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

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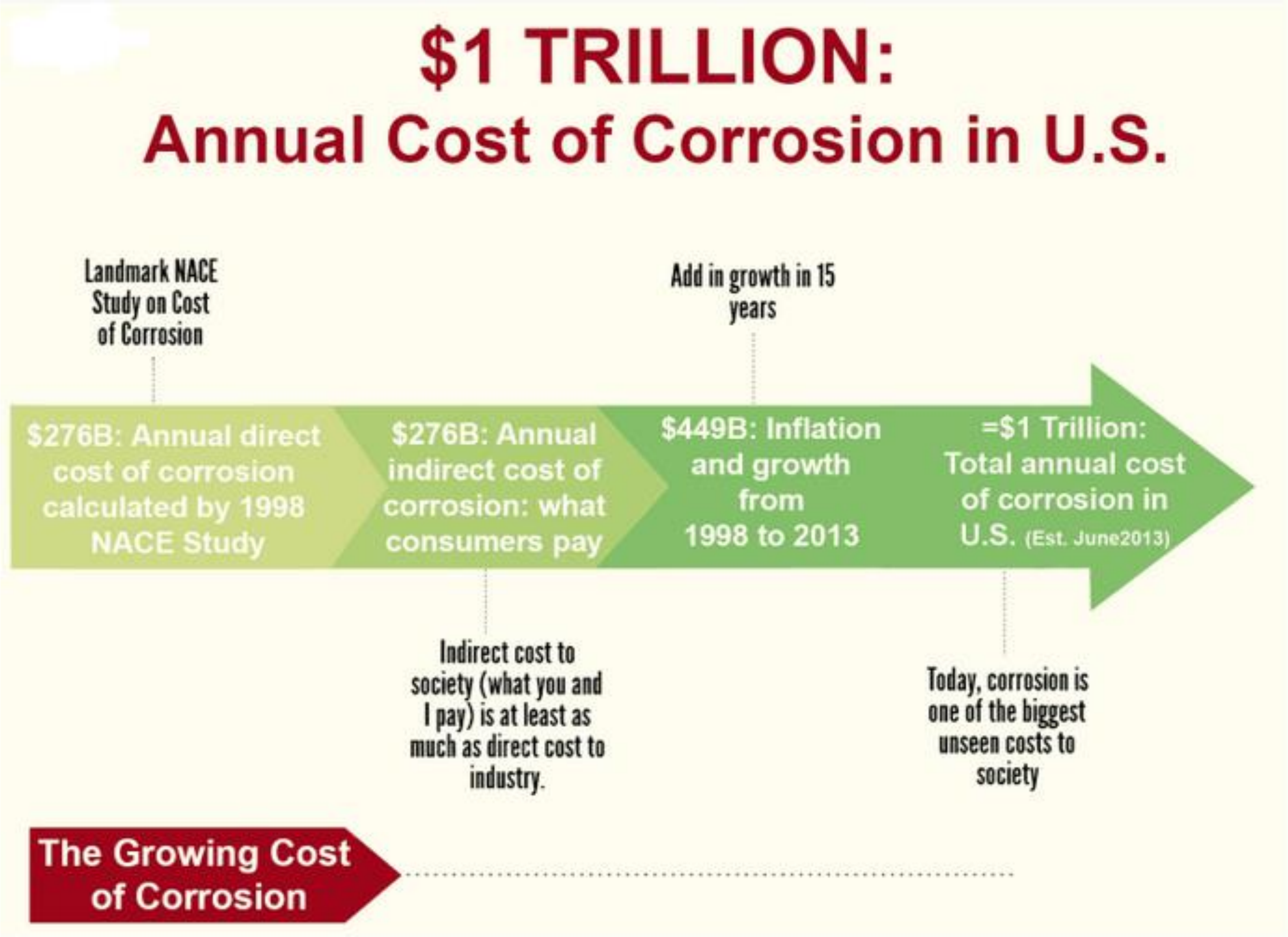
COST OF CORROSION

Corrosion will cost the US economy over $1.1 trillion in 2021. ~3.7% GNP

Direct & Indirect losses:

- **Direct loss: Material cost, maintenance cost, over-design, use of costly material**
- **Indirect losses: Plant shutdown & loss of production, contamination of products, loss of valuable products due to leakage etc, liability in accidents**



$1 TRILLION:
Annual Cost of Corrosion in U.S.

Landmark NACE Study on Cost of Corrosion

$276B: Annual direct cost of corrosion calculated by 1998 NACE Study

$276B: Annual indirect cost of corrosion: what consumers pay

Indirect cost to society (what you and I pay) is at least as much as direct cost to industry.

Add in growth in 15 years

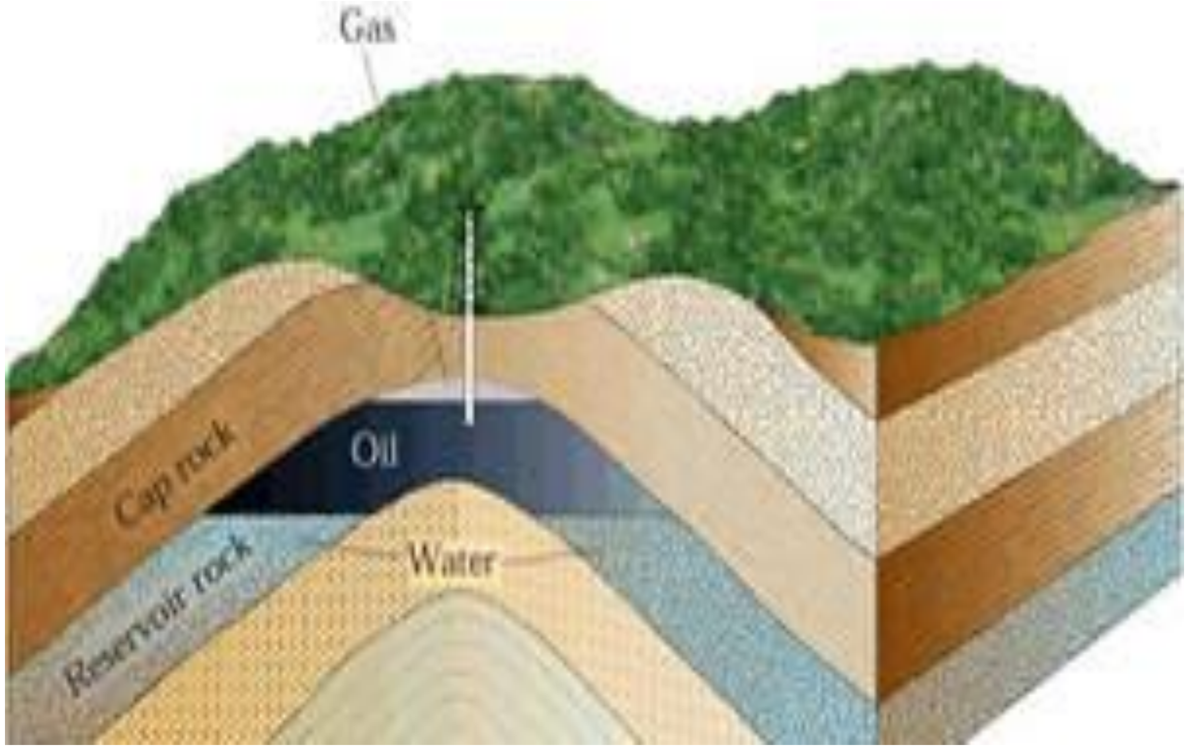
$449B: Inflation and growth from 1998 to 2013

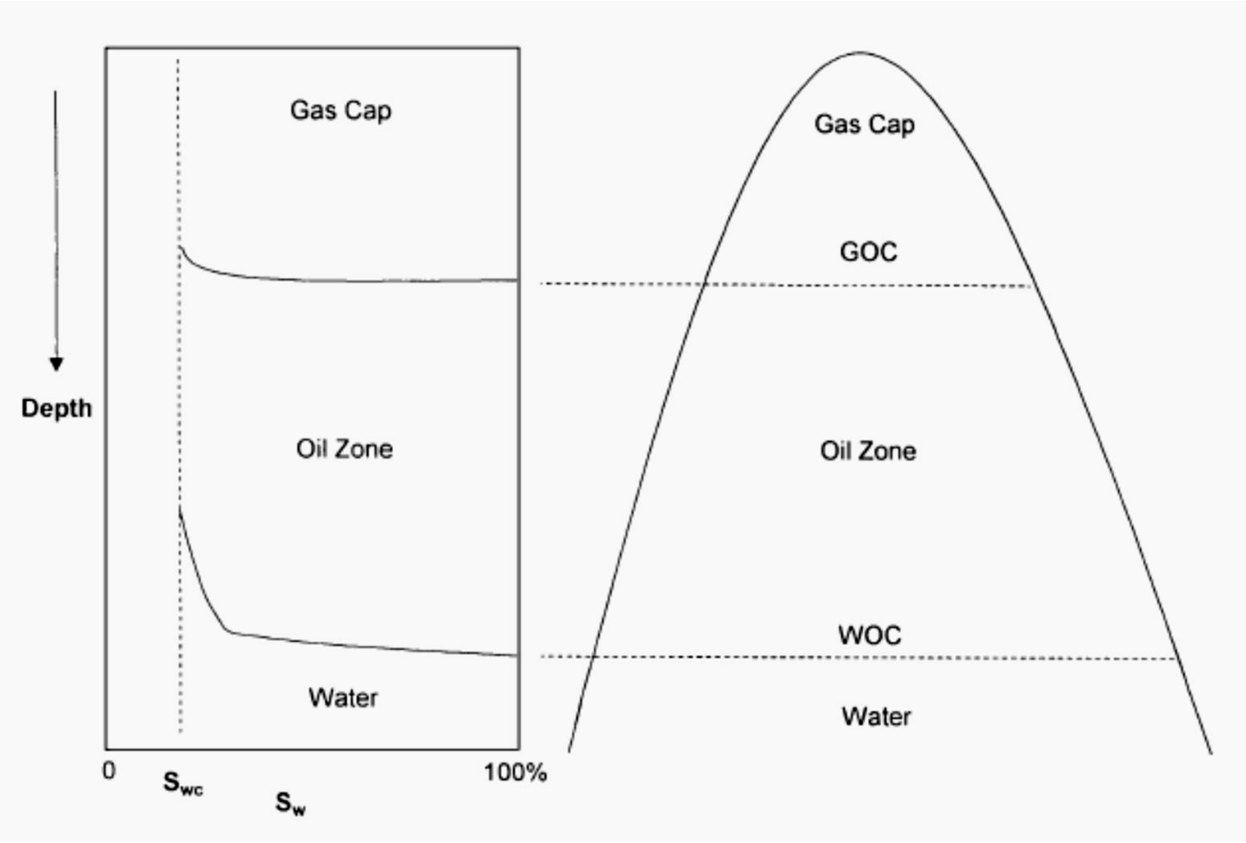
=$1 Trillion: Total annual cost of corrosion in U.S. (Est. June2013)

Today, corrosion is one of the biggest unseen costs to society

The Growing Cost of Corrosion

Oil well

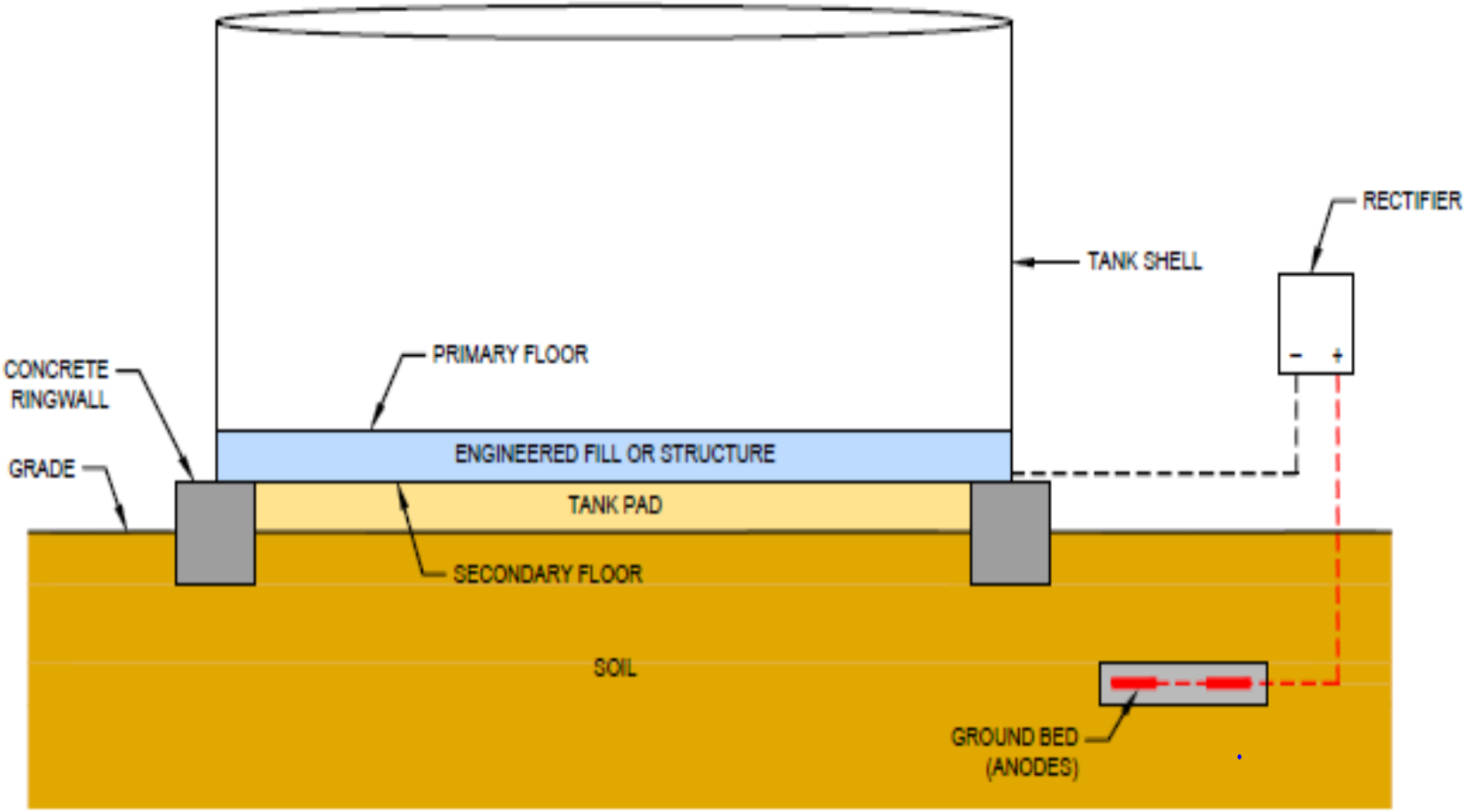

Gas
Oil
Cap rock
Water
Reservoir rock


Depth
Gas Cap
Oil Zone
Water
0
S_{wc}
S_w
100%
Gas Cap
GOC
Oil Zone
WOC
Water

Above ground Storage Tanks (ASTs)

