Study of Parameters Involved in the Production of Caustic Soda from Soda Ash using Lime-Soda Process

A Thesis

Submitted to the Department of Chemical Engineering in partial fulfillment of the requirement for the degree of Master of Science in Engineering (Chemical)

By

Tariq Mahmood Mannan

Department of Chemical Engineering

Bangladesh University of Engineering and Technology

Dhaka, Bangladesh

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BANGLADESH UNIVERSITY OF ENGINEERING AND TECHNOLOGY,
DEPARTMENT OF CHEMICAL ENGINEERING
CERTIFICATION OF THESIS WORK

We, the undersigned, certify that **Tariq Mahmood Mannan**, candidate for degree of Master of Science in Engineering (Chemical), has presented his thesis on the subject "Study of Parameters Involved in the Production of Caustic Soda from Soda Ash using Lime-Soda Process", that the thesis is acceptable in form and content, and that the student demonstrated a satisfactory knowledge of the field covered by this thesis in an oral examination held on December 15, 1998.

m.S. Islam

(Dr. M. Serajul Islam)
Associate Professor
Dept. of Chemical Engg.
BUET, Dhaka

Chairman,
Examination Committee

(Dr. Dil Afroza Beguim)
Professor and Head
Dept. of Chemical Engg.
BUET, Dhaka

Member (Ex-Officio),
Examination Committee

Akma Quader

(Dr. A.K.M.A. Quader)
Professor
Dept. of Chemical Engg.
BUET, Dhaka

Member,
Examination Committee

(Dr. M. Walliuzzaman)
Ex-Chairman, BCSIR
23/1 BUET Residential Area
BUET, Dhaka

Member (External),
Examination Committee

Abstract

This work is a study of the parameters involved in the production of caustic soda by the lime-soda process. Experiments were performed to determine the effect of reaction temperature on the per cent conversion of sodium carbonate using both analytical grade reagents and commercial grade reagents.

A temperature range of 60 to 100 °C was used for the experiments. The maximum conversion was found to be at 90 °C, corresponding to 93.4% conversion using AR grade reagents and 82.0% conversion using commercial grade reagents. Moreover, at this temperature filtration of the reaction products was found to be easier than that produced at lower temperatures. Therefore this temperature is considered to be the optimum temperature for carrying out the reaction.

Literature survey revealed that initial concentration of sodium carbonate of 10% to 20% (by weight) is used in industries. In these experiments the initial concentration of sodium carbonate was 20%. This was found to be satisfactory. The per cent conversion is also dependent on the initial concentration being higher at lower concentration of sodium carbonate.

The caustic soda produced contained unreacted sodium carbonate. No calcium residue could be detected. Separation of the carbonate from the caustic and the concentrating of the caustic were not performed experimentally.

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Chapter 1

Introduction

Caustic soda is the basic inorganic chemical which is used most extensively in industries. Its use is analogous to that of sulfuric acid as the industrial inorganic acid.

Industrially caustic soda is produced by two processes:

i) Chemical process, and

ii) Electrolytic process.

The chemical process is the classical method of caustic production. In this process, a solution of sodium carbonate is treated with calcium hydroxide to produce a precipitate of calcium and an aqueous solution of sodium hydroxide. After removal of the insoluble carbonate, the solution is concentrated to give various grades of caustic soda. This process is also known as the lime-soda process and the alkali produced is referred to as chemical caustic to distinguish it from that produced by electrolytic process.

Electrolytic methods for caustic production can be grouped into two processes, namely,

i) diaphragm-cell, and

ii) mercury-cathode cell methods.

Both processes work by the electrolytic decomposition of purified brine to produce weak caustic solutions and chlorine. Hydrogen and oxygen may also be produced. With the introduction of electrolytic methods for caustic and chlorine production, the lime-soda process declined. Initially mercury cell process (Europe and the far East) and diaphragm cell process (north America) were used for caustic production. But in view of the hazardous nature of mercury and the high salt content of diaphragm cell caustic, membrane cell process for caustic production is becoming the preferred process (Ref. 4,7). Membrane cell is a development of the diaphragm cell in which a semi-permeable membrane separates the brine at the anode from the cathode. The membrane only allows the transfer of cations and prevents the contamination of the caustic at the cathode by chloride ions (Ref. 4). Recently Chittagong Chemical Complex has started production in the 7000 MT caustic soda plant using ion-exchange membrane process (Ref. 8, 9). However, considering the high initial investment cost of and the need to use very pure brine solution for membrane cell process, there is renewed interest in lime-soda process for small scale production. This is verified by the fact that recently in Bangladesh a company has started commercial production of caustic soda based on the lime-soda process (Ref. 10).

Although the chemical reactions in the lime-soda process are well established, the exact conditions for industrial production are not given in texts. For indigenous development of this industry, the process parameters need to be studied. In particular, the effect of reaction temperature on conversion and subsequent separation needs to be determined.

Chapter 2

Literature Review

2.1 Historical background

Caustic soda has been produced from soda ash since shortly after the development of the Leblanc synthetic soda ash process in the early 18th century. Because of the incompleteness of the reaction, early caustic production was heavily contaminated with soda ash. As reaction conditions became better known, relatively pure caustic soda was produced in large quantities until World War I. When the electrolytic process for caustic and chlorine was developed, the lime-soda process could compete only with great difficulty and dwindled. Since 1968, in the United States caustic soda has been produced exclusively by electrolysis, and caustic soda is produced from soda ash only in isolated areas throughout the world (Ref. 3).

Even though the lime-soda process is no longer used to produce caustic soda for sale in the developed countries, the process is still employed in small- scale production for captive plant consumption. Of particular importance is the Kraft recovery process, on which "green" liquor (an aqueous solution of sodium carbonate) is limed to produce "white" liquor, or caustic soda, for return to pulp digesters. The process also finds limited use in the production of alumina, in which lime and soda ash are charged to bauxite digesters. Under the digester operating conditions, the reaction is not complete, resulting in a loss of efficiency and other difficulties. Consequently, most alumina plant prefer to charge caustic soda directly to the digesters (Ref. 3).

For the electrolytic production of caustic soda, diaphragm cells predominate in the United States, whereas mercury cells are prevalent in Europe and the Far East. There are a number of factors that have contributed to these preferences: (1) The relatively high voltage drop of mercury-arc rectifiers used to supply d-c power discouraged the use of large single cells (low voltage, high current) in Europe, and favored the use of a number of smaller cells operated in series (high voltage, low current). (2) Asbestos, needed for diaphragms, is native to Canada and the northern United States; mercury is produced in Spain and Italy. (3) Energy needed for evaporation of water to concentrate dilute caustic effluent from diaphragm cells has been more plentiful and lower in cost in the United States than in Europe. (4) Salt use for chlorine production in Europe, Japan, and Italy traditionally has been supplied and transported in the solid (ie, crystalline) form, which is ideal for use in mercury cells. (5) European consumers developed an early preference for the higher purity of mercury-cell caustic. Thus European producers found little incentive to make diaphragm-cell caustic with its higher salt content. Salt contamination problems of the Diaphragm-cell lead to the development of the membrane-cell which produce higher purity caustic (Ref. 3).

However, the electrolytic plants for caustic production need large initial capital investment and is economically attractive for large scale production. Moreover, there must also exist a ready market for the chlorine produced which in fact, is the main product with caustic soda as byproduct. In developing countries with capital constraints, the lime-soda process is still attractive for small scale caustic production (Ref. 2, 10).

2.2 Properties of Sodium hydroxide

2.2.1 Physical Properties

Pure, anhydrous sodium hydroxide (NaOH), molecular weight 39.998, is a white, somewhat translucent crystalline solid. In even moderate concentrations it is highly corrosive to skin. Because of this property, it is also known as caustic soda, a term widely used in industry. Caustic soda is very soluble in water and is highly alkaline. The properties of pure, anhydrous caustic soda are given in Table 2.2.1.1.

