A STUDY OF COMPLETE ANALYSIS OF CAUSTIC SODA FLAKES

Work done at

TRAVANCORE COCHIN CHEMICALS (TCC) LIMITED

Project work submitted to
MAHATMA GANDHI UNIVERSITY, KOTTAYAM
In partial fulfillment 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
2020-2023

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CERTIFICATE

This is to certify that the project work entitiled **“ A STUDY OF COMPLETE ANALYSIS OF CAUSTIC SODA FLAKES”** is an authentic work carried out by Mrs. AKSHAYA SHAJI (Reg.No:200021026724) in partial fulfillment of the requirements for the award of the degree of Bachelor of Science of Chemistry in Mahatma Gandhi University, under my supervision and guidance during the academic year 2020 – 2023.

Prof. SAJI K JOSE
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Place : Murickassery
Date :

DECLARATION

I, AKSHAYA SHAJI hereby declare that the dissertation entitled **" THE COMPLETE ANALYSIS OF CAUSTIC SODA FLAKES "** submitted to the **MAHATMA GANDHI UNIVERSITY,KOTTAYAM** in the partial fulfillment of the requirement for the award of the degree of Bachelor of Science in Chemistry is a record of orginal 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

Date : AKSHAYA SHAJI

ACKNOWLEDGEMENT

The satisfaction and euphoria that accompanied the successful completion of any task would be incomplete without mentioning those hands whose proper guidance served as a beam of light and crowned by efforts with success.

My sincere thanks to TRAVANCORE COCHIN CHEMICALS LIMITED at UDYOGAMANDAL for providing opportunity and guidance to do the project in their esteemed concern.

I express our heartfelt thanks and deep sense of gratitude to Mr. STEPHAN THOMAS (HR Manager and Officer of Training and Development), Mr. AMAL SEKHAR , Mrs. SINGU K.S , Trainers and all the other members of quality control department of TCC, Kochi for their invaluable guidance, useful discussion and encouragement to bring out this dissertation in a excellent manner. Finally i would like to thank all the staff of TCC who gave their support in this effort.

My sincere thanks to SAJI K JOSE (Head of department of chemistry), Pavanatma College, Murickassery other teachers for giving me a good guidance and encouragement. Further I express my extreme gratitude to our classmates for their timely discussion and information sharing which helped to complete this project work successfully. Also I express my gratitude to my parents.

Above all I thank the God Almighty for giving the unlimited support and encouragement for the successful completion of this project work.

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CHAPTER I

INTRODUCTION

CAUSTIC SODA (NaOH)

The main product of TCC is caustic soda which is produced by membrane electrolysis process. The reaction taking place can be represented as follows:

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

In the production of caustic soda large amount of Hydrogen and Chlorine are produced. The Hydrogen produced is used for manufacturing HCl by burning Chlorine in presence of Hydrogen and adding water and some Chlorine is liquefied. Various products are:

- Caustic soda lye
- Caustic soda flakes
- Chlorine
- Commercial HCl
- Sodium hypochlorite

Caustic soda is a basic alkali came into being in the latter half of the 19th century with the development of electrolysis.

TCC produces two types of caustic soda:

- Caustic soda lye
  It is a clear colourless, odourless and soapy liquid.

- Caustic soda flakes
  It is a white deliquescent solid in flakes form.

APPLICATION

- Chemical manufacturing

It is used mainly for pH control, neutralization, off gas scrubbing and catalysis. It is used in manufacture of organic intermediates, polymers and products such as propylene oxide, polycarbonate active reagents. Large amount of caustic soda is used in aluminium production.

- Pulp and paper

Caustic soda is used to pulp wood chips, to extract lignin during bleaching and to neutralize acid waste streams.

- Cleaning products

Caustic soda is used to produce household bleaches, polishers, soaps, detergents and other cleaning goods.

- Petroleum and natural gas

Caustic soda is used in the petroleum natural gas industry to process oil and gas into marketable products, especially by removing acidic contaminants. It is used to decrease corrosion of drilling equipments and to increase the solubility of drilling components by maintaining alkaline pH.

- Miscellaneous consumption

Caustic soda in water treatment, food processing and cotton mercury and flue gas scrubbing, mining, glass making, textile, dyes and adhesive preparation.

PHYSICAL PROPERTIES

- Caustic soda is brittle, white crystalline solid which readily absorbs moisture and CO_2 from atmosphere.
- It makes a yellow stain on paper and fabric.
- It is a white solid available in pellets, flakes and granules. It is also available as 32% and 50% caustic soda solution.
- It has a marked corrosive action of all human body tissue and hence the name caustic soda. Caustic means burning.
- Soluble in ethanol and methanol. It is insoluble in ether and other non polar solvents. It is deliquescent.
- Caustic soda is soluble in water and the reaction is exothermic.

CHEMICAL PROPERTIES

- With acids

  Caustic soda is primarily used in neutralization reactions to form sodium salts, because aqueous solutions of caustic soda is highly alkaline.

$$NaOH + HCl \rightarrow NaCl + H_2O$$

- With elements

A. It reacts with metals (Al, Zn and Sn) and other oxides to form complex anions such as AlO_2, SnO_2,etc..

$$2NaOH + Zn \rightarrow 2Na + Zn(OH)_2$$

B. Caustic soda reacts with weak acid gases like H_2S, SO_2, etc…

$$H_2S + 2NaOH \rightarrow Na_2S + 2H_2O$$
$$H_2S + 2NaOH \rightarrow Na_2SO_3 + 2H_2O$$

C. Organic acids reacts with caustic soda to form soluble salt.

- Preparation of hydroxides

From metallic solution, it precipitates the hydroxides of the metal

$$Fe(SO_4)_3 + 6NaOH \rightarrow 2Fe(OH)_3 + 3Na_2SO_4$$

- With ammonium salts

When treated with sodium hydroxide, ammonium salt decomposes and liberates ammonia.

$$NH_4Cl + NaOH \rightarrow NaCl + NH_3 + H_2O$$

CAUSTIC SODA FLAKES

It is a white deliquescent solid in flakes form. Caustic soda flakes have concentration of 98% to 99% NaOH. It is basic alkali used in manufacture of various articles of daily use like soap, paper, textiles, drugs, rubber and petroleum industries.

Caustic soda is used to produce a wide variety of cleaning products like household bleaches, polishes and cleaning goods. It is used in the petroleum and natural gas industry to process oil and gas into marketable products by removing acidic contaminates. It is used to decrease corrosion of drilling equipments and to increase the drilling mud components by maintaining an alkaline pH.

RAW MATERIALS USED FOR THE CAUSTIC SODA PRODUCTION

The main raw material used for the caustic soda production is common salt NaCl. About 3700 units of electricity is consumed for about 1.6 metric tons of salt per ton of caustic soda production.

VARIOUS STEPS IN THE PROCESS OF MAKING CAUSTIC SODA

The caustic soda production mainly involves two stages

1. The removal of impurities present in raw salt
2. Electrolysis

The raw salt used for electrolysis should be analyzed to estimate the amount of impurities in it. From this, the amount of chemicals needed for the removal of impurities can also be calculated.

ESTIMATION OF IMPURITIES

The raw salt contains Ca^{2+},Mg^{2+},SO_4^{2-} are the main impurities. The Ca^{2+}, Mg^{2+} are estimated as $BaSO_4$ by complexometric titration with EDTA solution. The insoluble residues and moisture in raw salt can be estimated as $BaSO_4$ by gravimetric estimation method and also for determining the composition of the salt.

1. Removal of impurities

- Calcium

Calcium is present as calcium sulphate in raw salt. It is removed as carbonate by treating the brine with soda as Na_2CO_3 in the dissolved form.

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$$

- Sulfate

Sodium sulfate in the brine is ordinary due to the treatment of $CaSO_4$ with Na_2CO_3. The common reactants to remove sulfates as $BaCl_2$ and $BaCO_3$.

$$Na_2CO_3 + BaCl_2 \rightarrow BaSO_4 + 2NaCl$$

$$Na_2SO_4 + BaCO_3 \rightarrow BaSO_4 + 2Na_2CO_3$$

Barium carbonate is preffered than $BaCl_2$ because of the low cost reagent. The settled precipitate can be discarded. If sulfate is present in 6gpL will affect the membrane of electrolysis.

