



ISSN: 2319-5967

ISO 9001:2008 Certified

International Journal of Engineering Science and Innovative Technology (IJESIT)

Volume 2, Issue 2, March 2013

A Study of Hydrochloric Acid Synthesis Process in a Chlor-Alkaly Industry

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Abstract- This paper includes a study on falling film type synthesis oven used in chlor-alkali industries for the synthesis of Hydrochloric acid is carried out on the basis of stack analysis reports (which show the efficiency of Hydrochloric acid synthesis oven - by analysing emission gases). The stack analysis reports indicated that excess Hydrogen and Chlorine are used for the production of desired quantity of Hydrochloric acid. The main objective of this study is to find out the causes of this problem and suggest possible remedies for the same. It is found that Hydrogen Chloride gas absorption into water depends on various factors such as property of absorbing water, defects in the oven, lack of proper monitoring etc. The remedies suggested include alteration in temperature, pressure and PH of absorbing water, providing venturi scrubbers, rectifying cracks in graphite blocks in the oven.

Index Terms- Cause and Effect Diagram, Hydrochloric Acid Synthesis Oven, Stacks Analysis Reports.

I. INTRODUCTION

This paper tries to conduct a case study on a Hydrochloric acid synthesis unit. Mainly five synthesis ovens are used to produce hydrochloric acid in the plant. Hydrogen, Chlorine and water are the raw materials for the production of hydrochloric acid. Hydrochloric acid is one of the main products in chlor-alkali industries. Hydrogen chloride gas is produced by the exothermic reaction of hydrogen and chlorine inside the furnace. Falling film type Hydrochloric acid synthesis furnace is used to produce Hydrochloric acid. A film of water falling through the small tubes gets mixed with HCl gas. The unabsorbed gas gets absorbed by secondary absorption system. The main possible problems in Hydrochloric acid synthesis unit are corrosion, improper combustion of hydrogen and chlorine, inefficiency in absorption system etc. A study on hydrochloric acid synthesis unit is carried out in a leading chlor-alkali industry. The objective of this study is to find out major problems in Hydrochloric acid synthesis unit and find out the remedies by which these problems can be minimized.

II. EXPERIMENTAL DETAILS

A. Problem Identification

Identification of loss prevention procedures is very essential for improving the performance of Chemical industries. The major hurdles faced by chemical industries include high power consumption, emission losses etc. Hydrochloric acid is one of the main raw materials required for various industries. 33% commercial Hydrochloric acid is generally produced in Chlor-alkali industries. To produce a unit tonne of hydrochloric acid, 330 kg of hydrogen chloride gas is required for which 320.96 kg of chlorine and 9.04 kg of hydrogen are used. However in real cases the quantity of chlorine used is quite higher than this theoretical requirement.

B. Process Description

1. Preparation of brine and primary purification

Sodium chloride or salt is fed into the saturator using bucket elevators, where it gets mixed with water. This solution water required concentration goes to precipitation tank where chemicals like Barium carbonate, sodium carbonate and caustic soda are added to remove sulphates, calcium and magnesium impurities. The solution then goes to the clarifier where the precipitators are allowed to settle. The clarified brine is passed through Anthracite filters. In the filtered brine solution chlorine content is completely removed by adding bisulphate. Caustic soda is also added to make the pH in between 8.5-9.5. Brine is to be admitted to the secondary purification system only after the desired purity level is attained.

