to the nucleus Ro is responsible for the thickness and the impenetrable nature of the film formed.

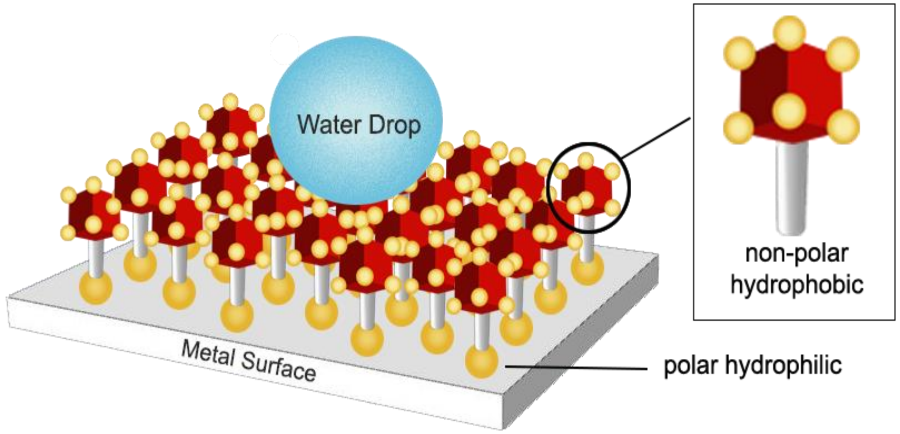




Adsorption to Surface

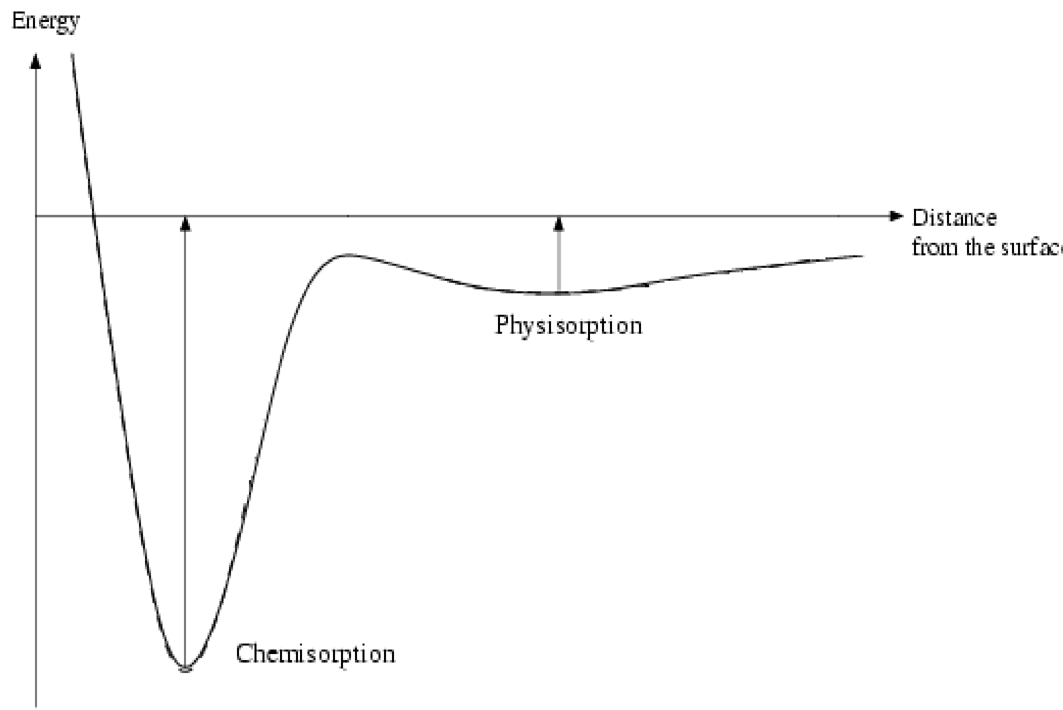
- VCIuse compounds that work by forming a monomolecular film between the metal and the water. In Film Forming Inhibitors, one end of the molecule is hydrophilic and the other hydrophobic.



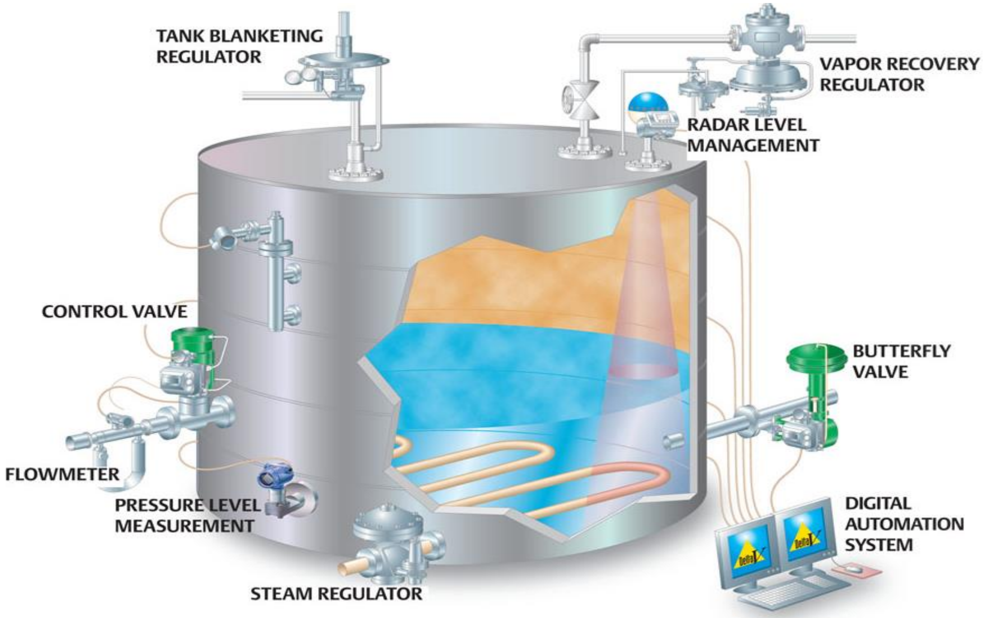


Chemisorption Vs Physisorption

- Chemisorption makes strong bonding between the inhibitor and the surface of the substrate resulting in a more stable protective film. But, the majority of corrosion damage to turbo-machinery systems occurs during shutdown period due to chemistry changes and stagnant condition in localized areas; therefore, a strong Physisorption corrosion inhibitor will provide satisfactory protection

