

# CORROSION ANALYSIS BY ACID CONCENTRATION IN OIL AND GAS PIPELINES

Chogule Izhaan<sup>1</sup>, Barad Rajdeepsinh<sup>2</sup>, M Mohit Samant<sup>3</sup>

<sup>1,2,3</sup>Undergrad students, Dept. of Petroleum Engineering, Uttarakhand University, Dehradun, India

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**Abstract** - Corrosion is one of the severe problem faced by the oil and gas industries. It is the gradual destruction of metals by chemical or electrochemical reaction with their environment. According to U.S. studies metallic corrosion causes a cost of \$276 million per annually. So, identifying the cause and control of corrosion in industries is very important. The main objective of this project is to identify the various causes that lead to corrosion in oil and gas pipelines and also to determine which element from the composition of pipe is contributing how much in corroding pipe using SEM technique. In this project we are studying the effects of - varying temperature while keeping the pipeline material & concentration of the solution constant and varying the concentration of the solution while keeping the material of the pipeline & temperature constant.

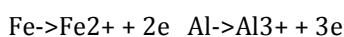
**Key Words:** corrosion, acid concentration, temperature effect, pitting, loss of pipe

## 1. INTRODUCTION

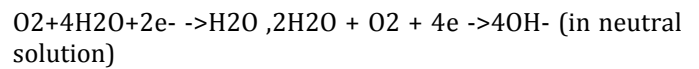
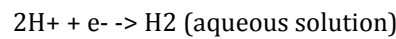
“Corrosion is an irreversible interfacial reaction of a material (metal, ceramic, polymer) with its environment which results in its consumption or dissolution into the material of a component of the environment. Often, but not necessarily, corrosion results in effects detrimental to the usage of the material considered. Exclusively physical or mechanical processes such as melting and evaporation, abrasion or mechanical fracture are not included in the term corrosion” – IUPAC, 1919. Corrosion is the loss of essential material which leads to loss of strength of the structure and subsequent failure. Also, it proves to be an economical setback and endangers the environment if the substance of harmful nature leaks out.

### 1.1 Corrosion Mechanism

Most metal corrosion occurs via electrochemical reactions at the interface between the metal and electrolyte solution. A thin film of moisture on a metal surface forms the electrolyte atmospheric corrosion. Corrosion normally occurs at a rate determined by equilibrium between opposing electrochemical reactions. The first is the anodic reaction, in which a metal is oxidized, releasing electrons into the metal. The anodic reactions are written below.



The other is the cathodic reaction, in which a solution species is reduced, removing electrons from the metal. Cathode gains the electrons from the anode by a metallic path where the electrons reacts with the ions in the electrolyte and causes a reduction in the positive ions. The common reactions at cathode is written below.



When these two reactions are in equilibrium the flow of electrons from each reaction is balanced, and no net electron flow occurs. The two reactions can take place on the one metal or on two dissimilar metals that are electrically connected. Since corrosion is actually a process involving electrochemical oxidation and reduction reactions. In order for the reaction to occur, the following conditions must exist:

- a chemical potential difference must exist between adjacent sites on a metal surface (or between alloys of a different composition)
- an electrolyte must be present to provide solution conductivity and as a source of material to be reduced at the cathode.
- an electrical path through the metal or between metals must be available to electron flow.

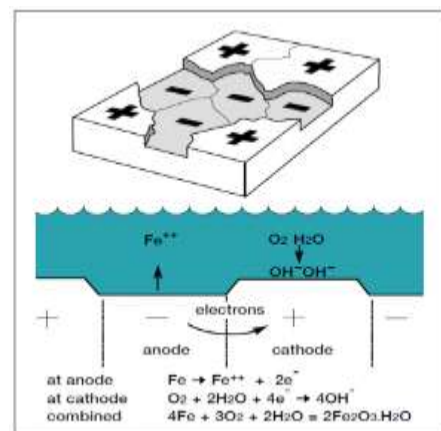


Figure 1. Corrosion mechanism

## 1.2 Effects of Corrosion

- Loss of production during a shutdown
- Replacement of corroded equipment
- High repair and maintenance cost such as repainting and wrapping
- Loss of efficiency

## 2. TYPES AND FACTORS AFFECTING OF CORROSION

### 2.1 Types of Corrosion

The most common type of corrosion in metals are uniform corrosion, electrochemical corrosion, galvanic corrosion concentration cell erosion corrosion, embattlement, stress corrosion, fusiform, corrosion fatigue intergranular, dezincification graphitization ,chemical reaction.