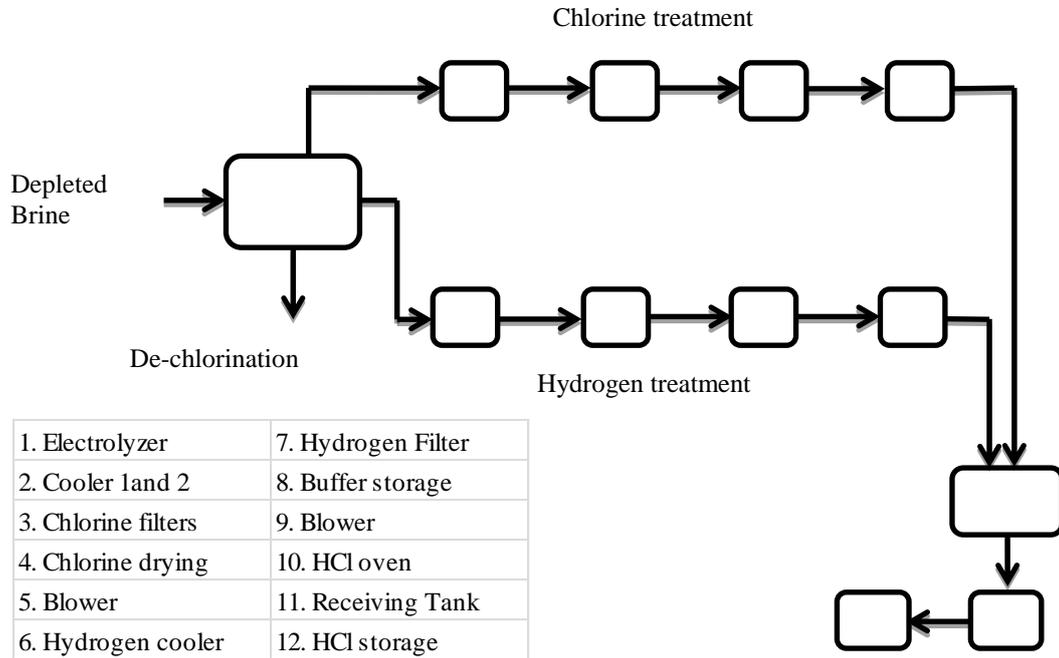


Fig 1: Hydrochloric acid process diagram

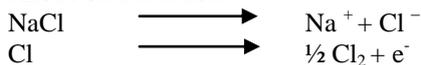
2. Secondary brine purification

The secondary brine purification system consists of four ion exchange filters. The primary purified brine is passed through the ion exchange filters where it undergoes an exchange process. Ion exchange materials are insoluble acids and bases, which when converted to salt remain insoluble. The most popular ion exchange materials are synthetic organic polymers. These ion exchange materials are used in columns in which the solution containing ionic impurities like calcium and magnesium. These impurities come in contact with the resin usually through downward flow through the resin bed. The saturated resin is then regenerated to its original state by using acid and alkali solution. The regenerated resin is then reused. The purity of the feed brine in the membrane cell process affects the performance and life of the membrane.

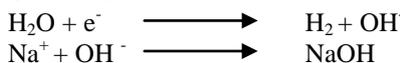
3. Electrolysis

The secondary purified brine is fed to brine head tank after cooling and is admitted to electrolysis. Demineralized water is also admitted to the electrolysis. Direct current (DC) supply is connected to the anode and cathode and the current is applied to the electrolyzed. During electrolysis, 32% concentration caustic soda is produced at the cathode. Hydrogen gas is also formed at the cathode chamber and Chlorine formed at anode. Chlorine is pumped into storage tank, hydrogen and chlorine gas goes to their respective treatment sections.

Anode side reaction



Cathode side reaction



The chlorine gas coming from the electrolyzers is water vapor saturated according to the electrolysis temperature of 80-90°C. The gas is cooled down in two steps with two titanium plate-type heat exchangers, Cl2 Cooler 1, and Cl2 Cooler 2. Cl2 Cooler 1 is operated with cooling water and the chlorine is cooled down from 90°C to 55°C. The cooling water flow rate is adjusted manually from a regulating valve at the water outlet side. The Cl2 temperature is maintained on thermometer.



ISSN: 2319-5967

ISO 9001:2008 Certified

International Journal of Engineering Science and Innovative Technology (IJESIT)

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In the second stage cooling, chlorine is cooled down to 25°C by means of chilled water and the flow rate is manually adjusted by regulating control valve at the water outlet side. Temperature recorder is used to monitoring temperature of chilled water. Both high and low temperature limits are alarmed in the control panel. The function of this filter is mainly to separate the brine mist (aerosols) carried along with the gas. The filter unit consists mainly of filter body and cartridge internals of glass fiber. Water is continuously sprayed into the gas stream inlet to the filter to keep the cartridges wet and so avoid undue pressure drop increase. Water to be sprayed in the chlorine stream entering the filter is adjusted and monitored through flow meter. The moisture containing chlorine coming from the second cooling stage is dried by means of sulphuric acid. The drying is performed in one single Cl₂ drying tower. The tower consists of two drying sections. In the first section, chlorine gas is dried by means of 78% H₂SO₄, which is circulated over a packed column. Final drying is performed with 98% H₂SO₄ in the top part of the tower consisting of five tunnel trays. Chlorine gas is fed at the bottom part of the tower and is dried by streaming in counter current acid flow. Water is absorbed in the first drying section and the corresponding amount of absorption heat is generated there. The drying performance of the tower is best at low acid temperature. So that's why reason absorption heat from circulating acid is removed with chilled water using 78% H₂SO₄ cooler. The 78% H₂SO₄ is continuously recalculated through the packed column with circulation pump. Hydrogen from the electrolyzer is fed to the cooling unit to reduce the room temperature by a heat exchanger and cooling tower system. The hydrogen gas coming from electrolyzer may contain salt materials can be removed by filtration process. The hydrogen gas is then fed to the hydrogen holder to store. This hydrogen storage is a buffer storage system. The storage tank is placed above the water tank and float on the water. This method reduces the impact of explosion. This stored hydrogen is fed to the hydrochloric acid synthesis unit for producing hydrochloric acid.