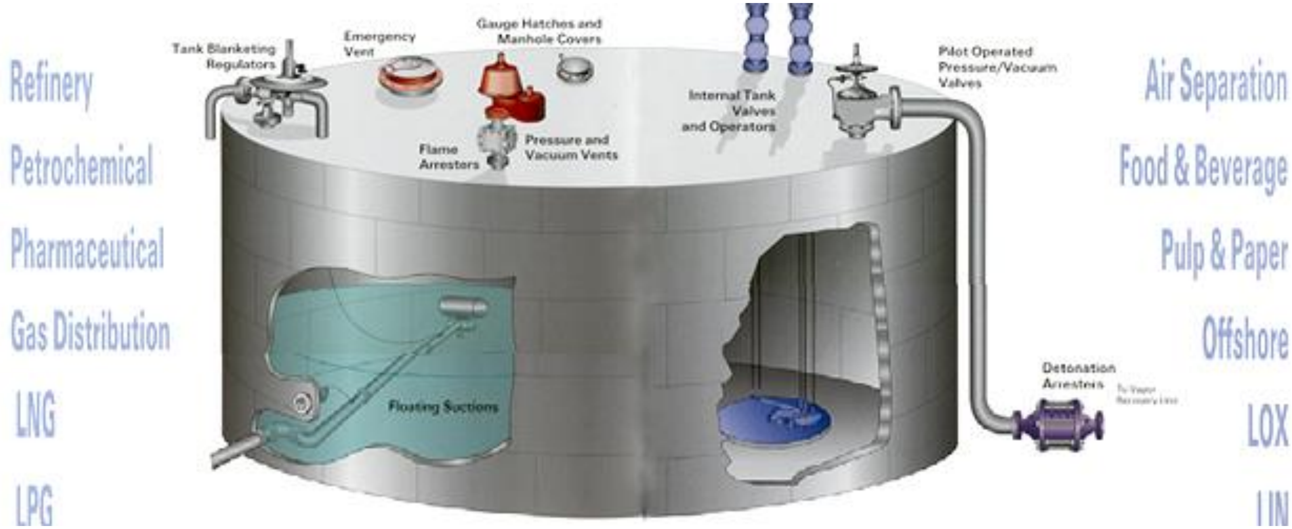


Tank Blanketing



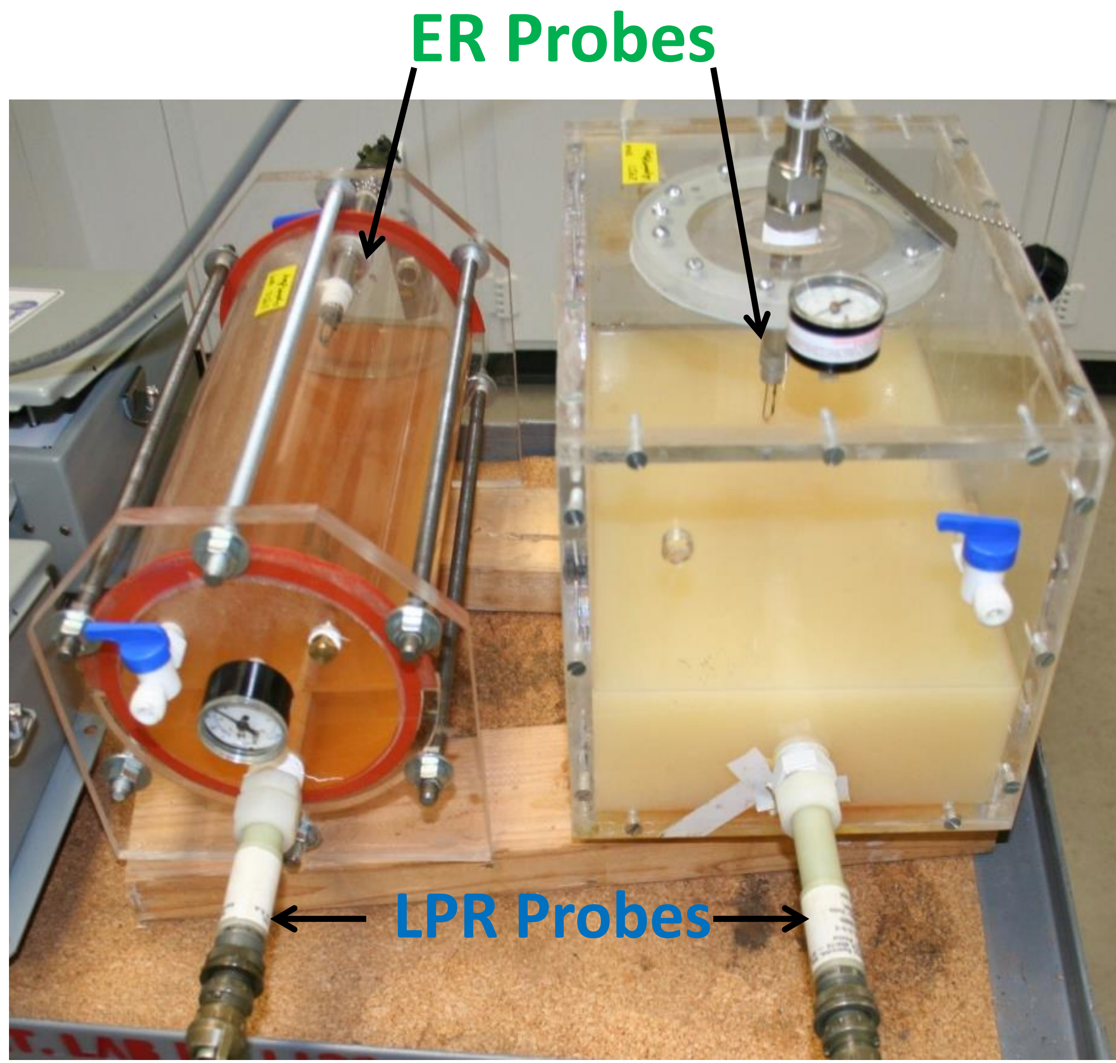
- Nitrogen is used in a wide range of industries to either prevent degradation of food, chemicals and metallic vessels due to atmospheric oxidation and corrosion, or to enhance safety by preventing the possibility of combustion, for instance when solvents are being stored.
- The presence of nitrogen keeps oxygen level low and Humid air in the head space is replaced by high purity, inert, dry nitrogen.
- Nitrogen effectively displaces all oxygen from the system and stops the corrosion reaction by eliminating the cathodic oxygen reaction. The dew point of 95% nitrogen is approximately -40°F, which enables it to absorb significantly more moisture than compressed air.
- From a corrosion point of view, air is roughly 20% oxygen, 80% nitrogen. Since fuels require oxygen to combust, reduced oxygen content in the vapor space lowers the risk of unwanted combustion.

Tank Blanketing - More Details



- To effectively blanket a tank, the system must be capable of pressurizing the vapor space and accurately maintaining that pressure.
- There are various ways to achieve a blanket. One method involves continuous purging, whereby blanketing gas introduced into the tank as a continuous flow exits through a vent or other opening. This method requires more gas and is not always effective in maintaining an inert atmosphere.
- Another approach uses a simple, direct-operated pressure-reducing valve (PRV) to blanket the tank. However, these devices are best suited for a continuous flow rate.
- Pressure variations can be an issue.
- This results in poor control, wasting of blanketing gas, and possibly not maintaining the necessary atmosphere within the tank.
- Nitrogen blanketing has been successfully used in many industries for protection of plant equipment, but it requires constant maintenance of the gas levels and additional equipment with a valve system for control.

Test setup for steel LPR and ER probes using 10% VpCI or nitrogen blanketing at 10 psi applied pressure.

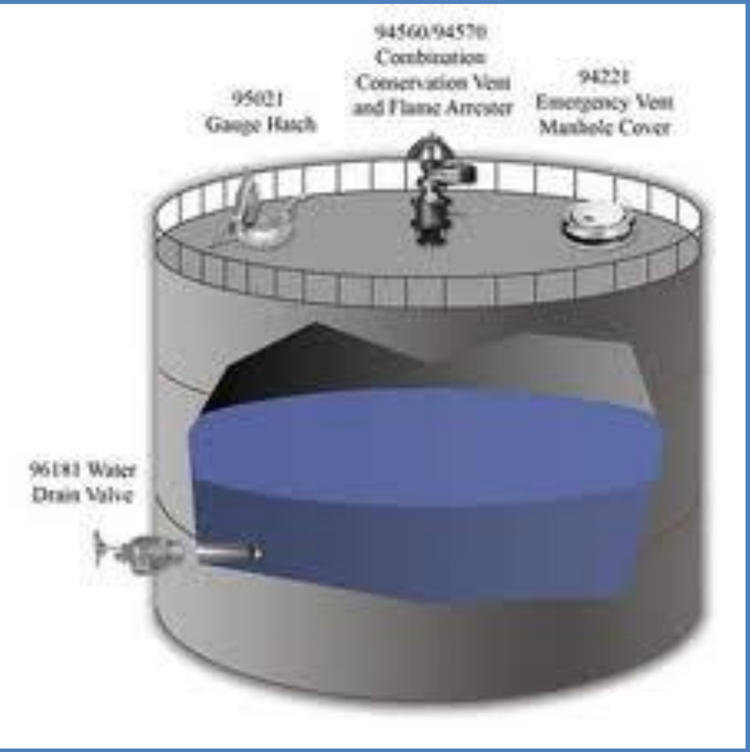


Linear Polarization

- CORRATER® systems operate on the fundamental principle that a metal corroding through oxidation will generate a small electrical current.
- A CORRATER® instrument determines the corrosion rate by measuring the current from a small applied potential difference between the two electrodes.
- CORRATER® systems measure the instantaneous corrosion rate of a metal in a conductive fluid using the linear polarization resistance measurement technique.