Table 2.2.1.1 Physical Constants of Pure Sodium Hydroxide (Ref. 3)

molecular weight	39.998
specific gravity, 20 °/4 °C	2.130
melting point, °C	318
boiling point at 101.3 kPa, °C	1390
index of refraction	1.3576
latent heat of fusion, J/g	167.4
heat of transition, alpha to beta, J/g	103.3
heat of formation from the elements:	
alpha form, kJ/mol	422.2
beta form, kJ/mol	426.60
transition temperature, °C	299.6
solubility at 20 °C, g/100 g water	109

In water solution, depending on concentration, caustic soda can form five hydrates containing 1, 2, 3, 5, and 7 molecules of water, respectively. Hydrate formation is exothermic; caustic solutions generate heat when further diluted with water. With concentrations of 40% or greater, the heat generated can raise the temperature above the boiling point, resulting in sporadic, dangerous eruptions of the solution. Any dilution of caustic from concentrations greater than 25% should be done cautiously (Ref. 3).

2.2.2 Chemical Properties

Aqueous solutions of sodium hydroxide are highly basic and especially useful in reaction with weakly acidic materials where weaker bases such as sodium carbonate are ineffective.

Sodium hydroxide will neither burn nor support combustion, although in its reaction with amphoteric metals, such as aluminum, tin, and zinc, hydrogen gas is generated which may form an explosive mixture. A major use of sodium hydroxide is to form sodium salts, thus neutralizing strong acids and solubilizing water-insoluble chemicals through the formation of the sodium salt. Sodium hydroxide is also useful in the precipitation of heavy metals as their hydroxides, and in the control of acidity of aqueous solutions (Ref. 3).

Reaction with Mineral Acids. Caustic soda reacts with all mineral aids to form the corresponding salts. It also reacts with weak-acid gases, such as hydrogen sulfide, sulfur dioxide, and carbon dioxide. Typical reactions are:

$$H_2S + 2\,NaOH \rightarrow Na_2S + H_2O \qquad (2.2.2.1)$$

$$SO_2 + 2NaOH \rightarrow Na_2SO_3 + H_2O \qquad (2.2.2.2)$$

$$CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O \qquad (2.2.2.3)$$

With appropriate equipment and operating conditions, the stronger acid gases can be selectively separately from carbon dioxide with a reasonable degree of efficiency.

This is practiced commercially in the preferential removal of hydrogen sulfide from natural gas that contains carbon dioxide (Ref. 3).

Reaction with Metals. Caustic soda reacts with amphoteric metals and their oxides to form soluble salt. For example, hydrated alumina forms sodium aluminate:

$$A(OH)_3 + NaOH \rightarrow NaAlO_2 + 2\ H_2O \qquad (2.2.2.4)$$

This reaction is the basis for the extraction of alumina from bauxite by the Bayer process.

The precipitation of soluble metals from aqueous solutions is also of industrial importance. Thus magnesium may be precipitated from seawater as the first step in the production of magnesium metal or magnesium oxide:

$$MgSO_4 + 2\ NaOH \rightarrow Mg(OH)_2 + Na_2SO_4 \qquad (2.2.2.5)$$

The precipitation of metals as their hydroxides is becoming increasingly important for pollution control. Nearly complete metal removal can be accomplished by precipitating and settling, providing an acceptable effluent for disposal (Ref. 3).

Reaction with Organic Acids. All organic aids also react with sodium hydroxide to form soluble salts. However, saponification of esters to form the corresponding salt of the organic acid and an alcohol is of greater industrial importance. The reaction of caustic soda with fatty acid triglycerides to form soap and glycerol is typical:

$$C_3H_5(OOCR)_3 + 3\ NaOH \rightarrow C_3H_5(OH)_3 + 3\ RCOONa \qquad (2.2.2.6)$$

Another common reaction of caustic soda is dehydrochlorination; eg, the reaction of propylene chlorohydrin and sodium hydroxide to form propylene oxide:

$$ClC_3H_6OH + NaOH \rightarrow C_3H_6O + NaCl + H_2O \qquad (2.2.2.7)$$

This reaction is often referred to as an internal coupling. Many other coupling reactions are also well known, such as the reaction of cellulose, caustic, and monochloroacetic acid, to produce the sodium salt of carboxymethylcellulose. The first step in this reaction is similar to that used in mercerizing cotton, and in the preparation of rayon via cellulose xanthate (Ref. 3).

Because of the complexity of some sodium hydroxide reactions with natural products, simple chemical reactions cannot be written to describe them. In this category are such reactions as the solubilizing of cotton in rubber reclaiming, the dextrination of starch, scouring of cotton, refining of vegetable oils, and the removal of lignin and hemicellulose in the Kraft pulping process (Ref. 3).

2.3 Uses of Caustic Soda

Caustic soda is used industrially in numerous ways, some of which are listed below (Ref. 1,3):

a) manufacture of vast number of other chemicals,

b) refining of Kraft process pulp to higher alpha cellulose content,

c) making of viscose silk or rayon,

d) making wood pulp (soda process),

e) petroleum refining,

f) making detergents,

g) making soaps,

h) textile processing,

i) rubber reclaiming,

j) mercerizing,

k) recovering of tar acids,

l) metal processing,

m) water and acid waste stream treatment,

n) pH control,

o) paint removing,

p) disinfectant,

q) alkaline bottle washing formulations,

r) pharmaceuticals,

s) food processing,

t) renovating anion exchangers in deionizers and for other purposes.

2.4 Available Grades of Caustic Soda

Different grades of anhydrous caustic such as USP, C.P., reagent, and commercial are available in the form of flakes, granulated, ground, sticks, lumps, and drops (pellets). The common grades based on sodium oxide (Na_2O) content are 60 per cent (77.4 per cent sodium hydroxide, NaOH), 70 per cent (90.3 per cent sodium hydroxide, NaOH), 74 per cent (95.48 per cent sodium hydroxide) and 76 per cent (98.06 per cent sodium hydroxide). Aqueous solutions (containing about 50 per cent and 73 per cent sodium hydroxide) are available and weigh about 12.5 lb per gallon (Ref. 2).

Regular-grade 50 % diaphragm-cell caustic is suitable for most end uses, and accounts for about 85% of the caustic soda consumed in the United States. Other uses, such as in rayon manufacture, the synthesis of alkyl aryl sulfonates, and the regeneration of anion exchange resins, require a higher purity caustic. Mercury-cell caustic satisfies these requirements easily. In order to compete for the high purity markets, however, the producers of diaphragm-cell caustic have spent a great deal of time and effort on purification processes. Crystallization of caustic soda by cooling to form the monohydrate or dihydrate has been investigated extensively and proven technically, although it has never been used commercially in the United States (Ref. 3).

The ammonia extraction process, however, has been used for many years. Essentially anhydrous ammonia is mixed with 50% caustic which forms a two-phase system. The ammonia phase extracts salt and sodium chlorate together with some caustic soda and water. The second phase, consisting of about 62% caustic soda, is essentially free of salt and sodium chlorate, but contains some ammonia. It is separated and flash-distilled in a fractionating tower which recovers nearly anhydrous ammonia (Ref. 3).

The still bottoms of salt, sodium chlorate, and caustic soda are generally used by producer for their alkalinity value, eg, the neutralization of acid. The 62% caustic is either diluted to 50% or else further evaporated to 73% or anhydrous grades for sale (Ref. 3).

73% Caustic Soda. In the freezing-point curve, there is a relatively flat area from 65-74% caustic soda. Over this range of concentrations, caustic soda freezes at about 62 °C, permitting it to be concentrated and shipped, with some latitude in the concentration. Nominal 73% caustic remains in the liquid state at a temperature of 62 °C, and can be handled as a liquid as long as it is kept above this temperature. However, at concentrations greater than 74%, the temperature required to keep the product liquid rises very sharply. For storage, customers who buy the 73% grade almost invariable dilute it to 50%, at which concentration it remains in the liquid state at room temperature. The objective of concentration, then, is to save freight costs by removing extra water. Using 50% caustic as feed, evaporation to 73% is usually accomplished in a single-effect, moderate-pressure, natural-circulation evaporator. Nickel is required on the caustic side of the evaporator to avoid corrosion and iron contamination. Because no additional salt crystallization occurs, the complications of salt handling, encountered when concentrating to 50%, are avoided. The evaporation system is usually controlled on the basis of the specific gravity and temperature of the product. The product is stored and shipped at elevated temperatures in tanks with proprietary organic linings (Ref. 3).