4. Hydrochloric Acid Production

The unit consists of the HCl synthesis unit, Steam Ejector, HCl Collecting Tank. The synthesis of HCl is performed by combustion of H₂ and Cl₂ gas. Both the reaction and absorption heat in water are highly exothermic. The reaction is;



For optimum combustion and low free chlorine content in acid, the gases are burnt with about 10% excess volume flow of hydrogen and the content of free chlorine can so be reduced. The HCl gas which contains inerts and the previously mentioned excess of hydrogen is absorbed in de-mineralized water in the falling film absorber to produce hydrochloric acid of max.33% w/w. The acid flows by gravity to the HCl Collecting Tank. The unabsorbed gas from the oven is sent to the secondary absorption and the remaining HCl gas is absorbed in counter flow to the de-mineralized water. The heat generated during the combustion and absorption is eliminated from the jacket cooled graphite blocks by cooling water. The de-mineralized water, which is used for the absorption of the HCl gas, is fed to the top of the oven from where it flows by gravity via the pickings to the falling film absorber of the synthesis. The quantity is controlled according to the concentration of the produced hydrochloric acid and assures constant quality over the full load range of the unit.

5. Design Features of HCL synthesis furnace

The construction material of the HCl Furnace is Diabon, which is an impregnated graphite material and it consists of a combustion chamber and a graphite burner, and a isothermal falling film absorber, which are built as an integral part of the wall of the combustion chamber. Absorber and combustion chamber are incorporated in a steel shell. It serves as a cooling jacket. That unit is protected with a diabon bursting disc due to over-pressure (max. 1.3 bars) initiate the discharge of the hydrogen chloride vapors at the top of the unit. Rupture disc absorbs explosions and the steel shell will resist to even more violent explosions. The unit is connected to the cooling water circulation system. The maximum allowable cooling water pressure is 0.4 bars.

III. RESULT AND DISCUSSION

A. Identifying Causes of the Problem

Defects in oven like blockage in HCl vents, cracks and damage in pipe lines cause leakage and incomplete absorption of gas. Lack of attention and training in controlling pneumatic valves are also contributed to the

problem. Presence of moisture, PH, temperature and pressure are to be noticed. Incomplete reaction, incomplete absorption is cause to the problem.

