STUDY AND ANALYSIS OF THE PRODUCTION OF LIQUID CHLORINE BY MEMBARANE CELL PROCESS

WORK DONE AT

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MAHATMA GANDHI UNIVERSITY, KOTTAYAM

In partial fulfilment of the requirement
for the award of the degree of Bachelor
of Science in Chemistry

Submitted by

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DEPARTMENT OF CHEMISTRY

PAVANATMA COLLEGE

MURICKASSERY

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CERTIFICATE

This is to certify that the project work entitled **"STUDY AND ANALYSIS OF THE PRODUCTION OF LIQUID CHLORINE BY MEMBRANE CELL PROCESS"** is an authentic work carried out by **Ms. DELLA TOMY (Reg No: 200021026715)**in partial fulfilment of the requirements for the award of the degree of Bachelor of Science in Chemistry in Mahatma Gandhi University, under my supervision and guidance during the academic year 2020 – 2023.

Prof. SAJI K JOSE
Head of the Department
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Place: Murickassery

Date:

DECLARATION

I**, DELLA TOMY** hereby declare that the dissertation entitled **" STUDY AND ANALYSIS OF THE PRODUCTION OF LIQUID CHLORINE BY MEMBRANE CELL PROCESS"** submitted to **MAHATMA GANDHI UNIVERSITY, KOTTAYAM** in partial fulfilment of requirement for the award of degree of Bachelor of Science in Chemistry is a record of original project done by me under the guidance of **Mr.AMAL SUDHAKARAN** and **Ms.SINJU K.S**, Quality controller officers **Travancore Cochin Chemicals Ltd.(TCC),**during the period Of June 27th to July 1st 2022.

Place: Udyogamandal

Signature of Candidates

DLLA TOMY

Date:

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CONTENTS

CHAPTER 1

INTRODUCTION

Chlorine is the 11th most abundant element in the lithosphere. It is highly reactive and hence rarely found in free state.it exist in mainly in the form chlorides .in sea water it is present as 2.9 wt. % NaCl and 0.3 wt.% $Mgcl_2$. In salt deposits formed by evaporation of seawater, Cholrine is present in large quantities as rock salt (NaCl) and sylrite (KCl), together with bischofite($MgCl_2.6H_2O$),carnite($KClMgCl_2.6H_2O$), Tachhydrite ($CaCl_2.2MgCl_2.12H_2O$) and others. Occasiony it is found as heavy metal chlorides, usuy in the form of double salts as atacamite($CuCl_2$,$3Cu(OH)_2$). Plants and animals always contain chlorine in the form of chloride or free HCl.

Cl_2 is formed by oxidation of HCl or chloride such as Manganese dioxide, Permangantes, Dichromate, Chlorates or Bleaching powder .Oxygen from the atmosphere act as an oxidizing agent in the presence of catalysits .There is mainly two methods for the preparation of chlorine ,Deacon Process and Weldon Process.

Weldone Process:

$MnO_2 + 4HCl \longrightarrow MnCl_2+Cl_2+2H_2O$

Here the yield is very low about 35%

Deacon Process:

$4HCl+O_2 \longrightarrow 2Cl_2+2H_2O$

Here the yield is about 65%

In 1800 A.D CRUICKSHANK first prepared chlorine electrochemicy in this process a diaphragm cell or a mercury cell is used. Currently 95% pf world's production of Cl2 done by using the chloro-alkali process. Today world's capacity of chlorine is more than 80*106 tones/annum.

Now in TCC the major method used for the production of chlorine is Membrane Cell Process.

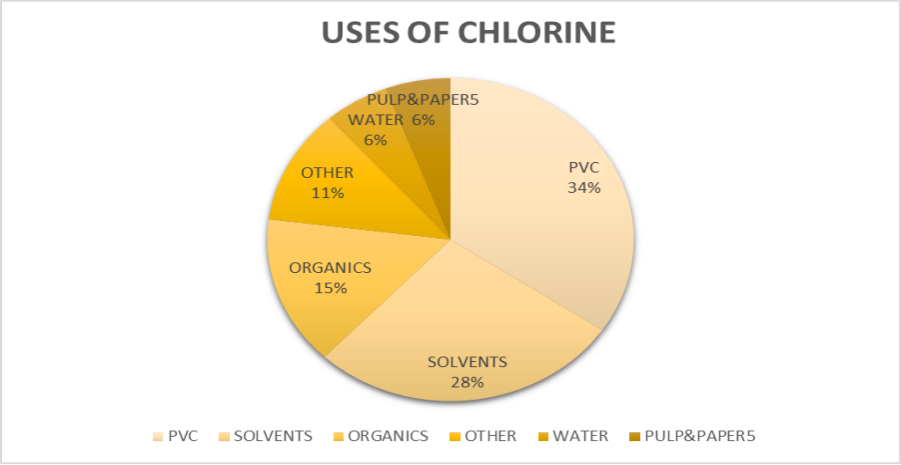
THE PRODUCTION OF LIQUID CHLORINE IN TCC

