
CORROSION BASICS, IMPACTS AND REMEDIES

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ABSTRACT

The strong need of this paper emerged after multiple observations of appearance of corrosion phenomenon in the existing oil & gas production fields. The same concern was sounded in various discussions with senior colleagues from safety & integration disciplines. The need was also apparent in the consciousness/ worriedness of integration managers in the green field in the process of handover of asset from projects to operation team.

This paper was written to provide brief idea about corrosion to graduates, engineers and supervisors in operations team and others disciplines engineers who are working in hydrocarbon industry as well other industries but do not have much exposure to corrosion.

Key Words: Corrosion, Integration, Linear Polarization Resistance, Electro-Chemical Noise

Introduction:

The word corrosion is derived from the Latin verb “corrodere” which means “ to gnaw” indicating how these substances seems to ‘gnaw’ their way through the flesh. Sometimes the word Caustic is used as synonym, but by convention “ Caustic” generally refers only to strong bases, particularly alkalis and not to acids, oxidizer or other non-alkaline corrosives. The term “acid ” is often used imprecisely for all corrosives.

A low concentration of a corrosive substance is usually an irritant. Corrosion of non-living surface such as metals is a distinct process. Corrosives are different from poisons, in that corrosives are immediately dangerous to the tissues when they come in contact, while poisons may have systematic toxic effects that require time to become evident. Colloquially, corrosives may be called “poisons” but the concepts are technically distinct. There is nothing, however which precludes a corrosive from being a poison, which is there are substance that are both corrosive and poisons.

Corrosion in layman's language can be said as damage. If damage is there, then it has to be associated with cost, safety, negative impacts on environment. The cause of corrosion comes as results from the chemical interaction of metal with environment and may be uniform in nature or localized. Physical and chemical conditions of the environment influence both rate and type of attack, the nature of corrosion products, the way in which metallic properties themselves are affected and the corrosion control measure needed.

Corrosion is an electrochemical process whereby metal reacts with its environment to form an oxide or other compound. This process is comprised of three elements; an anode, a cathode and an electrolyte. The anode is the site of the corroding metal, the electrolyte is the corrosive medium that enables the transfer of electrons from the anode to the cathode and the cathode forms the electrical conductor in the cell that is not consumed in the corrosion process.

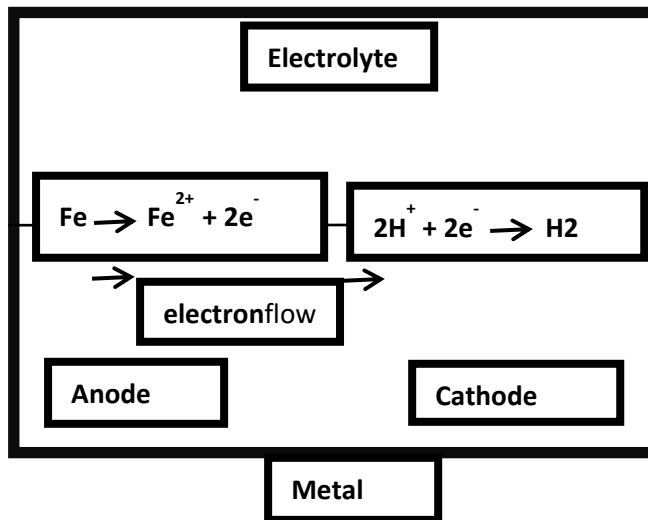
When metal is exposed to a corrosive solution (the electrolyte), the metal atoms at the anode site lose electrons are then absorbed by other metal atoms at the cathode site. The cathode in contact with the anode via the electrolyte, conducts this exchange in an attempt to balance their positive and negative charges. Positively charged ions are released into the electrolyte capable of bonding with other groups of atoms that are negatively charged.

In the Oil & Gas industries, Carbon dioxide CO_2 and Hydrogen sulphide (H_2S) are commonly present and water is there as catalyst for corrosion. When water combines with CO_2 and H_2S , in the environment and performs reactions as following:



There may be a combination of the above two reactions if both gases are present.

This process can be presented schematically in diagram as following:



This diagram separates an electrolytic reaction which is different than a chemical reaction.

Reasons for Corrosion:

There can be many reasons for corrosion but some of these which are most common in practice listed as below.

a) Presence of electrolytes:

Acid solutions make rusting go faster. In industrial areas where air is seriously polluted, there are high concentrations of CO_2 , SO_2 , N_2O . These gases dissolve in rain water to give "Acid rain" which makes Iron object rust faster.