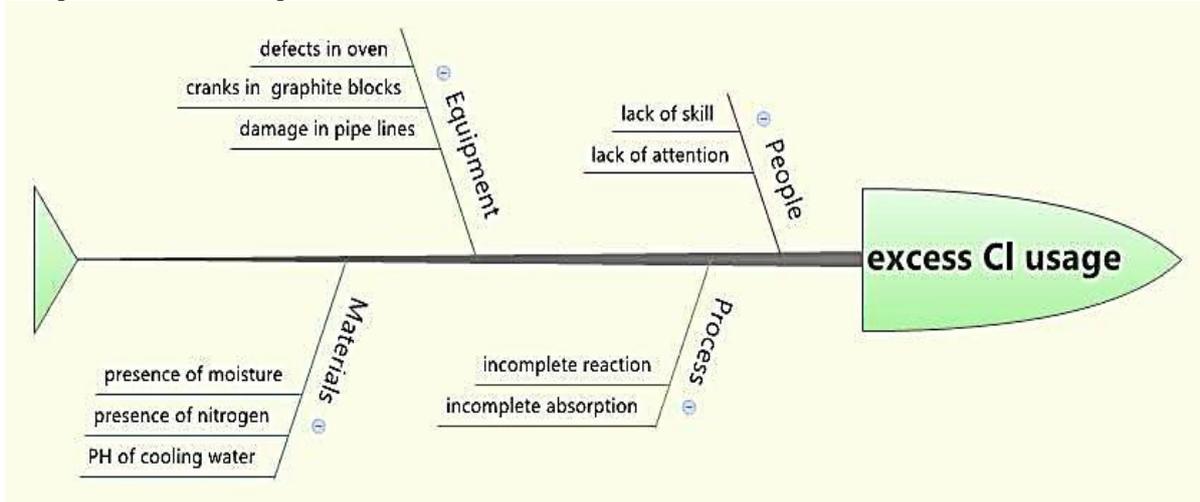


Fig 2: cause and effect diagram

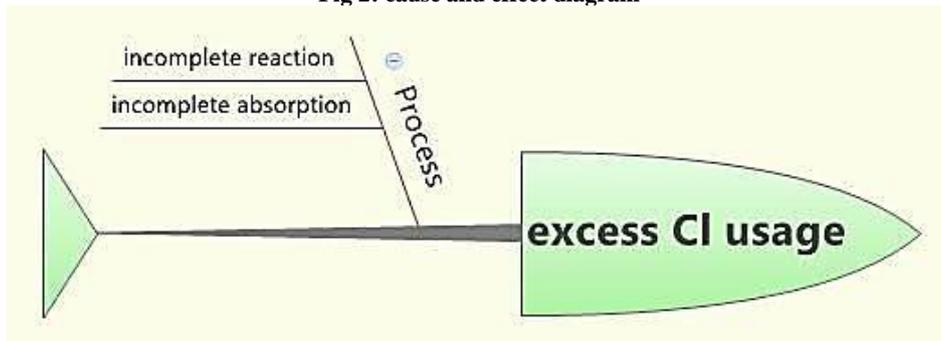


Fig 3 : Revised cause and effect diagram

B. Data Collection

The emission from each oven is selected for analysis. The emission quantity of each oven is collected and described in the tables given below.

Table 01: stack analysis report on July.

GASES	OVEN-1	OVEN-2	OVEN-3	OVEN-4	OVEN-5
HCl GAS	37.43	36.71	37.22	45.93	38.28
CHLORINE GAS	11.67	10.38	10.69	8.53	9.18
HYDROGEN GAS	NIL	NIL	0.14	0.20	NIL

Table 02: stack analysis report on June.

GASES	OVEN-1	OVEN-2	OVEN-3	OVEN-4	OVEN-5
HCl GAS	36.35	40.17	42.81	37.90	40.55
CHLORINE GAS	11.35	9.96	10.58	9.10	7.48
HYDROGEN GAS	NIL	NIL	NIL	NIL	NIL

Table 03: stack analysis report on May.

GASES	OVEN-1	OVEN-2	OVEN-3	OVEN-4	OVEN-5
HCl GAS	45.34	35.87	36.69	36.20	37.76
CHLORINE GAS	10.86	8.36	9.82	10.43	7.75
HYDROGEN GAS	NIL	NIL	NIL	NIL	0.32

Table 04: stack analysis report on April.

GASES	OVEN-1	OVEN-2	OVEN-3	OVEN-4	OVEN-5
HCl GAS	37.54	34.46	36.21	38.14	40.17
CHLORINE GAS	8.98	11.38	11.63	10.29	8.80
HYDROGEN GAS	NIL	0.18	NIL	NIL	0.26



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Table 05: stack analysis report on March.

GASES	OVEN-1	OVEN-2	OVEN-3	OVEN-4	OVEN-5
HCl GAS	38.40	35.77	38.08	35.37	44.25
CHLORINE GAS	10.46	9.91	9.81	9.33	10.11
HYDROGEN GAS	NIL	NIL	NIL	NIL	NIL

Table 06: allowable concentration of flue gases

GASES	Concentration(mg/Nm ³)
Hydrogen Chloride gas	35
Chlorine	15
Hydrogen	2

C. Data Analysis

Bar charts was plotted based on the above data and are shown in figures given below. All Histogram of March, April, May, June and July reveals that the quantity hydrogen chloride gas emission is more. The quantity of hydrochloric acid is more than 35mg/Nm³.

