Gaseous Corrosion & Its Effects: Brief Study

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***Abstract*— This paper synopsis describes the effect from gaseous corrosion on equipment as well as on the processed product. It specifically includes the driving force of corrosion and its outcome from the gaseous contamination along with the cause by main source. Hence, corrosion by vapors and its generation is also discussed with parameters to overcome.**

***Keywords*— Oil & Gas Industry, Corrosive Gases**

I. Corrosion In Oil & Gas Industry

Precisely, in petroleum industry the most common gases/vapors that cause corrosion to the equipment or transmission lines are those which come along with it naturally during extraction or some of them are naturally present in the liquid state in it and upon changing its state into gas/vapor, become corrosive in nature. This thing is common, whether, there is an oil field or gas field, and the contaminants almost remain the same with some exceptions. Although, there are some additives that is added during the refining or purification process which may also form some by-products that should be removed as they are corrosive in nature also. Detailed explanation will be provided in the upcoming sections. The most common corrosion causing gases/vapors are: SOx, NOx, H_2S, and CO_2.

II. Main types of corrosion Present

There are basically three main types of corrosion present in the gas/oil industry on the basis of the causing agent. This should not be confused with equipment corrosion. The types are as under:

- *Sweet Corrosion*

Sweet corrosion is mainly caused by Carbon dioxide (CO_2), as it causes to form Carbonic Acid (H_2CO_3) and acts as an active proton donor causing acidic effect to propagate during the processing of gas/oil. Along with it also contaminates the piping system as well as the process equipment, forming dead spots.

- *Sour Corrosion*

Sour corrosion is mainly caused by Sulphur and its relevant compounds. So far, the biggest source is H_2S which presents naturally in natural gas and crude. While during processing, it can cause to generate SOx which later may transform to Sulphuric Acid which acts as a strong dehydrating as well as corrosive agent.

- *Oxygen Based Corrosion*

While Oxygen is itself not so corrosive in nature but being an oxidizing agent, it contributes in increasing corrosion population. Bacterial growth in pipe due to excess deposition of moisture propagates more in the presence of Oxygen that is aerobic environment. Detail will be discussed shortly.

III. Contaminants Present In Natural Gas

Natural gas and its constituents that is other gaseous fuels like Butane and Propane are not itself contaminant whether in raw form or refined form. The two-main undesirable content are water vapor and hydrogen sulfide (H_2S) which is corrosive in nature. Water condensate is corrosive[1] for the process plant equipment but its severity becomes high when it dissolves acid in it, although, it is not as severe as H_2S and other sulfur based compounds. Carbon dioxide is also objectionable in natural gas due to its acid forming nature and also because it lowers the heating value of the natural gas. Hence, proper removal is necessary.

IV. How Water Vapor & H_2S Is Removed?

The simplified process depicts that, in industry, there is a compression system that compresses the gas followed by a cooling system to remove the water content. Glycols are also widely used for its high affinity with water and chemical stability. Activated Alumina, Silica Gel and concentrated solutions of Sodium thiocyanate is widely used in this regard. Monoethanolamine is widely used as a solvent to remove Hydrogen Sulfide followed by various scrubbing process.

V. What Will Happen If Water Vapors Remain In Natural Gas?

If water present in most fuel gas is not removed, unduly high corrosion chances will occur in the transmission lines and trouble may also result in the form of Hydrates which can cause line stoppage of various plant equipment. Freezing of valves and regulators in cold weather can also cause difficulty. The worst among this would be the formation of MIC** whose main cause of formation is excessive moisture environment but requires aerobic conditions to proceed its population.

VI. **Microbiologically Influenced Corrosion (MIC)

It comes under the shadow of Oxygen based corrosion. It is actually bacterial population that forms in the transmission/pipelines. It is mentioned here because its cause of formation is gas and its outcome is in the form of corrosive gas too. In aerobic environment, the cultural growth leads to the formation of acidic gases like HCl and it also cause to metabolize Sulphur and its gases to accelerate attack on steel.

VII. Addition Of Odorant In Natural Gas?

Usually, Sulphur based liquid or Merceptans is used as an odorant in the natural gas to identify leakages or to identify the gas. Under standard condition this isn't corrosive but on distribution system this can cause corrosion. Hence non-sulfur based additive like Methethyl pyrazine is encouraged to use although, Dimethyl Sulfide and Ethan thiol is still used in this regard.

