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Research Article

Advantageous approach for boron ores used in cement production: optimization of dehydration

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ABSTRACT

Boron with a certain water content is used for industrial purposes, including cement production. It is necessary to perform and optimize heat treatments and determine the water content. The heat treatment is applied to boron ores that must be used for cement production. However, these processes take time and increase costs. With this study, it will be possible to obtain boron products with the desired properties in a shorter time by determining the optimal parameters for dewatering processes. Colemanite and ulexite ores were reduced to a grain size of 44 microns by ore dressing processes and subjected to dewatering. The Taguchi method was used to optimize the dehydration of colemanite and ulexite ores. The orthogonal design of experiments method $L_{18}(6^1 3^2)$ 3 factors, 18 trials was chosen to determine the design of experiments. The changes in the H_2O-CaO-Na_2O-B_2O_3 concentrations were determined on the basis of the analyses performed. TG/DTA analyses were carried out for comparison with the dehydration processes. In the optimization processes performed using the Taguchi method, the maximum water removal was achieved with 1 g of ore and a period of 6 hours. H_2O removal was 98.42% at 650 °C for colemanite and 99.1% at 300 °C for ulexite. It has been shown that the dehydration of ulexite and colemanite ores can be optimized and the boron product with the desired properties can be obtained in a short time, which is an advantage for its use in the cement industry. It is expected that this study will serve as an important basis for future applications of B_2O_3 cement.

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1. Introduction

Boron ores are commonly known as borates and borosilicates. They are always associated with oxygen in mineral deposits (Helvacı 2015). They generally contain B_2O_3. They gain value depending on the amount of crystal water (H_2O) (Helvacı 2017; Çelik et al. 1994; Tunç et al. 1997; Şener et al. 2000). The most commonly used species in the industry are borax, colemanite and ulexite. Colemanite; among boron minerals, it is the most abundant type. It contains Ca, is transparent, colorless, and occurs in the form of crystals. Its density is 2.42 g/cm^3 and its hardness is 4.0-4.5 on the Mohs hardness scale (DPT 2001). It dissolves very poorly in water, but can easily dissolve in acid and acid salts (Akyıldız 2012). In Türkiye, it is concentrated in some regions of Balıkesir, Kütahya, Bursa, and Eskişehir (Ulusoy 2012). Chemical formula: ($2CaO.3\ B_2O_3.5H_2O$) and its B_2O_3 content is 50.8%. Ulexite; It is generally found in the form of soft, highly moist, and fibrous crystals. The hardness is 2.5 and the specific gravity is 1.955 g/cm^3. Its chemical composition is ($Na_2O.2CaO.5\ B_2O_3.16H_2O$) and in pure form, it contains 42-43% B_2O_3 (Çelik 2007).

Boron products are light, resistant to stress and chemical effects, and are mostly used in the chemical and cosmetic industries, photography, paint, leather, and cement industries (Topçu and Soyhan 2022; Kurtuluş and Kurtuluş 2021). Anhydrous boron (B_2O_3) has been used in cement production for many years. Research has shown that cement made with anhydrous (pure) B_2O_3

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significantly improves its properties (Demirel and Nasıroğlu 2017). In one study, mixed cement was made by adding boron waste with the same B_2O_3 content to the cement in varying proportions. Strength and durability tests were conducted with these cements. It was found that the mineral additives used in cement production not only have a positive impact on the environment but also have a positive impact on costs by saving natural raw materials and energy. These studies are important in order to recycle industrial waste in various sectors, eliminate environmental problems, and contribute to the country's economy. It is obvious that boron minerals and waste are suitable for cement production in the world, especially in our country. The use of boron minerals and wastes, which do not have negative effects on cement properties and do not contain harmful components, offers great advantages in cement production (Eyyüboğlu 2013; Oruç et al. 2004). In particular, the studies carried out jointly by Boren National Boron Research Institute and Turkish Cement Manufacturers Association (TÇMB) and industrial scale cement production in Denizli and Göltaş cement factories are one of these studies (Demirel and Nasıroğlu 2017). In their study, Elbeyli et al. (2003) added "boral gypsum" produced during the manufacture of colemanite (heat treated) to Portland cement and investigated its effects on mechanical properties. TGA, XRD, and gradual heating were applied as heat treatments. Boron was added to Portland cement at the clinker stage in an amount of 5-7% of the cement weight and subjected to heat treatment. Gradual heating was carried out at a rate of 10 °C/min up to 500 °C. At the end of the experiments, no change in strength was observed in the non-heat-treated (5%) specimens with boral gypsum addition, while the strength of the heat-treated (5%) specimens with boral gypsum addition increased by 25%. Pehlivanoğlu et al. (2013) investigated the effects of boron compounds on the setting time of Portland cement, boron-active belite cement, and calcium aluminate types of cement. Boric acid was added to these cement samples at a dosage of 0.25% and 1%. It was found that despite the increase in the amount of boric acid, the initial and final setting times also increased.

In another study in which colemanite and ulexite minerals were added to mortar samples, unheated and heat-treated colemanite minerals were added separately to the mortar. The minerals were subjected to heat treatment at 150 °C-24 hours and 600 °C-6 hours. In this study conducted by Şener et al. (2000), it was observed that the minerals completely lost their moisture at 150 °C. It was found that the prolongation of setting times by heat treatments at 150 °C and 600 °C further increased for the colemanite mineral. For this reason, heat treatment may be considered appropriate in cases where a longer setting time is required at lower additive rates (Durmuş 2016). The results of the setting time tests in this study are consistent with the results of the studies by Olgun et al. (2006) and Pehlivanoğlu et al. (2013), which state that boron additives increase the setting times. Based on the results of the bending and compression tests of heat-treated specimens with colemanite additive, it was found that the heat-treated colemanite mineral has no effect on mechanical strength.

The use of boron minerals and boron waste in cement has become a very important issue in recent years. In cement production, the use of boron increases the durability of concrete. Boron cement is especially preferred in the construction of concrete roads and dams. In order to investigate the usability of boron cement in concrete road construction and its effect on the performance of the road, a 1600 m long concrete road was constructed, 1000 m of which was located in the Black Sea region (Yenialaca 2009). The use of boron in cement production is not a new practice. Considerable improvements have been observed in the properties of cement produced using pure B2O3. With this in mind, appropriate studies have been initiated in our country and it has been determined that colemanite may be the most suitable mineral. When colemanite, a boron mineral, is used in cement production at the rate of 8%, it lowers the burning temperature of the clinker and improves the properties of the cement (Eyyüboğlu 2013). Boron cement; shows better properties than Portland cement in terms of parameters such as strength, water and gas permeability, and heat of hydration. Low heat of hydration significantly reduces cooling requirements, especially for mass concrete. Calcium borates are very useful plasticizers, as they reduce the viscosity and surface tension of the melt in the rotary kiln during cement production (Boren 2016).

