

Optimization by Using the Taguchi Method of Boric Acid Production by Dissolving Flash Calcined Colemanite in Water Saturated with SO₂

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ABSTRACT: Turkey has the largest boron reserves in the world with a rate of approximately 72%. The most common commercial boron reserves in Turkey are colemanite, tincal, and ulexite. Boric acid, which is the most commonly used boron compound in Turkey, is obtained from the dissolution of colemanite with sulfuric acid. In the present study, an aqueous medium saturated with sulfur dioxide instead of sulfuric acid was used in order to obtain boric acid. Colemanite ore was flash calcined at various temperatures and optimum dissolution conditions of the ore obtained in water saturated with SO₂ were examined via the “Taguchi Method”. In the trials, flash calcination temperature (500, 600, 700, 800 °C), reaction temperature (50, 60, 70, 80 °C), solid-liquid ratio (0.15, 0.20, 0.25 and 0.30 g/mL), grain size (-500+355, -355+212, -212+150, and -150 µm), and reaction time (15, 30, 45, and 60 minutes) were selected as the parameters and velocity of gas flow and mixing speed were considered as constant in all the experiments. In addition, experiments were carried out at atmospheric pressure. Accordingly, optimum conditions were found as flash calcination temperature of 500°C, reaction temperature of 50°C, grain size of -212+150 µm, solid-liquid ratio of 0.30 g/m, and reaction time of 60 minutes. The estimated dissolution under these conditions was 99.47% and dissolution of 100% was obtained in the experiments conducted. The aim of the study was to obtain more economical and high-purity boric acid compared to sulfuric acid via an environmentally friendly process without any waste.

Keywords: Sulfur dioxide; Flash calcination; Calcined colemanite; Optimization; Boric acid.

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INTRODUCTION

Boron is one of the most used elements in the world due to its superior properties. Boron minerals and products have a wide range of uses and these areas are increasing. The usage areas of boron minerals and their products, which are used commercially in a wide and various fields, are increasing. Nearly 10% of the produced boron minerals are consumed directly as minerals, while the remaining portion is used to obtain boron products. Boron minerals and products; It is used in many industries such as glass, ceramics, cleaning and whitening, anti-burning agent, agriculture, nuclear applications, textile and metallurgy.

In the field of boron technology, in order to increase production and develop production methods, it is necessary to make the necessary investments in new production technology according to the characteristics of the ores and to create resources in different alternatives [1].

Boron ores and boron compounds are strategically located in industrialized countries with a wide range of applications. There is no doubt that boron compounds will maintain their importance both today and in the future. In this respect, the production of boron compounds from boron ores and the development of these compounds as a variety or quality are important in terms of meeting the needs of the world countries.

Turkey has approximately 72% of the boron reserves worldwide. Most frequently found ores are colemanite, tincal, and ulexite. These ores are both consumed directly in various industries and employed in the production of various boron compounds. Boric acid is the mostly consumed boron compound. It is directly utilized in various industries and it is also the starting material in the production of boron end products.

Assessment of boron ore, which take place among the most important underground wealth in Turkey, production of new products from such ores, and development of alternative, economical, and more environment-friendly technologies for the existing products are of vital importance. In the present study, economical and also more environmental-friendly technology that can be an alternative to the existing processes in the production of boric acid was inspected.

Pyrometallurgy is one of the branches of extractive metallurgy and its primary purpose is to gain precious metals, to apply a series of heat treatments to the ore, and to have the material expose to physical and chemical

changes as a result of these treatments. In the calcination, one of the essential pyrometallurgical processes, CO₂, bound water, and organic substances are removed by exposing the solid material to a thermal decomposition process.

The implementation of heat treatment to the ores is generally performed in three ways. The first one is the calcination process in a classical rotary furnace, the second is the calcination in a fluidized bed, and the last one is flash calcination. As calcination process takes hours in classical calcination, the calcination process in the fluidized bed takes minutes. However, flash calcination process is performed in seconds. In addition, in flash calcination, the ore is suddenly subject to a thermal change and thus, the ore structure will be quite different from the ore that is subject to classical calcination. In calcination process, the most important parameters are temperature, heating rate, type of the material used, residence time in the reactor, and the grain size. Today, two experimental methods are used in flash calcination processes. In the first method, the material is generally in steady position. In the other experimental method, the material sample is continuously fed in the calcination furnace. The most commonly used reactor types in the studies with continuous material flow are stream flow reactor, free-fall reactor, and suspension reactors. When the reactor systems are considered, the residence time in the stream flow and suspension reactors can be adjusted by changing the velocity of the gas flow supplied to the reactor, the position of the collector, and the diameter of the reactor. However, the residence time in free-fall reactors is determined by reactor size and the grain size [2].

All the boron ores containing crystallization water loss the crystallization water via heating. Although colemanite loses its crystallization water, it is structurally disintegrated by cracking due to the internal stresses caused by heat. During the heating process of colemanite to this temperature, the original weight of the mineral decreases and the calcined product becomes more active chemically. In the study of Çelik and Suner [3] regarding the cracking characteristics of colemanite and ulexite, it was observed that ulexite did not significantly decompose into fractions with temperature while colemanite crackled. In the thermodynamic evaluation of fourteen boron minerals, it was found that only colemanite had crackling property.

There are numerous studies in the literature investigating solubility of colemanite and other boron ores in various solvents and optimization of the solubility. In the study, *Küçük et al.*, examined the solubility kinetics of colemanite ore from the Kestelek region in the water saturated with SO_2 [4]. In the literature, there is also a study conducted by *Korucu et al.* [5] regarding the examination of optimization of uncalcined colemanite ore in water saturated with SO_2 . The other four studies using Taguchi method also investigated the optimization of dissolution of ulexite ore in waters saturated with SO_2 and NH_4Cl solutions [6-8]. However, in the literature numerous studies have been conducted on the calcined boron ores [9-14]. Also, there are many studies in the literature about the solubility of original and calcined colemanite with various reagents and optimization of the solubility and alternative methods are recommended for the production of boric acid [15-28].

