LABORATORY-SCALE PRODUCTION OF COMMERCIAL GRADE CALCIUM CARBONATE FROM LIME-SODA PROCESS

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Received 20 May 2008; received in revised form 17 June 2008

Abstract: Quality precipitated calcium carbonate has much demand in various chemical and allied industries as filler, surface coating, whitening, adhesive etc. A study was carried out by modifying classical lime-soda process to obtain high quality precipitated calcium carbonate. The experiments were carried out in two stages using commercial and analytical grades of sodium carbonate and lime as reactants. After causticization, the filtrates from the washing of calcium carbonate were used to prepare all solutions for reactions in next stage. The precipitated calcium carbonate obtained from the process was analyzed and comparisons were made with the commercially available precipitated calcium carbonate produced from carbonation method. The calcium carbonate produced from causticization was superior to those produced by carbonation method in the country. The crystal structure of carbonate was calcite.

Keywords: *Causticization; Settle Volume; Bulk Density; Yield.*

INTRODUCTION

Precipitated calcium carbonate is one of the most versatile mineral fillers and is used in a wide range of products including paper, paint, plastic, rubber, ink, textiles, chalks, sealants, adhesives etc. United States Pharmacopoeia (USP) grades are used in dentifrices, cosmetics, foods and pharmaceuticals. Crescent Chemicals Ltd. and Usha Chemicals Ltd. are the producers of precipitated calcium carbonate in Bangladesh. The total production capacity of these plants is 20,000 tonnes per year against yearly consumption of 44,000 tonnes and the rest 24,000 tonnes per year of calcium carbonate is imported.

Precipitate Calcium carbonate can be produced by several methods such as [1]:

a. Carbonation Method
b. Calcium Chloride-Sodium Carbonate Double Decomposition Method
c. Lime-Soda Method

The carbonation method is the unique method of calcium carbonate production to-day and is widely used commercially.

The lime-soda process is the classical method of producing caustic soda. In this process, a solution of sodium carbonate is treated with excess calcium hydroxide producing liquid caustic and byproduct precipitated calcium carbonate. The quality of precipitated calcium carbonate formed in this process is not good replacement of commercial precipitated calcium carbonate. The byproduct calcium carbonate is handled in three following different ways [2]:

- "reburned" in rotary kilns to recover lime
- sent to cement plant for use as one of its main raw materials of cement
- disposed as waste when it cannot be sold or used

The present yearly demand for caustic soda and chlorine in Bangladesh are 80,000 tonnes and 3600 tonnes respectively. The demand for chlorine is being met locally while the production capacity of caustic soda in the country is only 20,000 tonnes per year. The rest 60,000 tonnes of caustic soda per year are imported [3]. Because of limited demand of chlorine, the growth of chlor-alkali industry in Bangladesh has been stopped. Considering reality (attractive demand of caustic soda and calcium carbonate) in Bangladesh, lime-soda process can be the right route for making caustic soda as it requires less investment per unit capacity.

The profitability of lime-soda process can be made attractive by improving the quality of the byproduct precipitated calcium carbonate and its efficient recovery. White colour, low alkalinity, free from harmful impurities and non abrasiveness are some prime requisites of calcium carbonate for use as a whitening, filler and coating. If byproduct precipitated calcium carbonate can be produced in such form by modification of the conventional process, the process can be commercially exploited.

This paper deals with obtaining quality precipitated calcium carbonate from modified lime-soda process which involves two stage reaction for completing conversion of soda ash to caustic soda.

EXPERIMENTAL

Causticization was carried out in the laboratory by using both analytical and commercial grades of

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lime and sodium carbonate as reactants. The assay of analytical and commercial grades of lime and sodium carbonate are shown below in Tables 1 to 4. A series of batch reactions were performed keeping lime as limiting reactant in the first stage for each batch. In second stage, sodium carbonate was the limiting reactant by having excess lime.

