RECOVERY OF CALCIUM CARBONATE

FROM 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

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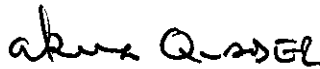
DEPARTMENT OF CHEMICAL ENGINEERING

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We, the undersigned, certify that **Syed Ahmad Imtiaz,** candidate for the degree of Master of Science in Engineering (chemical), has presented his thesis on the subject **"Recovery of Calcium Carbonate from Lime-Soda Process"** .The thesis is acceptable in form and content, and the student demonstrated a satisfactory knowledge of the field covered by this thesis in the oral examination held on the 30th August, 1999.
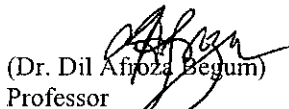
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ABSTRACT

Economy of the production of sodium hydroxide by lime soda process in the context of Bangladesh, depends largely on the recovery of a good quality $CaCO_3$ from the sludge formed during the causticization reaction:

$Ca(OH)_2 + Na_2CO_3 = 2NaOH + CaCO_3$. However, there is no published information available on the recovery of $CaCO_3$ from the sludge. The present study aims to develop a process scheme for the recovery of $CaCO_3$ from this sludge. Furthermore, it was planned to study the effect of lime quality on the optimum reaction time for causticization of soda ash, settling time for the slurry from causticization, and characteristics of the recovered calcium carbonate. Effect of the temperature on the drying time for the recovered $CaCO_3$ cake was also studied.

Causticization of soda ash solution was carried out in laboratory scale with three different grades of lime at 90°C and atmospheric pressure. The three grades of lime were designated as AR grade, Analytical grade and Commercial grade lime containing 96%, 90% and 59% $Ca(OH)_2$ respectively. To gain an understanding of the optimum time for reaction, conversion data as a function of time for reaction were obtained. The optimum reaction time for all three grades of lime was approximately 2 hours, while percent conversion depended on the purity of the lime and varied from 75 to 80 percent.

Study of the settling behavior of the slurry from causticization reactor revealed that settling of slurry from commercial grade lime was completed after 80 minutes, while that from analytical grade lime required more than 3 hours.

Conventionally in lime soda process after causticization caustic soda solution is recovered by decantation and filtration and the filter cake containing $CaCO_3$ is reburnt to recover $Ca(OH)_2$ for the process. For making the process economically feasible a scheme was developed for the recovery of $CaCO_3$ from the filter cake. The scheme basically utilizes recovery stages. Each recovery stage consists of washing of filter cake with water, further causticization by heating half an hour and subsequent vacuum filtration. It showed that including up to three recovery stages the conversion of lime to sodium hydroxide increased and at the same time the alkalinity of the recovered $CaCO_3$ decreased.

Drying data for the finally recovered $CaCO_3$ cake were obtained in the temperature range 120°C to 220°C. At 120°C drying completed after 2 hours while at 220°C it took only 30 minutes to dry the filter cake. Color of the $CaCO_3$ was observed visually. No appreciable discoloration was noticed within this temperature range. It was evident that the color of the recovered $CaCO_3$ is purely dependent on the color of the lime which is used for causticization.

Finally characterization of the recovered $CaCO_3$ was done. Carbonate content of the recovered $CaCO_3$ from commercial grade lime is 87% and impurities in this powder is 10.5%. The pH of the saturated solution of this $CaCO_3$ is 10.2. This product may find use as filler in plastic and rubber industries.

ACKNOWLEDGEMENTS

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CHAPTER – ONE

Introduction
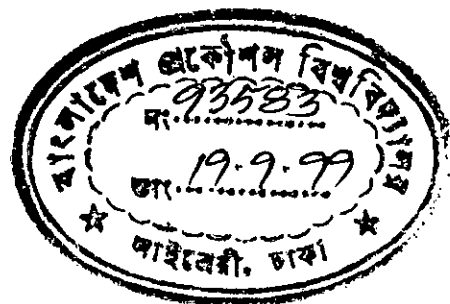
Caustic soda is one of the most extensively used alkalis in industries. Industrially caustic soda is produced by chemical process and electrolytic process.

The chemical process is the classical method of caustic production. Since shortly after the development of LeBlanc synthetic soda ash process in the early 18th century caustic soda was produced by reacting soda ash with lime. With the invent of electrolytic method the importance of lime-soda process began to decline. As the demand for chlorine, a byproduct of electrolytic process, increased lime-soda process could hardly compete with electrolytic process. Since 1968, in the United States caustic soda for sale has been produced exclusively by electrolysis, caustic soda is produced from soda ash only in isolated areas throughout the world. However, considering the high initial investment cost, high price of power and the need to use very pure brine solution for membrane cell there is a renewed interest in lime soda process for small scale production. This is verified by the fact that recently in Bangladesh a company has setup a plant for commercial production of caustic soda based on the lime-soda process.

The profitability of lime-soda process largely depends on the efficient recovery of calcium carbonate as shown in the profitability analysis in appendix A.7. Although lime-soda process is an established one, but the main objective has been to attain

increase of yield of caustic soda and in most cases the sludge from lime soda process was burnt to recover lime. Hence, the sludge from the lime soda process did not receive much attention. White color, low alkalinity, freedom from harmful impurities and nonabrasiveness are some of the prime requisites of $CaCO_3$ for use as a whiting and filler. For the indigenous development of lime soda process the recovery steps need to be studied.

CHAPTER – TWO

LITERATURE REVIEW

2.1 Introduction

Calcium carbonate occurs in nature as limestone. Depending on the requirement, ground limestone is sometimes directly used as whiting and filler. It is also used for production of lime. Purity and quality of these products depend mostly on the quality of the limestone. A detailed study of the geology, occurrence and mineralogy can reveal many important aspects. Of the processes for producing precipitated calcium carbonate, lime-soda process deserves some importance from our country's perspective. Much study has been done in the operating conditions of lime-soda process. The dominant objective being production of caustic soda, the causticization sludge did not receive much attention. Nevertheless, these studies have paved the way for making the present study.

This review includes geology, occurrence and mineralogy of limestone, production of lime, different production processes of calcium carbonate, and a detailed description of different studies made on the operating conditions of lime- soda process.

2.2 Limestone

Limestone is one of the most basic raw materials of industry and construction. The annual world production is incalculable but has been estimated at 2×10^9 metric tons in 1970s(Ref.3).

2.2.1 Classification of Limestone

Limestone may be classified according to origin, chemical composition, texture of stone and geological formation. Chemically it is composed primarily of calcium carbonate, $CaCO_3$, and secondarily of magnesium carbonate, $MgCO_3$, with varying percentages of impurities. Limestone is generally classified into the following three types:

(i)   **Calcite:** The carbonate content is essentially calcium carbonate with no more than 5% magnesium carbonate. Calcite that is fire white can be used in the manufacture of calcium carbonate pigment. Another variety that is off white, despite excellent chemical purity, is of little or no significance in the manufacture of pigments.

(ii)   **Magnesian:** This contains both carbonates with a magnesium carbonate content of 5-20%.

(iii)   **Dolomite:** Magnesium carbonate content of this rock is over 20% but not more than 45.6%, with the balance $CaCO_3$. It has no significance in the manufacture of pigments.

Similarly, limes calcined from these stone types are identified as high calcium, magnesian and dolomitic limes.

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2.2.2 Geology:

Limestone, as a constituent of earth's crust, is a rock of sedimentary origin from material precipitated by chemical and organic action on drainage water. Calcium is a common element, estimated to comprise 3-4% of the earth's crust, and the calcium constituent of limestone have come originally from igneous rocks. By the action of various eroding and corroding forces, including the solution of carbonic and other mineral acids, the rocks are disintegrated and calcium is dissolved and removed in the drainage water emptying into the sea. The amount of material removed in this manner is astonishing. It is estimated that Thames River in England annually carries more than 550,000 metric tons of dissolved materials, of which approximately two thirds is calcium carbonate(Ref.3). This represents the removal of about 62 MT of limestone per square kilometer from the drainage area involved.

Upon reaching the ocean, some of the dissolved calcium carbonate may be reprecipitated because of its lower solubility in the sea. Surface evaporation and temperature changes may reduce the carbon dioxide content of the water, causing precipitation of calcium carbonate from saturated conditions. By far the largest portion of the limestone in existence today is of organic origin formed through skeleton building processes of marine life. The lime remaining in solution following chemical precipitation is utilized by many different varieties of sea lives, such as corals, foraminifera, mollusks, chara and echinoderms to form shells and skeletons, which ultimately accumulate on the sea bottom.

The skeletal structures are almost pure calcium carbonate and are frequently found intact in such limestone as chalk and marl.

The calcareous sediment produced in either manner may become contaminated during deposition with argillaceous, siliceous, or ferruginous silts, which affect the chemical composition and nature of the resulting limestone. The size and shape of the calcareous particles, together with conditions of pressure, temperature, and solvent action to which a deposition is subsequently exposed, are factors that influence the physical characteristics of the stone.

The origin of magnesian and dolomitic limestone is uncertain; it is generally believed and considerable evidence supports the theory that, it is formed by direct chemical replacement of the calcium in the limestone by magnesium from waters high in magnesium salts. Several small deposits of dolomite appear to have originated through the coprecipitation of both carbonates. Ultimately land upheavals or recession of the oceans left the deposit as part of the land mass(Ref.1).

2.2.3 Impurities:

The chemical composition and properties of lime and limestone depend upon the nature of the impurities and degree of contamination of the original stone.

Alumina in combination with *silica* is present in limestone chiefly as clay, though other aluminum silicates in the form of feldspar and mica may be found. When present in appreciable quantities, on calcination, yield limes with hydraulic properties. Limestone containing 5-10% clayey matter yield feebly hydraulic limes, those containing 15-30% produce highly hydraulic limes Ref.3). Siliceous matter other than clay may occur in the

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free state, as sand, quartz and flint, in the combined state as feldspar mica, talc and serpentine. Metallurgical and chemical limestone should contain less than 1% alumina and 2% silica.

Iron compounds, normally are in the form of limonite ($Fe(OH)_3$) and pyrite (FeS_2). Occasionally, hematite, magnetite, marcasite and other forms of iron are found in limestone.

Sodium, potassium, sulfur and *phosphorus* compounds are rarely present in any extent in limestone and volatilize during burning. Sulfur and phosphorus compounds are objectionable impurities in chemical lime and limestone.

Analyses of typical sample of high-calcium, magnesian and dolomitic limestone found in United States are listed in Table 2.2.1.

2.2.4 Physical Properties of Limestone and Limes

The chemical and physical properties of limestone vary tremendously, owing to the nature and quantity of impurities present and the texture. These same factors exert a marked effect on the properties of limes derived from diverse stone types. In addition calcination and hydration can profoundly influence the properties of lime. Therefore many of the characteristics assume a range of values.

Color: The purest form of calcite and magnesite are white, often with an opaque cast, but most conventional limestone, even relatively pure types, are gray or tan. The presence of carbonaceous impurities can render the grays dark, even approaching black. The presence

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of iron influences the tan, brown, pink, and buff colors of some limestone. Impurities, such as pyrite, marcasite and siderite may alter the surface color through weathering.

Quicklime is usually white of varying intensity, depending upon chemical purity; some species possess a slight ash-gray, buff or yellowish cast. Invariably quicklime is lighter in color than limestone from which it is derived. Hydrated lime except for hydraulic and impure hydrates, are extremely white in color, invariably whiter than their quicklime.

Odor: Except for highly carbonaceous species, most limestone is odorless. Quick and hydrated limes possess a mild characteristic odor that is difficult to describe except that it is faintly musty or earthly but not offensive.

Table 2.2.1 Analyses of different types of limestone found in US

	Calcite	Magnesian	Dolomite
CaO	54.54	45.65	31.20
MgO	0.59	7.07	20.45
CO_2	42.90	43.60	47.87
SiO_2	0.70	2.55	0.11
Al_2O_3	0.68	0.23	0.30
Fe_2O_3[c]	0.08	0.20	0.19
SO_3[d]	0.31	0.33	
P_2O_5		0.04	
Na_2O	0.16	0.01	
K_2O		0.03	
H_2O		0.23	
Other		0.06	

Solubility: High calcium limestone is only very faintly soluble; in cold CO_2-free water it is often regarded as insoluble. Between 17 and 25°C, its solubility is only 14-15 mg/L. As temperature increases so does the solubility until at 100°C solubility increases to 30-40 mg/L. This faint solubility at elevated temperature accounts for the accumulation of primary $CaCO_3$ in steam boilers. Carbondioxide exerts a mild solvent action on $CaCO_3$ and increases its solubility in direct proportion to the increase of CO_2 pressure

There are no solubility values for quicklime because the oxide is hydrated to its hydroxide before dissolving. Contrary to limestone in CO_2-free water, the solubility of hydrate is in inverse proportion to temperature, decreasing with rising temperature. Figure 2.2.1 displays how temperature changes influence lime's solubility. Although data on the solubility of magnesium hydroxide are discordant, the solubility is extremely faint. On an equivalent basis this is about one-hundredth the solubility of $Ca(OH)_2$.
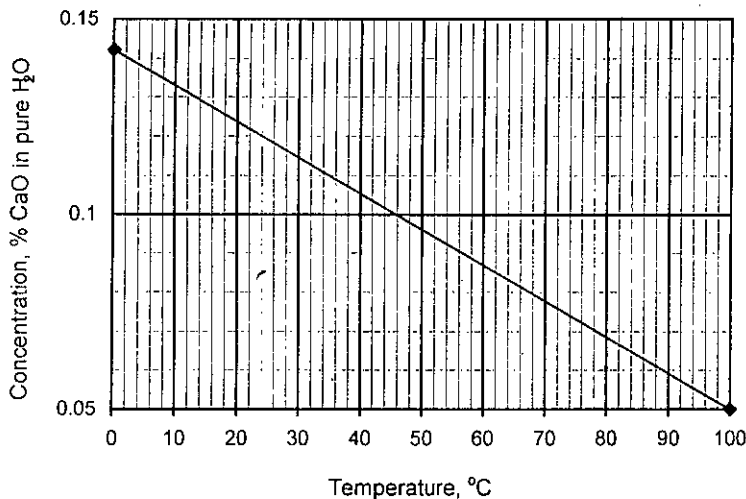
Fig.2.2.1 Solubility of lime in water(Ref.3)

2.3 Preparation of Lime

Limestone is first calcined to calcium oxide. Then water is added to this calcium oxide to form either hydrated lime or milk of lime.

Calcination of Limestone: Lime burning consists in driving out carbondioxide gas from limestone by heat. This occurs at a comparatively high temperature, because the decomposition absorbs heat. The thermochemical equation is:

$$CaCO_3 \rightarrow CaO + CO_2; \Delta H = 42900 \text{ cal.}$$

The heat of decomposition is 41,000 cals per mol of $CaCO_3$. Although theoretically a temperature of $898^{o}C$ is sufficient to decompose limestone with one atmosphere of CO_2 vapor pressure, the rate of dissociation is slow.

The temperature at the decomposition zone is nearly $1050^{o}C$ under kiln condition. Sometimes the temperature rises as high as $1200^{o}C$. At these high temperatures the structure changes and the grains of calcium oxide breakup into a number of smaller spherical particles. Upon holding at such temperatures, the size of the grains increases while their number diminishes. This dense lime presents less surface and requires a much longer time for dissolving. Such lime is called over burnt or dead burnt lime. Besides giving slow reaction rate it may cause difficulties by lowering settling rate in the causticizing operation. Properly burnt lime is practically cream white and readily hydrated to loose, pure-white powder.

Hydration of Lime: Lime is comparatively an active base. Hydrating consists in converting the oxide to hydroxide by adding just enough water to the lump so that the

mass disintegrates and turns white, but does not become pasty or wet. The thermo-chemical equation for hydration of lime is:

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s); \qquad \Delta H = - 15,540 \text{ cal.}$$
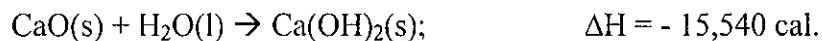
Various types of machines called hydrators have been designed for hydrating the lump lime. Two types of hydrators are commonly used in industries .First one, *Kritzer type*, consists of sections of stationary cylinders, one on top of another with a rotating screw ribbon in each cylinder. Second type, *Schaffer hydrator*, consists of a number of shelves placed one on top of the other with revolving rabbles on them.

Lumps of lime are charged onto the top and a small excess of water over the theoretical quantity necessary to form $Ca(OH)_2$ is sprinkled over them. The stirring action helps to distribute the water and scrape the lime along. Finally the hydrated lime is discharged through the bottom.