Either 73% regular or 73% purified caustic can be produced, using 50% regular or 62% ammonia-extracted caustic, respectively, as the starting material. The determining factor in the use of 73% caustic is usually the cost of concentrating as opposed to the cost of shipping the extra water in a 50% solution (Ref. 3).

Anhydrous Caustic. Prior to about 1950, anhydrous caustic was produced by evaporation of the water from 50% or 73% caustic solution in direct-fired, cast-iron pots. In the production of high volume chemicals, however, the economics favor a continuous process. For this purpose a tubular, flash-type evaporator was developed which is still being used. Heat is supplied by direct firing, by Dowtherm heat transfer fluid, or by a eutectic mixture of molten potassium nitrate, sodium nitrite, and sodium nitrate. Nickel or Inconel are commonly used as construction materials. Because sodium chlorate corrodes these metals at elevated temperatures, it must be removed or destroyed. This is not a serious problem with purified caustic, since chlorate has already been removed. However, a reducing agent such as sugar, must be added to regular-grade caustic before concentration (Ref. 3).

2.5 Materials of Construction

Nickel is by far the preferred metal for handling caustic soda at all concentrations and temperatures, including molten anhydrous caustic up to 480 °C. The high cost and limited availability of nickel, however, precludes its use for most applications. Nickel and/or its alloys are, therefore, used only for equipment that requires precision tolerances, for caustic solutions at elevated temperatures, or where high solution velocities are encountered such as in centrifugal pumps (Ref. 3).

For almost all caustic-handling applications, mild steel is quite adequate. The corrosion rate of caustic solutions on steel at ambient temperature is less than that of water.

When caustic soda solution concentrations exceed 20% at temperatures in excess of 60 °C, stress cracking may occur. Stress cracking can be greatly reduced or eliminated by annealing the metal. Corrosion also becomes a general problem at temperatures above 60 °C, and it accelerates with increasing temperatures. Thus the use of steel is not recommended at elevated temperatures. For such conditions nickel alloys are usually suitable. The chrome-nickel stainless steels are more resistant than mild steel to caustic corrosion. They are frequently used as construction materials, especially in food processing. Chlorides present in regular diaphragm-cell caustic, however, may cause chloride stress cracking of austenitic stainless steels at elevated temperatures. In general, corrosion resistance is proportional to nickel content. Amphoteric metals, such as aluminum, tin, and zinc, are attacked rapidly by caustic soda solutions.

Neither they nor their alloys, such as brass or bronze, should be used in contact with caustic or its solutions (Ref. 3).

Plastics and plastic-lined steeled are now commercially available as construction materials. Fiberglass-reinforced plastic tanks of Derakane vinyl ester resin are suitable for many applications, provided that they are protected from mechanical damage. Several types of plastic are also commonly used for lining pipe. From a cost and performance consideration, polypropylene is probably superior for this application. At moderately high temperatures, the fluorocarbon plastics have been used successfully as pipe linings (Ref. 3).

2.6 Transportation

Liquid-caustic soda solution is classified by the Department of Transportation (DOT), USA as a corrosive liquid. It must be transported in containers conforming to DOT specifications. DOT regulations covering handling and labeling must also be followed. The Manufacturing Chemists Association (MCA), too, has a recommended warning label for containers of both caustic soda solution and anhydrous caustic soda. Anhydrous or dry caustic soda is also regulated by the Department of Transportation.

Approximately one-fourth of the caustic soda produced in the United States is shipped in barges as a 50% solution. Tank cars for shipping caustic soda, usually insulated and equipped with external heating coils, are made of nickel-clad steel, or they are lined with an organic coating, to minimize iron contamination. Tank trucks also play an important role in the transportation of 50% caustic soda. Caustic soda is also produced in anhydrous solid form, for shipment to facilities that are not equipped to handle liquid caustic (Ref. 3).

2.7 Safety

Caustic soda is a highly hazardous chemical. As such, no attempt should be made to handle it without first reviewing its properties and safety precautions.

Because of the hazards of handling caustic soda, all persons doing so should wear proper protective clothing and equipment. Chemical worker's safety goggles should always be worn. Depending upon the possibility of exposure, additional protective clothing and equipment may be required, such as a full face shield, a caustic-resistance apron or suit, rubber gloves, boots, and possibly a dust-type respirator.

Disposal of waste or spilled caustic soda must meet all federal, state, and local regulations. Only properly trained personnel should undertake spill cleanup. Accidental spills of dry caustic soda must be shoveled up, and the area flushed with water. Dilute acid, preferably acetic acid, may be used to neutralize the final trace of caustic. Spilled or waste-caustic-soda solution should never be discharged directly into sewers or streams. It should first be cautiously diluted with water, and then converted to a neutral salt by treatment with acid (Ref. 3)

2.8 Industrial Methods for Caustic Production

Industrially caustic soda is manufactured by two processes:

i) electrolytic, and ii) chemical.

In the electrolytic process for the manufacture of sodium hydroxide, an electric current is passed through a sodium chloride (salt) solution in specially designed cells. The salt brine is decomposed by the current to form a 10 to 12 per cent sodium hydroxide solution, with hydrogen gas forming at the cathode and chlorine gas at the anode as co-products. Two types of cells, the mercury cathode and diaphragm, are used in the United States. Figure 2.8.1 shows the flow diagram of both the processes.

The Mercury Cell Process. The mercury-cell process actually involves two cells. In the primary electrolyzer (or brine cell), purified, saturated brine containing approximately 25.5 wt % sodium chloride flows through an elongated trough that is inclined slightly from the horizontal. In the bottom of this trough a shallow sheet of mercury, the cathode, flows concurrently with the brine. Closely spaced above the cathode, an anode assembly is suspended which consists of horizontal blocks of graphite or dimensionally stable (titanium-base) anodes. Current flowing through the cell decomposes the brine that is passing through the narrow space between the electrodes, liberating chlorine gas at the anode and sodium metal at the cathode. The chlorine gas is accumulated above the anode assembly and discharged to the purification process (Ref. 3).

As it is liberated at the surface of the mercury cathode, the sodium immediately forms an amalgam which essentially eliminates the reaction with water in the brine to form caustic soda and hydrogen, and reaction with dissolved chlorine (Ref. 3).

Decomposer. From the electrolyser, dilute amalgam is fed to a separate packed-bed reactor (the decomposer, denuder, or soda cell) where it reacts with water.

$$\text{Na-Hg} + H_2O \rightarrow Na^+ + OH^- + \tfrac{1}{2} H_2 + Hg$$

Mercury cells are usually operated so as to maintain a 21 – 22 wt % concentration of salt in the spent brine discharging from the electrolyzer. This corresponds to a decomposition of 15 – 16 % of the salt during a single pass (Ref. 3).

Mercury Losses. The mercury used in a mercury cell represents a significant portion (10 – 15%) of the total investment in the cell. Depending on cell size, the amount required ranges from 680 to 1360 kg/(t.d) of chlorine capacity. Prior to government regulation, mercury losses from mercury-cell plants ranged from 135 to 225 g/t chlorine. At the operating temperatures of electrolyzers and decomposers, mercury has a measurable vapor pressure; even with cooling, mercury is lost in the product and waste streams from a plant. Recent EPA regulations limit effluent discharge to 0.28 g mercury per metric ton of product for existing plants, with additional 50% reduction for new plants. To meet these regulations, in addition to elaborate filter systems, mercury-cell plants have also had to install more efficient coolers to condense mercury vapor (Ref. 3).