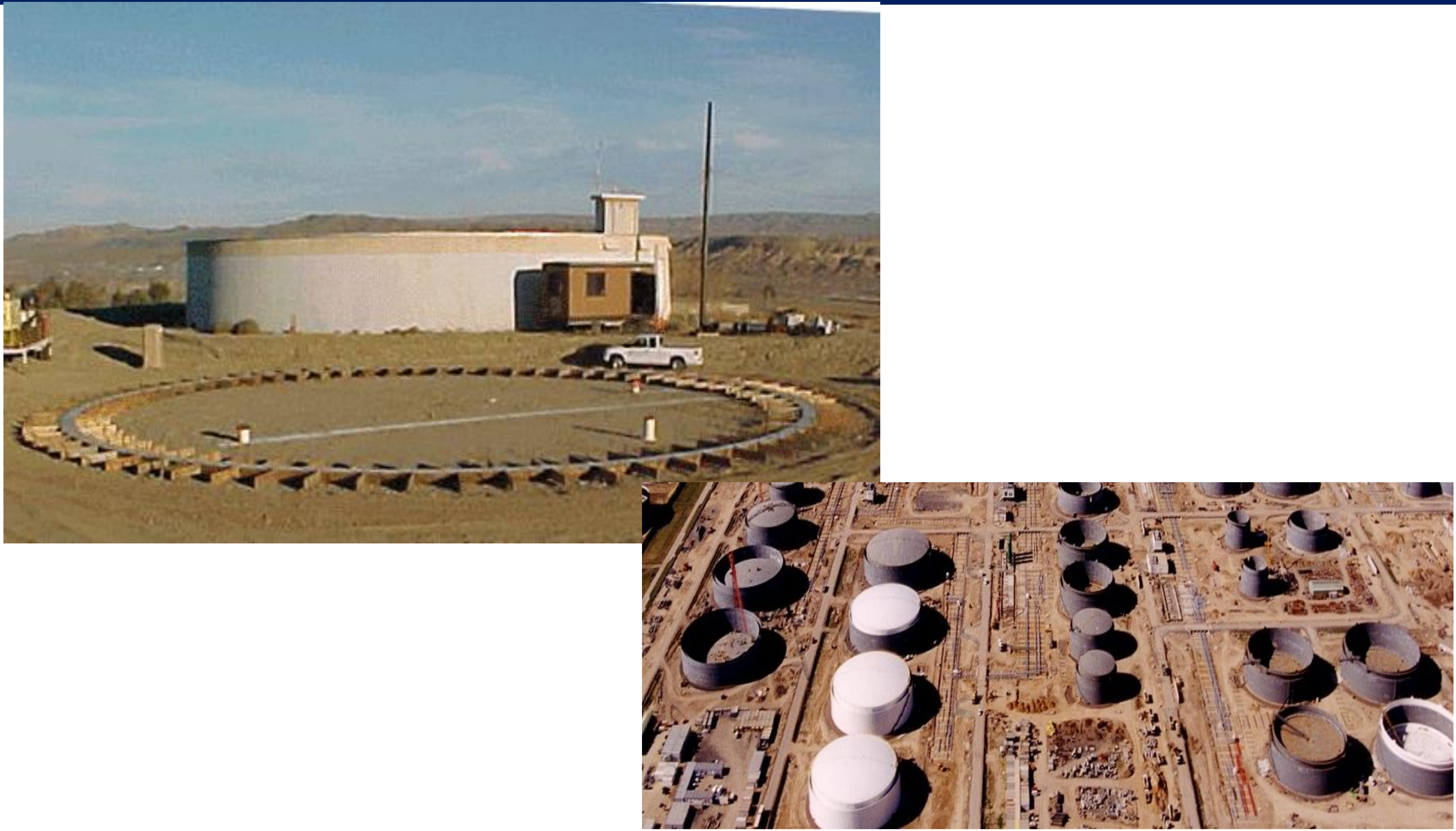
- Corrosion of soil side bottoms of above ground storage tanks (ASTs) causes the formation of pits that allows product leakage into the environment that in most cases are a catastrophic disasters. This specific type of corrosion is called soil side localized corrosion, and forms in the gaps between the metal tank bottom and the soil/concrete slab it rests on. Most of these tanks are located in coastal areas, high ambient humidity and/or rainfall causes moisture to seep between the metal bottoms and soil (bottom bed). This problem also shows up when sand bed between the two bottoms becomes saturated with water over time and causes corrosion of the soil side of the upper tank bottom.

- **Typical double-bottom breakout tank**



Pitting Corrosion of the bottom of AST can lead to a environmental disaster

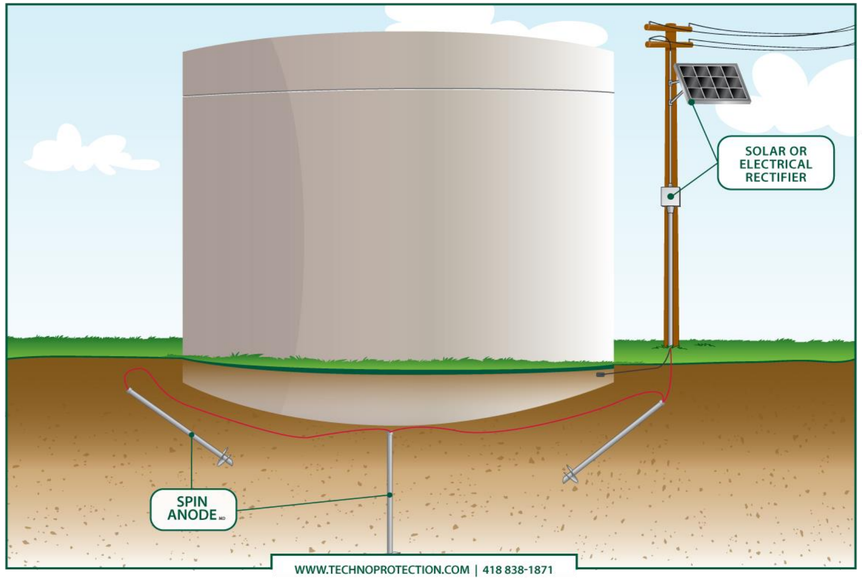
Pitting Corrosion of the bottom of AST can lead to a environmental disaster

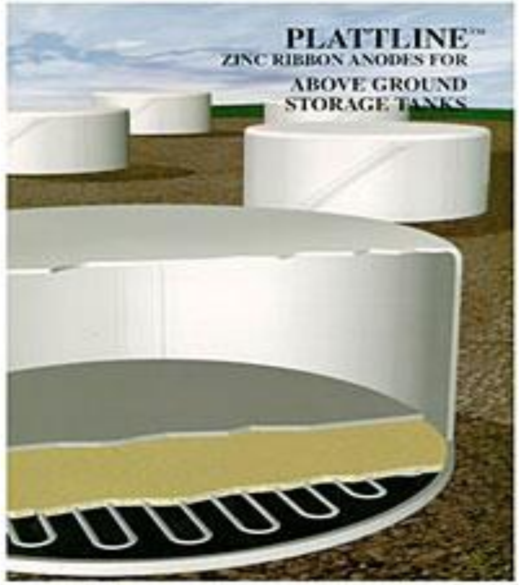


Common Tank Foundation Design

How to avoid Corrosion/leakage of the AST

- Proper Design and corrosion resistance steel selection
- Cathodic Protection
- Use Corrosion Inhibitors: Vapor Corrosion Inhibitors (VCI) is an effective method to protect the metal surfaces of the tank bottom, at the sand/bottom interface





- Determine effectiveness of the mass-loss based methods for corrosion monitoring
  - Mass-loss coupons
  - Electrical resistance probes
  - UT-based mass-loss coupons
- Monitoring using the coupons and comparison with the tank bottom soil-side indications
- Determine correlation between tank bottom corrosion and a variety of parameters such as resistivity, pH, bacteria concentration, corrosive species such as chloride

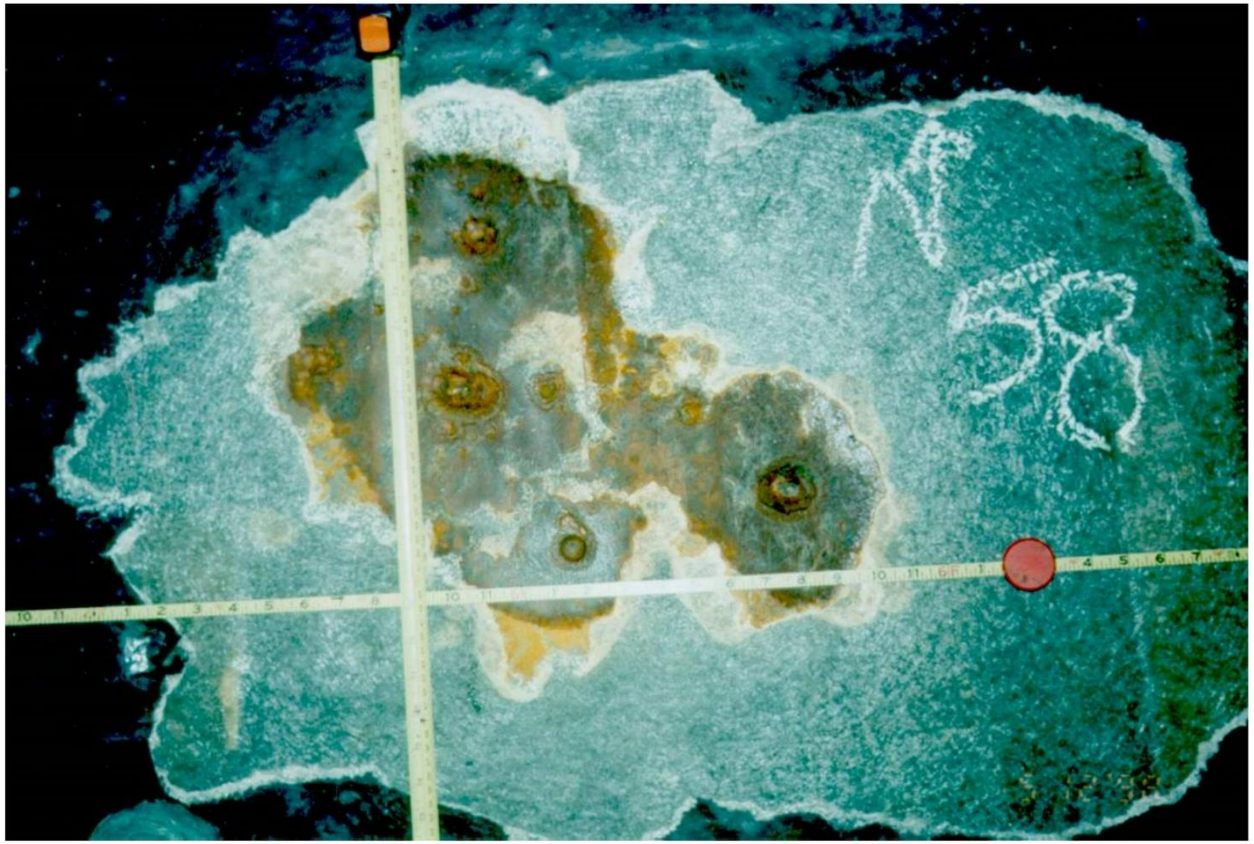
Aboveground Storage Tanks: Age and Bottom Condition

Historically Holes Weren’t Patched with Steel Plates (1951 tank)

Proudly Serving Ontario | 175 YEARS

Fibreglass Linings

Applied over welding flaws, pits, holes, etc.



