

PRODUCTION OF MARINE CHEMICALS IN PAKISTAN

Part IV. Optimization of Parameters for the Production of Light Weight Magnesium Carbonate from Sea Bittern

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(Received September 23, 1993 ; revised April 5, 1995)

Sea bittern can serve as a basic raw material for the production of light weight magnesium carbonate. Experiments have been carried out to optimize various parameters which affect the bulk density of the product. It has been observed that the rate of agitation and the concentration of reactants are the controlling factors. Choosing as suitable combination of the rate of agitation (280/560 rpm) and the concentration of reactants (Mg^{++} 20-25 gml^{-1}), (Na_2CO_3 250-265 gml^{-1}), light weight magnesium carbonate of bulk density 0.1-0.125 gml^{-1} can be prepared which is in demand in the local market.

Key words: Sea bittern, Magnesium carbonate, Parameters.

Introduction

The light variety of magnesium carbonate contains a crystalline species of magnesium hydroxy carbonate (hydromagnesite), whereas the heavy variety, in addition to hydromagnesite, also contains magnesite in certain proportions [1]. Both light and heavy weight varieties of magnesium carbonate are prepared by reacting solutions of magnesium salt (or sea bittern which contains sufficient magnesium ions) and sodium carbonate [2-7]. The essential difference between preparation of the two varieties is that the former requires controlled conditions of mode and time of addition, concentration of reactants, degree of agitation and temperature etc. Previously, efforts were made to study separately, the effect of each variable. However, no comprehensive or integrated attempt was made to study all involved parameters in a single 'go'. The main objective of the research, reported here, was to investigate the parameters which affect bulk density and optimize them.

Bittern, the mother liquor left after the recovery of sodium chloride from sea water, has been utilized for the production of various industrial chemicals [8,9]. Thus locally available sea bittern can also be used as a basic raw material in the production of light weight magnesium carbonate.

Experimental

Experiments were carried out utilizing commercial grade dried soda ash (approx. 85% by weight) and sea bittern (around 30°Be) having an average composition on weight basis: NaCl 11.5%, KCl 1.7%, $MgCl_2$ 8.1% and $MgSO_4$ 6.2% [9]. Soda ash solution of a suitable concentration was added to the bittern solution diluted to the desired concentration in a reactor of standard design fitted with a speed controlled stirrer.

In the first set of experiments, the aliquot soda ash solution of proper concentration was fed almost instantaneously (within 5-10 sec) to the bittern solution containing a stoichiometrically equivalent amount of Mg^{++} ions in a continuously stirred reactor. In order to collect time concentration data, samples of slurry were taken out at various time intervals up to 1800 sec and analysed for Mg^{++} ions and sodium carbonate content [10].

Both the second and third sets of experiments were conducted in semi-batchwise fashion following the same procedure. However, the levels of variables in each set were chosen differently. In the second set (pilot set), combinations of the levels of variables were chosen at random, whereas in the third set, choice was strictly according to the rules of factorial planning [11]. In these sets aliquot soda ash solution was added within 6 min to the bittern solution as explained earlier, through a specially designed perforated ring, placed below the stirrer. The temperature of reactants was maintained at 32-35°C throughout the experiments [5]. After addition of the soda ash solution, stirring was continued for 10 to 15 min. Then the product was filtered off, dried, ground and the bulk density determined by the ASTM method [12]. A minimum of two experiments were carried out for each combination.

It is difficult to evolve a precise relationship amongst bulk density and divergent conditions involving temperature, concentration of reactants, agitation rate, time and mode of addition etc., however, by properly devising the experiments, effect of the levels of characteristic variables could be assessed on bulk density. Hence a problem solving technique was adopted to evaluate the effect of various combinations of parameters of bulk density. Experimental studies were di-

vided into three sets, each planned to obtain specific information. On the basis of a literature survey [5] and our previous experience, some of non-property parameters such as temperature, time and method of addition were standardized. This in turn resulted in eliminating the effect of these parameters and in confining this investigation to the study of two variables only, concentration levels and rate of agitation.

The first set of batchwise experiments was aimed at studying changes in concentration of reactants with time whence one constituent (soda ash) was instantly added to the other. The second set of experiments (a semi batch operation) was designed to acquire data regarding maximum and minimum levels of variables and their effect on bulk density. The third set of experiments (also semi-batchwise) was based on factorial planning which reduced the number of experiments and also made this study more systematic. According to the methods, various combinations of low (-) and high (+) levels of parameters are chosen and the property or characteristics to be studied in the present case the bulk density is noted as a response [11]. Such a technique is particularly useful in situations where no precise relationship could exist between the desired property and the variables which govern it. For operational convenience, in case of factorial planning, the effect of concentration levels on bulk density was investigated in two separate sets with agitation rate of 280 and 560 rpm. respectively. The choice of concentration levels of the two reactants was made in the light of results of previous sets and literature survey [5].