- Magnesium

Mg^{2+} present as $MgCl_2$ and $MgSO_4$ in the brine solution is precipitated by treating with caustic soda and hydrated lime. Caustic soda is preffered in TCC to avoid excess impurities problem with hydrated lime. Moreover the NaOH is used which produces sodium chloride as a byproduct can be reused in the plant.

$$MgSO_4 + 2NaOH \rightarrow Mg(OH)_2 + Na_2SO_4$$

$$MgCl_2 + 2NaOH \rightarrow Mg(OH)_2 + 2NaCl$$

During the above treatment the Na_2SO_4 produced is removed by treating with Na_2CO_3 before adding NaOH. This is because the $Mg(OH)_2$ precipitated is in the form of a large delicate gelatinous flow which tends to settle rapidly. In doing so, it traps the suspended slow setting and finally divided crystalline turbidity is also decreased.

2. Electrolysis

There are three types of cell such as diaphragm cell, mercury cell and membrane cell used for electrolysis. Now a days the mercury cells are not used because of the pollution problems. Compared to diaphragm cell membrane cells are more efficient. Hence they are used in TCC for electrolysis.

Continuous caustic fusion

It is done in CCF plant. CCF plant is mainly for concentrating 32% sodium hydroxide lye to 50% sodium hydroxide lye and then to 98% - 99% sodium hydroxide melts which is converted as flakes. The 32% sodium hydroxide is stored in the main storage tank, as a part of which goes for sale. The remaining part of 32% lye is passed through three evaporators Ev1, Ev2, Ev3.In the first evaporator the caustic soda lye is heated using vapours generated in Ev1 is then drawn by a vacuum pump through a condenser and thus Ev1 is working under vacuum and at 70 – 80 degree Celsius. In the outlet from Ev1 is 40% caustic soda lye using 9Kg/cm^2 steam from boiler. A portion of 50% caustic soda lye cooled and solid.

PROCESS OF MAKING CAUSTIC SODA IN TCC

In TCC caustic soda is produce by the electrolysis of common salt. The ion exchange membrane cell consists of 20 electrolysis at 61KADC load and 95% current efficiency in the AGC plant.

The composition of the raw salt for electrolysis in common salt as per the specification of TCC.

NaCl	94% maximum on wet basis
SO_4^{2-}	0.48% maximum on wet basis
Ca^{2+}	0.16% maximum on wet basis
Mg^{2+}	0.06% maximum on wet basis
Insoluble residue	0.04% maximum on wet basis
Moisture	4% maximum on wet basis

The following are the chemical used for the removal of impurities.

Commercial Na_2CO_3 and $BaCO_3$ brought from the standard companies (used for removing calcium, sulphate) sodium hydroxide with minimum concentration 32% Fe≤ 10ppm (used for removing magnesium).

Hydrochloride with minimum concentration for 30%

Fe ≤ 10ppm(used for adjusting Ph)

MEMBRANE CELL PROCESS AND PLANT DESCRIPTION

In TCC, caustic soda is produced by the electrolysis of common salt.

The following are the chemicals used for the removal of impurities:

- Commercial Na_2CO_3 and $BaCO_3$ brought from standard companies used for removing Ca and sulphates.
- NaOH and minimum concentration of 32%, Fe ≤ 10ppm used for removing Mg.
- HCl with minimum concentration of 30%, Fe ≤ 10 ppm used for adjusting pH.

During the caustic soda production chlorine and hydrogen gases are also produced in TCC. The process of manufacturing involves the following steps:

- Primary brine purification
- Secondary brine purification
- Electrolysis
- Brine chlorination
- Chlorine treatment
- Hydrogen treatment

TCC consists of three plants. They are:

- Brine purification plant
- Membrane plant
- Continuous caustic fusion plant(CCF)

BRINE PURIFICATION PLANT

1. Primary brine purification

The primary brine purification involves brine saturation, precipitation and filtration.

- Brine saturation

There are two saturators. One is in operation and other as stand by the saturators filled with raw salt by means of buckets elevator and feed hopper learn brine. Dechlorinated brine of 210gpl sodium chloride is fed to saturated bottom through a dip pipe. The lean brine is mixed with salt and saturated brine leave from top through a strainer. The undissolved impurities are removed from bottom of the saturator periodically. About

5 – 6m^3/hour water is passed continuously through bottom of saturator for brine make up in whole brine system.

Brine loss occurs in electrolysers due to water transportation to the catholytic chamber. The salt charging rate is adjusted to get a brine concentration of 310gpl in saturator overflow.

- Precipitation

Saturated brine overflows into a precipitation tank A and B which are in serious and minor treatment with $BaCO_3$,Na_2CO_3 and NaOH lye respectively. Precipitation of brine impurities such as sulphates, calcium and magnesium takes place in the above tanks during the mixing of chemicals.

The precipitated brine is passes to the feed well of clarifier through a strain pot. A solution of 1% flock prepared in the flocculent tanks is added to the strainer pot by means of metering pump.

About 90% of solids are settled in the clarifier and are removed from bottom draining to brine sludge or effluent drain.

- Filtration

Four anthracite filters are provided for brine filtration. Normally three filters will be in service and one is stand by a centrifugal pump forces the clarified brine through the filters. The filtered brine is made acidified by mixing with 30% HCl in a mixture. The pH is adjusted to 4-5 and brine is collected in filtered brine tank. This is done to supply in ionic form of calcium and magnesium in secondary brine purification system in filtered brine chlorine contents is completely removed by adding $NaHSO_3$ to the inlet line to filtered brine pump. Also caustic soda in ionic form and also caustic soda is added to get the brine of pH in between 8.5- 9.5. Secondary purification unit cannot accept brine of pH below this range. Purification is also collected in secondary brine receiving tank. The clear brine is admitted to the electrolysis through the anode chamber.

2. Secondary brine purification

The secondary brine purification consist of ion exchange process, it remove traces level of brine impurities present in the brine. The clear brine is admitted to the electrolysis in anode chamber after heating in the heat exchanger.

ION EXCHANGE PROCESS

The ion exchange materials are insoluble acids and bases. The cation exchange materials are insoluble substances with fixed electronegative charge. These fixed charges are associated with mobile ions of opposite charge and these relative affinities account and the ion exchange process.

Most popular ion exchange materials are synthetic organic polymers having granular shape. The ion exchange resins are used columns in which solution containing ionic impurities such as Ca2+ and Mg2+ is in contact with the resin and finally equilibrium is reached. The saturated resin can then be regenerated to its original states by using HCI and NaOH solution. The regenerated resin is then ready for service. The chemical structure for chelating ion resin is micro porous. In TCC stirring divinyl benzene phosphate Na^+ ionic form is used. This process mainly include in membrane cell, added to get brine of pH in between 8.5-9.5. Secondary purification unit cannot accept brine of pH below this range. Filtered brine can be directly admitted to dechlorinated brine tank through a heat exchanger to the secondary brine purification unit.

CONTINUOUS CAUSTIC FUSION PLANT

It is used to concentrate 32% caustic soda lye to either 50% caustic soda lye or 99% caustic soda flakes.

Instrument used

Estimation of calcium and magnesium as sulphate in the sample after ion exchange process is measured by spectrophotometer.

Spectrophotometer

Spectrophotometry as the name implies is an instrument composed of two units. A spectrometer which produces light of definite wavelength and a photometer to measure the intensity of transmitted or absorbed light. Thus this serves as a device for the measurement of relative energy. The spectrophotometer is an instrument which measures the amount of light of a specified wavelength which passes through a medium. According to Beer's law, the amount of light absorbed by a medium is proportional to the concentration of absorbing material or solute present.