Eliminating Product-side Corrosion with Internal Linings

- **Single and double bottom tanks with concrete pads:**
  - VCIs can be applied at the pad surface, during out-of-service conditions.
  - VCIs can be applied through leak-detection slots, slots need to align with the dead shell ports, but this option is not preferred by tank operators.
  - VCI mixed with concrete: will have to evaluate concrete properties, outside the scope of this project, not preferred.
  - Underside of the concrete not accessible, double bottom.
  - Single bottom: VCIs cannot be applied underside of the leak-prevention barriers
    - *HDPE liner*
    - *ClayMax™ liner*
  - Current plan: developed an experimental system to study VCI application and migration on concrete pad
    - *Two control experiments (with and without VCI)*
    - *Migration experiment*

- Monitoring the long term compatibility of VCI and Cathodic Protection of tank bottom

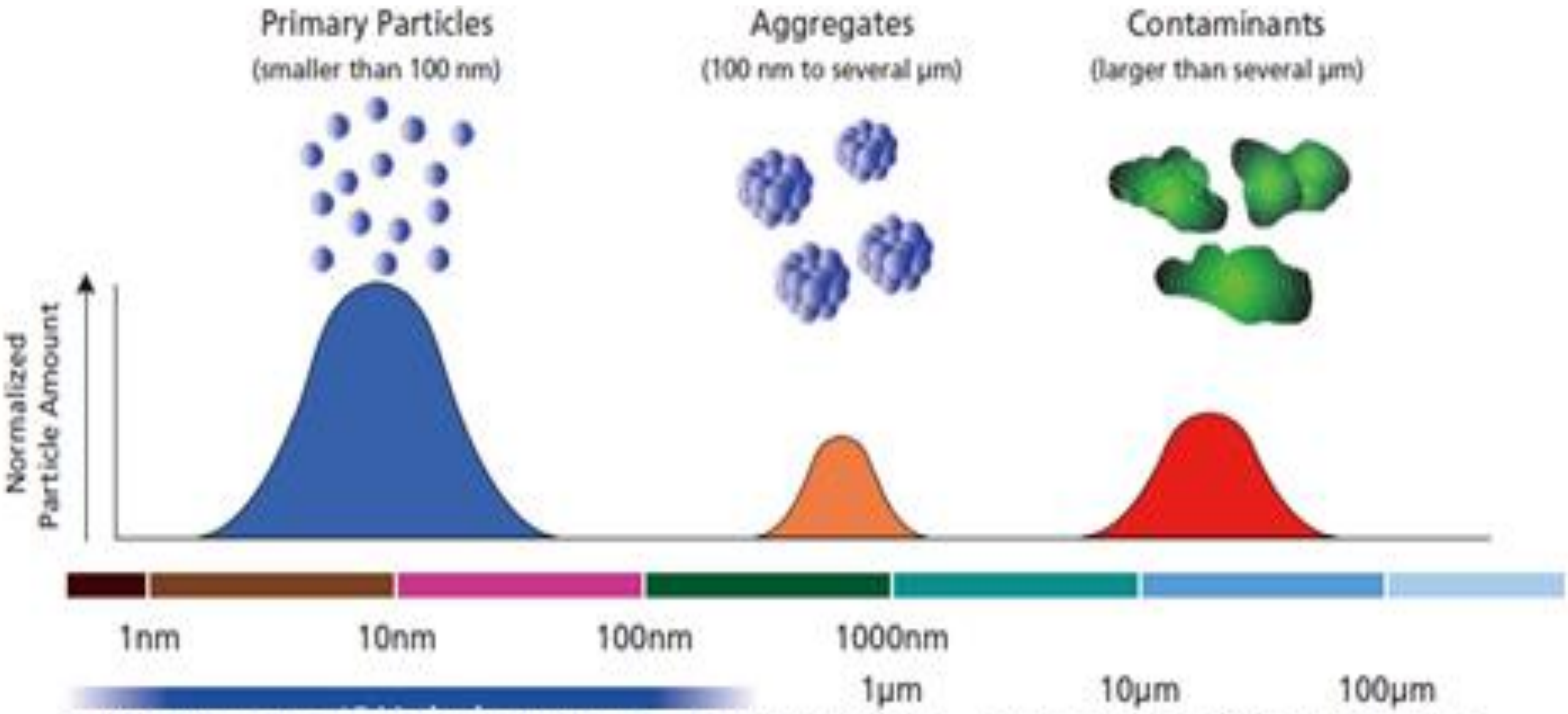
Corrosion Inhibitors

- Corrosion inhibitors are chemical compound add to system to lower corrosion.
- 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.

NANO-VCI Mechanism

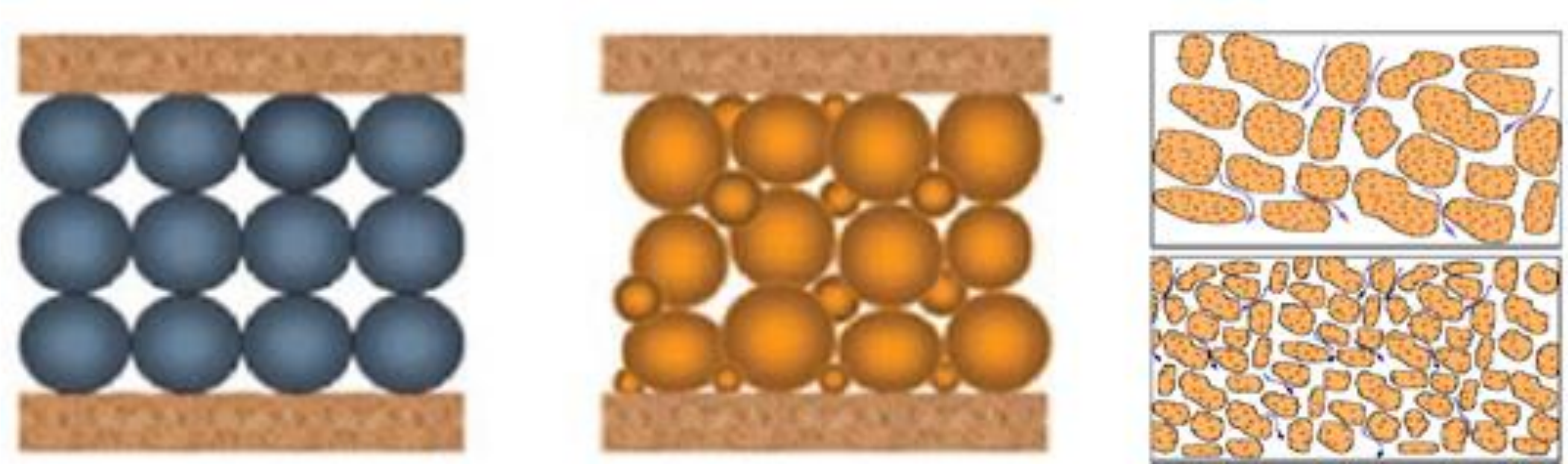
- NANO-VCIs transport inhibitor to the metal surface and interact with the metal substrate to form a protective film.
- When added to a liquid coating, the inhibitors become active.
- A good level of corrosion protection can be obtained with an inhibitor that forms a passive micro-phobic layer on the metal surface using micron sized powder particles in water.

Particle Size



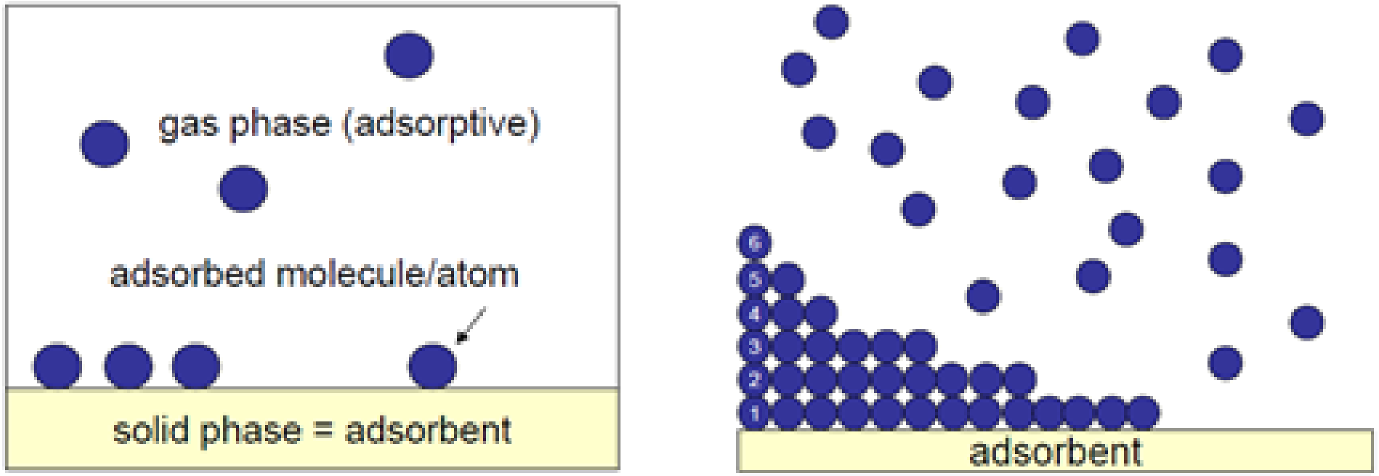
Relative size for particles, aggregates and corrosive species.

Particle Size Influence



- Particle size variation can lead to ingress of corrosive species that may attack the surface of the metal.

Adsorption Isotherms



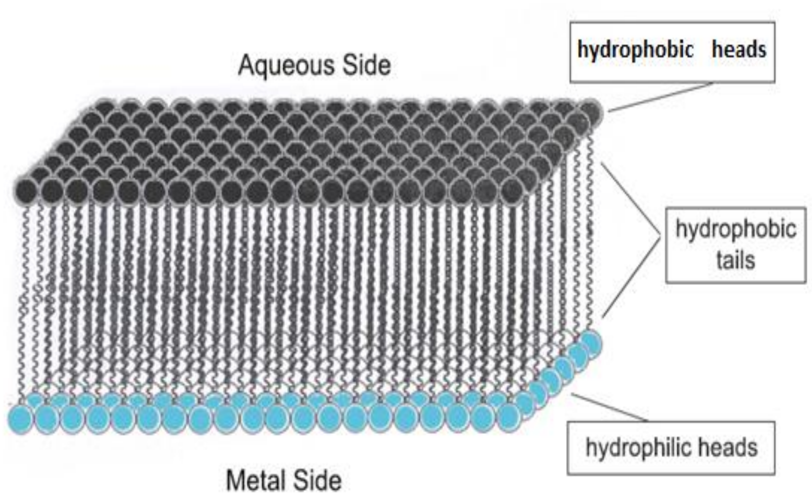
Atomic models for possible types of surface coverage, monolayer or multiple particle deposition on the metal.

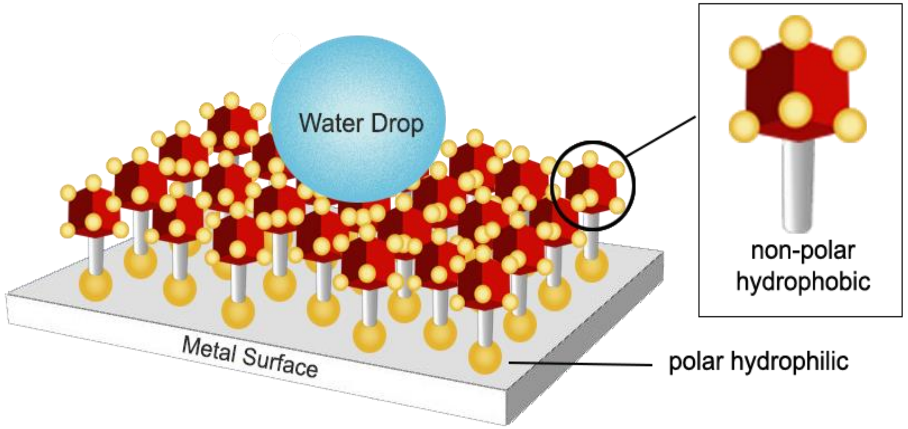
Adsorption Isotherm - Langmuir

- Irving Langmuir developed an isotherm that models gases adsorbed to solid surfaces.
- It is a semi-empirical isotherm with a kinetic basis derived from 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 adsorption sites are equivalent and each site can accommodate only one molecule.
  2. The surface is energetically homogeneous and adsorbed molecules do not interact.
  3. There are no phase transitions.
  4. Only a monolayer is formed. Adsorption only occurs on localized sites on the surface, not with other adsorbates.

How VCI Inhibitor Works

- VCIs use 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.

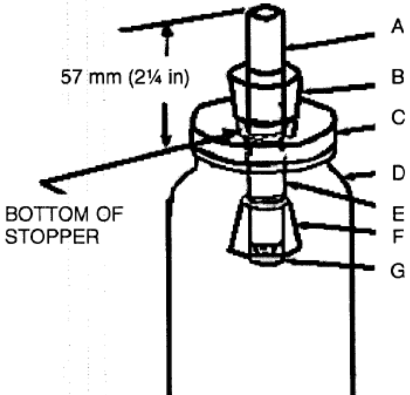


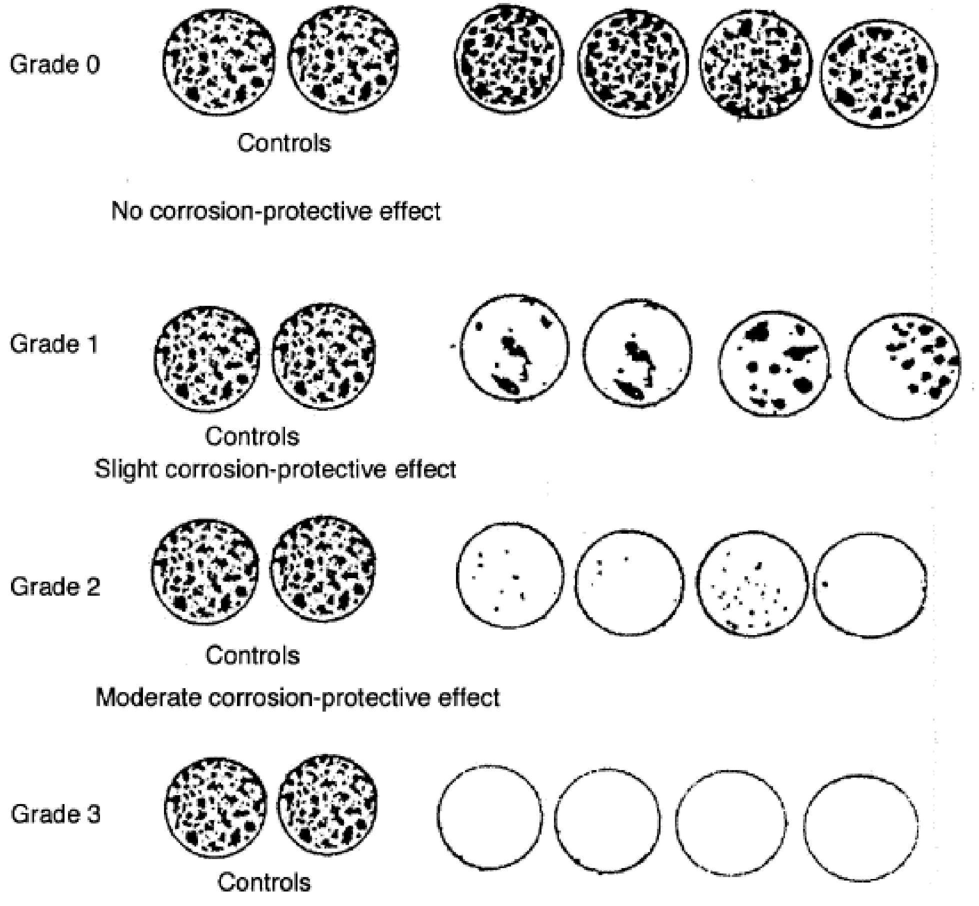


Experimental Procedure

- Corrosion behavior of carbon steel (UNS G10180) samples were studied in two different vapor corrosion inhibitors with coarse particles size (~150 um, V_pCI 309) and vapor corrosion inhibitors with nanoparticles size (~100 nm, V_pCI 309 DPM), Dense Phase Mill (DPM) is a special pulverized for heat sensitive powders using the NACE TM 208-2008 Standard Test Method.
- This laboratory test method evaluates the vapor inhibiting ability (VIA) of various forms of VCI materials for temporary corrosion protection of ferrous metal surfaces.

