

METHODS OF PRODUCTION AND PROCESS SELECTION

1. KEL – CHLORINE PROCESS:

This process was developed by KELLOG, which uses HCl as a raw material from the waste gases of a fluorinated hydrocarbon plant. Concentrated sulphuric acid and 1% nitrosylsulphuric acid are used as catalysts.

Sulphuric acid catalyst is fed from the top of the stripper column. The HCl gas reacts with the catalyst to form nitrosyl – chloride. O₂, the ultimate oxidizing agent blows the remaining HCl out of the H₂SO₄, which becomes more concentrated and then get cooled in the flash vaporizer. This acid is then fed back into the process. Nitrosyl – chloride, HCl, O₂ and water vapour flows as gaseous streams into the oxidizer and reacts there, resulting increase in the temperature. In the absorber rest of the HCl is oxidized. Concentrated H₂SO₄ acid is fed at the top, reacts with the oxides and N₂ to form nitrosyl – sulphuric acid, absorbs the water that has formed and is fed back into the stripper.

The cooled dried chlorine gas still contains 2% HCl and up to 10% O₂. Both are removed by liquefaction.

On the account of the aggressive nature of the chemicals, expensive materials, such as tantalum plated equipment and pipes must be used.

2. OXIDATION OF HCl BY NITRIC ACID:

The nitrosyl – chloride route to chlorine is based on the strongly oxidizing properties of nitric acid.

The practical problem lies in the separation of the chlorine from HCl and other gaseous components. The dilute nitric acid must be concentrated for further use. Corrosion problems are severe.

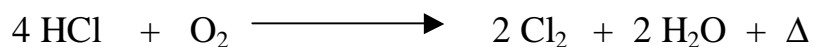
3. DEACON PROCESS:

Air oxidizes HCl in vapour phase, over a hot copper containing catalyst (CuCl_2). The principal difficulties of fugitive CuCl_2 , low Cl_2 composition in the exit stream, limited available materials of construction with high maintenance and poor catalyst activity makes this process unsuitable.

4. AIRCO – PROCESS:

The Air Reduction Company has made a number of developments in the basic Deacon process in recent years using both air and O_2 . The net result indicates that the process is practical today from an industrial by product containing HCl.

HCl is mixed with air or O_2 and preheated in a heat exchanger and sent to the fluidised bed reactor that operates at 300°C to 500°C .



The product gases from reactor is cooled to 110°C and fed to the product gas cooler where substantially all the water from reaction is

condensed. The top stream of the product gas cooler contains mainly Cl_2 , O_2 , N_2 , H_2O and HCl . This stream is sent to product gas absorber where the HCl gas is absorbed with 22% HCl solution and the rest of the gases leave the absorber from the top. This stream is then taken to liquefaction system from which the pure chlorine is obtained.

This process is chosen for the production since the problem of catalysis has been solved by the use of improved copper base catalyst bodies with at least one year of useful activity, utilizing rare earth as promoters and accelerators in a special reverse in flow reactor which makes the reaction self sustaining without the addition of external heat. New methods, materials of construction and engineering technique make this process economically feasible.

PROCESS DESCRIPTION

HCl is mixed with air, fed into a fluidised bed reactor containing cupric chloride catalyst, and maintained at a suitable temperature in the range of $300 - 500^\circ\text{C}$. HCl in the feed reacts with oxygen or oxidizes to give chlorine and water. The product gas containing chlorine, water, unchanged HCl and inert gases are passed to a packed tower cooler/ scrubber, operating somewhat above the atmospheric pressure. In the tower the gases come in contact with 33 – 36% HCl , thereby cooling the insoluble gases and absorbing the unchanged HCl . The acid enters the tower at 20°C . Most of the water and some amount of HCl contained in the product gas are dissolved in the acid. The liquid effluent coming out of the scrubber is split up into two streams. One stream is passed to the top of the scrubber through a cooler, which lowers the temperature to 20°C while the other is sent to the top of a stripper column (Expeller). In the stripper, the HCl present in the