Electrical Resistance

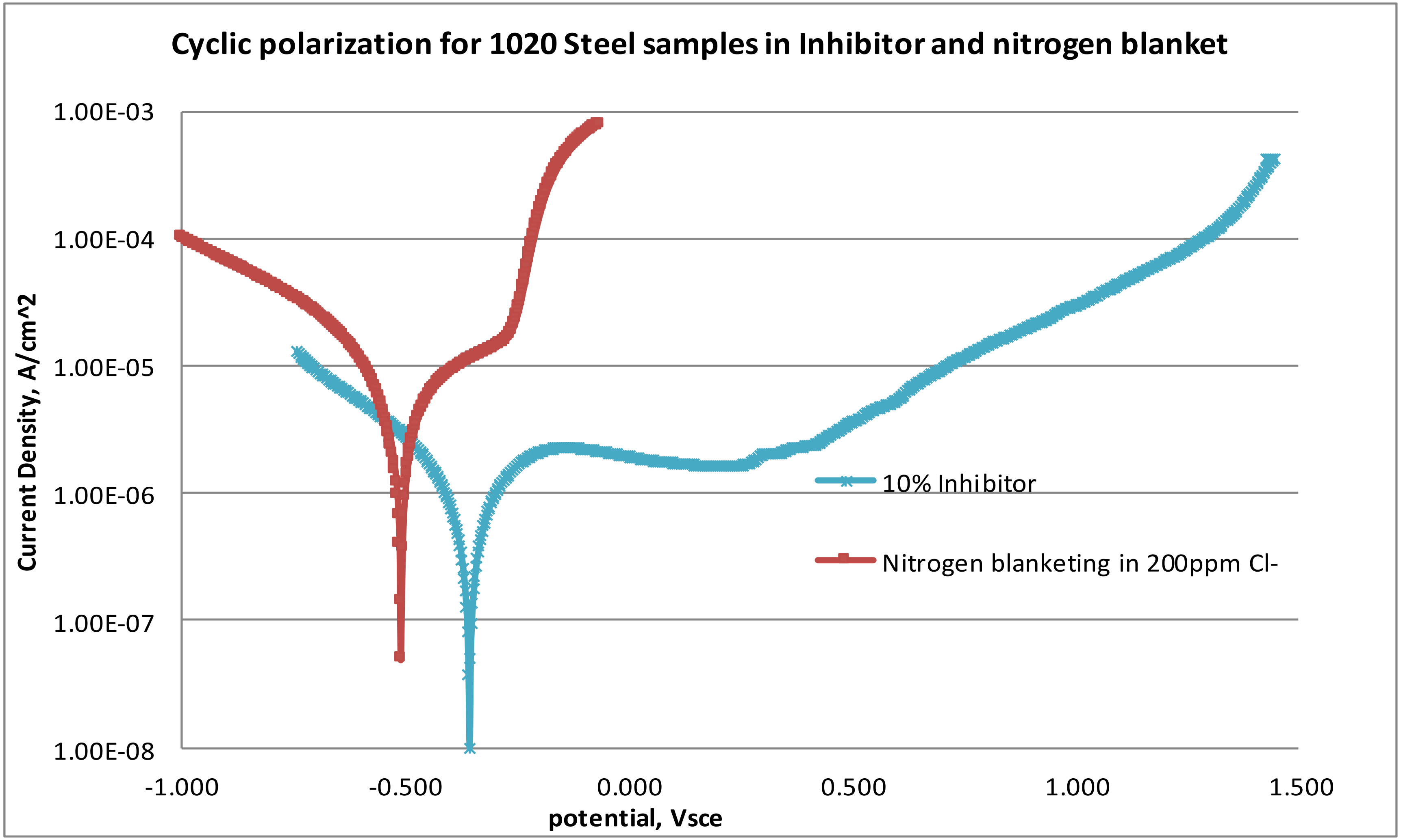
- Corrosion rate measurements are made using the electrical resistance method.
- Essentially, the instrument measures the resistance of the probe element which changes over time, as metal loss occurs.
- The rate of change is directly proportional to the corrosion rate.
- The reduction in cross-sectional area (A) of an element of metal or alloy as it corrodes results in an increase in the electrical resistance (R) of the element. The relationship is given by: $R = \rho L/A$, where resistivity (ρ) and length (L) of sample contribute to the measured resistance.


94560/94570
Combustion
Conservation Vent
and Flame Arrester
95021
Gauge Hatch
94221
Emergency Vent
Manhole Cover
96181 Water
Drain Valve

