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AN OPTIMIZATION STUDY ON DISSOLUTION OF THE CALCINED COLEMANITE MINERAL IN METHYL ALCOHOL BY CO_2 IN AN AUTOCLAVE SYSTEM USING TAGUCHI METHOD

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ABSTRACT
The process of optimizing the dissolution of colemanite ore ($2CaO.3B_2O_3.5H_2O$) in methyl alcohol by CO_2 in a high-pressure reactor was evaluated by using the Taguchi method. Optimum conditions for the cholemanite mineral were determined to be as follows: reaction temperature: 140°C, reaction time: 50 min, calcination time: 240 min, calcination temperature: 450 °C, solid-liquid ratio: 1/6 g.mL^{-1}, mixing rate: 500 cycle/min, pressure: 20 bar, grain size: -100 mesh and the amount of $CaCl_2$: 7.5 g.

Keywords: Colemanite, optimization, taguchi method.

1. INTRODUCTION

Boron is abundantly found in nature and the world's largest boron mineral reserve is located in Turkey. Boron is an economically valuable mineral that is not found in its natural state, but forms borate minerals with alkali and alkaline earth metal oxides of elements like sodium, calcium, and magnesium (Alkan and Doğan, 2004). Among these minerals, tincal, pandermite, ulexite, and colemanite have the highest percentages of boron reserve and production (Demirbaş et al. 2000). Colemanite chemically known as $2CaO.3B_2O_3.5H_2O$ is a boron mineral widely found in Turkey and is commercially valueable (Bayca, 2013). It is highly important to develop these boron reserves that form one of the most important underground treasures of Turkey, obtain new products from these reserves, and develop alternative economic and more environmentally-friendly technologies for present products. The most used source to obtain boron compounds in industry is boric acid (B_2O_3) (Şayan et al. 2006). Boric acid is formed as a result of reactions of boron minerals with various acid solutions.

In this study, the purpose is to develop an environmentally-friendly method to produce trimethyl borate by using colemanite ($2CaO.3B_2O_3.5H_2O$) and CO_2. The purpose of this study is to investigate optimum conditions for the dissolution of colemanite ore in methanol by CO_2 in a high-pressure controlled and high temperature reactor using the Taguchi method, and to develop an alternative process to produce trimethyl borate.