Milk of Lime: Lime is so sparingly soluble that its solution would be too dilute for general purpose. Therefore it is introduced usually in the form of a suspension called milk of lime. In milk of lime there is an equilibrium between the solid lime and the lime that has gone into solution, small as it is. The amount dissolved is again in equilibrium with the calcium and hydroxide ions in solution. Thus,

$$Ca(OH)_2 \Leftrightarrow Ca(OH)_2 \Leftrightarrow Ca^{++} + 2OH^-$$

(Solid)   (diss.)

As the reaction goes on (i.e. say as the OH⁻ ions are used up) more $Ca(OH)_2$ dissociates and in turn more $Ca(OH)_2$ dissolves(Ref.2).

2.4 Production of Calcium Carbonate

Calcium carbonate powder is produced by two processes; Natural process and Precipitation method. These are described in the following sections.

2.4.1 Natural Process:

In this process good quality limestone are ground for manufacturing calcium carbonate. The limestone used to make natural calcium carbonate must be carefully selected to assure good color and a minimum of metallic or abrasive impurities. In some instances physical or chemical beneficiation or both is used to upgrade the feed stone for the grinding mills. The processes for making natural calcium carbonate suitable for paper coating are shown in Fig. 2.4.1.
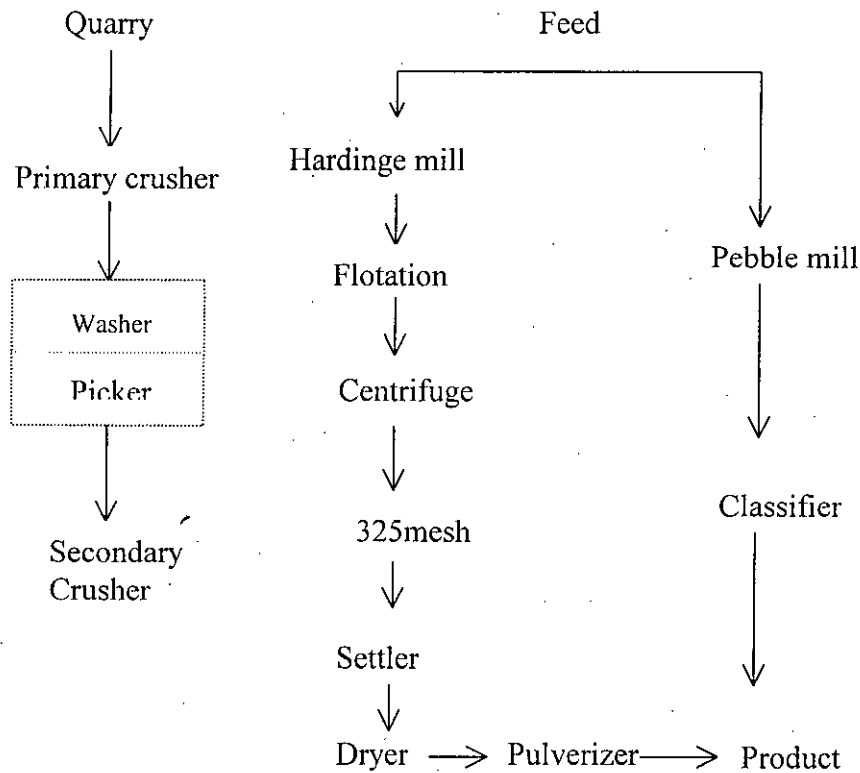
Figure 2.4.1 Processing steps for producing fine ground
limestone by the natural process (Ref.1)

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The finest product from either the wet or dry system are 99.5 percent finer than 15 µm with a mean particle size of approximately 2.5 µm. The U.S. paper coating industry refers to this product as fine-ground limestone (FGL). Two other grades intermediate-fine-ground limestone (IFGL) and ultrafine-ground limestone (UFGL) are also sometimes referred. Both of these products require more intense grinding than does FGL.

2.4.2 Precipitation Method

In all processes for making precipitated calcium carbonate, limestone is first calcined in a kiln bringing about decomposition into carbon dioxide gas and quicklime. The quicklime (CaO) or in some instances, lime hydrate [$Ca(OH)_2$] is given a rough screening before being slaked with water to form milk of lime. The purity activity, particle size, concentration and temperature of the milk of lime have a pronounced effect on the physical properties of the end product . Production of precipitated calcium carbonate by different methods is also referred in literature (Ref.1) as recarbonation of lime. The recarbonation of lime is done by the following three processes:

- Carbonation method ,

- Lime-soda process.

- Calcium chloride-sodium carbonate double decomposition method.

The processing steps of these three methods for producing precipitated calcium are shown in Fig. 2.4.2
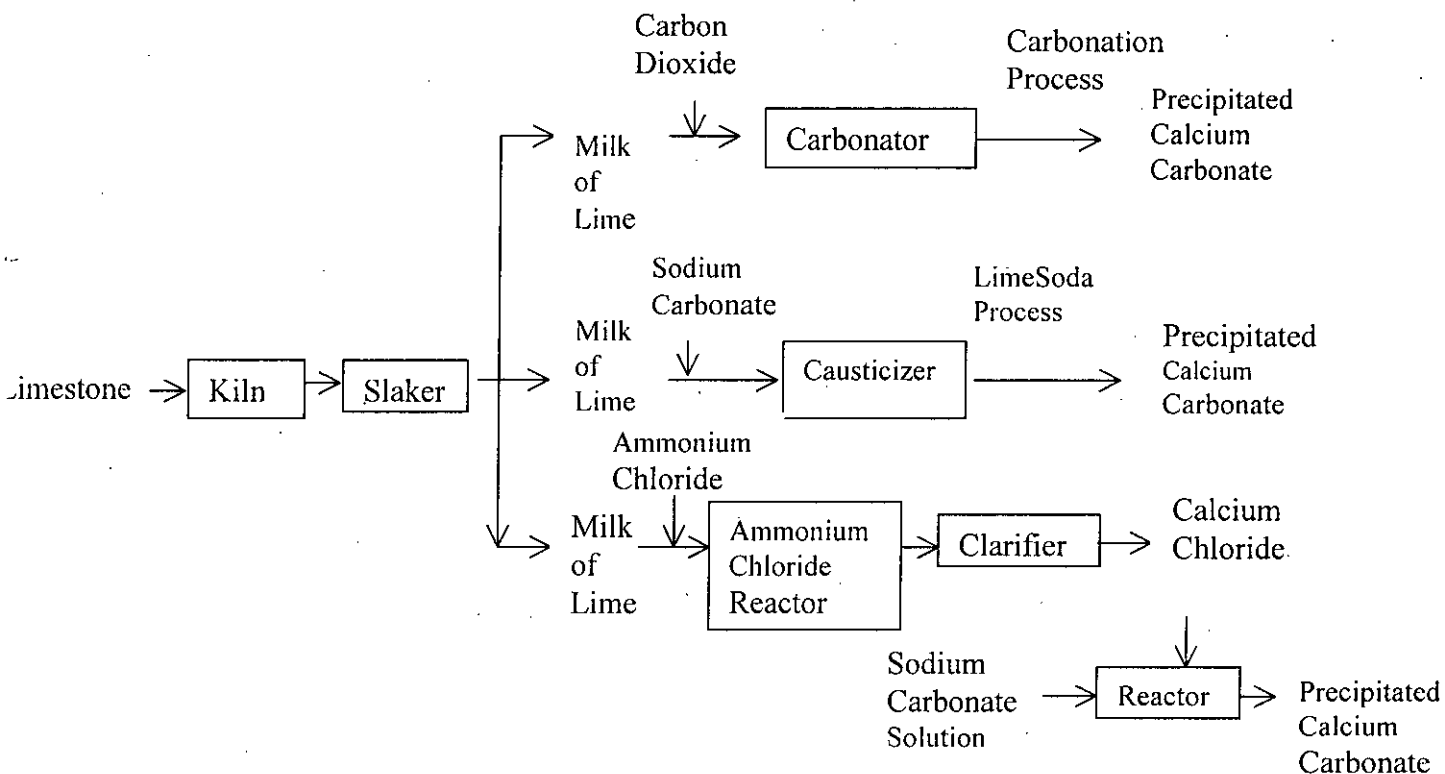
Fig.2.4.2 Processes used for making precipitated calcium carbonate(Ref.1)

2.4.2.1 Carbonation Method:

This is the most common method used for production of calcium carbonate powder. In the carbonation process the kiln gas is bubbled through the milk of lime. Carbon dioxide and milk of lime react according to the following reaction:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$
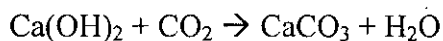
The simplicity of the chemical equation belies the complexity of the reaction.

The main focus of the process is on control of physical features of the precipitated calcium carbonate. The particle shape and size are determined by the reaction conditions, which include variables such as:

a) Concentration

b) Starting temperature

c) Temperature profile

d) Type and degree of agitation

e) pH

f) Solution rates

g) Auxiliary materials added.

Of the three processes for producing precipitated calcium carbonate, this is the most complex one(Ref.1). However, it is most widely used because it uses the most readily available and lowest cost raw materials.

2.4.2.2 Lime-Soda Process

In lime-soda process, sodium carbonate and milk of lime are reacted to produce sodium hydroxide and calcium carbonate according to the following reaction:

$$Ca(OH)_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaOH$$
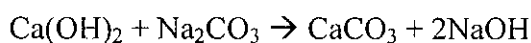
Here also the physical properties of the final calcium carbonate are determined by the reaction condition. This reaction is commonly known as causticization reaction. The dependence of causticization on different parameters are described below.

Causticization Equilibrium: The equilibrium of causticization reaction depends upon the low solubility product of Ca^{++} and CO_3^{2-} ions causing the removal of solid $CaCO_3$ from solution. As the reaction proceeds, the concentration of sodium hydroxide increases. This increase, by common-ion effect, greatly decreases the solubility of calcium hydroxide until ultimately it is no more soluble than calcium carbonate and the following equilibrium is set up:

$$Na_2CO_3 + Ca(OH)_2(s) \Leftrightarrow 2NaOH + CaCO_3(s)$$
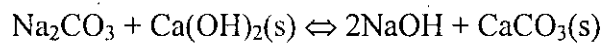
Thus equilibrium is reduced to that between sodium carbonate and sodium hydroxide. Therefore,

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

By substituting the solubility product of $Ca(OH)_2$ and $CaCO_3$ and rearranging the final expression obtained is:

$$\frac{\left(2OH^-\right)}{\left(CO_3^{2-}\right)} = \frac{K'}{\sqrt{CO_3^{2-}}}$$

where K' is the square root of K. This mathematical expression of equilibrium

reveals the more dilute the soda solution, the higher will be the conversion percentage(Ref.2). The effect of initial concentration on percentage conversion is shown in Fig. 2.4.3.
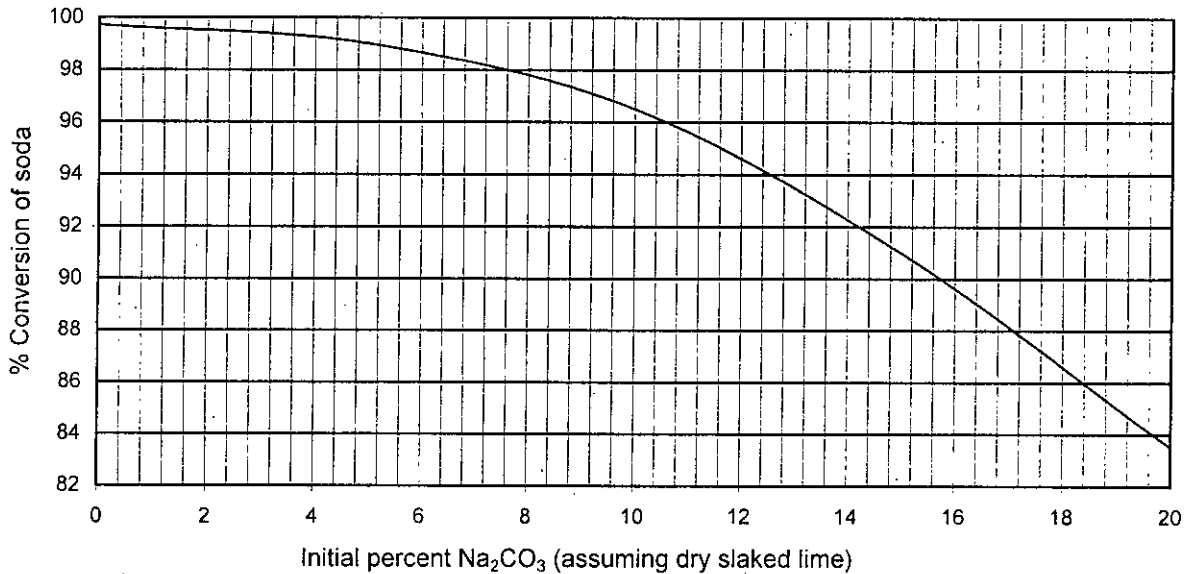
Fig.2.4.3 The causticization equilibrium (Ref.2)

Since the conversion is higher in dilute solution, a balance is stuck between the additional fuel cost required to evaporate the more dilute solution and the advantage of higher conversion. In actual practice 11 to 12 percent sodium carbonate solution is used.

Conversion as a Function of Temperature: The effect of temperature on conversion had been studied by Mannan (Ref.5). Experiments were carried out with two different grades of lime, namely analytical grade with more than 96% $Ca(OH)_2$ and commercial grade with approximately 60% $Ca(OH)_2$ were used for causticization. The results of the experiments are graphically represented in Fig. 2.4.4 It shows conversion is highest around 90°C.
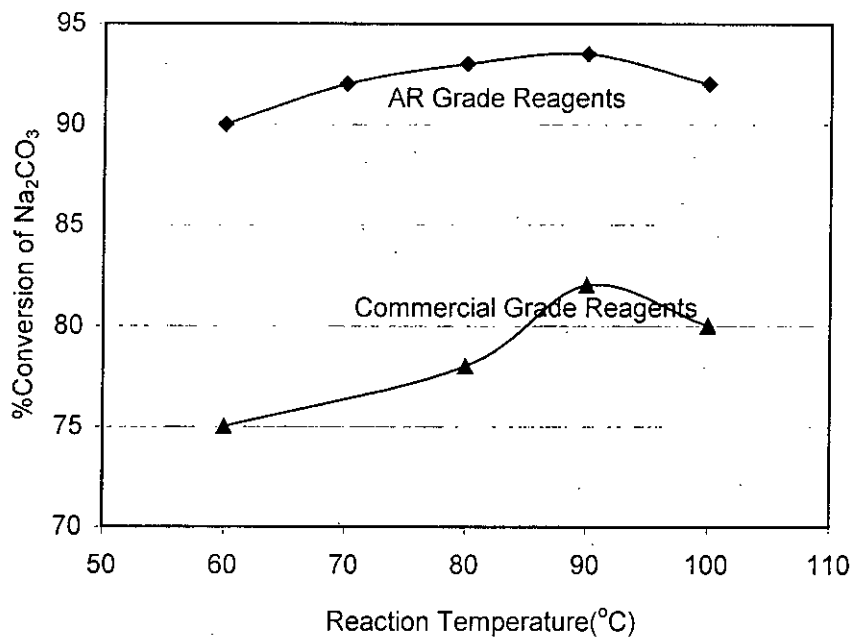
Fig.2.4.4Effect of Temperature on Conversion(Ref.5)
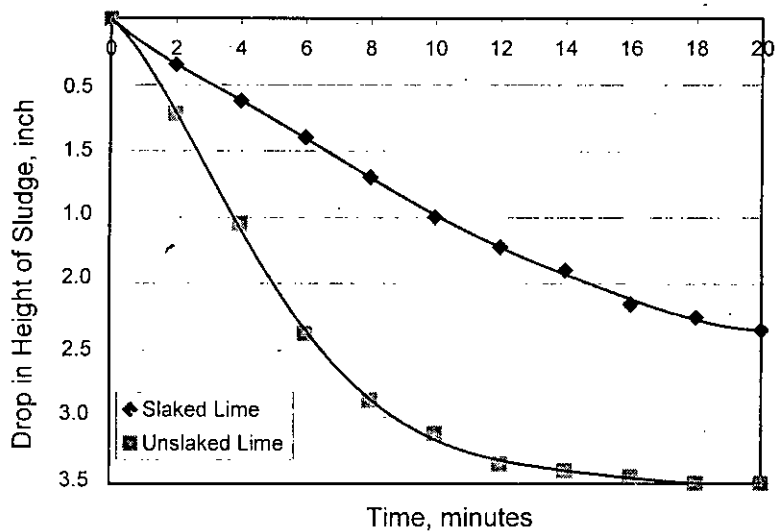
Figure 2.4.5. Settling Curve after Causticization with
Slaked and Unslaked Lime(Ref.4)

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Effect of Lime Quality on Conversion and Settling of Slurry: The percentage conversion for slaked lime is higher than unslaked lime for identical condition(Ref.4). However, the free settling rate shows a reverse trend. Settling curves for slaked and unslaked lime are shown in Fig.2.4.5

Batch Causticizing Process: Soda solution is made up in storage tanks at a specific gravity of 1.13 This solution is causticized in large tanks with flat bottoms. Steam is used to heat and a compressed air line is provided for agitation. There is also arrangements for mechanical stirring. Lime is added in lumps or as milk of lime(Ref.2).

