International Journal of Recent Technology and Engineering (IJRTE)
ISSN: 2277-3878 (Online), Volume-8 Issue-2, July 2019

Atmospheric Pollutant Analysis and Corrosion Simulation over LPG Transporting Pipelines in Sriperumpudur – Vadakal Industrial Site

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Abstract: ***An Organization has to abide national safety legislation procedures so as to maintain business moral and workers safety. To ensure this, management has to do the following active monitoring steps like Hazard Identification, detailed Risk Assessment, drafting Safe Work procedure, Supervision and Training to Workers. While doing Risk Assessment the likelihood for the hazard to occur and the intensity of damage it would create should be properly calculated. Along with that, the effectiveness of existing control measure and the recommendations for advanced control measures also to be suggested. In general, incidents are happening mainly due to defect in Safety management, technical Job factor or individual factors. The accidents are happening mainly due to unsafe act or unsafe condition. Unsafe act includes Individual negligent behavior like, not wearing personal protective equipment, not carrying out the task as per the instruction, not carrying out the inspection or preventive maintenance as per the procedure etc., . Unsafe conditions include defective equipment in the work place, improper Housekeeping in the work site etc. In Petrochemical plants, as volatile Hydrocarbon exist in the process area, the chances for fire oriented emergencies are unavoidable if unsafe act or unsafe condition not identified and controlled appropriately. In a crude oil refinery or downstream petrochemical units, mostly flammable substances like Petrol, Diesel, Superior Kerosene, Aviation Turbine Fuels and Liquefied Petroleum Gas (LPG) would be the refined products. These products processed in distillation columns, stored in tanks, bullets and transported through pipelines. As this process equipment's and distribution networks especially Pipeline grids are exposed to atmosphere the natural phenomenon called Atmospheric Corrosion is unavoidable. Atmospheric Corrosion may happen if the atmospheric pollutants interact with humidified air an electrochemical reaction leads to Corrosion. This electrochemical reaction would affect the Pipeline structures very badly results in puncture on pipeline surface leads to flammable substance leakage.***

To control this corrosion, along with proactive engineering control measure, ambient air quality analysis, corrosion simulation and corrosion monitoring should be done.

Index Terms: Electrochemical, LPG, Unsafe act, Unsafe Condition

Revised Manuscript Received on 30 July 2019.

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I. INTRODUCTION

LPG is heavier than air. Mostly LPG stored and transported in liquid form, but when it release or leak to atmosphere it changes into gaseous form. This leaked gases created a flammable vapor cloud and leads to explosion named as Unconfined Vapor Cloud Explosion. It is evident that most of the accidents in LPG Terminals and Filling stations are mainly due to leakage of gases. This leakages may occur either from storage bullets, from pipelines, vents or from the valves. In oil and gas industry the gas leakage is due to many reasons like: Unsafe acts of workers while operating the pipeline components, failure of any specific parts like valve or defective welding joint, not following standard operating

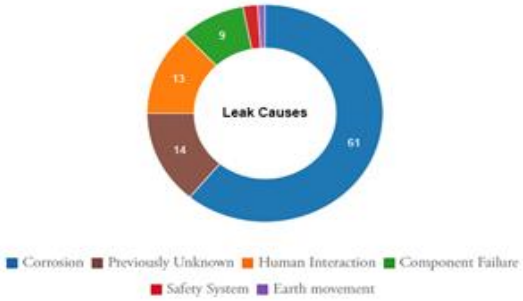

Fig. 1: Causes for Leaks

procedure while operating the pipeline. But the statistics are clearly indicating that the leakage is occurring in the pipeline majorly due to corrosion. In terms of percentage, 14% of leaks are occurring due to unknown reasons, 13% is due to human interaction, 9% is due to component failure, 61% is mainly due to corrosion. LPG is transported through pipelines inside the filling plants and they exposed to atmosphere. Due to corrosion, pipelines may rupture and gas leak may occur. In general as per the legal requirements, at regular intervals organization would do pressure testing for the pipelines to confirm its structural integrity.