#### 2.1 Electro chemical corrosion

The main components of electrochemical cell are, Anode, cathode, a metallic conductor between the anode and cathode, an electrolyte. The cell shown in figure 2, an electric current will flow through the electrolyte and metallic conductor. As because of oxidation reaction in anode, anode will corrode. Reduction reaction proceeds at cathode. Hydrogen gas produced at the anode insulates the cathode from electrolyte, by a protective gas layer. As a result, current flow will stop, thus polarizing the cell. The presence of oxygen or some depolarizing elements reduce this effect and continues the cell function. If a voltmeter is placed instead of metallic conductor, the potential difference across the metal electrodes can be determined. This potential difference is due to contact between dissimilar metallic conductors or because of the concentration difference. It is not compulsory that the metal sample should completely immersed in solution, it should be in contact with the moist soil for corrosion.

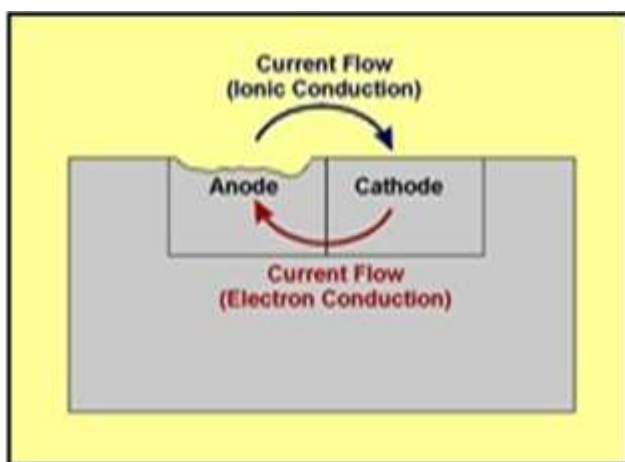


Figure 2. Electrochemical corrosion

#### 2.2 Galvanic corrosion

It is a type of electrochemical corrosion in which two metals of different type in contact are exposed to corrosive atmosphere. The more negative electrode potential metal anode will corrode. This way of corrosion can be minimized by (a) avoiding galvanic couples and (b) usage of insulating material between the two metals. This type of corrosion is also known as dissimilar metal corrosion. Commonly found in unusual places and it causes the most professional problems. Galvanic series of the metal gives how the galvanic current flows between the two metals and which metal will corrode when they are in contact or near each other in ground.

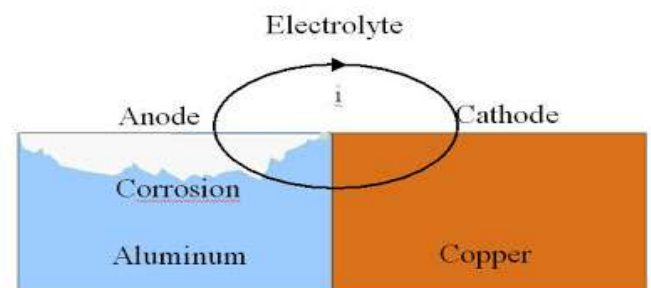


Figure 3. Galvanic corrosion

#### 2.3 Uniform corrosion

Uniform corrosion is the corrosive attack over the entire surface area. General thinning takes place continuously till failure. This can be considered as the most important form of corrosion. Uniform corrosion is easily measured and predicted, making huge failures are very rare. It cannot be easily identified that whether corrosion is happening or not. Corrosion can be controlled by cathodic protection, use of coatings or paints or simply by specifying a corrosion allowance. Uniform corrosion creates various colors and appeal to a surface. Sometimes it creates the patina by naturally tarnishing copper roofs and the rust hues produced on weathering steels. Oxygen is the main factor for uniform corrosion.

### 2.2 Factor affecting corrosion

The factors which affects the corrosion rate are

- Nature of the metal
- Nature of the environment
- Nature of the electrolyte

#### 2.2.1 Nature of the metal

a) Position in the galvanic series:

The corrosion extent depends on the position of metal in the galvanic series. As the oxidation potential is grater the

corrosion rate is also higher. The metal higher up in the galvanic series acts as anodic and corrosion occurs, if two metals are in electrical contact. The greater is the difference in the position of galvanic series, the faster is the corrosion of anodic metal. The difference in position depends the extent and severity of corrosion.

b) Relative area of anode and cathode

As the area of cathode is higher, the rate of corrosion is also higher. The metal higher up in the galvanic series acts as anodic and corrosion occurs, Because the electrons demand will be more. So, dissolution of metals at anodic regions will be also high.