Typical visual patterns for rating VIA test results





Grade 0 – No corrosion-protective effect

Grade 1 – Slight corrosion-protective effect

Grade 2 – Moderate corrosion-protective effect

Grade 3 – Good corrosion-protective effect

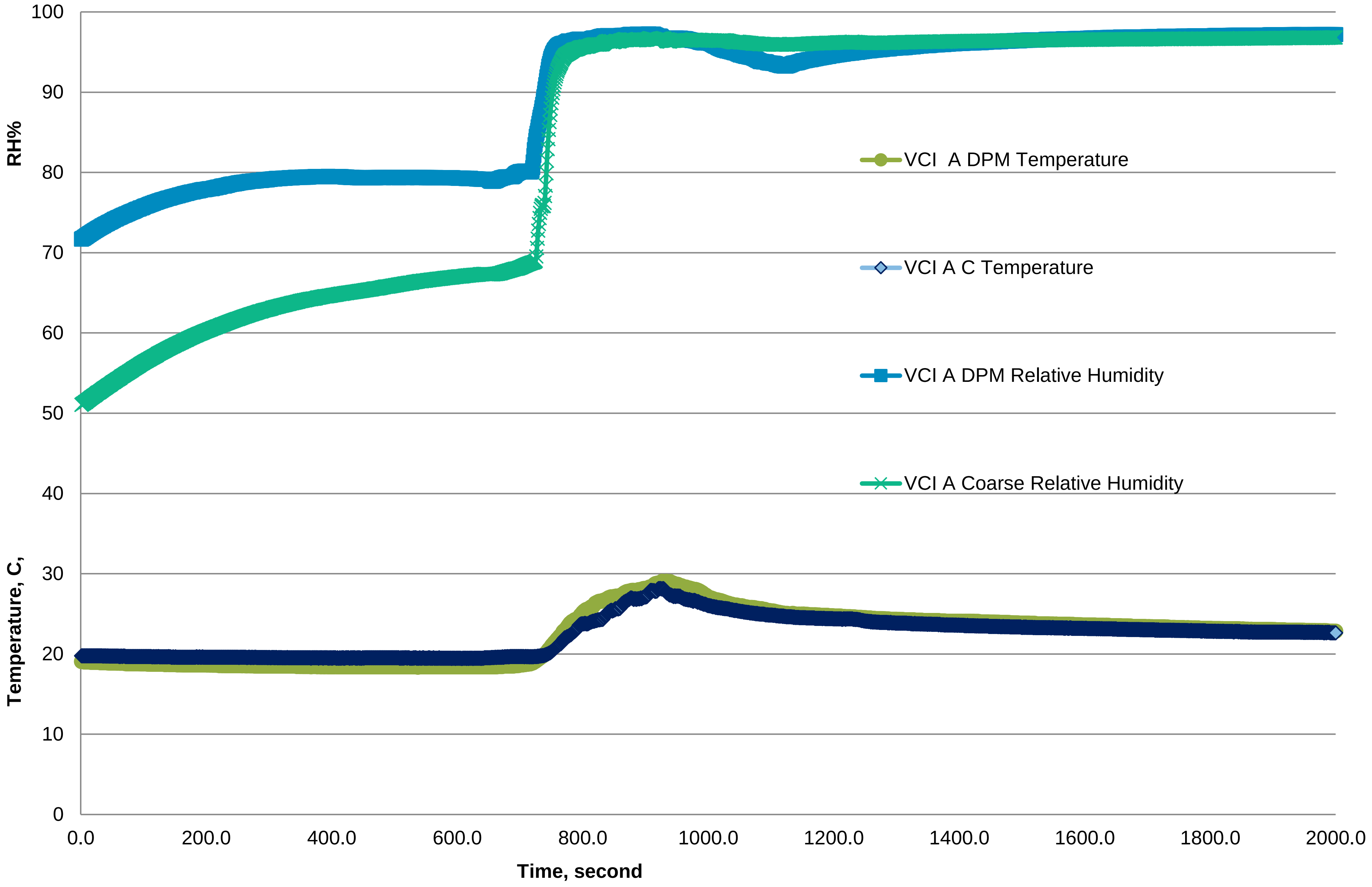
Grade 4 Same as Grade 3 except examined under 10X magnification.

Excellent corrosion-protective effect.

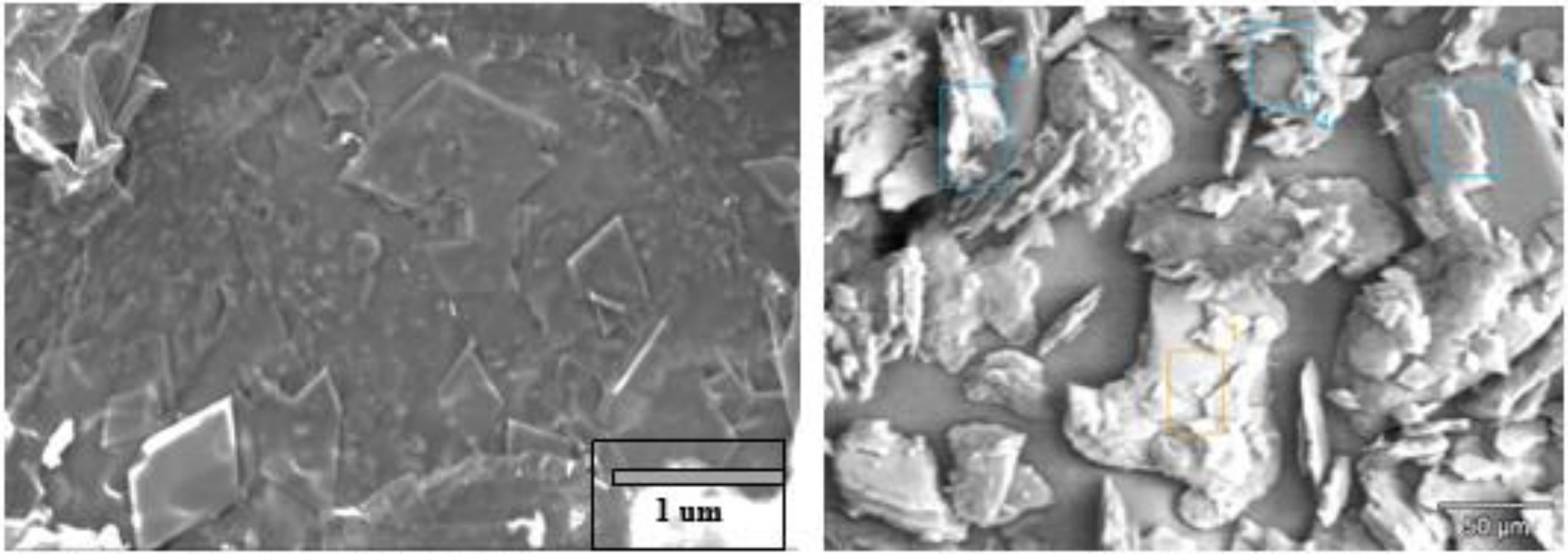
The VIA Corrosion Test Method, NACE TM 208

- The VIA corrosion test method provides for standard conditions in a test jar of warm air, saturated with water, absent any contaminants.
- Water vapor and VCI transport were confirmed and corrosion protection was evaluated in this test method.
- The VIA tests consisted of four steps of sample conditioning (saturation) for 20 hours at 22 ^{o}C, cooling cycle at 2^{o}C, pre-warming at 50^{o}C, followed by three hours at 22 ^{o}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: grade 0 through grade 4.
- To have a valid test, control samples 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.

Temperature and RH% monitoring during the VIA TM 208 tests on VCI



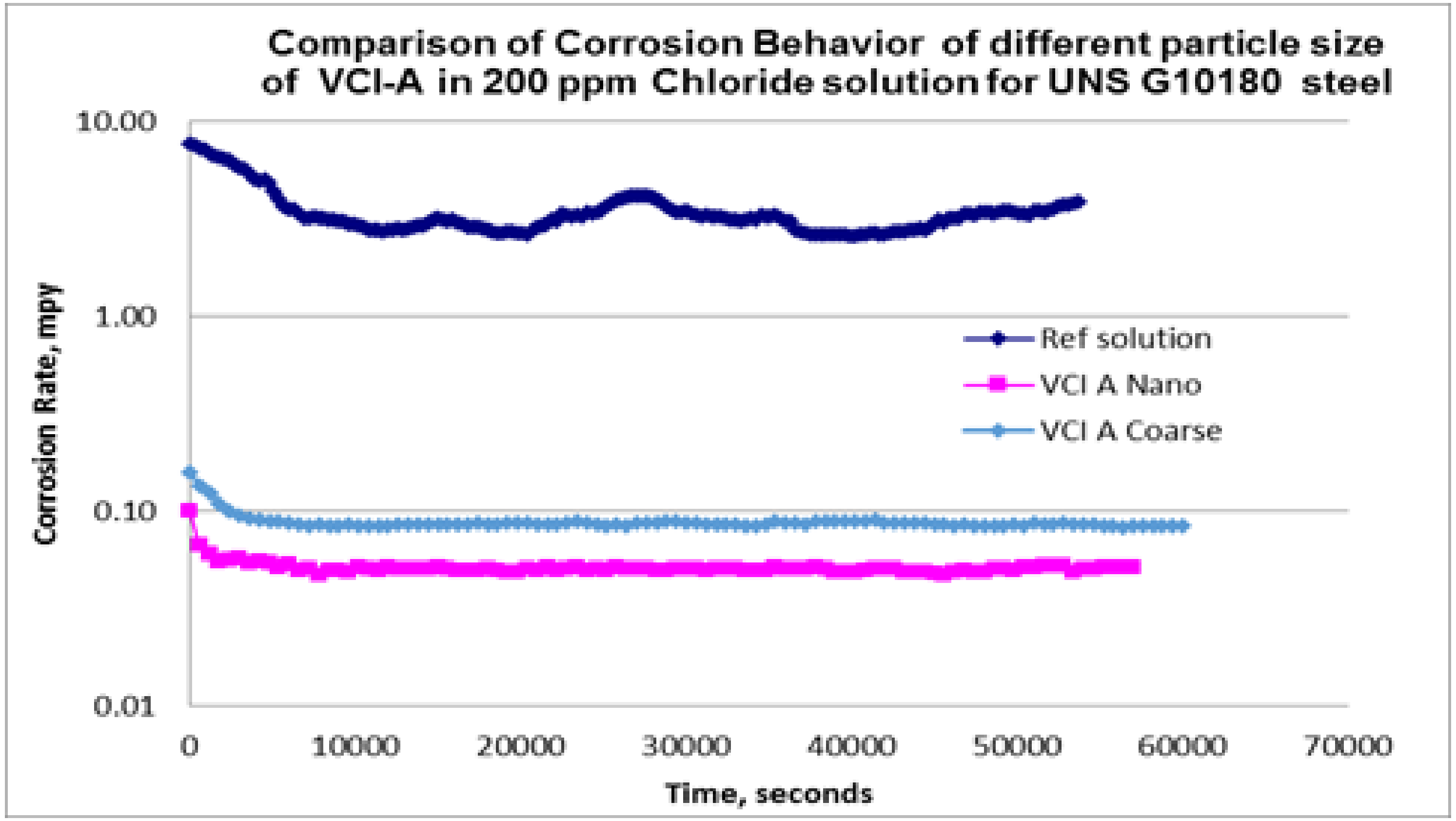
Comparison of Particle Size: VCI-A (DPM) platets of ~500nmx 2-5 nm thick