In order for boron ores to be used in industry, they must undergo certain processes such as crushing, grinding, and dewatering, and the water of crystal in their structure must be removed. Calcination/dehydration processes must be applied to remove the crystal water bound in their structure (Kılcı 2011). As can be seen, boron ores are offered for industrial use by removing the chemically bound water they contain through calcination or dehydration processes (Kayandan et al. 2004). The main purpose of dehydration of boron minerals is to prepare the ores for commercial use, i.e., to give them a higher useful and economic value by releasing the crystal water they contain (Tunç et al. 2001; Şener et al. 2000). Thus, calcined boron ores can be used in many industries. Şener and Ozbayoğlu (1994) conducted a study on the calcination processes of ulexite and colemanite minerals (which are endothermic). In this study, they mixed colemanite and ulexite and calcined them at 400-450 °C for half an hour. They found that the colemanite ore crumbled and dissolved, while the ulexite ore did not break and turned into a porous, hard structure.

In addition to the dehydration processes, which are important for the use of boron ores in industrial applications, some optimization processes can also be carried out for these heat treatments, which bring both time and economic benefits. One of these methods is the Taguchi method. The general idea of the Taguchi method is to fit small factorial or orthogonal arrangements of experimentally calculated elements to assembly variations and to perform estimated calculations. This method can be applied to all open or closed functions (Samtaş and Gülesin 2005). The Taguchi method is an experimental design method that attempts to minimize product and process variability by selecting the most appropriate combination of levels of controllable factors versus the uncontrollable factors that cause product and process variability (Baynal 2005). Applying parameter design in the Taguchi method to optimize a process with multiple performance characteristics involves the following steps: the determination and calculation of performance characteristics and the selection of process parameters that can be evaluated, the provision of the number of parameter levels for the process and the interaction between possible process parameters, the selection of the appropriate orthogonal arrangement, the determination of process parameters in the orthogonal arrangement, the management of experiments based on the arrangement of the orthogonal arrangement, analysis of experimental results using ANOVA and performance characteristics, selection of optimal process parameters, verification of optimal process parameters (with all verification experiments) (Çopur et al. 2004; Kocadağistan 2007). The Taguchi method occupies a very important place in the technological and scientific development of quality and has brought a completely different perspective to the definition of quality (Kumsal 1994). In a study, the formation of calcium carbide slag by the Taguchi method and its use in the production of CaO briquettes by calcination processes was investigated. In this study, since the disposal of calcium carbide slag (CCS), obtained as a by-product during the Acetylene gas process, poses an environmental problem, it is aimed to use CCS in the preparation of calcium oxide (CaO) briquettes for reuse in calcium carbide production. As parameters; binder types (phosphoric acid (H_3PO_4), molasses, and corn syrup), binder amount (1, 3, and 5%), briquette pressure (20, 28, and 36 MPa), calcination temperature (800, 900, and 1000 °C), and calcination time (30, 45, and 60 min.) was selected. The effect of these parameters on the strength of the CaO briquettes was examined using the Taguchi approach (Altıner 2018). In another study, the optimization of the dissolution of calcined colemanite mineral in methyl alcohol by CO_2 in the autoclave system was investigated using the Taguchi method. In the study, the process of optimizing the dissolution of colemanite ore in methyl alcohol with CO_2 in a high-pressure reactor was evaluated using the Taguchi method (Kızılca and Çopur 2017).

2. Materials and Method

2.1. Materials

In the experiments, colemanite and ulexite ores obtained from Etibank Bor mines were used (Fig. 1). Chemical analysis results of colemanite and ulexite ores are given in Table 1.

Table 1. Analysis results of colemanite and ulexite ores.

Compound	Colemanite	Ulexite
	%	%
B_2O_3	50.97	43.1
CaO	27.18	13.8
Na_2O	-	7.6
H_2O	21.85	35.4

Fig. 1. Ulexite and colemanite ore samples.

Laboratory-type jaw crusher, ball mill, and mechanical sieve were used in ore size reduction processes. In the sieving process, 60 mesh (283 micron/0.28 mmx0.28 mm mesh size, 60 mesh, 0.14 mm wire diameter, 23.62 mm/number of holes) and 325 mesh (43 micron/0.043 mmx0.043 mm mesh size, 325 mesh, 0.035 mm Standard sieves with dimensions (wire diameter, 127.952 mm/number of holes) were used. A muffle furnace (Nabertherm, Germany) with a maximum temperature of 1100 °C was used for dehydration experiments. TG analyses were performed with differential thermal analysis and thermogravimetric analyzer (DTA-TG system, SETARAM Labsys 3.0). Other materials; 35 mL porcelain crucible, desiccator, OHAUS-PA214C brand precision balance, and other experimental materials.

2.2. Method

In the sample preparation process of ulexite and colemanite ore for dehydration experiments, a 500 g sample was taken by cone and quartering method and was first crushed to 60 mesh (250 micron) size in a jaw crusher, and then ground to 325 mesh (45 microns) size in a ball mill. Approximately 200 g ore samples to be used in the experiments were sieved using a mechanical sieve and the samples were made ready for dehydration processes. In the Taguchi method, the experimental design was planned first. The problem was defined, performance characteristics were determined, and the design was realized. Parameter design is carried out in order to determine the factors and levels that affect the target value of the performance characteristic and make this optimum. There are two stages in parameter design; robust design and orthogonal arrays. Robust design is an optimization method applied to introduce new technologies in the design of products and processes (Taguchi et al. 1999; Şanyılmaz 2006). After the robust design, an orthogonal array selection was made, which determines how all experimental combinations will be carried out. Thus, fewer experiments were performed with a larger number of factors (Özden 2020; Mercan 2019). The values used in the experiments were converted to S/N (signal/noise) ratios and analysis of variance (ANOVA) was performed (Danışman and Yalçındağ 2023). In order to verify the optimal factor levels determined by the Taguchi method, a confidence interval was created for the average response value under optimal conditions (Yılmaz and Keskin 2019). Dehydration experiments were carried out to verify the data found in the experiments performed with the Taguchi method. In order to determine the experimental plan in the optimization studies of the dehydration of colemanite and ulexite ores (Taguchi method), orthogonal layout experimental design method $L_{18}(6^1 3^2)$ 3 factors, 18 experiments were selected. In optimization experiments, dehydration temperature, dehydration time, and ore amount were selected as experimental parameters. The data obtained as a result of the experiments were evaluated according to Eq. (1) for each level of each parameter and performance criteria were calculated.

$$\text{Smaller – better } S/N_S = -10log\left(\frac{1}{n}\sum_{i=1}^{n} y_i^2\right) \quad (1)$$

For the dehydration temperature of ulexite ore, 300 °C was chosen in the parameter levels, and it was aimed to obtain precise data against the possibility of variations in weight differences at temperatures of 350 and above. The parameters used in the optimization experiments are arranged as given in Table 2.