c) Purity of the metal

The impurities create heterogeneity galvanic cells are set up with distinct anodic and cathodic areas in the metal .The corrosion rate depends on impurities .If the percentage of impurity is more, faster the rate of corrosion also. In zinc impurities, such as Pb and Fe leads to the formation of small electrochemical cells at the impurity part.

d) Physical state of the metal:

Unevenly distributed stresses in metals leads to easy corrosion. The areas under stress acts as anode corrode faster. Caustic embrittlement occurs in stressed parts such as bends, joints etc.

e) Nature of the oxide film:

Metals such as Mg, Ca and Ba forms its oxides on the metal surface, this oxide are porous so oxygen can easily diffuse to the metal surface and corrosion continues. In case of metals like Al, Cr and Ni form oxides, but it is non porous and its volume is comparatively more than the volume of metal. So, oxygen cannot diffuse in to the metal surface and prevents further corrosion.

f) Solubility's of the products of corrosion:

If the corrosion product formed on the surface of the metal is soluble, then no problem, corrosion proceeds very rapidly .Incase if the corrosion product is insoluble, it will form a protective film on the metal surface and it suppresses further corrosion to occur.

2.2.2 Nature of the environment

a) Temperature:

The reaction rate and diffusion of ions increases with increase in temperature. So, corrosion rate also increases with increases in temperature. A passive metal becomes active at a higher temperature.

b) Humidity:

The corrosion rate is very slow in normal atmospheric dry conditions but with presence of moisture, corrosion rate increases. Because the oxygen acts as a medium for the oxygen to diffuse in to the air and setting up an electrolyte and forms an electrochemical or concentration cell for

corrosion. When the relative humidity of air reaches 80% the rusting of iron also increases.

c) Effect of pH

The effect of pH and electrode potential of a metal corrosion can be clearly understood from pourbix diagram.

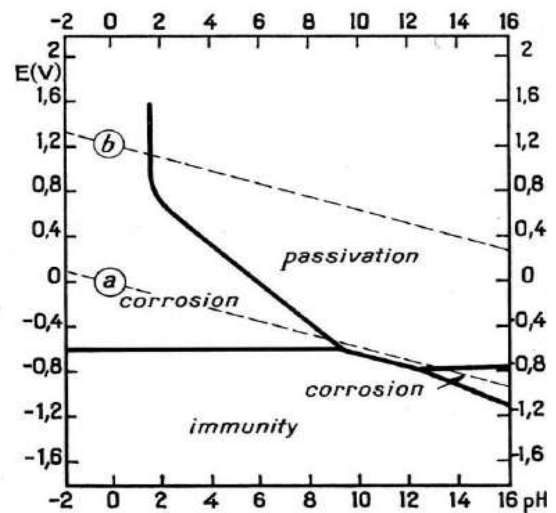


Figure 4. Pourbix diagram of iron in water highlighting different zones of corrosion.

By applying positive potential, the corrosion rate of iron can be decreased by moving into the passivity region. From this diagram, it is evidently clear that rate of corrosion can also be reduced by increasing the pH by alkali addition without any change in potential. The diagram clearly indicates that the corrosion rate can also be reduced by increasing the pH of the solution by the addition of alkali without disturbing the potential.

2.2.3 Nature of the electrolyte.

The electrolyte nature also influences the corrosion rate. Silicate ions, in the electrolytes form insoluble silicates and it prevents further corrosion. The presence of chloride ions in electrolytes destroy the protective film and further corrosion at the surface occurs. If the conductance of solution more, the more current passes through the solution, and corrosion rate increases. The corrosion rate increases with the increasing amount of oxygen. The area where concentration of oxygen is lesser becomes anodic and corrosion begins. Some cases corrosion happens under metal washers where oxygen diffusion cannot occur readily. Buried pipelines and cables passing through different soils suffers corrosion due to differential aeration. Lead pipe through clay gets corroded fastly, because it is less corroded.



### 3. CORROSION IN OIL AND GAS INDUSTRY

#### 3.1 Pipeline Corrosion

Pipeline has an important role in the oil and gas industries throughout the entire world. Transportation of oil and gas from producers to ultimate consumers through long distance pipelines. There are a number of pipelines are used for transportation purposes. According to a study, 65% of corrosion were due to external corrosion and 34% were due to internal corrosion. The corrosion accidents in natural gas transmission pipeline, 36% were by external corrosion and 63% were by internal corrosion. Stress corrosion cracking and microbial corrosions are the other type of corrosion in pipelines. Some reports shows that oil companies pipeline ruptured due to corrosion and oil spillage occurred, resulted in environmental pollution and finally caused ecological damages. The cost of corrosion is around 3% -5% of world GDP. The most of the underground pipelines were made of ASTM 5L grade specification carbon steels. Carbon manganese. The underground pipelines exposed to water, soil, are very susceptible corrosion. Without any protections, these pipelines deteriorate fast. Due to the corrosion, the structural integrity of pipelines weakens and make it an unsafe medium for transportation of hazardous materials. The common pipeline corrosions are uniform corrosion, galvanic corrosion, pitting corrosion, selective leaching, crevice corrosion, intergranular deterioration, cavitation and erosive corrosion, erosion corrosion, stray current corrosion, stress corrosion.