After sufficient lime has been added and the desired conversion level attained the liquor is allowed to settle for about 2 hours. The clear portion is drawn off through swing pipe. This gives lye containing about 10 percent sodium hydroxide. The lime sludge, with whatever lye remains, is washed with the third liquor from a previous batch, the stirrer is started and the liquor heated with steam. After settling, this gives the second liquor that may be added to the lye tank. This slime is again washed with the fourth liquor in a similar way; this gives the third liquor, which is used for second washing and also for making soda solution for causticization. Finally the slime is further washed with fresh water, giving the fourth liquor.

This washed slime containing a little alkali that remains, is washed out and sent to waste. A batch of causticization can be made in every 2½ to 3 hours; but this, coupled with the time for washing, settling and decantation, makes the cycle for each tank about 16 hours.

Continuous Dorr Causticizing Process: Figure 2.4.6 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 percent 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.

After the desired conversion level has been attained, the solution is settled in thickeners,
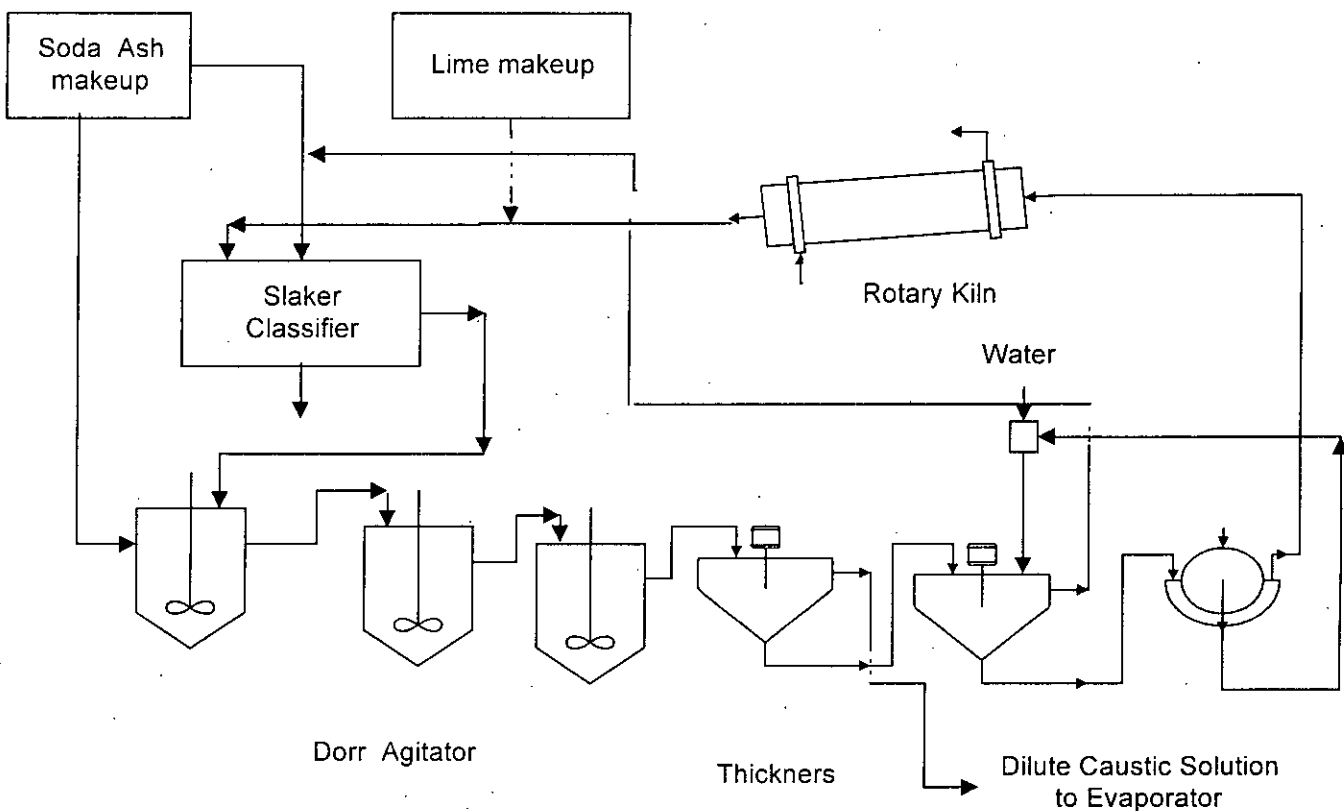
Figure 2.4.6 Continuous Causticizing Plant (Ref.5)

usually of multi-tray design and consisting of two or three units in series. The overflow from the first thickener is run to the evaporators for concentration or is used as a finished

product. The solution contains 10 to 12 percent sodium hydroxide and is an obtained at above 90 percent conversion based on sodium carbonate.

Sludge from the bottom of the first thickener is pumped to a second thickener, where hot water and 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 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 limekiln to furnish reburnt lime. 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 the causticizer to start the process.

Concentration of Caustic Solution: The lye from the strong liquor storage tanks is concentrated in multiple-effect vacuum evaporators, having generally two or three effects. Ordinarily, the caustic liquor from last effect has a concentration up to 50%.

2.4.2.3 Calcium Chloride Sodium Carbonate Double Decomposition:

Milk of lime is reacted with ammonium chloride, freeing the ammonia as gas and forming a calcium solution which, after purification, is reacted with soda ash solution to form calcium carbonate. The overall reaction is:

$$Na_2CO_3 + CaCl_2 \rightarrow CaCO_3 + 2NaCl$$
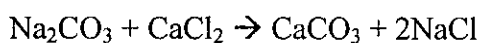
This process can be controlled by addition times, rate and method of agitation, concentrations, pH and reaction temperature. It is the simplest of the three

processes but requires a low cost source of calcium chloride to be economically attractive. Commercial plants are located adjacent to solvay process synthetic ash facilities.

2.5 Physical and Chemical Properties of Calcium Carbonate:

The physical properties of calcium carbonate vary according to grade, raw materials and method of manufacture. The physical properties for calcium carbonate are shown in Table 2.5.1 and the chemical properties in Table 2.5.2. As might be expected, the chemical purity of the precipitated products is normally superior to that of the ground limestone.

Table 2.5.1: Typical physical properties of calcium carbonate pigment (Ref.3)

	Natural		Precipitated	
	FGL	UFGL	Calcite	Aragonite
Specific gravity	2.71	2.71	2.71	2.93
Index of refraction, mean	1.58	1.58	1.58	1.63
Hardness (Mohs scale)	3.0	3.0	3.0	3.5
Decomposition temperature ^{0}C	← 800-900 →			
Valley abrasion, mg	25	10	5	8
Brightness percent (GE)	95	96	98	99
Oil absorption, cc/100 g	13	23	30	55
Surface area, m^2/g	3.2	9.6	6.8	8.5

Table 2.5.2: Typical Chemical Properties of Calcium Carbonate Pigments (Ref.1)

	Type 1	Type 1	Type 3	Type 4
$CaCO_3$, percent	96.63	98.36	98.43	98.62
$CaSO_4$, percent	-	0.08	0.78	0.63
$MgCO_3$, percent	2.43	0.7	0.37	0.21
Al_2O_3, percent	0.28	0.09	0.07	0.01
SiO_2, percent	0.37	0.1	0.04	0.02
FeO_3, percent	0.09	0.07	0.06	0.01
NaCl, percent	-	-	-	0.1
H_2O loss at 110^oC, percent	0.2	0.6	0.25	0.3
pH (saturated solution)	9.1	9.4	10.3	8.5

Type 1 is a ground limestone. Actual values will fluctuate over a moderate range

reflecting variations within and between various stone deposits.

Type 2 is a calcium carbonate formed by the following reaction:
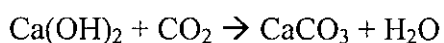
$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$

Type 3 is a calcium carbonate formed by the following reaction:

$Ca(OH)_2 + Na_2CO_3 \rightarrow 2NaOH + CaCO_3$

Type 4 is a calcium carbonate formed by the following reaction:

$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$
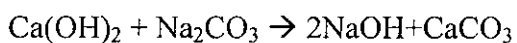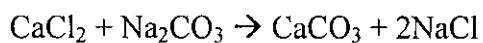
2.6 Grades of Calcium Carbonate:

Transmission photomicrographs for the precipitated calcium carbonate calcite (PCC–C) and precipitated calcium carbonate aragonite (PCC – A) are shown in Figures 2.6.1 a, b, c, d.
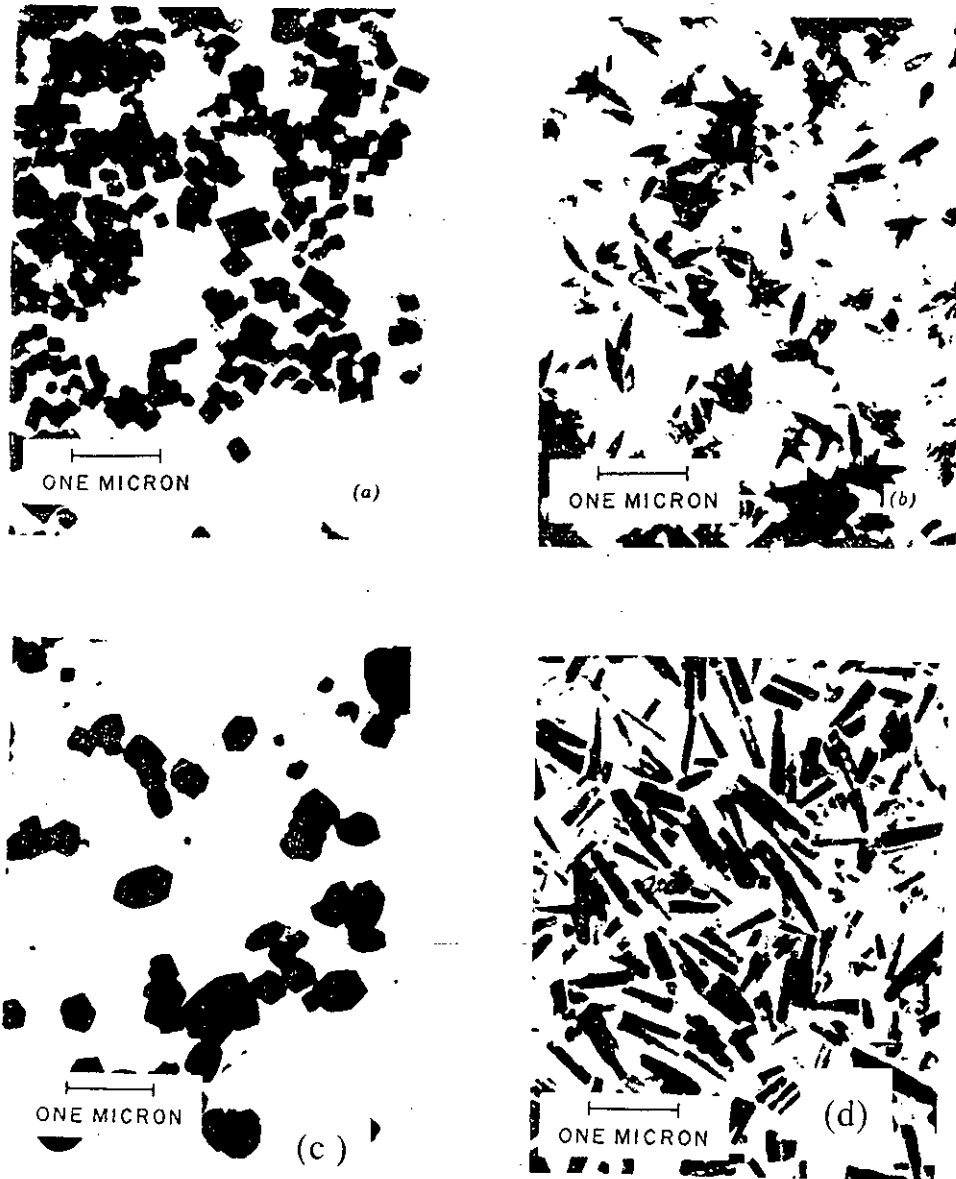
Fig. 2.6.1 Transmission photomicrographs showing precipitated (a) calcite in rhombohedral form; (b) calcite in scalenohedral form; (c) calcite in novel barrel-shaped prismatic form; and (d) aragonite in acicular form.

Scanning photomicrograph for representative standard coating grades of calcium carbonate are shown in Fig. 2.6.2 a, b, c, d. It can be seen from Fig. 2.6.2, the precipitated materials are much more uniform and finer in particle size than the ground lime stone.
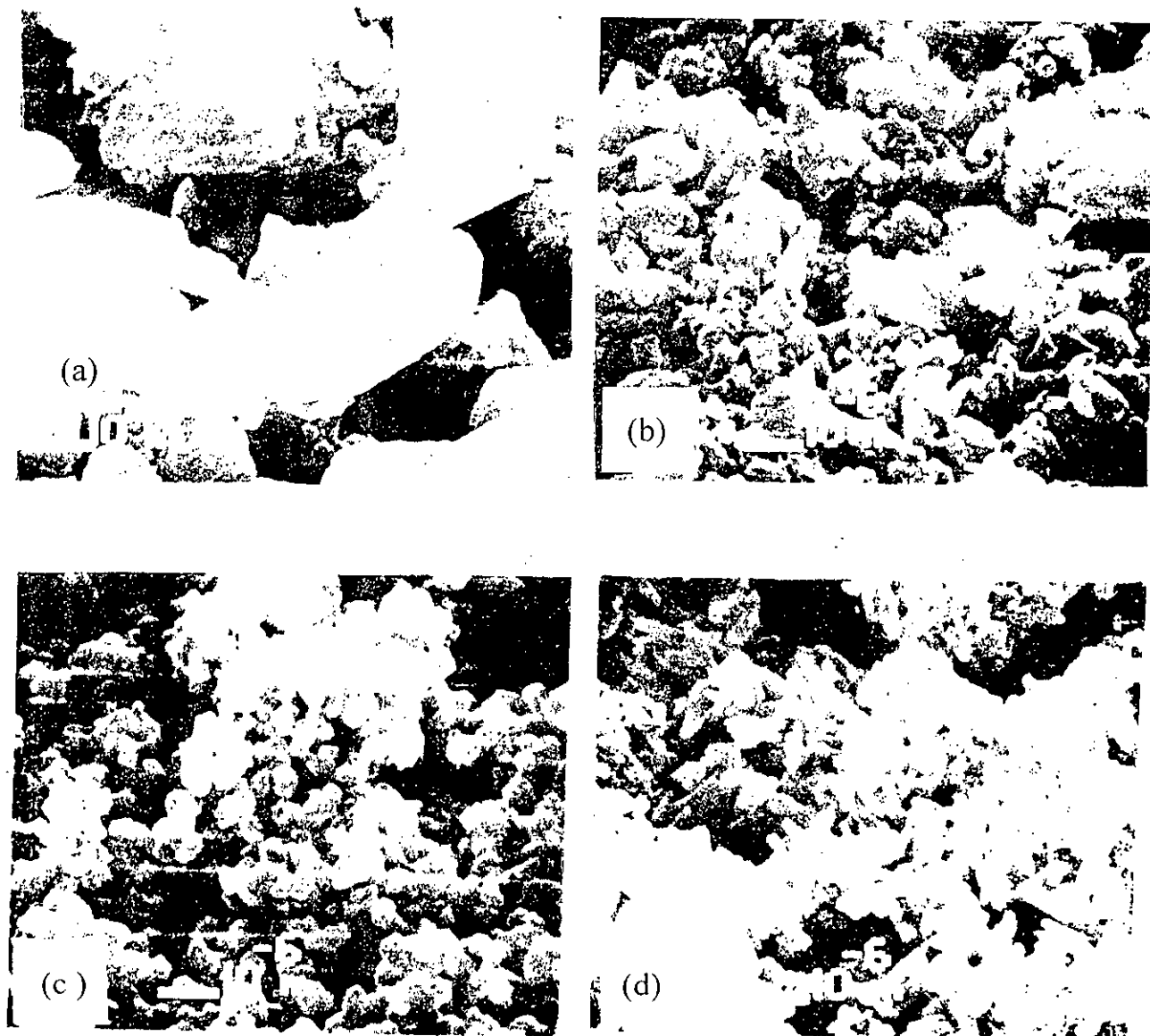
Fig. 2.6.2 Scanning photomicrographs of calcium carbonates showing (a) fine-ground limestone (FGL); (b) ultrafine ground limestone (UFGL); (c) precipitated calcium carbonate, calcite (PCC-C); and (d) precipitated calcium carbonate, aragonite (PCC-A) (reference bar = 1 μm).