Reagents

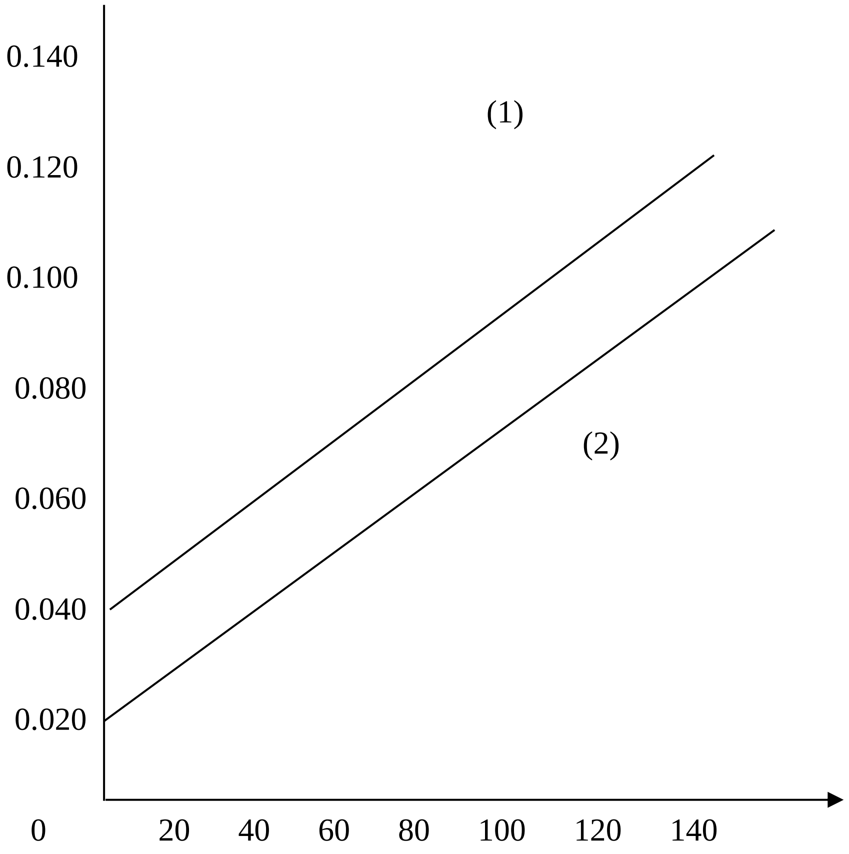
- HNB solution (Hydroxyl Naphthol Blue)
- 10mg per litre calcium standard solution
- Alkali buffer solution (3N)
- 1M EDTA solution

Apparatus

- DR 5000 UV-Visible spectrophotometer (HACH make)
- 100ml plastic graduated cylinders
- Ten settle pipette
- Brine-secondary filter outlet

ANALYSIS OF BRINE SAMPLE

Measures the absorbance of brine by developing color as above without adding calcium standards. The concentration graph the concentration is directly measured from the intercept corrected calibration graph. The value obtained is the sum of calcium and magnesium as calcium in microgram of brine.



Mg/I : Mg/I calcium spike

Ca, Mg : X axis Mg/I calcium spike

Y axis absorbance at 620nm

Found : (1) Standard addition calibration

(2) Intercept corrected calibration

Caliberation of the instrument

Measure out 100ml purified brine using 100ml plastic graduated cylinder in to 125ml plastic Erlenmeyer flask. Using ten settle pipette add 0.0, 0.2, 0.4, 0.6, 0.8 and 1ml of 100mg per litre calcium standard solution to five flasks to get 0, 20, 40, 60, 80 and 100m microgram per litre calcium standards. Add 1ml of prepared

HNB dye solution and mix well. Press the two times (two minutes), add the prepared brine into each of the matched cells. Label one of them as EDTA and the other as 'sample'. Place the sample cell into the sample compartment. After the time beeps, zero the instrument by pressing zero ABS to the EDTA cell add one drop of EDTA. Mix well and press three times (three minutes). Place EDTA into the sample compartment and press READ key on hearing the beep sound. Repeat the above steps with 20, 40, 60 and 80 microgram per litre standard solution.

Subtract the absorbance of 0 micrograms per litre standard from all the absorbance readings and plot absorbance against concentration. Measure all absorbance at 620nm.

MEMBRANE CELLS

Membrane cell consist of semi-permeable copolymer to separate the anode and cathode compartments. The membrane allow to pass sodium ion but reject hydroxyl group. Perflurosulphuric acid polymer. (Na+ ions) is the 1stly used membrane. The ASAHI glass company implemented bipolar as with multiple layer membrane. It consists of perflurosalphonic acid polymer coated on one side with a florocarboxylic acid polymer. The membrane cell operates using more concentrated brine and produce more pure and concentrated products 32% sodium hydroxide. Such product requires only 7.15Kg of water to be evaporated to produce sodium hydroxide such products require only 7.15Kg of H_2O to evaporate to produce metric ton of 50% caustic soda.

The membrane cell consumes least electricity when compared with mercury cell and diaphragm cell and also it have 95% current efficiency. Membrane is the most critical component of the cell technology and for current efficiency and cell voltage and hence energy consumption is greatly depends on quality.

Heat ion exchange membrane separator should be high selectivity of the transport of Na

- Negligible transport of chloride, hypochlorite and chlorite ion.
- Zero back migration of hydroxide ion
- Low electrical resistance
- Good mechanical properties and long term stability for practice use. In TCC Chloralkali electrolyser consists of flemion type membrane is a co-polymer of Tetrafluroethylene, Teflon (CF_2-CF_2) and Perflurovinyl ether polymer (CF_2-O-CF_2-CF_2-COO)$_n$.

ION EXCHANGE MEMBRANE CELL PROCESS

For electrolysis secondary purified brine is being fed to the anode chamber and the purified water to the cathode chamber. While applying a DC current the reaction of the substance in the electrolyser will take place.

- Reaction in anode chamber

In anode chamber electrolysis of sodium chloride occurs turning CI^- ions into Cl_2, on the cathode chamber through the ion exchanger membrane in the separator, chlorine gas is separated and analyte is recycled through a circulation pipe

$NaCl \rightarrow Na^+ + CI^-$

$Cl^- \rightarrow \frac{1}{2} Cl_2 +$ electron

Reactions in cathode chamber

In cathode chamber decomposition of water occur, produces hydrogen gas and hydroxide ion. The OH^- ions from caustic soda get together with Na^+ ions that passed through the membrane generated H_2 gas and caustic soda flows up to cathode gas separator by gas life effect, where H_2 gas is separated.

H_2O+electron→ $H^+ + OH^-$

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

Water in the anode chamber will move to the cathode chamber through the membrane by electro-osmosis. Hydroxide ion if any diffuse from the cathode chamber to anode chamber will produce O gas, Hypochlorite &chlorate by reacting with Cl_2 gas and O_2 gas generated in the cell during caustic soda production is tested using orsat apparatus.

$NaOH + Cl_2 \rightarrow NaCl + HOCl$

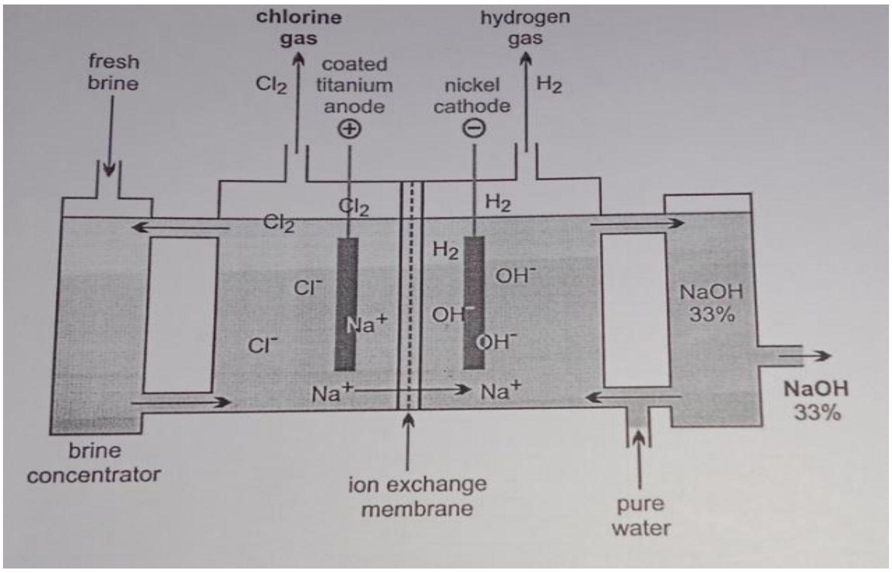
$6NaOH + 3Cl_2 \rightarrow 5NaCl + NaClO_3 + 2H_2O$

$2NaOH + Cl_2 \rightarrow \frac{1}{2} O_2 + 2NaCl + H_2O$

For producing highly pure caustic soda and also to avoid the mercury pollution, mercury cell were replaced by membrane cell in TCC.

The membrane cell produced from ASAHI glass company Ltd Japan and UHDE with 175 tones caustic soda production capacity per day.