Solid wastes are generated at the boron concentration facilities and they are generally stocked in tailings impoundments. Thus, thousand tons of ore are stocked. Since boron, as in the stocks, dissolves in water at a considerable amount, B_2O_3 content of this ore, that is stocked in the open mining area, dissolves with rain and snow waters and merges with rivers, lakes, and underground waters. Such water with increasing boron level increases the boron content of the ground when it is used for irrigation purposes. This also adversely affects many plants grown on these grounds.

There are numerous studies regarding the elimination of SO_2 in flue gases, and hundreds of processes have been developed. Electrochemical processes make great contributions to in the elimination of sulfur dioxide pollution. Publications by various researchers are issued in this regard. In addition, another type of process applied in desulfurization processes is to have flue gases contacts with basic substances in dry or aqueous media. There are various processes regarding this issue.

When the literature studies are examined, it has been observed that there are studies on optimization of solubility of colemanite ore in original form and classical calcination and optimization of the solubility and also studies on solubility of flash calcined colemanite in waters saturated with CO_2 and optimization of the solubility; however, no study on optimization of solubility of flash

calcined colemanite in waters saturated with SO_2 was found.

Today, in Turkey boric acid is obtained through the reaction of colemanite with sulfuric acid, so that gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is obtained as the by-product in this process. There is a significant amount of loss of boron during the reaction and the gypsum formed could not be evaluated because there is no practical relevant situation although there are studies on this issue. On the other hand, the crystalline boric acid obtained in the process contained sulfate pollution due to the sulfuric acid used and calcium and magnesium pollution due to calcium and magnesium carbonates in the ore. This pollution reduced the market value of the produced boric acid and the obtained crystalline boric acid is washed with water to compensate this and remove these pollutions. The crystalline boric acid is washed with water. This causes both loss of boric acid and entry of more water in the process, thus negatively affects the costs. However, because of abundant water used in the process, water with limited amount of boric acid is sent to the tailings dam, thus, a loss is present in both boric acid and a negative condition is encountered in environmental pollution. In this sense, it is even crucial to create new environmental-friendly processes and technologies in order to produce boric acid in a cheaper and purer manner and also, to preserve the environment in the present world where competition is highly increasing. The aim of the study is to develop an alternative, economical, and more environment-friendly process in the production of boric acid.

EXPERIMENTAL SECTION

Preparation of the Materials

Colemanite ore employed in the studies was supplied from Bursa (Turkey) Kestelek region and the ore was used as extracted directly from the mine without eliminating the impurities. The ore was crushed with a laboratory-sized crusher and milled by using a grinder. The milled ore was decomposed in $-500\mu\text{m}+355\mu\text{m}$, $-355\mu\text{m}+212\mu\text{m}$, $-212\mu\text{m}+150\mu\text{m}$, and $-150\mu\text{m}$ fractions by using ASTM-standard sieves. Each fraction was subject to flash calcination process at the calcination temperatures stated in the design. Table 1 shows the chemical analysis of the colemanite ore.

Table 1: Chemical analysis of the colemanite ore.

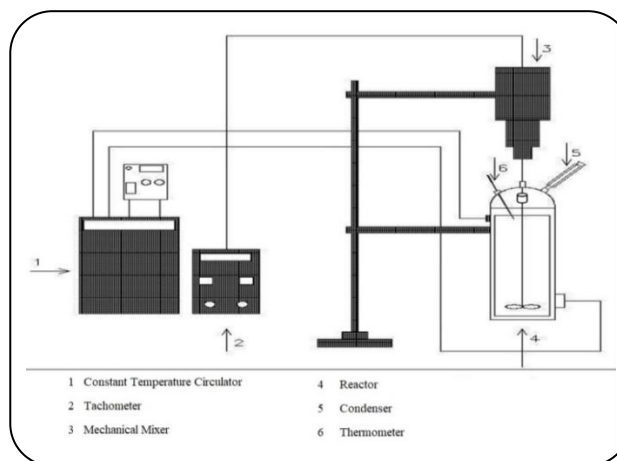
Properties			H ₂ O% (depending on the structure)	SiO ₂ + Other impurities
Grain sizes	B ₂ O ₃ %	CaO%		
-500 μm +355 μm	40.56	21.82	17.47	20.15
-355 μm+212 μm	42.31	22.76	18.22	16.71
-212 μm+150 μm	43.83	23.58	18.87	13.72
-150 μm	42.44	22.83	18.28	16.45

Experimental study

A 250 mL double-walled glass reactor was used in the dissolution experiments. A mechanical mixer for the mixing process, a constant temperature circulator for keeping the reaction temperature constant, and a condenser for preventing solvent losses caused by evaporation were used. In the dissolution processes, 100 mL purified water was filled in the reaction vessel each time, the reaction vessel and its content were saturated with SO₂ gas after bringing to the reaction temperature, and the vessel content was mixed at 500 rev/min in each experiment. The experiments were performed based on other parameters and levels specified in the design, the mixing process was terminated at the end of the specified periods, and B₂O₃ assignment was determined in the filtrate after the reaction vessel was filtered [29]. Fig. 1 shows the experimental setup in which the dissolution experiments are carried out.

Flash calcination experiments were carried out in a vertical free-fall calcination furnace with a diameter of 6.7 cm and a length of 120 cm. The pipe used in the furnace is a stainless chrome-nickel material and is resistant to high temperatures. There is a thermocouple in each heating zone of the furnace, and the temperature of the furnace can be controlled automatically. In order to prevent heat losses in the furnace, the furnace is insulated with a zirconium blanket. A spiral material feeding unit was built to feed material at a constant flow rate. In order for the material fed from above to be taken from below, a plug-in material collection container was built at the lower end of the pipe in the furnace.

Flash calcination process of the samples was conducted in the furnace shown in Fig. 2. Before starting the experiments, the furnace was adjusted to the desired temperature. After the desired temperature was reached, the material collecting vessel was attached to the lower part of the furnace. The calcined ore required for each test in the experimental design given in Table 3 was obtained

**Fig. 1: Experimental setup used in the dissolution process.****Fig. 2: Flash Calcination Furnace.**

from the samples, whose chemical composition given in Table 1, from the upper part of the furnace by feeding at a flow rate of 5 g/min. After the calcined colemanite ore, which descended with the free-fall movement, was collected in the material collecting vessel, it was transferred to the sample collection vessels for analysis. Experimental conditions were determined by keeping the heating rate and the residence time in the reactor constant, other parameters such as calcination temperature and grain size, which are used to understand the effects of the flash calcination process, into the design.