In the dehydration process, the temperature of the furnace was adjusted according to the determined parameters and the weighed colemanite and ulexite ores were placed in porcelain crucibles and placed in the furnace. Each sample, whose dehydration process was completed, was left to cool in the desiccator together with the crucible to prevent moisture, was weighed and the weight differences were recorded. TG analyzes were performed with differential thermal analysis and thermogravimetric analyzer (DTA-TG system, SETARAM Labsys 3.0). Analyzes were performed using an aluminum oxide crucible at a heating rate of 10 °C/min. The process flow diagram of the working method is given in Fig. 2.

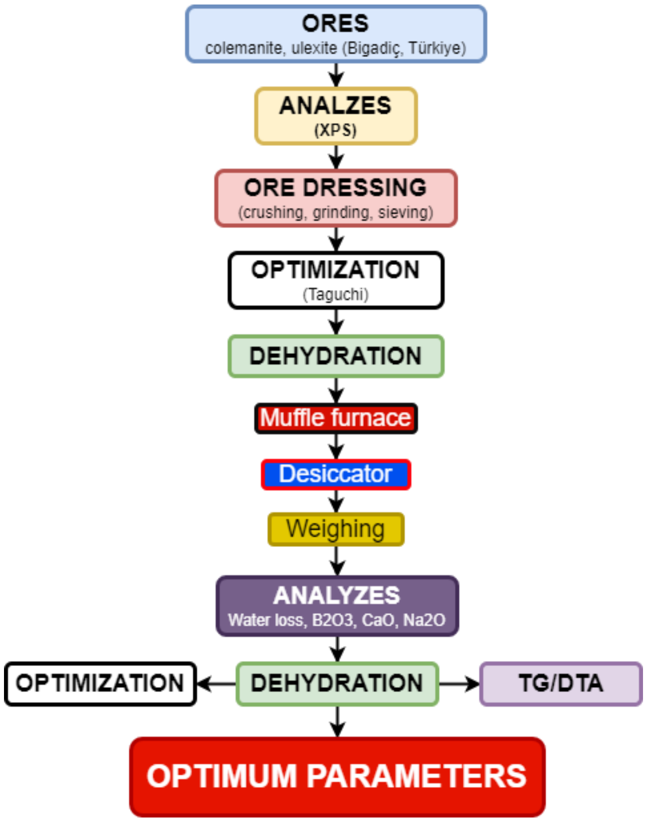

Fig. 2. Process flow diagram.

Table 2. Parameters used in optimization of dehydration of colemanite and ulexite ores.

Ore	Parameters	Level					
		1	2	3	4	5	6
Colemanite	Dehydration temperature (°C)	400	450	500	550	600	650
	Dehydration time (h)	2	4	6	-	-	-
	Amount of ore (g)	1	3	5	-	-	-
Ulexite	Dehydration temperature (°C)	50	100	150	200	250	300
	Dehydration time (h)	2	4	6	-	-	-
	Amount of ore (g)	1	3	5	-	-	-

3. Results and Discussion

3.1. Optimization of the dehydration process of colemanite and ulexite ores

The parameters selected for the optimization of dehydration processes to be applied to colemanite and ulexite ores and the water concentrations in the ores at the end of the experiments are given in Table 3. After the experimental groups determined according to the Taguchi method were completed, dehydration experiments were carried out to verify the data obtained and compared with these data.

Figs. 3 and 4 were prepared by considering the results calculated for both ores as the y-axis and the levels of the parameters as the x-axis. The first part in Figs. 3 and 4 shows the temperature levels, the second part shows the time levels and the third part shows the ore amount levels. Considering the S/N_S ratio, the point where the performance criterion has the lowest value indicates the best level of the relevant parameter. When the test results are examined, the parameter values that give the best results for colemanite ore using the Taguchi method are; 650 °C temperature, 6 h time, and 1g ore amount. For ulexite ore, the parameter values that give the best results; it is 300 °C temperature, 6 h time, and 1g ore amount. Since the obtained levels were not included in the $L_{18}(6^1 3^2)$ 3 orthogonal experiment design plan, it was necessary to conduct another experiment for these levels.

In the verification experiment conducted for colemanite, 98.42% H_2O removal was calculated for 650 °C, 6 h, and 1 g ore amount. In the verification experiment conducted for ulexite, 99.1% H_2O removal from ulexite ore was calculated for 350 °C, 6 h, and 1 g ore amount. These values are the highest H_2O removal values reached as a result of dehydration experiments. This shows that the required value in the Taguchi method has been achieved.

Table 3. Experimental plan to be used in optimizing the dehydration of colemanite and ulexite ores and the obtained H_2O removal amounts.

Time (h)	Amount of ore (g)	Dehydration temperature (°C)		Total amount of H_2O remaining in the ore after the dehydration process (%)	
		Colemanite	Ulexite	Colemanite	Ulexite
2	1	400	50	9.44	34.66
4	3	400	50	8.38	34.81
6	5	400	50	7.30	34.51
2	1	450	100	3.64	30.27
4	3	450	100	4.85	24.79
6	5	450	100	5.48	29.09
2	3	500	150	4.15	29.50
4	5	500	150	4.09	23.52
6	1	500	150	3.64	22.21
2	5	550	200	2.17	9.15
4	1	550	200	2.92	8.51
6	3	550	200	2.80	7.50
2	3	600	250	3.40	5.82
4	5	600	250	1.88	4.62
6	1	600	250	1.95	4.67
2	5	650	300	1.72	3.09
4	1	650	300	0.70	2.63
6	3	650	300	1.33	1.39

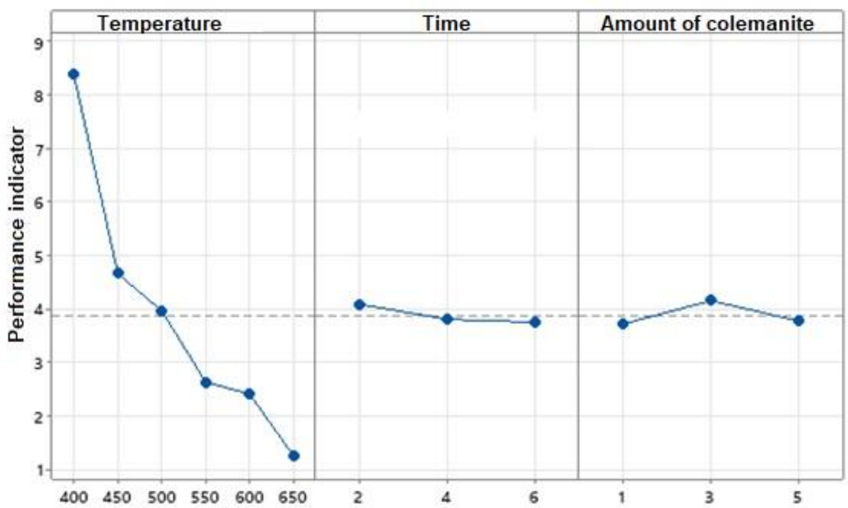

Fig. 3. According to the data obtained as a result of optimization experiments, the effect of temperature, time, and ore amount on the total H_2O amount (colemanite).