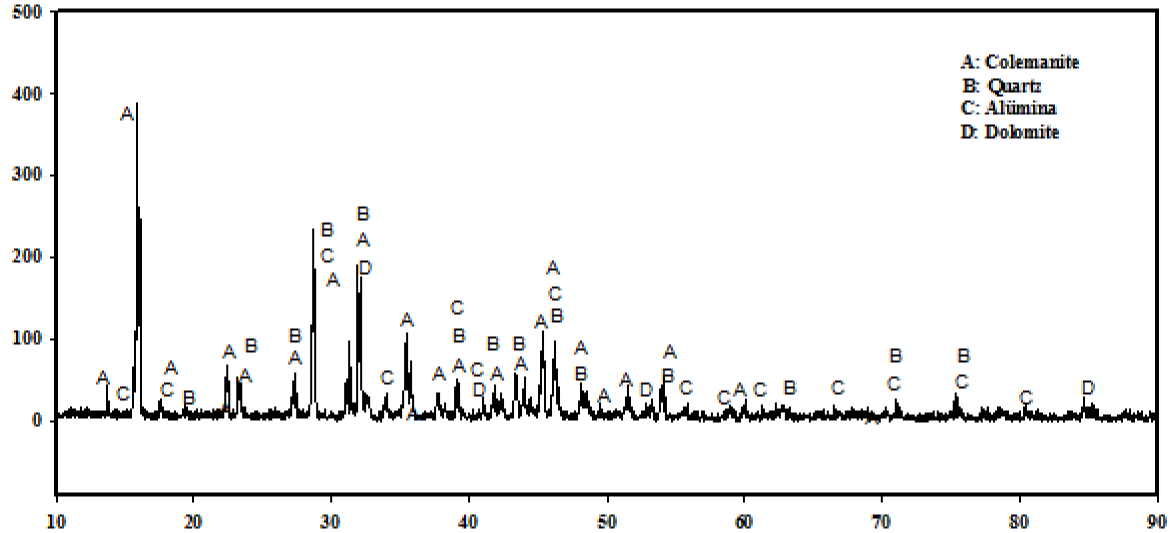
2. LITERATURE REVIEW

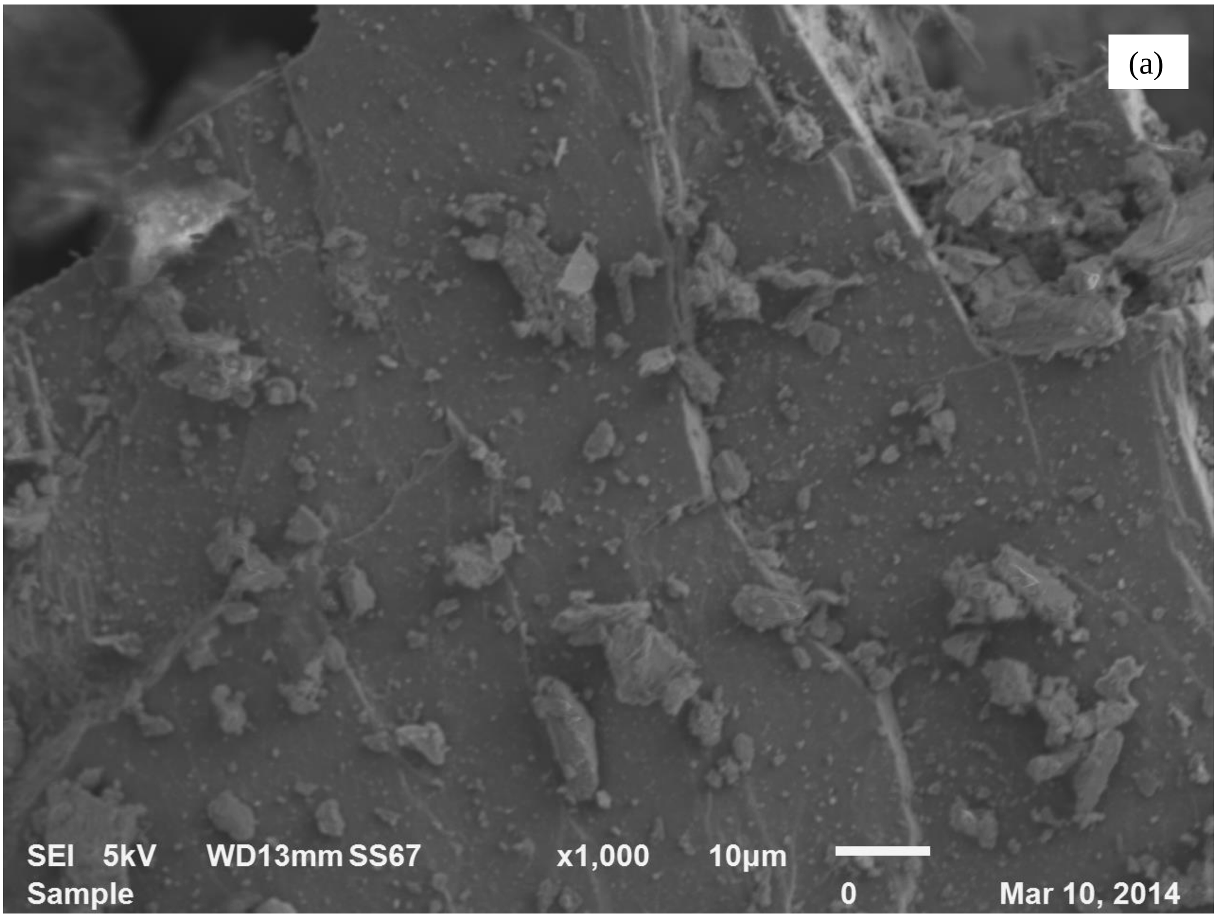
In the literature, the dissolution of boron minerals in various acid solutions was investigated, for example hydrochloric acid (Sis et al. 2015), phosphoric acid (Copur et al. 2000; Doğan and Yartaşı, 2014), sulphuric acid (Uysal et al. 2015), oxalic acid (Alkan and Doğan, 2004; Bayca et al, 2013), citric acid (Çiftçi, 2012), ammonium chloride (Alkan et al. 2013), ammonium sulfate (Kocakerim et al. 2007), propionic acid (Bulutçu et al. 2008) water saturated with chlorine gas, water saturated with both sulphurdioxide and carbondioxide (Kocakerim and Alkan, 1988; Şayan et al. 2006).

3. METHODOLOGY AND DATA

Colemanite ore used in this study was obtained from Bursa, in Turkey's Kestelek region. The ore was ground and separated after sieving by standart sieves into four fractions: 297+250, -250+177, -177+149, and -149+125 µm. Mineralogical analysis of the ore was done by X-ray diffraction (XRD), while its elemental analysis was done by Scanning Electron Microscopy-Electron Dispersive Spectroscopy (SEM-EDS). The result of XRD analysis is shown in Figure 1. The colemanite mineral, based on EDS results, as shown in Figure 2, includes 24.13% B, 57.91% O, 12.40% Ca, 4.20% C, 0.24% Mg, 0.30% Al, 0.67% Si, and 0.50% K. Thus, a majority of colemanite consists of B, O, Ca and C, while Mg, Al, Si and K exist in small quantities.