Taguchi method

Due to the fact that well-designed and analyzed pre-production experiments significantly contribute to making an accurate analysis regarding the optimization of industrial processes, improvement of product quality, and reduction in costs, statistical experimental designs are used for this purpose. In the classical experiment design, which is costly and not safe; only one factor is changed and all the other factors are kept constant. However, in the statistical experiment design, systematically, numerous factors are changed at the same time. When the effects of the factors are examined in detail, suitable steps can be taken for process control.

According to Taguchi, the stage where the most decisive work can be done in improving the quality of the product is the parameter design stage, for both product and process design. The aim in parameter design is to reduce both the manufacturing and lifetime cost of the product by minimizing the variation that may arise in the product.

Process parameter design is used to define optimal levels and settings for controllable manufacturing process parameters. In both parameter designs, the aim is to minimize the variation in the product and process by optimally choosing the values of the controllable factors (parameters) against the variance-creating and uncontrollable factors in the product and process[30].

Taguchi Method runs according to the principle of minimum number of experiments in order to minimize the costs [31]. This method is distinguished from other statistical experimental design methods since it examines the effective parameters in an experiment in two groups (controllable and uncontrollable) and many parameters at more than two levels. In general, the performance characteristic of each product or process should have a nominal or target value. The purpose is to decrease changeability in this target value. Optimum working conditions should always provide the same or very close performance values in various working environments or at various times. The optimization criteria should control the changeability in the performance value at the minimum level. According to Taguchi, such optimization criteria are the performance statistics. The optimum levels of parameters are detected using the following performance statistics formula

For larger and better;

$$SN_L = 10\text{Log} \left(\frac{1}{n} \sum_{n=1}^n \frac{1}{y^2} \right) \quad (1)$$

For smaller and better;

$$SN_S = 10\text{Log} \left(\frac{1}{n} \sum_{n=1}^n y^2 \right) \quad (2)$$

Where n : repeated number of experiments, y : B_2O_3 dissolution fraction. In a process, in case the purpose is to obtain the highest value and the parameter level provided to achieve maximum SN_L is optimum. If the purpose is to obtain minimum, the parameter levels provided to achieve maximum SN_S are optimum [32]. The following equation is used to estimate the performance value corresponding to the optimum working conditions detected in the Taguchi method.,

$$Y_{it} = \mu + X_i + e_i \quad (3)$$

Where Y_{it} : is the estimated performance value of the i th experiment, X_i : is the total efficiency dimension of the parameter levels used in the i th experiment, μ : is the mean value, and e_i : is the experimental error. If the experimental results are in the form of percentages, before calculating the Y_{it} value, the percentage values are converted into decibel value by $\Omega_i = -10 \cdot \text{Log}(y_i / (1 - y_i))$ formula. In this formula, $\Omega(\text{db})$: decibel value, y_i : Dissolution fraction of the i th experiment.

Equation 3 is used to estimate the experimental data in order to detect whether or not the additional model is suitable. Thus, confidence limits should be determined for the estimated error[33]. Estimated error refers to the difference between the observed Y_{it} and the estimated Y_{it} . The confidence interval for the estimated error (S_e) is calculated by using the below-mentioned equations.

$$S_e = \pm 2 \sqrt{\left(\frac{1}{n_0} \right) \sigma_e^2 + \left(\frac{1}{n_r} \right) \sigma_e^2} \quad (4)$$

$$\sigma_e^2 = \frac{\text{error sum of squares}}{\text{deg of freedom for error}} \quad (5)$$

$$\frac{1}{n_0} = \frac{1}{n} + \left[\frac{1}{n_{A_i}} + \frac{1}{n} \right] + \left[\frac{1}{n_{B_i}} + \frac{1}{n} \right] + \left[\frac{1}{n_{C_i}} + \frac{1}{n} \right] + \quad (6)$$

Where S_e refers to the confidence interval of two standard deviations, n refers to the number of experiments in the experimental design, n_r refers to the number of repetitions of the verification experiment, and n_{A_i} , n_{B_i} , n_{C_i} , ...

Table 2: Design parameters and levels.

Codings	Parameters	Levels			
		1	2	3	4
A	Calcination temperature (°C)	500	600	700	800
B	Reaction Temperature (°C)	50	60	70	80
C	Grain size (µm)	-500+355	-355+212	-212+150	-150
D	Solid-Liquid Ratio (g/mL)	0.15	0.2	0.25	0.30
E	Time (min.)	15	30	45	60

Table 3: Experimental plan and results of the design.

Experiment No	A	B	C	D	E	B ₂ O ₃ % 1st trial	B ₂ O ₃ % 2nd trial
1	1	1	1	1	1	87.90	88.70
2	1	2	2	2	2	89.00	90.80
3	1	3	3	3	3	93.80	95.00
4	1	4	4	4	4	99.90	99.80
5	2	1	2	3	4	95.97	92.57
6	2	2	1	4	3	81.30	80.79
7	2	3	4	1	2	99.90	99.80
8	2	4	3	2	1	99.90	96.00
9	3	1	3	4	2	85.70	88.60
10	3	2	4	3	1	84.00	84.10
11	3	3	1	2	4	97.25	93.45
12	3	4	2	1	3	99.90	99.53
13	4	1	4	2	3	80.00	78.80
14	4	2	3	1	4	99.90	99.80
15	4	3	2	4	1	57.00	54.40
16	4	4	1	3	2	69.34	69.35

refers to the number of *i*th levels of A, B, C parameters. When the estimated error is outside these limits, it is assumed that this model is not proper [33].

RESULTS AND DISCUSSION

Effect of the Parameters on Dissolution

L₁₆ (4⁵) Taguchi factorial fractional experimental design plan was made considering the examination of 5 parameters determined for this study and 4 different levels for each parameter. Table 2 shows the parameters and levels and Table 3 shows the experimental plan and the obtained results.