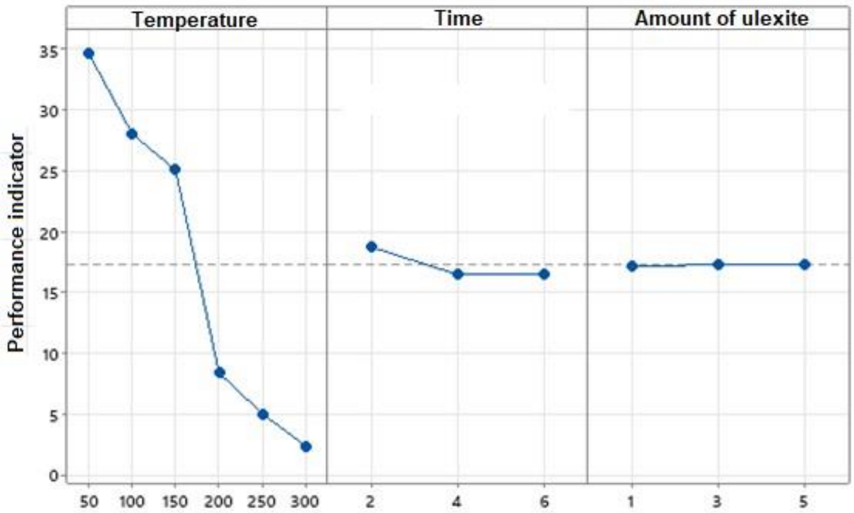

Fig. 4. According to the data obtained as a result of optimization experiments, the effect of temperature, time, and ore amount on the total H_2O amount (ulexite).

In the optimization study, the response table for the averages of colemanite and ulexite ores is given in Table 4, and the model summary is given in Table 5. The regression equation obtained for the total amount of H_2O removed was calculated with Eq. (2) (for colemanite) and Eq. (3) (for ulexite).

Total amount of H_2O removed = (3.880+4.493 colemanite temperature_400+0.777 colemanite temperature _450 + 0.08 colemanite temperature_500 -1.25 colemanite temperature _550+1.47 colemanite temperature _600- 2.63 colemanite temperature _650-0.165 amount of ore _1+0.272 amount of ore _3 - 0.107 amount of ore_5 0.207 duration_2 - 0.077 duration_4 - 0.130 duration_6) (2)

Total amount of H_2O removed = (17.263+ 17.40 ulexite temperature_50+ 10.79 ulexite temperature_100+ 7.81 ulexite temperature_150- 8.88 ulexite temperature _200- 12.23 ulexite temperature _250- 14.89 ulexite temperature _300+ 1.485 time_2- 0.783 time_4- 0.702 duration_6- 0.105 amount of ore_1+ 0.038 amount of ore_3 + 0.067 amount of ore_5) (3)

Table 4. Response table for means.

Level	Colemanite			Ulexite		
	Dehydration temperature (°C)	Time (h)	Amount of ore (g)	Dehydration temperature (°C)	Time (h)	Amount of ore (g)
1	8.373	4.087	3.715	34.660	18.748	17.158
2	4.657	3.803	4.152	28.050	16.480	17.302
3	3.960	3.750	3.773	25.077	16.562	17.330
4	2.630	-	-	8.387	-	-
5	2.410	-	-	5.037	-	-
6	1.250	-	-	2.370	-	-
Delta	7.123	0.337	0.437	32.290	2.268	0.172
Rank	1	3	2	1	2	3

Table 5. Model summary.

	S	R-sq	R-sq(adj)	PRESS	R-sq(pred)	AICc	BIC
Colemanite	0.826	94.59%	88.51%	27.61	72.62%	95.59	61.38
Ulexite	1.96128	98.92%	97.70%	155.788	94.52%	126.73	92.53

Effects of the factors on H_2O removal are seen according to the variance analysis results from Table 6. While the dehydration temperature of colemanite ore was effective within the 94.32% confidence interval, the ulexite ore dehydration temperature was found within the 98.21% confidence interval. Duration and ore amounts are less effective for both ores.

Table 6. Analysis of variance for colemanite and ulexite ores.

Colemanite							
Parameters	DF	Seq SS	Distribution (%)	Adj SS	Adj MS	F-Value	P-Value
Temperature (°C)	5	94.320	93.53	94.3199	18.8640	27.67	0.000
Time (h)	2	0.674	0.67	0.6744	0.3372	0.49	0.627
Amount of ore (g)	2	0.393	0.39	0.3929	0.1965	0.29	0.757
Error	8	5.454	5.41	5.4538	0.6817	-	-
Total	17	100.841	100.00	-	-	-	-
Ulexite							
Parameters	DF	Seq SS	Distribution (%)	Adj SS	Adj MS	F-Value	P-Value
Temperature (°C)	5	2790.43	98.21	2790.43	558.085	145.08	0.000
Time (h)	2	19.87	0.70	19.87	9.934	2.58	0.136
Amount of ore (g)	2	0.10	0.00	0.10	0.051	0.01	0.987
Error	8	30.77	1.08	30.77	3.847	-	-
Total	7	2841.17	100.00	-	-	-	-

3.2. Dehydration experiments

In the dewatering experiments, colemanite and ulexite ores were weighed as 1, 3, 5 g, placed in porcelain crucibles, placed in the furnace and the experiments started. After the heat treatment at temperatures of 300-650 °C for colemanite and 50-350 °C for ulexite, weight differences were taken and the amount of water removed was determined. It was aimed to remove more than 90% of the water content of the ores at the beginning of the experiment. According to the chemical formulas of colemanite and ulexite minerals, it was determined that 1 g of B_20_3 contains 0.2185 g and 0.354 g of crystal water, respectively. Calculations made after the dehydration experiments were completed showed that while the H_2O content decreased, the B_2O_3, Na_2O and CaO concentrations increased.

