A STATISTICAL APPROACH TO EVALUATE FACTORS AFFECTING MAGNESIUM AMMONIUM SULPHATE PRODUCTION

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ABSTRACT

A statistical screening designs were conducted to determine the effective factors affecting the production of magnesium ammonium sulphate fertilizer. The screening designs were based on 16 run design. The conversion of Mg was chosen as a measure for the production of $Mg(NH_4)_2(SO_4)_2$ fertilizer from a reaction of slurry solutions (gypsum and dolomite) with ammonium hydroxide in presence of CO_2 gas. The most significant factors affecting the Mg conversion were reaction time followed by CO_2 flow rate. Temperature was insignificant in the range studied. Mathematical equation was developed to predict the percentage Mg conversion.

Key words:

Magnesium ammonium sulphate, Screening design, Factorial design.

INTRODUCTION

Magnesium ammonium sulphate is considered an important multicomponent fertilizer required by certain plants to provide them with combinations of N_2, S and MgO in one package. This is an efficient method to distribute multicomponent fertilizers to the soil. The production of $Mg(NH_4)_2 (SO_4)_2$ is carried out by reaction of gypsum and dolomite with ammonium hydroxide in presence of CO_2 gas [1]. The materials used for production usually contain several impurities which affect the product quality. The production rates are affected by operating variables such as reaction time, slurry concentrations, CO_2 flow rate and solution temperature. Therefore, before finding the effects of impurities on product quality, it is necessary to determine first the effect of the process variables on the production rate.

Usually it is most efficient to estimate the effects of several variables simultaneously in a statistical experimental design [2,3]. The relative importance of independent or factor variables can be ascertained from Plackett-Burman screening design. This design is based on a simplified first order empirical model, but will also yield information indicating overall curvature, or deviations from linear model, and give an indication of the presence of interaction effects among variables.

Plackett-Burman screening design has several sizes (8,12 and 16), each has its merits and drawbacks, depending on information that is desired [4,5].

In general, the screening design program provides valuable information for chemical process industries particularly when more than one variable of potential importance are present [6,7]. The present study aims at determining, by means of screening designs, the significant factors affecting the production of magnesium ammonium sulphate and interactions among variables.

2. EXPERIMENTAL WORK

2.1. Screening Design

A 12 run Plackett-Burman was chosen to investigate the importance of parameters listed in Table I. The high, low and intermediate values of the factor levels are also listed in Table (I). The choice of factor level was based on pre-screening tests and conditions appropriate to industrial practice.

Table (I) Variables and their levels used in the screening design

Variable	Low	Factor level center	High
x1 Soild concn. (gm/l)	10	20	30
x2 CO_2 flow rate (l/min.)	0.612	1.39	1.73
x3 Reaction time (min.)	10	35	60
x4 Temp. (^oC)	25	30	35
x5- X 11 Dummy			

Table (II) shows the matrix of the design, with each variable at two levels, "plus" denotes the high level, and "minus" low level. Although 11 variable can be studied in this design, only four variables were studied, leaving the rest of variables as dummies to estimate the presence of interaction among variables. Studies on 8 run screening size was not satisfactory to give useful information on interactions and variables significance.

To estimate curvature effects and experimental error, three center point runs were added to the design runs. The order in which the runs were done was randomized. The center points were evenly spaced over the experimental run orders.

2.2 Solution Preparation

Tests were conducted using synthetic slurries for each design point. Pure $CaCO_3$ was heated at 900°C for at least three hours to produce CaO. Slurries were prepared by mixing the proper amount of CaO, MgO, $CaSO_4.2H_2O$ according to the molecular weights. Then, stoichiometric amount of ammonium hydroxide was added and slurry completed to 1 L by distilled water.

2.3 Carbonation Process and Analysis

Proper CO_2 flow rates were passed through the slurry which at different required temperatures. At the end of reaction periods the slurry was filtered and Mg ion was analyzed by EDTA, in addition to sulphate and ammonia [8].

3. Results and Discussions

Table (II) shows the values of response (Y), % Mg conversion, observed for each of the 12 runs and the summation of responses and the factor effect. Table III shows the response results obtained from center points runs and an example of factor level calculation.

Table III. Factor effect determination procedure and example.