Statistical Calculations

Regarding the determination of the parameter levels causing the solubility of flash calcined Colemanite in water saturated with SO₂ to be maximum, no. (1) SN_L equation was employed. In order to find the parameter levels causing the solubility to be maximum, dissolution fractions were used and SN values from no.1 equation were found. graphics in Fig. 3 show the results calculated based on the SN_{mean} marginal mean performance statistics for the parameters levels via the SN_L values. Equation No. (3) was employed for estimation of the performance

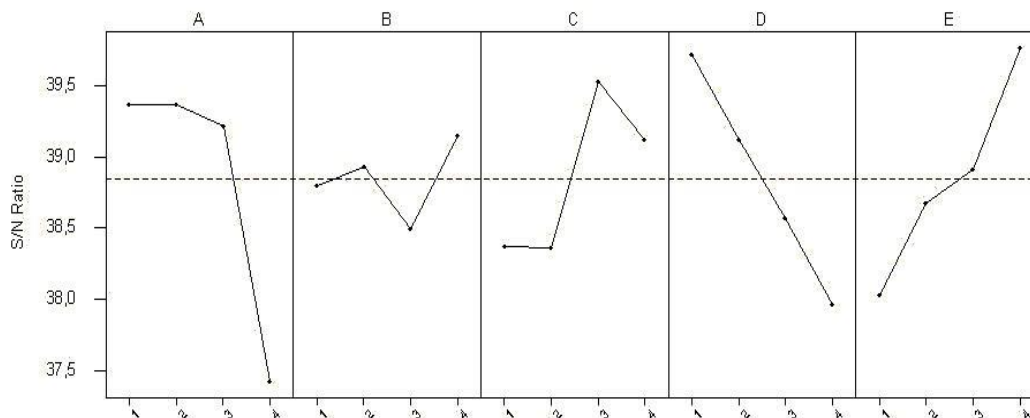


Fig. 3: SN_{mean} based on the parameter levels for the design

value of the parameter levels causing the SN_{mean} value to be maximum.

Fig. 3 reveals that the parameter levels making the SN_{mean} value maximum were A2, B4, C3, D1, and E4. Thus, the parameter values making the dissolution fraction of colemanite maximum would be A2, B4, C3, D1, and E4. Accordingly, optimum conditions were found as flash calcination temperature of 600°C, reaction temperature of 80°C, grain size of -212 μm + 150 μm , solid-liquid ratio of 0.15 g/mL, and reaction time of 60 minutes. Percentile dissolution estimated under optimum conditions ($B_2O_3\%$) was 100.00% and experimentally found value was also 100.00%. Fig. 3 reveals that the difference between 500°C and 600°C for the calcination temperature was scarcely any. In their study, Şener and Özbayoğlu [34] stated that colemanite was exposed to hydroxylation at 380°C and sintering at 650°C. In the current study, 500 and 600°C corresponded to this interval and this verified the absence of any difference among these temperatures. Also, at 700°C, it is close to 650°C, where colemanite undergoes hydroxylation. However, the effect is quite high after 700°C, and the sudden change of this effect causes the efficiency value to be higher than other parameters. Analysis of variance confirms this.

Moreover, given that the use of high solid-liquid ratios is a factor chosen in industrial scale processes, and less energy cost will be obtained by selecting a lower reaction temperature, it was investigated whether 100% solution can be achieved at other parameter levels and it was estimated that 100% resolution could be achieved at parameter levels A1, B1, C3, D4, and E4 (namely flash calcination temperature of 500°C, reaction temperature of

50°C, grain size of -212 μm + 150 μm , the solid-liquid ratio of 0.30 g/mL, and reaction time of 60 minutes). Accordingly, the estimated dissolution value was found as 99.47% and experimentally found value as 100.00%. Confidence interval (Se) was calculated as $\pm 3.45\%$.

Due to the fact that high solid-liquid ratio, working at low flash calcination temperature, and low reaction temperature will be preferred in industrial-scale processes, optimum conditions were accepted as flash calcination temperature of 500°C, reaction temperature of 50°C, solid-liquid ratio of 0.30g/mL, reaction time of 60 min., and grain size range of -212 μm +150 μm . Also in all the studies, a mixing speed of 500 rev/min and SO_2 gas flow rate at the saturation value was kept constant and experiments were carried out at atmospheric pressure. The fact that the estimated value was very close to the experimental value and within the confidence interval showed that there was no internal interaction between the parameters and the model was sufficient to explain the effect of the parameters.

An alternative condition can also be considered as given in situation 3 in Table 4. Here, only the reaction temperature was selected as a higher temperature than 80°C. The advantage of such a situation can be stated as follows: More boric acid crystals can be obtained in the crystallization to be done by cooling the saturated solution, obtained at a higher temperature, to lower temperatures and the amount of boric acid that may be present in the wastes can be reduced. In addition, additional decomposition processes may be required to remove the boric acid crystals that were precipitated in a process conducted at low temperatures. When all of these are

Table 4: Optimum working conditions in the experiments and percentile B₂O₃ amount in the observed and estimated solution.

Parameters	1st situation*		2nd Situation**		3rd Situation***	
	Value	Level	Value	Level	Value	Level
A. Flash Calcination temperature (°C)	600	2	500	1	500	1
B. Reaction Temperature (°C)	80	4	50	1	80	4
C. Grain Size (µm)	-212+150	3	-212+150	3	-212+150	3
D. Solid/Liquid Ratio (g/mL)	0.15	1	0,30	4	0.30	4
E. Reaction Period (minute)	60	4	60	4	60	4
Observed value (%)B ₂ O ₃	100		100		100	
Estimated value (%)B ₂ O ₃	100		99,47		100	
Confidence interval (%)B ₂ O ₃	96.55-100		96.02-100		96.55-100	

*Optimum values according to the SN_L values** Optimum conditions selected according to the SN_L values

*** Alternative optimum condition

Table 5: Analysis of variance on optimization experiment.