Table 1: Assay of Analytical Grade Soda Ash

Component	Percent
Na_2CO_3	≤99.5-100.5
Chloride (Cl^-)	≤0.0125
Sulphate ($SO_4^=$)	≤0.025
Arsenic (As)	≤0.001
Lead (Pb)	≤0.0005
Iron (Fe)	≤0.005

Table 2: Assay of Analytical Grade Calcium Oxide

Component	Percent
CaO	≥97
Chloride (Cl^-)	≤0.05
Sulphate ($SO_4^=$)	≤0.5
Insoluble in HCl	≤0.1
Lead (Pb)	≤0.005
Iron (Fe)	≤0.05

Table 3: Assay of Commercial Grade Soda Ash

Component	Percent
Na_2CO_3	≤95.00
Moisture	4.00

Table 4: Assay of Commercial Grade Slaked Lime

Component	Percent
$Ca(OH)_2$	93.00
$CaCO_3$	3.00
Moisture	1.00
SiO_2	0.40
Mg	0.59
Fe	0.01
CO_2	1.50
Dead burnt lime	0.50

A two-litre three necked round bottom heat resistant glass flask was used as causticizer. The size of the central neck was 45/40 mm and the other two side necks were 32/29 mm. The stirrer was fitted through the central neck of the flask and was driven by an electric motor. Calcium hydroxide was kept in suspension by agitation. The other two necks were used to place condenser and thermocouple. Rubber stoppers with provision for installing stirrer, condenser and thermocouple were placed on the necks.

Two-stage causticization for both analytical and commercial grade reactants was performed in the laboratory. First stage was carried out keeping lime at 90% of its stoichiometric amount while the second stage was performed with 50% excess lime. In the initial batch 12.5% sodium carbonate solution was prepared by taking 105 g available soda ash in 735 ml water in a beaker. For subsequent batches the first washed solution of both stage obtained from this batch was recycled and fresh sodium carbonate was added into the recycle stream as makeup. The amount of calcium oxide was charged as described earlier. Each stage of causticization is followed by decantation, vacuum filtration, analysis of product caustic soda, and drying and analyzing of calcium carbonate.

The reactants were charged through the neck fitted with thermocouple by taking it out. Cooling water was supplied countercurrently to condenser. The causticizer was sealed (using stirrer, condenser, and thermocouple in three necks) and the stirrer was then switched on. Heating of solution was started by keeping switch on of electro-mantle to raise the temperature of the solution at 90^0C and it was maintained for 2.5 hrs. The pressure in the causticizer was maintained at atmospheric pressure by keeping the top of condenser open. After causticization for the stipulated time, the stirrer and heating mantle were switched off and the stirrer, thermocouple and condenser were removed from the flask and the valve for condenser cooling water was closed. The slurry was then poured into a beaker for settling. The clear solution was decanted after completion of the settling of the slurry, and the thick dense slurry was sent to vacuum filtration to separate caustic solution from calcium carbonate precipitate. The clear solution and filtrate were collected, analyzed and amount of sodium carbonate in the solution was determined. Caustic solution from first stage was charged for second stage causticization using 50% excess lime to achieve maximum equilibrium conversion of sodium carbonate to caustic soda.

The byproduct calcium carbonate cake from each stage contains a substantial amount of caustic soda in its pore space. To recover caustic soda from calcium carbonate, it was washed thrice as shown in Figure 1.

The cake deposited on the filter paper from last washing stage was dried in an electric oven. Initially cake was placed on tray with filter paper. The temperature of dryer was set at 100^0C and the cake was kept at this condition for about an hour. The cake was then removed from filter paper and disintegrated manually. The cake was then dried for several hours at 110^0C. Finally, the calcium carbonate thus obtained was analyzed. The laboratory work undertaken to complete the causticization in a batch process is schematically shown in Figure 1.

