

KINETIC STUDIES AND REACTOR DESIGNING FOR THE PRODUCTION OF LIGHT WEIGHT MAGNESIUM CARBONATE

Nayeemuddin*, S Naeem Mahmood, S Burhanuddin Abdali, M Habib and Mohsin Ali

PCSIR Laboratories Complex, Karachi-75280, Pakistan

(Received 4 August 1995; accepted 16 May 1998)

Studies have been undertaken to investigate kinetic data for producing light weight magnesium carbonate from magnesium sulphate and commercial soda ash solution. Using factorial planning, series of batch-wise experiments were carried out in a 25 lit capacity stirred tank reactor (S.T.R.) at three concentration levels of the reactants (viz. low, medium and high) and two agitation levels (viz. 280 and 560 r.p.m.). It has been observed that initial concentration of Mg^{++} ions has pronounced effect both on the yield of the desired product and reaction kinetics. Whereas the agitation level/Reynolds number (within range of 6000 to 17000) has insignificant effect on the said parameter. The optimum concentrations of the reactants at which the concentration - time plot is linear are: Mg^{++} ions 20 g l^{-1} and Na_2CO_3 270 g l^{-1} . The data obtained has been applied to design C.S.T.R. which suggests that a single tank reactor (0.6 m^3) operating within the range of 30 - 45 r.p.m. would be economically feasible to produce 125 Kg h^{-1} of light weight magnesium carbonate.

Key Words: Kinetic studies, Light weight magnesium carbonate, Design of reactor, Material balance, Order of reaction.

Introduction

The earlier work (Nayeemuddin *et al* 1995) concerning the production of light weight magnesium carbonate from sea bittern was restricted to the development of a systematic process and optimization of the related parameters. The variables investigated and optimized using factorial planing technique comprised, concentration of reactants, degree of agitation, time of addition and mixing time allowed to complete the reaction as far as possible. The investigation however, lacked basic information on reaction kinetics in the presence of slurry and depleted concentration ranges. Study of kinetics is imperative for estimating the rate of reaction, its relationship with concentration of reactants and degree of agitation. It is also found helpful for preparing cost estimates of reactor and prediction of changes if any, in operating conditions. Accordingly, a series of experiments, essentially batchwise, was arranged in stirred tank reactor and the data extended to design a continuous reactor. The studies were carried out at three concentration levels of the reactants and two levels of agitation. It was also investigated that which of the two reactants had more dominating effect on kinetics and the corresponding optimum concentration level. The study of temperature and pressure has been excluded from the present investigation, because the former has already been optimized (Wintershall 1965) and the latter would not be a parameter as the reactants are in liquid phase. Availing the opportunity, Reynolds number has

*Author for correspondence

also been calculated in a couple of instances to explain the effect of agitation level.

Materials and Methods

Studies have been carried out utilizing the solutions of dried commercial soda ash and magnesium sulphate. Experiments were arranged at three concentration levels of Mg^{++} ions namely low ($20\text{-}21\text{ g l}^{-1}$) medium ($27.5\text{-}30\text{ g l}^{-1}$) high (36.8 to 37.7 g l^{-1}) whereas the concentrations of sodium carbonate ($250\text{-}280\text{ g l}^{-1}$) were selected at random. In all the experiments, the aliquot of soda ash solution of certain concentration was instantly fed (within 5 to 10 seconds) to the stoichiometrically equivalent amount of magnesium sulphate solution of chosen concentration in a 25 litre tank reactor of standard design (Dengbigh and Turner 1972) fitted with stirrer and speed controlling device.

In order to collect data in respect of change of concentration with time, the contents of the tank were kept stirred for 30 min after the addition of soda ash samples of slurry were taken out at definite time intervals, weighed immediately, filtered off under vacuum and the filtrate collected into a filtering flask containing cold distilled water to arrest further reaction between unreacted reactants. The filtrate and washings were transferred to a volumetric flask, diluted to a known volume and analysed for Mg^{++} contents; the analytical results were reported as g l^{-1} of slurry (Table-1). Each set of experiment was repeated at three concentration levels and two levels of agitation (280/560 r.p.m).