As a result of the experiments, 99.56% of the water in the colemanite ore was removed at 650 °C, 1 g of ore, and a period of 6 hours. As can be seen from Fig. 5, H_2O removal amounts were more efficient in the use of 1 g of ore. As a result of the experiments conducted with 1 g of ore, the lowest water removal amount was found to be 98.31% at the end of a 1-hour period at 650 °C (Fig. (5a)). In dehydration processes performed with 1 g ore samples, approximately 94% of the existing water could be removed even after 4 hours. Values close to these results were obtained for 3 and 5 g ore samples (Figs. 5(c-e)).

When looking at the changes in the H_2O amounts of ulexite ore Figs. 5(b-d-f), it is seen that the water contents begin to decrease in 1, 3, and 5 g ore samples in the temperature range of 50-100 °C. The increase in water loss was accelerated in the temperature range of 150-200 °C and reached its maximum level in the temperature range of 200-350 °C. Above 350-400 °C, the decrease in the amount of H_2O became stable, and almost all (99.5%) of the water in the ore was removed. It is seen that the weight decrease that occurs in dehydration processes after 50 °C corresponds to the physical release of water. As a result of the experiments, 99.67% of the water in the ore was removed at 350 °C, 1 g of ore and a period of 6 hours (Fig. 5(b)) (Şener and Özbayoğlu 2000).

As a result of the experiments, it is seen that there is an increase in B_2O_3 concentrations in both ores (Figs. 6(a-c-e)). For colemanite ore, the amount of B_2O_3, which was 50.97% at the beginning of the experiments, reached its maximum value of 64.93% at the end of 650 °C, 1 g ore, and 6 hours (Fig. 6(a)). As can be seen from Fig. 6, B_2O_3 amounts are higher when using 1 g of ore. As a result of the experiments, it is seen that there is an increase in the amount of B_2O_3 in ulexite ore, similar to that in colemanite ore (Figs. 6(b-d-f)). The amount of B_2O_3, which was 43.1% at the beginning of the dehydration experiments, reached its maximum value of 66.57% at the end of 350 °C, 1 g ore, and 6 hours (Şener and Özbayoğlu 2000; Kayandanet al. 2004; Eti Maden 2022).

As a result of the experiments, it was determined that there was an increase in the amount of CaO in both ores. The CaO amount of 27.18% determined for colemanite at the beginning of the experiments reached its maximum value of 34.63% at the end of 650 °C, 1 g of ore and 6 hours. As can be seen from the graph drawn according to the data obtained as a result of dehydration experiments, CaO amounts were more efficient in the use of 1 g of ore (Figs. 7(a-b-c)). Similar results were found for ulexite. The CaO amount of 13.8%, which was calculated at the beginning of the experiments for ulexite, reached its maximum value of 21.3% at the end of the experiments at 350 °C, 1 g of ore, and a period of 6 hours (Figs. 7(b-d-f)).

When the amount of Na_2O found in ulexite ore, unlike colemanite, was examined; there was also an increase in the amount of Na_2O. The amount of Na_2O, which was 7.6% at the beginning of the dehydration experiments, reached its maximum value of 11.79% at the end of 350 °C, 1 g ore, and 6 hours (Figs. 8(a-b-c)).

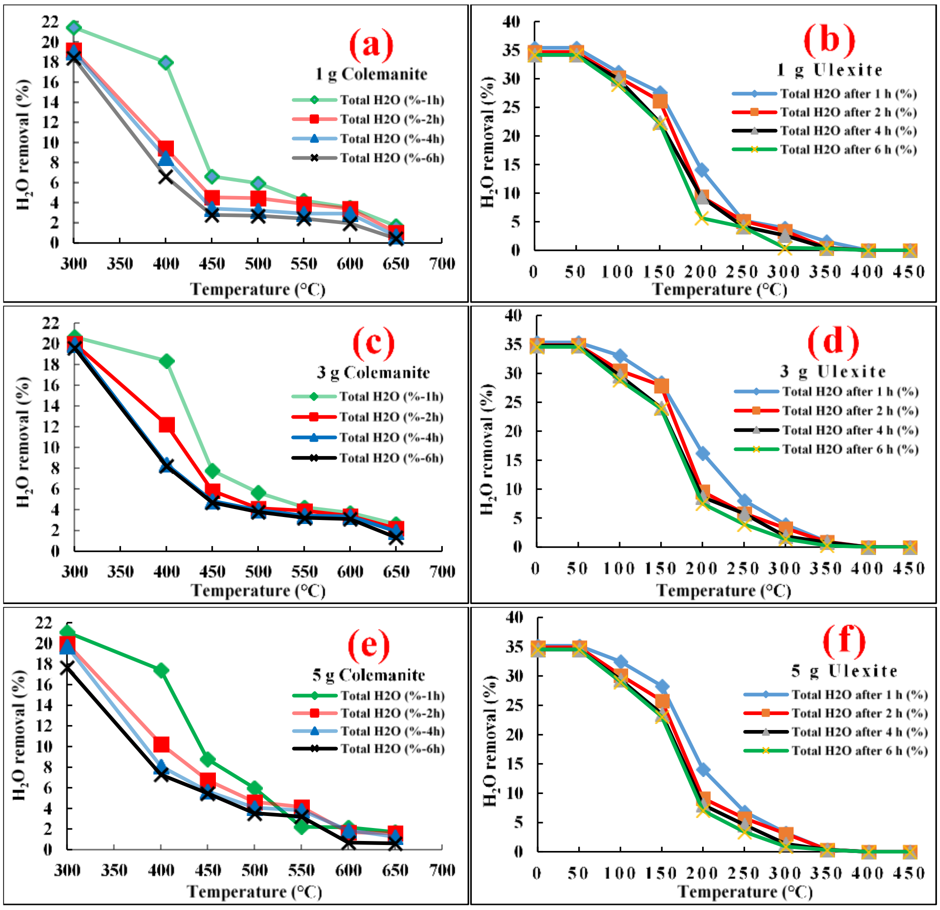

Fig. 5. H_2O removal amounts of 1, 3 and 5 g colemanite and ulexite ores after 1, 2, 4 and 6 hours of dehydration (%).