Chlorine is a co product obtained in the process of manufacture of caustic soda .Soda is a chemical used for the manufacturing of plastics, various organic and inorganic chemicals, Petrochemicals ,textile, paper Industries and pharmaceuticals. It is the traditional water purification agent, chlorine and chlorine compounds on pharamaceutical industries has served billions of life since the discovery. About 51532 metric tone chlorine is produced in TCC per annum. Liquid Chlorine is manufactured in the liquefactions plant of TCC.

USES OF CHLORINE

During the span of chlorine industry in the world , the largest single use been in the manufacture of pulp and paper .In the early period of the industry , the 2nd largest use was in sanitation for sewage treatment and purification of water .Later on the demand increased because of the invention of new compounds. Some of the major use of chlorine are listed below.

1. Producing insectisides like DDT, BHC etc and pesticides like aldine
2. In purifying drinking water and sterilisers sewage effluents
3. For manufacturing PVC and ied copolymers
4. For producing chloramines and its organic derivatives
5. For upgrading titanium content in limelite



PHYSICAL PROPERTIES OF CHLORINE

PROPERTIES	
Atomic Number(Z)	17
Atomic Mass(A)	35.453g
Stable Isotope Mass	35,37g
Melting Point(M.P)	-110^0C
Boiling Point(B.P)	-34^0C
Critical Temperature(T_c)	144^0C
Critical Pressure (P_c)	$7.71x10^5$N/m^2
Critical Density	565 Kg/m^3
Density at 0^0C	3.213Kg/m^3
Density relative to air	2.48Kg/m^3
Enthalpy of fusion ΔH_f	90.33 KJ/kg
Enthalpy of vaporisation ΔH_v	90.33 KJ/Kg
Standard Electrode Potential E^0	287.1 KJ/Kg
Enthalpy of dissociation ΔII_d	1.359 V

CHEMICAL PROPERTIES

1. REACTION WITH WATER

Chlorine is moderately soluble in water(0.3% -0.7%)depending on the temperature of water.

$$Cl_2+H_2O \longrightarrow HClO+HCl$$

2. REACTION WITH METALS

Metals react with chlorine to form ionic chlorides , with most of these compounds being soluble in water .Some of the metal chlorides are insoluble in water . AgCl and $PbCl_2$ are examples of insoluble metal chlorides. Gaseous or liquid chlorine usuy does'nt have an effect on metals such as Fe ,Cu ,Pt and Ag at temperatures below 230^0 F.

$$2Na(s)+Cl_2(g) \longrightarrow 2NaCl(S)$$

$$Ca(s) +Cl_2(g) \longrightarrow CaCl_2$$

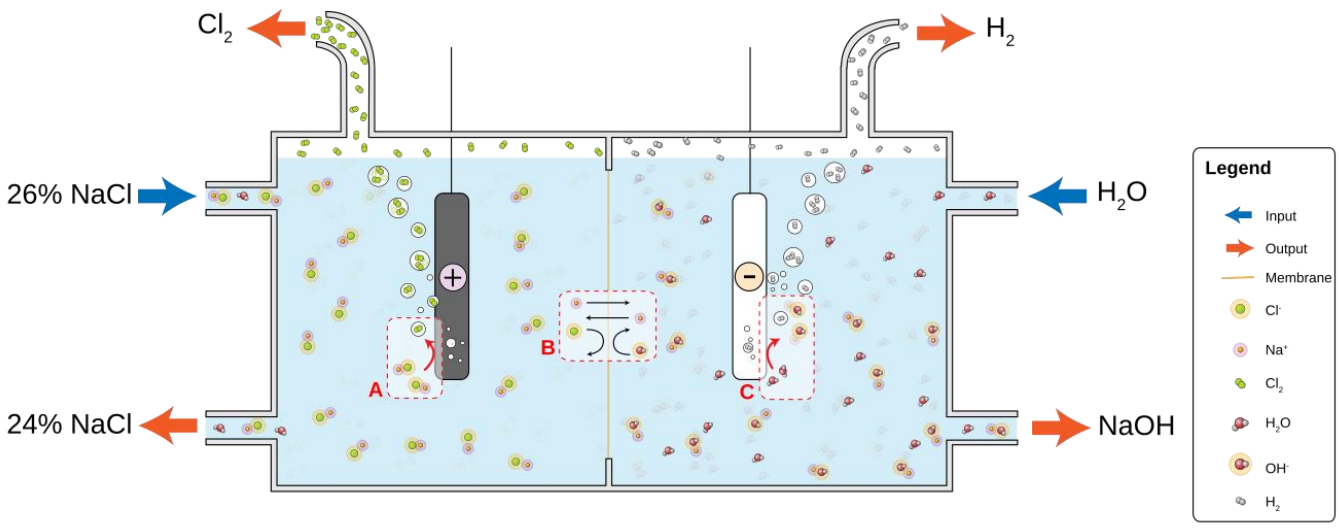
$$Mg (s)+Cl_2 (g) \longrightarrow MgCl2$$