Parameters	Degrees of freedom (DF)	Sum of squares (SS)	Mean of squares (MS)	F _{Experimental}	C _r (%)
A Flash Calcination temperature (°C)	3	1663.40	554.47	279.08	35.46
B Reaction Temperature (°C)	3	132.80	44.27	22.28	2.71
C Average grain size (µm)	3	666.27	222.09	111.78	14.13
D Solid/Liquid Ratio (g/mL)	3	1134.23	378.08	190.30	24.14
M Reaction Period (minute)	3	1045.98	348.66	175.49	22.24
Error	16	31.79	1.99		
Total	31	4674.46			

F_{Table(3.16)}0.95=3.24, F_{Table(3.16)}0.99=2.46

considered, alternative situation given in Table 4 can also be evaluated as an optimum condition. Table 4 shows the optimum levels of the design parameters and the numerical values for these levels, and alternative operating conditions, respectively.

Experimentally found F_{Experimental} value and F_{Table} values were compared and it was determined whether or not the parameters were efficient. If F_{Experimental} > F_{Table}, the relevant parameter was effective on the performance value. If F_{Experimental} < F_{Table}, the relevant parameter was not effective on the performance value. Table 5 shows the analyses of variance for design experiments.

When table 5 was examined, it can be seen that F_{Table} values of all the parameters were smaller than the F_{Experimental} values. This means that all the parameters selected in optimization are effective on the performance value.

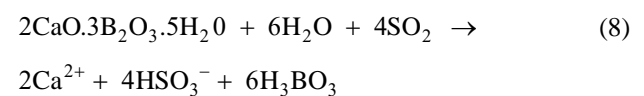
The effectiveness of each parameter (in %) can be determined from the equation below [8].

$$\% \text{ Effect of Parameter } (C_r) = \frac{SS_i - (DF_i)(MS_{i,\text{Error}})}{SS_{i,\text{Total}}} \times 100 \quad (7)$$

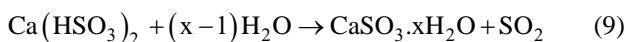
CONCLUSIONS

The main conclusions drawn from the present study can be expressed as follows:

In dissolution experiments; flash calcination temperature, reaction temperature, grain size, solid/liquid ratio, and reaction time were used as the parameters. The reaction conducted is as follows.

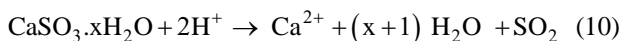


Also, the byproducts in this process were $\text{Ca}(\text{HSO}_3)_2$ and $\text{CaSO}_3 \cdot x\text{H}_2\text{O}$. $\text{Ca}(\text{HSO}_3)_2$ degrades when the solution is heated and calcium sulfide precipitates according to the

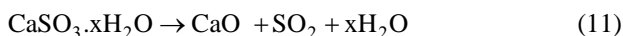


reaction. When the solubility of calcium sulfide in 100mL water at 20°C [35] is considered as 0.0059 g, since the by-product forming in the reaction will remain in the solid waste, it will become possible to obtain the boric acid product with high purity. SO_2 produced in this reaction can be used again in the process. When required, SO_2 can be recovered by processing or calcining $\text{CaSO}_3 \cdot x\text{H}_2\text{O}$ with cheap acids and it can be used in the process.

In case acid is used



In case of calcination;



It is thought that sulfur dioxide can form and recovered in the process according to the above mentioned reactions.

In chemical industry, which is an important sector in environmental pollution, one of the alternatives for preventing environmental pollution, is to develop environmental-friendly technologies, which may be the most important one. Negatives in the today technology were mentioned earlier in the article.

On the other hand, in boric acid forming as a result of the reaction of colemanite with SO_2 , the absence of sulfate in the medium, and the solubility of calcium sulfide approximately 55 times less than calcium sulfate[36] will yield cleaner boric acid crystals compared to the sulfuric acid process. In this regard, it will not be necessary to wash the crystalline boric acid in centrifuges or a smaller number of washes may be sufficient. Colemanite, used in this process, is dissolved with SO_2 in the solution medium and the suspensions obtained were easily filtrated and solutions containing boric acid were obtained. Also, it was observed in the experiments that the clay and the solution containing CaSO_3 solid can be filtered more easily than clay and CaSO_4 solid[37]. It is thought that duly use of colemanite with SO_2 will be a better process in terms of the products to be obtained.

A study regarding the optimization of colemanite ore in water saturated with SO_2 was conducted by *Korucu et al.* [5].

However, in the said study, ore was used without calcining. In the current study, ore was subject to flash calcination process. It was considered that the calcined samples obtained via both classical calcination and flash calcination processes would show better dissolution than the original samples. In a study of *Korucu et al.* [5], the reaction temperature and grain size, which were found as optimum conditions, were found to be the same in the current study. However, 100% dissolution was obtained by calcined ore at a higher solid/liquid ratio (0.30 g/mL). In addition, while the mean B_2O_3 ratio in the original core is about 42%, this ratio reached to 48% in calcined ore. Thus, a sample that was richer in terms of B_2O_3 was obtained.

Although the optimum conditions from Fig. 3 were A2, B4, C3, D1 and E4, since the reason for choosing the 2nd case as the optimum condition was discussed in the *statistical calculation* section, it is not mentioned here to avoid repetition. In addition, considering that the solubility of boric acid is greater at high temperatures and more crystals can be obtained when cooled to low temperatures, the 3rd situation, where the reaction temperature is higher, is also proposed. The 3rd situation is only a recommendation, not the optimum condition found from the analysis. Of course, the negative cost of rising to high temperatures should also be considered.

As a result, 100% dissolution was obtained with calcined ore obtained at 500°C by taking the reaction temperature as 50°C, solid/liquid ratio of 0.30g/mL, reaction time of 60 min, and the grain size of -212 μm +150 μm .

The predicted and observed dissolution values are very close to each other. Thus, it may be concluded that the additive model is adequate for describing the dependence of the dissolution process on the various parameters.

Since optimum conditions determined by the Taguchi method in a laboratory environment are reproducible in real production environments as well; the findings of the present study may be very useful for processing on an industrial scale.