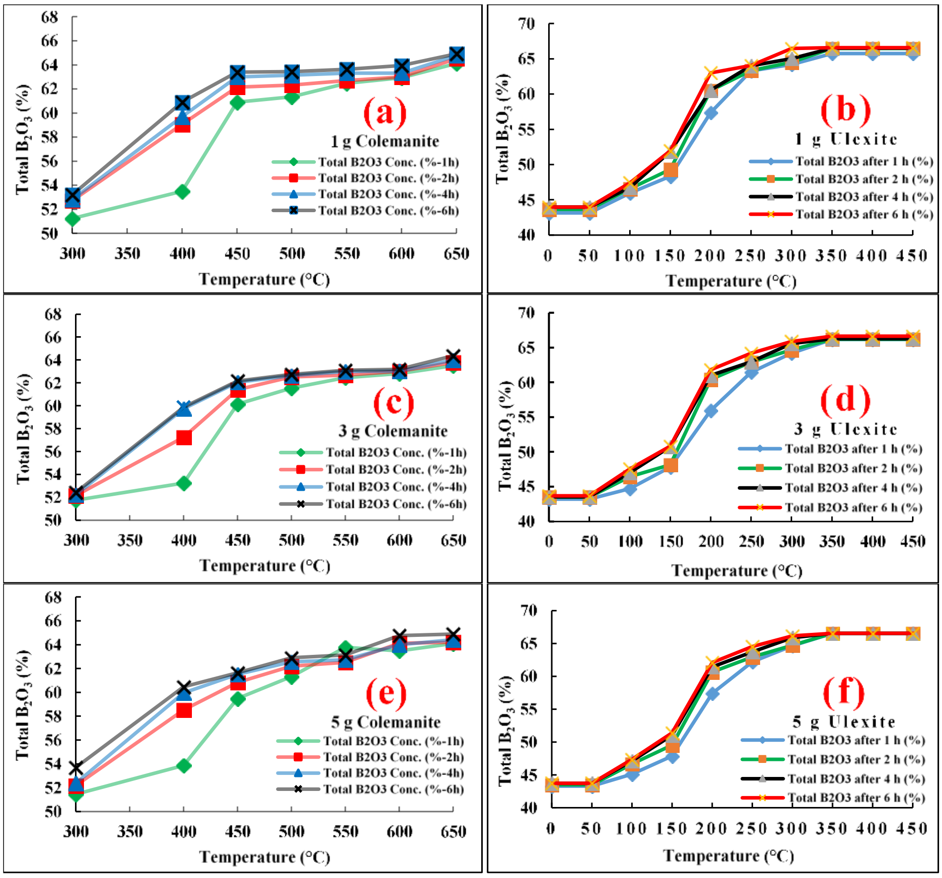

Fig. 6. B_2O_3 concentrations of 1, 3, and 5 g colemanite and ulexite ores after 1, 2, 4, and 6 hours of dehydration (%).

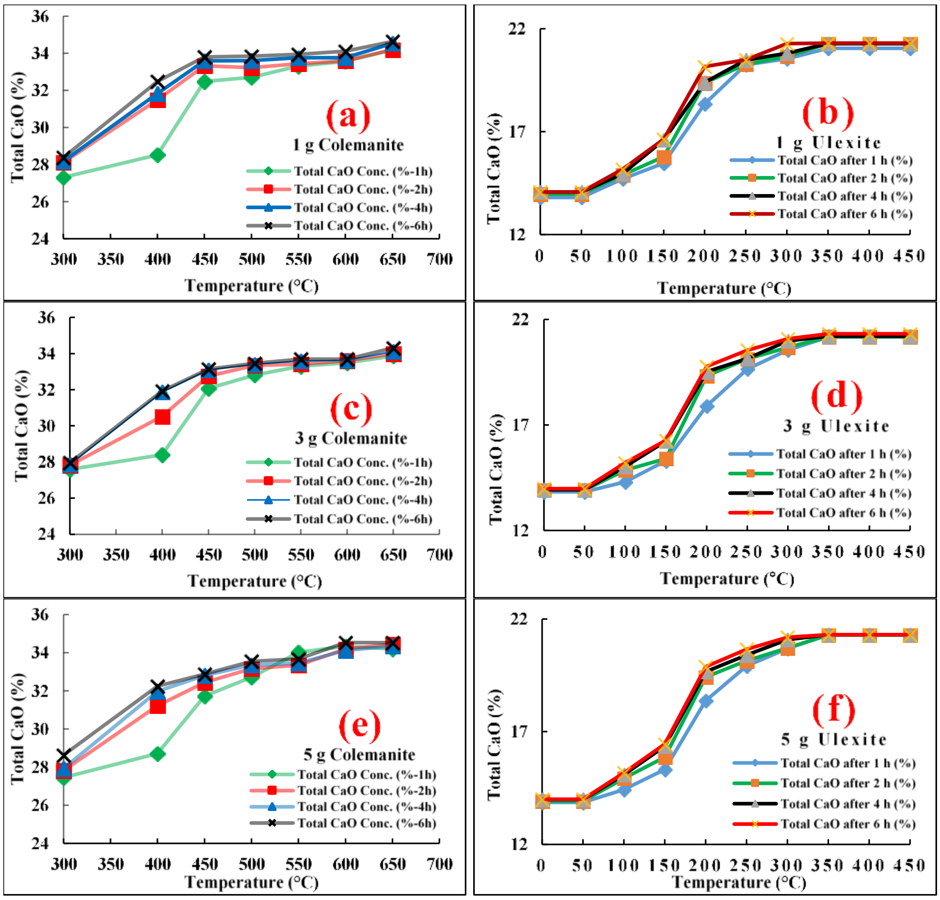

Fig. 7. CaO concentrations of 1, 3, and 5 g colemanite and ulexite ores after 1, 2, 4, and 6 hours of dehydration (%).

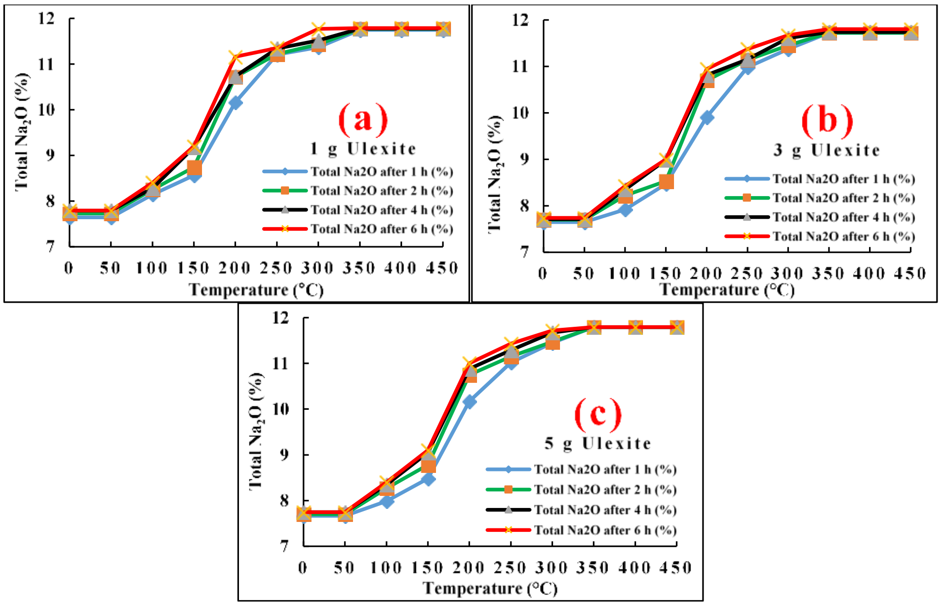

Fig. 8. Na_2O concentrations of 1, 3, and 5 g colemanite and ulexite ores after 1, 2, 4, and 6 hours of dehydration (%).