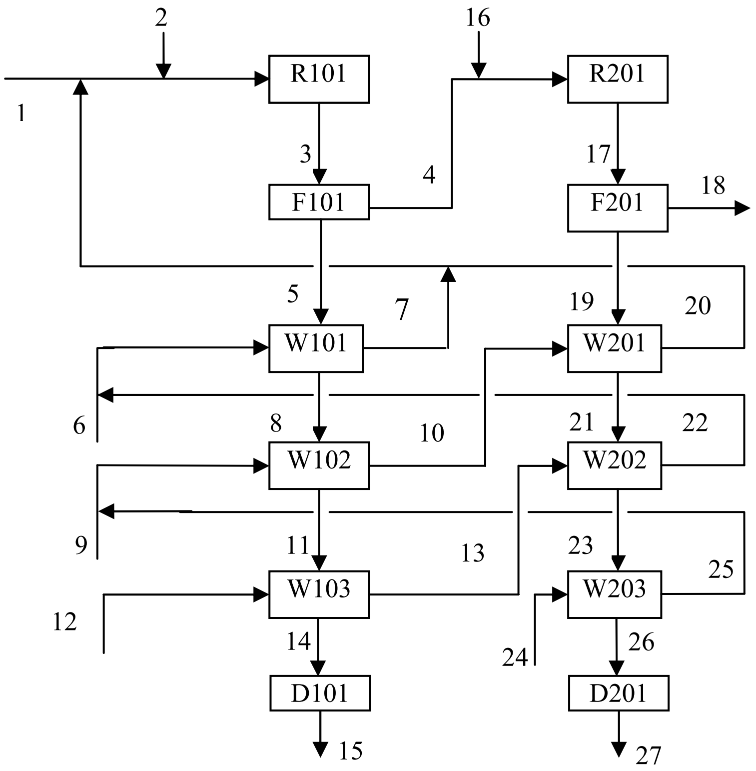


Figure 1: Block Diagram for Experimental Setup Performed in the Laboratory to Carry Out Causticization Reaction in two-stage

1: Fresh sodium carbonate feed to reactor
2: Lime feed to reactor (90% of stoichiometric amount)
3: Total effluent from first causticizer
4: First stage product caustic solution
5: Byproduct calcium carbonate from stage 1
8: First washed calcium carbonate
7: First washed solution from stage 1 used as recycle stream for next batch
6/9/12: Fresh water to stage 1
10: Second washed solution from first stage
11: Second washed calcium carbonate
13: Third washed solution from first stage
14: Washed calcium carbonate
15: Dried calcium carbonate
16: Lime feed to second causticizer
17: Total effluent from second causticizer
18: Product sodium hydroxide from second stage
19: Byproduct calcium carbonate from stage 2
20: First washed solution from stage 2 used as recycle stream for next batch
22: Second washed solution from second stage
24: Fresh water feed to second stage
25: Third washed solution from second stage
26: Washed calcium carbonate from second stage
27: Dried calcium carbonate from second stage
R101: First causticizer
F101: First causticizer outlet filter
W101: First calcium carbonate washer after first causticizer
D101: First stage outlet calcium carbonate dryer
R201: Second stage causticizer
F201: Second stage outlet filter
W201: Second stage outlet calcium carbonate first washer
D201: Second stage outlet calcium carbonate dryer

RESULTS

Table-5 provides conversions of lime and sodium carbonate, and overall conversion of sodium carbonate for two stage causticization reactions.

The calcium carbonate produced by this process was analyzed in the laboratory at Crescent Chemicals Ltd., Gazipur. Table-6 lists various measured parameters that determine the quality of precipitated calcium carbonate.