MEMBRANE CELL



Metal anode:

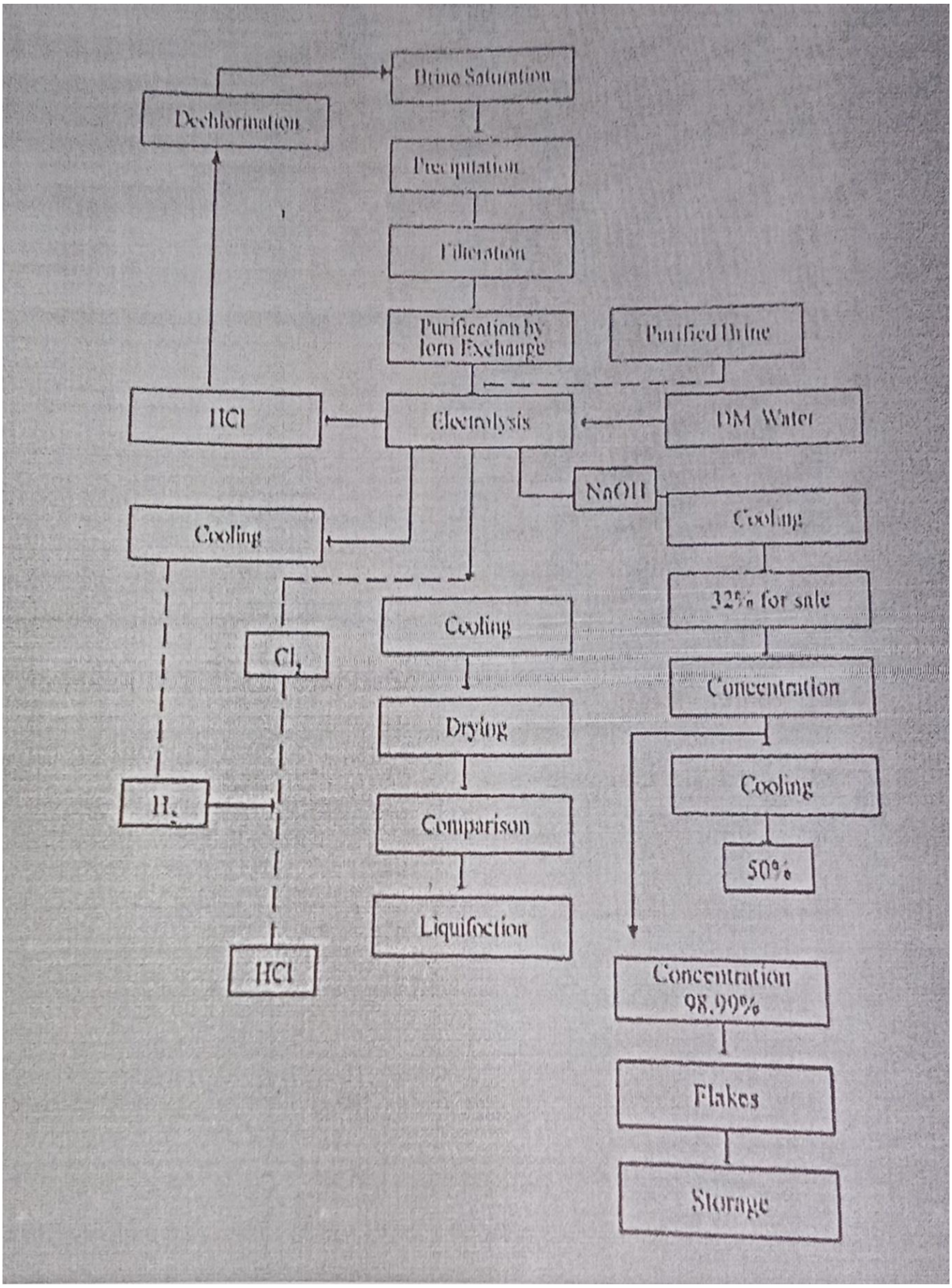
Both the frame and mesh are made up of titanium cathode with ruthenium oxide.

Metal cathode:

The frame is made up of stainless steel and the mesh is copper coated with nickel and Raney nickel.

FLOW DIAGRAM OF THE MEMBRANE CHLOR – ALKALI PROCESS

CHAPTER II


Brine Saturation
Dechlorination
Precipitation
Filteration
Purification by Iorn Exchange
Purified Brine
HCl
Electrolysis
DM Water
NaOH
Cooling
Cooling
32% for sale
Cl_2
Cooling
Concentration
Drying
H_2
Comparison
Cooling
50%
Liquifoction
HCl
Concentration 98.99%
Flakes
Storage

AIM AND OBJECTIVES

The Travancore Cochin chemicals limited, popularly known as TCC, caustic soda is manufactured in large scale in TCC Caustic soda is a basic alkali entering in to the manufacture of a host of articles of daily use like soap, paper, textiles, drugs, and rubber and petroleum products. Hence the aim of project is understand the purity of sodium hydroxide

Analysis of impurities like $NaNO_{2,}$ Na_2CO_3,Fe, Mn, Chlorates & matter insoluble in color-alkali manufacturing industry.

To identify caustic soda flakes in manufacturing units meets ISI standard

CHAPTER III
EXPERIMENTAL METHODS

SAMPLING OF FLAKES

For taking the sample, scrap off 50mm of material from the top center, the quantity of sample so drawn should not be less than 200mg and the mass of the total material taken out should not exceed 1Kg. Mix the quantity of the material (so collected from any particular bay on clean dry surface rapidly.) The sample should be placed on a clean dry and air tight alkali glass containers. Each sample container should be sealed air tight after filing and marked with full details of sampling, the data of sampling & batch number.

Determination of NaOH and Na_2CO_3

Aim

Estimate percentage of NaOH and Na_2CO_3 in caustic soda flakes, using standard HCI.

Solid NaOH has property of absorbing CO_2 from the air. Consequently it is never obtained in pure state. Caustic soda flakes contain the impurities like Na_2CO_3 etc… To determine the purity of caustic soda flakes we have to evaluate how much amount of NaOH and Na_2CO_3 are present in it. Both NaOH and Na_2CO_3 can be determined simultaneously by conducting double titration. For that flakes are accurately weighed and titrated against standard HCI using phenolphthalein and methyl orange as indicators. When phenolphthalein is used the whole of

NaOH and half if Na_2CO_3 have been reacted and remaining half reacts when orange is added. From the titre values, calculations are made and percentage of NaOH and Na_2CO_3 are determined.

Phenolphthalein:

$NaOH + HCI \rightarrow NaCl + H_2O$

Methyl orange:

$Na_2CO_3 + HCI \rightarrow NaHCO_3 + NaCl$

$NaHCO_3 + HCI \rightarrow NaCl + H_2O + CO_2$

Both NaOH and Na_2CO_3 of material were determined simultaneously conducting double indicator titration. The flakes were taken in a small weighing bottle and accurately about 3 gram of material was transferred into a 250ml wide mouth conical flask containing exactly 30ml 1N HCI dilute with a little of freshly prepared CO_2 fresh water two drops of phenolphthalein indicator was added.

Titre the contents of flakes against 1N HCI. Very near to end point which is indicated by fading of pink color, note down the volume of 1N HCI used for titration. Continue the titration with N/20 HCI till the end and continue the titration against N/20 HCI. End point is yellow orange red. Note the titre value

Percentage of NaOH =

$[(30 + V_1)+V_2 - V_3/(20\times N_1)]N_1 \times 40/1000 \times 100$ / weight of sample

Where,

N_1 = Normality of 1N HCI

N_2 = Normality of N/20 HCI

V_1 = Volume of 1N HCI

V_2 = Volume of N/20 phenolphthalein.

V_3 = Volume of N/20 methyl orange

[Percentage of $Na_2CO_3 = (2V_3 \times 1/20 \times 53/1000 \times 100)$/weight of flakes)

Determination of Sodium Chloride

Aim

Estimate the amount of chloride as sodium chloride caustic soda flakes using mercuric nitrate.

When chloride ions are titrated with mercury (II) nitrate solution in presence of sodium of nitroprusside indicator, the mercury (II) nitrate solution was converted into mercuric chloride.

$$Hg(NO_3)_2 + 2NaCl \rightarrow HgCl_2 + 2NaNO_3$$

$$Hg(NO_3)_2 + Na_2[Fe(CN)_5NO]2H_2O \rightarrow Hg[Fe(CN)_5NO] + 2NaNO_3 + 2H_2O$$

The excess $Hg(NO_3)_2$ solution reacts with sodium nitroprusside and form soluble mercuric salt. The first appearance of turbidity is the end point of the reaction

10 gram of solid flakes sample was weighed accurately into a conical flask. Dilute it to 100 ml using demineralized water. Neutralize the solution by adding concentrated HNO_3. Then add sodium nitroprusside indicator and titrate the solution against 0.01N $Hg(NO_3)_2$ from burette. The end point is the appearance of turbidity due to the formation of $Hg[Fe(CN)_5 NO]$. Note the titre value.