Only selected combinations are tested in the Taguchi method. These combinations are determined by considering the studies in the literature. The parameters affecting the operation are known. Experiments are made by determining the levels of the parameters. However, experiments can be analyzed using methods such as stochastic optimization algorithms[38, 39].

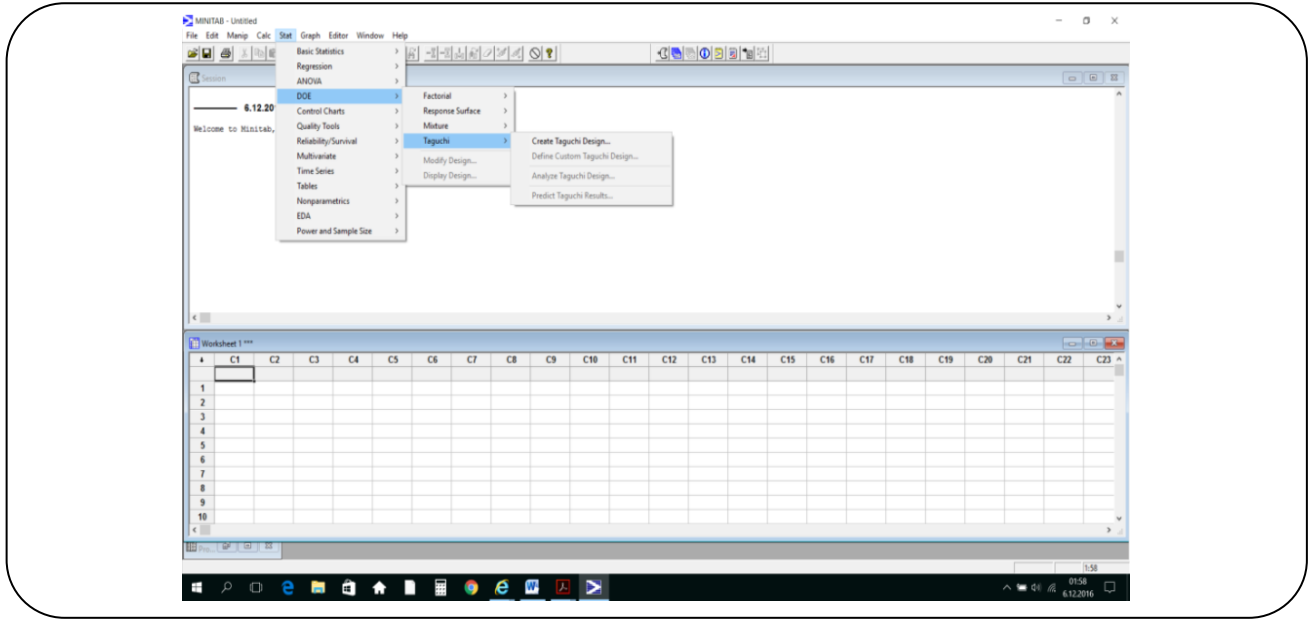


Fig A1.

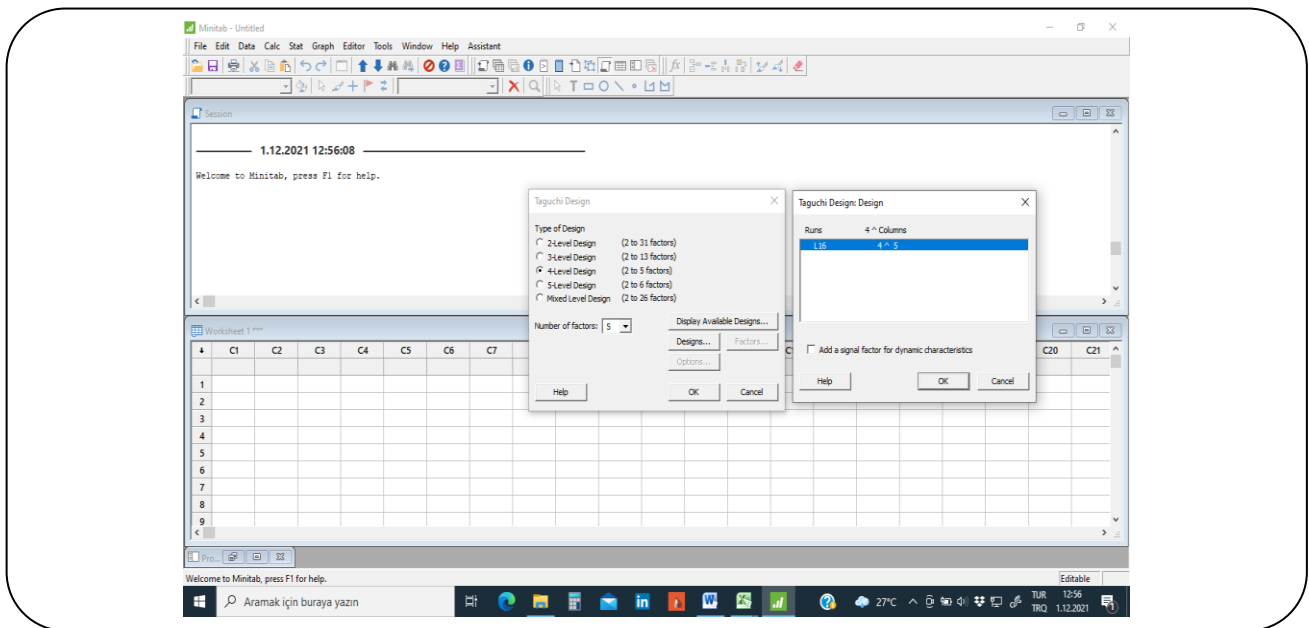


Fig A2.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Using of Package Program

The following describes how the data and graphics of this work were obtained with the Minitab Package Program. Firstly, the Minitab program is run. Stat, DOE, Taguchi, and Create Taguchi Design menus are clicked from the top menu, respectively, as shown in Fig. A1.

