Aegis Tech Line

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CORROSION IN OIL & GAS PRODUCTION

Corrosion is the destruction of a metal by chemical or electrochemical reaction with its environment (Uhlig's Corrosion Handbook). Electrochemical corrosion normally applies in oil and gas production.

The corrosion process requires the following:
Anode: Iron (Fe) from steel reacts to forms iron ions (Fe++) that go into solution, and two (2) electrons that travel through the conductor to the cathode
Cathode: Two (2) electrons formed at anode react with Hydrogen (H+) in the water to form Hydrogen (H_2) gas
**Conducting Solution:** Water with dissolved minerals
Conductor: Steel - pipe/tubing/casing/sucker rod/etc.

Anodes and Cathodes exist throughout the steel due to differences in electrical potential across grain boundaries. Corrosion rate units are typically described in Mils Per Year (mpy). A mil is a thousandth of an inch, so mpy is then thousandth of an inch/year. In the metric system it is measured in millimeters per year or mm/year. The corrosion rate is then the loss of that amount of thickness of the steel in a year's time. Corrosion is generally NOT uniform across the entire area of the steel. Pitting may occur and cause unexpected early failure – it only takes one hole in the steel structure used in oil & gas production to cause a failure.

ANODES AND CATHODES IN STEEL

Alloying iron with carbon (usually 0.2 to 1%) produces steel (low-alloy steel). Steel is a far stronger metal than iron and is therefore better suited for use in the oilfield. Other components can also be added to iron to enhance the corrosion-resistance properties of the resulting steel. These include manganese (Mn), chromium (Cr), molybdenum (Mo) and nickel (Ni) to name a few. Some of the carbon added to the iron is insoluble and forms iron carbide (Fe_3C). This accelerates the cathodic processes necessary for corrosion to take place, accelerating the corrosion rate. One of the major, ubiquitous impurities in steel is sulfur, and it is a major source of corrosion instability. Grain boundaries are also areas that are chemically active. When iron solidifies during casting, the atoms that are randomly distributed in the liquid state arrange themselves in a crystalline array. This ordering usually begins simultaneously at many points in the liquid. As these blocks of crystals and grains meet, there is a mismatch in the boundaries. There are areas of higher energy. Impurities in the liquid metal tend to accumulate at these grain boundaries. These accumulations of impurities are more susceptible to chemical attack than the iron surface itself.
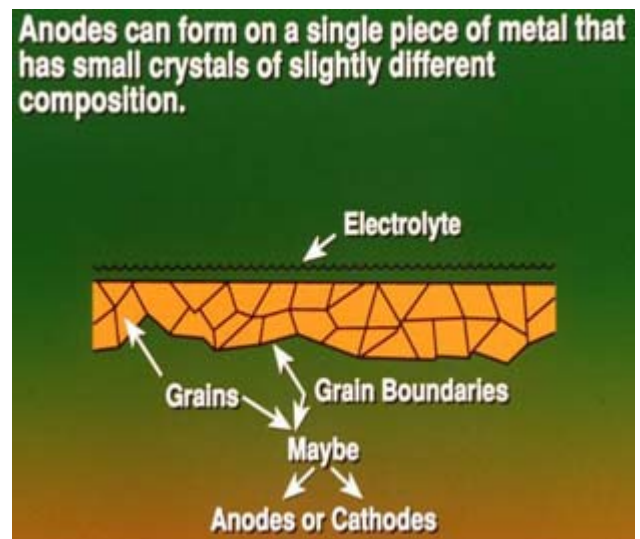
MAJOR CAUSES OF CORROSION IN THE OILFIELD

There are numerous causes of corrosion that attack the steel used in oilfield wells, pipelines and surface equipment. Salt water that may be naturally occurring in the wells or may be introduced by the producers is a conductor. One of the major corrosion mechanisms is acid gases. Hydrogen sulfide (H_2S) is an acid gas that can occur naturally in the formation or can be the result of contamination introduced into the formation by the producers. The H_2S can react with the iron in the steel producing iron sulfide (FeS) as a corrosion product.