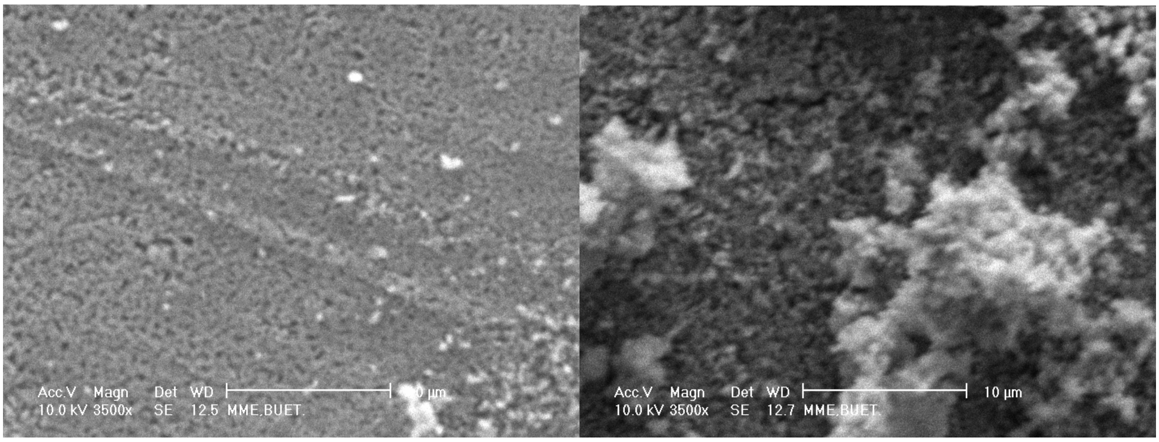
The commercial precipitated calcium carbonate produced by Crescent Chemicals Ltd. using carbonation method as well as calcium carbonate produced by this method was analyzed in the laboratory. Crystal structures were determined by chemical and Scanning Electron Microscope (SEM) method. The crystal structure of each product was found to be calcite. Table-7 shows these results. Figure-2 shows the Scanning Electron Microscopic view of calcite structure.

Table 5: Summary of Results Obtained for Conversions of Lime and Sodium Carbonate to Caustic Soda in Two Stage Causticization

Grades of Reactants	**Stage No**	**% Conversion(to NaOH)**		**% Overall Conversion(to NaOH)**
		Basis: $CaO/Ca(OH)_2$	**Basis: Na_2CO_3**	**Basis: Na_2CO_3**
Analytical	1	94.8-95.1	86.0-86.7	94.0
	2	32.0-35.8	49.0-55.2	
Commercial	1	97.0-97.5	87.6-87.8	94.0
	2	22.0-30.0	34.0-50.0	

Table 6: Analytical Results of Precipitated Calcium Carbonate Produced by Lime- soda Process

	Product Calcium Carbonate using Analytical Grade Reactants	Product Calcium Carbonate using Commercial Grade Reactants
Calcium Carbonate, %	98.30	96.67
Calcium Oxide, %	1.22	1.27
Iron (Fe), ppm	468	1073
Bulk Density, g/ml	0.784	0.579
Settle Volume, ml/min	8/25	13/25
Moisture, %	0.40	0.24
Colour	Brilliant White	White



(a) **(b)**

Figure 2: Calcite Crystal Structure of Precipitated Calcium Carbonate Determined by SEM Method; (a) Analytical Grade Reactants (b) Commercial Grade Reactants

Table 7: Analytical Results of Precipitated Calcium Carbonate in the Laboratory

	Product Calcium Carbonate using Analytical Grade Reactants	Product Calcium Carbonate using Commercial Grade Reactants	Commercial Calcium Carbonate
Calcium Carbonate, %	98.3-99	96.2-97	97.06
Calcium Oxide, %	0.2-0.4	0.3-0.4	0.375
Crystal Structure	Calcite	Calcite	Calcite

Table 8: Comparison of Laboratory Produced $CaCO_3$ with Commercial Grade

	$CaCO_3$ Produced in the Laboratory		Commercial $CaCO_3$ by Carbonation Process (Crescent Chemicals Ltd.)
	Analytical Grade Reactants	Commercial Grade Reactants	
Calcium Carbonate, %	98.30	96.67	96.00
Calcium Oxide, %	1.22	1.27	0.12
Iron (Fe), ppm	468	1073	>1000
Bulk Density, g/ml	0.784	0.579	0.4-0.45
Settle Volume, ml/min	8/25	13/25	18/25
Moisture, %	0.40	0.24	0.50
Color	Brilliant White	White	White