3.3. Optimization

The data obtained as a result of the experiments carried out according to the parameters selected for the optimization processes carried out by applying the Taguchi Method and the verification experiments carried out with the dehydration experiments are given comparatively in Table 7. When Table 7 is examined; Among the parameters selected according to the Taguchi Method, the parameters with the highest values are as follows: for colemanite ore; 650 °C, 4 h and 3 g ore amount, and for ulexite ore: 300 °C, 6 h and 3 g ore amount. In Tables 5 and 6, the effects of the factors on H_2O removal were examined according to the analysis of variance results. It was determined that dehydration temperature was more effective, while time and ore amounts were less effective, in the confidence intervals of 98.21% (for colemanite) and 94.32% (for ulexite).

Table 7. Validation of the experimental results.

Ore	Temperature (°C)	Time (h)	Amount of ore (g)	Optimization-Verification			
				H_2O	B_2O_3	CaO	Na_2O
Colemanite	400	2	1	9.44	59.06	31.50	-
	400	4	3	8.38	59.75	31.87	-
	400	6	5	7.29	60.46	32.25	-
	450	2	1	4.53	62.15	33.32	-
	450	4	3	4.84	62.06	33.10	-
	450	6	5	5.47	61.65	32.88	-
	500	2	3	4.15	62.51	33.34	-
	500	4	5	4.08	62.56	33.36	-
	500	6	1	2.70	63.45	33.85	-
	550	2	5	4.15	62.51	33.34	-
	550	4	1	2.91	63.32	33.77	-
	550	6	3	3.22	63.09	33.69	-
	600	2	3	3.40	63.00	33.60	-
	600	4	5	1.88	63.99	34.13	-
	600	6	1	1.94	63.95	34.11	-
	650	2	5	1.60	64.20	34.44	-
	650	4	1	0.69	64.77	34.54	-
	650	6	3	1.32	64.36	34.32	-
	650	6	1	0.44	64.93	34.63	-
Ulexite	50	2	1	34.66	43.65	13.97	7.73
	50	4	3	34.81	43.54	13.93	7.71
	50	6	5	34.51	43.74	14.00	7.75
	100	2	1	30.27	46.58	14.90	8.25
	100	4	3	24.79	47.00	15.04	8.35
	100	6	5	29.09	47.39	15.17	8.40
	150	2	3	29.50	48.15	15.41	8.53
	150	4	5	23.52	51.05	16.35	9.05
	150	6	1	22.21	51.96	16.63	9.20
	200	2	5	9.15	60.68	19.42	10.75
	200	4	1	8.51	60.55	19.38	10.73
	200	6	3	7.50	61.79	19.77	10.94
	250	2	3	5.82	62.91	20.13	11.14
	250	4	5	4.62	63.71	20.39	11.29
	250	6	1	4.67	64.05	20.49	11.35
	300	2	5	3.09	64.73	20.71	11.47
	300	4	1	2.63	65.04	20.81	11.52
	300	6	3	1.39	65.86	21.08	11.67
	350	6	1	0.49	66.46	21.27	11.77

As a result, the parameter values that give the best results using the Taguchi method are; are for colemanite 650 °C for temperature, 6 h for time and 1 g ore amount, for ulexite 350 °C, 6 h for time and 1 g ore amount. Since the obtained levels were not included in the orthogonal experimental design plan, additional experiments were conducted for these levels, the obtained values are shown in Table 7 (with red color) and the results were confirmed.

3.4. Thermal analysis

Structural or chemical changes that may occur in colemanite ore were determined by TG/DTA analysis and compared with dehydration test results. The changes occurring here are explained by the temperatures at which the endothermic and exothermic peaks obtained during the measurement occur (Figs. 9 and 10). When the TG/DTG curves of the colemanite mineral were examined, no mass change occurred at temperatures up to 300 °C. It was observed that heating from 300 to 800 °C led to mass losses in two consecutive steps. It is seen that the colemanite sample undergoes rapid water loss in the temperature range of approximately 350 °C-450 °C, where an endothermic reaction occurs and thermal decomposition occurs. According to the DTA curve, it was determined that there were sharp peaks in the range of approximately 389°C-404 °C. Rapid water loss and irregular stresses in the crystal matrix cause expansion in the ore structure, allowing crystal transformation to occur as the temperature increases in the fractures that occur as a result of these internal stresses (Çelik and Suner 1995).

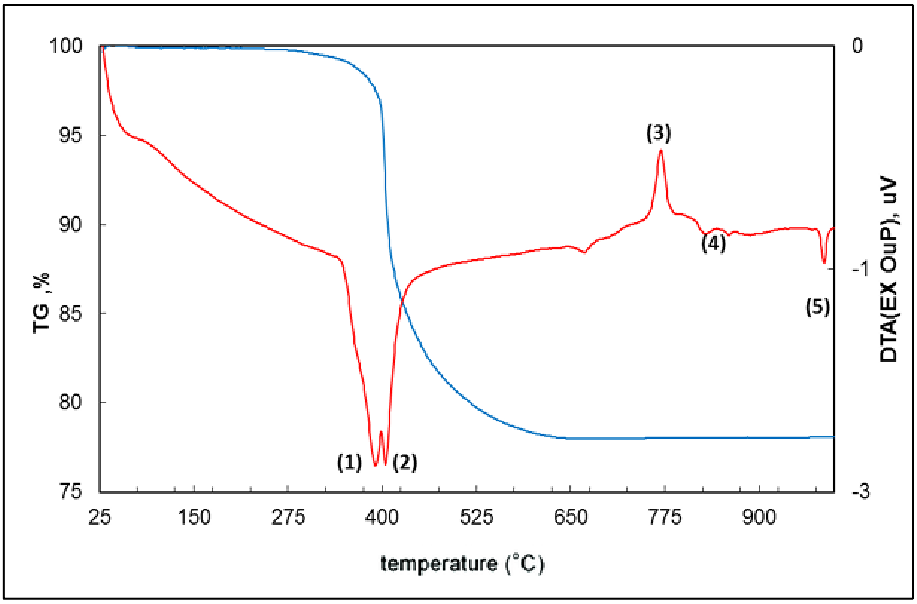

Fig. 9. TG/DTA curve of colemanite ore.

It has been determined that the decomposition of the ulexite mineral begins at 76°C and continues up to 240 °C. According to the TG/DTA curve, it was determined that there were 8% and 17% mass losses at the peaks at 146°C and 173°C. As heating continued, removal of the remaining OH− groups occurred, with peaks at 398°C and 718°C. It has been determined that water is completely released at temperatures up to 600 °C. As seen in Fig. 10, while a mass loss of approximately 14% occurred in the first stage, a mass loss of 4% was observed after 400 °C. The maximum peaks for these mass losses were determined from the TG/DTA curve as 109°C and 447°C, respectively.