H_2S Corrosion

Carbon dioxide (CO_2) is another acid gas that often occurs naturally in the formation. This gas can react with the iron in the steel to produce iron carbonate ($FeCO_3$) as a corrosion product. Oxygen (O_2) is a soluble gas that can react with the iron in the steel to produce iron oxide (Fe_2O_3) as a corrosion product generally called rust. O_2 solubility decreases with increasing water temperature.

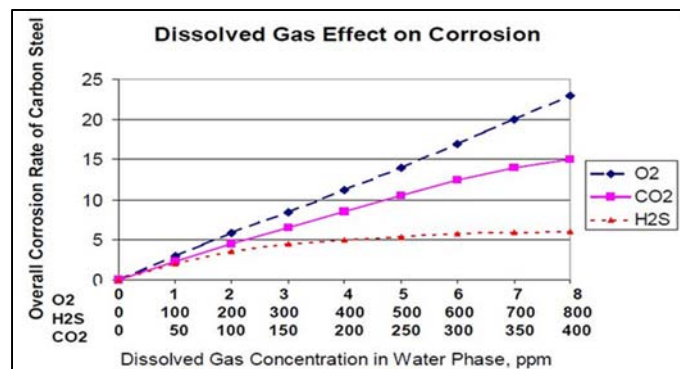**MIC in Wet Gas Pipeline**   **MIC at Prudhoe Bay**
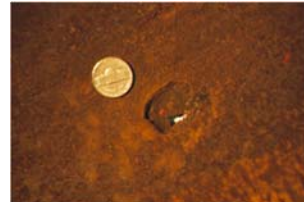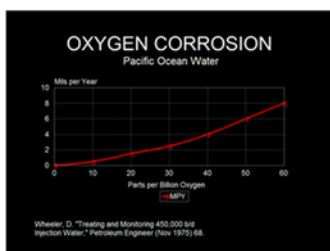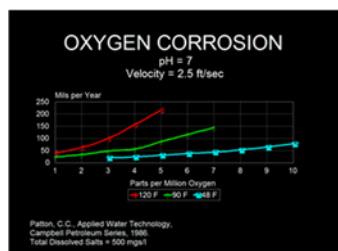
Acids also attack the steel. Acids can be naturally occurring organic acids or hydrochloric acid (HCl) introduced into the wells or surface equipment for a variety of reasons (for example, acidizing).

OTHER CAUSES OF CORROSION

There are other causes of corrosion that are typically not prevented using corrosion inhibitors. Galvanic cells are produced when dissimilar metals are in contact with each other. Examples where galvanic cells can develop are:
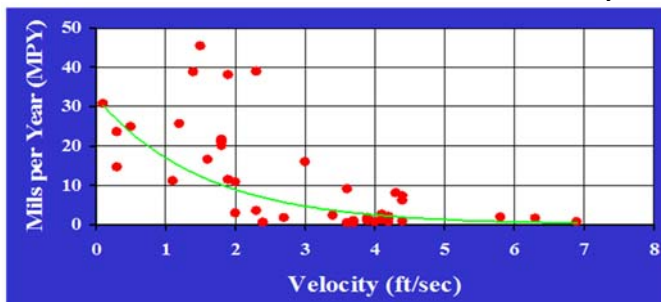
- Pipe to pipe coupling of different metals
- Weld material used in fabricating pipeline, gathering lines or other oilfield metal structures
- Different grades of steel in contact with each other

Electrolysis produced from stray electrical currents from grounding, electrical equipment, etc. Mechanical damage to steel from sand erosion (or other particulates), wear from moving metal-to-metal contact, nicks or cuts in the steel surface (particularly if coated) and bends in the steel that produce cracking in the metal surface.

Erosion Corrosion

Poor heat treatment during steel production that results in high corrosion rate in heat affected zone (HAZ).

Bacteria, and more specifically sulfate-reducing bacteria (SRB), can lead to severe isolated pitting in the surface of the steel underneath a colony of bacteria. This type of corrosion is called Microbial Induced Corrosion (MIC) and can be particularly severe in stagnant or near stagnant conditions.