When this is done, the following screen image (Fig A2) is displayed. In this screen view, we choose the number of parameters of your design and the level of each parameter

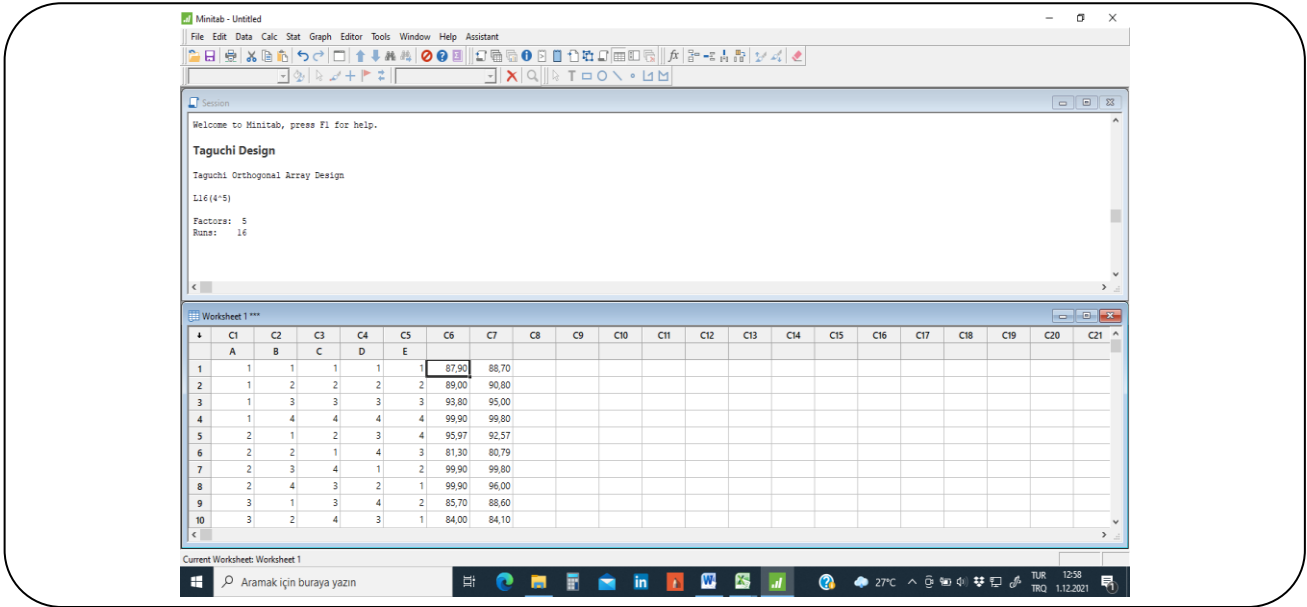


Fig A3.

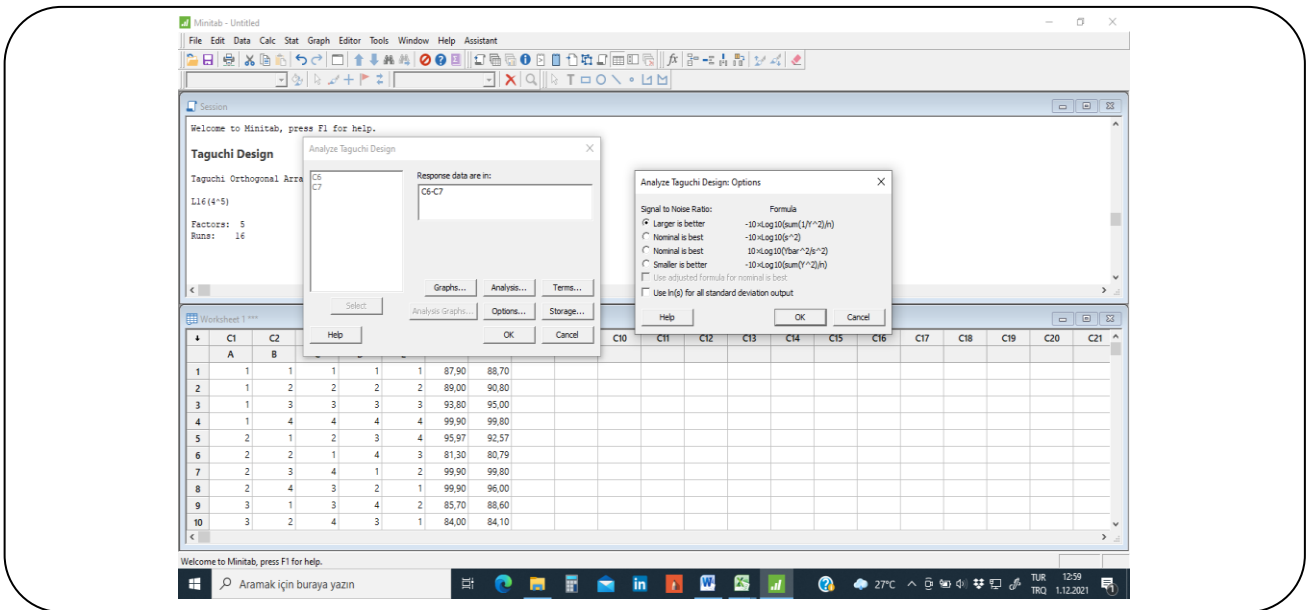


Fig A4.

(For example, we chose 5-parameter and 4-level $L_{16}(4^5)$ experimental designs at the beginning of our experiments). Then we determine the experiment number by pressing the “Design” button. If there are no alternative experiment numbers, click on the existing design and we will push OK key. If there is a design of the desired number of experiments is selected.

Then by pressing OK key, You can get the following image (Fig A3) again. The experiment plan you selected is

placed in the bottom box of the screen. Enter the data obtained in the columns without numbers (eg C6 and C7) in the box (The test results are entered in the columns C6 and C7 as each test is repeated at least twice). If three or more repetitions are made, other results must be entered in columns C8, C9,..... (Data entry in only one column will not yield results).