1. Center point response (% conversion) = 15, 13.25 and 16.
2. Average value (Y) = 14.75
3. $S + \sqrt{(Y_i - Y)^2/(r-1)} = 1.39$

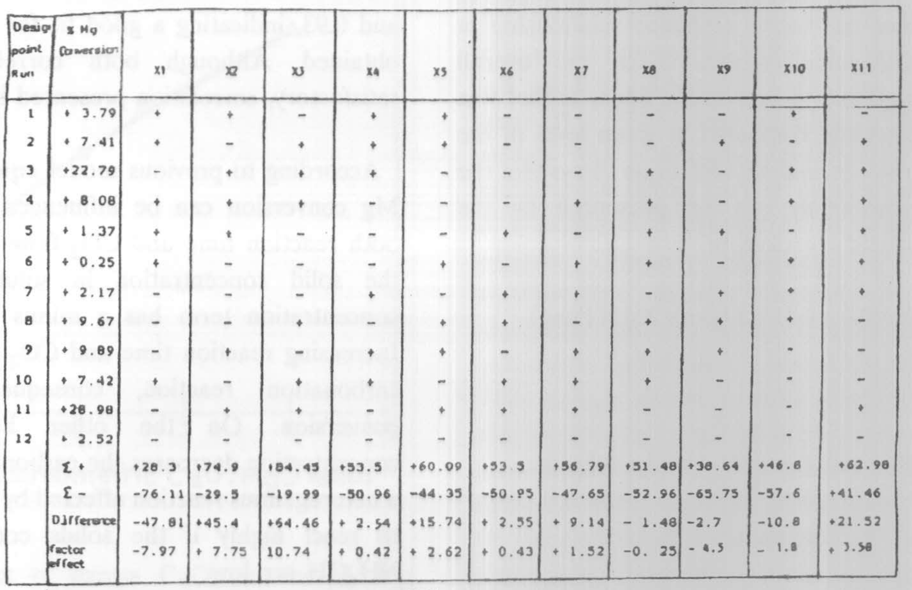
   whre r = 3
4. $$\text{Factor effect } X_i = \frac{\text{response at high } x_i - \text{response at low } X_i}{\text{half of the number of factirial runs}}$$
5. Example for X_3 i.e response for reaction time in the design Factor effect $= \dfrac{84.43 - 19.19}{12/2} = 10.74$

In any screening design, the calculated factor effect establishes the best estimate of the relative importance of a factor. The precision of the estimate is generally stated in the form of a confidence interval, which is an interval said to include the "true" effect at a stated confidence level. Factor effects whose confidence interval passes through zero are considered to be statistically insignificant at chosen confidence level. Calculation of factor effects and confidence interval, based on 95% confidence level, for the present study are listed in Tables IV. As can be seen from Table IV, within the range of factors levels considered in the design, the CO_2 flow rate is the most significant factor followed by reaction time and solid concentration in slurry.

Reaction temperature is statistically insignificant factor in the design experiments. The fact that temperature was not significant may be due to the small range of temperature studied (25-35°C). However, further increase in temperature may decrease the solubility of CO_2 gas in the solution, consequently carbonation reaction decrease. Excessive higher temperatures may also causes ammonium hydroxide to evaporate before it take an effective role in the reaction.

The effect of dummy factors is also shown in Table IV. These factors are a measure of any interaction among independent variables in the system. Since all the dummy factors include zero in their response except X9 which represent interaction between variables X1X3 or X2X4 (Table II). Since X4 represents temperature in this design

Table (II). Statistical design and results for 12 rum system.



Design point Run	% Mg Conversion	X1	X2	X3	X4	X5	X6	X7	X8	X9	X10	X11
1	+ 3.79	+	+	−	+	+	−	−	−	−	+	−
2	+ 7.41	+	−	+	+	+	−	−	−	+	−	+
3	+22.79	−	+	+	+	−	−	−	+	−	+	+
4	+ 8.08	+	+	+	−	−	−	+	+	−	+	+
5	+ 1.37	+	+	−	−	−	+	−	+	+	−	+
6	+ 0.25	+	−	−	−	+	−	+	+	−	+	+
7	+ 2.17	−	−	−	+	−	+	+	−	+	+	+
8	+ 9.67	−	−	+	−	+	+	−	+	+	+	−
9	+ 9.89	−	+	−	+	+	−	+	+	+	−	−
10	+ 7.42	+	−	+	+	−	+	+	+	−	−	−
11	+28.98	−	+	+	−	+	+	+	−	−	−	+
12	+ 2.52	−	−	−	−	−	−	−	−	−	−	−
	Σ +	+28.3	+74.9	+84.45	+53.5	+60.09	+53.5	+56.79	+51.48	+38.64	+46.8	+62.98
	Σ −	-76.11	-29.5	-19.99	-50.96	-44.35	-50.95	-47.65	-52.96	-65.75	-57.6	+41.46
	Difference	-47.81	+45.4	+64.46	+ 2.54	+15.74	+ 2.55	+ 9.14	− 1.48	-2.7	-10.8	+21.52
	factor effect	-7.97	+ 7.75	10.74	+ 0.42	+ 2.62	+ 0.43	+ 1.52	-0. 25	- 4.5	− 1.8	+ 3.58

Table IV. Summary of factor effect intervales at 95% confidence limit.