Percentage of chloride as sodium chloride =

titre value × strength of [$Hg(NO_3)$] × 59.45 × 100/(1000 ×weight of flakes)

Equivalent weight of sodium chloride = 58.48

Determination of Iron

Aim

Estimate the amount of iron in caustic soda flakes using potassium thiocyanate solution.

Nitric acid oxidizes iron from ferrous state to ferric state. Ferric reacts with thiocyanate to give an intense red colored complex, which remains in the solution. Ferrous iron does not react. The color is due to ferric thiocyanate. The solution contains the complex, $Fe(CN)_6$ having used coloration.

$Fe^{3+} + 3CNS^{-} \rightarrow Fe(CN)_3$

$Fe^{3+} + 6CNS^{-} \rightarrow [Fe(CNS)_6]$

Iron is estimated calorimetrically by visual comparisons

10g of flakes is taken in a beaker. Dilute to 50ml & neutralize with concentrated hydrochloric acid. Add 5ml excess sodium chloride and boil. Add 1ml HNO_3 to the boiling Solution. Cool and make up to 100ml. Pipette out 50ml of made up solution into nesslers tube, add 5ml of made up solution into nesslers tube, add 5ml of 5% HCI & 5ml 5% KCNS solution. Make up the solution into 100ml. In another nesslers tube take all the reagent except the sample in the same quantity and then go on adding by means of burette drop by drop of 0.01g/L Fe solution till the red color matches.

Fe(ppm)=

volume of standard solution consumed × 0.01/(1000) ×100/(50)×10^6/(weight of sample)

Determination of sulfate

Aim

Estimate the amount of chloride as sulfate in caustic soda flakes using $BaCl_2$ solution.

Sulfate is present in the caustic soda in the form of Na_2SO_4 ion present in a definite volume of sample solution is precipitated in the presence of dilute HCl as barium sulfate by adding $BaCl_2$.

$Na_2SO_4 + BaCl_2 \rightarrow BaSO_4 + 2NaCl$

Weigh accurately about 50g of flakes into 400ml beaker. Dissolve in it about 100ml water and cool. Neutralized the solution with Conc. HCI and add about 20ml in excess. Boil to decompose all the carbonates filter through Whatman no.41 filter paper and then wash the paper till. It's chloride free. Collect the filtrate of washings into 400ml beaker. Boil and add 20ml of hot 10% $BaCl_2$ solution with vigorous stirring. Digest for 3-4 minutes and allow to stand for minimum four hours.

Filter through Whatman no.41 paper & wash the precipitate to free it from chemicals then it take into No.4 sintered glass crucible which is previously weighed. Dry to constant weight in an oven at 110degree Celsius. Cool the crucible in a desiccators weighed and calculate the weight of the $BaSO_4$ obtained.

Percentage of Na_2SO_4 = Weight of precipitate × 142/ (233.36) x 100/ (weight of sample)60.86 × weight of the precipitate/(weight of the sample)

Equivalent weight of Na_2SO_4 =142g

Equivalent weight of $BaSO_4$ = 233.36g

Determination of silica

Aim

Estimate the amount of silica present in caustic soda flakes

Silica is determined colorimetrically by visual comparisons.

Weighted accurately about 10g the solid sample in to beaker. Dissolve in 100ml of H_2O. Neutralize it with dil.H_2SO_4 and made up to 100ml. Take 10ml of this into Nesslers cylinder and added excess of acid to bring the PH of this solution to 1.5 to 1.6. Add 5ml of ammonium molybdate solution and allow to stand for 5minutes. Then add 5ml of sodium citrate solution and 2ml of reducing olefin solution. Dilute the concerts to 50ml mask of the Nesslers cylinder. Observe the blue color. In another Nesslers cylinder take all the ingredients of the 1" cylinder except the sample material. Add to this by means of a burette, standard 0.01N silica solution drop by drop with shaking till the color of the solution matches that the test cylinder.

Percentage of silica =titre value x 0.01/(1000)× 100/(10)× 100/(weight of sample)

Determination of copper

Aim

Estimate the percentage of the copper in caustic soda flakes.

Copper is estimated colorimetrically by visual comparisons.

Weighted out 10g of material to the nearest 0.1g& transfer it into a 400ml beaker. Dissolve it in 50ml water and neutralize with conc. H_2SO_4 using litmus paper. To the neutralize solution add NH_4CI and conc.NH_4OH to the precipitate out iron. Heat the solution to coagulate the precipitate filter the precipitate through a Gooch crucible with an washings in a beaker Cover the beaker with a watch glass and evaporated to a volume of about 70ml. Transfer the solution to 100ml Nesslers cylinder. To this add 2ml citric acid solution and add NH_4CI.

Solution till pH becomes 8.5. Mix thoroughly and then add 10ml of gum acacia solution. 5ml of tetrasodiumpyrophosphate solution, 10ml of sodium diethyl dithiocarbonate solution and then dilute to 100ml dark with distilled water. To another Nesslers cylinder, add 2ml of citric acid solution, dilute NH_4OH, 10ml gum acacia solution. 5ml of tetra sodium pyrophosphate, 10ml of sodium diethyl dithiocarbonate solution and then dilute to 100ml dark with distilled water. To another Nesslers cylinder, add 2ml of citric acid solution, diluted NH_4OH, 10ml gum acacia solution. 5ml of tetra sodium diethyl dithiocarbonate, 10ml of sodium diethyl dithiocarbonate solution and then 2ml standard 0.01g/1 copper solution. Make up to 100ml mark with distilled water &shaken well. Compare the color produced in two cylinders.

Cu (ppm) = Titre value× 0.01/(1000)× 100/(10)×10^6/(weight of the sample)

Determination of manganese

Aim

Estimate the amount of manganese in caustic soda flakes.

Manganese is estimate colorimetrically by visual comparisons.

Weighed about 10g of flakes and transferred to 100ml beaker and dissolved it about 40ml H_20. To this solution add 10-15ml of phosphoric acid and 0.6-0.8g of potassium periodate. Heat the solution to boiling for 20minutes. Cool the solution to room temperature and transfer it to 100ml Nesselers cylinder make to mark with distilled water mix well. Compare the color with other Nesslers cylinder containing Iml of standard manganese solution and all the reagents except test solution treated similarly under similar condition with the same amount of reagent for the same as in the test solution and make up to 100ml mark

Mn (ppm)=titre value × 0.01/(1000)× 10^6/ (weight of the sample)

Determination of chlorates and perchlorates

Aim

Estimate the amount of chlorates and perchlorates in the caustic soda flakes.

A little excess of ferrous ammonium sulfate added to the slightly acidified solution of caustic soda flakes, oxidized quantitatively for the chlorate present in the caustic soda. The chlorate is estimated by back titrating, excess ferrous ammonium sulfate with potassium permanganate.

$NaClO_3+6FeSO_4+3H_2O \rightarrow 3[Fe_2(SO_4)_3]+NaCl+3H_2O$

$2KMnO_4+3H_2SO_4 \rightarrow K_2SO_4+2MnSO_4+3H_2O+5[0]$

$10FeSO_4 +5[0]+H_2SO_4 \rightarrow [5Fe(SO_4)_3]+H_2O$

Weigh completely about 50g of caustic soda sample into a 400ml beaker. Dissolve it into 200ml distilled water and cool. Add 20ml of the acid in excess and transfer the contents of beaker into 500ml conical flask. Add 2ml of 0.2N ferrous ammonium sulfate solution. Close the flask with at Bunsen value and boil the contents gently from 15minutes. Allow the flask to cool at room temperature. After cooling, titrate the contents of flask against 0.02N $KMnO_4$ solution slowly with stirring still a pink color persists. Now take the volume as V_2 run a blank by titrating 25ml of 0.02N ferrous ammonium sulfate containing 5ml of phosphoric acid and 200ml of H_2O against 0.02N $KMnO_4$ proceeding in the same as that of test. Note the volume as V_1.

Sodium chlorate (ppm) = $(V_1 - V_2) \times 0.02x\ 17.74/(1000) \times 10^{\wedge}6/(M)$

Where,

V_1 - volume of $KMnO_4$ in blank

V_2- volume of $KMnO_4$ in sample

M- Mass of sample

Determination of nickel

Aim

Estimate the amount of nickel in caustic soda flakes

Nickel present in the sample solution is precipitated as the insoluble nickel ammonium sulfate by alcoholic solution of dimethyl glyoxime.