3. REACTION WITH ORGANIC COMPOUNDS

Chlorine reacts with many organic compounds to form chlorinated derivatives. Some reactions can be extremely violent, especiy those with hydrocarbons, alcohols and ethers. Proper methods must be followed, whether in laboratory or plant, when organic materials are reacted with chlorine.

MEMBRANE CELL PROCESS

Membrane cell process makes use of brine and a membrane cell with positive and negatively charged electrodes. The anode oxidises the chloride ion which loses an electron become free chlorine gas . the hydrogen ions are pulled at the cathode and form hydrogen gas.the semi-permiable membrane of the cell ows for the sodium ions to travel to second chamber,where they react with water to produce NaOH



MEMBARANE CELL PROCESS

ADVANTAGES OF MEMBRANE CELL PROCESS

- Reduced power consumption
- High purity of product
- Flexibility of operation
- Elimination of environmental problems
- Lesser space requirements
- Reduction of operating costs

PROCESS PRINCIPLE

ELECTROLYSIS OF BRINE

Electrolytic cell consist of an ion exchange membrane with titanium anode and copper cathode. Brine is admitted to the anode compartment and DM water to the cathode compartment. As the DC current passes through the electrode the Na+ ions passes through the membrane to the cathode compartment where it reacts with OH- ions producing NaOH and H_2.