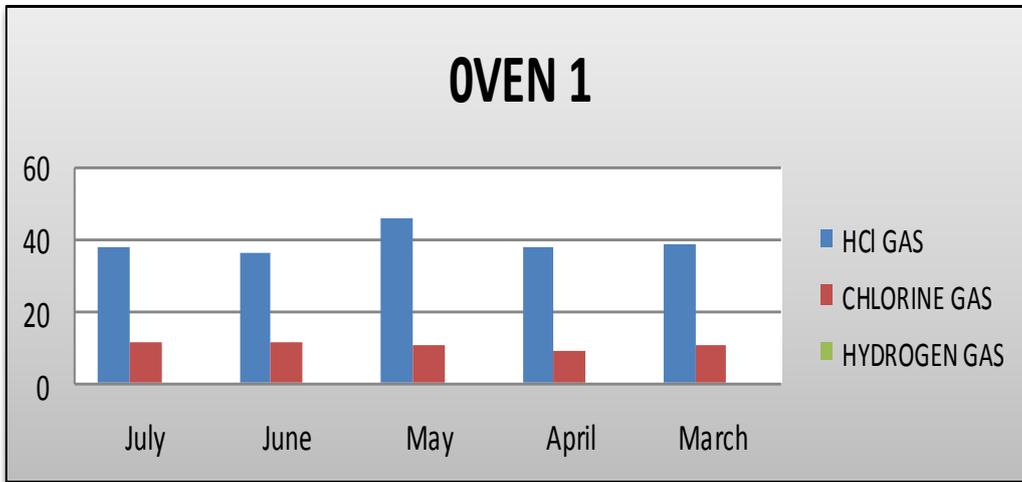


Fig 4: Stack analysis report of emission of oven 01.

Based on stack analysis in oven 01, the maximum Hydrogen Chloride gas emission was on May 2012 and emission on July, June, May, April and March was more than the allowable limit. Emission of Chlorine was less than the allowable limit.

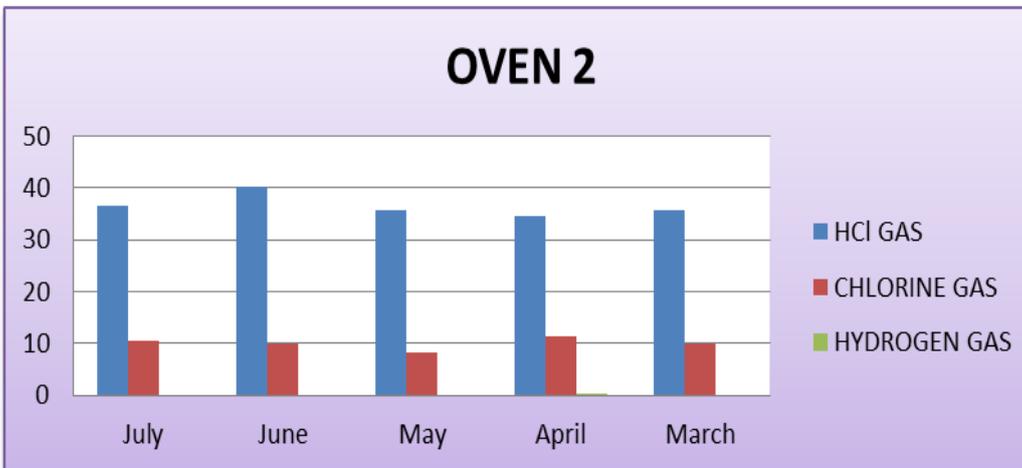


Fig 5: Stack analysis report of emission of oven 02.

Based on stack analysis in oven 02, the maximum Hydrogen Chloride gas emission was on June 2012 and emission on July, June, May, April and March was more than the allowable limit. Emission of Chlorine was less than the allowable limit.