Variable	Value
X_1 soild concn.	-7.96 ± 3.45 *
X_2 CO_2 flow rate	+ 17.59 ± 3.45 *
X_3 reaction time	+ 10.74 ± 3.45 *
X_4 temperature	+ 0.42 ± 3.45
X_5 Dummy	+ 2.62 ± 3.45
X_6 Dummy	+ 0.43 ± 3.45
X_7 Dummy	+ 1.52 ± 3.45
X_8 Dummy	- 0.24 ± 3.45
X_9 Dummy	- 4.5 ±3.45*
X_{10} Dummy	- 1.8 ± 3.45
X_{11} Dummy	- 3.58 ± 3.45

* Means factor effects which are statistically significant at 95% confidence level.

Example to calculate the value of confidence level interval for actor effect:

$$\text{The interval value} = \pm \frac{t\,S}{\sqrt{N/4}}$$

where,

n = number of design point = 12 runs

s = standard deviation center point = 1.39

r = degree of feedom 2 (from center point)

t = student variable at 95% confidence level = 4.303

$$\text{Therefore, the interval values is} = \frac{4.303 * 1.39}{\sqrt{12/4}} = \underline{3.45}$$

and not statistically significant, therefore, X2X4 set is not significant. The combination X1X3 is significant (solid concentration and reaction time).

If the system is linear, the centrad of all the design points and average response from center points should be equal. If, however, the system deviates from linear model, overall curvature can be estimated as the difference between the average response of the center points and the average response of the design points. Table V shows the calculation of the curvature effect for the design. At 95%

confidence level, the confidence intervals on curvature is 3.63 ± 3.68 which is not statistically significant.

When responses and factors are continuous in scale, it is useful to consider the factor response relationship in terms of a mathematical model. Since the overall curvature are insignificant a first order linear model was considered to predict the responses at given level of the variables. The regression analysis technique shows that the percentage Mg conversion can be presented by the following mathematical correlation:

$$\% \text{ Mg} = 0.581 - 0.389(S) + 6.61(CO_2) + 0.2115(\text{Time}) + 0.24(T). \quad (1)$$

where: (S) = % solid concentration in solution;

(CO_2) = CO_2 flow rate in l/min. ;

(Time) = time in minutes;

(T) = temp. in°C

Table V. Estimate of curvature effect.

Variable	Mg % conversion effects
Center point average	14.75
Design point average	11.12
Curvature effect *	3.63
Confidence interval at 95% confidence level **	3.63 ± 3.68

* curvature effect = Center point average - Design point average

** Confidence interval = curvature effect + ts $\sqrt{1/N + 1/C}$

The R^2 and R values of the correlation are 0.83 and 0.91. If the interaction between solid concentration and reaction time (X1X3) are considered, the following correlation can present the % Mg conversion as follows:

$$\% \text{ Mg} = -6.728 - 0.171(S) + 5.813(CO_2) + 0.344(\text{Time}) + 0.151(T) + 6.45\text{E-}03\ (S.\text{Time}) \quad (2)$$

The R^2 and R values for the above correlation are 0.86 and 0.93, indicating a good fit for the experimental data obtained. Although both correlations fit the data satisfactory, correlation presented by equation 2 is better.

According to previous model equation obtained, the % Mg conversion can be influenced greatly by increasing both reaction time and CO_2 flow rate and by deceasing the solid concentration in solution, since the solid concentration term has a minus sign in the equation. Increasing reaction time and CO_2 flow rate enhance the carbonation reaction, consequently, increases Mg conversion. On the other hand, increase solid concentration decreases the carbonation reaction which is a heterogenous reaction affected by the activity of CO_2 gas to react highly if the solids concentrations in liquid NH_4OH are low.

Effect of excess CaO.MgO on % Mg conversion.