DISCUSSION

This work was concerned with enhancing conversion of sodium carbonate by adopting multi-stage operations. In practice, 12.5% sodium carbonate solution is used in industry to produce caustic soda and equilibrium conversion of this concentration is about 94%. But the average conversion in single stage causticization is not much over 90%. Hence the first stage of causticization was carried out with 90% stoichiometric amount of lime. The purpose of performing this stage was to get 100% conversion of lime i.e., to get high quality precipitated calcium carbonate. In the case of commercial grade reactants, dry calcium hydroxide and sodium carbonate were used to carry out causticization and the conversion from first stage was about 97.5%, but that for analytical grade was about 95%. The reagent grade quick lime used was from an old stock. The exact physical state of the lime was unknown. What has led to conversion lower than expected (calculated) is difficult to explain. But the overall conversion found from each grade was about 94%, remained same for each type of reagent. The commercial precipitated calcium carbonate produced by Crescent Chemicals Ltd. as well as calcium carbonate produced from this method was analyzed in the laboratory. Crystal structures determined by chemical method of each product were found calcite which was also observed by Scanning Electron Microscope (SEM) method. Figure-2 shows the Scanning Electron Microscopic view of calcite structure. The analysis of byproduct calcium carbonate was carried out in the laboratory at Crescent Chemicals Ltd. Table-6 shows result of this analysis and Table-8 shows comparison among produced calcium carbonate by present study to commercial precipitated calcium carbonate produced at Crescent Chemicals Ltd. For analytical grade reactants, the calcium carbonate percent was found about 98.3% as against 96.67% for commercial grade reagents.

Table 7 shows the laboratory analysis of precipitated calcium carbonate produced by carbonation and lime-soda process. The result clearly indicates the quality of product precipitated calcium carbonate obtained from both methods is identical. The calcium oxide content was same for each grade of product.

The bulk density of product calcium carbonate obtained from this process was higher than the product obtained by commercial carbonation process. Presence of Iron, settle volume, colour, etc also affect quality of calcium carbonate.

The bulk density is very important criteria of precipitated calcium carbonate for consuming the product in paper, plastic, ceramic, rubber industries etc. The major problem of in commercial processes is low bulk density of their product calcium carbonate. As a result they can not expand their market in those sectors like paper making industries where high bulk density is the prime requisite of precipitated calcium carbonate. The colour of the product calcium carbonate was also white.

Calcium carbonate occurs in nature either of two polymorphs: calcite or aragonite. The crystal form of calcite is hexagonal form and aragonite is in orthorhombic system. In the commercial forms of precipitated calcium carbonate, where aragonite predominates, crystals have parallel sides and large length to width ratios.

The production of caustic soda from lime-soda process is not cost effective if it is produced using conventional one stage process. The conventional one-stage process may be replaced by present two-stage lime-soda process. In present lime-soda process, the byproduct calcium carbonate is highly pure, comparable with commercially available calcium carbonate. The byproduct calcium carbonate has a great demand in various industries as filler, coating, adhesive etc., so this two stage lime-soda process may play an important role in partial fulfilling the demand of caustic soda and calcium carbonate. Marketing of this quality byproduct calcium carbonate will improve the economic viability of lime-soda process in Bangladesh. Thus, Multi-stage causticization can pave the way for achieving equilibrium conversion of sodium carbonate to sodium hydroxide as well as obtaining purer calcium carbonate in the first stage by using lime as the limiting reactant.

CONCLUSION

The by-product calcium carbonate obtained from this modified process was pure. The quality of this product was comparable with the commercially available precipitated calcium carbonate produced by carbonation method. In the case of analytical grade reactants, the calcium carbonate produced was 98.3%, which was 96.67% for commercial grade reactants. The crystal structure of precipitated calcium carbonate was found to be calcite.

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