Sodium Chloride also makes iron rust more quickly. i.e Seawater which has high salt content approx 3.6 % in Atlantic & Pacific Oceans.

Due to higher concentration of Ions, corrosion rate may order of 0.1mm/ yr.

(Presence of soluble salt other than sodium chloride may also assist rusting.)

b) Heat:

An increase in temperature always increases rate of chemical reaction, including rusting.

c) Humidity:

Normally corrosion starts when relative humidity exceeds around 65%. In the areas where humidity is (80%-95%) during winter & (60% to 80%) during summer. This results in iron rusting five times faster, than in winter.

In waters when Lime & Carbonic Acid is in equilibrium called an equilibrium water. In this water, sufficient Carbon dioxide is in solution to stabilize the carbonate and can be expressed as follows:



Provided the minimum hardness is about 2.2 mill equivalent, these waters form layers of mixed lime and rust that safeguard the steel piping against further corrosion. If water contains an excess of Carbonic acid, when prevents the formation of protective layers, there is a danger of corrosion of unprotected steel in the presence of oxygen.

d) Contact With Less Reactive Metal

Consider iron and copper plates joined together and put in water containing dissolved oxygen. Iron loses electrons more readily than copper. Hence, iron forms anode and copper as the cathode of an electrochemical cell. In this case, iron rusts even more quickly than when there was no copper.

e) Other Factors

Other factors that speed up rusting include the presence of sharply pointed regions in the iron piece, or a high concentration of dissolved oxygen in water.

Hydrogen Corrosion Monitors:

Considering the prevalence of hydrogen based corrosion, cracking and blistering in the oil & gas industry, monitoring for hydrogen production and activity provides a good basis for proactive monitoring. There is a direct relationship between the amount

of hydrogen inside or permeating through the tank or pipe wall and corrosion activity, the greater the amount of hydrogen production, the greater the corrosion.

Other corrosion monitoring systems that may be used in conjunction with or in place of hydrogen monitoring system include:

i) Coupons:

Coupons directly monitors for corrosion by way of placing a metal coupon inside the pipe for a period of time , then removing it to evaluate the pipes corrosion environment and potential wall loss.

ii) Electrical Resistance (ER) Probes:

Directly monitor for corrosion by conducting and evaluating an electrical signal as corrosion occurs, the electrical resistance of the unit increases proportionally.

iii) Linear Polarization Resistance (LPR):

Directly monitors for corrosion by sending an electrolyte down through the pipe between two monitors to determine the polarization resistance, which is inversely proportional to the corrosion rate.

iv) Electro-Chemical Noise (ECN):

ECN records the naturally occurring fluctuations in current and voltage noise between electrodes to determine corrosion –the higher the fluctuations the greater the corrosion.

v) Ultrasonic Scan:

Hand held device scans for wall thickness at any given point.

vi) Field Signature Method (FSM):

Measures metal loss by comparing voltage readings between pin pairs to a reference plate.

Methods for Reducing the Corrosion Rate:

The methods suggested are as following:

- a) Apply corrosion inhibitors
- b) Apply Hydrate preventers
- c) Reduce water wetting
- d) Increase the pH
- e) Reduce the CO₂ partial pressure
- f) Select optimized material
- g) Avoid flow disturbances

a) Apply Inhibitors:

Traditional inhibition contains surface –active compounds which adhere to the surface and prevent corrosion. This type of inhibitor will lose its efficiency above a certain wall shear stress. This limit is influenced by the aggressiveness of the environment and the type of inhibitor. High flow velocities improve inhibitors distribution, but the production rate should not be so high that inhibitors are removed from the surface. For smooth pipes inhibitors efficiency is sometime quoted to be as high as 95%.

b) Apply Hydrate Preventer:

It has been shown that DEG, MEG and methanol can be reduced the corrosion rate considerably. Use of Glycol reduces the corrosion rate most probable because it reduces the concentration on the walls. Shell experiments (Troll Pipeline) with radio activity-marked glycol showed that the glycol added for hydrate prevention most probably reached the top of the pipeline, and ensured that an acceptably-low corrosion rate can be achieved in the pipeline.

c) Reduce Water Wetting:

The oil producing wells water content increases over the life of well, since water wetting of the steel wall depends on the type, viscosity, density, and temperature of the oil, interfacial tension between water soil. And local flow conditions.