Microbial Induced Corrosion Rate vs Fluid Velocity

OTHER FACTORS INFLUENCING CORROSION

There are other factors influencing corrosion as follows:

- Chlorides: Influence corrosion inhibitor solubility and water conductivity
- Temperature: Corrosion rate generally increases with increasing temperature
- Pressures: Solubility of CO_2 and H_2S increases with increasing pressure
- Velocity: Can accelerate MIC when low, or accelerate CO_2 corrosion when high
- Wear/Abrasion: Such as sucker rods rubbing on inside of tubing
- Solids: Such as sand, scale which strips protective films and erodes metal
- Oxygen in Combination with CO_2 or H_2S: Can increase corrosion rate significantly
- Corrosion rate is typically worse at bends or elevation changes, especially if welds are present
- Other chemicals:
  - Frac fluids
  - Enhanced Oil Recovery (EOR) chemicals
- Oil/water ratio and type of oil
  - If oil is the external phase and the water is emulsified or dispersed, this minimizes corrosion
    - However, in low velocity pipelines water can fall to the bottom and build-up in low spots
    - Oil pipelines containing <1% water have shown corrosion at the bottom.
  - Heavy oils may have natural corrosion inhibition properties.
  - In condensates, corrosion can be significant even at very low water cuts.
    - Condensate does not oil-wet the pipe.
  - Some oils contain elemental sulfur, which can be extremely corrosive to steel.
- High volumes of methanol injection to prevent hydrates can make corrosion worse
  - Oxygen is substantially more soluble in methanol than in water
    - Addition of oxygen corrosion inhibitor can prevent
  - Methanol is more volatile than water and will vaporize if injected in hot areas

  - As it condenses as the pipeline cools it can cause "top of the line" corrosion, which is difficult to inhibit with continuous injection.
  - Batch filming of inhibitor between two pigs has been found to work on "top of line" corrosion

CORROSION PREVENTION

There are numerous methods to prevent corrosion that are dependent on the causes of corrosion. To minimize corrosion caused by O_2, there are methods are to exclude, remove, scavenge or inhibit the O_2. These include:
- Nitrogen or dry gas blankets on tanks
- Seal the annulus of wells
- Maintain compressor or pump seals to prevent oxygen ingress
- Vacuum towers often used on surface water or seawater used in water floods to remove oxygen
- Scavenge with sulfite or bisulfite if oxygen exclusion fails

To minimize corrosion caused by H_2S use a corrosion inhibitor. In some cases where the H_2S content is relatively low, the H_2S is scavenged and converted to a noncorrosive material.

To minimize corrosion caused by CO_2, use methods to inhibit the CO_2.

To minimize the effect of bacteria and Microbial Induced Corrosion:
- Utilize frequent batch treatment with biocide
- Frequently pig pipelines to remove solids and bacteria on pipe walls in conjunction with biocide treatment
- Control fluid velocity to maintain flow at 5 to 6 feet/second or higher
- Batch treatment before any shut-in

CORROSION INHIBITORS

Corrosion inhibitors form semi-permanent protective coatings, or "oil-wet" films on the steel surface. Corrosion inhibitors are usually water soluble or water dispersible since corrosion takes place at the water-steel interface. Since the corrosion inhibitor partitions into the water phase, it is

carried to the steel by the water. The corrosion inhibitor is usually added continuously to the corrosive fluids at dosages of 10 to 1,000 parts per million (ppm) where the injected corrosion inhibitor can treat a significant portion of the system, or where the facilities (injection pump, downhole delivery system, chemical tanks, etc.) exist to treat individual wells. Batch treatments using treater trucks are the typical alternative used in pumping wells due to lack of power, and the cost of chemical injection pump and related infrastructure to apply corrosion inhibitors continuously on individual wells. Pipelines may be batch treated (usually with planned pig runs) in addition to continuous injection especially if "top of the line" corrosion is predicted or has been experienced.