CHAPTER – THREE

Statement of the Objectives

For indigenous development of lime-soda process it is very important to recover the byproduct calcium carbonate from the filter cake. The whole of the profitability of the process depends on efficient recovery and marketing of calcium carbonate. Though lime-soda process is an established one but there is not much information available on the recovery steps.

This research work is aimed to study in general the separation steps in the production of caustic soda using lime-soda process. The major objective is to recover good quality alkali free calcium carbonate from the sludge of lime-soda process. To attain this the following things were studied.

(a) Conversion data as a function of time were obtained for determining the optimum time for causticization.

(b) A scheme was developed for recovery of caustic solution and at the same time removal of alkalinity of calcium carbonate powder,

(c) Drying data were obtained for filter cake and optimum time for drying was determined.

(d) Effect of lime quality on the color of calcium carbonate powder was studied by causticizng with lime of different grades.

CHAPTER – FOUR

Experimental

Experiments were conducted in four stages consisting of causticization of soda ash, separation of caustic solution and sludge by decantation and filtration, recovery of $CaCO_3$ and drying of filter cake. The basic experimental setup for causticization was the same as used by Mannan (Ref.5).Additional setups were used for vacuum filtration and CO_3 content determination. Setup and procedures of these experiments are described in the subsequent sections.

4.1.1 Setup for Causticization

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. 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 opening 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 of 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. Fig. 4.1.1 shows a schematic diagram of the experimental setup .
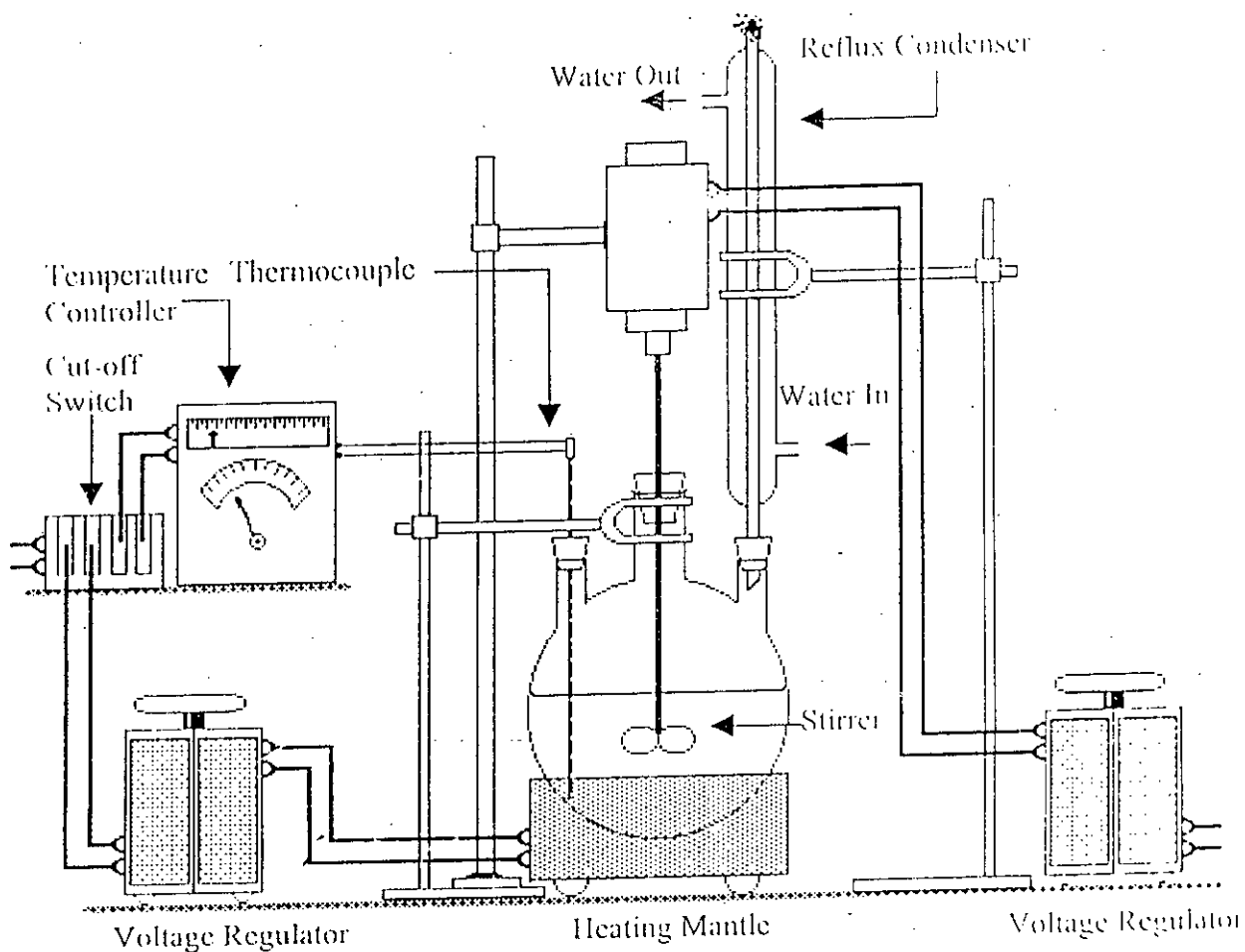
Fig.4.1.1 Schematic Diagram of Experimental Setup (Ref.5)

4.1.2 Procedure for Causticization

100 g of anhydrous sodium carbonate was dissolved in 685 ml water in a beaker to make 12.5% solution and poured it into the three necked flask. After the solution has reacted, the desired lime, 10% excess of the stoichiometric amount was weighed and poured into the flask. The three necks of the flask were sealed and stirrer was switched on. The valve for condenser cooling water was opened. After causticizing for the stipulated time the stirrer and heating mantle were switched off and the stirrer, thermocouple and condenser were removed from the flask. The slurry was then poured into a beaker for settling.

4.1.3 Bulk Settling Test

For bulk settling test a measuring cylinder with its height graduated in centimeter was used. The slurry from the reactor was directly poured into the cylinder and height of the solid-liquid interface was recorded with time.

4.1.4 Setup and Procedure for Vacuum Filtration

After completion of the settling of slurry, the clear solution was decanted and the thick dense slurry was sent to the vacuum filter for recovering caustic solution and reducing the heating load in the dryer. The schematic diagram of the setup for vacuum filtration is shown in Fig. 4.1.3. A vacuum gauge was fitted on the suction

line to measure the vacuum and the surge tank was used for making the applied vacuum steady. All the filtrations were conducted at a vacuum of 4 inches of mercury.
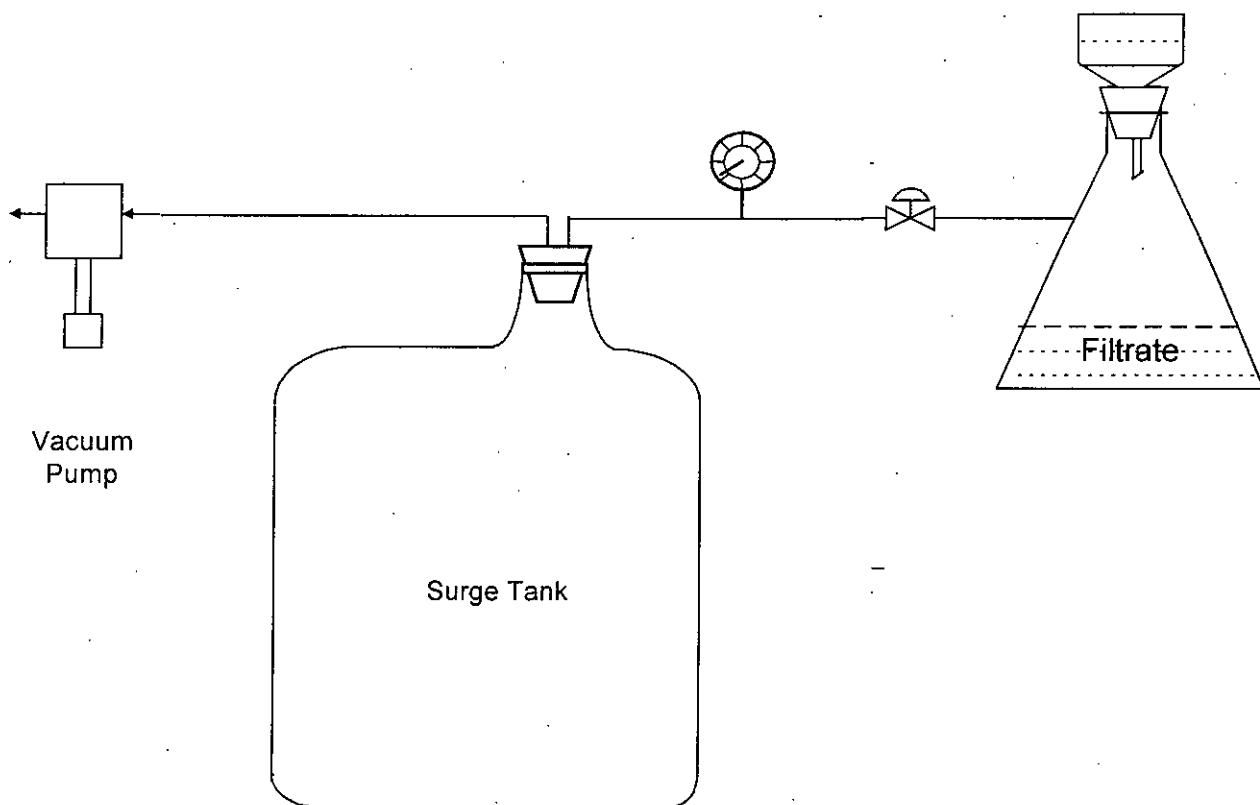
Figure 4.1.2 Setup for Vacuum Filtration

4.1.5 Drying of the Filter Cake

The filter cake from the vacuum filter was spreaded over the tray in a thin layer of about ¼ inch thickness. Filter cakes from different runs were dried at 120°C, 150°C, 180°C and 220°C. Weight loss of the cake with time was recorded for

drawing the drying curves. Effect of temperature on the color of $CaCO_3$ was also observed visually.

4.2 Recovery of Caustic Solution and Removing the Alkalinity of $CaCO_3$

After causticizing for about 2 hours the slurry was left for settling. The clear caustic solution was decanted from top and the thick slurry was sent to vacuum filter. The filtrate and the decanted solution made the strong liquor. The lime sludge was then washed with about 100g water. Together with the wash water the lime sludge with unconverted soda was sent to the causticization reactor. Again, it was causticized for about half an hour and the then the slurry was filtered in the vacuum filter. This gave the 1st wash liquor. This whole step was again repeated twice giving respectively 2nd and 3rd wash liquor. This recovered caustic solution also contained Na_2CO_3. Samples of wash liquor from each stage were drawn and titrated with HCl using phenolphthalein and methyl orange double indicator method. Thus, the NaOH and Na_2CO_3 content of the solution was determined. Simultaneously, samples of filter cake were also collected after each recovery step and these were titrated with HCl using phenolphthalein as an indicator. This gave the total alkalinity and $Ca(OH)_2$ content of the filter cake. Details of the analytical procedure are given in appendix A.4. Process scheme for $CaCO_3$ recovery is illustrated in Fig. 4.2.1

Causticization stage

Na$_2$CO$_3$
(12.5% soln)
Ca(OH)2
10% excess of
the stoichiometric
amount

Filter Cake
to 1st recovery
stage

Strong liquor
7.56% NaOH

1st recovery stage

Water

Filter
cake

Filter cake to
2nd recovery

First wash liquor
3.1%
NaOH(w/w)

2nd recovery stage

Water

Filter
cake

Filter cake to
3rd recovery
stage

2nd wash liquor
1.61%
NaOH(w/w)

3rd recovery stage

Water

ter
ce

Filter cake to dryer

First wash liquor
0.71%
NaOH(w/w)
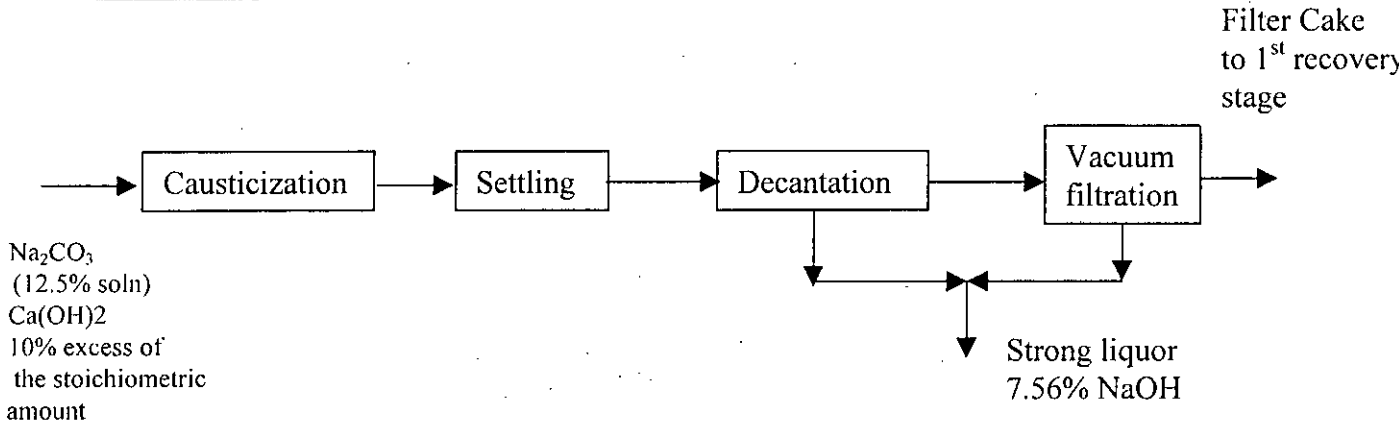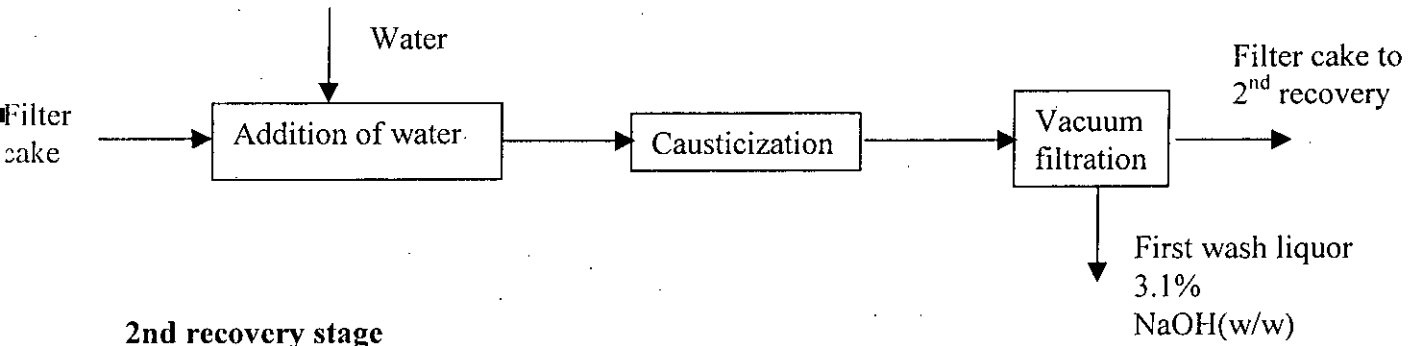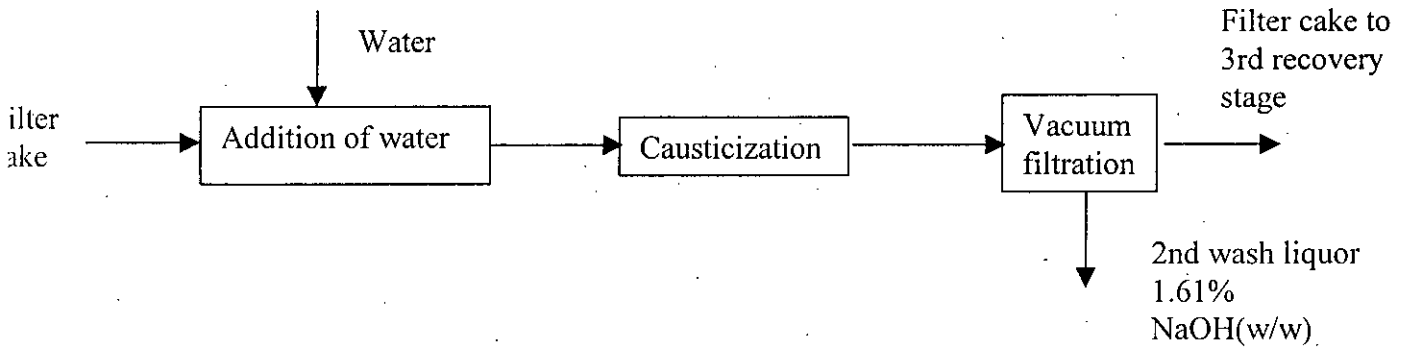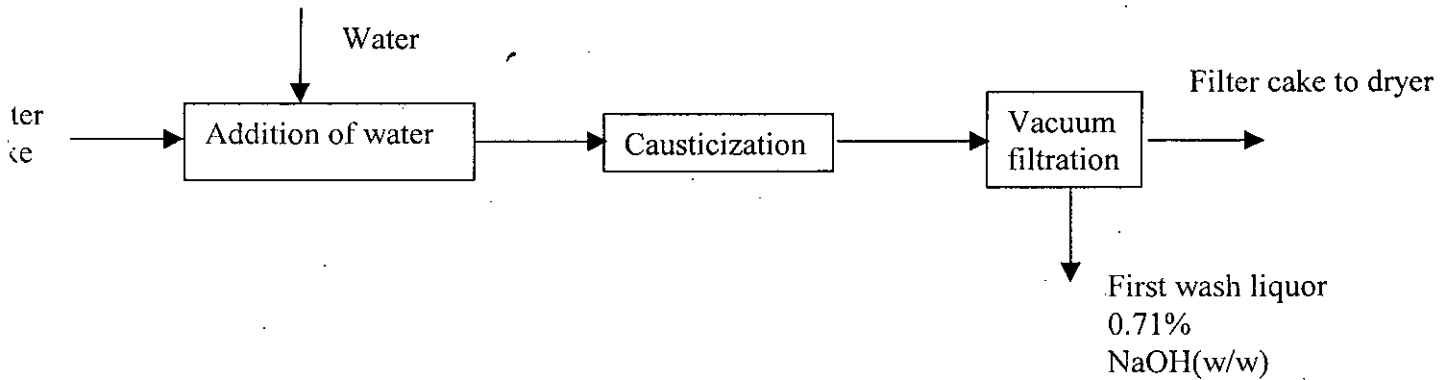
Fig. 4.2.1 Block diagram of process scheme for causticization and recovery of CaCO$_3$