Results and Discussion

Examination of the data viz. drop in concentration of Mg^{++} against time (Table-1) indicates that it may be divided into three distinct regions, each corresponding to a definite time range. The first one consisting of several subregimes and lasting only about 0.5 to 1 min. may be denoted as instantaneous regime, during which rate of reaction is too fast to be measured. The second phase, namely the intermediate reaction regime starts after 1 min. and continues upto 12 min. The third one, characterized by a slow reaction regime which continues from 12 min. onwards, is of no significance. Consequently from the point of view of application to process design, the study of kinetics of intermediate regime is of practical value and is therefore highly desirable. Further, review of Table-2, reveals that the conversion of Mg^{++} to magnesium carbonate is proportional to its initial concentration level. For low conc-level of Mg^{++} (20 g l^{-1}), the conversion is 89.5 to 90%, for medium conc-level of Mg^{++} (27.5 to 30 g l^{-1}), it is around 91.8 to 94% and for high conc-level it is in the range of 93% to 95.5%; which is in conformity to the basic laws of chemistry.

At this stage an objective analysis of the mechanics of S.T.R. for the reaction under-study would lead to useful conclusions in respect of the conditions to be maintained in the reactor and interpretation of kinetic data of the resistance to mass transfer built up as a result of quick precipitation of magnesium carbonate during instantaneous regime. It may be considered with fair degree of confidence that in subsequent regime a very good majority of feed(s) elements on entering the reactor, first get diluted and then react. This in practice, nevertheless, calls for appropriate designing of the stirring and feeding systems. In an efficiently designed and properly operated reactor(s), agitation level should be enough to disperse the entering feed through reactor body, so that the local concentration variations are minimized. This in turn would be helpful in maintaining the steady state conditions

in the tank(s). Any departure from conditions which may arise due to improper design or operation is likely to disturb the steady state conditions. In addition, the tank(s) should be operated at concentrations of reactants lower than that attained at the end of the instantaneous regime. This is essential for two reasons. Firstly the kinetics of the instantaneous regime is not known and secondly the reaction in this regime results into heavy weight variety of the product.

As there exists distinct difference both in the mechanics of mass transfer and the kinetics of the three regimes, each may be categorized separately by suitably reclassifying the time as reported in Tables 1 & 2.

The plots drawn from the data (Table-1) at three levels of concentrations (Figs. 1a, 1b, 1c), reveal that the drop in concentration against time in respect of $20 \text{ g l}^{-1} Mg^{++}$ is linear, whereas it is non-linear for higher Mg^{++} ions concentration. This in turn suggests that at low concentration (around 20 g l^{-1}) of Mg^{++} ions, the reaction is of zero order which has been reported to be a common phenomenon in case of solutions (Fazal-i-Hussain and Ghaziuddin 1978). Further it is also evident that the concentration level of soda ash solution has insignificant effect within the range of 250 to 280 g l^{-1} . It is also transpired from the studies that agitation level/Reynolds Number in the chosen range has quite insignificant effect on the degree of conversion. Higher agitation rates/Reynolds number beyond 6500 would be undesirable as the result will be the increased energy cost.

These investigations have established that the initial concentration of Mg^{++} has pronounced effect both on the conversion into the desired product and the kinetics of reaction optimum being around $20 \text{ g l}^{-1} Mg^{++}$ (ions). On the other hand, the concentration of sodium carbonate at given agitation level/Reynolds Number does not appear to have any significant bearing on the kinetics and conversion even upto 270 g l^{-1} (Table 2). Therefore, in order to carry out material balance for g l^{-1} the reactor of 3 tons per day capacity plant (125 Kg

Table 1
Drop in molar concentration of Mg^{++} ions

Time in Sec		Low Conc. of Mg^{++} Ions				Medium Conc. of Mg^{++} Ions				High Conc. of Mg^{++} Ions			
		280 r.p.m.		560 r.p.m.		280 r.p.m.		560 r.p.m.		280 r.p.m.		560 r.p.m.	
$Mg \text{ g l}^{-1}$		20	20	20.8	20	28.8	27.5	29.5	29.9	36.8	37	37.7	37.5
$Na_2CO_3 \text{ g l}^{-1}$		264	270	253	270	270	268	270	265	280	250	271	266
0	Instantaneous - regime (I)	0.822	0.822	0.855	0.822	1.184	1.134	1.122	1.185	1.48	1.52	1.55	1.55
60	Intermediate regime (II)	0.287	0.279	0.246	0.234	0.259	0.263	0.2	0.2	0.259	0.296	0.22	0.263
180		0.259	0.254	0.226	0.213	0.246	0.250	0.189	0.195	0.254	0.287	0.22	0.259
360		0.205	0.198	0.185	0.16	0.22	0.235	0.123	0.113	0.193	0.185	0.2	0.15
540		0.131	0.14	0.12	0.11	0.150	0.170	0.099	0.112	0.133	0.15	0.14	0.10
720	Slow regime (III)	0.085	0.08	0.09	0.086	0.08	0.102	0.074	0.08	0.086	0.123	0.078	0.082
1080		0.083	0.078	0.086	0.082	0.08	0.095	0.069	0.07	0.078	0.106	0.078	0.069
1800		0.080	0.069	0.082	0.078	0.074	0.094	0.069	0.065	0.078	0.106	0.061	0.061