Results and Discussion

A critical review of the data, viz. concentration of reactants against time (Table 1a and 1b), suggested that the reaction was spontaneous. Within first 30 sec, the concentration

of the respective reactant dropped substantially (from 31.5 to

TABLE 1 (a): CHANGE IN CONCENTRATION OF REACTANTS AT 140 RPM.

Time in seconds	Mg ⁺⁺ ions gml ⁻¹		Na ₂ CO ₃ gml ⁻¹	
	Experiment A	Experiment B	Experiment A	Experiment B
00	31.55	31.64	206.22	207.96
30	05.20	05.10	22.50	22.22
60	05.00	05.00	21.80	21.79
90	04.80	04.80	20.91	20.92
120	04.60	04.50	20.00	19.61
150	04.60	04.30	20.00	18.74
180	04.40	04.00	19.00	17.43
240	03.00	03.00	13.00	13.00
300	02.50	02.40	10.89	10.46
360	02.00	02.00	08.70	08.717
900	01.20	01.00	05.02	04.359
1800	00.90	00.80	03.92	03.486

TABLE 1 (b): CHANGE IN CONCENTRATION OF REACTANTS AT 280 RPM.

Time in seconds	Mg ⁺⁺ ions gml ⁻¹		Na ₂ CO ₃ gml ⁻¹	
	Experiment A	Experiment B	Experiment A	Experiment B
00	31.07	31.07	207.05	207.05
30	05.60	05.80	23.90	23.80
60	05.40	05.60	23.50	23.50
90	05.20	05.30	22.60	22.66
120	05.00	05.00	21.79	21.79
150	04.90	04.80	20.95	20.92
180	04.60	04.70	20.04	20.48
240	04.20	04.30	18.30	18.74
300	03.90	04.00	16.99	17.43
360	03.80	03.80	15.69	15.56
900	01.70	01.60	07.40	06.97
1800	01.00	00.90	04.35	03.92

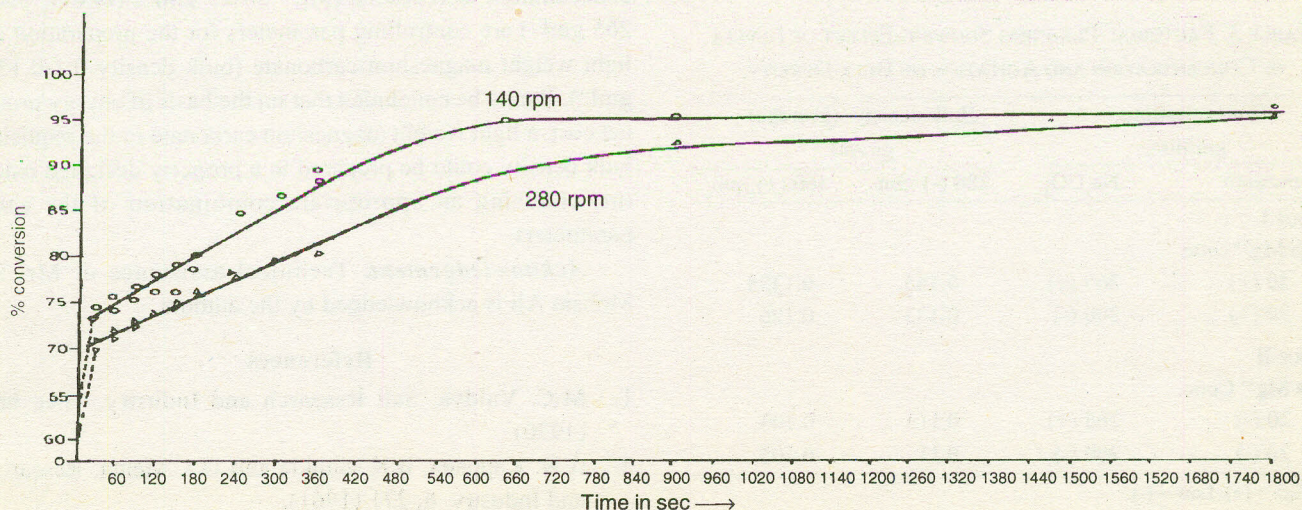


Fig. 1. % Conversion of Mg⁺⁺ vs time in sec.