4.3 Determination of Percentage Conversion of Soda Ash

For determining the percentage conversion of soda ash with time it is necessary to recover all the caustic solution from the filter cake. So, after decantation and vacuum filtration the filter cake was washed with large excess of water (1000 ml) in two stages and filtered in the vacuum filter. The total recovered solution was then titrated against standard HCl using phenolphthalein and methyl orange double indicator method.

CHAPTER – FIVE

Results and Discussions

The experiments were carried out using soda ash of commercial grade and lime of three different grades, namely, Analytical Reagent grade (AR grade), Analytical grade and Commercial grade. The assay of the AR grade and Analytical grade were readily available from the manufacturers. Using the available analytical facilities at the Chemical Engineering Department, a partial analysis of the commercial grades were made in the laboratory. Assay of different grades of lime together with the analytical procedure and set up used are given in appendix A.5.

The single kinetic study made in this research work is the effect of reaction time on conversion of soda ash. The results of the investigation regarding the effect of reaction time on the conversion for different grades of lime are presented in Figure 5.1 .It can be seen from this figure that, initially the conversion is very high, after one hour it gets slower and at two hours it is extremely slow. Curves are similar in nature for all the three grades of lime However the lime with higher $Ca(OH)_2$ content results in higher conversion . This can be explained from the fact that, due to the higher $CaCO_3$ content in the commercial grade lime the dissociation of $Ca(OH)_2$ and Na_2CO_3 to a certain extent is suppressed in the solution. However, the maximum conversion attained by AR grade lime is 74.8% at 2 hour against 93.4% conversion after 1 hour reaction at 90°C reported by Mannan(Ref.5).This discrepancy is because, the analytical procedure followed in the present study is

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different from the analytical procedure followed by Mannan(Ref.5). In the previous study the amount of unconveted Na_2CO_3 in the solution was determined and the rest amount was accounted as converted soda ash. But in actual case some soda ash also remains in the calcium carbonate powder as a complex. So, it is better to determine the conversion of Na_2CO_3 by determining the total amount of NaOH in the solution. For the present study this convention was followed for determining the conversion of Na_2CO_3.

The data for multistage recovery of caustic solution have been summarized in Table 5.2.1 and 5.2.2 for analytical grade and commercial grade lime respectively. The data are also presented in Figures 5.2.1 and 5.2.2. It is evident from the histograms that both for the analytical grade and commercial grade lime the percentage recovery can be improved by including recovery steps in the process. It can be seen that the caustic liquor from the third recovery stage is very weak

(Table 5.2.1 and 5.2.2). Addition of any further recovery stage may not be feasible. Again, the analysis of the caustic mud indicates that the alkalinity of the recovered calcium carbonate can be lowered to a reasonable value. Comparing the alkalinity values of caustic mud from two grades of lime it can be concluded that it is easier to remove the alkalinity of the $CaCO_3$ from the commercial grade lime than from the analytical grade. This may be because the precipitate from commercial grade lime was coarse while analytical grade lime produced fine precipitate that has a higher liquid retaining capacity.

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The bulk settling test data of causticization slurry are given in Table 5.3. The settling behaviour of the slurry is evident from Fig. 5.3. It shows that the settling rate of the slurry from commercial grade lime is much higher than the slurry from analytical grade lime. While the settling of slurry from the commercial grade is nearly complete at about 80 minutes the corresponding value was more than three hours for the analytical grade . This higher rate may be due to the presence of more clay and $Mg(OH)_2$ in the commercial grade lime than the analytical grade lime. Due to the hydraulicity of these impurities the slurry from commercial grade lime has a higher settling rate than the slurry from analytical grade lime.

The drying data of the finally recovered filter cake from different grades of lime is given in appendix A.7 and the distinguishing features have been summarized in Fig. 5.4.1 through Fig. 5.4.6. It is evident from the moisture content vs. time curve that the initial moisture content of all the filter cakes were not the same due to lack of proper control in vacuum filtration. After about 10 minutes drying there is a point where the moisture content of all the cakes are almost the same. Taking this point as a basis drying time vs. drying temperature curves (Fig. 5.4.2 and 5.4.4) have been plotted. Drying time vs. drying temperature curves using the actual data has also been plotted. Both types of plot show that the drying time decreases very rapidly with the increase of drying temperature. For the filter cake from commercial grade lime at 120°C it took 2 hrs. to completely dry the filter cake, while it took only 40 minutes at 220°C. This has also been reflected in the drying rate vs. moisture content curves. There are some scattered points in the curves

particularly at low drying temperature(120^0C), because the drying mass in the tray was given a manual agitation.

Now about the color of the product, drying temperature have a little effect on the color of calcium carbonate powder. It was observed that at 220^oC there formed a yellowish crust over the surface of the product. Despite this, the product from AR grade lime was bright white while the product from commercial grade lime was off white . It can be concluded that the color of the product is purely dependent on the color of the lime which is used for causticization. Impurities such as iron, silica and carbonaceous materials present in the lime in turn are responsible for the discoloration of calcium crbonate.

Table 5.1: Percent Conversion of Different Grades of Lime with Time

Time min	AR Grade Lime	Analytical Grade Lime	Commercial Grade Lime
	% Conversion	% Conversion	% Conversion
20	66.26	62.03	60.75
40	-	66.83	-
60	76.4	70.69	70.85
90	78.3	75.73	74.06
120	79.77	78	75

Table 5.2.1: Multistage Recovery of Caustic Solution (Analytical Grade Lime)

	Volume of solution (ml)	Sp. Gr. of solution	Concentra-tion of solution % NaOH (w/w)	Cumula--tive % recovery of NaOH	Total Alkalinity & Ca(OH)$_2$ content of filter-cake (m. eq. NaOH/g)	Wt. of Dry filter-cake (g)
Decantation	340	1.112	10.15	53.55	-	
Vacuum filtration	75	1.112	10.15	65.32	2.62	
1st stage recovery	165	1.060	5.33	77.94	1.87	105
2nd stage recovery	150	1.027	2.40	83.09	1.42	
3rd stage recovery	105	1.016	1.38	85.14	1.27	

Table 5.2.2:Multistage Recovery of Caustic Solution (Commercial Grade Lime)

	Volume of solution (ml)	Sp. Gr. of solution	Concen-tration of solution % NaOH (w/w)	Cumu--lative % recovery of NaOH	Total Alkalinity & Ca(OH)$_2$ content of filter-cake (m. eq. NaOH/g)	Wt. of Dry filter-cake (g)
Decantation	500	1.1085	7.56	57	-	
Vacuum filtration	115	1.1085	7.56	70	1.93	
1st stage recovery	125	1.0340	3.10	75.90	1.32	140
2nd stage recovery	140	1.0190	1.61	78.33	0.88	
3rd stage recovery	135	1.0084	0.71	79.68	0.763	

Table 5.3: Bulk Settling Test Data for Causticization Slurry from Lime of Different Grades

Time, min	Analytical Grade Lime	Time, min	Commercial Grade Lime
	Height of Inter-phase, cm.		Height of Inter-phase, cm.
2	32	2	31
4	31.2	4	29
6	30.4	6	27
8	29.1	8	25.2
10	28.7	10	23
12	28.0	12	21
14	27.2	14	19.3
16	26.5	16	17.8
18	25.4	18	16.6
20	24.7	20	15.7
24	23.4	22	14.8
28	22.1	24	14.2
36	19.7	28	13.3
40	18.7	30	12.8
51	16.5	32	12.5
55	15.9	34	12.2
60	15.2	37	11.8
70	14.3	45	10.9
75	13.9	50	10.6
195	10.9	80	9.2
After 24hrs.	10.3	After 24hrs.	8.5
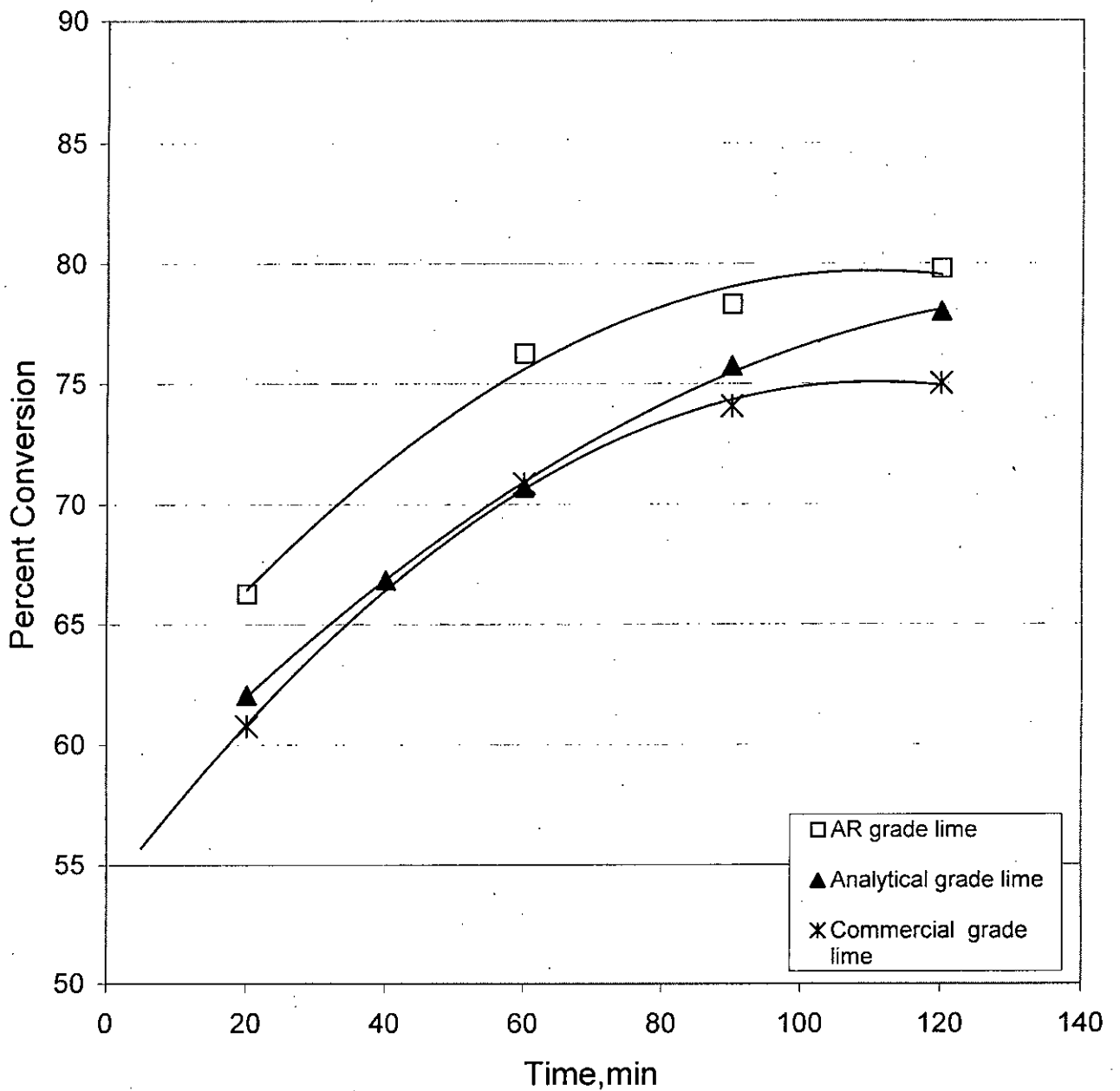
Fig.5.1 Percentage Conversion of Na_2CO_3 for Different Grades of Lime vs. Time; Caustic soda in Filter Cake Recovered with Excess Water(Ratio of Solid to Water= 1 : 7 to 10)
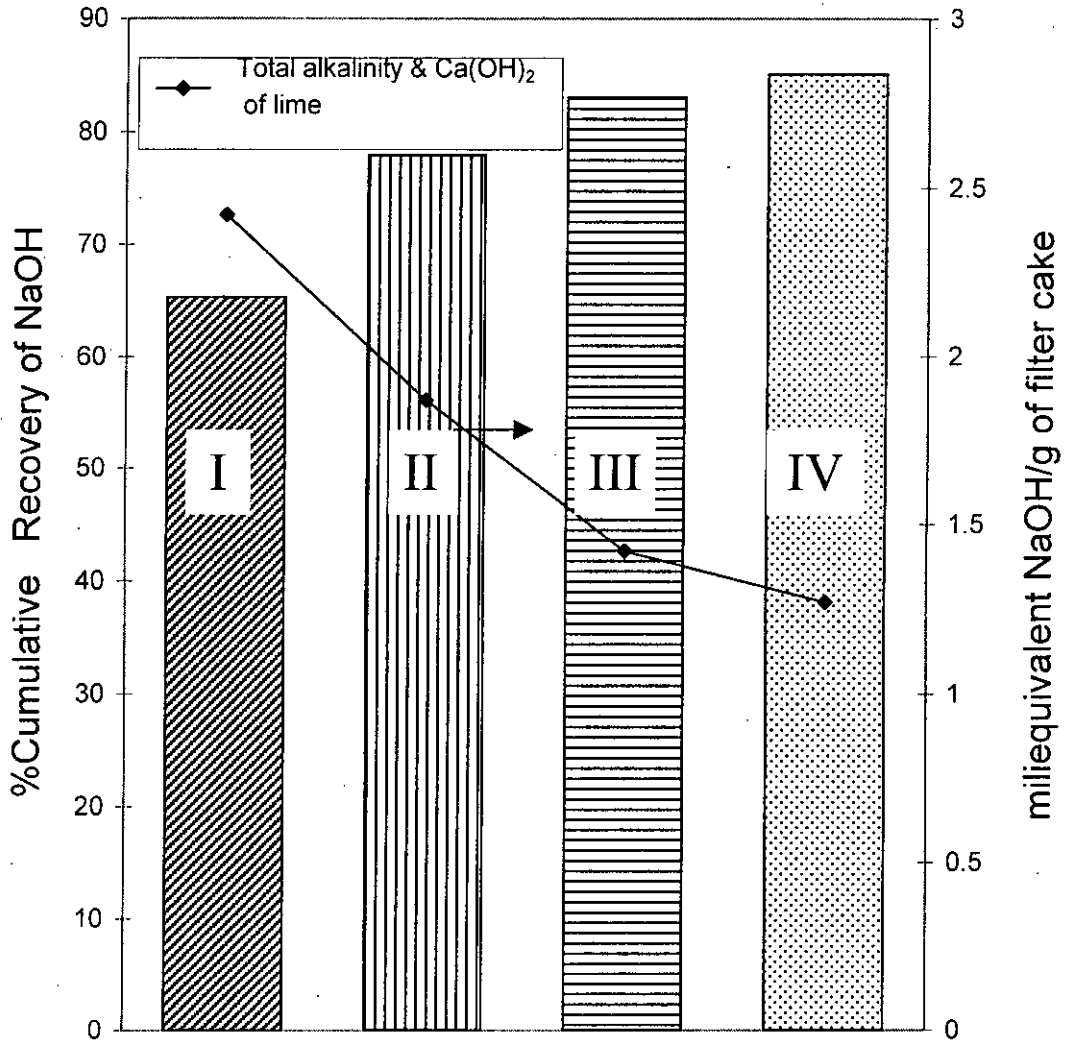
Fig.5.2.1 Multistage Recovery of Caustic Solution by
Causticizing Analytical Grade Lime