ANODE REACTION

$NaCl \longrightarrow Na^+ + Cl^-$

$2Cl \longrightarrow Cl_2 + 2e^-$

CATHODE REACTION

$H_2O \longrightarrow H^+ + OH^-$

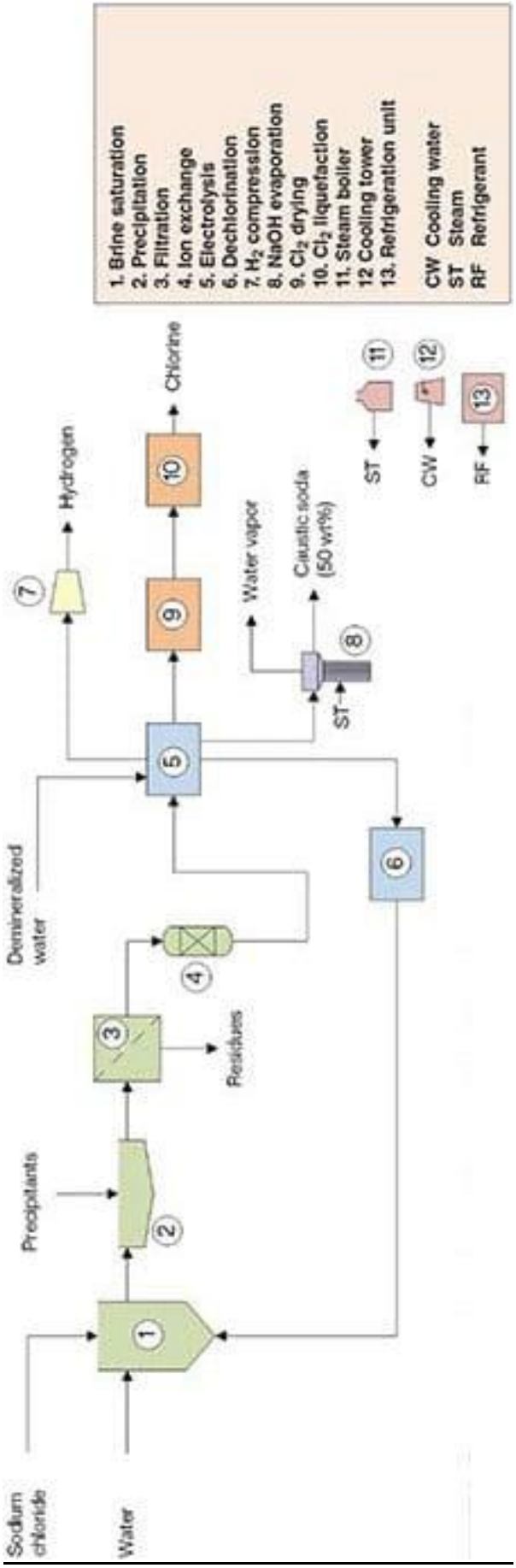
$Na^+ + OH^- \longrightarrow NaOH$

$2H^+ + 2e^- \longrightarrow H_2$

OVER REACTION

$2NaCl + 2H_2O \longrightarrow 2NaOH + H_2 + Cl_2$

LIQUID CHLORINE MANUFACTURING



PROCESS DESCRIPTION:

The process of manufacture of liquid chlorine and employing ion exchange membrane cell technology involving the following steps

- Primary brine purification
- Secondary Brine purification
- Electrolysis
- Brine dechlorination
- Cl_2 treatment
- Cl2 liquefaction

DESCRIPTION

- PRIMARY BRINE PURIFICATION

Saturation- there are two saturators, one is operation and another one is standby. The raw salt from the salt storage area is fed to the saturator of capacity 45m^3 from the top using a bucket elevator, pay loader and feed hopper. About 5 to 6m^3/hr. Process Water is added to saturator. Depleted brine is fed to the bottom of the saturator through a dip pipe for the preparation of saturated brine. A strainer is provided at the top for the removal of macro size suspended impurities. This brine solution is obtained from the saturator is having a concentration 310g/L. This brine solution is taken out as over flow the saturator, and goes to the precipitation tank.

Precipitation- $BaCO_3$ and Na_2CO_3 are also fed to the precipitation tank A & B respectively from separate chemical tank A, in precipitation tank A, the sulphate in the brine solution is precipitated as $BaSO_4$ and in the precipitation tank B, the Ca content in the brine is precipitated as $CaCO_3$. The outlet from the

precipitation tank B is fed to the mixer tank where caustic soda lye is added in order to precipitate magnesium as $Mg(OH)_2$. Air agitation is provided in a chemical tanks and precipitation tanks for better mixing. Samples from the precipitation ranks are taken from the sampling point for checking its calcium and sulphate value if the values are taken from the particular limit the feed rate from the chemical tank is increased vice-versa. Brine from the mixer tank is taken to a strainer where it is mixed with flocculent and fed to the clarifier of 2000 m^3 capacity. The flocculent (sodium poly acrylate) is pumped from flocculent tank. Flocculent helps adhere the smaller precipitates and enhances the settling of precipitates. Here the settling is due to gravity 90% of the precipitate is settled as a sludge and is removed from the clarifier bottom. The sludge from the clarifier is pumped for land filling

- SECONDRY BRINE PURIFICATION
  ION EXCHANGE PROCESS

The steam of saturated brine from anthracite filters going for secondary brine purification plant is divided into FSTL and US filters. There are two US (A&B) filters and two FSTI (A&B) filters. Generally the resin is micro porous styrene divinyl benzene in Na^+ ionic form. These two filter can be in operation at the same time one acts as primary filter and other as polishing filter, i.e. if A is primary B will be polishing and vice versa. If there is some problem, one filter is isolated while other remains in operation. Analysis is done for checking Ca and Mg concentration in the filtrate using Hack Spectrophotometer. The secondary brine purification plant is designed by US Filter Corporation with a maximum capacity of treating $55m^3$/hr primary purified alkaline brine using ion exchange process. The purity of feed brine in the ion exchange membrane electrolytic process is very important as it largely affects the performance and life of the ion exchange membrane. Primary brine purification with anthracite filters will not meet the specified brine quality for admitting to the electrolyser. The Ca and Mg impurities in the primary purified brine reacts with the resin is generated by treating with HCl and NaOH.

- ELECTROLYSIS

The salt is dissolved in the water and the concentration is made to 310gm/L. Below 260gm/L , water electrolysis takes place with NaCl dissociation in the anode compartment of the electrolyser. This results in the combination of hydrogen and chlorine, which can form an explosive mixture Concentration above 310gm/L can lead to crystallization at the operating temperature, resulting in the accumulation of Naci in the pipelines and the vessels which resulting in choking.

- BRINE DECHLORINATION

The step brine dechlorination is meant for removing the free chlorine and chlorate ion formed in depleted brine system will make brine purification impossible. Accumulation of a huge amount of chlorate ions in the brine system is harmful for both membrane and anode. The system includes the depleted brine receiver, vacuum dechlorinated brine receiver.