VCI-A Nano-size particle

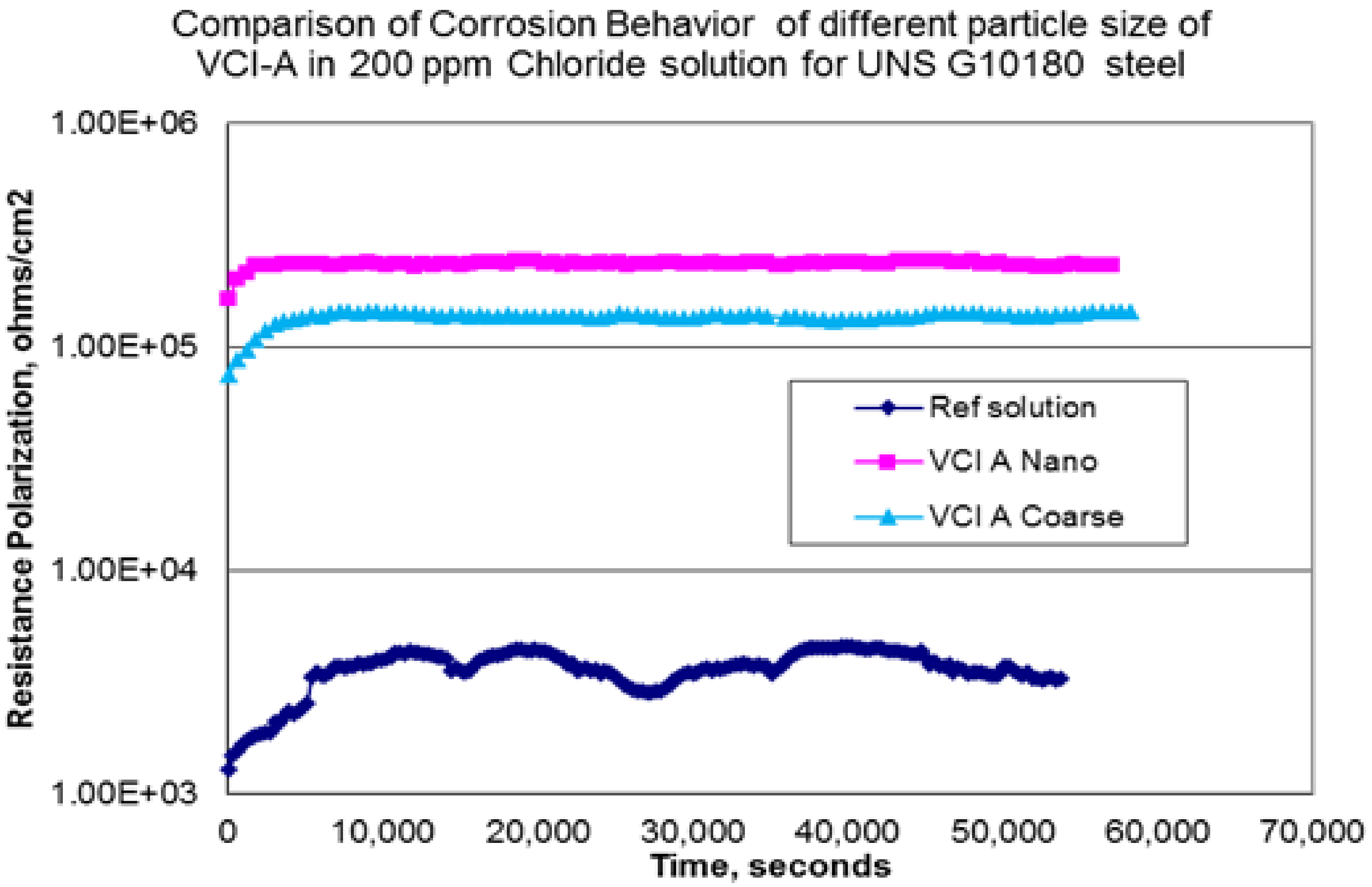
VCI-A Coarse particle

Corrosion Rate



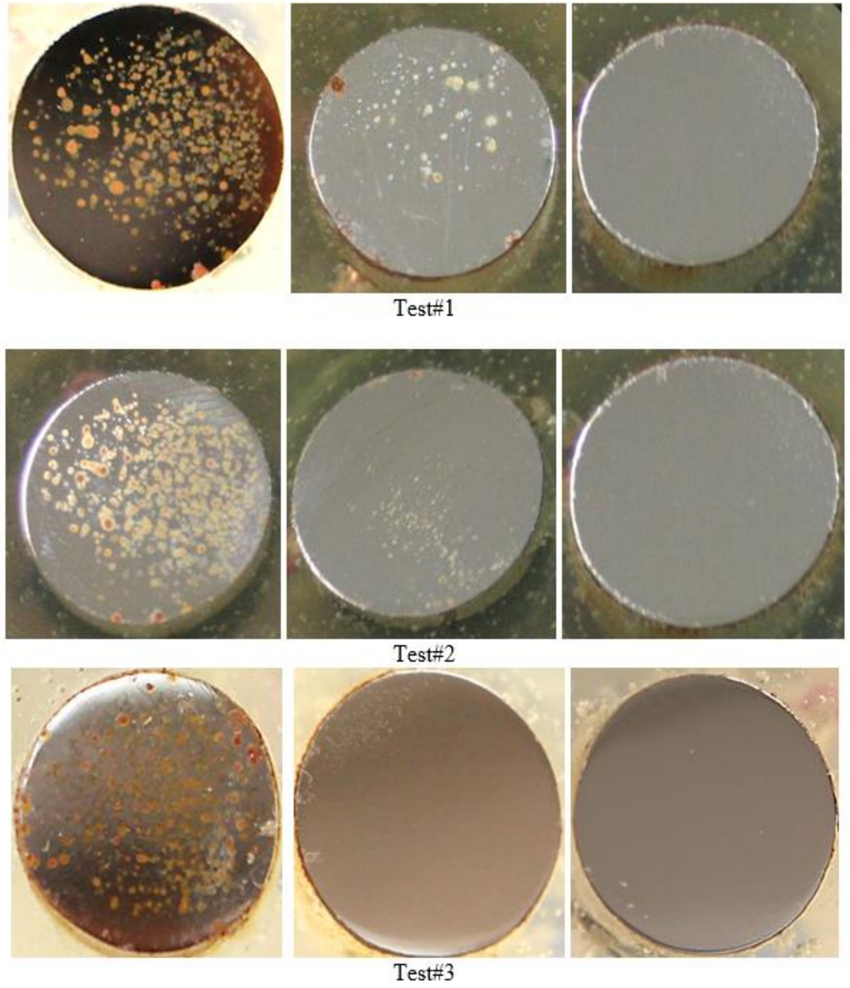
Comparison of corrosion behavior of different particle size for VCI-A in 200 ppm chloride solution for UNS G10180 steel.

Resistance Polarization



Comparison of polarization resistance for different particle size of VCI-A in 200 ppm chloride solution for UNS G10180 steel.

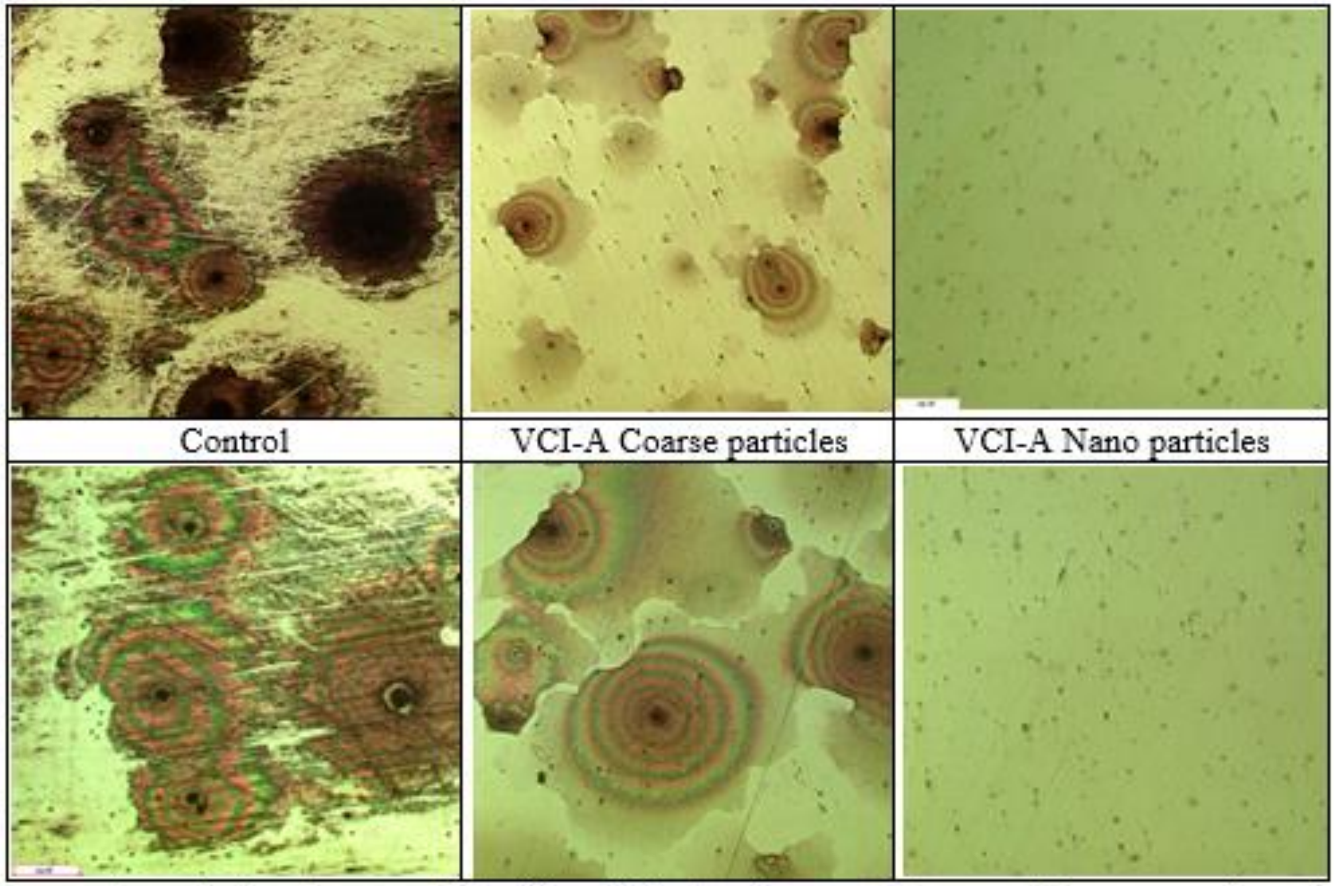
Photographs after VIA Tests



Photographs of steel samples after VIA tests and their corrosion rating; shows superior performance for VCI-A Nano exposed samples.

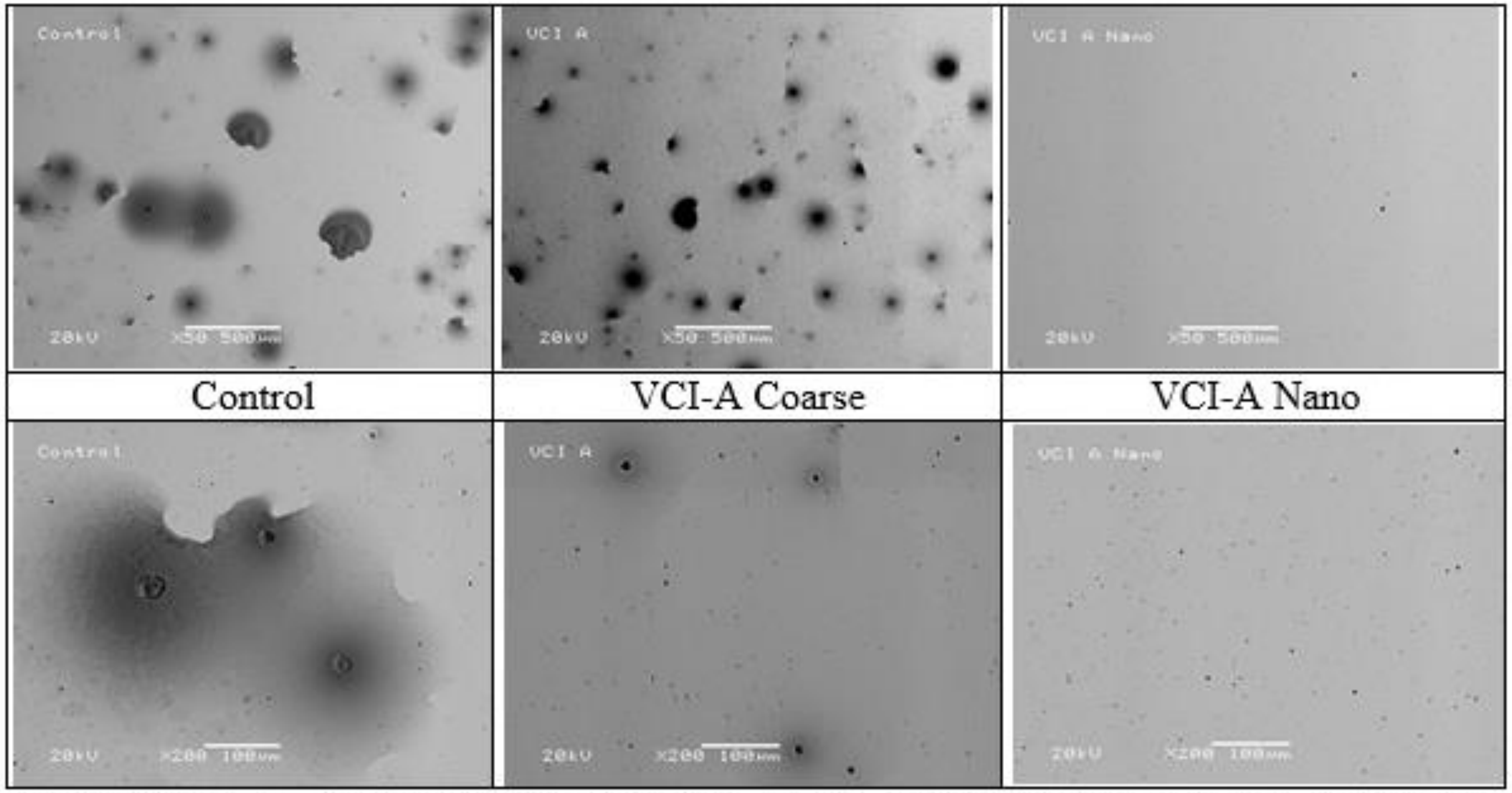
The corrosion rating per TM-208 indicated: control sample had Grade 0, while VCI-A coarse rating was Grade 2, and VCI-A Nano rating was Grade 4.