StageI   After digestion
StageII   After 1st washing of filter cake
StageIII After 2nd washing of filter cake
StageIV After 3rd washing of filter cake
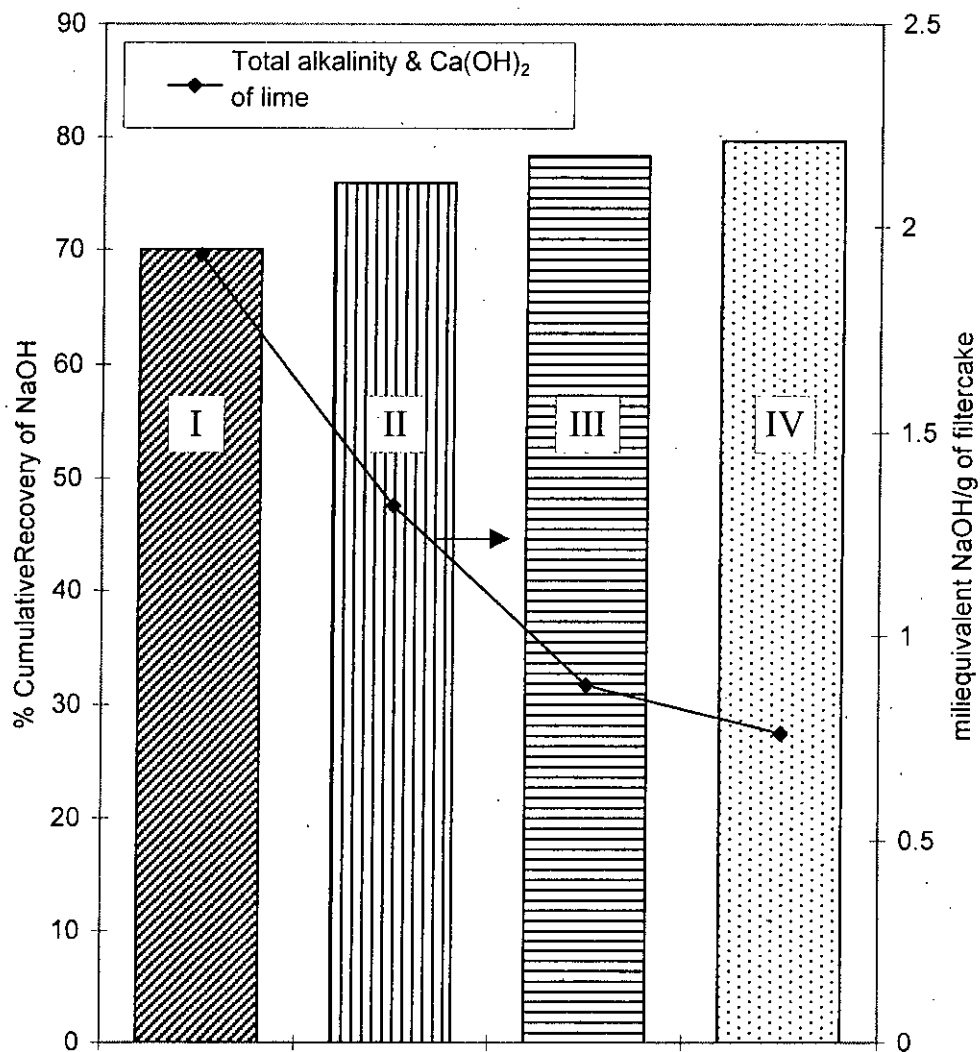
Fig.5.2.2 Multistage Recovery of Caustic Solution by
Causticizing Commercial Grade Lime

StageI   After digestion
StageII After 1st washing of filter cake
StageIII After 2nd washing of filter cake
StageIV After 3rd washing of filter cake
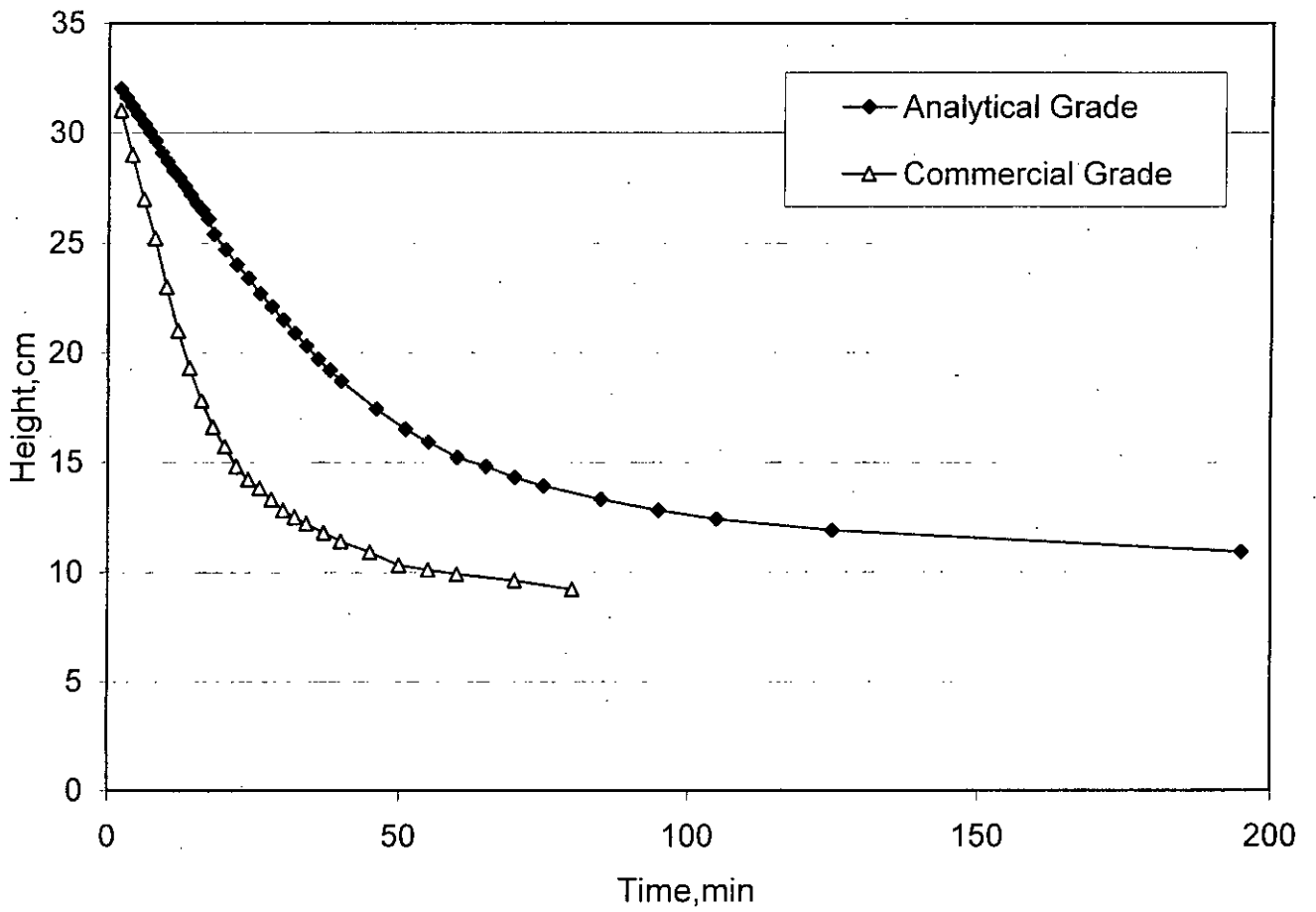
Fig.5.3 Settling Curves after Causticizing withAnalyticalgrade
and Commercial grade lime
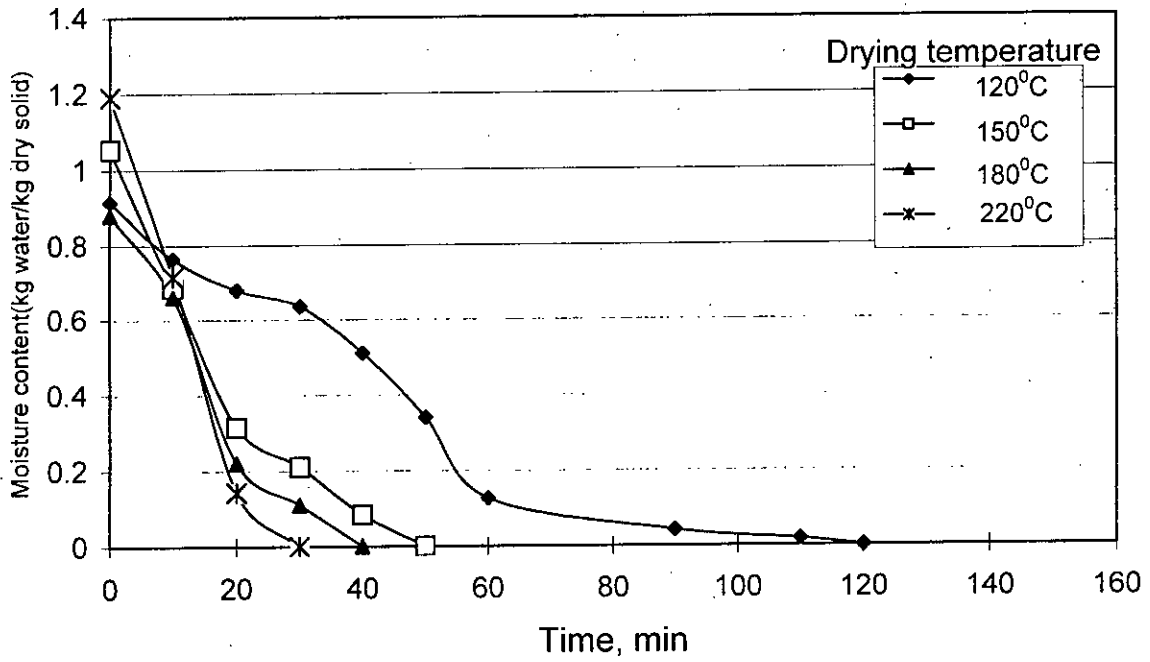
Fig.5.4.1 Moisture Content vs. Time at Diffrent Temperatures for Drying Calcium Carbonate Cake (AR grade lime)
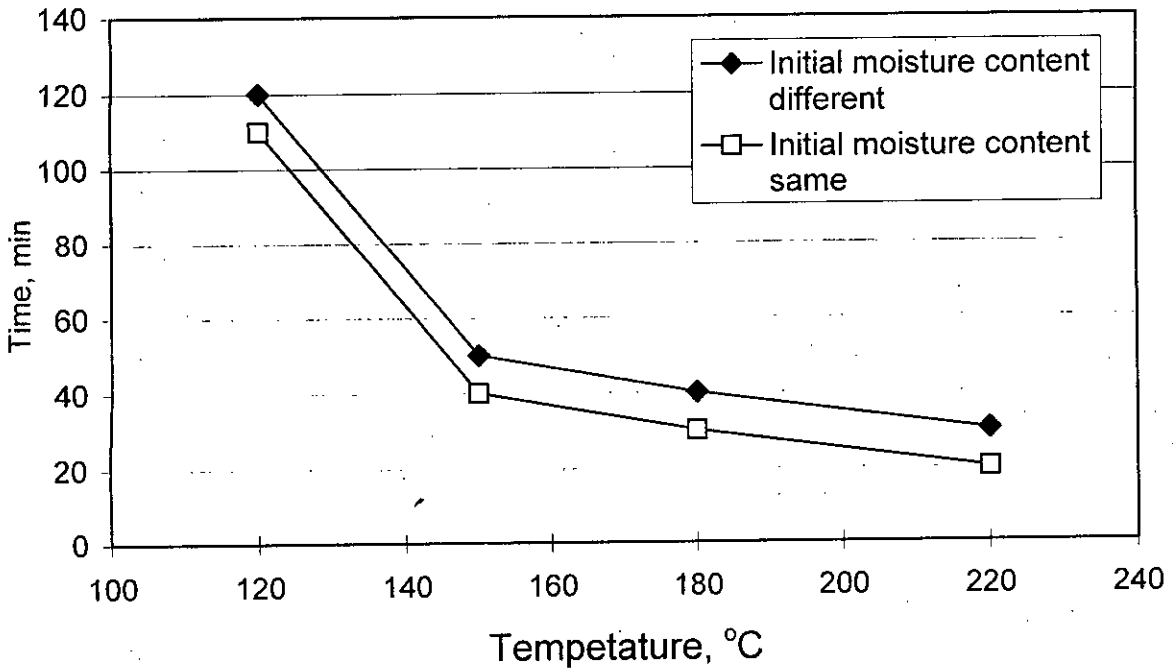
Fig.5.4.2 Drying Time vs.Drying Temperature for Drying Calcium Carbonate(AR grade lime)
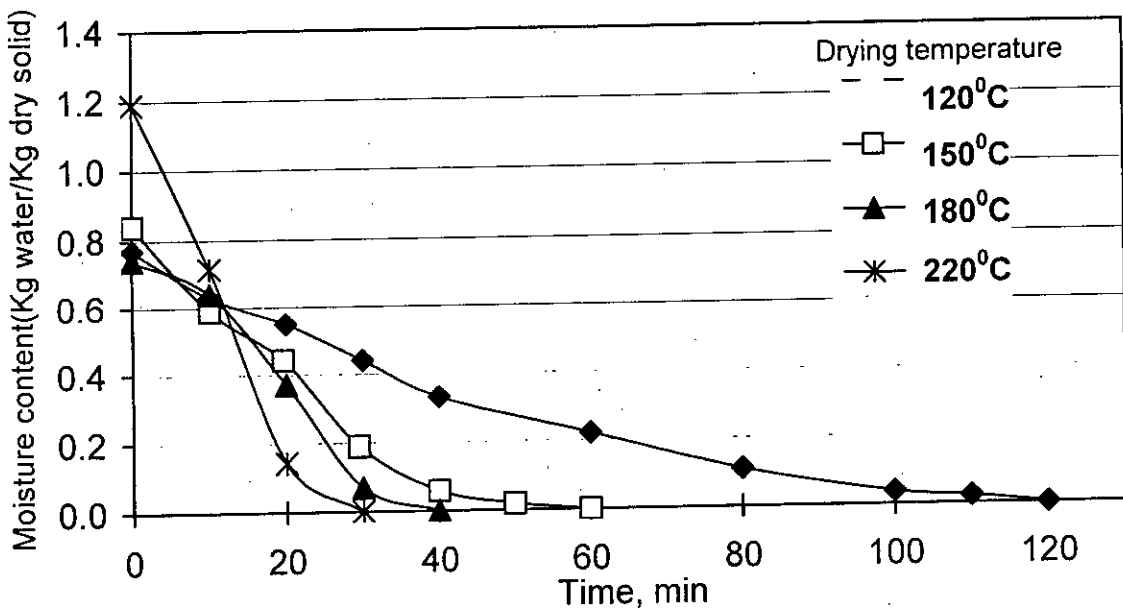
Fig.5.4.3 Moisture Content .vs. Time at Different Temperatures for Drying Calcium Carbonate Cake(Commercial grade lime)
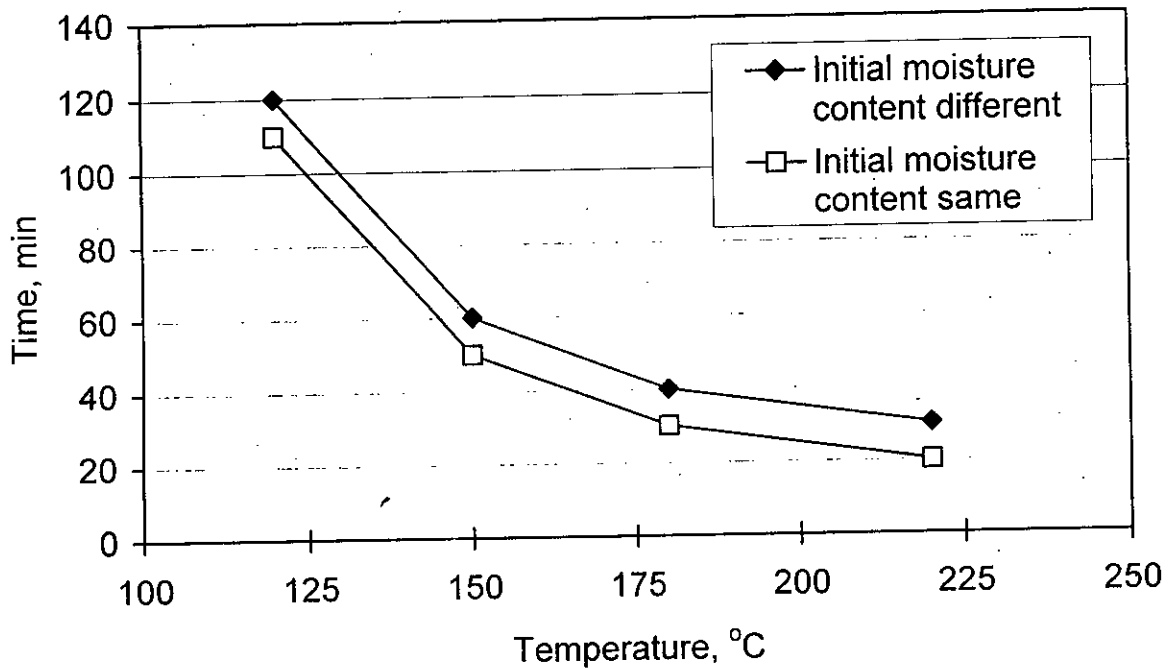
Fig.5.4.4 Drying time vs. Temperature for Drying Calcium Carbonate Cake(Commercial grade lime)
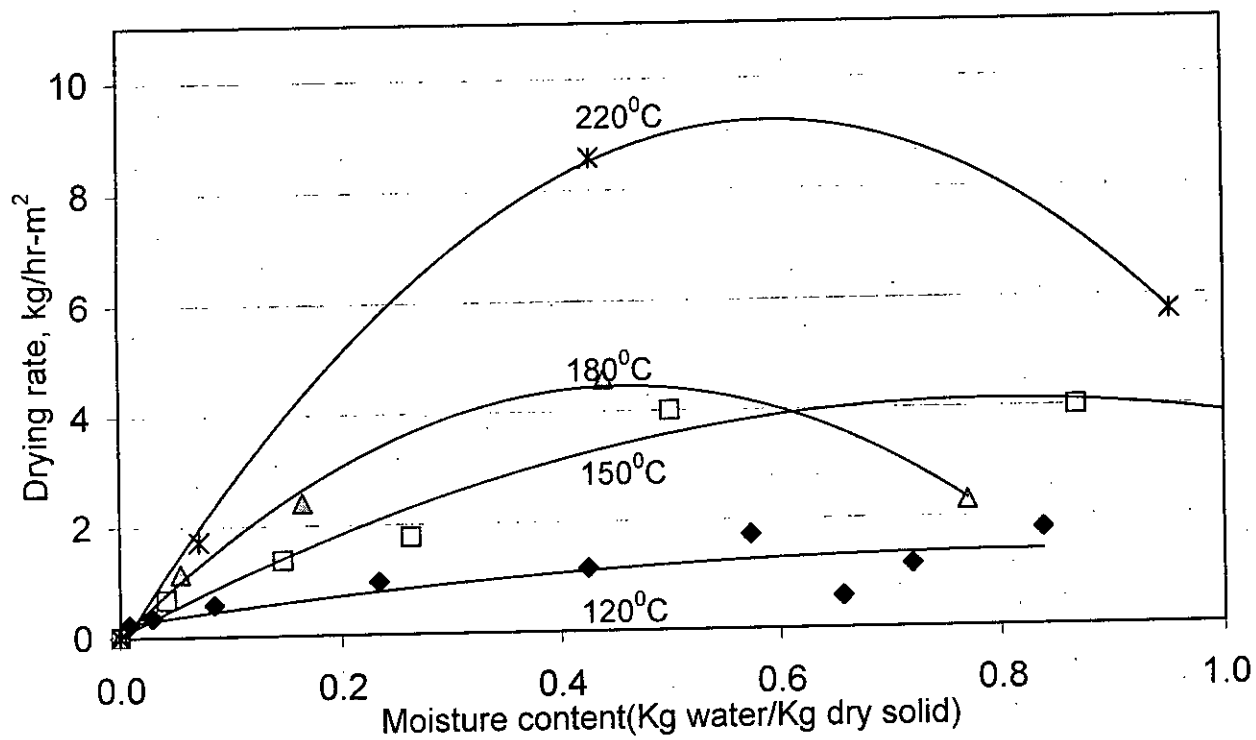
Fig.5.4.5 Drying rate .vs. Mositure content(AR grade lime)
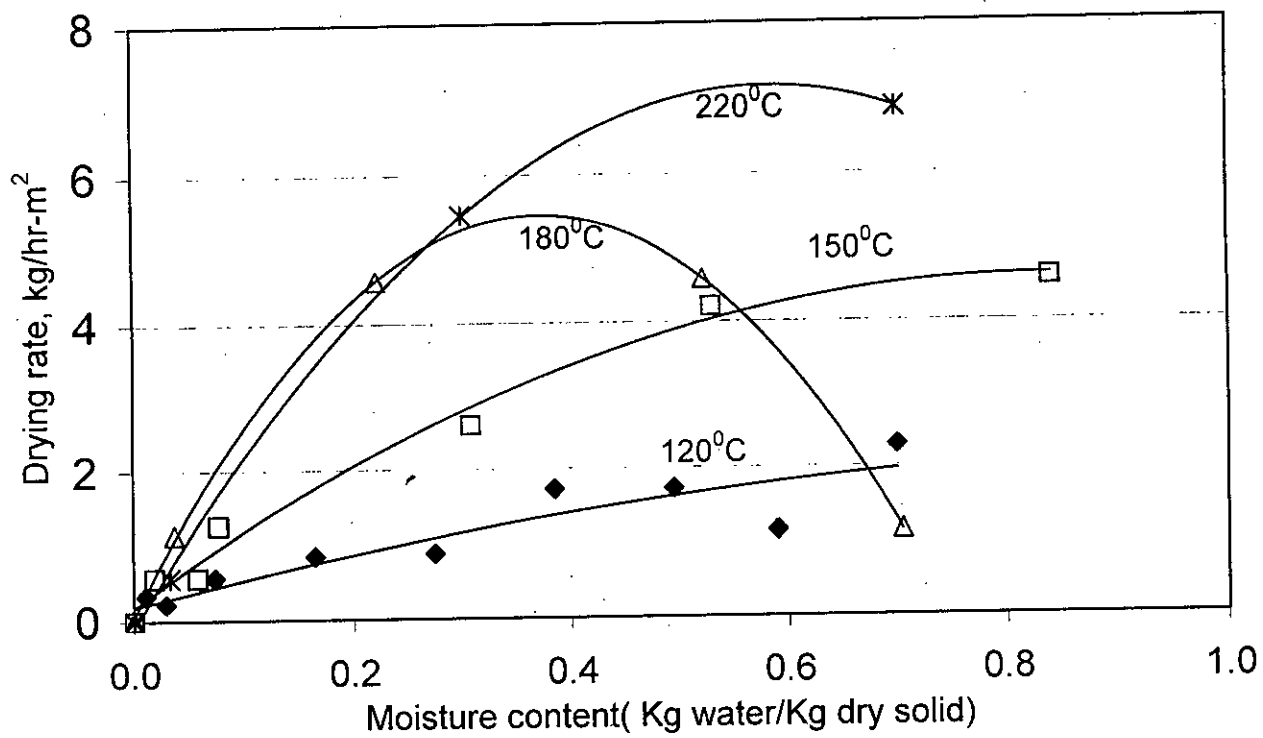
Fig.5.4.6 Drying rate.vs. Moisture content(Commercial grade lime)