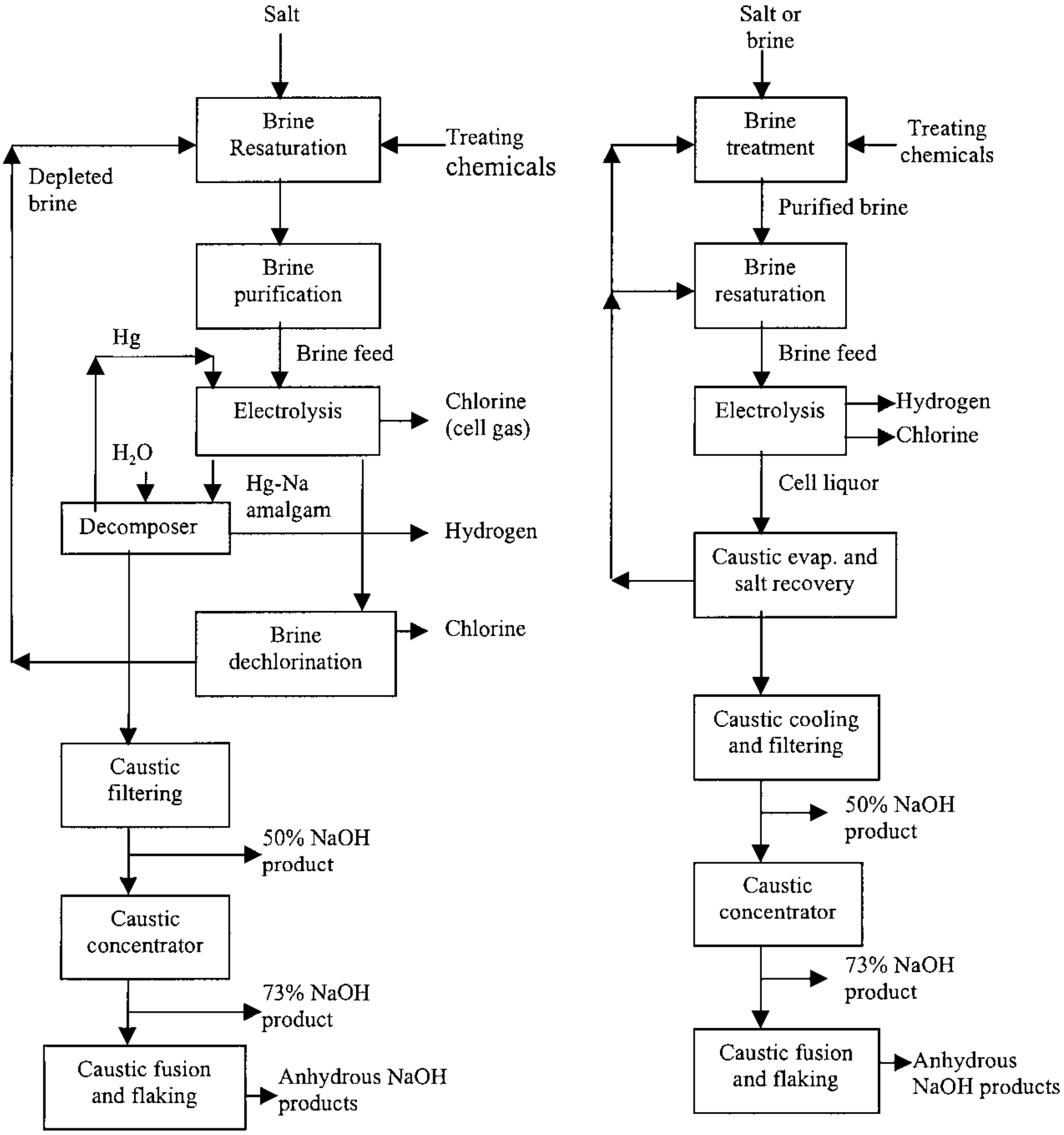
Diaphragm Cells. Chlor-alkali diaphragm cells produce chlorine and sodium hydroxide by electrolysis of saturated brine. A diaphragm is employed to separate the chlorine liberated at the anode, and the hydrogen and caustic soda produced at the cathode. Without the diaphragm to isolate them, the caustic soda and chlorine would react to form sodium hypochlorite, with further reaction to produce sodium chlorate.

Modern diaphragm cells employ vertical electrodes and a cathode-supported diaphragm. Asbestos is vacuum-deposited on the cathode to form the diaphragm, which separates the feed brine, or anolyte, from the caustic-containing catholyte. Purified brine enters the anode compartment and percolates through the diaphragm into the cathode chamber (Ref. 3).

In the diaphragm cell, saturated brine (ca 25 wt % NaCl) is decomposed to approximately half of its original concentration in a pass through the electrolyzer as compared to a 16 % decomposition of salt per pass in mercury cells.

Electrolytic decomposition of water and hypochlorous acid forms oxygen at the anode. When dimensionally stable anodes are used, oxygen leaves the cell with the chlorine. With graphite anodes some of the oxygen reacts with the graphite and/or the binder to form carbon dioxide. Particles of graphite break off, tending to plug the diaphragm, with a resulting gradual loss of diaphragm permeability. After 90 – 100 days of operation the diaphragm becomes inoperable and the asbestos must be replaced. Precipitation of calcium and magnesium hydroxides on the catholyte side of the diaphragm may also create blocking problems. Hydrochloric acid is added to the brine entering the anode compartment to neutralize back-migrating hydroxyl ions and to suppress formation of hypochlorous acid, both of which are damaging to graphite.

As in mercury cells, chlorine discharges from the anode compartment, together with small amounts of oxygen, carbon dioxide, and hydrogen. The catholyte solution discharging from the cell contains about 10% caustic soda and 14% sodium chloride (Ref. 3).



a) Mercury-cathode-cell operation **b) Diaphragm-cell operation**

Figure 2.8.1 Flow diagrams of electrolytic caustic production (Ref. 3)

Manufacture by Lime Soda Process. In the lime-soda process, a solution of sodium carbonate (soda ash) is treated with calcium hydroxide (slaked lime) to produce a precipitate of calcium carbonate and an aqueous solution of sodium hydroxide. The following equilibrium is set up:

$$Na_2CO_3 + Ca(OH)_2 \leftrightharpoons 2\,NaOH + CaCO_3 \qquad (2.8.1)$$

The above reaction never reaches completion but an equilibrium is set up. There are always some calcium hydroxide and calcium carbonate present in the solid phase, when the equilibrium state is attained.

$$Na_2CO_3 + Ca(OH)_2\,(\text{solid}) \leftrightharpoons 2\,NaOH + CaCO_3\,(\text{solid}) \qquad (2.8.2)$$

By the application of Law of Mass Action, we have (Ref. 5):

$$K = \frac{(2Na^+)^2(2OH^-)^2}{(2Na^+)^2(CO_3^{2-})} = \frac{(2OH^-)^2}{(CO_3^{2-})} \qquad (2.8.3)$$

From this, it is obvious that in order to have a high conversion, the soda ash solution should be dilute. The effect of initial concentration on % conversion is shown in figure 2.8.2.

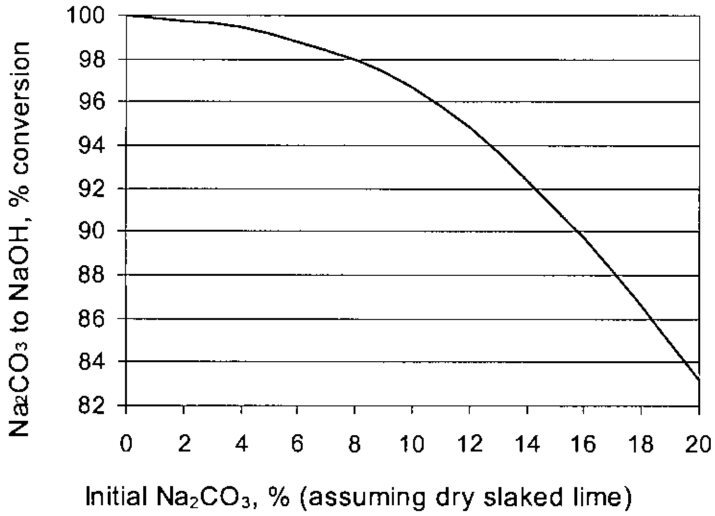


Figure 2.8.2 Causticization equilibrium (Ref. 3)

The heat of reaction is ΔH = 2100 cal which is not appreciable. The value of K and therefore, equilibrium is not materially altered by change in temperature. However, the rate of settling of calcium carbonate and the speed of reaction increase with the increase in temperature. In practice the reaction is carried out at the boiling point of the solution. Since the conversion is higher in dilute solution, a balance is struck between the additional fuel cost required to evaporate the more dilute solution and the advantages of higher conversion. In actual practice 11 to 12 per cent sodium carbonate solution is used (Ref. 1).