Optical Micrographs



Optical micrographs of steel samples after VIA tests; superior performance is seen for VCI-A Nano exposed samples.

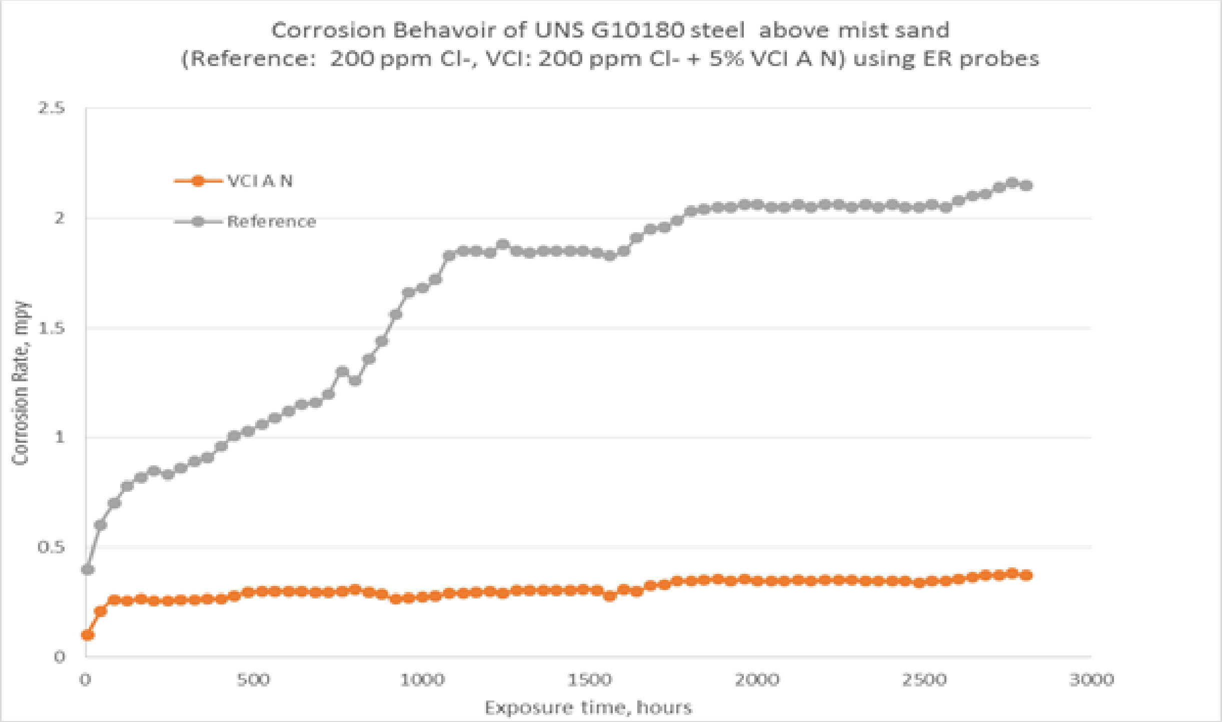
SEM Micrographs

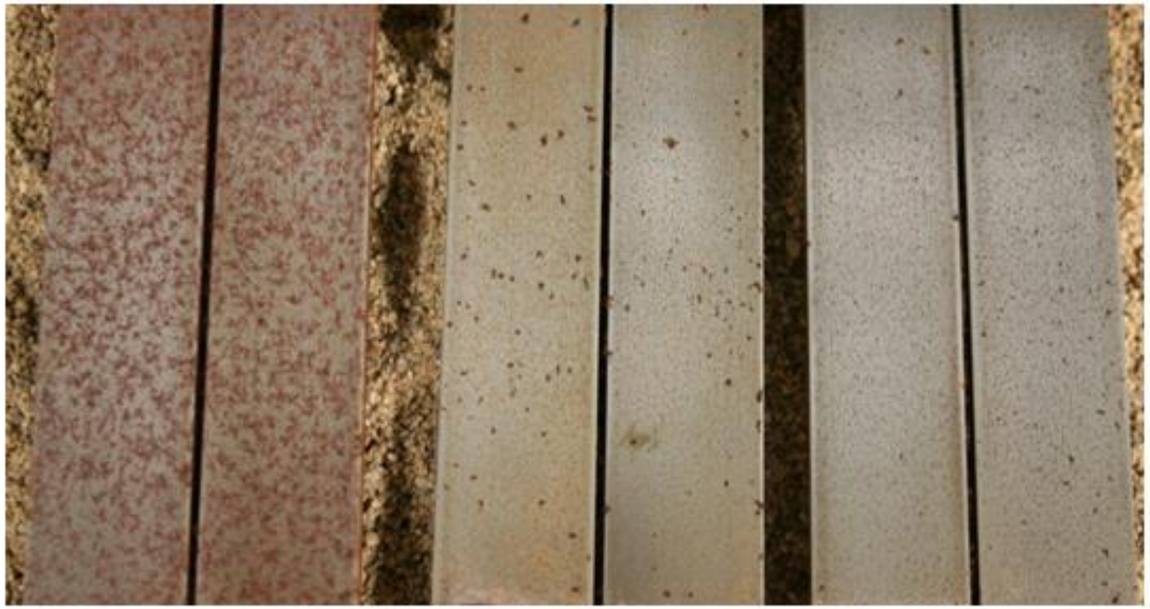


Control | VCI-A Coarse | VCI-A Nano

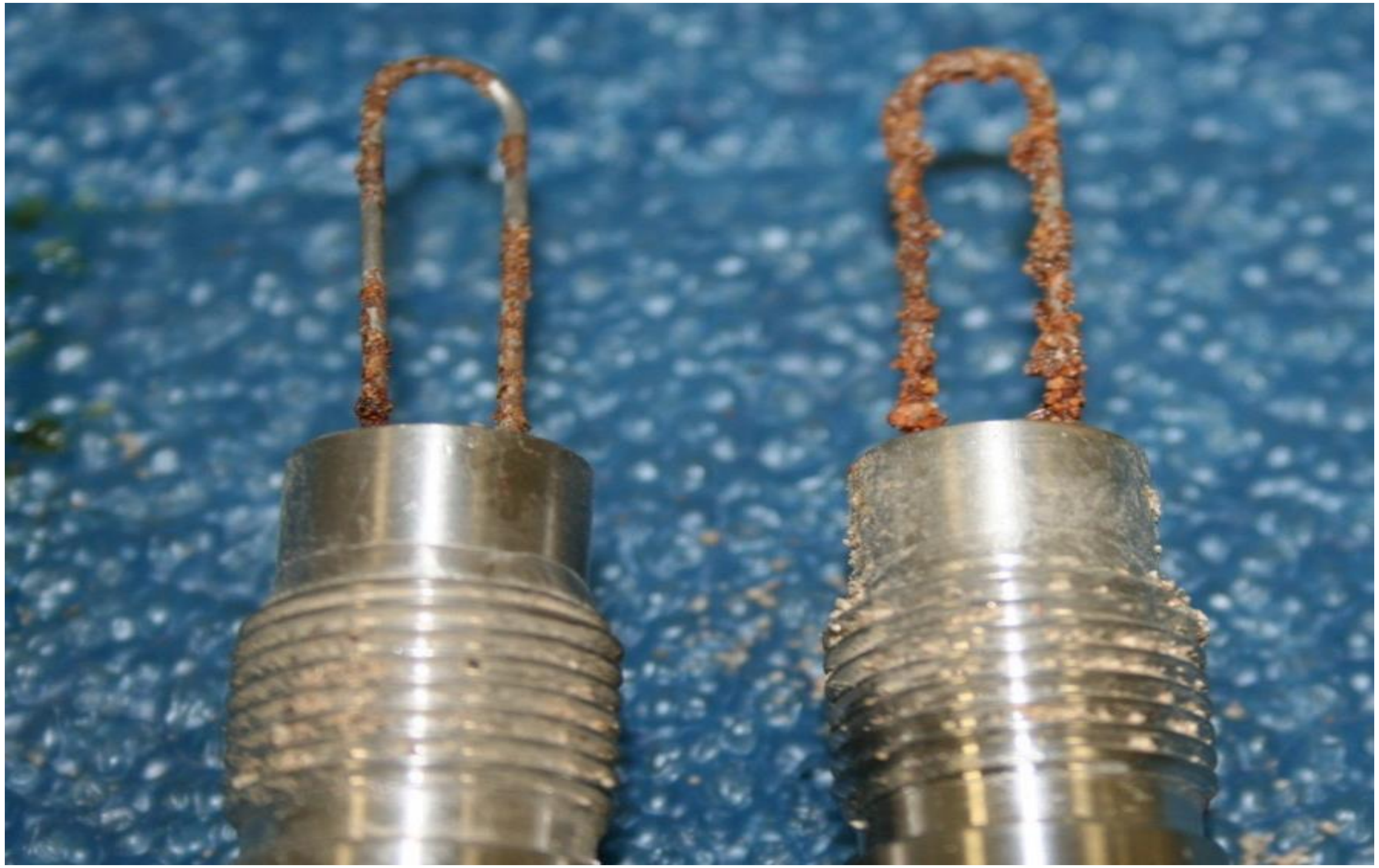
SEM micrographs of steel sample after VIA tests. Superior performance for VCI-A Nano exposed samples. The black dots on the VCI-A Nano samples are mainly alloy inclusions.

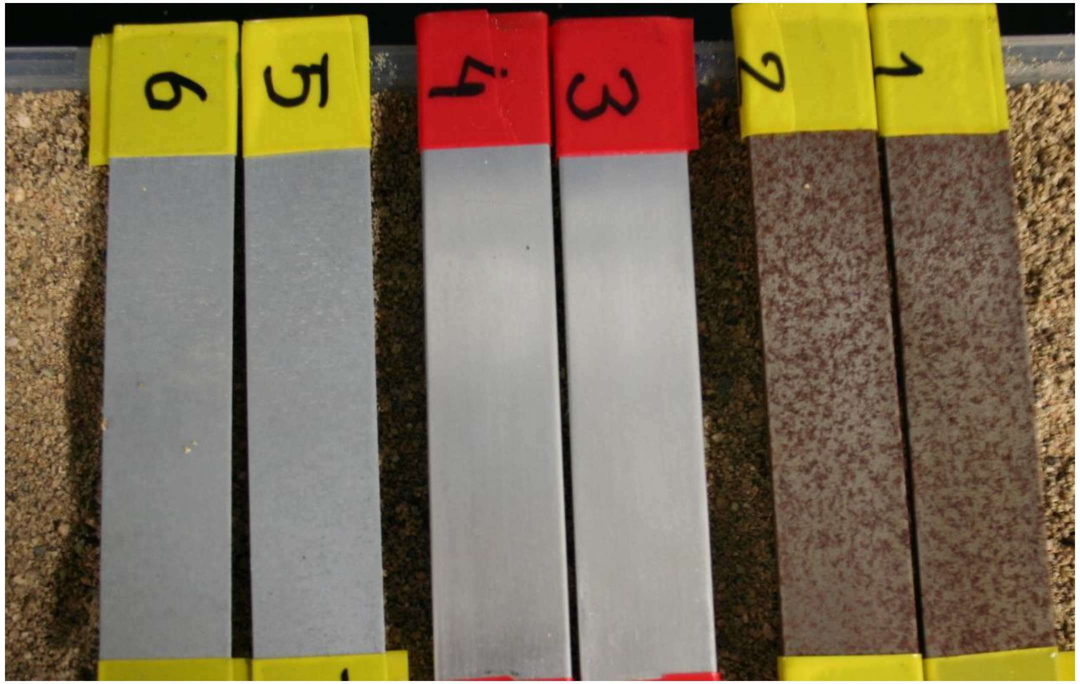
Comparison of corrosion behavior of UNS G10180 steel, continuous exposure Misted Sand tests (150 days above mist sand corrosion tests, 200 PPM Cl- solution added to sand bed every 72 hrs).