The conservative approach is to assume continuous water wetting and calculation. Corrosion rate is function of various parameters as given above.

d) Increase The pH:

The increase in pH has large impact on protective film formation and the corrosion rate. At high pH (6-7), protective films are more easily formed because the solubility of Fe^{++} is reduced by several order of magnitude ($\ll 1$ ppm) below the solubility in pure water & CO_2 when the pH is increased. The low solubility also implies that protective films will not be easily dissolved. Protective films are formed can therefore only be removed mechanically or by erosion.

The pH can be increased artificially in gas condensate lines by adding pH stabilizers alone or together with the hydrate preventer (Glycol, Methanol etc)

e) Reduce CO_2 Pressure:

Reduction of the total pressure by half by choking will reduce the CO_2 partial pressure. Generally speaking reduce total pressure will reduce the corrosion rate.

f) Select Optimal Carbon Steel:

Various studies have shown that Chromium can improve the corrosion resistance of carbon steel. Pipeline material with 0.5% Chromium is presently being considered for offshore use by several Oil companies in Norway.

g) Avoid Flow Disturbance:

The local near-wall turbulence level can be significantly behind grooves and obstacles such as weld beads. This can destroy protective corrosion product films or the inhibitor film locally, and increase corrosion rate considerably. The

welding method and other design and construction procedures should be selected to give a minimum of flow disturbance in the pipeline.

Select Corrosion –Resistant Alloys (CRAs):

Stainless steel are generally immune to well fluids with high CO₂ and salt concentration and can be an alternative material for especially for aggressive wells.

Suggestion and Way Forward:

It is required to fight corrosion however available corrosion prediction models have uncertainties which will generally improve as more laboratory and field data accumulate. Due to complicity in the different modeling studies. To get more accurate assessment and understanding of corrosion prudent suggestions are as following:

- 1) It will be prudent to use multi experience people as core team in study so that study will deliver complete package recommendations.
- 2) Imbed Corrosion chemical engineer in the team can provided various input related to recommendation of different chemicals in the separate service or mixed service i.e water or oil & gas or Condensate & Gas.
- 3) Fluid flow expert surely add more value in the study by providing input in the of fluid behavior in the different phase i.e Water, Oil, Gas and condensate phases.
- 4) Gate keeper for maintenance activities will do value addition to the study by providing historical data of operations which can be plotted and extrapolated for recommendation from study.
- 5) Presence of experienced Biologist will lead new field of research.

Reference:

1. A.Cinitha, P.K Umesha, Nagesh R Iyer, KSCE Journal of Civil Engineering, 18 (6), 1735-1744 (2014)
2. Shaw, B.A. & Kelly, Electrochemical Society Interface, 15. 24-26 (2006) , 10.1149/2.F06061IF
3. Yannawar, Dr. Vyankatesh, Golden Research Thoughts, 3. 1-3 (2013)
4. H.S. Issacs, J. Electrochemical Soc., 149, S85-87 (2002)
5. H.H. Uhlig, s , J.Electrochemical Soc., 125, 85C (1978)
6. Alam, I.A and M.Sadiq , Metal Contamination of Driking Water from Corrosion of distribution pipes , Environmental Pollution , 57(2), 167-178 (1989)
7. Natesan M., Venkatachari G., Palaniswamy N., Rajeswari A., Corrosion the Journal of Science and Engineering , Vol 64 No2, 92-100 (2008)
8. R. D. Braun, "Solubility of iron(II) carbonate at temperatures between 30 and 80° ," Talanta, vol. 38, no. 2, pp. 205–211, 1991.
9. S. Nešić and K.-L. J. Lee, "A mechanistic model for carbon dioxide corrosion of mild steel in the presence of protective iron carbonate films—part 3: film growth model," Corrosion, vol. 59, no. 7, pp. 616–628, 2003
10. S. Sim, P. Corrigan, I. Cole, and N. Birbilis, "Use of aqueous solutions to simulate supercritical CO2 corrosion," Corrosion, vol. 68, no. 4, pp. 045004-1–045004-11, 2012.
11. Y.-S. Choi and S. Nešić, "Determining the corrosive potential of CO2 transport pipeline in high pCO2-water environments," International Journal of Greenhouse Gas Control, vol. 5, no. 4, pp. 788–797, 2011