

# Natural Gas Pipeline Corrosion- Steel

## External Corrosion aided by Liquid Saturation of Steel from Internal Pipeline Products.

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Natural gas transmission pipelines are far more susceptible to external corrosive attack than similar operating oil pipelines. To explain the difference, it is proposed that the internal liquid content of the natural gas transmission pipeline may actually promote corrosive chemical reactions on the outside steel surface of the pipeline.

It is common knowledge when given enough time that steel will eventually absorb a high concentration of hydrocarbon and other liquids within the grains structure itself. A welder that attempts to cut and weld "in-service" natural gas pipelines will realize that the steel contains contaminants that will react with the weld metal deposited and cause blisters and hard compounds to develop. Special weld procedures are developed with the most common remedy is to bake out the steel for several hours at high temperatures to evaporate most of the liquids/gas contained within the steel prior to welding.

Corrosion of underground natural gas and liquid petroleum pipelines occurs in a variety of forms and requires specialized mitigation methods to detect and control. Stress corrosion cracking (SCC) is a form of electrochemical corrosion that results in clusters or colonies of cracks on the external surface of the affected pipeline.

According to the Federal Pipeline & Hazardous Materials Safety Administration (PHMSA), the majority of pipeline incidents caused by SCC are found on natural gas pipelines rather than hazardous liquid pipelines. However, SCC can manifest itself wherever the right combination of factors exists. External SCC of underground pipelines has been the most common issue, however, it has become apparent that internal SCC, as a result of exposure to alcohols, also can pose a threat to pipelines. Both ethanol and methanol are potent SCC agents.

This paper examines the probability that liquid contamination of the internal surface of a natural gas transmission pipeline can penetrate the steel matrix and promote corrosion on the outside surface of the steel pipeline. The external surface will corrode where the protective coating has been disbanded allowing electro chemical communication through the steel matrix and provide the necessary ions for transfer of the chemical processes that cause corrosion.

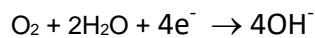
Corrosion of steel takes place readily when there is a plentiful supply of oxygen and hydrogen ions to facilitate the electrochemical corrosion processes. Water and hydrocarbon penetration of the steel/iron matrix is aided by dissociation of water and other compounds that are in contact with the steel surface and by internal operating pressure. The penetration is similar to a reverse osmosis process where the membrane is a steel pipeline. The pathway will be along grain boundaries and dislocations in the crystal

formations in the steel. The saturation and development of electrical communication is slow process so it will take several years in service for the external corrosion issues to manifest themselves.

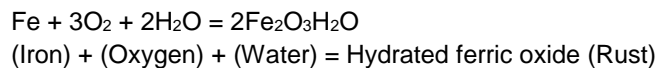
### Basic Corrosion Chemistry for Iron Corroding into Rust

Iron  $\text{Fe} \rightarrow \text{Fe}^{n+} + n \text{ electrons}$  the iron atom can lose some electrons and become a positively charged ion. This allows it to bond to other groups of atoms that are negatively charged.

Wet steel rusts to give a variant of iron oxide so the other half of the reaction must involve water ( $\text{H}_2\text{O}$ ) and oxygen ( $\text{O}_2$ ) to produce negatively charged material



This material will combine with the iron  $\text{Fe}$  and electrons to produce



This series of steps tells us a lot about the corrosion process.

- (1) Ions are involved and need a medium to move in (usually water)
- (2) Oxygen is involved and needs to be supplied
- (3) The metal has to be willing to give up electrons to start the process
- (4) A new material is formed and this may react again or could be protective of the original metal
- (5) A series of simple steps are involved and a driving force is needed to achieve them

Interfering with the steps involved allows the corrosion reaction to be stopped or slowed to a manageable rate.

The reaction is slow in pure water because there are actually two reactions taking place at separate sites. At one site the reaction is the oxidation of the iron to produce ferric oxide and electrons that enter the metal. At the other site the reaction is the reaction of these electrons to reduce water to hydrogen gas. The electrons move rapidly through the metal, but if the reaction is to proceed rapidly electrolytic charge must also move rapidly through the water and in pure water it doesn't.

However, when a salt is dissolved in water it forms an electrolytic solution that will conduct electricity. (The salt is an electrolyte. Many acids and bases form conductive solutions in water and are also electrolytes.) The electrolyte carries electric current through the solution from one site where the iron is oxidized to ferric oxide to another site where hydrogen gas ( $\text{H}_2$ ) is produced.