#### 3.2 Effects of internal corrosion on pipelines

Internal corrosion is a major problem to the oil and gas pipelines. It occurs when the internal surface wall of pipeline is exposed to CO<sub>2</sub>, H<sub>2</sub>S and chlorides. The damage of corrosion is a function of the concentration and combination of particular components inside the wall. Corrosion may also cause by the presence of microorganism. Internal corrosion due to the chemical attack on the interior surface of the pipe. It is a major problem in crude oil pipelines, crude oil itself is not corrosive, but water can cause corrosion. The density difference between the oil and water leads, water to settle down bottom and leads corrosion. Crude oils containing more heavy crude is not corrosive. Settling of solid particles is another reason for corrosion. This creates a water wetting environment. This leads to corrosion, if the flow condition allows to settle the sediments. But internal corrosion happens only when the flow conditions allow these materials to accumulate in the pipeline surface for long time. Internal corrosion in pipelines can be divided in to 3 categories: Sweet corrosion, Sour corrosion and Sulphate acting bacteria. Sweet corrosion occurs where carbon dioxide and water present in pipeline. Carbon dioxide dissolves in water and form carbon monoxide which reacts with the pipeline surfaces and forms corrosion. The temperature pressure and flow rate affects the rate of corrosion. Sour

corrosion occurs when the pipeline fluid contains H<sub>2</sub>S and water. The hydrogen sulphide causes metallic losses. In this hydrogen sulphide dissolved in water to form weak acid. In this case, the corrosion product is iron sulphide or iron carbonate and forms a semi protective layer. Prevents further corrosion. Sulphide stress cracking occurs when material is subjected to stress and exposed to sulphide environment



Figure 5. completely corroded pipeline.

#### 3.3 Damages due to corrosion

##### 3.3.1 Appearance

Automobiles are painted, because rust surfaces are pleasing to eye. badly corroded and rusted equipment in plant will give bad impression to the observer. In rural area it would cheaper to make metal thicker than to apply coatings.

##### 3.3.2 Maintenance and operating cost

Substantial savings can be obtained through the usage of corrosion resistant materialistically fool attention of corrosion engineer and process design personnel can eliminate substantial maintenance cost.

##### 3.3.3 Plant shut down

Frequently plants are shut down and portion of plant stops working because of unexpected corrosion failures. Sometimes these are not because of the process procedures, they are due to the operating procedures.

##### 3.3.4 Contamination of production

In some cases, market value of a product is directly related to the purity and quality of the product. freedom from contamination is a vital factor in manufacturing and handling transparent plastics foods semiconductors etc. in some cases a small amount of corrosion will cause ions in to the solution and which results catalytic decomposition of the product.

### 3.3.6 Effects on safety and reliability

The hazardous materials such as hydrochloric acid, sulphuric acid radioactive substances and other chemicals demand some construction materials that minimize corrosion. Failure of a small component results in the destruction of the entire structure.

### 3.4 How to control corrosion in oil and gas industry

Four common methods are commonly used to control corrosion in oil and gas industry pipelines. They are usage of

- Coatings
- Cathodic protection
- Corrosion inhibitors
- Material selection

## 4. SAMPLE PREPARATION

The test specimens were machined from Mild Steel pipe that was obtained from Gujarat Gas. It was a "ASTM 106 GRADE B" Steel pipeline which is most used pipelines in oil and Gas Industry

- The steel specimens were made by cutting square of size 4.4cm\*2.3cm having thickness of 1 cm.
- The surface finishing procedure recommended by ASTM with the polishing procedure used as standard practice in metallographic laboratories. Specimen preparation or polishing is very necessary to study the microstructure because the microscope makes use of the principle of reflection of light to obtain the final image of the metal structure. Following steps were taken during the preparation of sample.
- A reasonably flat surface of the specimen was achieved by using a fairly coarse file or by grinding, after intermediate and fine grinding carried out by using emery papers progressively finer grade.
- Grinding was done to remove the coating that was present on the upper surface of the sample to prevent corrosion but for the complete exposure of the sample we needed to remove all the coatings that will interrupt the exposure of sample to our provided solution.