The process may be operated on a batchwise or a continuous basis. Figure 2.8.3 shows sheet of the process. Lime is used in lumps or as milk of lime. This is mixed with soda ash in the agitator in the desired proportion. This is mixed with wash water from a previous stage and agitated for two to three hours. The mixture goes to decanters to remove the precipitated calcium carbonate from the caustic soda solution. The slurry still contains some caustic and is subject to further washing and the washings being returned to the cycle again. The lime sludge practically free from caustic is reburnt or discharged (Ref. 5).

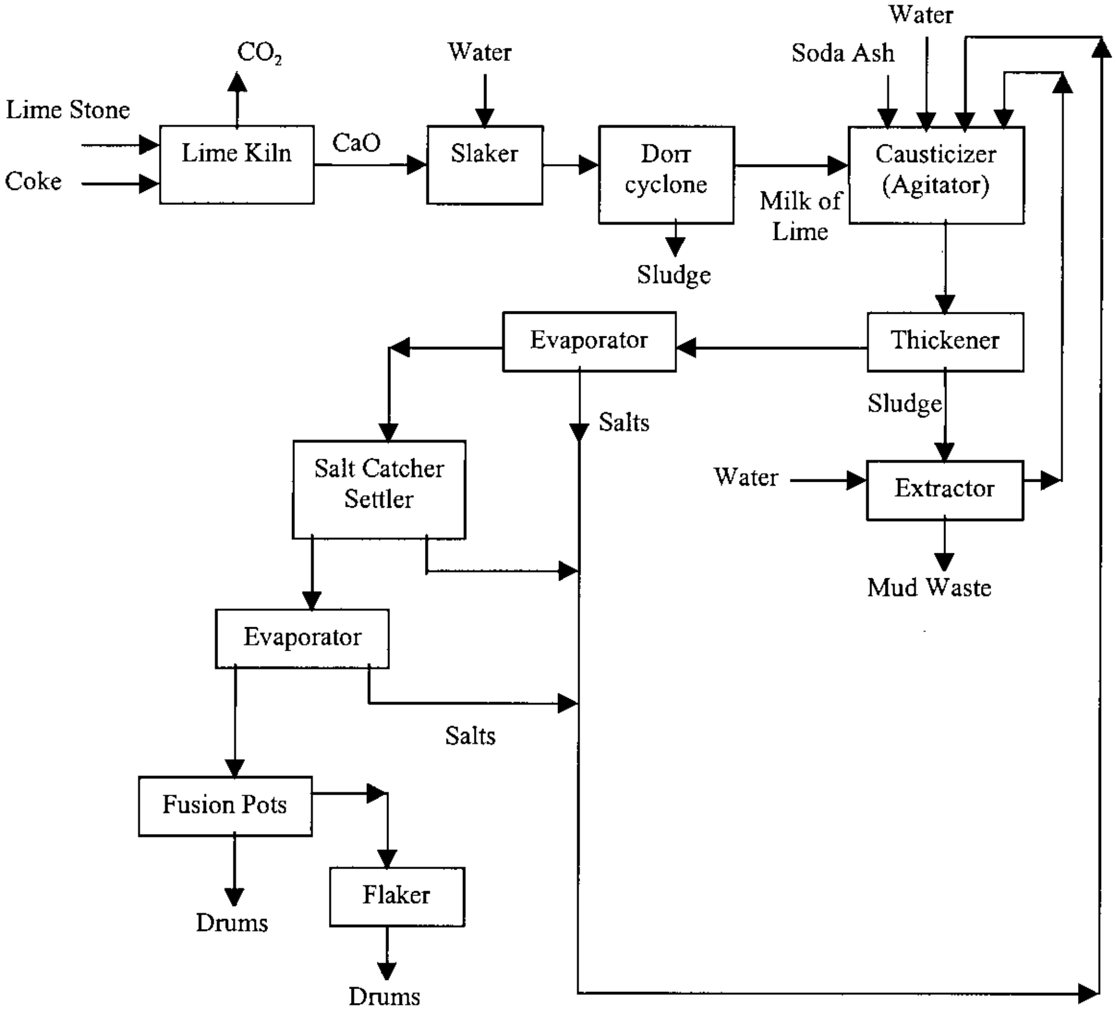


Figure 2.8.3 Flow sheet of a Caustic Soda Plant Producing Chemical Caustic (Ref. 5)

The ten per cent caustic solution from the decanter or thickener goes to the multiple effect evaporators, where it is evaporated to 50 per cent caustic soda. Impurities such as soda ash, salt, sodium sulfate separate out and are allowed to settle down before final removal. If caustic flakes are desired the solution is further concentrated to 75 per cent in a single effect evaporator and then in direct fired thick grained, cast iron pots. The product is sent to a flaker, where it is cooled to form flakes and packed in drums (Ref. 5)

In the batch process, the sodium carbonate solution from storage tank is run by gravity into the causticizer. The tank is provided with steam line to heat the liquor to 80° to 90°C. Compressed air is provided for agitation. The soda solution is adjusted to 10-11 per cent dilution. The tank is also provided with a mechanical agitator. Lime is added to a steel basket having perforated bottom which partially dips in the soda solution, in small lumps. Sometimes milk of lime is preferred to the lumps (Ref. 5).

After the desired amount of lime has been added and the equilibrium is reached as shown by titration, the liquor is allowed to settle for 1 to 3 hours. The clear liquor containing about 10 per cent caustic is drawn by a swing pipe. The lime sludge is washed with the washings of a previous batch, a number of such tanks being provided. The washing of the sludge is usually done counter current. The whole cycle takes about 16 hours (Ref. 5).

Continuous Dorr Causticizing Process. Figure 2.8.4 shows the flow sheet of the Dorr Continuous Process. The whole process consists in the application of Dorr agitator and Dorr thickener. Soda solution containing about 18 – 20 per cent of soda is mixed with either slaked lime or milk of lime in the first Dorr agitator. Usually three such agitators are used. Overflow from one agitator is fed to the second one and so on. They are set at different levels so that the solution runs by gravity (Ref. 5).

After agitating for about 1 hour, the solution is settled in thickeners, usually of the multitray design and consisting of two or three units in series. The overflow solution from the first thickener is run to the evaporators for concentration or is used as a finished product. The solution contains 10 to 12 per cent sodium hydroxide and is obtained at a conversion of 95 to 96 per cent based on sodium carbonate (Ref. 2).