Contributing factors to drive the formation of an electrolyte into the steel matrix of pipeline includes the internal operating pressure of pipeline and the process of osmosis. The high operating pressure

increases the internal molecular movement and subsequent collision rates to enable the process to advance. Similarly, water from the outside of the pipeline does not enter the steel matrix completely due to the pressure being lower, however the outside environment will provide dissolved oxygen in the to the corroded area to complete the formation of corrosion products. The drive for supplying fresh oxygen from the outside environment to the corrosive site is aided by the phenomena that water will travel to a higher salt (or any solute) concentration solution. When the steel matrix is saturated, the solute concentration will attract fresh water. This natural process is called osmosis and can be demonstrated when fresh water will tend to migrate through a membrane to the salt solution on the other side.

The internal operating pressure the pipeline will also drive any water present on the inside surface through the steel matrix as it acts like a semipermeable membrane. The water produced by reverse osmosis has a comparatively low pH and has little or no alkalinity. This means that the water lacks its hardness to function like a buffer and will be highly corrosive when reacting on the outside surface of the pipeline.

**A summary of the corrosion issues is presented below. Actual corrosion issues that cause failures usually involve several types of corrosion that are discussed.**

### **1-UNIFORM CORROSION 30% of failures**

Uniform corrosion occurs over the majority of the surface of a metal at a steady and often predictable rate.

Uniform corrosion can be slowed or stopped by using the five basic facts;

- (1) Slow down or stop the movement of electrons
  - (a) Coat the surface with a non-conducting medium such as paint, lacquer or oil
  - (b) Reduce the conductivity of the solution in contact with the metal
  - (c) Apply a current to the material (see cathodic protection).
- (2) Slow down or stop oxygen from reaching the surface. Difficult to do completely but coatings can help.
- (3) Prevent the metal from giving up electrons by using a more corrosion resistant metal higher in the electrochemical series. Use a sacrificial coating which gives up its electrons more easily than the metal being protected. Apply cathodic protection. Use inhibitors.
- (4) Select a metal that forms an oxide that is protective and stops the reaction.

### **2- LOCALISED CORROSION 70% of failures**

## **2.1 GALVANIC CORROSION**

This can occur when two different metals are placed in contact with each other and is caused by the greater willingness of one to give up electrons than the other. Three special features of this mechanism need to operate for corrosion to occur:

- The metals need to be in contact electrically
- One metal needs to be significantly better at giving up electrons than the other
- An additional path for ion and electron movement is necessary.

Prevention of this problem is based on ensuring that one or more of the three features do not exist.

Break the electrical contact using plastic insulators or coatings between the metals.

Select metals close together in the galvanic series.

Prevent ion movement by coating the junction with an impermeable material, or ensure environment is dry and liquids cannot be trapped.

## **2.2 PITTING CORROSION**

Pitting corrosion occurs in materials that have a protective film such as a corrosion product or when a coating breaks down. The exposed metal gives up electrons easily and the reaction initiates tiny pits with localized chemistry supporting rapid attack. Control can be ensured by:

- Selecting a resistant material
- Ensuring a high enough flow velocity of fluids in contact with the material or frequent washing
- Control of the chemistry of fluids and use of inhibitors
- Use of a protective coating
- Maintaining the material's own protective film.

Note: Pits can be crack initiators in stressed components or those with residual stresses resulting from forming operations. This can lead to stress corrosion cracking.

## **2.3 SELECTIVE ATTACK**

This occurs in alloys such as brass when one component or phase is more susceptible to attack than another and corrodes preferentially leaving a porous material that crumbles. It is best avoided by selection of a resistant material but other means can be effective such as:

- Coating the material
- Reducing the aggressiveness of the environment

- Use of cathodic protection

## **2.4 STRAY CURRENT CORROSION**

When a direct current flows through an unintended path and the flow of electrons supports corrosion. This can occur in soils and flowing or stationary fluids. The most effective remedies involve controlling the current by:

- Insulating the structure to be protected or the source of current
- Earthing sources and/or the structure to be protected.
- Applying cathodic protection
- Using sacrificial targets.

## **2.5 MICROBIAL CORROSION**

This general class covers the degradation of materials by bacteria, moulds and fungi or their by-products. It can occur by a range of actions such as:

- Attack of the metal or protective coating by acid by-products, Sulphur, hydrogen Sulphide or Ammonia
- Direct interaction between the microbes and metal which sustains attack.

Prevention can be achieved by:

- Selection of resistant materials
- Frequent cleaning
- Control of chemistry of surrounding media and removal of nutrients
- Use of biocides
- Cathodic protection.

## **2.6 INTERGRANULAR CORROSION**

This is preferential attack of the grain boundaries of the crystals that form the metal. It is caused by the physical and chemical differences between the centres and edges of the grain.

It can be avoided by:

- Selection of stabilized materials
- Control of heat treatments and processing to avoid susceptible temperature range.