$NiSO_4+2C_4H_8O_2N_2 \rightarrow Ni(C_4H_70_2N_2)_2+H_2SO_4$

From the mass of dimethyl glyoxime complex the mass of nickel is calculated by that 288.26g complex contains 58.59 of Nickel.

10g of flakes are accurately weighed and neutralize with dilute hydrochloric acid, boil and add to it a few drops of conc.HNO_3. Cool and make up to 100ml. Take 50ml from made up solution, add little potassium bitatarate to make to 100ml. Take 50ml from made up solution, add little potassium bitatarate to mask the iron. Then add a little bromine water to oxidize nickel and neutralize with ammonia. Add dimethyl glyoxime and compare the color with standard 0.01g/L solution.

$$\text{Ni (ppm)} = \text{volume of standard solution consumed} \times \frac{0.01}{1000} \times \frac{100}{50} \times \frac{10^6}{\text{weight of sample}}$$

Determination of matter insoluble

Aim

Estimate the percentage of matter insoluble present in caustic soda flakes.

Weighed accurately about 50g of the material and transfer it into 600ml beaker and add 300ml of H_2O and stirring until dissolved. Add conc. Hydrochloric acid. Till the solution just alkaline to that add phenolphthalein. Bring to boil and allow the solution to settle on the hot plate for 15minutes.Filter through a weighed gooch crucible no:4 and wash with hot water to free it from alkali allowing water to drain completely after each washings. Dry it in an oven for 1 hour at 105 to 110 Degree Celsius. Cool it. In a desiccators and weighed.

$$\text{Percentage of matter insoluble} = \frac{\text{weigh of insoluble} \times 100}{\text{weight of sample}}$$

Determination of sodium nitrate

Aim

Estimate the amount of sodium nitrate in the caustic soda flakes.

The sample solution is neutralized with 1.1 H_2SO_4 and add indigo as indicator shows the presence of $NaNO_2$.If $NaNO_2$ is present, sample solution neutralized with 1.1 H_2SO_4 is titrate against N/20 $KMnO_4$ till permanent pink color persists.

$$2KMnO_4+3H_2SO_4 \rightarrow K_2SO_4+2MnSO_4+H_2O+5[0] +5NaNO_2 + 5NaNO_3$$

Weighed out 10g of flakes and dissolves in water, neutralize with 1.1 H_2SO_4 then to boil, add 2ml indigo indicator. If the color disappears it shows the presence of $NaNO_2$.If there is the presence of $NaNO_2$, 10g of flakes is dissolve in water,neutralize with 1.1 H_2SO_4 , cooled and then titrated against standard N/10 $KMnO_4$. End point is pink color.

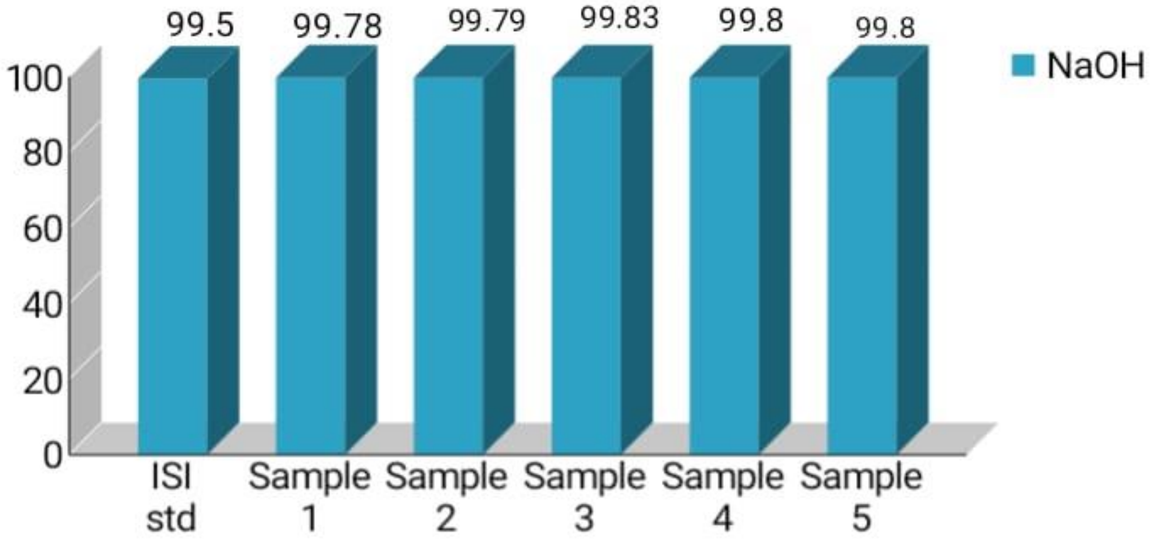
$$NaNO_2 = \frac{\text{Titre value} \times NKMnO_4 \times 60 \times 10^6}{2 \times 1000 \times \text{weight of sample}}$$