Results

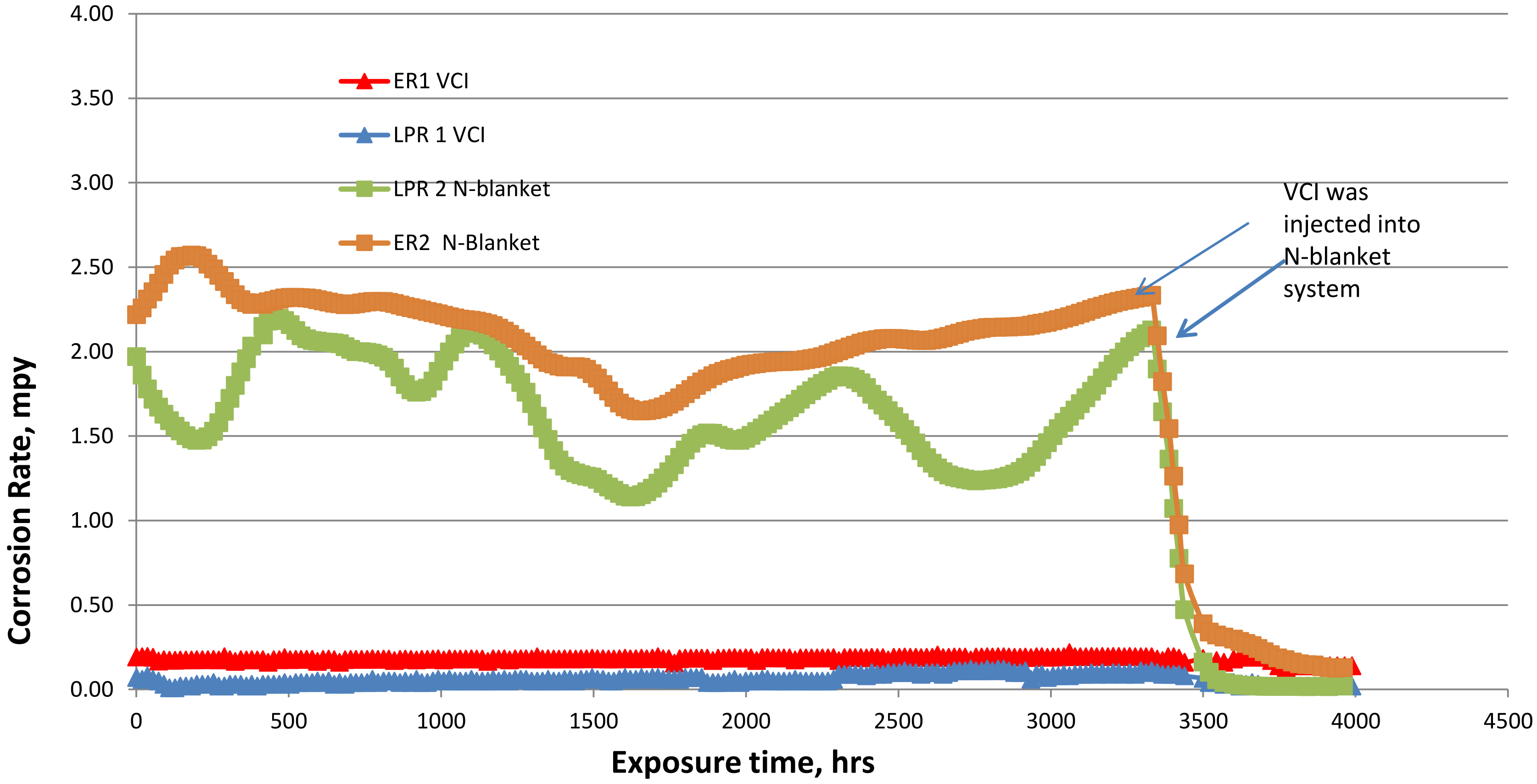

0207
0208

Electrochemical polarization behavior of the 1020 Steel samples in 10% VCI and nitrogen blanket in 200 ppm chloride ions solution.



Corrosion Rate results (LPR and ER)

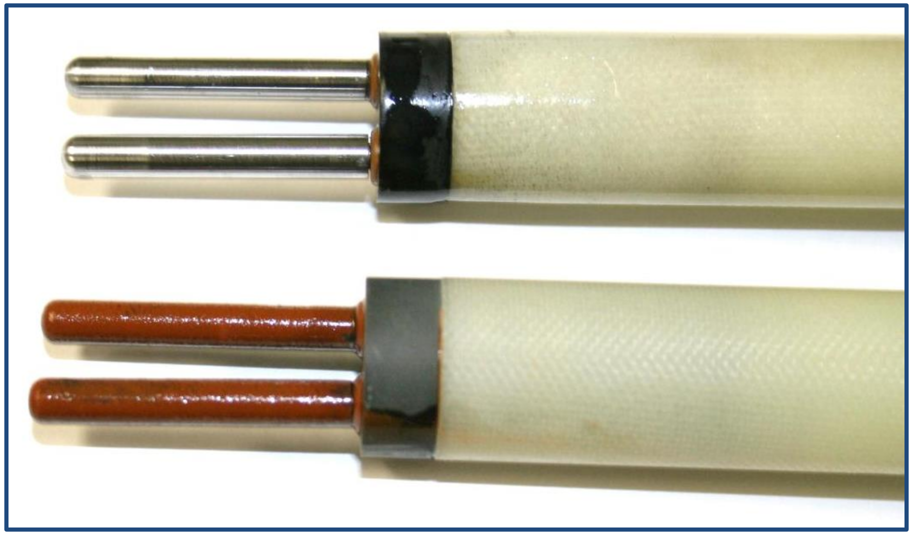
Comparison of corrosion behaviors of UNS G10200 Steel samples in Inhibitor and Nitrogen blanketing (10 psi) protection systems

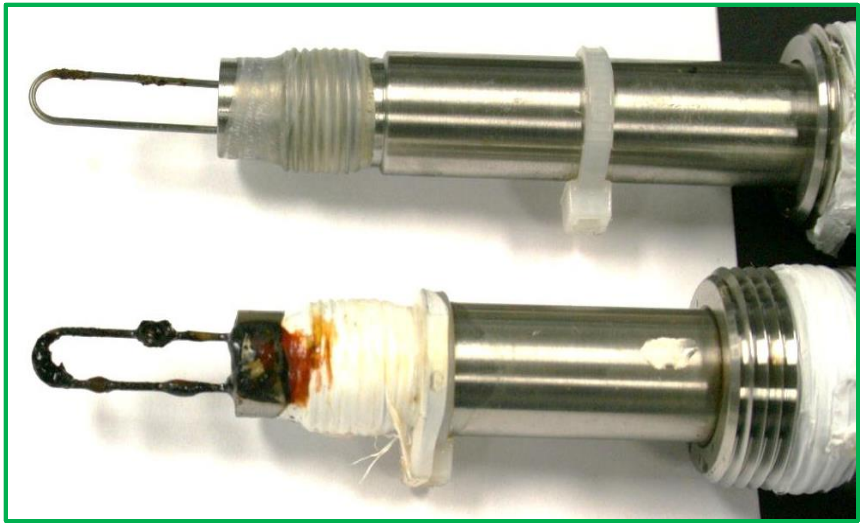


There is a much lower corrosion rate for steel samples protected by VpCI (average corrosion rate of 0.04 mpy), while nitrogen blanket coverage resulted in higher corrosion rate, regardless of technique used to monitor (average corrosion rate of 1.8 mpy).

Probes

Comparison of corrosion on LPR probes (left) in VCI and nitrogen blanket protection system, showing no rust formation on VCI protected steel samples, while nitrogen blanket protected steel samples covered with a thick red rust.