Reference VCI-A Coarse VCI-A Nano

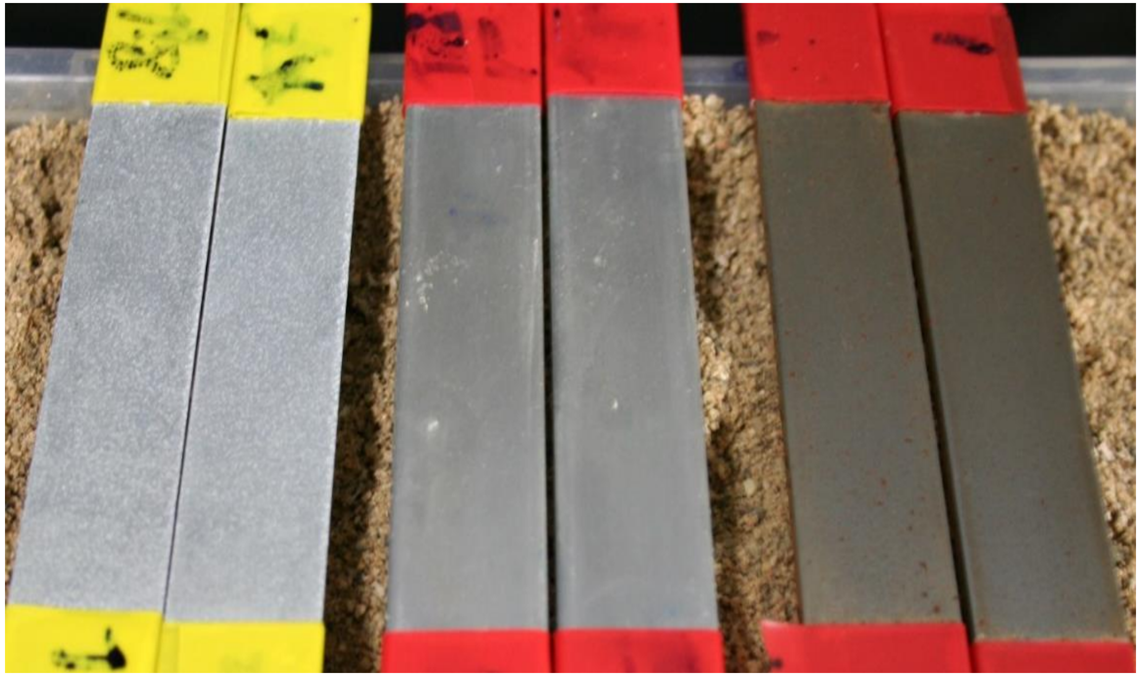




Galvanized steel
Control tests:

2024-T3 Aluminum alloy

UNS G10180 steel



Galvanized steel
VpCI 309 DPM

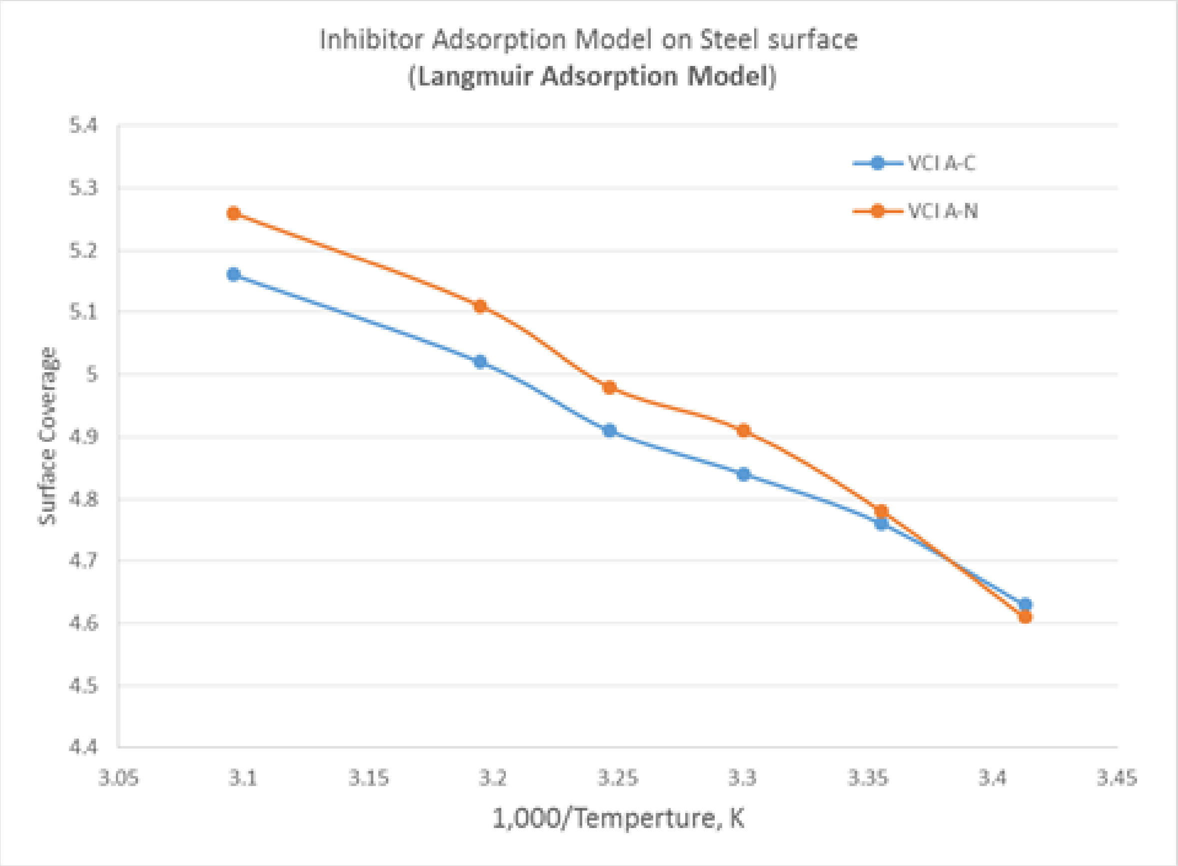
2024-T3 Aluminum alloy

UNS G10180 steel

The Adsorption Isotherm Relationship

- The adsorption isotherm relationship between surface coverage and temperature for both VCI-A coarse and VCI-A Nano inhibitors on the surface of steel is roughly:
- -16,740 J/mol for the nanoparticle size inhibitor, and -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.

Adsorption Energy



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.

How to measure particle velocity?

- Almost all industrial flows are turbulent.
- Almost all naturally occurring flows on earth, in oceans, and atmosphere are turbulent.

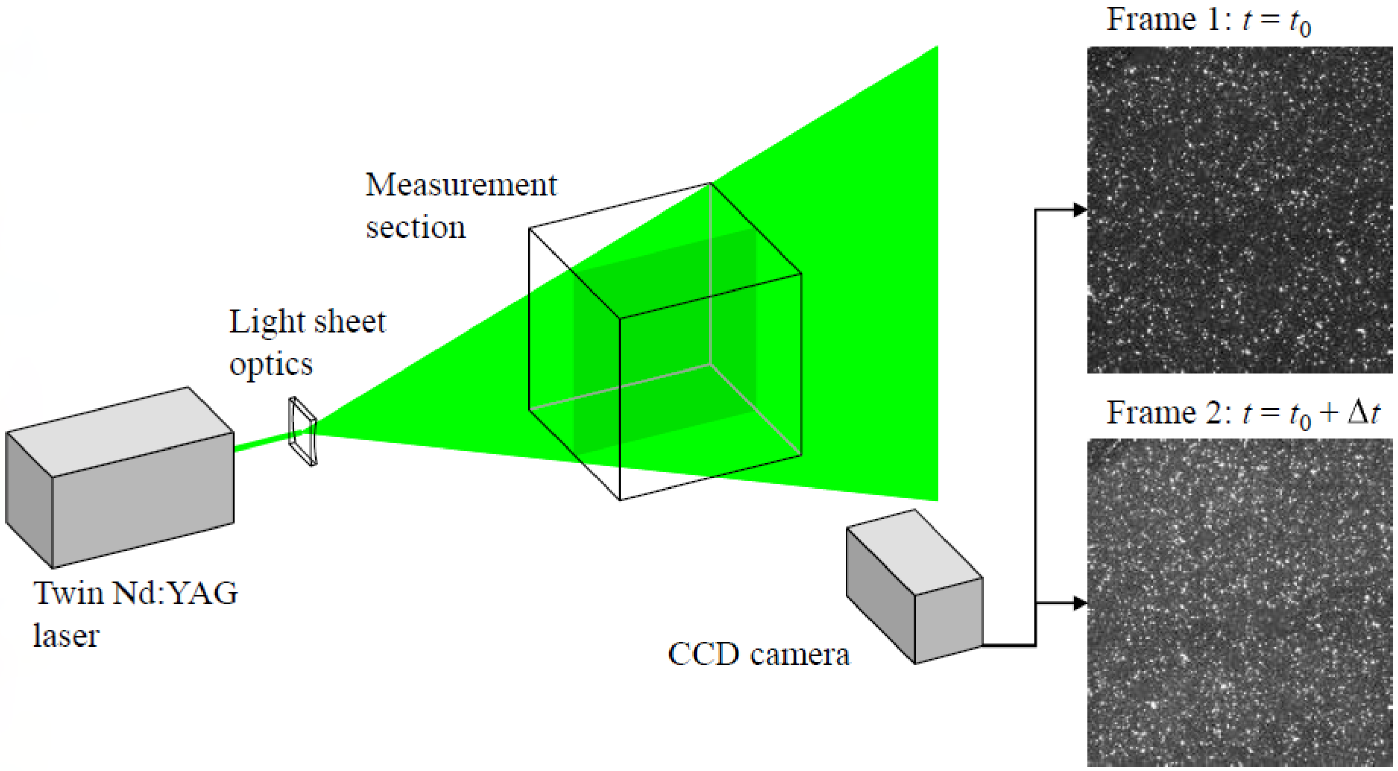
$$\rho \frac{Du_i}{Dt} = \frac{\partial \tau_{ij}}{\partial X_j} + \rho f_i - \frac{\partial p}{\partial X_j}$$

- Turbulent motion is 3D, vortical, and diffusive ⇨ governing Navier-Stokes equations are very hard (or impossible) to solve.
- Measurements are easier

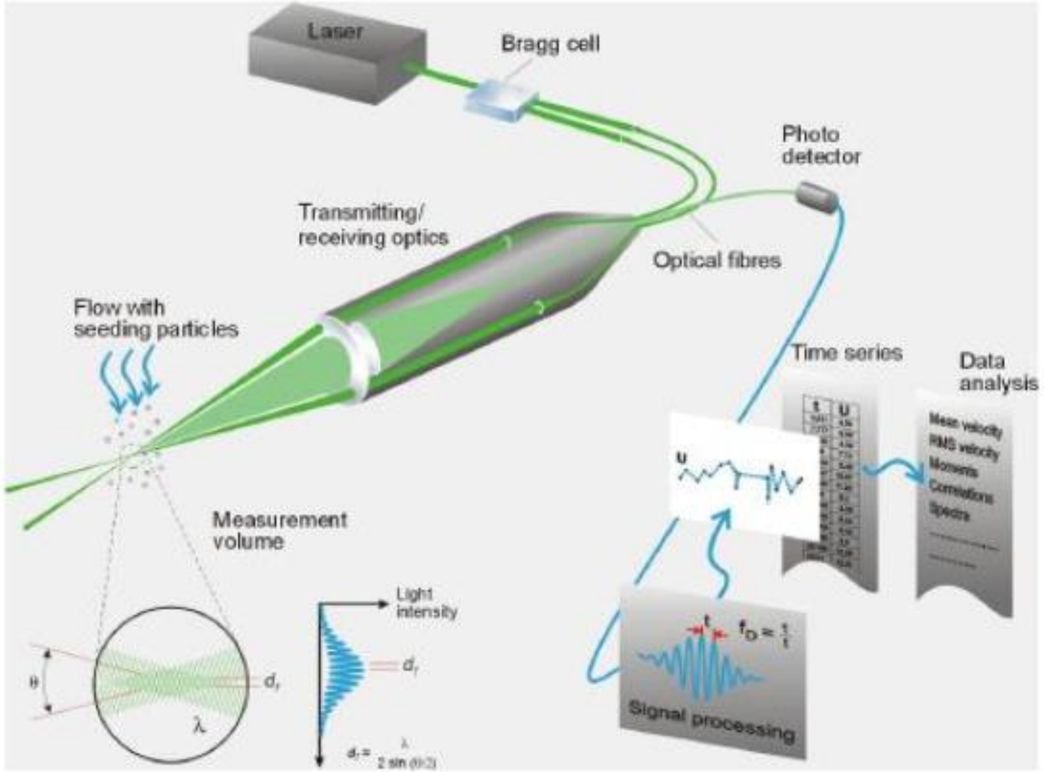
Current research activities

Particle Image Velocimetry (PIV):

Imaging of tracer particles, calculate displacement: local fluid velocity



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 flows, or the linear or vibratory motion of particles. The measurement with LDA is absolute, linear with velocity and requires no pre-calibration.

LDA

A high resolution -single point technique for velocity measurements in turbulent flows

Basics:

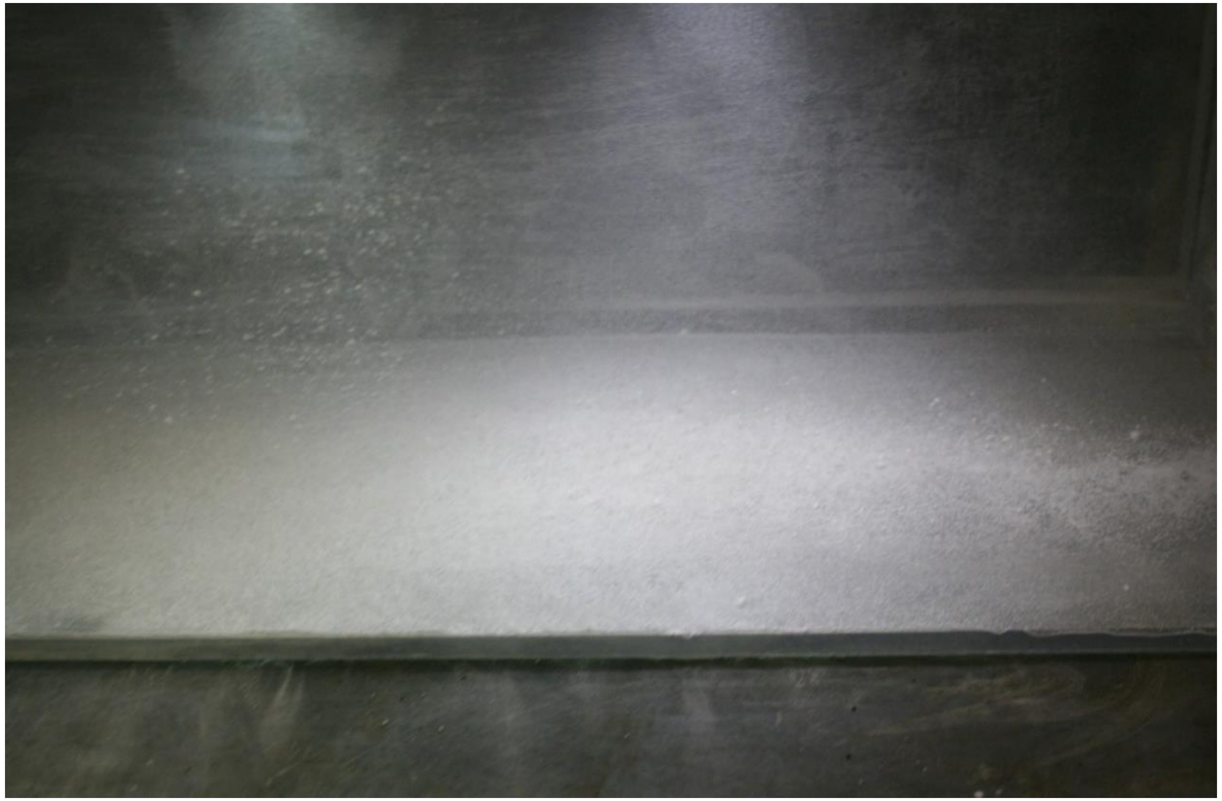
Seed flow with small tracer particles

Illuminate flow with one or more coherent, polarized laser beams to form a MV (measurement volume)