Figure (1) shows the effect of the excess amounts of MgO.CaO than stoichiometric ratio on the % Mg conversion. The results indicate that increasing CaO.MgO increases the percentage Mg conversion. For example, for reaction time 60 min. at 25°C, with 1.73 l/min. CO_2 and 10 % solid, the % Mg conversion values are 28.98, 41.5 and 61 for 1:1, 1:2 and 1:4 excess amounts of CaO. MgO than stoichiometric ratios. The great enhancement in % Mg conversion is due to the fact that reaction rates are increased with increasing the percentage of MgO presence in the reactant material.

Effect of excess ammonium hydroxide on % Mg conversion.

The results shown in Figure 2. indicate that increasing NH_2OH amounts than stoichiometric ratios decreases the % Mg conversion. This is due to a rapid formation of ammonium sulphate compound instead of Mg ammonium sulphate compound. The sulphate analysis of the compounds support this observation.

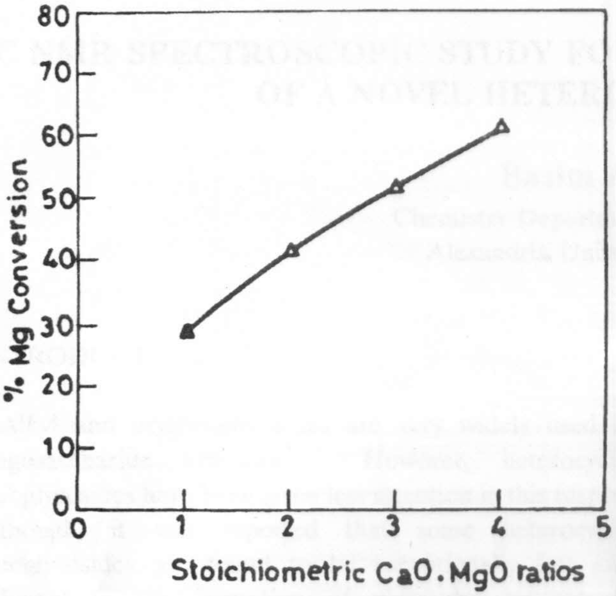


Figure 1. The effect of excess CaO. on the % Mg conversion at the following conditions: reaction time 60 min., temp. 25^{o}C \, solid concn. 10% and CO_2 1.73 l/min.

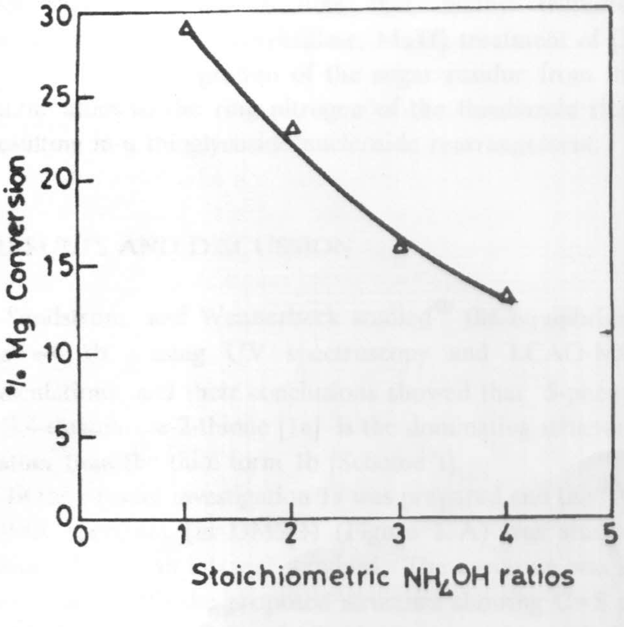


Figure 2. The effect of excess NH_4 OH on the % Mg conversion at the following conditions: reaction time 60 min., temp. 25^{o}C, solid conc. 10% and CO_2 1.73 l_y/min.

4. CONCLUSIONS

The screening design tests show that CO_2 flow rate is the most significant variable in the production of magnesium ammonium sulphate followed by reaction time and solid concentrations, whereas temperature in the range 25 - 35°C is not significant. The statistical design permits with minimum experimental runs to develop a model which can be used to predict the % Mg conversion as a measure of production of magnesium ammonium sulphate. Higher amounts of MgO.CaO than stoichiometric amount increase the percentage Mg conversion on the other hand, higher amounts of ammonium hydroxide decreases the conversion.

The design shown permits a reference base to study additional factors required in the production of magnesium ammonium sulphate process. Future studies with additional different types of screening designs are useful for comparative reasons to support the approach on the importance of screening design approach to our case and similar chemical processes.

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