- SODIUM BISULPHATE PREPARATION

Sodium bisulphate tank has two parts, the upper part is for dissolving bisulphate and lower part is for storage of dissolves sodium bisulphides. DM water is taken in the upper part, calculated amount of bisulphite power is charged and agitator is started for proper mixing. When desired concentration is achieved, open the inner connection valve, admit the solution to the lower part and then pump to the dechlorination and primary purification.

- CHLORINE TREATMENT AND LIQUEFACTION

Chlorine treatment and liquefaction involves cooling, washing, filtration, drying, compression, liquefaction, storage and chlorine unloading.

- COOLING AND WASHING

Chlorine leaving the cells will be at a temperature of 80°C and pressure of 10 mm WC. This is cooled to 30°C in the first stage at chlorine cooling tower. At the inlet of the wet chlorine filter, water spraying is provided for chlorine washing. The main chlorine line branches are dipped in chlorine vacuum seal tank. The seal tank are provided for controlling the wide pressure fluctuation in the chlorine line during the abnormal condition. Water is admitted to seal tanks for level make up and is collected in chlorine water tank and recycled to the system using condensate pump. Excess chlorine water is admitted to depleted brine tank.

- FILTRATION

Final traces of sodium chloride mist from Cl_2 are removed by admitted to wet chlorine filter. The filtration efficiency is improved by injecting water at the rate of 300l L/hr into the chlorine gas before it enter the filter. Filtered chlorine is further cooled to -15°C by passing through a second stage cooler in which chilled water is used for cooling.

- DRYING

The drying unit is of packed bed type. The packing material is rashing rings and this helps in providing longer contact time, larger surface area of contact resulting in efficient moisture removal. 98% H_2SO_4 enters the tower from the top then moist chlorine vapours are fed at the bottom, resulting in a counter current contact between the two. H_2SO_4 will not react with Cl_2 and hence the reaction is between H_2SO_4 and moisture while flowing downwards and becomes more and more dilute.

The acid is again pumped to the top of the tower after passing through a heat exchanger for cooling. H_2SO_4 given at the top. Dry Cl_2 leaving out from the top of the tower is fed to an acid separator for removal of the traces of acid present, if any acid trickles down through the trays, acid is fed to the top tray. The concentrated acid is gets diluted as it goes down through the packing. The tower made of PVC and is surrounded by FRP for providing mechanical strength mainly during high temperature softening of PVC.

- COMPRESSION

Chlorine gas enters a suction near the rotary compressor. The compressor first filled with 98% H_2SO_4 up to a certain level leaving some space for Cl_2 inlet. The Cl_2 from the suction drum enters a rotary compressor from one end. This compressor has a special kind of fixed cone arrangement for the smooth suction and delivery of Cl_2 gas. The cone is fixed at particular position, suction and delivery occurs according to the movement of the impeller. The advantages of taking H_2SO_4 as a compression fluid include its ability to absorb traces of moisture from chlorine vapour without reacting with it. The compressor and the circular impeller are placed inside the elliptical casing. The compression of Cl_2 vapours takes place in the elliptical position. When the impeller rotates, H_2SO_4 compresses Cl_2 to a certain pressure and is delivered from the other end. The compressed Cl_2 outlet contain some amount of H_2SO_4 and hence it is fed to a centrifugal acid separator where acid is recovered at the bottom.

- LIQUEFACTION

The compressed Cl_2 is pumped to the acid mist eliminator for the removal of acid mist carried over. Mist eliminator consists of a cartridge of terry wool. When compressed Cl_2 enters the mist eliminator, terry wool allows the passage of the Cl_2 vapour but absorb fine droplets of H_2SO_4. H_2SO_4 is collected at the bottom of the Cl_2 vapour are removed from the top. This acid is collected in a separate drum. The liquefier is covered with thermocol, cement, etc. so as to maintain the low temperature.

This Cl_2 enters the liquefier, which is a plate and frame heat exchanger the liquid Freon is also enter the heat exchanger from the receiver through an expansion valve. Freon gas is sucked by Freon compressor from the upper part of the heat exchanger the sudden expansion creates the cooling effect and this property is used for liquefaction process. The Cl_2 is liquefied by using the heat of vaporization of Freon.

- STORAGE

The liquid Cl_2 is stored in four process vessel each having 50MT capacities Cl_2 is filled to certain level for providing space for liquid Cl_2 due to expansion at high temperature.