VIII. HCl Vapor Corrosion In Petroleum Refining

Boot Water: An Important Overhead Component

One important factor shall be discussed in the next part i.e. Crude Tower Overhead Corrosion and the parameter that relates to it is the Overhead water content. This water is tested frequently to check the amount of Iron or any traces of contaminated components as well as due to the hydrolysis in desalter HCl vapors are produced which comes out as an overhead side product from the crude tower and pre – flash tower causing severe corrosion to the upper section as well as to the condenser tubes. Thus, the importance of testing is significant to ensure safety as well as prevention from damages.

Crude Tower Over Head Corrosion: How Can It Be Prevented?

This is one of the most common problem usually encountered in Petroleum Refineries. The problem actually originates from the desalter, the three main salt content present in crude are NaCl, $MgCl_2$, $CaCl_2$ and out of these the heat stability are as under:

$$NaCl > CaCl_2 > MgCl_2$$

Hence, Sodium Chloride remains unaffected while Magnesium Chloride tends to hydrolyze at elevated temperature usually at crude tower's flash zone releasing HCl vapors and the usual severe outcomes are in the form of:

- Loss of atmospheric distillation tower's tray material/plugging.
- Corrosion of condenser tubes and reflux drum

A single stage desalter approximately removes around 90% of the salt content as compared to 99% removal from double stage removal. Here, the question arises, why don't we utilize this to prevent corrosion? – The answer is – Magnesium Chloride is a troublesome salt and its removal is not that easy whether to use a single stage or multi stage. The HCl vapor attack is continuously regenerated by reaction with H_2S because usually there's an excess of H_2S inside the crude tower.

$$HCl + Fe \text{ yields } FeCl_3 \text{ and then } FeCl_3 + H_2S \text{ yields } FeS_2 \text{ and } HCl$$

This unfortunately leads to another factor to consider, HCl liberated out from the crude tower has usually a greater affinity for water and as long as no water is present the HCl vapors are non – corrosive in nature but as the overhead water droplets tend to condense, it dissolves all HCl and become highly corrosive in nature. The pH of HCl vapor without mixing with water condensate is about 2 while after dilution it increases to about 5.5 – 6.5.

On the similar manner, naturally crude oil contains Naphthenic Acid which is highly corrosive in nature whether in vapor form or condense form hence, observation of the acid content present in crude is very necessary and for this, TAN (Total Acid Number) test is being widely used.

How To Take Prevention Measures?

The following actions should be taken to overcome this issue:

- Effective desalting to remove the maximum content of Magnesium Chloride.
- Caustic injection to control Chlorides in the reflux drum boot water.
- Sufficient addition of neutralizing additives.

Usually, Ammonia gas is injected at the bottom of the pre – flash column/distillation column also, Concentrated Caustic is added in the crude to suppress any acidic content to prevent corrosion. Zinc and Kerosene based mixture is also used to protect the inner side of the equipment as it forms a protective coating inside.

Generally, there are several corrosion types on the basis of equipment and may vary but in industry two types of corrosion are witnessed mostly by the corrosive gases like HCl, SOx, NOx, H_2S etc. and these are:

- *Pitting*

All the pipeline system must have some weak spots present and gases with corrosive nature cause to accumulate here and forms localized corrosion effect as it penetrates in metal and form holes which can cause leakage. This is most widely witnessed in condenser/heat exchanger tubes.

- *Crevice*

This type of corrosion happens at the joints or confined space where fluid presence is limited but to some extent. Gaskets, seals, flanged joints are more susceptible to this kind of corrosion.

IX. Corrosion In Fertilizer Industry

There may be numerous source of corrosion which varies from plant to plant. Since, in the Nitrogen industry, Urea is one of the most common an essential product widely used as a fertilizer. When Urea solution is heated at low pressure for prilling purpose, it thermally breaks down into highly corrosive Ammonium Cyanate followed by Isocyanic Acid which evaporates in the overhead section of the equipment and condenses back and this condensate tends to contaminate the Urea as well as the equipment.

$$NH_2CONH_2 \rightarrow NH_4CO \rightarrow HNCO + NH_3$$

Ammonium Carbamate is more corrosive in nature and has higher affinity for the hottest section in the equipment to corrode, this thing usually witnessed in the Stripper and to overcome this, air is injected to form ad oxide layer inside but this method cause further problems. Hence, since 1980, Duplex (Ferric-Austenitic) Steel has been using in the industry as it is highly corrosive resistant.

X. Equipment That Are Mostly Affected By Corrosion

Although, there are several equipment that may get affected by gaseous corrosion specifically but the most common among them includes:

- Heat Exchanger and Condenser Tubes, gaskets ad flanges.Valves and miscellaneous industrial fittings.
- Transmission pipelines.
- Distillation/pre-flash column overhead section.Accumulator in refinery.

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