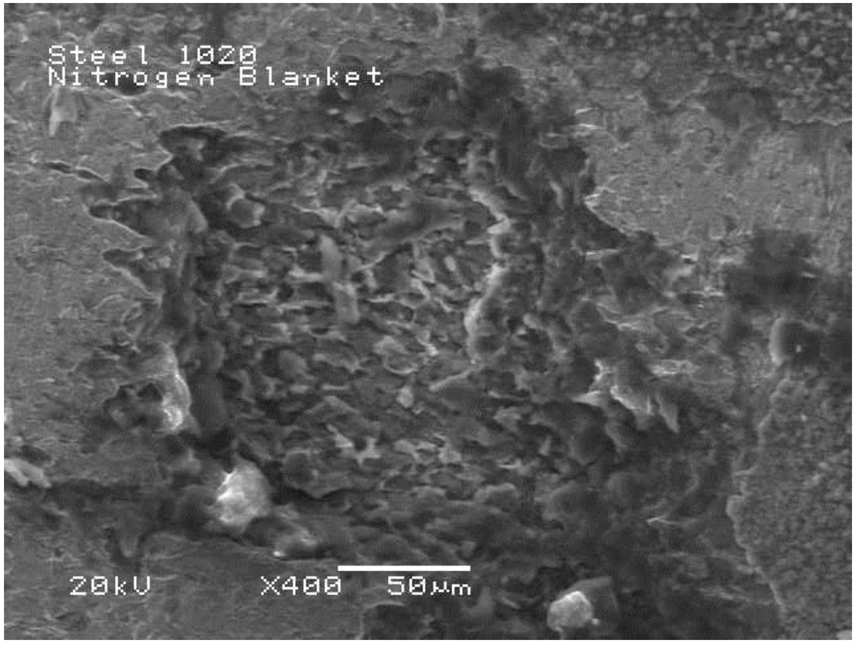


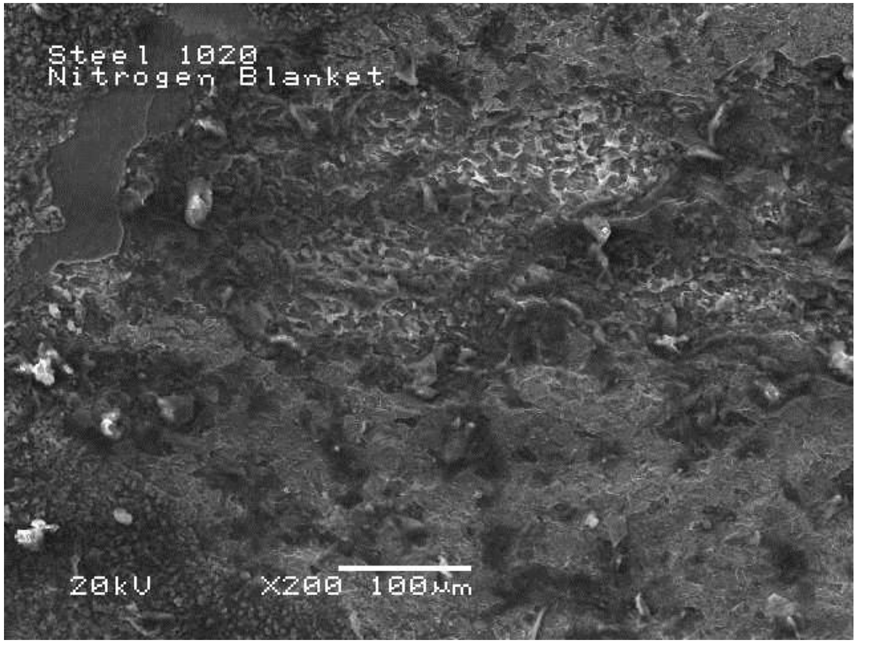


Comparison of corrosion on ER Probes (right) in VCI and nitrogen blanket protection system. There is minor rust formation on the VCI protected steel sample (average corrosion rate of 0.18 mpy), while nitrogen blanket protected steel samples covered with a thick red rust (average corrosion rate of 2.4 mpy).

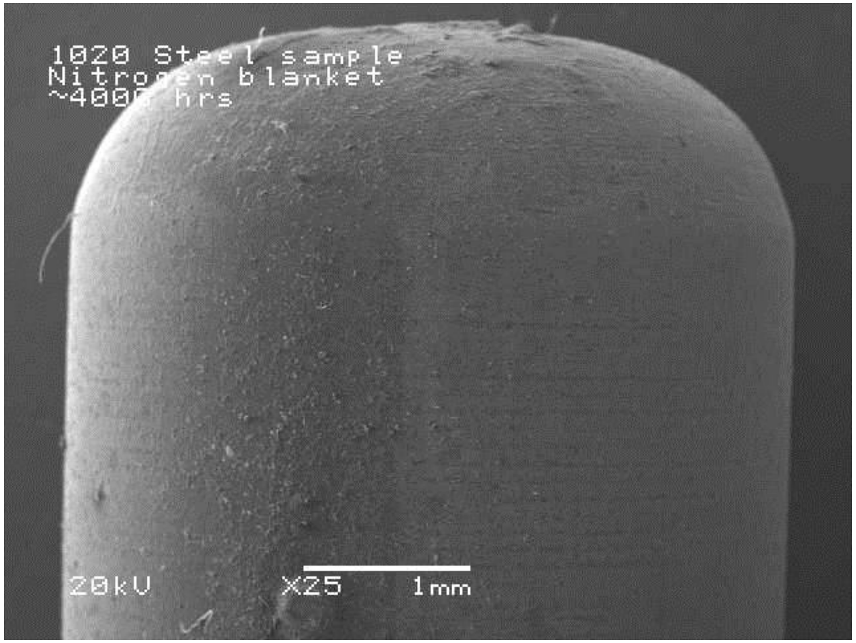
SEM

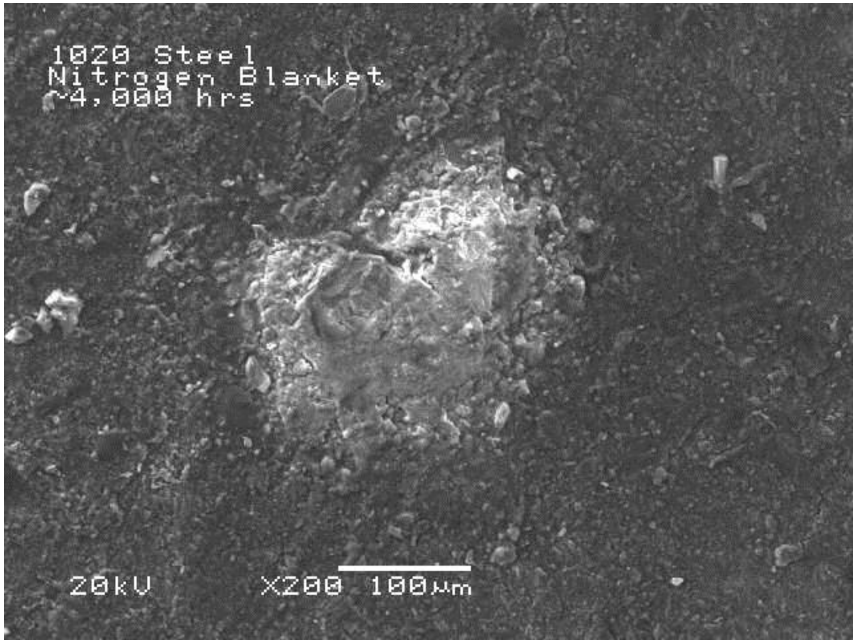
SEM micrographs of the LPR Probes (1020 steel) in nitrogen blanket protection system, show severe corrosion attacks on the samples surfaces.