However, the corrosion may happen in between the testing periods and possibility of gas leakages could be unavoidable. The main challenge in Atmospheric corrosion is, it is a chronic process and difficult to judge at what time period and under which specific spot over the pipeline corrosion may occur. Governments have strictly instructed to maintain appropriate corrosion control measures in the LPG Terminals and Filling stations. Though the Organizations are implementing the same, they are facing difficulty in maintaining the effectiveness of the control measure mainly due to economic reasons and lack of man power.

II. PROBLEM DEFINITION AND PROPOSED METHODOLOGY

The atmospheric corrosion damage over LPG transporting pipeline is unpredictable. The external corrosion monitoring is very challenging and it is difficult to calculate how much corrosion can happen. The middle size LPG storage terminals may unable to invest much money and implement costlier corrosion control measure. However, if the corrosion rate has identified appropriate control measures can be implemented. To determine the corrosion rate, the following steps to be followed. Ambient air quality analysis to be done. As the analysis is about Atmospheric corrosion, the pollutant and the concentration of corrosive agents to be determined. After that appropriate corrosion simulations to be done. By doing this analysis, the impact of corrosion level in that specific site can be determined and appropriate effective control measure can be determined. The proposed methodology as follows:

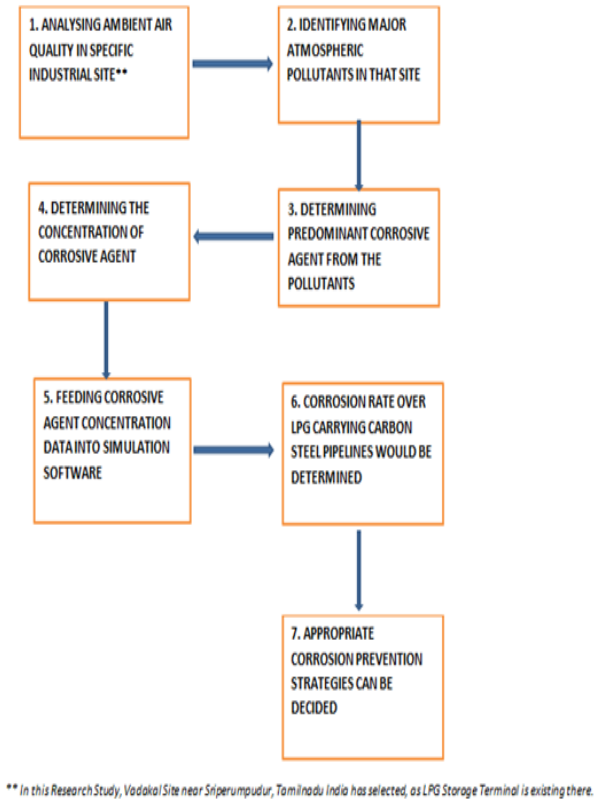

Fig. 2: Proposed Methodology

III. ATMOSPHERIC POLLUTANT ANALYSIS

Sriperumpudur Vadakal Industrial site, Ambient air quality analysis has done with the below procedure

Step 1: Gathering air quality report near Vadakal location

Step 2: Determining the Moisture percentage near the site

Step 3: Calculating Atmospheric Pollutant concentration in ppm

Step 4: Identifying the possible Corrosive substance near the site

Step 5: Determining the concentration of Corrosive agents near the site

Step 6: Determining the pH of primary corrosive agent to proceed with simulation

The air quality reports have gathered around the plant location with reference to Central Pollution Control Board (CPCB), Chennai division (web site http://www.airpollutionapi.com) and tabulated below:

Pollutants	**Day I -III : 05th Apr 2019 to 07th Apr 2019**		
	Morning	**Evening**	**Average**
Ambience Temperature	34 °C	31 °C	33°C
Relative Humidity	51%	68%	60%
Ozone (O_3) µg/m^3	22.76	6.60	14.68
Oxides of Nitrogen (NOx) µg/m^3	2.52	0	1. 26
Oxides of Carbon (Cox) µg/m^3	580	1983.33	1281.67
Oxides of Sulphur (Sox) µg/m^3	6.98	4.31	5.65