CORROSION INHIBITOR ATTRIBUTES

Corrosion inhibitors are usually a complex mixtures of organic chemicals. They must be pumpable under cold conditions particularly for use where the winters approach arctic conditions. This would include deep-water applications offshore. Corrosion inhibitors must be designed not to degrade in hot environments such as in deserts or tropical zones. They must be thermally stable for use in high temperature production. They must be designed so as not to cause foaming or emulsions in produced oil and water. The lower the toxicity or hazard class the better in case of a spill, or where produced fluids containing the corrosion inhibitor end up in the environment. In some cases, this is regulated such as in the North Sea. Corrosion inhibitors must have the right solubility in the water at system temperature.

CORROSION INHIBITOR CHEMISTRY

Oilfield corrosion inhibitors are typically composed of one or more primary components and could include some secondary components depending on the application of the corrosion inhibitor and field conditions. Primary components of corrosion inhibitors include the following:

- Primary, secondary, or tertiary amines or amine salts
- Imidazolines and amides and salts
- Quaternary ammonium chlorides
- Phosphate esters
- Fatty acids and salts
- Fatty acid dimers and trimers and salts

- Naphthenic acids and salts

Secondary components of corrosion inhibitors include the following:
- Emulsion preventer (usually polyols, sulfonates or alkyl phenol/formaldehyde resin alkoxylates)
- Surfactants to adjust solubility in brine at system temperature
- Anti-foam or defoamer
- Glycol and/or alcohol pour point depressant
- Neutralizing acid or base to adjust pH of final formula

TESTING AND SELECTION OF CORROSION INHIBITORS

Testing in the laboratory should simulate the conditions in the field as closely as possible. This includes the following:
- Temperature and Pressure
- Brine chemistry and type of oil – field fluids may be used
- Partial pressure of H_2S and/or CO_2
- Velocity of produced fluids simulated with flow loops or rotating steel coupons
  - A range of velocities should be simulated, since flow conditions may change during the life of the field, or may vary within the field especially in pipeline gathering systems
- In cases where sand production is severe, it may also be used in testing
- Tests conducted to meet requirements identified above
  - Pour point
  - Emulsion and foaming tendency
  - Heat stability
  - Toxicity and hazard rating

Field trials on individual, groups of wells or selected portions of pipelines may be conducted to ensure the efficacy of work done in the laboratory

LABORATORY CORROSION TESTING

The typical laboratory testing used to evaluate the performance of corrosion inhibitors based on field specifications is included below.
- Wheel Test
  - Low velocity/low pressure

- - Temperature to 180°F
- Bubble Test
  - Low velocity/low pressure
  - Temperature to 180°F
- Rotating Cylinder Electrode (RCE)
  - High velocity/low pressure
  - Temperature to 180°F
- High Temperature, Pressure, and Velocity Testing
  - HP/HT rotating coupon
  - HP/HT rotating cylinder
  - HP/HT flow loop

LABORATORY CORROSION TESTING - CORRELATION TO FIELD APPLICATION

Laboratory testing produces good results about the performance of corrosion inhibitors. Laboratory testing produces an estimate or approximation of the concentration of corrosion inhibitor that will be required in the field. Experience indicates that it will generally require more chemical in the field to yield the results obtained in the laboratory. There are reasons for this difference including:

- Corrosion inhibitors adsorb on solids found in the produced fluids and are therefore not available to adsorb onto the steel
  - This results in more corrosion inhibitor required to "satisfy solids demand"
- Variations or fluctuations in production rates and oil/water ratio then those used in testing and selection of corrosion inhibitors in the laboratory
- Field experience indicates that higher concentrations of corrosion inhibitors are desired to film the pipe in case injection pumps fail

Keeping the systems clean will improve corrosion inhibition. Removing scales, sand, waxes or anything else that can stop inhibitor from reaching steel surface will improve the performance of the corrosion inhibitors. Corrosion inhibitors are NOT 100% effective at preventing corrosion – they reduce corrosion rates but do not completely prevent corrosion.