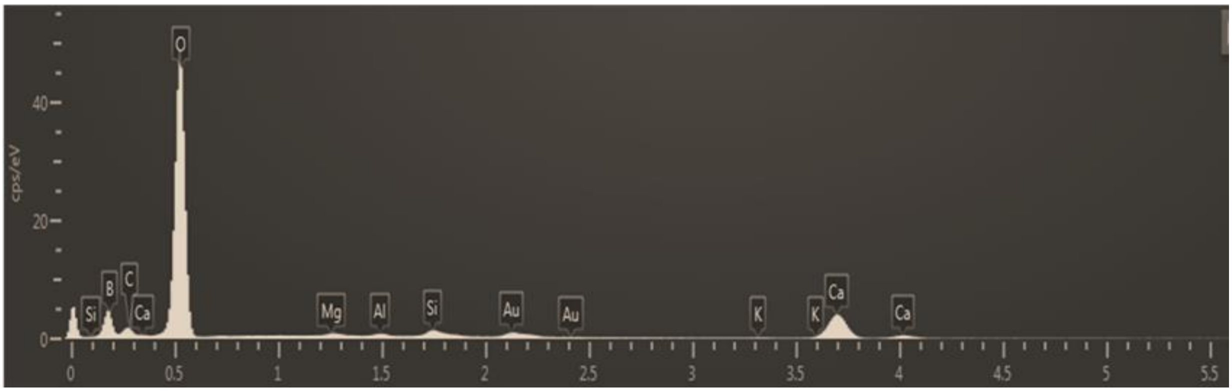
Figure 1: XRD Pattern of the Colemanite Mineral





(b)

Figure 2: SEM Micrograph (a) and EDS Pattern (b) of Colemanite Mineral



The Taguchi method is an experimental design method that tries to minimize variabilities in the product and process from uncontrollable and changeable factors by selecting the optimum combination of controllable factors. An orthogonal series a special form of the fractional factorial design is used in this method. How this method differs from other statistical experimental design methods is that it evaluates the parameters affecting an experiment in two separate groups: i. e. controllable and uncontrollable parameters, and enables the researchers to examine numerous parameters at more than two levels. Because uncontrollable parameters cause high costs, it is appropriate to investigate levels of controllable parameters to minimize effects of uncontrollable parameters. Generally, the performance characteristic of each product or process should have a nominal or target value. The purpose is to decrease the variability around that target value. Optimum operating conditions to be determined at the end of the experimental study should usually give the same or similar performance values under different operating conditions or times. The optimization criteria to be used for this purpose should control the variability around the performance value at a minimum level. In the Taguchi method, such an optimization criterion is the performance statistics, SN (signal to noise ratio). The equations below are used to calculate the performance statistics (Pignatiello, 1988; Phadke, 1989):

Larger the better:

$$SN_L = -10\mathrm{Log}\left[\frac{1}{n}\sum_{i=1}^{n}\frac{1}{Y_1^2}\right] \quad (1)$$

Smaller the better:

$$SN_S = -10\mathrm{Log}\left[\frac{1}{n}\sum_{i=1}^{n}Y_i^2\right] \quad (2)$$

Nominal is the best:

$$SN_S = -10\mathrm{Log}\left[\sum_{i=1}^{n}Y_i^2/S^2\right] \quad (3)$$

where n is the number of repeated experiment; y_i is the performance value; SN_L, SN_S, and SN_T indicate performance statistics. If the purpose in a process is to reach maximum value, parameter levels, making the SN_L value maximum are optimum. If the purpose is to obtain the minimum, then parameter levels making the SN_S maximum are optimum. In the Taguchi method, if the experiment corresponding to optimum operating conditions is not available in the experimental plan, an additional model can be used by utilizing Equation 4 to estimate the performance value, i.e. dissolution percentage.