After that, we click on Stat, DOE, Taguchi, and Analyze Taguchi Design menus respectively. In the window

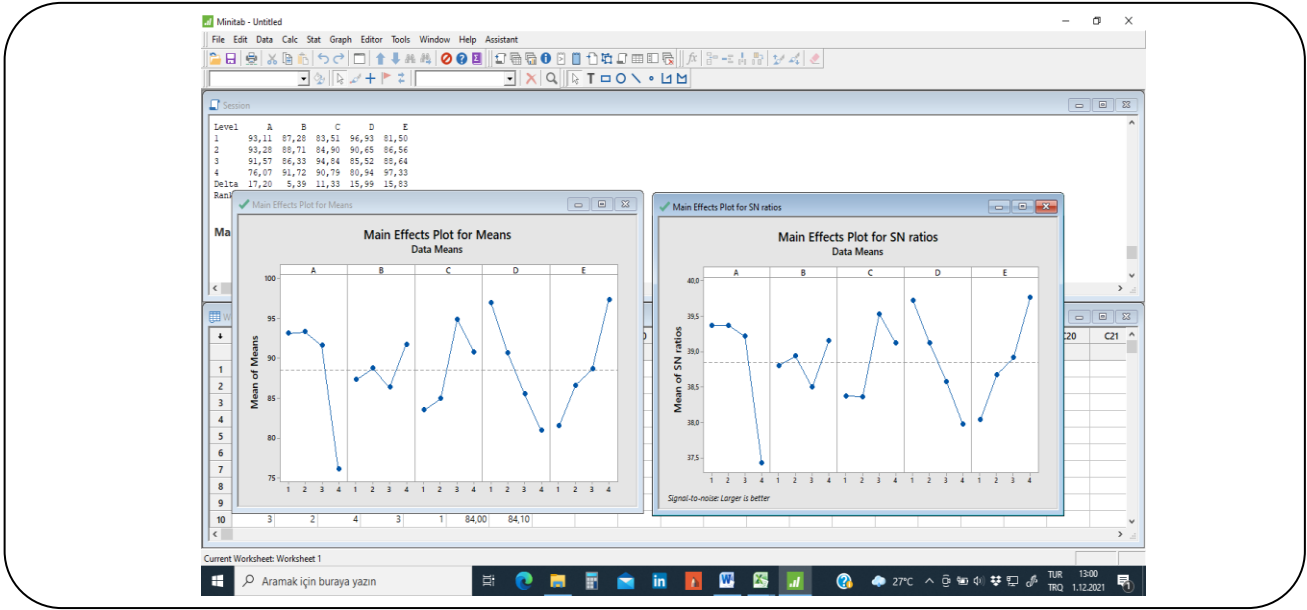


Fig A5.

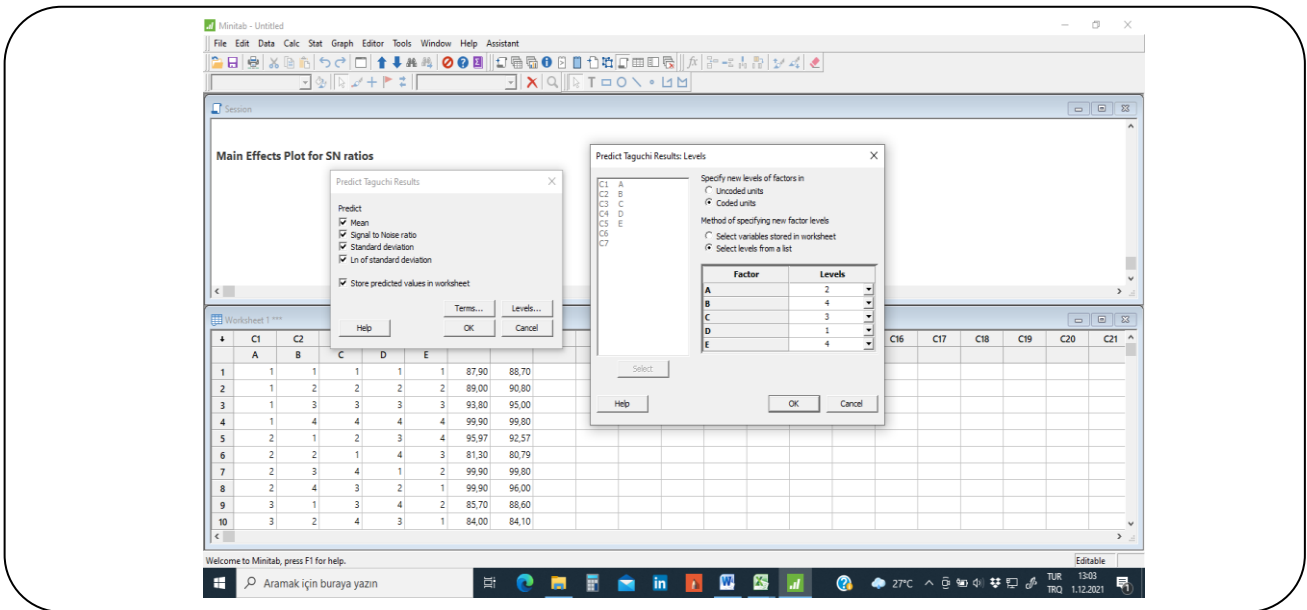


Fig A6.

that will open we will select C6 and C7 in the "response" data section. We then use the "options" key to select the performance statistic formula we will use for analysis. (In our study, the larger the better was chosen). After confirming the selection by pressing the OK key, we can make the analysis by pressing OK again (Fig A4).

The program will give us both data and graphs of S/N and average values (Fig A5). Here, the optimum conditions are found by taking the points where the S/N

value of each parameter is maximum (for example, in the graph below, A2, B4, C3, D1, and E4 values are the points where the S/N values are maximum).

The next step is to see if this determined experiment has been carried out. If the A2, B4, C3, D1, and E4 experiments were not performed, you can also guess from the same menu what the result will be when this experiment is done.

This time, after clicking the space on the top of the program,

the Stat, DOE, Taguchi and Predict Taguchi Results menus are clicked. By clicking "Levels" in the open window, the predicted levels are entered manually and the value of the analysis is obtained by pressing "OK" key (Fig A6). In order to confirm this value, the experiment is performed under optimum conditions and the result is compared and interpreted.

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