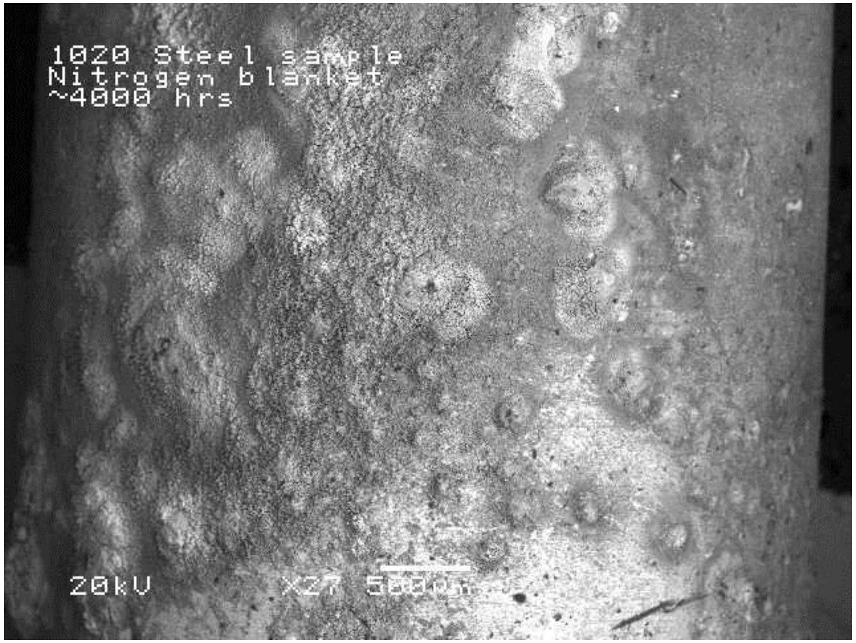


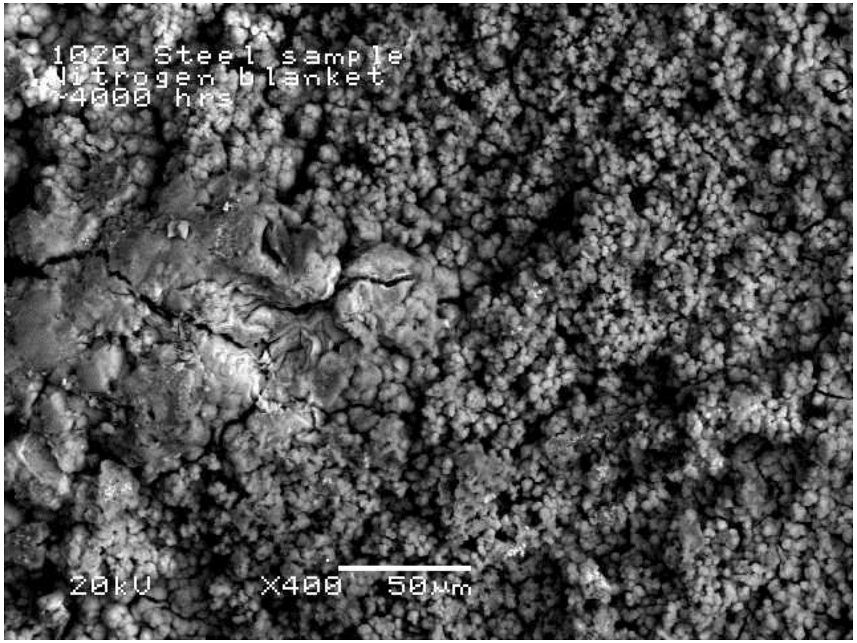
SEM micrographs of the LPR Probes (1020 steel) in nitrogen blanket protection system, show severe corrosion attacks on the sample surfaces. The thick red rust was removed to show severity of corrosion attack.



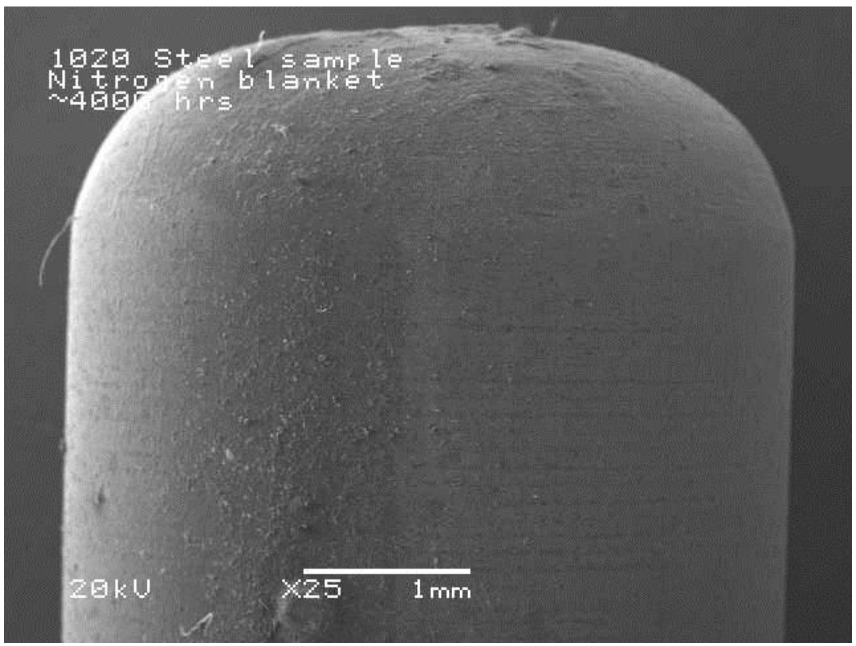


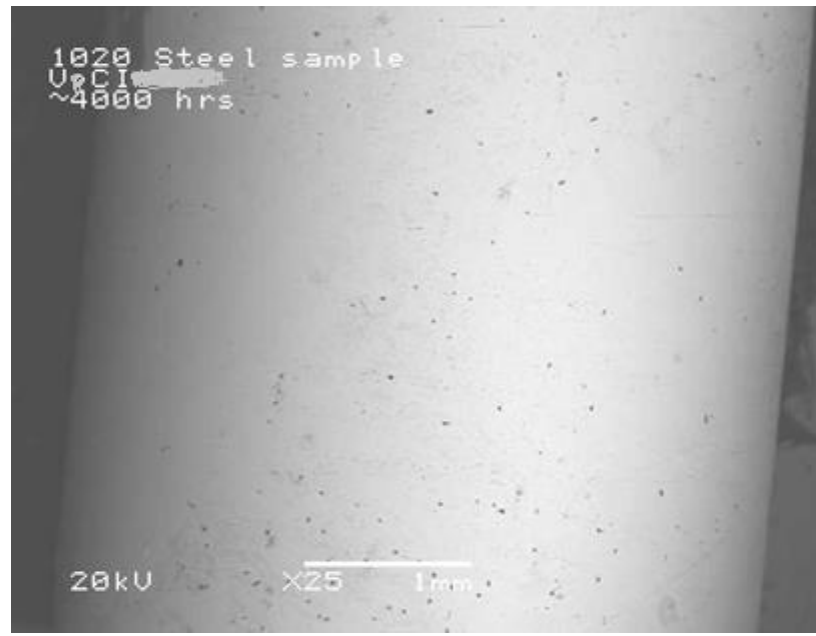
SEM micrographs of the LPR Probes (1020 steel) in nitrogen blanket protection system, show more severe corrosion attacks on the sample surfaces.