CORROSION MONITORING – INDIRECT

Once the corrosion inhibition program is implemented in the system, the efficacy of the program should be monitored to demonstrate the performance of the program. There are several indirect monitoring techniques that are typically used in the oilfield. One of the indirect methods used to monitor the corrosion inhibition program is the installation of steel coupons in the production flow of the system:

- Usually installed for a minimum of 30-day period
- Coupons are extracted, cleaned, weighed and inspected at scheduled intervals
- Corrosion rate is calculated from weight loss, coupon dimensions, and exposure period
- The amount of pitting is noted and pit depths may be measured
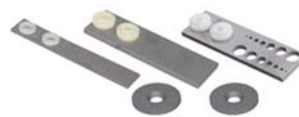
Flat Coupons   **Disc Coupons**

Retractor for Coupons – 1500 psig

Another indirect monitoring technique is to run iron "counts" on samples of the produced water.

- Analyze water from system for concentration of iron (Fe)
- Calculate the Pounds/Day to account for variations in water volumes
  - Pounds/Day = 0.00035 x (mg/L Fe) x (Bbls/Day water)
- This technique assumes that the iron found in the produced water is the result of corrosion of steel pipe rather than naturally occurring from the formation.

Another indirect monitoring technique is to run manganese "counts" on samples of the produced water.

- Analyze water from system for concentration of manganese (Mn)
- Calculate the Pounds/Day to account for variations in water volumes

- - Pounds/Day = 0.00035 x (mg/L Mn) x (Bbls/Day water)
- This technique assumes that the manganese found in the produced water is the result of corrosion of steel pipe rather than naturally occurring from the formation.

Other forms of indirect monitoring of the effectiveness of the corrosion inhibition program include electronic monitoring of the system.
- Electrical Resistance (ER) is one form of electronic monitoring:
  - Probe installed in system to be monitored
  - Based on principle that electrical resistance increases as cross section area of steel specimen is reduced (e.g. due to corrosion loss)
  - Multiple electrical resistance readings are taken using a handheld meter
  - The change in electrical resistance with time is used to calculate corrosion rate

Corrosometer   **Corrosometer Probes**

- Linear Polarization Resistance (LPR) is another form of electronic monitoring:
  - A two-electrode probe is installed in system
  - A potential is applied across the probes and the corrosion current is measured
  - Corrosion rate is read directly using handheld meter
  - Must have enough water in the system for LPR to function properly

Corrater   **Corrater Probes**

CORROSION MONITORING – DIRECT

In addition to the indirect corrosion monitoring techniques described above, there are also techniques that are "direct" methods for monitoring the condition of the system and demonstrating the efficacy of the corrosion inhibition program. The direct corrosion monitoring methods include:
- X-ray of the pipe wall
- Ultrasonic measurement of pipe wall thickness
- Use of pipe spools that can be physically examined by using a bypass, or during shutdown
- Physical Examination and inspection
- Smart-pigging of pipelines
- Magnetic testing in well tubing

LIMITATIONS OF CORROSION MONITORING METHODS

There are a few limitations of the various methods described above that are available to monitor the corrosion inhibition program. These limitations include:
- Selection of location for installing ER or LPR probes or coupons is critical
  - The most convenient location to install the probes or coupons may NOT be the location where corrosion may occur

Monitoring Location Example

NACE Standard RP0775-2005 – Item No. 21017

	Average Corrosion Rate		Maximum Pitting Rate (See Paragraph 2.5)	
	mm/y [A]	mpy [B]	mm/y	mpy
Low	<0.025	<1.0	<0.13	<5.0
Moderate	0.025-0.12	1.0-4.9	0.13-0.20	5.0-7.9
High	0.13-0.25	5.0-10	0.21-0.38	8.0-15
Severe	>0.25	>10	>0.38	>15

[A] mm/y = millimeters per year
[B] mpy = mils per year

- Software is available to predict the most likely location of corrosion in pipeline systems and estimate the corrosion rate. Software models are often used in pipeline design. Aegis has access to the ECE-5 Electronic Corrosion Engineer Model, Norosok Corrosion Rate Calculator and various in-house Excel spreadsheet models.
  - The effectiveness or accuracy of these models depends on the parameters used in the software to predict corrosion rate:
    - CO_2 and H_2S concentrations and partial pressure
      - Sulfide stress cracking
      - Chloride stress cracking
    - Total Pressure
    - Temperature
    - Fluid/Gas velocity
    - Elevation (low spots, bends, abrupt elevation changes)
    - Water chemistry
    - Gas Composition

CORROSION RATE EVALUATION

The corrosion rate measured or determined by the various monitoring methods used should be evaluated to determine if that rate represents a "good" corrosion rate based on the efforts used to mitigate corrosion in the system. In the absence of any other information, the NACE guidelines can be used in that evaluation.