TABLE 1: COMPOSITION OF SAMPLE

SR NO.	ELEMENT	CONTENT
1.	CARBON	<30%
2.	MANGANESE	<0.29% - 1.06%
3.	PHOSPHOROUS	<0.035%
4.	SULPHUR	<0.035%
5.	SILICON	>0.1%
6.	CHROMIUM	<0.40%
7.	COPPER	<0.40%
8.	MOLYBDENUM	<0.15%
9.	NICKEL	<0.40%
10.	VANADIUM	<0.08%

### Chemicals Required

- HCl of various normalities
- H2SO4 of various normalities

### Apparatus Used

- Hack Saw
- Bench Vice
- Emery Papers
- Angle Grinder
- Beaker

## 5. EXPERIMENTAL WORK

### 5.1 WEIGHT LOSS EXPERIMENT (to study effect of concentration)

#### 5.1.1 Solution Preparation

- A (.01N,.03N,.05N&.07N) HCL solution preparation by adding .0897 ml of conc. HCL to 100ml distilled water.

#### 5.1.2 Sample Preparation

- A metal piece dipped in 1N HCl solution for 10 minutes.
- It will be cleaned using steel wool in order to remove the rust and then dried.

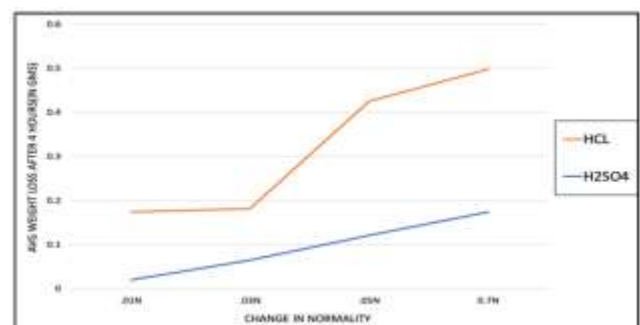


Chart 1: Average weight loss vs Concentration

## 5.2 WEIGHT LOSS EXPERIMENT (to study effect of temperature)

### 5.2.1 Solution Preparation

- Solutions of HCl of concentrations 1N HCl was prepared respectively.
- Solutions of H<sub>2</sub>SO<sub>4</sub> of 1N H<sub>2</sub>SO<sub>4</sub> was prepared.

### 5.2.2 Sample Preparation

- The metal coupons will be cleaned by immersing them in 1N HCl solution for 10 minutes and they will be subsequently cleaned using steel wool.

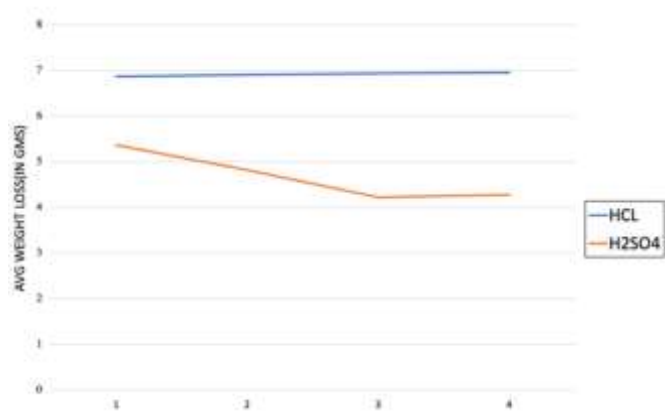


Chart 2: Average weight loss vs Temperature

## 5.2 Observing Pitting Corrosion

A reasonably flat surface of the specimen was achieved by using a fairly coarse file or by grinding after grinding carried out of emery paper of progressively finer grades. Here the specimen was first grinded by 80 grit paper to remove scratches that were produced at right angles due to filing operation. Grinding was then continued on 120 grit paper again, polishing until previous scratch marks were removed. The process is repeated with 180 grit, 220 grit and 320 grit and 400 grit emery papers.



Figure 5. Pitting observed under the microscope

## REFERENCES

- [1] ASMT, Metals Handbook, vol. 3, Properties and Selection of in : Stainless Steels, Tool Materials and Special-Purpose Metals, 1980, pp. 6.
- [2] G. Frankel, "Pitting corrosion of metals: A review of the very critical factors in the field," 1998.
- [3] Electrochemistry and Corrosion: Overview of the techniques Princeton Applied Research, 801 S. Illinois Avenue, Oak Ridge, TN 37830.
- [4] R. P. V. Cruz, A. Nishikata, and T. Tsuru, "Pitting corrosion mechanism of stainless steels under wet-dry exposure in chloride-containing environments," Corrosion science, vol. 40, pp. 125-139, 1998.