- UNLOADING

Unloading of liquid chlorine from the storage tank is done by dry compressed air.

- FILLING

The liquid Cl_2 in the process vessel in the Cl_2 liquefaction plant is transferred and stored in five horizontal storage tanks, each having 50MT capacities, at the cylinder filling station. During Cl2 transfer the liquid chlorine storage is maintained about 3 kg/cm^2 pressure and an air pressure of 9-10 kg is applied at the top of the liquid chlorine in process vessel tank. Here air used must be dry to avoid the formation of nascent oxygen.

During the filling process an air pressure around 9 kg/cm^2 is applied at the top of the storage tank and hence Cl_2 comes out to a common header to different filling point. The Cl_2 line is provided with lagging in order to avoid the evaporation and reaction due to high temperature. The Cl_2 is filled in large cylinder called tonners having 900 kg capacity. The gross weight of the cylinder is about 1500kg.

The tonners contain two high capacity valves at one end. The cylinder should be placed such that the purge valve is at the top and the liquid chlorine is allowed to enter through the bottom valve. After while pressure inside the cylinder is increased and it opposes further entry of liquid Cl_2. Then the gaseous Cl_2 is purged in order to decrease the pressure inside the cylinders, thus enhancing further filling of liquid Cl_2. These purged Cl_2 vapour are fed to the absorption tower in the soda bleach plant. These cylinder ends are curved inwards to withstand extra pressure developed.

Small cylinder having 100kg. 80kg, and 50kg liquid Cl_2 capacities are also used for the supply of liquid Cl_2. The various uses of Cl_2 include bleaching, water treatment, and etc. One unit volume of chlorine vapours occupies 460 times the volume of liquid chlorine.

CHAPTER 2

AIM AND OBJECTIVE

In TCC, liquid chlorine is a bi-product got in production of caustic soda by membrane cell process. Aim of the project is to understand how the production of liquid chlorine is carried out and also to study how to control the quality of liquid chlorine, its raw material. As we said above chlorine is a bi-product membrane cell process, it is important to maintain the quality of the feeding brine solution. The impurities in brine is reduced by complete precipitation of impurities through the ion exchange resin. The excess dosage of chemicals helps in it. A major quality control tests involved in ISO 9000 specification have been studied and result have been discussed.

CHAPTER 3
EXPERIMENTAL METHODS

LIQUID CHLORINE SAMPLE COLLECTION

Sample is drawn from the cylinder filling line using regulating valves and analysis of the liquid chlorine samples are made and the values are noted

- **PURITY OF CHLORINE**

100 ml chlorine gas is taken in the gas samplping burette of orsat gas analysis apparatus keeping liquid in the bottle and the liquid in the burette at the same level close the three way stopper and absorb the chlorine gas in 20% caustic filled in the absorption pipette.

$$\% \text{ by volume of } Cl_2 \text{gas} = \frac{\text{Volume of the gas absorbed} \times 100}{\text{Total volume of gas taken in burette}}$$