CHAPTER – SIX

Conclusions and Suggestions

6.1 Conclusions

The objectives which were set at the beginning of the research work has been fulfilled in most cases. There was some success in removing the alkalinity of calcium carbonate, pH of the saturated solution of the recovered calcium carbonate was 10.23. At the same time high conversion rate was also attained.

It also came out that addition of a vacuum filtration step in the process can recover strong caustic soda liquor and decrease the heating load of the dryer. Study of the drying behavior of the recovered $CaCO_3$ filter cake reveals that for practical purpose $220^{o}C$ will suffice for drying, and at this temperature there is no appreciable discoloration of $CaCO_3$. As detailed analysis of the commercial grade lime could not be done , the impurities which are responsible for the poor color of $CaCO_3$ could not be identified. But it can be stated with confidence that the impurities present in lime are responsible for the poor color of $CaCO_3$.

6.2 Suggestion for Future Work

To attain the main goal for the indigenous development of lime soda process in Bangladesh, it is suggested that the following works should be undertaken.

i)   Detailed analyses of different grades of lime available.

ii) In cooperation with the lime producers calcination of limestone should be studied and optimum operating conditions to be established so that there is no unburnt calcium carbonate in the lime.

iii) Recycle of the weak caustic soda solution recovered from the washing of sludge, for making the entire process more efficient.

iv) To make the $CaCO_3$ powder free of $Ca(OH)_2$ there are two alternatives. Firstly, treatment of the $CaCO_3$ sludge by passing CO_2 gas for transforming into $CaCO_3$. Secondly, use of excess soda ash in the causticization step, so that there will be no free $Ca(OH)_2$ in the sludge.

v)   Lime soda process should be studied in pilot plant scale

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APPENDICES

A.1 Determination of the calcium content of lime

For determining the calcium content of lime calcium was precipitated as calcium oxalate, $CaC_2O_4.H_2O$, by treating a hot acidic solution of calcium solution with ammonium oxalate solution, and slowly neutralizing with aqueous ammonia solution:

$$Ca^{2+} + C_2O_4^{2-} + H_2O = CaC_2O_4.H_2O$$
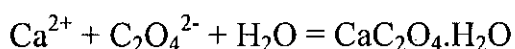
The precipitate was washed with water to remove Cl^- and then dissolved with dilute H_2SO_4. This liberated oxalic acid, which was then titrated with standard potassium permanganate solution.

Procedure:

i)   Sufficient sample was weighed accurately to contain approximately 0.2 g of calcium into a 400 or 600 cm^3 beaker with a clock glass and provided with a stirring rod.

ii)   10 cm^3 of water was added, followed by about 15 cm^3 of dilute hydrochloric acid (1:1).

iii) The mixture was heated until the solid has dissolved, and boiled for several minutes in order to expel carbon dioxide. The sides of the beaker and clock glass were rinsed, and the solution was diluted to 200 cm^3.

iv) A solution of 2.0 g of ammonium oxalate in 50 cm^3 of water was added.

v) Two drops of methyl orange indicator was added and dilute ammonia solution (1:1) was added dropwise with stirring until the mixture is neutral or faintly alkaline.

vi) The solution was allowed to stand for an hour. Precipitate of calcium-oxalate formed at the bottom of the beaker.

vii) The precipitate was transferred over a filter paper, and washed with excess water until the precipitate is free from Cl$^-$.

viii) Washed precipitate was transferred into a conical flask, and about 20 ml of H$_2$SO$_4$ (1:1) was added to dissolve the precipitate.

ix) The total volume of the solution was made to 500 ml in a graduated flask.

x) 25 ml of the resulting solution was pipetted out into a conical flask, heated to 60°C and titrated against 0.01 N KMnO$_4$ with constant stirring. The end point was noted when the faint pink color persisted for 30 seconds.

Sample Calculation:

Commercial grade lime

Wt. of sample= 0.4 g

Table A1: Results for titration of oxalic acid solution

Obs. No.	Volume of $KMnO_4$, ml	Avg. volume of $KMnO_4$, ml	Strength of $KmnO_4$, N	Volume of stock solution, ml
1	45.1			
2	45.0	45.0	0.01	25
3	44.9			

$$V_1S_1 = V_2S_2 \qquad \text{Volume of } KMnO_4, \; V_1 = 45$$

$$S_2 = \frac{45 \times 0.01}{25} \qquad \text{Strength of } KMnO_4, \quad S_1 = 0.01 \; N$$

$$= 0.018 \; (N) \qquad \text{Volume of Oxalic acid solution } V_2 = 25 \; ml$$

Strength of oxalic acid solution, S_2

Total wt. of oxalic acid in 500 ml stock solution = 0.405 g

$$\equiv 0.162 \; g \; Ca$$

A.2: Determination of the carbonate content of lime and calcium carbonate

The carbonate content of lime was determined by expulsion and displacement method. The setup of the apparatus is shown in Figure A.2.
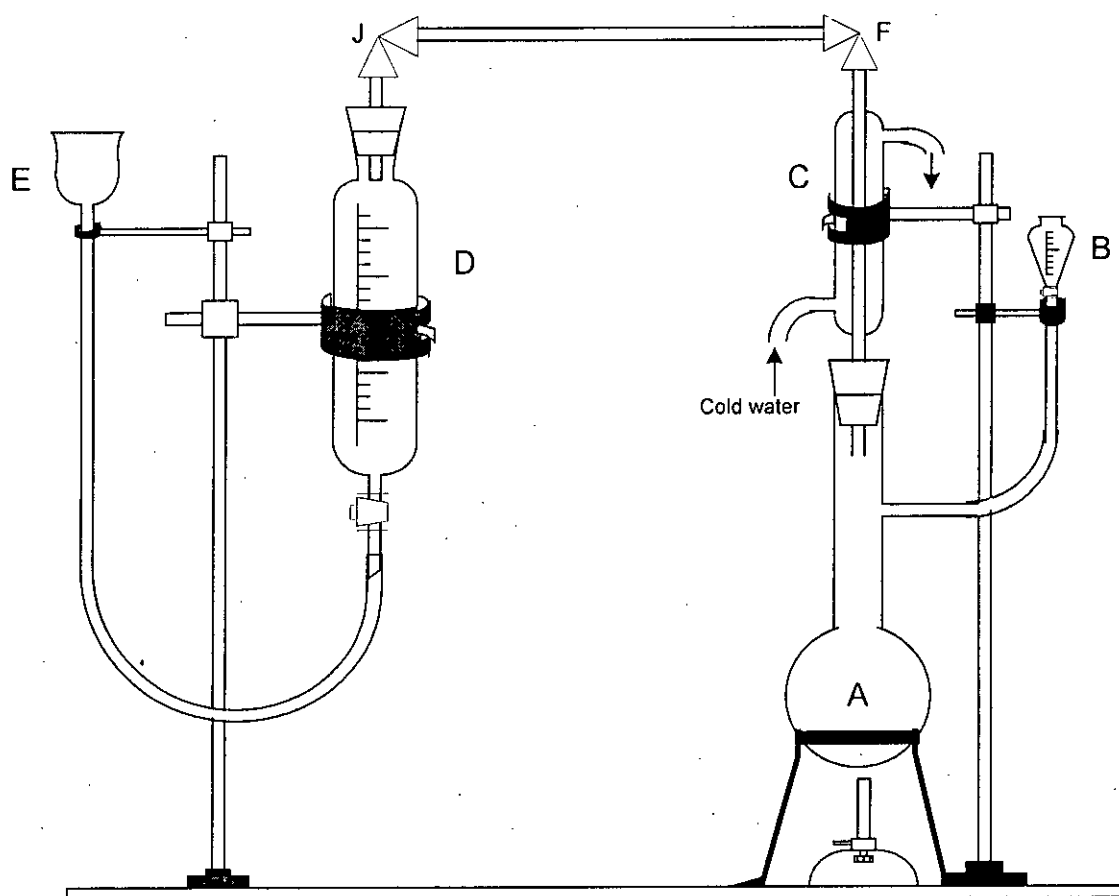
Figure A..2 Apparatus setup for determination of carbonate content

Procedure

i)   About 1 g of commercial lime containing calcium carbonate was placed in the generation flask A. The CO_2 collector burette, D was filled with water up to valve J.

ii)   50 c.c. of 10 N H_2SO_4 was runned into the flask from funnel B.

iii) The flask was heated to boiling, and CO_2 gas was collected through the condenser C into the burette D.

iv)   The apparatus was left for about half an hour to cool down to ambient temperature.

v)   With the leveling funnel E, the volume of CO_2 was noted from the displaced water volume in burette D. Ambient temperature, T_1 and pressure, P_1 were also recorded.