Table I: Vadakal Site – Ambient Air Quality

The **Absolute Humidity** calculation as follows

Relative Humidity = (Pw /P sat (T)) x 100

Pw = Partial Pressure of Water

P_{Sat} *= Saturation pressure of Water*

T = Specific Ambient Temperature

Average Relative Humidity in Vadakal site is 60%

Average Ambient Temperature in the site is 33 ℃

Table II: Saturation Pressure for Water

Saturation Pressure of Water (mm Hg)

T(°C)	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
30	31.824	32.007	32.191	32.376	32.561	32.747	32.934	33.122	33.312	33.503
31	33.695	33.888	34.082	34.276	34.471	34.667	34.864	35.062	35.261	35.462
32	35.663	35.865	36.068	36.272	36.477	36.683	36.891	37.099	37.308	37.518
33	37.729	37.942	38.155	38.369	38.584	38.801	38.018	39.237	39.457	39.677
34	39.898	40.121	40.344	40.569	40.796	41.023	41.251	41.480	41.710	41.942

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By referring Saturation Pressure Water Table at 33 ℃,

Psat= 37.729 mm Hg

0.6 = (Pw/37.73 mm Hg) => Pw = 22.64 mm Hg

Absolute Humidity = Mass of Water Vapor / Mass of Air

Pw Mw / (P-Pw)*Ma

Pw = Partial pressure of Water = 22.64 mm Hg

Mw - Molecular weight of Water = 18 gram of water/Mole

P = Total Pressure = 760 mm Hg

Ma = Molecular weight of dry air = 29 gram air/mole

Absolute Humidity = (22.64 mm Hg x 18 g of water/mole) / ((760 mm Hg - 22.64 mm Hg) x 0.029 kg air/mole)

= 407.52/21.38 = 19.06 g of water/kg of Air

Density of air = 1.225 kg/m3

=> 19.06 g of water / kg of air x 1.225 kg/m3 = 23.35 g of water/m3 of air

The **atmospheric pollutant concentration** in Table I data converted from micro gram/m^3 of air = gm / m^3 of air (1 gram = 10^6 micro gram)

Table III: Vadakal Site – Ambient Air Quality (in gm)

Pollutants	Average Concentration gm/m^3 air
Relative Humidity	23.35
Ozone (O_3)	0.00001468
Oxides of Nitrogen (NOx)	0.00000126
Oxides of Carbon (Cox)	0.00128
Oxides of Sulphur (Sox)	0.00000565

From the above table it is evident that the concentration of Oxides of Carbon is more. So it is considered as corrosive agent and further analysis has done. Oxides of Carbon on reacting with humidified air, carbonic acid (H2CO3) would be formed. Carbonic acid by reacting with carbon steel (Fe) pipes, corrosion is occurring

Carbonic Acid from Oxides of Carbon

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

By using (thermobook.net) stoichiometry calculator the amount of carbonic acid that can be formed near the site has found out. The pH of the carbonic acid has calculated using Weight method in which the weight of carbonic acid is 0.00186 gm and volume of solution (water) is 0.02335 liter of water. The conversion factor applied is (1000 gm of water = 1 liter of water). Based on the ambient air quality analysis the following points are summarized: (i) Oxides of Carbon is predominant than other atmospheric pollutant near Vadakal site. (ii) As per pH scale, Carbonic acid can cause severe corrosive damage than other acids. (iii) As more automobile movement are there for loading and unloading near the selected site, Carbonic acid concentration can be considered between 4 and 5. (iv) This concentration can be considered for further corrosion simulation.

IV. MULTIPHYSICS CORROSION SIMULATION

Atmospheric Corrosion is a multiphysics electrochemical reaction in which film of electrolyte formed by interaction of moisture present in the air and oxygen .Oxidation and reduction reaction would occur results in considerable material loss of metal. Carbon steel pipeline is mostly used to transport LPG. It is evident from the ambient air quality analysis that Carbon di oxide and Carbonic acid are the primary atmospheric pollutant acting as a corrosive agent in Vadakal Industrial site. So, carbon di oxide (CO_2) corrosion simulation over carbon steel pipes has initiated for further progress. To simulate the above scenario open source corrosion simulation software has used. The following steps are tailed to progress with the simulation.