incoming stream from the product gas cooler is stripped off and hence a gas containing around 98% HCl (the other constituents being water and chlorine) leaves the stripper from the top that is fed back into the reactor. A mixture of water and HCl containing 20 – 22% HCl leaves from the base of the expeller at a temperature of 147°C, which is fed to a HCl absorber through a cooler and the flow rate is maintained around 1000 kg/ hr. In the absorber, almost all of the HCl coming from the product gas cooler/ scrubber are absorbed. The liquid leaving the base of the HCl absorber contains 33 – 36% of HCl which is then mixed with fresh 36% HCl and then fed to the top of the expeller. The gaseous chlorine leaving the top of the HCl absorber column is then dried and sent to liquefaction unit to get pure liquid chlorine.

The workings of various equipments are described as follows:

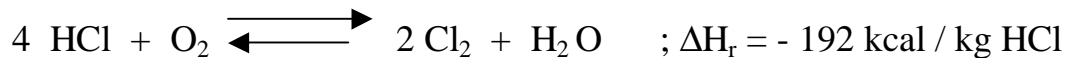
1. The catalytic reactor consists of a U – shaped steel container with “Foamsil” lined catalyst container. Both feed and discharge ports are at the bottom. Periodic reversal of flow, controls reaction temperature, preheats the feed. The copper catalyst acts as an efficient heat regenerator. Gases leaves the reactor slightly below 200°C
2. In the cooler, product gas is scrubbed by cold 33 – 36% HCl solution. Substantially all the water of reaction condenses to produce a concentrated solution of HCl, which is stripped of its HCl content in the expeller described below. The cooler is internally lined with non – corrosive material.
3. In the absorber, the cooled reactor gas stripped of its water content is absorbed in cold 20 – 22% HCl solution in a falling film unit of karbate and plastic construction. It leaves as 33 –

35% solution, which is then stripped in the expeller. The absorbing liquid (22% HCl) is the cooled “foots” of the expeller.

4. The expeller or stripper is a karbate packed tower which is fed with strong & cold HCl solution which is stripped to produce a product of 98% HCl gas and foots as close as 20% solution of HCl. The water build up is discharged from the system by stripping HCl as gas, in a separate system.
5. The dry gas from the absorption tower is then fed to the liquefaction unit where most of the sniff gases and O₂ is removed and chlorine emerges as the pure liquid.

THERMODYNAMIC CONSIDERATIONS

The oxidation of hydrogen chloride is a reversible reaction and hence the feasibility of the desired forward reaction is highly dependent upon various factors such as temperature, pressure, etc. Arnold and Kobe have studied the effect of varying these factors. They have calculated the thermodynamic functions of hydrogen chloride and chlorine from spectroscopic measurements. The reaction is:



The equilibrium constant K for this reaction has been calculated from the following equation.

$$-\Delta G^\circ / T = 2.303 R \log K$$

where ΔG° = change in free energy of the reaction

$$= - 274460 + 8.65 T - 0.00229 T^2 + 0.263 \times 10^{-6} T^3$$

T = temperature
R = gas constant

Effect of other variables:

Pressure:

Increase in the pressure gives an increase in the HCl conversion and hence increase in the chlorine content. However, the pressure chosen for operation is only 1 atm. This is done after considering the economics point of view of the plant. High-pressure operation involves the compression of gases, which requires considerable amount of money. Secondly, the reactor will have to be designed to withstand the pressure too. At high pressure, the equipment is highly prone to failure due to stress corrosion cracking.

Dilution of oxygen with inert gases:

If pure oxygen is used instead of air, higher content of chlorine is obtained in the product gas. At 350°C, the HCl conversion increases by 2%. And the chlorine recovery also becomes simpler. But due to the high cost of O₂ as compared to the air, one usually goes for air.

Hydrogen chloride / Air Ratio:

Increasing the excess oxygen content from 0 to 300% increases the conversion by 10% at 700°K, but the chlorine content decreases by 12%. Thus the cost of recovery increases.