Sample Calculation:

Commercial grade lime

Wt. Of lime = 1.0 g

Volume of CO_2, V_1 = 85 ml

Ambient Temperature = 30°C

Ambient pressure = 760 mm Hg.

Vapor pressure of water at 30°C, $p^* = 31.82$ mm Hg

Volume of CO_2 at STP, $V = V_1 \times \dfrac{P_1 - p^*}{760} \times \dfrac{273}{273+T}$

$$= 85 \times \frac{760-31.82}{760} \times \frac{273}{303} = 73.38 \text{ ml}$$

Wt. of $CO_2 = 44 \times \dfrac{73.38}{22.4 \times 10^3} g = 0.144$ g

Wt. of $CaCO_3 = \dfrac{100}{44} \times 0.144 = 0.328$ g

Calcium carbonate content of lime $= \dfrac{0.328}{1.0} \times 100\% = 32.8\%$

A.3: Determination of Na_2CO_3 content of Washing Soda

The Na_2CO_3 content of washing soda was determined by titrating against standard hydrochloric acid.

Procedure

i)   About 3.6 g of washing soda was weighed, dissolved in distil water, and made up to 250 cm^3 in a graduated flask.

ii)   25 cm^3 of the solution was titrated with 0.1 N HCl using methyl orange as an indicator. Color changed from colorless to faint pink.

Sample Calculation

Wt. of sample = 3.53 g.

This was dissolved in water and made up to 250 cm^3.

Table A.3   Results of titration of Na_2CO_3 solution with HCl.

Experiment	Volume of HCl, ml	Concentration of HCl, N	Volume of stock solution, ml
1	25.2		
2	25.1	0.1	10
3	25.1		

Average volume of HCl, V_1 = 25.1 ml

Strength of HCl, N = 0.1 N

Volume of Na_2CO_3 solution, $V_2 = 10$

Strength of Na_2CO_3 solution, S_2

$V_1 S_1 = V_2 S_2$

$$S_2 = \frac{V_1 S_1}{V_2}$$

$$= \frac{25.1 \times 0.1}{10} = 0.251 \text{ (N)}$$

250 ml solution contains $\quad 0.251 \times 53 \times \dfrac{250}{1000} g$

$$= 3.33 \text{ g } Na_2CO_3$$

Thus, percentage of Na_2CO_3 $\quad = \dfrac{3.33}{3.5} \times 100\%$

$$= 95.1\%$$

A.4: Analysis of Caustic Soda Solution

The caustic soda solution from lime soda is a mixture of NaOH and Na_2CO_3. This has been determined by titrating against standard hydrochloric acid using phenolphthalein and methyl orange double indicator method.

At the phenolphthalein end point all the hydroxide is neutralized and the carbonate is converted into hydrogen-carbonate.

$$OH^- + H^+ = H_2O$$

$$CO_3^{2-} + H^+ = HCO_3^-$$
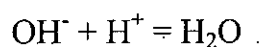
Another titration is performed with methyl orange, indicator. At the end point all the hydroxide and carbonate are neutralized.

$$OH- + H^+ = H_2O$$

$$CO_3^{2-} + 2H^+ = H_2CO_3$$

$$H_2CO_3 = H_2O + CO_2$$
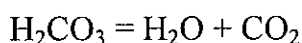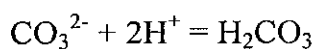
Procedure:

i)   25 ml of caustic solution was transferred to a conical flask with a pipette.

ii)   2-3 drops of phenolphthalein was added into the solution.

iii)   The solution was titrated with 0.486 N HCl. Color changed from pink to colorless.

iv)   Another titration was done exactly following the above procedure with methyl orange indicator. Color changed from colorless to faint pink.

Sample Calculation

Multistage Recovery of Caustic Solution after Causticizing with Analytical Grade lime. (Ref. Table 5.2.1)

Table A.4: Results for titration of caustic solutions

	Total Volume of Solution, ml	Volume of caustic stock solution titrated, ml	Volume of HCl at phenolphthalein end point, ml	Volume of HCl at methyl orange end point, ml	Strength of HCl, N
Decantation and vacuum filtration	415	10	60.7	63.3	0.486
1st recovery stage	165	10	28.9	29.7	0.486
2nd recovery stage	150	10	13.1	13.5	0.486
3rd recovery stage	105	10	7.4	7.6	0.486

Decantation and vacuum filtration stage

For 10 ml of stock solution

Volume of HCl required to neutralize OH^- and convert

CO_3^{2-} to HCO_3^- v = 60.7ml

Volume of HCl required to neutralize OH^- and CO_3^{2-}, V= 63.3 ml.

Therefore, volume of HCl required to neutralize OH^- = v − (V − v)

                                                     = 60.7 − (63.3 − 60.7)

$$= 58.1 \text{ ml}$$

Volume of acid required to neutralize $CO_3^{2-} = 2(V - v)$

$$= 2 \times 2.6$$

$$= 5.2 \text{ ml}$$

Wt. of NaOH in 10 ml stock solution $= 1.13$ g

Total wt. of NaOH in 415 ml solution $= 46.87$ g

Wt. of Na_2CO_3 in 10 ml stock solution $= 0.139$

Total wt. of Na_2CO_3 in 415 ml solution $= 5.55$ g

Using the above procedure;

For 1st recovery stage

Total wt of NaOH recovered $= 9.01$ g

Total wt of Na_2CO_3 recovered $= 0.68$ g

For the 2nd recovery stage

Total wt. of NaOH recovered $= 3.703$ g

Total wt. of Na_2CO_3 recovered $= 0.31$ g

For the 3rd recovery stage

Total wt. of NaOH recovered $= 1.47$ g

Total wt. of Na_2CO_3 recovered $= 0.108$ g

Total wt. of recovered NaOH $= (46.87 + 9.01 + 3.70 + 1.47)$ g

$$= 61.06 \text{ g.}$$

% Recovery $= \dfrac{61.06}{71.7} \times 100\%$

$$= 85.16\%$$

A.5 Assay of Different grades of lime and soda ash.

Table A.5.1 Assay of AR grade lime

$Ca(OH)_2$	min. 96%
$CaCO_3$	max 3%
SiO_2	max. 0.1%
Cl	max. 0.005%
SO_4	max 0.2%
Pb	max. 0.005%
Fe	max. 0.05%
Ammonium Oxalate	max 2.5%

Table A.5.2 Assay of Analytical grade lime

$Ca(OH)_2$	min. 90%
Al, Fe and Insolubles	max. 1.0%
As	max. 0.0004%
Cl	max. 0.01%
Pb	max. 0.001%
SO_4	max. 0.2%

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Table A.5.3 Assay of commercial grade lime

Ca(OH)$_2$	58.8%
CaCO$_3$	32.8%
H$_2$O	3%

Table A.5.4: Assay of soda ash

Na$_2$CO$_3$	95%
H2O	3%

A.6 Assay of CaCO₃ powder.

Table A.6.1:   Composition and properties of $CaCO_3$ after causticizing
with commercial grade lime

$CaCO_3$	87%
$Ca(OH)_2$	10.5%
pH of saturated solution	10.23
Color	off white
Particle size	70%passed through 100mesh

Table A.6.2: Composition and properties of commercially available
precipitated $CaCO_3$

$CaCO_3$	98%
$Ca(OH)_2$	-
pH of saturated solution	9.72
Color	bright white

A.7.1: Drying Data (AR grade lime)

Drying temperature 120°C

Wt of tray = 640 g

Drying area = 0.0525 m^2

Time min	Wt of tray + filtercake, g	Wt of liquid, g	Moisture content g liq/g dry solid	Avg. Moisture content	Drying rate kg/hr-m^2
0	868	110	0.915	0.839	2.057
10	850	92	0.763	0.72	1.143
20	840	82	0.678	0.657	0.571
30	835	77	0.635	0.573	1.714
40	820	62	0.51	0.425	1.143
60	800	42	0.34	0.234	0.952
90	775	17	0.127	0.085	0.571
110	765	7	0.042	0.0295	0.343
120	760	2	0.017	0.0085	0.229
130	758	0	0	0	0
140	758				

A.7.2: Drying Data (AR grade lime)

Drying temperature 150°C

Wt of tray = 625 g

Drying area = 0.0525 m^2

Time min	Wt of tray + filtercake, g	Wt of liquid, g	Moisture content g liq./g dry solid	Avg. Moisture content	Drying rate kg/hr-m^2
0	820	100	1.053	0.868	4.0
10	785	65	0.684	0.5	4.0
20	750	30	0.316	0.263	1.143
30	740	20	0.21	0.147	1.37
40	728	8	0.084	0.042	0.914
50	720	0	0	0	0
60	720	0			

A.7.3: Drying Data (AR grade lime)

Drying temperature 180°C

Wt of tray = 650 g

Drying area = 0.0525 m^2

Time min	Wt of tray + filtercake, g	Wt of liquid, g	Moisture content g liq/g dry solid	Avg. Moisture content	Drying rate kg/hr-m^2
0	820	80	0.88	0.77	2.29
10	800	60	0.66	0.44	4.57
20	760	20	0.22	0.165	1.14
30	750	10	0.11	0.055	1.14
40	740	0	0	0	0
50	740	0			

A.7.4: Drying Data (AR grade lime)

Drying temperature 220°C

Wt of tray = 620 g

Drying area = 0.0525 m^2

Time min	Wt of tray + filtercake, g	Wt of liquid, g	Moisture content g liq/g dry solid	Avg. Moisture content	Drying rate kg/hr-m^2
0	850	125	1.19	0.952	5.714
10	800	75	0.714	0.428	8.57
20	740	15	0.143	0.715	1.714
30	725	0	0	0	0
40	725	0	0		

A.7.5: Drying Data (Commercial grade lime)

Drying temperature 120°C

Wt of tray = 635 g

Drying area = 0.0525 m^2

Time min	Wt of tray + filtercake, g	Wt of liquid, g	Moisture content g liq/g dry solid	Avg. Moisture content	Drying rate kg/hr-m^2
0	875	105	0.77	0.7	2.286
10	855	85	0.63	0.59	1.143
20	845	75	0.55	0.495	1.714
30	830	60	0.44	0.385	1.714
40	815	45	0.33	0.275	0.875
60	800	30	0.22	0.165	0.85
80	795	25	0.11	0.074	0.57
100	775	5	0.037	0.0295	0.35
110	772	2	0.015	0.011	0.23
120	770	0	0		
130	770	0	0		

A.7.6: Drying Data (Commercial grade lime)

Drying temperature 150°C

Wt of tray = 640 g

Drying area = 0.0525 m^2

Time min	Wt of tray + filtercake, g	Wt of liquid, g	Moisture content g liq/g dry solid	Avg. Moisture content	Drying rate kg/hr-m^2
0	900	130	1.0	0.845	4.573
10	860	90	0.69	0.53	4.573
20	820	50	0.385	0.308	2.290
30	800	30	0.23	0.077	2.290
40	780	10	0.077	0.058	0.572
50	775	5	0.0385	0.019	0.572
60	770	0	0	0	0
70	770	0	0		

A.7.7: Drying Data (Commercial grade lime)

Drying temperature 180°C

Wt of tray = 625 g

Drying area = 0.0525 m^2

Time min	Wt of tray + filtercake, g	Wt of liquid, g	Moisture content g liq/g dry solid	Avg. Moisture content	Drying rate kg/hr-m^2
0	860	100	0.74	0.705	1.14
10	850	90	0.67	0.520	4.57
20	810	50	0.37	0.222	4.57
30	770	10	0.074	0.037	1.14
40	760	0	0	0	0
50	760	0	0		

A.7.8: Drying Data (Commercial grade lime)

Drying temperature 220°C

Wt of tray = 635 g

Drying area = 0.0525 m^2

Time min	Wt of tray + filtercake, g	Wt of liquid, g	Moisture content g liq/g dry solid	Avg. Moisture content	Drying rate kg/hr-m^2
0	890	105	0.7	0.5	6.86
10	830	45	0.3	0.166	4.57
20	790	5	0.033	0.0165	0.577
30	785	0	0	0	0
40	785	0	0		

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A.8: Profitability analysis for lime soda process

Plant Capacity: 2000 MT/year 50% Caustic solution

Purchased equipment cost + Installation cost = Tk. 1,76,000/-[*]

Cost Estimation Table [**]

Direct Cost	Ratio	Cost (Tk.)
Purchased equipment-delivered	100	1,26,61,800
Purchased equipment installed	39	49,38,100
Instrumentation and controls	13	16,46,000
Piping (installed)	31	39,25,100
Electrical (installed)	10	12,66,100
Buildings (including services)	29	36,71,900
Yard Improvements	10	12,66,100
Service facilities (installed)	40	50,64,700
Land	6	7,59,700
Total Direct Plant Cost	293	3,70,99,000

[*] Source: Prospectus of J.H. Chemical Industries Limited, Daily Janakantha, June 17, 1998.

[**] Reference: Peters, M.S. & Timmerhaus, K.D., Plant Design and Economics for Chemical Engineers, 4th ed., p. 183.

Indirect Cost	Ratio	Cost (Tk.)
Engineering and supervision	32	40,51,700
Construction expenses	34	43,05,000
Total direct and indirect costs	359	4,54,55,800
Contractor's fee	18	41,78,300
Contingency	36	45,58,200
Fixed capital investment	413	5,22,93,200
Working capital	74	93,69,700
Total Capital Investment	**487**	**6,16,62,900**

Estimation of Total Product Cost

	Amount	Cost
Na_2CO_3	1743.3 MT/yr	1,91,73,000
Lime	2196 MT/yr	76,86,000
Total Raw materials Cost		2,68,59,000

I. Manufacturing Cost

A. Direct Production Cost

Raw material	2,68,54,000
Operating labor (5% of raw materials cost)	13,42,950

	Direct supervisory and clerical (10% of operating labor)	1,34,295
	Maintenance of repairs (5% of fixed capital investment)	13,07,337
	Operating supplies (10% of cost for maintenance)	1,30,733
	Laboratory charges (10% of operating labor)	1,34,295
	Total Direct Production Cost	2,99,08,610

B. Fixed Charges

	Depreciation	30,60,337
	Local Taxes (4% of fixed capital investment)	20,91,728
	Insurance (4% of fixed capital investment)	5,22,932
		56,74,947

C. Plant-overhead cost (50% of operating labor) — 6,71,475

Total Manufacturing cost = 3,62,55,082

II. General Expenses

A. Administrative costs

(15% of costs of operating labor,

supervision and maintenance) — 4,17,687

B. Distribution and selling costs

(10% of Total product cost) — 44,17,323

C. Financing (5% of total capital investment) — 30,83,145

79,18,155

Total Product Cost — 4,41,73,237

Sales: Caustic soda (50% solution)   Tk. 4,50,00,000

       2000 MT/yr at Tk. 22,500/MT

       Calcium carbonate   Tk. 2,96,00,000

       2196 MT/yr at Tk. 10,000/MT

Total Income	=	Tk. 7,46,00,000
Gross earnings	=	3,04,26,763
Gross earnings cost (Tax 30%)	=	91,28,028

             Net profit   **Tk.   2,12,98,734**