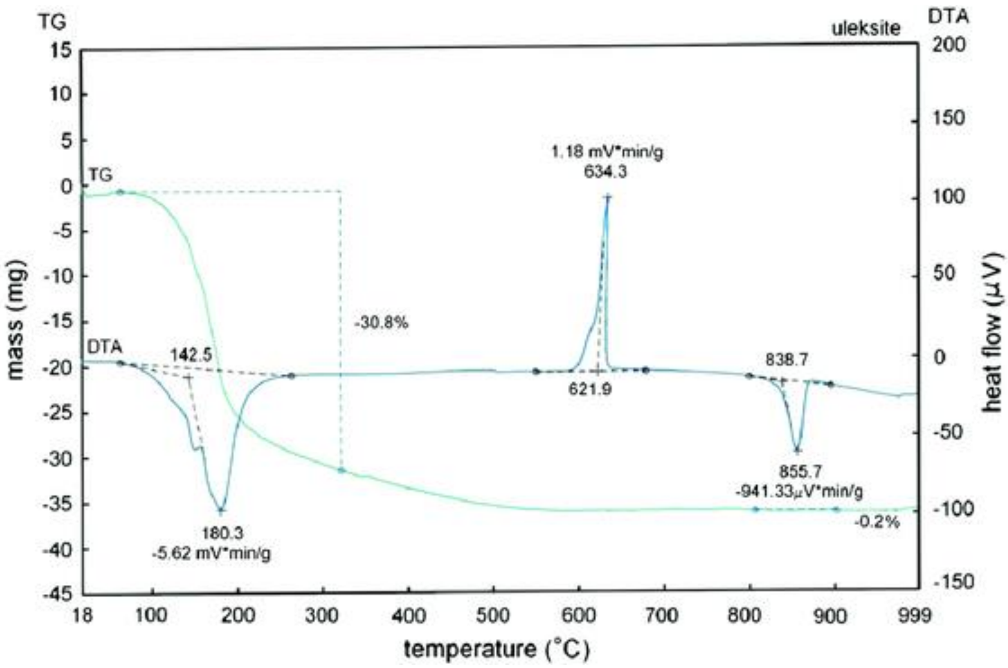

Fig. 10. TG/DTA curve of ulexite ore.

4. Conclusions

In this study, the dehydration of colemanite and ulexite ores and their optimization according to the Taguchi method were investigated in order to obtain anhydrous boron ores that can be used in cement production. The results found at the end of the study are stated as follows;

It was determined that approximately 98% of the chemically bound water in the colemanite ore was removed in the temperature range of 650-700 °C, the B_2O_3 grade increased to 65% and the amount of CaO increased to 35%. It was determined that approximately 99% of the chemically bound water in the ulexite ore was removed in the temperature range of 350-400 °C, the B_2O_3 grade increased to 67%, the amount of CaO increased to

21% and the amount of Na_2O increased to 12% (Yıldız 2004; Kayandan et al. 2004; Eti Maden 2022).

The optimum parameters determined according to the Taguchi method are (for colemanite) 650 °C temperature, 6 h time, and 1 g ore amount and (for ulexite) 350 °C, temperature, 6 h time, and 1 g ore amount (Kızılca and Çopur 2017). To determine the experimental plan selected according to the Taguchi Method, it has been proven that optimum results can be achieved with the orthogonal layout experimental design method $L_{18}(6^1 3^2)$ 3 factors, 18 experiments.

As a result of dehydration processes, it has been observed that colemanite and ulexite ores release the chemically bonded water they contain after a certain temperature and time by giving off heat to the environment and undergoing structural changes. The minerals, which were dehydrated by leaving their chemically bonded waters, crumbled to micronized sizes. Amorphous structures were observed at temperatures above 600-650 °C. While the decrease in the amount of crystal water depending on the ore amounts was around 1% at the initial temperatures, approximately 99% of the crystal water was removed at 350-450 °C in ulexite and at 600-700 °C in colemanite (Şener and Özbayoğlu 1994).

In dehydration experiments, solubility was decreased at temperatures above 450 °C (for ulexite) and 650 °C (for colemanite). It has been determined that run-of-mine ulexite and colemanite ores should be calcined in the temperature range of 350-350 °C and 650-700 °C, respectively. It has been shown that no treatment is required above these temperatures. It has been determined that as a result of the dehydration processes performed on run-of-mine ulexite ores for use in industrial applications, the tenors of colemanite and ulexite ores increase and anhydrous boron ore can be obtained (Kayandan et al. 2004; Eti Maden 2022).

The calcined colemanite ore crumbles into microns, but the main impurity, the clayey materials, leaves its amorphous structure and turns into a more shaped structure under the influence of the calcination temperature. When the sample containers are examined, it is seen that the sample surface is smooth. When mixed, it was observed that the parts that were slightly larger in terms of density and size were collected at the bottom. This reveals that during dehydration, the vapor of chemically bound water mixes the sample as it leaves the environment, and thus classification occurs. Such observations also reveal that the sample is calcined. It is seen that the weight reduction that occurs in dehydration processes corresponds to the physical release of water (Şener and Özbayoğlu 1994).

Using the Taguchi Method, the number of experiments to be carried out in the dehydration process was reduced to 18 experiments, and optimum results and parameters were achieved through this design. In this way, it has been shown that the necessary savings can be achieved in terms of economy and time, and the same results can be obtained with a small number of experiments (Altıner 2018). This means that additional dehydration/calcination costs can be avoided, production costs can be reduced, and transportation and energy costs can be saved. This situation is expected to bring many advantages, especially in terms of marketing (Oruç et al. 2004). Because it is known that chemically bound water and other impurities in boron minerals increase transportation and energy costs in boric acid production. For this reason, boric acid producers primarily prefer "anhydrous" boron ores. In this way, it has been shown that the cost of additional enrichment can be reduced, sales prices can be increased, thus making a significant contribution to the economy, and the desired quality of boron ores can be obtained in a very short time.

The accuracy of the experiments was supported by comparing the data obtained as a result of both optimization and dehydration experiments with thermal analyses. The next step of this study should be studies on the use of boron ores in cement production according to their water content ratios.

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Author Contributions

All of the authors made substantial contributions to conception and design, or acquisition of data, or analysis and interpretation of data; were involved in drafting the manuscript or revising it critically for important intellectual content; and gave final approval of the version to be published.

Data Availability

The datasets created and/or analyzed during the current study are not publicly available, but are available from the corresponding author upon reasonable request.

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