## **2.7 CONCENTRATION CELL CORROSION (CREVICE)**

If two areas of a component in close proximity differ in the amount of reactive constituent available the reaction in one of the areas is speeded up. An example of this is crevice corrosion which occurs when oxygen cannot penetrate a crevice and a differential aeration cell is set up. Corrosion occurs rapidly in the area with less oxygen. The potential for crevice corrosion can be reduced by:

- Avoiding sharp corners and designing out stagnant areas
- Use of sealants
- Use welds instead of bolts or rivets
- Selection of resistant materials

## **2.8 THERMOGALVANIC CORROSION**

Temperature changes can alter the corrosion rate of a material and a good rule of thumb is that 10 C rise doubles the corrosion rate.

## **2.9 CORROSION CAUSED BY COMBINED ACTION**

This is corrosion accelerated by the action of fluid flow sometimes with the added pressure of abrasive particles in the stream. The protective layers and corrosion products of the metal are continually removed exposing fresh metal to corrosion. Prevention can be achieved by:

- Reducing the flow rate and turbulence
- Use of replaceable or robust linings in susceptible areas
- Avoiding sudden changes of direction
- Streamlining or avoiding obstructions to the flow

## **2.10 CORROSION FATIGUE**

The combined action of cyclic stresses and a corrosive environment reduce the life of components below that expected by the action of fatigue alone. This can be reduced or prevented by;

- Coating the material
- Good design that reduces stress concentration
- Avoiding sudden changes of section
- Removing or isolating sources of cyclic stress

## 2.11 STRESS CORROSION CRACKING

The combined action of a static tensile stress and corrosion which forms cracks and eventually catastrophic failure of the component. This is specific to a metal material paired with a specific environment. Prevention can be achieved by:

- Reducing the overall stress level and designing out stress concentrations
- Selection of a suitable material not susceptible to the environment
- Design to minimize thermal and residual stresses
- Developing compressive stresses in the surface the material
- Use of a suitable protective coating

### External Stress Corrosion Cracking

Three conditions are necessary for external SCC on underground pipelines (like other forms of SCC) to occur:

- (1) a susceptible metal,
- (2) a tensile stress of sufficient magnitude, and
- (3) a potent environment at the metal surface.

The carbon steels used to manufacture line pipe are susceptible to SCC in a number of environments, including two that develop beneath disbonded coatings underground.

Tensile stresses on underground pipelines originate from a number of sources, including residual stresses from pipe manufacturing and construction, internal operating pressure, damage to the pipeline, such as that caused by from dents and mechanical damage, and land movement. These stresses are usually can be in the hoop direction (e.g., from the internal pressure), resulting in axial cracks in the axial direction.

The majority of underground pipelines are externally coated and cathodically protected to mitigate corrosion. A potent environment must have access to the metal surface for SCC to occur. Accordingly, an intact, well-bonded coating will mitigate all forms of external corrosion, including SCC. The first step in the development of a potent environment at the pipeline surface is the disbondment of the coating, typically at defects in the coating.

Potent environments are associated with the presence of carbon dioxide in the soil, typically from decay of organic matter. The cathodic protection (CP) causes the pH of the electrolyte beneath the disbonded coating to increase and the carbon dioxide dissolves in the elevated pH electrolyte, resulting in a potent high pH-cracking environment containing carbonate and bicarbonate.

## 2.13 HYDROGEN DAMAGE

A surprising fact is that hydrogen atoms are very small and hydrogen ions even smaller and can penetrate most metals.

Hydrogen, by various mechanisms, embrittles a metal especially in areas of high hardness causing blistering or cracking especially in the presence of tensile stresses. This problem can be prevented by:

- Using a resistant or hydrogen free material
- Avoiding sources of hydrogen such as cathodic protection, pickling processes and certain welding processes
- Removal of hydrogen in the metal by baking.

## Hydrogen Embrittlement

Hydrogen diffuses along the grain boundaries and combines with the carbon, which is alloyed with the iron, to form methane gas. The methane gas is not mobile and collects in small voids along the grain boundaries where it builds up enormous pressures that initiate cracks. Hydrogen embrittlement is a primary reason that the reactor coolant is maintained at a neutral or basic pH in plants without aluminum components.

If the metal is under a high tensile stress, brittle failure can occur. At normal room temperatures, the hydrogen atoms are absorbed into the metal lattice and diffused through the grains, tending to gather at inclusions or other lattice defects. If stress induces cracking under these conditions, the path is transgranular. At high temperatures, the absorbed hydrogen tends to gather in the grain boundaries and stress-induced cracking is then intergranular.

Hydrogen embrittlement does not affect all metallic materials equally. The most vulnerable are high-strength steels, titanium alloys and aluminum alloys.

Sources of hydrogen causing embrittlement have been encountered in the making of steel, in processing parts, in welding, in storage or containment of hydrogen gas, and related to hydrogen as a contaminant in the environment that is often a by-product of general corrosion. If the presence of hydrogen sulfide causes entry of hydrogen into the component, the cracking phenomenon is often termed "Sulphide stress cracking (SSC)"