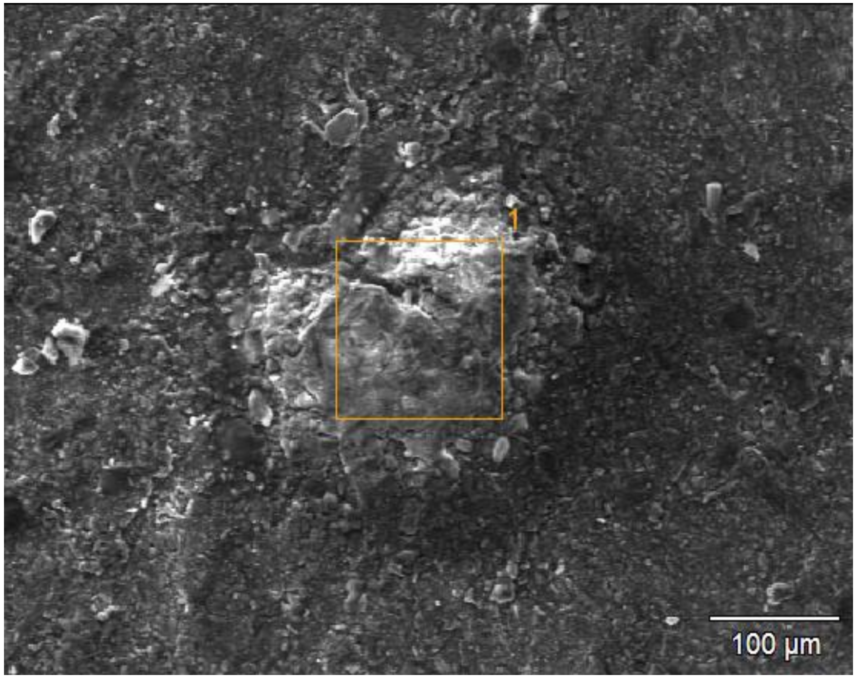


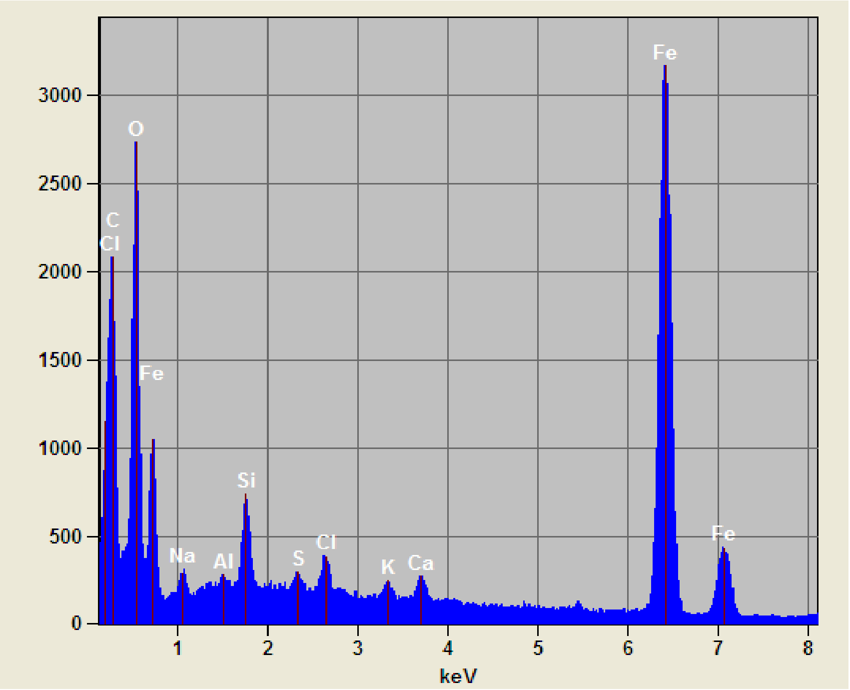
In comparison, SEM micrograph of LPR probe (right) in VCI shows a clean corrosion free surface for the VCI protected steel sample, no rust or corrosion reaction was detected.





SEM/EDAX analysis on the LPR probe (1020 steel) in nitrogen blanket protection system shows severe corrosion attack on the sample surfaces.

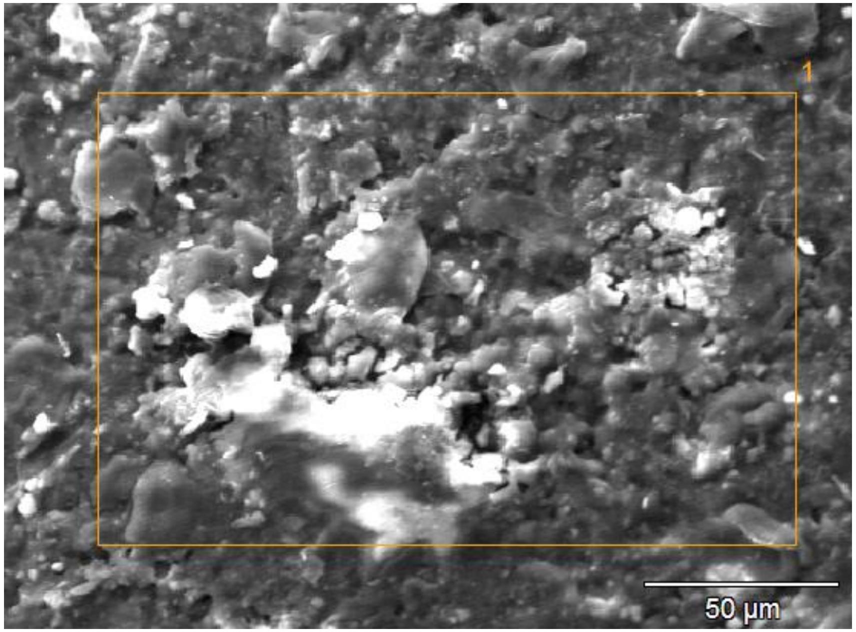


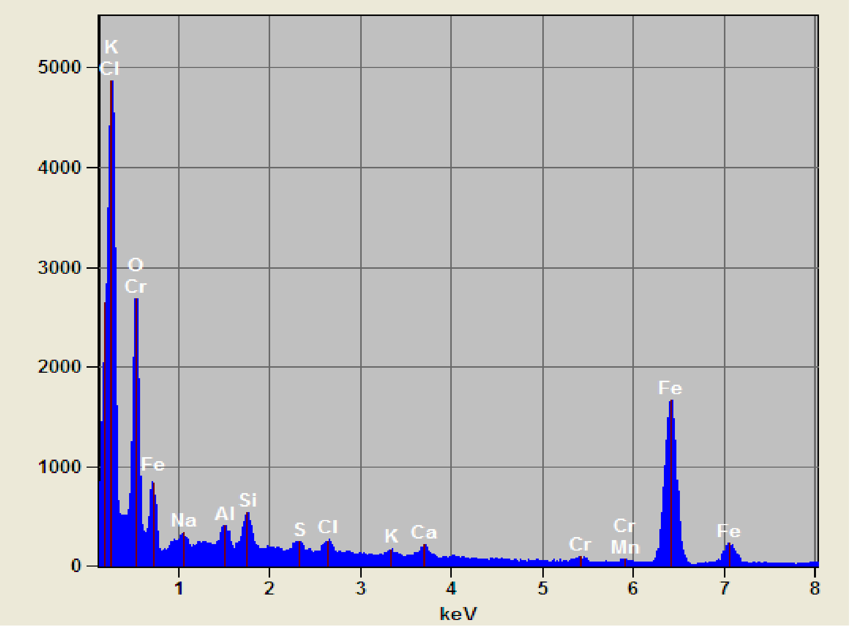


Weight %

	O-K	Na-K	Al-K	Si-K	S-K	Cl-K	K-K	Ca-K	Fe-K
N-steel(1)_pt1	18.62	2.92	0.39	3.29	0.60	1.41	0.66	1.13	70.97

SEM/EDAX analysis on the LPR probe (1020 steel) in nitrogen blanket protection system shows severe corrosion attack on the sample surfaces.