Table 2
Percentage conversion of Mg⁺⁺ ions

Time in Sec	Low Conc. of Mg ⁺⁺ Ions				Medium Conc. of Mg ⁺⁺ Ions				High Conc. of Mg ⁺⁺ Ions			
	280 r.p.m.		560 r.p.m.		280 r.p.m.		560 r.p.m.		280 r.p.m.		560 r.p.m.	
Mg gl ⁻¹	20	20	20.8	20	28.8	27.5	27.5	29.9	36.8	37	37.7	37.7
Na ₂ CO ₃ gl ⁻¹	264	270	253	270	270	268	270	265	280	250	271	266
0	Instantaneous - regime (I)											
60	Intermediate regime (II)											
180	65	66	71.2	71.5	78.2	76.72	83.6	83.12	82.5	80.52	85.6	83.03
360	68.5	69.1	73.56	74.1	79.2	77.87	84.5	83.5	82.8	81.1	85.6	83.29
540	77.5	76.03	78.36	80.53	81.25	79.2	89.9	90.46	86.95	87.82	87.09	90.32
720	82.9	82.96	85.96	86.61	87.33	84.95	91.8	90.85	91.21	90.13	90.96	93.54
1080	89.65	90.2	89.47	89.5	93.2	90.97	93.93	93.24	94.18	91.88	94.96	94.7
1800	89.9	90.5	89.9	90.0	93.2	91.59	94.34	94.09	94.72	93.0	94.96	95.54
1800	90.26	91.49	90.38	90.4	93.75	91.68	94.34	94.5	94.72	93.0	96.06	96.02
Reynolds number	6000				12000				8500			

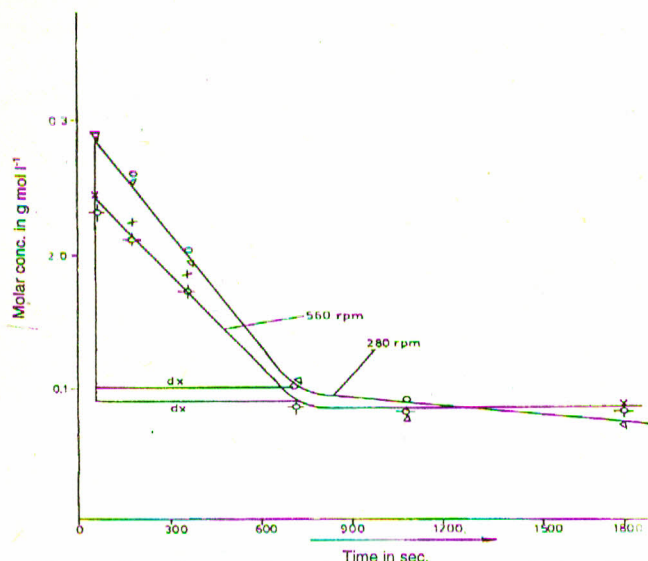


Fig 1a. Reaction profile at low concentration of Mg⁺⁺ ions showing drop in molar concentration.
At 280 RPM O = 20 gl⁻¹; Δ = 20 gl⁻¹, At 560 RPM + = 20.80 gl⁻¹; -○ = 20 gl⁻¹

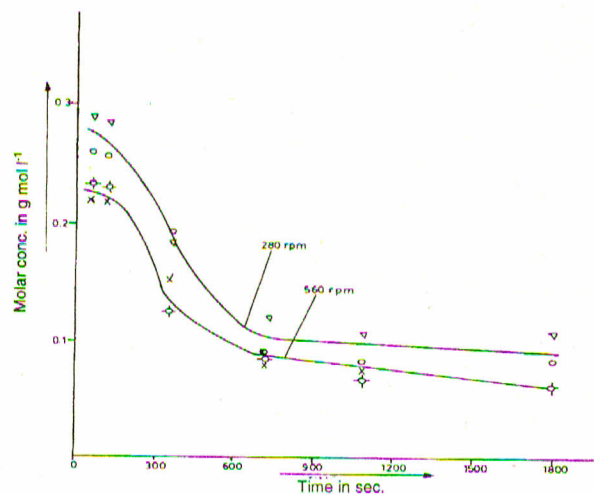


Fig 1c. Reaction profile at high concentration of Mg⁺⁺ ions showing drop in molar concentration.
At 280 RPM O = 36.8 gl⁻¹; Δ = 37 gl⁻¹, At 560 RPM + = 37.7 gl⁻¹; -○ = 37.7 gl⁻¹