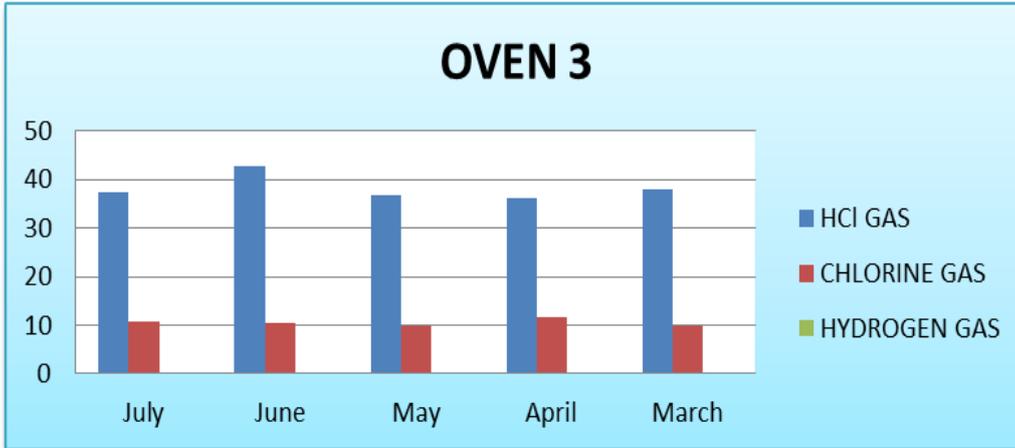


Fig 6: Stack analysis report of emission of oven 03.

Based on stack analysis in oven 03, the maximum Hydrogen Chloride gas emission was on June 2012 and emission on July, June, May, April and March was more than the allowable limit. Emission of Chlorine was less than the allowable limit.

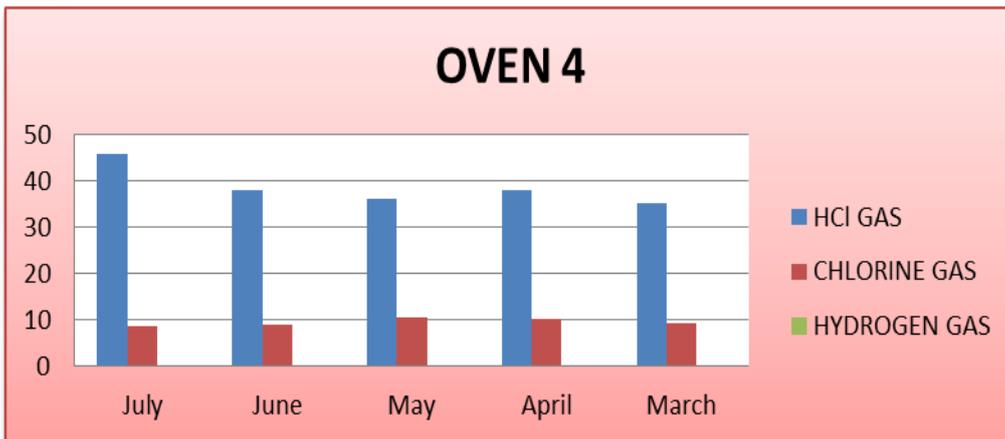


Fig7: Stack analysis report of emission of oven 04

Based on stack analysis in oven 04, the maximum Hydrogen Chloride gas emission was on July 2012 and emission on July, June, May, April and March was more than the allowable limit. Emission of Chlorine was less than the allowable limit.

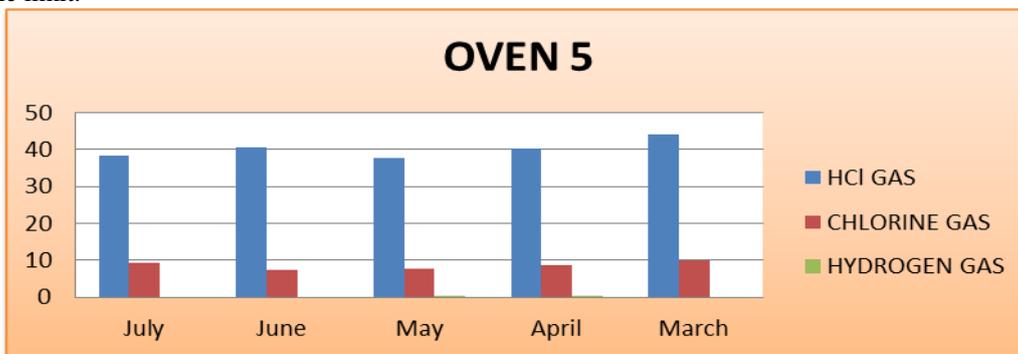


Fig 8: Stack analysis report of emission of oven 05

Based on stack analysis in oven 05, the maximum Hydrogen Chloride gas emission was on March 2012 and emission on July, June, May, April and March was more than the allowable limit. Emission of Chlorine was less than the allowable limit. The total contribution of each gas emitted from the HCl synthesis oven down below based on stack analysis report.