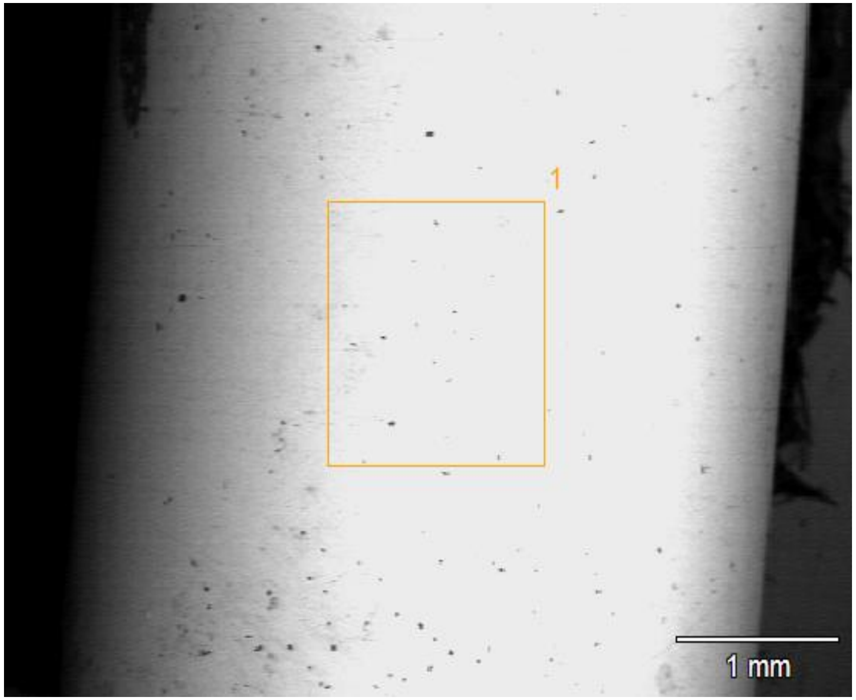


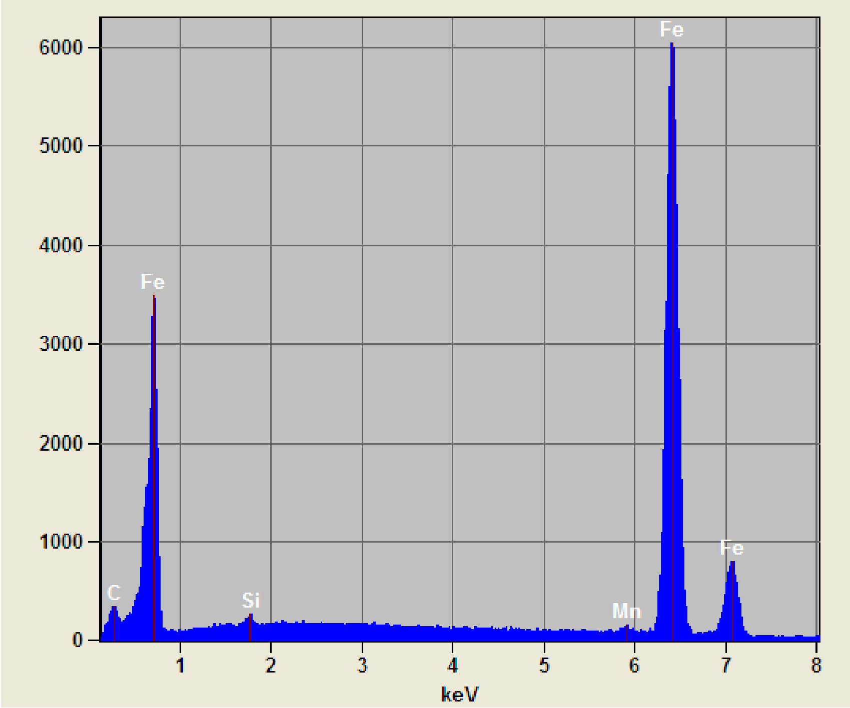


Weight %

	O-K	Na-K	Al-K	Si-K	S-K	Cl-K	K-K	Ca-K	Cr-K	Mn-K	Fe-K
N-steel(2)_pt 1	10.52	7.09	2.40	4.43	1.35	1.45	0.84	1.61	0.82	1.14	68.35

SEM/EDAX analysis on the LPR probe (1020 steel) in 10% Inhibitor + 200 ppm Cl ions show no corrosion attack on its surfaces after roughly 4,000 hours of continuous corrosion testing.

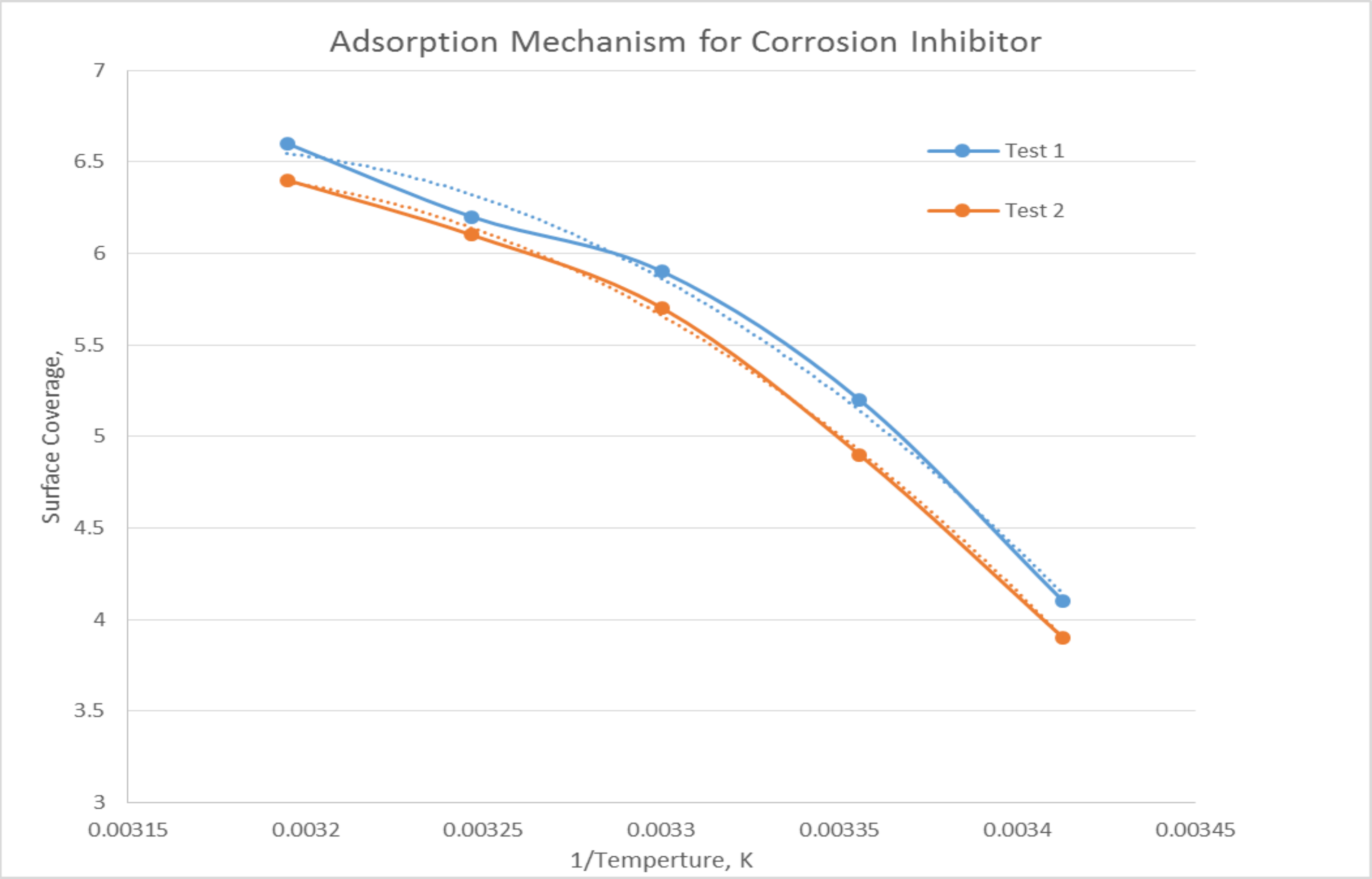




Weight %

	Si-K	Mn-K	Fe-K
Vci-steel(1)_pt1	0.52	0.89	98.59

Langmuir adsorption isotherm showing the relationship between surface coverage and temperature for VCI Inhibitor on the surface of steel. Adsorption Energy for the VCI inhibitor was roughly -10 to -14 kJ/mol, indicative of an inhibitor with strong physical adsorption to the metal surface



Conclusions

- The corrosion data have demonstrated that corrosion inhibitors have superior advantages over a nitrogen blanketing system in the presence of excessive salt and moisture.
- On average, the LPR corrosion rate measured less than 0.06 mpy for samples immersed in and exposed to the Inhibitor solution with no signs of corrosion.
- The immersed and nitrogen blanketed samples, in contrast, showed a corrosion rate of 1.78 mpy and were covered with a thick red rust.
- The ER probes showed a corrosion rate of 0.18 mpy for the Inhibitor treated samples, while the nitrogen blanketed samples showed a 2.12 mpy corrosion rate and the probes were heavily corroded.
- The electrochemical data acquired from corrosion tests showed that VCI inhibitor adsorption to the steel surfaces fits with the Langmuir adsorption isotherm; the enthalpy of adsorption was approximately -10 to -14 kJ/mol that suggests a physical adsorption compound
- Furthermore, when Inhibitor was injected into the nitrogen blanketed corrosion cell, the corrosion rate of the corroded steel probes dropped to less than 0.26 mpy in less than 20 hours. This shows a significant reduction in the corrosion rate by more than eight times.