- **MOISTURE CONTENT IN LIQUID CHLORINE**

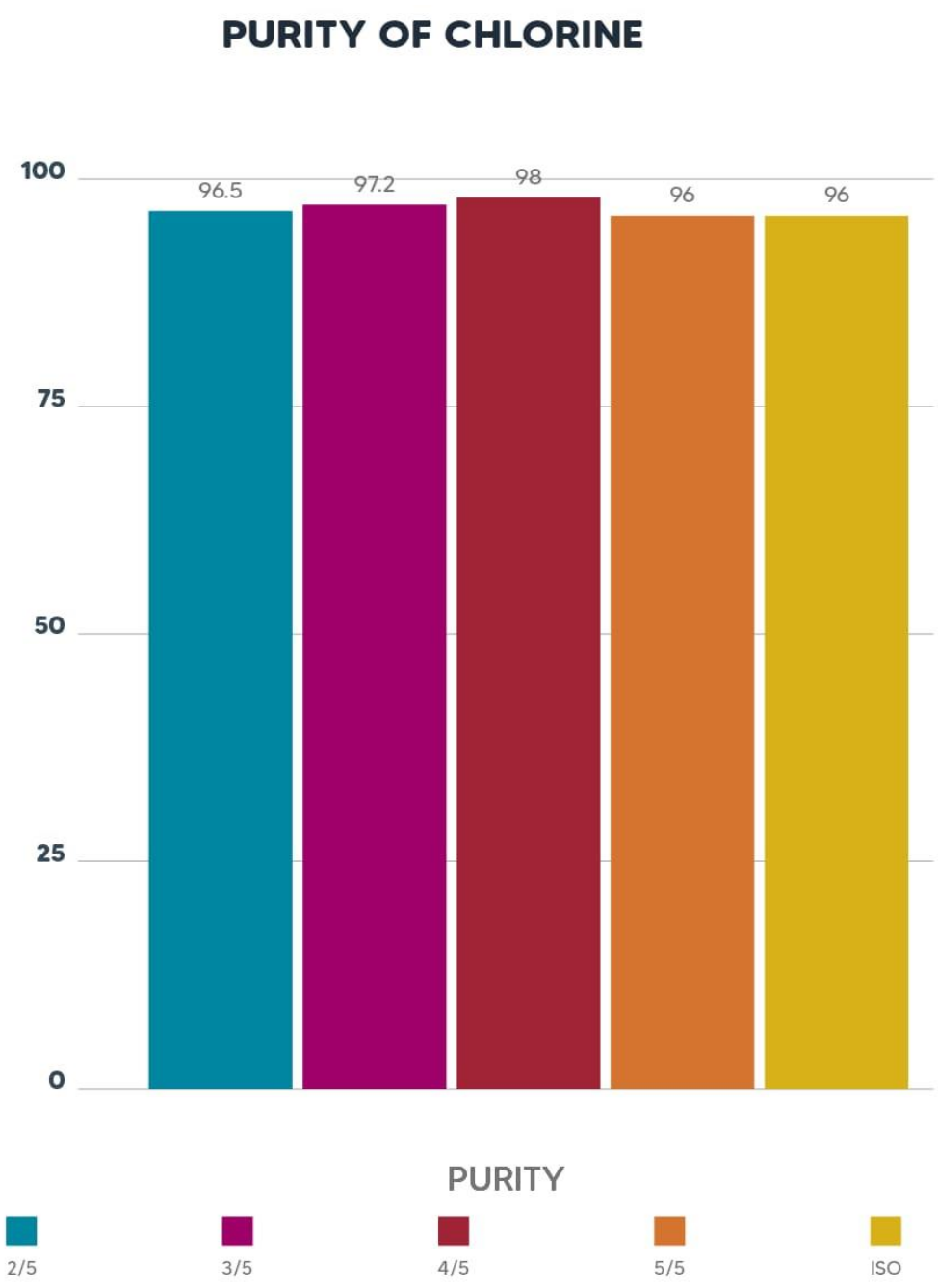
A 'U' tube filled with P_2O_5 is used as moisture absorber one end of the absorber is connected to the chlorine sampling point and the other to a SL gas absorbing bottle containing about 5L of 20% NaOH solution. Condition the absorber in the 'U' tube by passing chlorine for 30 minute. Disconnect the absorber tubes and weigh them accurately. Replace the caustic solution in the bottle with its contents and connect it to the absorber tube. Pass Chlorine slowly thorough the absorber for 4-5 hours at the rate of 252/hour. No chlorine is owed to escape through the caustic solution. This can be ensured by connecting the discharge of the caustic solution bottle to a gas bubbler containing starch KI solution. No change in colour indicates the absence of Cl_2.After 4-5 hours disconnect the 'U' tube and weigh accurately. The increase in weight gives the weight of moisture. Weigh the caustic solution bottle. Increase in the corresponding to the weight of Cl_2. Which has passed through absorber tube.

$$\text{Moisture content in Chlorine} = \frac{\text{weight of moisture in gram} \times 10^6}{\text{weight of the } Cl_2 \text{ passed in grams}}$$