Receive scattered light from particles passing through MV and interfere with additional light sources

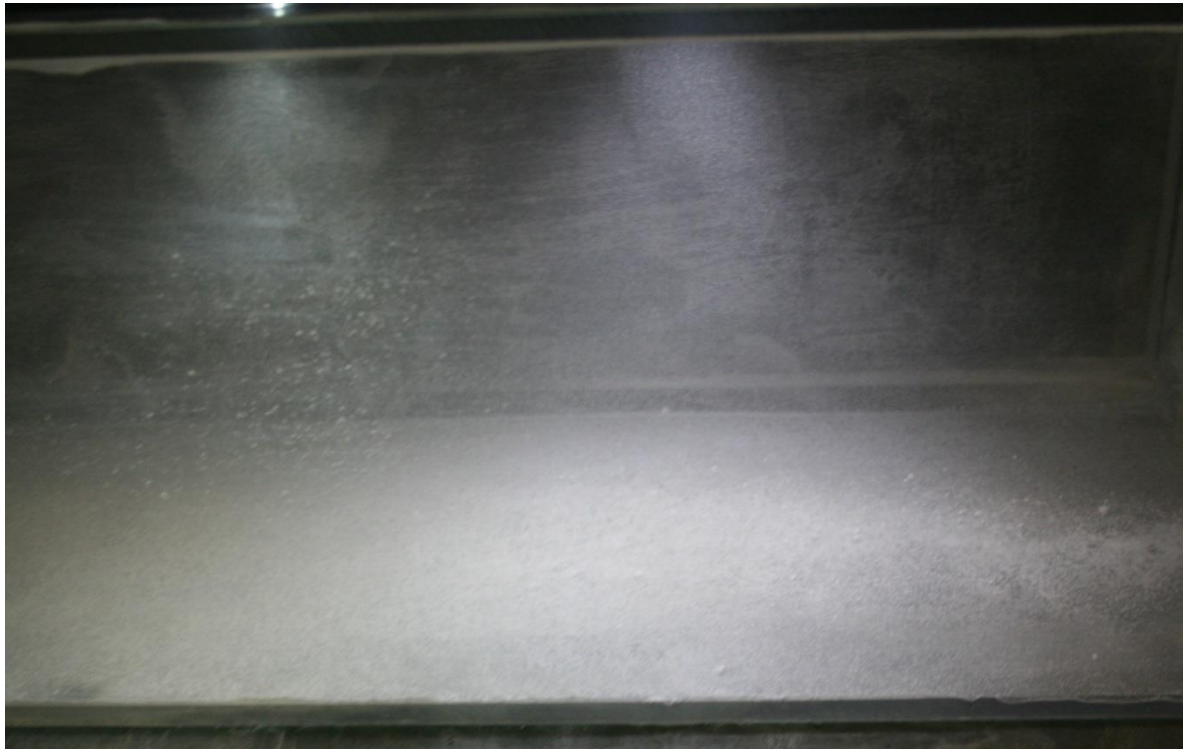
Measurement of the resultant light intensity frequency is related to particle velocity

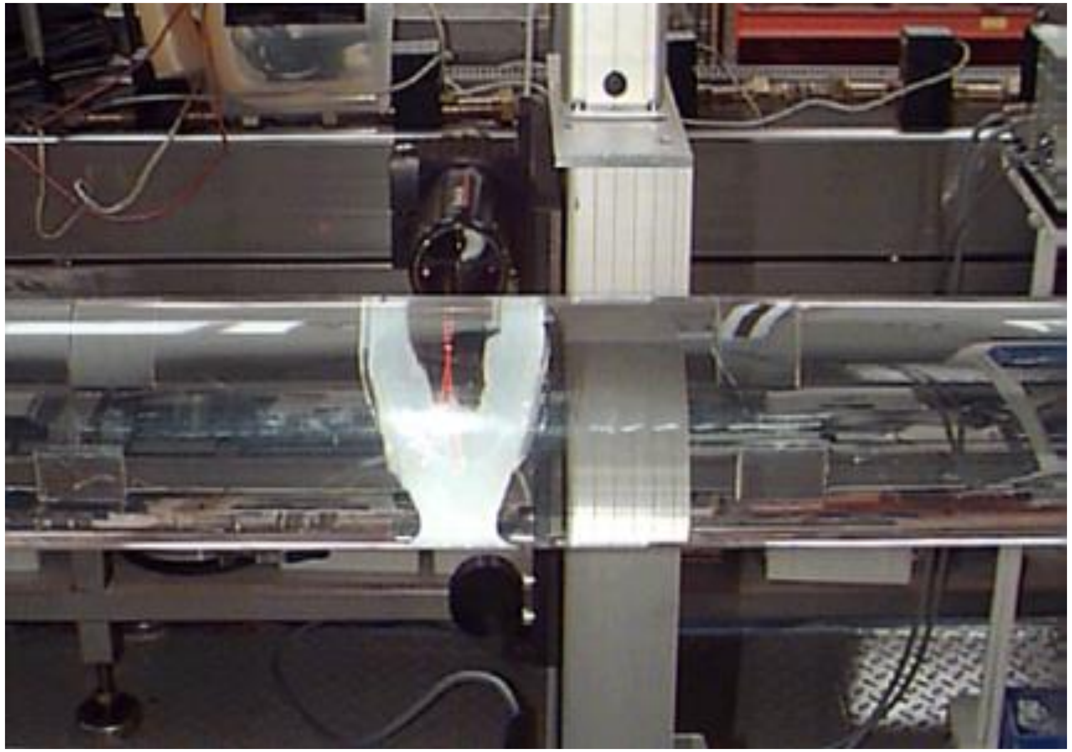
Fine VCI, 20 psi flow pressure

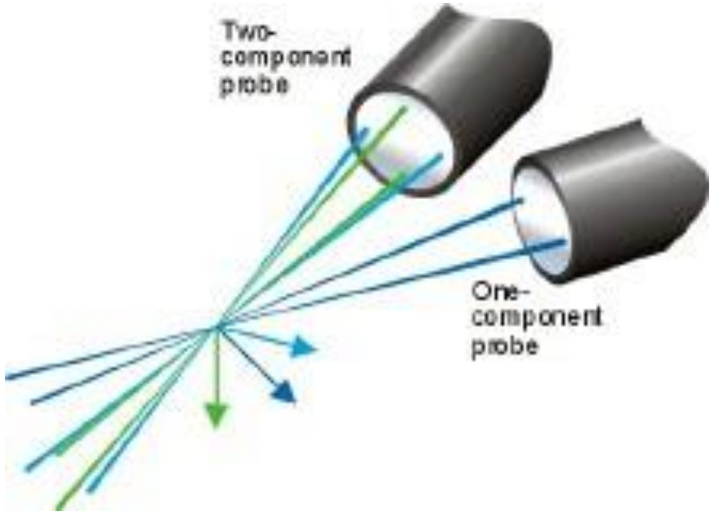


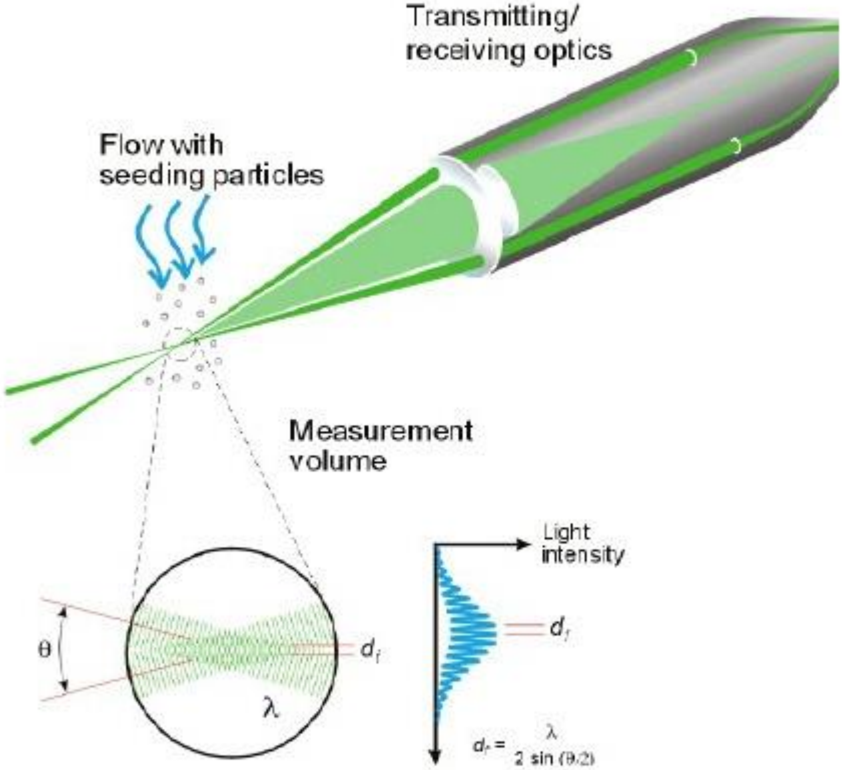
Coarse VCI, 20 psi flow rate

Measurement of velocity profiles in of VCI in box chamber





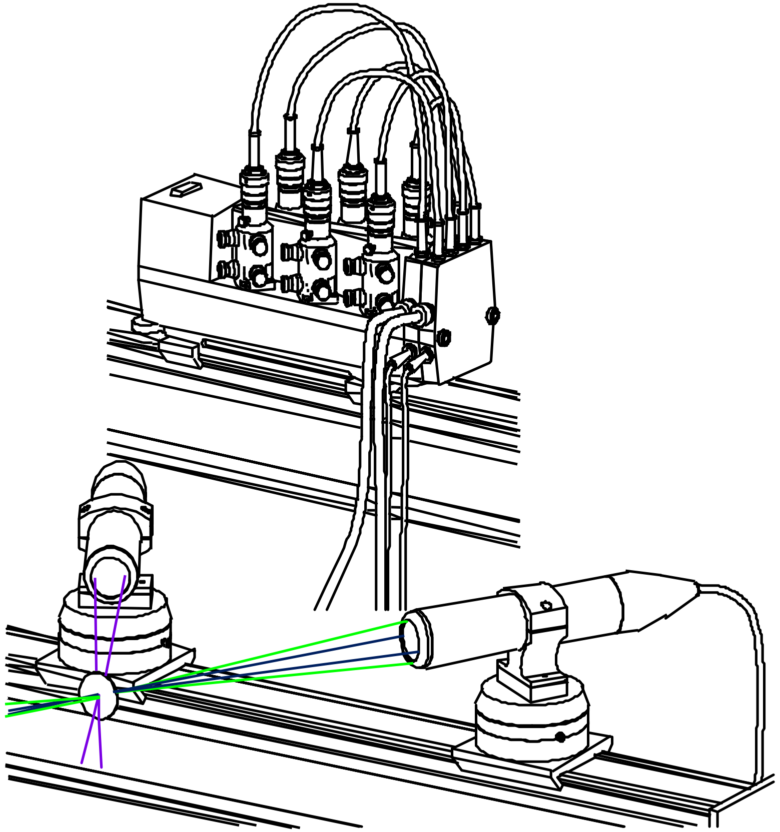




The probe and the probe volume.

FiberFlow set-up for 3D velocity measurements

- Measuring three velocity components requires three beam pairs.
  - Two pairs are emitted from a 2D probe
  - One pair from a 1D probe
- The two probes are aligned so their intersection volumes coincide.
- The velocity components measured by the beams from the 2D probe are orthogonal.
- The third velocity component can be orthogonalized by software.



Conclusions

- The nano-particle inhibitor (V_pCI 309 DPM) showed best corrosion rating grade of 4 (after VIA tests).
- Electrochemical corrosion tests showed more than 41% decreased corrosion rate for the nano-particle inhibitor .
- Surface coverage also appeared to improve due to the increased effective surface area and increased partial pressure of vapor inhibitors as powder particle size decreased.
- Adsorption energy was roughly -16,740 J/mol for nano-particle size inhibitor, and -13,660 J/mol for the coarse-particle size, indicating strong physical adsorption to the metal surface for both inhibitors.
- V_pCI 309 DPM (Nano-VCI) showed a stronger interaction with steel surface than the coarse inhibitor, leading to better corrosion protection.
- Changing the particles (going Nano-size powder) of inhibitors improve the flow and increase velocity by a factor of 2-3, means a better transport and more accessibility and coverage.

Current Research activities

Monitoring the long term compatibility of VCI and Cathodic Protection of tank bottom

Practical application of VCI into tank bottom, and life expectancy and re-injection intervals

- Acknowledgments

- Cortec Corp for supporting this project
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- Dept. of Transportation, Pipeline Safety