$$Y_i = \mu + X_i + e_i \quad (4)$$

where Y_i is the estimated performance value of the i^{th} experiment; µ is overall mean of the performance value; X_i is the overall activity size of parameter levels used in the i^{th} experiment; e_i is the experimental error. If experimental results are given in percentage, omega transformation of the obtained percentage values is performed before using the Y_i equation. Later, the omega value estimated for optimum conditions:

$$\Omega(\mathrm{db}) = -10\mathrm{Log}\left(\frac{1}{\mathrm{P}} - 1\right) \quad (5)$$

where Ω (db) is the db value of the omega transformed percentage value and P is % value of the product obtained experimentally. Because the Y_i equation calculated based on experimental results is point estimation, a confidence interval for the error of estimation must be constructed to decide whether an additional model is sufficient. The confidence interval is found by using the equation below (Çopur and et al. 2000; Çopur and Kızılca, 2015):

$$S_e = \pm 2\sqrt{\left[\frac{1}{n_0}\right] + \sigma_e^2 + \left[\frac{1}{n_r}\right]\sigma_e^2} \quad (6)$$

$$\sigma_e^2 = \frac{sum\ of\ squares\ due\ to\ error}{degrees\ of\ freedom\ for\ erro} \quad (7)$$

$$\frac{1}{n_o} = \frac{1}{n} + \left[\frac{1}{n_{Ai}} - \frac{1}{n}\right] + \left[\frac{1}{n_{Bi}} - \frac{1}{n}\right] + \left[\frac{1}{n_{Ci}} - \frac{1}{n}\right] \quad (8)$$

Where S_e is the confidence interval for the effects of parameters; σ_e^2 is the variance of the error; n_r is the number of repetition of validation experiments; *nAi*, *nBi*, *nCi*…, *Ai*, *Bi*, *Ci*…indicate the levels of experiments (Phadke, 1989). If the estimated error is out of these limits, the additional model is not necessary. Validation experiments are a good tool to determine whether there is an internal interaction between parameters controlling the process. If the value estimated for optimum conditions is close to the observed value, this phenomenon indicates that there is no internal interaction between parameters. Otherwise, there is an internal interaction.

Experiments were conducted in a high-pressure resistant, temperature-controlled steel reactor having a mixing setup. For the calcination studies, colemanite ore was poured in a steel plate of 5x25 cm and 2 mm thick. Calcination treatment was performed in an ash oven of 20x32 cm under conditions determined in the experimental design. Parameters determined for this system are calcination temperature and time, reaction temperature, solid to liquid ratio, pressure, grain size and amount of calcium chloride. For optimization, orthogonal series were used as the Taguchi experimental design (Roy, 1990). The solid substance and methyl alcohol determined in accordance with the solid to liquid ratio were added into the reactor, which was adjusted for the conditions determined. After the reactor content reached the desired temperature value, the experiments were initiated by adjusting the reactor pressure to the desired value with CO_2 gas. At the end of reaction, B_2O_3 analyses were performed in the precipitates of solutions by filtering them with a vacuum pump.

Parameters used in this study and selected values are shown in Table 1 while the experimental plan based on the $L^{18}(3^7)$ orthogonal series is shown in Table 2.

Table 1: Parameters Studied in Experiments and Their Levels

Parameters		Levels		
		1	2	3
A	Mixing rate (rpm)	500	700	
B	Calcination temperature (^oC)	400	450	500
C	Calcination time (dak)	120	180	240
D	Solid-liquid ratio (gmL^{-1})	1/4	1/5	1/6
E	Grain-size (mesh)	-80	-100	-120
F	Reaction temperature (^oC)	130	140	150
G	$CaCl_2$ amount (g)	7.5	10	15

Table 2: L^{18} (3^7) Orthogonal Array Experimental Plan and the Amounts of B_2O_3 Dissolved in the Experiments

Exp.no	A	B	C	D	E	F	G	%B_2O_3	%B_2O_3	%B_2O_3	%B_2O_3
1	1	1	1	1	1	1	7.5	83.46	82.95	83.49	83.50
2	1	1	2	2	2	2	10	94.86	94.70	94.51	94.65
3	1	1	3	3	3	3	15	96.14	95.14	95.85	96.11
4	1	2	1	1	2	2	15	87.32	86.75	87.11	87.20
5	1	2	2	2	3	3	7.5	94.63	93.90	93.80	93.85
6	1	2	3	3	1	1	10	96.37	95.87	96.10	95.90
7	1	3	1	2	1	3	10	93.88	94.12	93.50	93.95
8	1	3	2	3	2	1	15	95.34	94.90	95.20	95.32
9	1	3	3	1	3	2	7.5	94.45	95.25	94.15	94.30
10	2	1	1	3	3	2	10	96.14	97.20	95.99	95.85
11	2	1	2	1	1	3	15	87.16	86.95	87.01	87.19
12	2	1	3	2	2	1	7.5	95.30	95.20	95.21	95.25
13	2	2	1	2	3	1	15	94.74	94.70	94.81	94.80
14	2	2	2	1	1	2	7.5	97.97	97.90	97.99	97.85
15	2	2	3	2	2	3	10	85.88	84.99	85.94	85.90
16	2	3	1	2	2	3	7.5	97.02	97.12	97.22	97.25
17	2	3	2	3	3	1	10	79.49	79.54	80.10	79.85
18	2	3	3	1	1	2	15	94.99	94.45	94.91	94.90