5.5 gml⁻¹ for Mg⁺⁺ ions and from 207 to 23 gml⁻¹ for Na₂CO₃. Thirty seconds onward to the end of experiment, the decrease in respective concentrations was gradual at a diminishing rate whence final values were around 1 gml⁻¹ for Mg⁺⁺ ions and 3 gml⁻¹ for Na₂CO₃. Therefore, further treatment of primary data was considered imperative. Accordingly a graph was drawn for percentage conversion against time (Fig.1) which revealed the following: (i) About 72 to 77% conversion took place within first 30 sec. (ii) The relationship was linear between 30 and 360 sec, during which 82 to 88% conversion took place. (iii) After 6 min, the rate of conversion was non-linear and diminishing. This trend continued up to 9 min.

The total conversion after 15 min was around 95%. Thereafter, the curves became asymptotic to time axis, signifying that equilibrium condition had arrived under given conditions and additional conversion was not possible. (iv) During initial stages a gap in percentage conversion was also noted at two levels of agitation for the same period of time (Fig.1). Curiously enough, lower conversion was noticed at higher rpm (280), a phenomenon contrary to normal behaviour. Most probably this was caused by the formation of smaller size particles at higher rpm offering higher resis-

tance to mass transfer during the initial stages. However, the gap between conversion at the two levels decreased slowly and eventually became quite narrow at the end of 30 min suggesting that the rate of conversion was independent of rpm for a longer period of agitation and that continued agitation beyond 30 min would not enhance product yield or quality. It was also observed that instantaneous addition of reactant resulted the formation of heavy variety of the products. Hence in order to obtain the products of requisite bulk density, soda ash solution was added at a uniform rate within 9 min during which more than 82% of the conversion was achieved.

The results of the second set of experiments (Table 2) indicated that: (i) Generally, the rate of agitation was the controlling factor, over-shadowing the effect of concentration. (ii) At low rpm (140), the bulk density was found to be independent of concentration levels and moreover the product obtained was not of desired quality hence it was excluded from the scope of future studies.

Results of the factorial planning experiments (Table 3) confirmed that for a given combination of reactant concentrations, bulk density of the product was low at high rpm substantiating that agitation was the major factor for obtaining the desired product. It was also noted that for a given rate of agitation, the bulk density increased with higher Mg⁺⁺ ion concentrations.

In view of this, various combinations of low (-) Mg⁺⁺ ion concentrations and appropriate agitation rates could be chosen to obtain a product of the desired bulk density. If energy is a criterion, lower rpm (280) would be favourable while if lower bulk density is demanded, higher rpm level (560) should be chosen.

The experiments carried out during this study have thus established that the rate of agitation (280/560 rpm) and the concentration of reactants (Mg⁺⁺ 20-25 gml⁻¹, Na₂CO₃ 250-265 gml⁻¹) are controlling parameters for the preparation of light weight magnesium carbonate (bulk density 0.1-0.125 gml⁻¹). It may be concluded that on the basis of energy/product cost, a light weight magnesium carbonate of the requisite bulk density could be prepared in a properly designed reactor, choosing an appropriate combination of the said parameters.

Acknowledgement. Technical assistance of Mr. S. Mohsin Ali is acknowledged by the authors.

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TABLE 2. EFFECTS OF CONCENTRATION AND AGITATION RATE ON BULK DENSITY.

Experiment	RPM	Concentration of reactants (W/V)		Reaction time (sec).	Bulk density gm ml ⁻¹
		Mg ⁺⁺	Na ₂ CO ₃		
1	140	20	150	1800	0.185
	140	25	200	900	0.260
2	280	25	250	600	0.15
	280	23	200	900	0.14
3	560	20	250	600	0.09
	560	20	200	900	0.10

TABLE 3. FACTORIAL PLANNING SHOWING EFFECT OF LEVELS OF CONCENTRATION AND AGITATION ON BULK DENSITY.

Concentrations gm/litre		Bulk density (average) gm/ml	
Magnesium	Na ₂ CO ₃	280 (-) rpm	560 (+) rpm
GROUP I			
High Mg⁺⁺ conc.			
30 (+)	265 (+)	0.145	0.1325
30 (+)	200 (-)	0.133	0.126
GROUP-II			
Low Mg⁺⁺ Conc.			
20 (-)	265 (+)	0.113	0.103
20 (-)	200 (-)	0.11	0.105

High = (+). Low = (-).

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