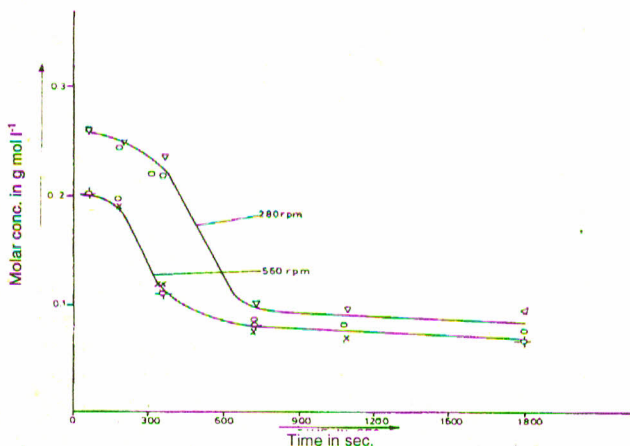


Fig 1b. Reaction profile at medium concentration of Mg⁺⁺ ions showing drop in molar concentration.
At 280 RPM O = 28.8 gl⁻¹; Δ = 27.5 gl⁻¹, At 560 RPM + = 29.5 gl⁻¹; -○ = 29.9 gl⁻¹

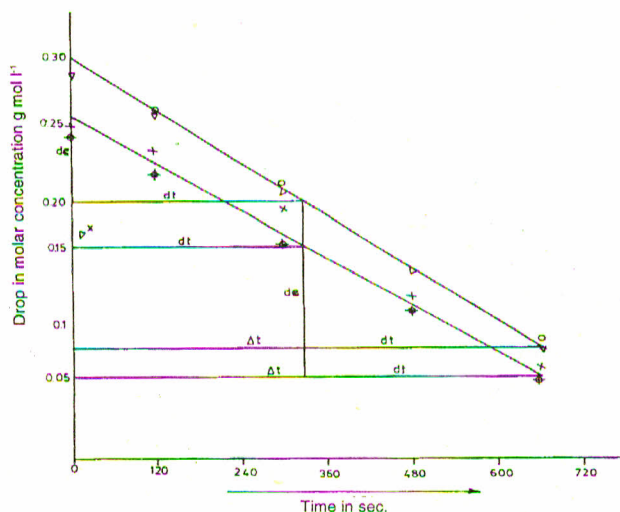


Fig 2. Intermediation reaction regime at low concentration of Mg⁺⁺ ions showing drop in molar concentration.
At 280 RPM O = 20 gl⁻¹; Δ = 20 gl⁻¹, At 560 RPM + = 20 gl⁻¹; -○ = 20 gl⁻¹

Table 3

Material balance basis 125 kg per hour of light weight $MgCO_3$ composition of feed (Mg : 20g l⁻¹ and Na_2CO_3 : 270 g l⁻¹)

Input			Output		
1. $MgSO_4$ Solution:		2182.64 kg	1. Light Weight Magnesium Carbonate		125kg. (90%)
i) $MgSO_4 \cdot 7H_2O$	380.74 kg		i) Pure product	112.5 kg	
a) Mg^{++}	36.05 kg		ii) Impurities	6.25 kg	
b) SO_4	142.3 kg		iii) Moisture	6.25 kg	
c) Impurities	15.8 kg		2. Effluents		2824.43 kg
d) Water of crystallization	180.77 kg		i) Na_2SO_4	189.4 kg	
ii) Water for Solution	1802.5 kg		a) Na^{++}	61.35 kg	
			b) SO_4^{--}	128.05 kg	
2. Na_2CO_3 Solution:		766.8 kg	ii) $MgSO_4$	17.86 kg	
i) Na_2CO_3 (Commercial)	184.85 kg		a) Mg^{++}	3.61 kg	
a) Na_2CO_3	157.12 kg		b) SO_4^{--}	14.25 kg	
Na ⁺			iii) Na_2CO_3	15.62 kg	
b) Impurities	27.72 kg		Na ⁺	6.78 kg	
ii) Water for solution	581.94 kg		iv) Impurities	36.95 kg	
			v) Water	2564.96 kg	
Total		2949.43 kg	Total		2949.43 kg