CHAPTER IV

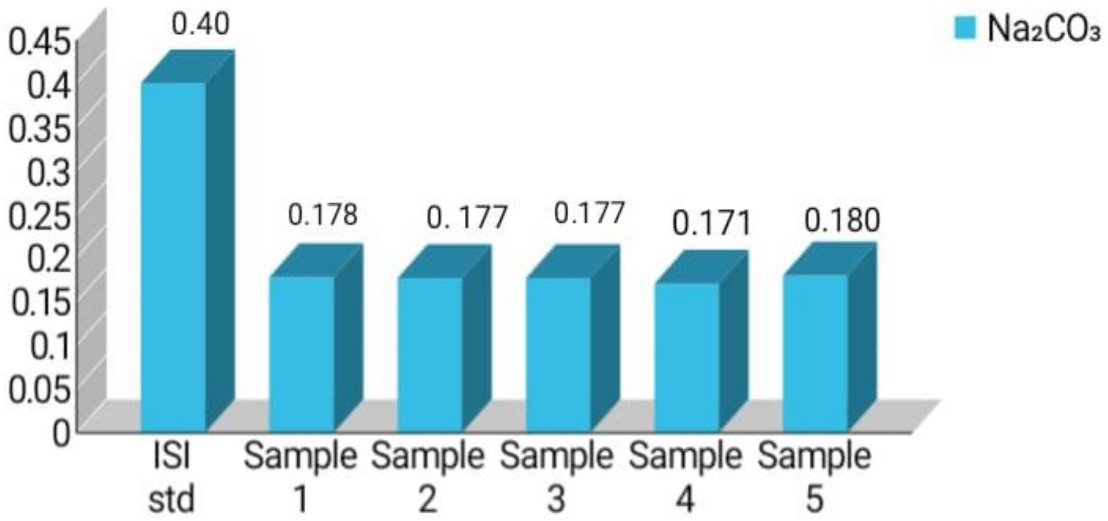
RESULT AND DISSCUSION

Analytical report of caustic soda flakes on dry basis

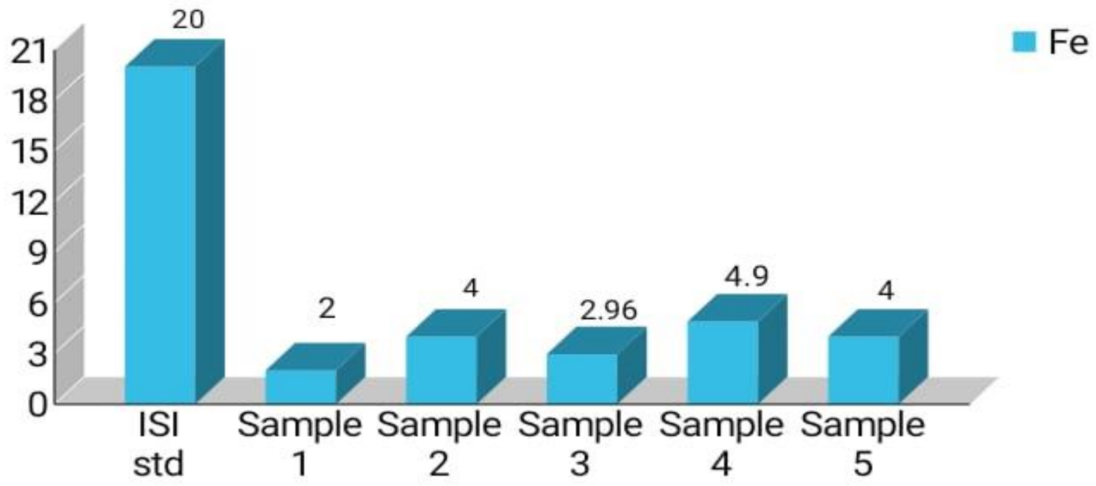
Dry basis								
Components	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	15252/1991
NaOH(%) by mass(a)	99.78	99.79	99.83	99.80	99.8	99.5	99.5	99.5
Na_2CO_3 by mass (b)	0.178	0.177	0.177	0.171	0.180	0.178	0.26	0.40
NaCl (%) by mass(c)	0.021	0.017	0.019	0.022	0.014	0.033	0.028	0.10
Fe(ppm) (d)	2	4	2.96	4.9	4	5.3	5	20
Ni (ppm) (e)	1	1.36	0.9	0.9	0.8	1	0.8	_
$NaNO_2$ (f)	Nil	Nil	Nil	Nil	Nil	Nil	Nil	_
Na_2SO_4 (%) by mass (g)	0.005	0.003	0.0056	0.004	0.003	0.003	0.003	0.10
SiO_2 (%) by mass (h)	0,002	0.006	0.0003	0.003	0.0003	0.0060	0.0059	0.02
Matter insoluble (i)	0.008	0,004	0.008	0.004	0,002	0,0036	0.0038	0.05
Cu(ppm) (j)	0.20	0.20	0.20	0.10	0.20	0.20	0.20	2.0
Mn(ppm) (k)	0.1	0.2	0.2	0.204	0.2	0.32	0.32	1.0
Chlorates (l)	NIL	1.358	Nil	Nil	1	1.25	1.24	10



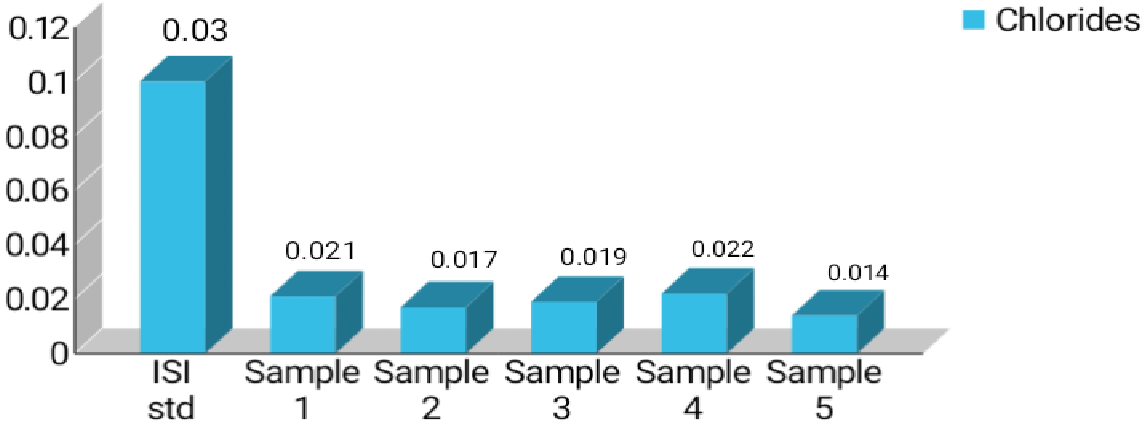
As per ISI standards the NaOH with purity greater than 99.5% is considered as pure. From the above data is clear that all samples are pure with purity greater than 99.5%. From this we come to know that NaOH made here is very pure and sample no.3 is very pure with 99.83% purity.



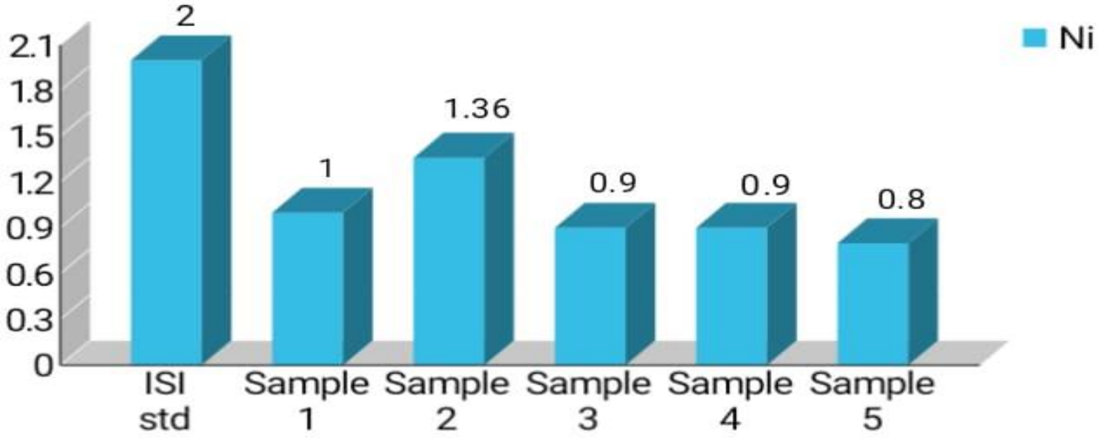
As per ISI standards the NaOH with Na2CO3 content less than 0.40 is considered as pure. From the above data is clear that all samples are pure with impurity less than 0.40.From this we come to know that NaOH made here is very pure and sample no.4 is very pure with Na2CO3 content less than with 0.171.



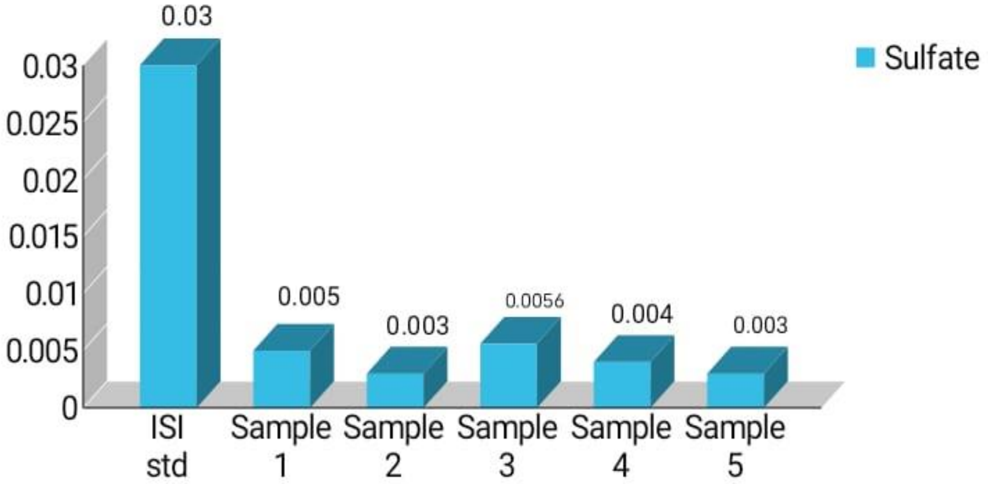
As per ISI standards the NaOH with Fe content less than 20 is considered as pure. From the above data is clear that all samples are pure with impurity less than 20.From this we come to know that NaOH made here is very pure and sample no.1 is very pure with Fe content less than with 2.



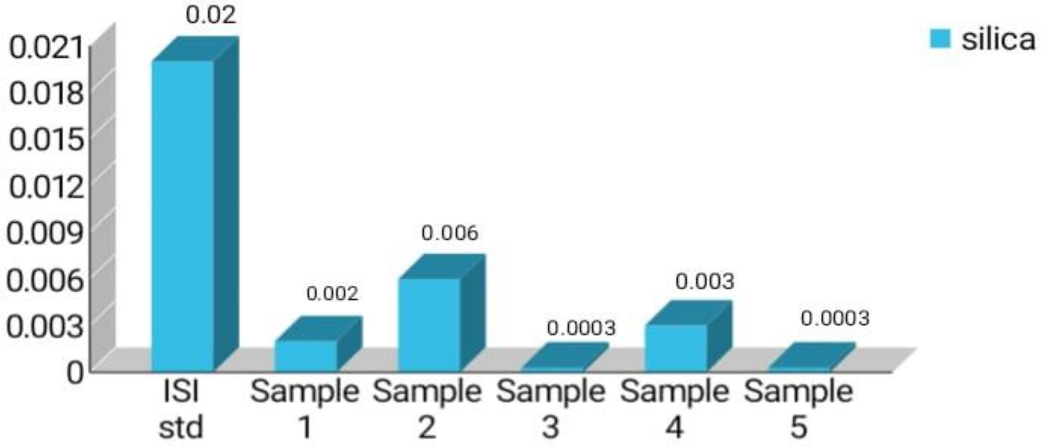
As per ISI standards the NaOH with chlorides content less than 0.03 is considered as pure. From the above data is clear that all samples are pure with impurity less than 0.03.From this we come to know that NaOH made here is very pure and sample no.5 is very pure with chlorides content less than with 0.014.