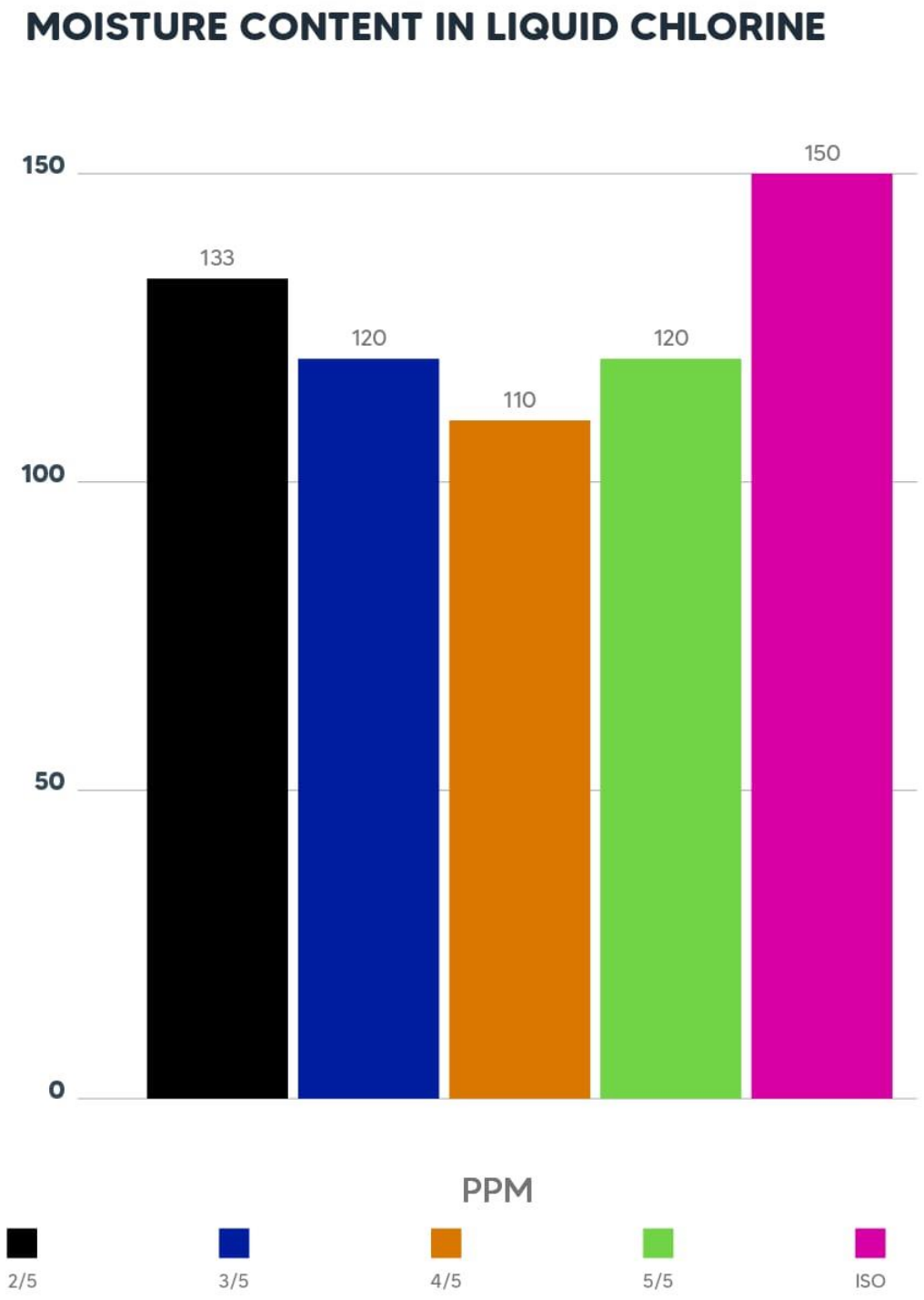
CHAPTER 4

RESULT AND DISCUSSION

SAMPLE NO	DATE OF SAMPLE COLLECTION	PURITY OF CHLORINE	MOISTUURE COTENT IN CHLORINE
1	02/05/2022	96.5%	133ppm
2	03/05/2022	97.2%	120ppm
3	04/05/2022	98%	110ppm
4	05/05/2022	96%	120ppm



As per ISO 9000 standards the chlorine with purity greater than 96% is considered as pure. From the above data is clear that all samples are pure with purity greater than 96%. From this we come to know that liquid chlorine made here is very pure and sample no:3 is very pure with 98 % purity.



As per ISO 9000 standards liquid chlorine with moisture content less than 150 ppm is considered to be selling. From the above data it is clear all samples taken are under ISO limits and sample no:3 is with the less moisture content.

CHAPTER 5

CONCLUSION

Chlorine, the most widely used disinfectant worldwide and the technological advances develop alternatives system that owed efficient use of chlorine in water disinfection. In our country, although liquid chlorination is used as disinfection for water treatment plants, on-site chlorine generators have begun to be recently used. In this study, information about mechanical equipment, working principle and storage conditions of the liquid chlorination are discussed.

With a global demand, Liquid chlorine is one of the important products widely used in many commercial application. The project was done on the "Manufacture of Liquid Chlorine by Membrane Cell Process" at Travancore Cochin Chemicals Ltd. in Udyogamandal, Kerala. The capacity of the plant is 65 tons per day. The project has covered the aspects in detail like material balance and energy balance. An elaborate design procedure has been worked out for shell and tube heat exchanger and the parameters were found out, also design the centrifugal pump employed in the process. Several aspects of safety and environmental concern were discussed.

CHAPTER 6

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