Table 3: L^{18}(3^7) Orthogonal Series

	A	B	C	D	E	F	G
Exp.No	**Mixing rate**	**Reaction temperature**	**Pressure**	**S/L ratio**	**Reaction time**	**Grain size**	**$CaCl_2$ amount**
1	500	130	10	20/200	40	-80	2.5
2	500	130	20	30/200	50	-100	7.5
3	500	130	30	40/200	60	-120	15
4	500	140	10	20/200	50	-100	7.5
5	500	140	20	30/200	60	-120	3.75
6	500	140	30	40/200	40	-80	10
7	500	150	10	30/200	40	-120	7.5
8	500	150	20	40/200	50	-80	15
9	500	150	30	20/200	60	-100	2.5
10	700	130	10	40/200	60	-100	10
11	700	130	20	20/200	40	-120	7.5
12	700	130	30	30/200	50	-80	3.75
13	700	140	10	30/200	60	-80	11.25
14	700	140	20	20/200	40	-100	2.5
15	700	140	30	30/200	50	-120	2.5
16	700	150	10	30/200	50	-120	7.5
17	700	150	20	40/200	60	-80	10
18	700	150	30	20/200	40	-100	7.5

3. FINDINGS AND DISCUSSIONS

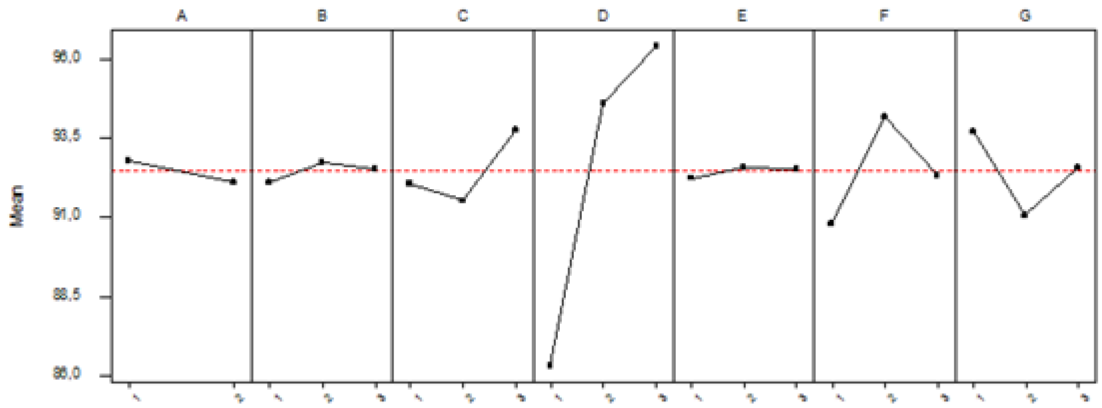
The reaction between colemanite, CO_2 and methyl alcohol can be expressed as follows:

$$2CaO.3B_2O_3.5H_2O+3CO_2+9CH_3OH \rightarrow 3H_3BO_3+3B(OCH_3)_3+2Ca(HCO_3)_2+4H_2O+CaCO_3 \quad (9)$$

Dissolution percentage values of B_2O_3 are shown in Table 3. Data obtained from the trials and analyses were evaluated by using the Minitab package program.

In the Figure 3, between the performance statistics and levels of parameters, the numerical value of maximum points shows the best value of the related parameter. Accordingly, the following were obtained: optimum operating conditions A_1 (mixing rate: 500 cycles/min), B_2 (calcination temperature: 450^oC), C_3 (calcination time: 240 min), D_3 (solid/liquid ratio: 1/6), E_2 (grain size: -100 mesh), F_2 (reaction temperature: 140^oC) and G_1 (the amount of $CaCl_2$: 7.5 g). Under these conditions, the passage ratio of B_2O_3 to the solution was found to be 98.4%. An F test was conducted to observe which parameters selected for optimization experiment designs are significant to the effects of impurities. Effective parameters were determined to be the solid-liquid ratio, reaction temperature, calcination time, and the amount of $CaCl_2$.

Figure 3: **The Effect of Each Parameter on the Optimization Criteria for B_2O_3.**



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