Table 4

Size of reactor with respect to residence time

Reynolds number	Entering Conc.(CAo) R. P. M.	Leaving Conc.(CA) R. P. M.	Difference (CAo - C)	$K = dc/dt$	Residence time θ (F) Sec.	Capacity $\theta'F = CAo - CA/k$	Reactor m/ft	Estimated R. P. M.	Suggested Capacity of Reactor m3	Suggested R.P.M.	
8500	0.300	0.085	0.215	0.01954	660	0.54	0.883/2.89	38*	0.60	0.915	30-45
17000	0.255	0.065	0.19	0.01727	660	0.54	0.883/2.89	76.8**	0.60	0.915	60-70

*Scaled-up on the basis of 280 r.p.m of Experimental unit; ** Scaled-up on the basis of 560 r.p.m. of experimental units.

h⁻¹) the concentration of reactants have been taken: Mg^{++} ions 20 g l⁻¹, sodium carbonate 270 g l⁻¹ and the conversion to the desired product is 90%. As for the product average analysis of the sample prepared under controlled conditions, it has been found to contain (i) 90% magnesium compound and (ii) 10% impurities and moisture. The material balance calculated on the basis of the above data proved to be instrumental in designing the reactor and has been presented in Table 3. As for r.m.p, it has been scaled-up on the basis of equal linear velocity of the tips.

Application to design. The reaction between sodium carbonate and Mg^{++} leading to the formation of magnesium carbonate is instantaneous, irreversible, equimolar reaction of the type: $A + B \rightarrow$ Products (Octave Levenspiel 1972) and as such appears to be of second order. The reactants in solution form are homogenous, but once they come in contact, instantaneous formation of insoluble phase

results into nonhomogeneity, which according to its degree, drastically impedes the rate of reaction. Under this condition there appears to be some relationship between drop in concentration and time which enables the measurement of kinetics.

Derivation of Working Relationship. A general material balance equation on any element (smallest possible amount) of reactant species may be written as follows (Dengbigh and Turner 1972): (Moles entering) = (Moles leaving) + (Moles reacting) + (Change of moles within the element).....(i)

It may be noted that the final form of the relationship developed, would be specific to the type of reactor, and the conditions to be maintained therein. In the light of the mechanism of reaction discussed in the preceeding paragraphs, the general equation may be modified to the following, "rate equation" for component "A" in respect of any continuous reactor (Dengbigh and Turner 1972).

(Rate of moles of A entering) = (Rate of moles of A leaving) + (Rate of moles of A reacting) + (Rate of change of moles of A within tank).....(ii)

The above equation may be written algebraically as follows (Coriga *et al* 1955) $F(C_{Ai}) = F(C_{Af}) + kv(C_{Af})^n + V(dCA/dt)$(iii)

Since a C.S.T.R. has been opted, wherein the conditions in the tank remain in steady state i.e. $dCA/dt = 0$, and $n = 0$, being zero order reaction, the above equation may be rewritten in the final form as follows: $F(C_{Ai} - C_{Af}) = K(V/F)$(iv)

Design of Reactor. Using the relationship of equation (iv) and the material balance data (Table 3), various parameters for both the degrees of agitation have been estimated and reported in (Table 4). It is evident from the data that higher r.p.m. neither significantly improves the conversion rate nor reduces the residence time; it rather results into increased energy consumption and hence may be dropped. Since the drop in concentration against time in the intermediate regime is linear Fig. 2 the increase in the number of tanks does neither affect the total

residence time nor the volume of the reactor. It is effect therefore suggested to use a single stirred tank reactor.

References

- Coriga T E, Young E F, Resercher C E 1955 Chemical engineering fundamentals, general consideration in reactor design-II. *Chemical Engineering Journal* 211-215.
- Denghigh K G, Turner J C R 1972 *Chemical reactor theory introduction*. E.L.B.S. Cambridge University press 2nd ed 8-10, 17,67.
- Fazal-i-Hussain, Ghaziuddin 1978 *Chemical kinetics physical chemistry*, 2nd ed, PP-290-293.
- Nayeemuddin, Mahmood S N, Abdali S B, Habib M 1995 Production of marine chemicals in Pakistan. Part-IV. Optimization of parameters for the production of light weight magnesium carbonate from sea bittern. *Pak J Sci Ind Res* 38 (8) 326.
- Octave Levenspiel 1972 *Chemical reaction engineering*. John Wiley & Sons Inc New York 2nd ed pp 10, America.
- Winter shall A G 1965 Magnesium carbonate and sodium sulfate. Budan and Alexander effmert, *Ger* 1 192, 165 (Cl. Colf)