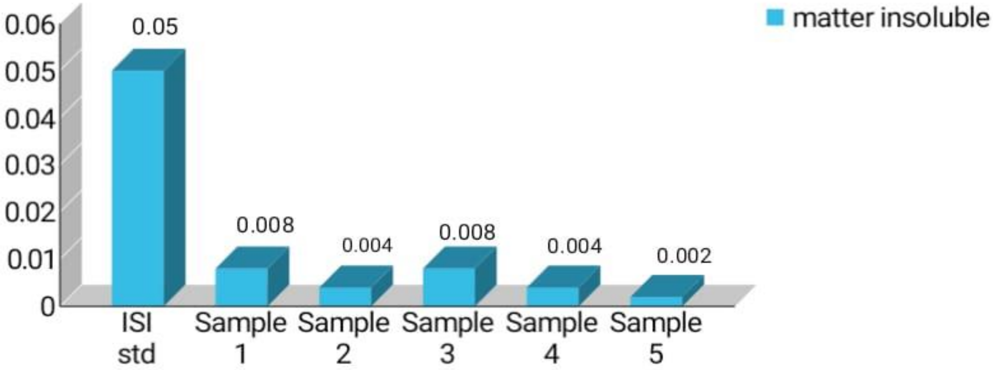
As per ISI standards the NaOH with Nickel content less than 2 is considered as pure. From the above data is clear that all samples are pure with impurity less than 2.From this we come to know that NaOH made here is very pure and sample no.5 is very pure with Nickel content less than with 0.8



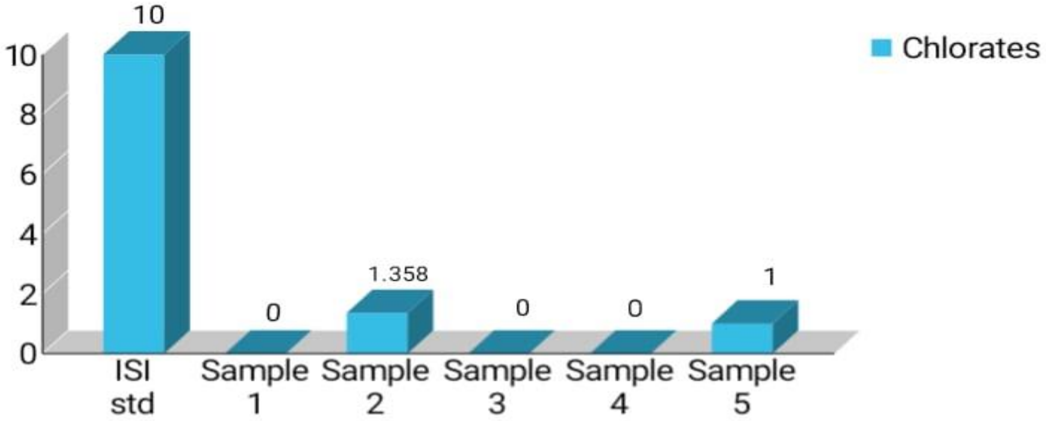
As per ISI standards the NaOH with Sulfate content less than 0.03 is considered as pure. From the above data is clear that all samples are pure with impurity less than 0.03 .From this we come to know that NaOH made here is very pure and sample no.5 is very pure with Nickel content less than with 0.003



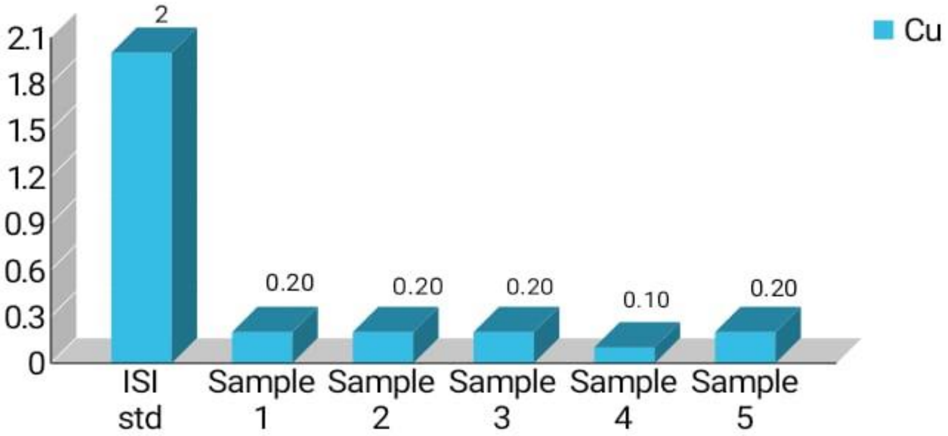
As per ISI standards the NaOH with silica content less than 0.02 is considered as pure. From the above data is clear that all samples are pure with impurity less than 0.02.From this we come to know that NaOH made here is very pure and sample no.3&5 is very pure with silica content less than with 0.0003.



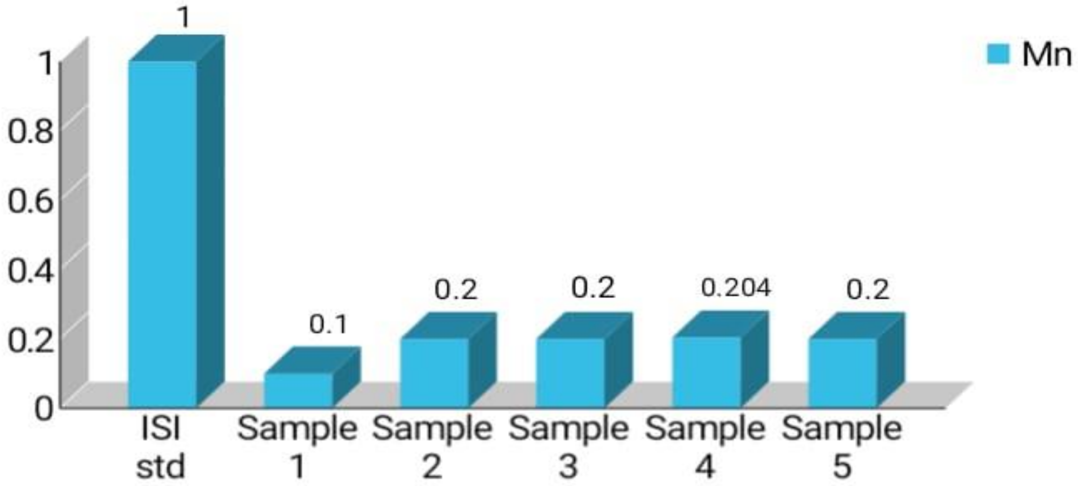
As per ISI standards the NaOH with matter soluble content less than 0.05 is considered as pure. From the above data is clear that all samples are pure with impurity less than 0.05.From this we come to know that NaOH made here is very pure and sample no.5 is very pure with matter soluble content less than with 0.002.



As per ISI standards the NaOH with chlorates content less than 10 is considered as pure. From the above data is clear that all samples are pure with impurity less than 10.From this we come to know that NaOH made here is very pure and sample no.1,3&4 is very pure with chlorates less than with 0.



As per ISI standards the NaOH with copper content less than 2 is considered as pure. From the above data is clear that all samples are pure with impurity less than 2.From this we come to know that NaOH made here is very pure and sample no.4 is very pure with copper less than with 0.10.



As per ISI standards the NaOH with manganese content less than 1 is considered as pure. From the above data is clear that all samples are pure with impurity less than 1.From this we come to know that NaOH made here is very pure and sample no.1 is very pure with manganese less than with 0.1.

CHAPTER V

CONCLUSION

The objective of this project is to find the various amounts of impurities present in the caustic soda flakes. To find out the quality of the product samples were analysed and concentration of the flakes were checked.Thus common impurities such as NaOH, Na_2CO_3,Fe,Mn,Matter insoluble and Chlorates were analyzed. Experiments showed that then given caustic soda samples are about 98% pure and reaches international quality.From this project it is clear that the caustic soda produced by chlor – alkali process meet high standard.

CHAPTER VI

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