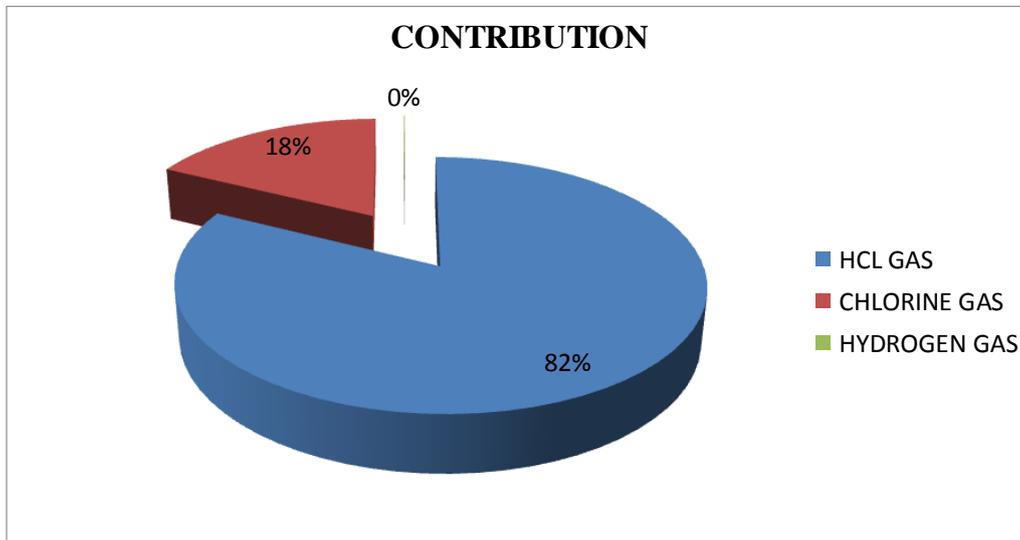


Fig 9: Total contribution of each gas in percentages

IV. SOLUTION AND DISCUSSION

After collecting and analysing the data, cause and effect diagram was drawn to identify the causes of excess usage of chlorine and hydrogen. The major cause of the problem was identified as incomplete absorption of HCl gas by the water. Methods by which to increase the absorption of HCl gas by the water.

A. Temperature of absorbing water

Increase in temperature will lower the solubility of gases (the gas will escape from solution, going back to the gas phase). Decrease in temperature of absorbing water, will increase the hydrochloric acid absorption due to negative enthalpy of solution. Hence providing an inter cooler in between secondary and primary absorption unit is desirable. [1, 2]

B. Effect of pressure

The solubility of gases increases when the pressure above the gas is increased. In other words, more gas will dissolve when pressure is increased. This is known as HENRY'S LAW (William Henry, English chemist). [1,2]

C. PH of absorbing water

Maximum absorption of hydrogen chloride gas is obtained, when the PH value of the water is 6-7.5. Hence use of de-mineralized water is essential for increasing the absorption of Hydrogen Chloride gas. [3]

D. Venturi scrubbers

Venturi scrubbers can absorb the remaining gas from the ovens. It is used in all most all chlor-alkali industries to increase tail gas absorption. [4]

E. Cracks in graphite blocks in the oven

Presence of cracks on graphite blocks in HCl oven cause the mixing of cooling water with acid and absorbing water which in turn reduces the absorption. In order to avoid this problem, lining with fiber reinforced plastic (FRP) on graphite blocks can be provided – which shall reduce crack propagation.

V. CONCLUSION

This study identified the causes of increased usage of chlorine and Hydrogen in HCl synthesis unit. The main reason for the problem is incomplete absorption of Hydrogen Chloride gas. It is found that Hydrogen Chloride gas absorption into water depends on various factors such as property of absorbing water, defects in the oven, lack of proper monitoring etc. Reduction in temperature will significantly increase the solubility of Hydrogen Chloride gas in water. Increase in pressure will definitely increase the absorption of Hydrogen Chloride gas. However the pressure should not go beyond the operation pressure. The solubility of Hydrogen Chloride gas is more within the PH range of 6-7.5. Hence use of de-mineralised water is essential for increasing the absorption of Hydrogen



ISSN: 2319-5967

ISO 9001:2008 Certified

International Journal of Engineering Science and Innovative Technology (IJESIT)

Volume 2, Issue 2, March 2013

Chloride gas. Providing venturi scrubbers, rectifying the cracks in graphite blocks in the oven by using FRP are also effective.

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