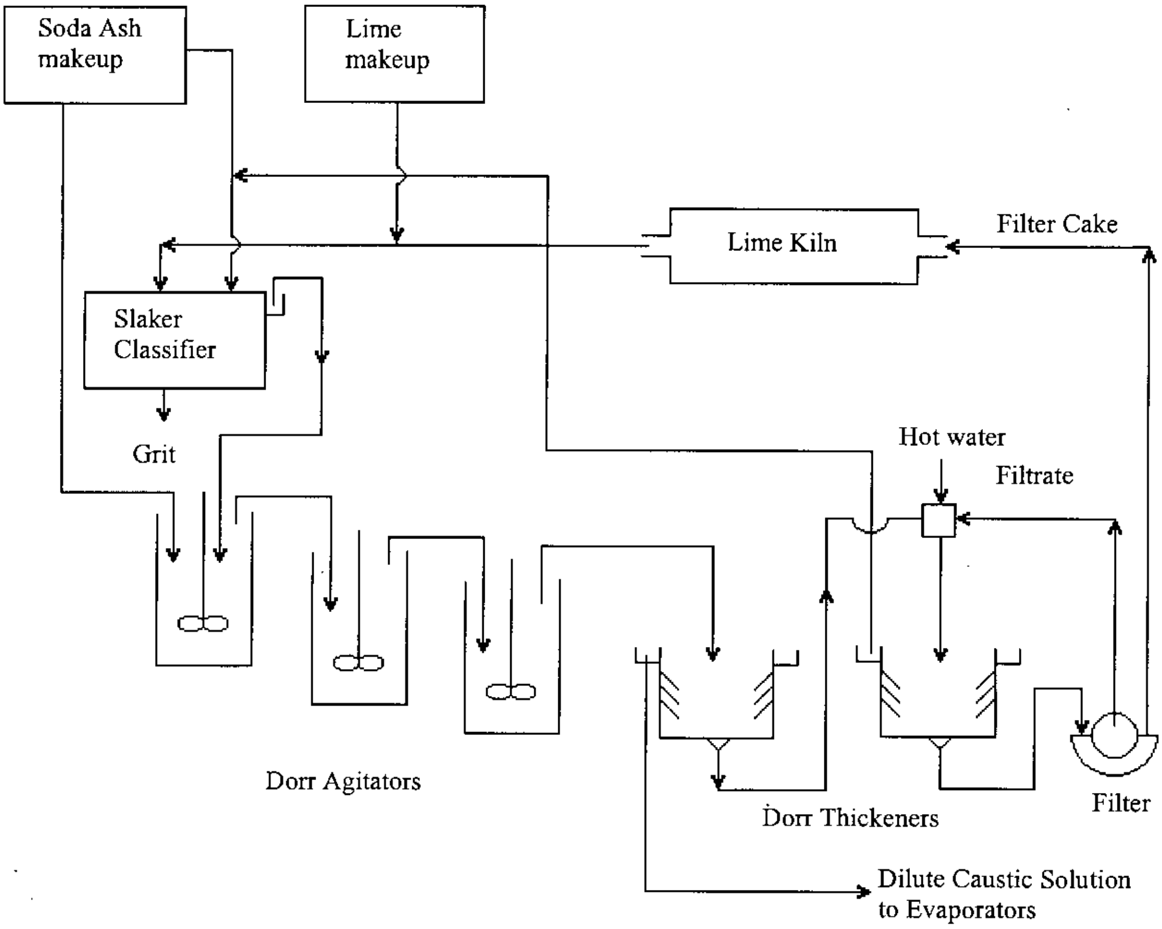


Figure 2.8.4 Continuous Causticizing Plant (Ref. 5)

The sludge from the bottom of the first thickener is pumped to a second thickener, where hot water and the filtrate from subsequent operation are added. The liquor overflowing from this thickener contains sodium hydroxide and carbonate in weak concentrations and is generally used as weak liquor to make up the original 20 per cent sodium carbonate solution. The sludge from the second thickener is filtered and washed. The filtrate is returned to the second thickener as mentioned, whereas the filter cake, which consists mostly of calcium carbonate, is sent to a lime kiln to furnish reburnt lime (calcium oxide). This material is fed along with the soda ash solution to a combination classifier-slaker, where milk of lime is formed and the grit removed to give the slurry, which is fed to causticizers to start the process (Ref. 2).

The clear liquor from the first thickener contains about 11 per cent sodium hydroxide and 1.7 per cent sodium carbonate. This weak solution is concentrated in multiple-effect evaporators to produce 50 per cent sodium hydroxide. As the concentration of sodium hydroxide increases, the sodium carbonate becomes less soluble and is finally precipitated so that the finished 50 per cent caustic soda solution contains only about 0.15 per cent sodium carbonate. After settling in another thickener, the clear solution is stored. The sludge from the bottom of the thickener is filtered on an Oliver filter; the filtrate is returned to the thickener. The filter cake, consisting mostly of unreacted sodium carbonate and whatever sodium chloride was present in the original soda ash, is returned to the causticizer. The 50 per cent sodium hydroxide solution is either sold from storage or concentrated further, as described previously (Ref. 2).

Chapter 3

Statement of the Objectives

Although lime-soda process for caustic production is a well-established process, literature does not give the exact operating conditions for industrial production. As has been mentioned previously this process is still attractive for small scale indigenous production of caustic for local market. So for the development of local expertise, the process parameters need to be studied. As a first step, laboratory scale production of caustic is necessary.

This work is an effort to investigate the parameters affecting the production of sodium hydroxide by lime-soda process using laboratory glass-wares. In particular, it is essential:

a) to study the effect of concentration on conversion,

b) to study the effect of temperature on conversion, and

c) to evaluate consequent separation problems, such as decantation and filtration,

d) and hence determine the optimum condition for caustic production.

As the quantitative effect of initial sodium carbonate concentration on conversion is given in literature, only the quantitative effect of reaction temperature on conversion was determined. Also the qualitative effect of reaction temperature on subsequent separation of product was studied. Experiments were performed using both analytical grade reagent and industrial (commercial) grade reagents and the optimum conditions for caustic production was determined.

Chapter 4

4.1 Experimental Setup

The experiment was carried out in a two liter three necked round bottom heat resistant glass flask. A stirrer was fitted through the central neck of the flask. The stirrer was driven by an electric motor whose speed was regulated manually by a variable transformer. A reflux condenser was fitted in one of the side necks, while a thermocouple was inserted into the remaining neck. Three rubber stoppers with holes drilled through their center for the passage of stirrer, condenser and thermocouple respectively were used to seal the openings of the flask.

The flask was heated by an electric heating mantle whose heating rate could be controlled by another variable transformer. The temperature within the flask was automatically regulated by a feedback temperature controller that sensed the temperature of the reacting mixture using the thermocouple and controlled the electric supply to the heating mantle by means of a cut-off switch. The temperature controller could be set at different desired temperatures for carrying out experiments at different temperatures. A laboratory thermometer was also used to check the temperature of the reacting mixture. Figure 4.1.1 shows a schematic diagram of the experimental setup, and Plate 4.1.1 is a photograph of the setup.

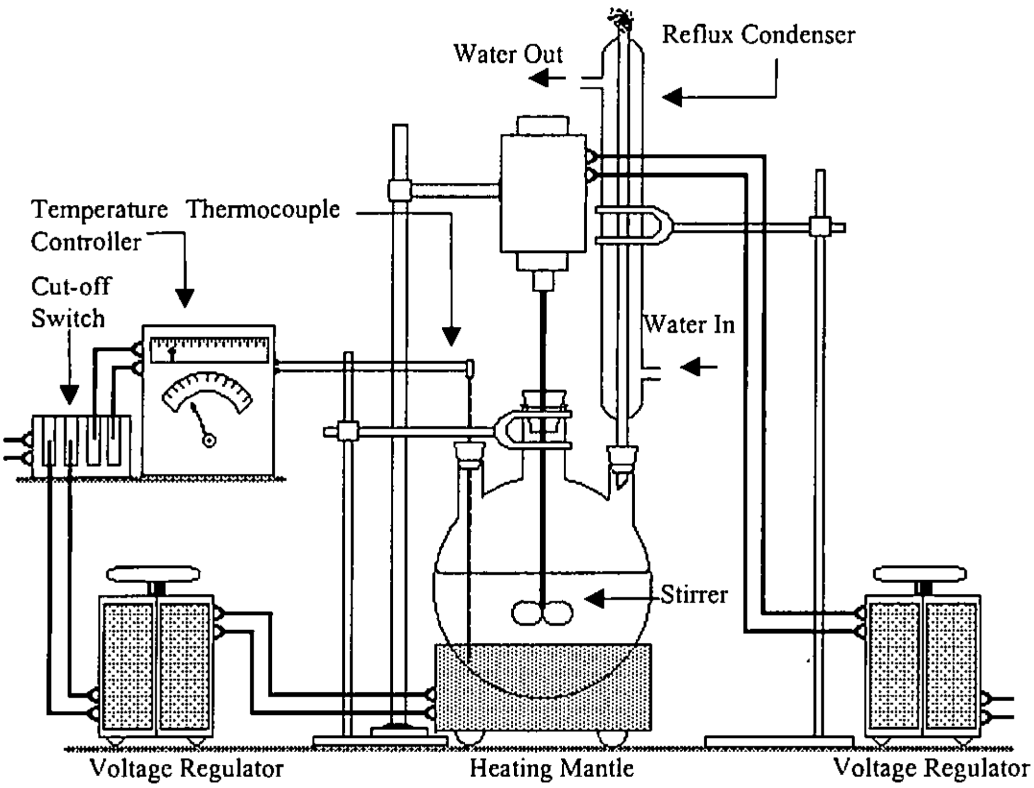


Figure 4.1.1 Schematic Diagram of Experimental Setup (Not to scale)