(i) Electrochemical corrosion reaction at the steel surface to be identified

Iron dissolution

$$Fe(s) \rightarrow Fe^{2+} + 2e^-$$

Proton reduction

$$H^+ + e^- \rightarrow H$$

Water reduction

$$H_2O + e^- \rightarrow H + OH^-$$

Carbonic acid reduction

$$H_2CO_3 + e^- \rightarrow H + HCO_3^-$$

(ii) The equilibrium reaction of electrolyte (humidified air (H_2O) and Carbon di oxide) to be recognized

$$H_2O(l) \Leftrightarrow H^+(aq) + OH^-(aq) \qquad K_1 = 6.418 \cdot 10^{-15}$$

$$CO_2(aq) + H_2O(aq) \Leftrightarrow H_2CO_3(aq) \qquad K_2 = 2.580 \cdot 10^{-3}$$

$$H_2CO_3(aq) \Leftrightarrow H^+(aq) + HCO_3^-(aq) \qquad K_3 = 1.251 \cdot 10^{-4}$$

$$HCO_3^-(aq) \Leftrightarrow H^+(aq) + CO_3^{2-}(aq) \qquad K_4 = 1.382 \cdot 10^{-10}$$

(iii) To determine the corrosion potential at the steel surface, appropriate boundary condition to be applied.

(iv) As corrosion is a mass transfer phenomenon, Diffusion co-efficient of species to be given as input

(v) As atmospheric corrosion has simulated, the following process parameters have considered.

Atmospheric pressure is kept as constant. pH and ambient temperature variations has done and fed into simulation software to generate Corrosion Rate data. After completing the atmospheric corrosion simulation of Carbon di oxide on Carbon steel pipes, Corrosion Rate graph has generated. This graph has plotted for different pH values of carbonic acid and ambient temperature. It is evident from the graph data that corrosion rate is proportional to the ambient temperature and inversely proportional to pH value. As per ambient analysis of Vadakal site, average ambient temperature ranges between 30 to 40 ℃ and the pH of carbonic acid is 4.7. The expected corrosion rate is 3.5 to 4 mm/year.

V. RESULTS AND DISCUSSIONS

Due to exposure to atmosphere, the external localized corrosion over LPG Pipelines is unavoidable which may leads to LPG gas leak results in fire and explosion. To take proactive control measure appropriate analysis of atmospheric pollutant where the LPG pipelines are running to be done. In this research, Vadakal Industrial site which is located near Sriperumpudur, Tamilnadu, India has selected. It has found that Oxides of Carbon is found to be the predominant pollutant in this site of average concentration 0.00128 gm/m3 air. After this, relevant electrochemical corrosion reaction related to Oxides of Carbon has studied and found Carbonic acid would cause corrosion for the pipeline. By applying stoichiometric calculation, pH of the carbonic acid has determined as 4.7 at the ambient temperature of 33℃ and Relative Humidity 60%. This data has given as input into Corrosion Simulation software and found that corrosion rate would range between 3.5 to 4 mm/year. In general, ASTM A106 grade pipeline of diameter between 40 mm to 300 mm with thickness varies between 4 mm to 7.1 mm has generally used to transport LPG. In case of bulk LPG transport to bullets high thickness pipe of 7.1 mm would be used. If the LPG terminal has located in Vadakal site, as per the above research study, the high volume carrying LPG pipelines would be corroded within 2 years. Based on this data, the frequency of protective coating, preventive maintenance schedule can be decided.

VI. CONCLUSION

In an oil & gas Industry the flammable gas leakages and related fire accidents are increasing mainly due to corrosion in the pipelines. The Atmospheric corrosion is very challenging one, as the corrosion damage may occur anywhere in the pipelines. The effective localized corrosion monitoring techniques have limitations like human interface requirements and costlier implementations. As the oil revenue is going down, the cost effective solution for corrosion monitoring would be acceptable in the Industry. In this research study, an attempt has made to study about the Atmospheric pollutant and its impact in corrosion over the carbon steel pipes. A specific Industrial site has selected and air quality analysis has done. Based on the data, Corrosion simulation has done and corrosion rate has determined which can be useful to decide the proactive corrosion monitoring and control method

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