Another method to evaluate the corrosion rate is to compare corrosion coupon rates over time and note changes in system parameters and corrosion inhibitor injection. A comparison to other indirect methods; iron counts, LPR probes, ER probes, etc. can be used to evaluate the corrosion rate. The operator will likely track well failure rates or rod/tubing failure rates as a performance measure of the effectiveness of the corrosion inhibition program. The direct monitoring methods described above can be used as measurement to verify the corrosion rate – particularly inspection, x-ray, ultrasonic, or smart-pig. If "failure is not an option", the operator **must** have direct measurement of corrosion rate. As mentioned above, the indirect methods of corrosion measurement and corrosion rate determination are only as good as the location that they are installed. In wells, coupons and probes are installed at wellheads and give you the corrosion rate AT THAT POINT.
- Downhole the tubing may be (and probably is) corroding at a higher rate

In pipelines, coupons and probes are installed at slug catchers, in risers at the plant, etc.
- What about the pipeline location that goes under a river or stream in the middle of nowhere?
- What about pipelines that comes in from 100 miles offshore and the coupon location is at the beach? The corrosion rate may be dramatically different between the beach and offshore.

AEGIS FACILITIES LOCATIONS

Corporate Headquarters *Houston* 4560 Kendrick Plaza Dr., #190 Houston, TX 77032 Tel: (855) 532-2033	**Permian Basin** *Midland* 2200 Market St. Midland, TX 79703 Tel: (432) 695-6285	**Permian Basin** *Abilene* 4657 FM 707 Abilene, TX 79606
Permian Basin *Breckenridge* 566 FM 2231 Breckenridge, TX 76424	**Permian Basin** *Forsan* 300 1st St. Forsan, TX 79720	**Permian Basin** *Lubbock* 13622 Hwy 87 S. Slaton, TX 79423 Tel: (806) 329-4609
Permian Basin *Monahans* 1332 PR Thrasher Ln. Monahans, TX 79756	**East Texas** *Kilgore* 4524 State Hwy 42 N. Kilgore, TX 75662 Tel: (903) 218-0058	**East Texas** *Raywood* P.O. Box 219 Raywood, TX 77582 Tel: (409) 550-5211
East Texas *Teague* 931 W. Hwy 84 Teague, TX 75860 Tel: (903) 218-4795 x1058	**South Texas** *Freer* 5743 Hwy 44 Freer, TX 78357 Tel: (361) 226-3103	**South Texas** *Asherton* 664 Hwy 190 Asherton, TX 78827
South Texas *Cuero* 424 U.S. Hwy 87 S. Cuero, TX 77954	**South Texas** *Jourdanton* 8229 S. State Hwy 16 Jourdanton, TX 78026 Tel: (830) 265-5595	**South Texas** *San Antonio* 311 N. Frank Luke Dr., #103 San Antonio, TX 78226
North Louisiana *Haughton* 140 Sligo Industrial Dr. Haughton, LA 71037 Tel: (318) 261-8333 x1056	**South Louisiana** *Elizabeth* 3552 Highway 10 Elizabeth, LA 70638 Tel: (318) 634-5252	**Mid-Con** *Ratliff City* P.O. Box 98, 1500 Old Hwy 7 Ratliff City, OK 73481 Tel: (580) 856-2015
Mid-Con *El Reno* 801 N. Willie L. Minor, #B-1 El Reno, OK 73036	**Mid-Con** *Hennessey* 1117 S. Main St. Hennessey, OK 73742	