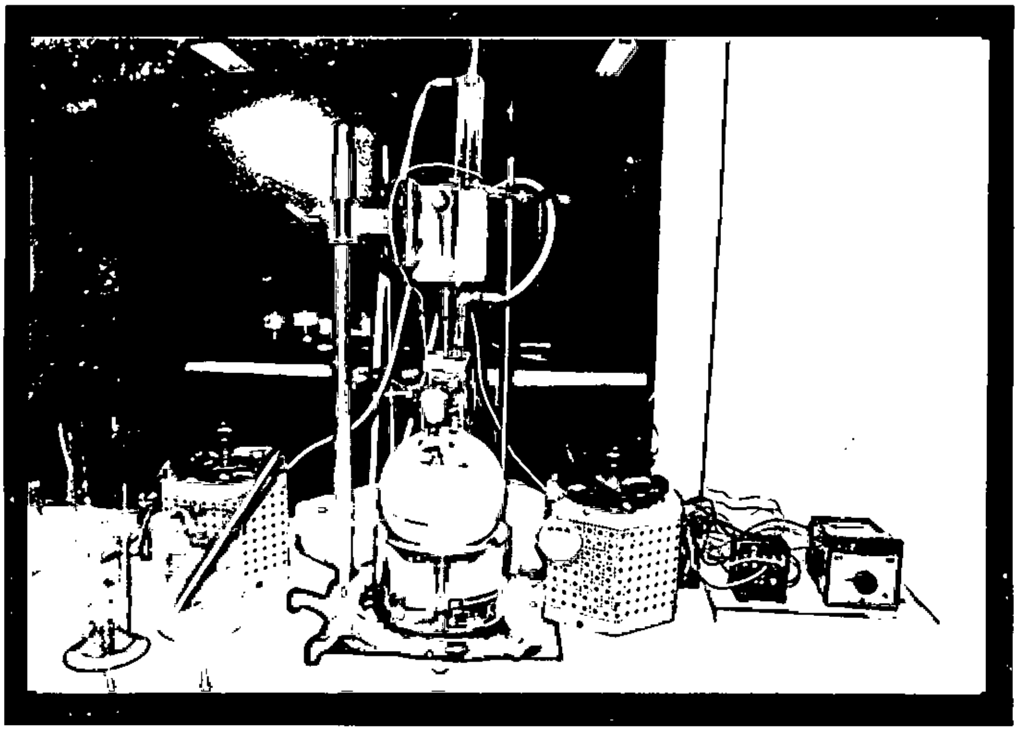


Plate 4.1.1 Photograph of the Experimental Setup

4.2 Experimental Procedure

125 g of anhydrous sodium carbonate was dissolved in 500 ml of hot water at the desired temperature in a beaker to make 20 % solution and poured into the three necked flask. The temperature controller was set at the desired temperature and switched on. Stoichiometric amount of calcium hydroxide was weighed and made into 20 % solution with hot water at the required temperature. The rubber stopper with the thermocouple was removed and the solution was poured into the flask. The thermocouple was reinserted and the stirrer switched on. After an hour the stirrer and heating mantle were switched off and the stirrer and thermocouple were removed from the flask.

The hot caustic solution was then filtered under vacuum. Any residue in the causticizing flask was washed with the filtrate and returned to the residue on the filter paper. Volume of filtrate was measured. The filtrate was then poured into a liter volumetric flask and diluted to one liter using distilled water. This was referred to as the stock solution.

The residue on the filter paper was washed with 500 ml distilled water and refiltered under vacuum. The filtrate was poured into a 500 ml volumetric flask and referred to as the wash solution. Plate 4.2.1 depicts the fitration setup.

Plate 4.2.1 Vacuum Filtration Setup

The amount of sodium hydroxide and sodium carbonate in both the stock and wash solutions were determined using standard titrimetric analysis as given in A.I. Vogel's "A Textbook of Quantitative Inorganic Analysis". First the total alkalinity due to the presence of OH^- and CO_3^{2-} ions in 10ml sample solution was determined by titrating with standardized hydrochloric acid (approximately 0.25N) using Methyl Orange indicator. Then the CO_3^{2-} ions of another 10ml sample were precipitated as $BaCO_3$ using excess barium chloride solution (0.25N). The remaining OH^- ions were determined by titrating with the standardized hydrochloric acid using Phenolphthalein indicator. The difference between the total alkalinity and that due to OH^- gave the amount of unreacted CO_3^{2-} ions present in the solution. Hence, knowing the initial amount of CO_3^{2-} taken (as sodium carbonate) the percent conversion was determined. Plate 4.2.2 shows titrimetric analysis being performed.

Plate 4.2.2 Titrimetric Analysis Setup

Chapter 5

5.1 Experimental Results and Observations

Two sets of experiments were carried out. In the first set, the effect of temperature on per cent conversion of sodium carbonate was determined using Analytical Grade reagents. The composition of the reagents are given in tables 5.1.1 and 5.1.2.

Table 5.1.1 Assay of Anhydrous Sodium Carbonate

Molecular Weight, M	105.99
Na_2CO_3	min. 99.5%
Loss of water on heating	Negligible
Chloride	< 0.005 %
Sulfate	< 0.01 %
Arsenic	< 0.0002 %
Iron	< 0.001 %

Table 5.1.2 Assay of Anhydrous Calcium Hydroxide

Molecular Weight, M	74.09
$Ca(OH)_2$	min. 96 %
$CaCO_3$	max. 3 %
Chloride	max. 0.005 %
Sulfate	max. 0.2 %
Iron	max. 0.05 %

125g of anhydrous Na_2CO_3 was dissolved in 500ml of distilled water to make the 20% solution in each case. 90.9g of anhydrous calcium hydroxide was dissolved in 364ml of distilled water to make the 20% solution. The experiments were carried out at temperature range of 60 to 100 °C, with one hour reaction time. Table 5.1.3 is a summary of the experimental results.

Table 5.1.3 Effect of Temperature on Conversion (Analytical Grade Reagents)

Temperature (°C)	% Conversion (Na_2CO_3 basis)	Conc. of NaOH Produced (wt.%)	Mass of dry Filter Cake (g)
60	90.5	8.5	126.2
70	92.3	9.1	125.6
80	93.1	9.2	126.7
90	93.4	9.3	126.5
100	92.1	9.7	126.3

Qualitative analysis of both stock solution and wash solution showed that there was no calcium present. So it is reasonable to assume that all the calcium remained in the filter cake. It is also assumed that only trace amount of sodium remains in the cake.

The second set of experiments were performed using commercial grade reagents. Although commercial grade anhydrous sodium carbonate was available in local markets, commercial grade anhydrous calcium hydroxide could not be found. Therefore, a drying test was performed on a batch of commercial slaked lime to determine the moisture content. Moisture content was found to be approximately 38%. For lack of analytical facilities to determine the exact concentration of impurities in the slaked lime, such as carbonate, iron, etc. it was assumed that the calcium hydroxide content was 60%. Therefore, 125g of commercial sodium carbonate (assumed approximately same composition as AR Grade) dissolved in 500ml of distilled water was reacted with 145.4g of commercial slaked lime mixed with 364ml water in this set of experiments for one hour. The results are summarized in table 5.1.4 below.

Table 5.1.4 Effect of Temperature on Conversion (Commercial Grade Reagents)

Temperature (°C)	% Conversion (Na_2CO_3 basis)	Conc. of NaOH Produced (wt.%)	Mass of dry Filter Cake (g)
60	75.6	6.9	107.0
80	79.0	7.3	106.3
90	82.0	7.9	108.0
100	79.6	7.5	108.0

It was also found that as the reaction temperature was increased it became easier to filter the reaction products and the clear caustic solution separated more easily from the insoluble precipitate if allowed to settle. Moreover, at higher temperature it was also easier to make the initial carbonate and lime solution. In case of lime, only the AR grade calcium hydroxide formed a solution at temperature above 80 °C while at lower temperature and for commercial slaked lime only a slurry could be formed. Also at higher temperature it was easier to pour the slaked lime solution than at the lower temperature.

5.2 Discussion

The effect of temperature on conversion can best be seen from graphical representation of the results as shown in figure 5.2.1. The results indicate that for maximum conversion of sodium carbonate to sodium hydroxide the reaction temperature of 90 °C is best.

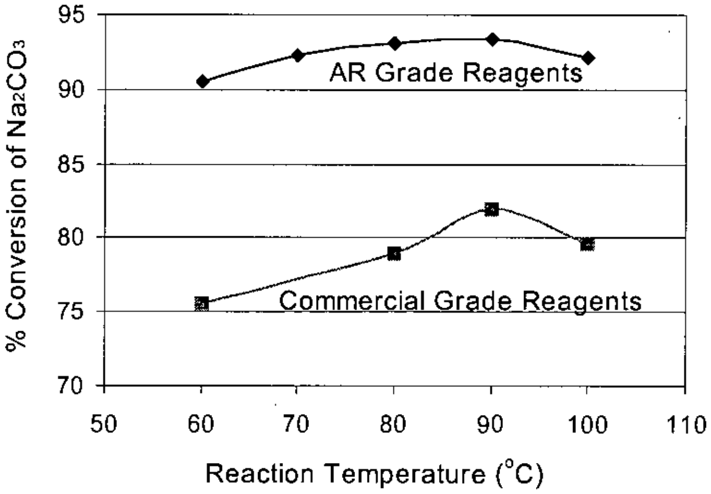


Figure 5.2.1 Effect of Temperature on Conversion (1 hr. reaction time)

The general trend of the curves is that at higher temperature the conversion is higher. This is to be expected from chemical kinetics as at higher temperature the rate of reaction would increase. As the reaction time was limited to one hour, it can be argued that at lower temperature the reaction rate is not fast enough to reach equilibrium within the time period. The parabolic nature of the % conversion curves can also be justified. As given in literature (Ref. 1, 3, 5), the equilibrium is dependent on the concentration of carbonate and hydroxide ions present. At 100 °C, loss of water from the reaction flask by evaporation is substantial and therefore the concentration of sodium carbonate does not remain at the 20% initial value poured into the flask but gradually increases. Although, efforts had been made to keep the flask sealed to prevent loss of water, it was not possible to make it perfectly air tight as a hole is required to insert the stirrer and there must be some clearance space for the stirrer to rotate. At a higher concentration of sodium carbonate the per cent conversion is lower than at a lower concentration as reported previously. Therefore the parabolic nature of the curves is justified.

The effect of temperature on conversion of the analytical grade reagents is less marked than that for the commercial grade reagents. This is because the AR grade calcium hydroxide formed a solution more easily than its commercial counterpart, and reactions between two solution phases is faster than that between solid-solution phases. At higher temperature the commercial grade lime went into solution faster as can be predicted from chemical kinetics and hence the reaction rate also increased. The shifting of the commercial grade reagents conversion curve to about 11% below that of the AR grade reagents' conversion curve is a result of the assumption of composition of the commercial grade reagents. As the amount of impurities like carbonate, iron, sulfate, etc. in the commercial slaked lime was not determined, the amount of the reagent used in the experiments was less than that required stoichiometrically. Therefore the calculated % conversion of sodium carbonate was less than the true result. However, whatever maybe the composition of the commercial grade reagents the general trend of the conversion curve is valid.

It must be noted that the temperature controller kept the reaction temperature within ±3 °C of the set point. Therefore the reaction temperatures are accurate only to ±3 °C of the stated vales.

5.3 Conclusion

From the experiments carried out it can be said that the optimum temperature for caustic production is about 90 °C using the lime-soda process. Also at this temperature the subsequent separation of the caustic from the calcium carbonate precipitate is easier than that at a lower temperature. While carrying out the reaction at lower temperature would decrease the cost of heating the solution, a lower conversion would make it costlier to separate the caustic from the unreacted carbonate. Also it would be more expensive to concentrate the more dilute caustic solution resulting from lower conversion.

An initial concentration of 20% sodium carbonate as used during these experiments is also recommended as the per cent conversion is reasonably high (82%) for commercial grade reagents. A lower concentration would increase the per cent conversion but would give weaker caustic solutions, which would be more expensive to concentrate.

5.4 Recommendation for Future Work

In the first step of the development of a process, laboratory scale work needs to be carried out. As this work has been done in this thesis project, the next logical step would be to set up a pilot plant to study the process. Also further work in the filtration separation of the caustic from the precipitated carbonate and the separation of the unreacted sodium carbonate from the caustic must to be done to better understand the process. Once these requirements have been fulfilled we would be in a position to develop our own plants using our acquired knowledge and operate them at optimum conditions.

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APPENDIX – A

Analytical Procedures

Determination of a mixture of Carbonate and Hydroxide. In the method used in this thesis the total alkali (carbonate + hydroxide) was determined by titration with standard acid, using methyl orange as indicator. In a second portion of the solution the carbonate was precipitated with slight excess of barium chloride solution and without filtering, the solution was titrated with standard acid using phenolphthalein as indicator. The latter titration gave the hydroxide content, and by subtracting this from the first titration, the volume of acid required for the carbonate was obtained.

$Na_2CO_3 + BaCl = BaCO_3$ (insoluble) $+ 2NaCl$

Procedure. A 10 ml sample of the stock or wash solution was taken using an accurately graduated pipette in a conical flask. The solution was titrated with standard 0.25 N-hydrochloric acid, using methyl orange as indicator. Two titrations were carried out that did not differ by more than 0.1 ml. This gave the total alkalinity (hydroxide + carbonate). Another 10 ml sample of the solution was warmed to 70 °C and 0.25 N barium chloride solution was slowly added from a burette in slight excess, i.e., until no further precipitate was produced. After cooling to room temperature, a few drops of phenolphthalein was added to the solution, and titrated very slowly and with constant stirring with standard 0.25 N-hydrochloric acid; the end-point was reached when the color just changed from pink to colorless. The amount of acid used corresponds to the hydroxide present.

This method yielded only approximate results because of the precipitation of basic barium carbonate in the presence of the hydroxide. More accurate results were obtained by considering the above titration as a preliminary one in order to ascertain the approximate hydroxide content, and then carrying out another titration as follows. 10 ml of the solution was treated with standard hydrochloric acid to neutralize most of the hydroxide, then heated and precipitated as before. Under these conditions, practically pure barium carbonate was precipitated. Then the titration was carried out as before.

APPENDIX B

Detailed Calculations

Experiment carried out at 100 °C (AR Grade Reagents).

Raw materials:	Na_2CO_3 = 125g,	dissolved in	Water = 500ml
	$Ca(OH)_2$ = 90.9g	dissolved in	Water = 364ml

Volume of stock solution = 750ml, made to 1000ml with distilled water

Volume of wash solution = 500ml.

Mass of dry filter cake = 126.3g.

Strength of standard $HCl_{(aq)}$ = 0.2504N

Table B1. Results for Titration of Stock Solution

Vol. of Stock Solution	Vol. of $HCl_{(aq)}$ (Methyl Orange)	Vol. of $HCl_{(aq)}$ (Phenolphthalein)
10ml	78.9ml	72.4

Table B2. Results for Titration of Wash Solution

Vol. of Stock Solution	Vol. of $HCl_{(aq)}$ (Methyl Orange)	Vol. of $HCl_{(aq)}$ (Phenolphthalein)
10ml	23.9ml	22.2

For 10ml of stock solution

Volume of acid required to neutralize OH^- and CO_3^{2-} = 78.9 ml

Volume of acid required to neutralize OH^- = 72.4 ml

Therefore, Volume of acid required to neutralize CO_3^{2-} = 6.5 ml

Na_2CO_3 unreacted in 10 ml of stock solution = 6.5 * 0.2504 = 1.628 meqv.

Na_2CO_3 unreacted in 1000ml stock solution = 162.76 meqv.

For 10ml of wash solution

Volume of acid required to neutralize OH^- and CO_3^{2-} = 23.9 ml

Volume of acid required to neutralize OH^- = 22.2 ml

Therefore, Volume of acid required to neutralize CO_3^{2-} = 1.8 ml

Na_2CO_3 unreacted in 10 ml of wash solution = 1.8*0.2504 = 0.451 meqv.

Na_2CO_3 unreacted in 500ml wash solution = 22.54 meqv.

Total Na_2CO_3 unreacted = 162.76 + 22.54 = 185.3 meqv

Total Na_2CO_3 taken = 125g = 2358 meqv

Total Na_2CO_3 reacted = 2172.7 meqv

$$\% \text{ Conversion of } Na_2CO_3 = \frac{2172.7}{2358} * 100 = 92.1\%$$

Concentration of NaOH in original stock solution

$$= \frac{72.4 * 0.2504}{10} * \frac{1000}{750} = 2.417 \text{ N}$$

$$\cong 2.417 * 40 \text{ g/lt} = 96.7 \text{ g/lt}$$

$$\cong 9.7 \text{ wt. } \%$$