DOI: 10.32571/ijct.467098 **E-ISSN:2602-277X**

International Journal of Chemistry and Technology

http://dergipark.gov.tr/ijct

Research Article

Optimization of dissolution of ulexite by pure CO_2 gas in aqueous medium under pressure and production of sodium pentaborate

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Received: 03 October 2018, Revised: 27 October 2018, Accepted: 30 October 2018

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Citation: Selimoglu, V. **;** Kocakerim, M. M. *Int. J. Chem. Technol.* **2018**, 2 (2), 123-128.

ABSTRACT

The obtain of the boron compounds from Ulexite which is one of the most important ores of Turkey is important. In this study, optimization of dissolution of ulexite by pure CO_2 was investigated in aqueous media under pressure in according to Taguchi method. Temperature, particle size, solid-to-liquid ratio, reaction time and pressure were chosen as parameters for the studies carried out in a high pressure-high temperature reactor. After dissolution experiments, optimum conditions for the dissolution of ulexite were found as 75 g/300 g water (A_1) for solid-to-liquid ratio, 15 bar (B_3) for CO_2 pressure, 80 °C (C1) for temperature, 60 min (D_3) for time and -150µm (E_1) for particle size. The solutions obtained under optimum conditions were dried using a spray drier. Further, after the solution was concentrated, it was crystalized by cooling, and the crystals were filtered and dried. Chemical analyzes exhibited that the products obtained in both cases are sodium pentaborate ($Na_2B_{10}O_{16}$) with different water contents.

Keywords: Ulexite, carbon dioxide, sodium pentaborate, Taguchi method.

Basınç altında üleksitin saf CO_2 gazı ile sulu ortamda çözünürleştirilmesinin optimizasyonu ve sodyum pentaborat elde edilmesi

ÖZ

Türkiye'nin en önemli cevherlerinden biri olan Ulexitten bor bileşiklerinin elde edilmesi önemlidir. Bu çalışmada, basınç altında sulu ortamda saf CO_2 ile üleksitin çözünmesinin optimizasyonu Taguchi metoduna göre araştırıldı. Bir yüksek sıcaklık ve basınç reaktöründe gerçekleştirilen çalışmalarda sıcaklık, tane boyutu, katı/sıvı oranı, reaksiyon süresi ve basınç parametreler olarak seçildi. Çözünme denemeleri sonunda üleksitin çözünmesi için optimum şartlar; katı/sıvı oranı için 75 g/300 g su (A_1), CO_2 basıncı için 15 bar (B_3), sıcaklık için 80 ℃ (C_1), süre için 60 dak (D_3) ve tane boyutu için -150 µm (E_1) olarak bulundu. Optimum şartlarda elde edilen çözeltiler bir püskürtmeli kurutucu kullanılarak kurutuldu. Ayrıca, çözelti konsantre edildikten sonra soğutularak kristallendirildi. Kristaller süzüldü ve kurutuldu. Kimyasal analizler her iki halde de elde edilen ürünlerin farklı su içerikli sodyum pentaborat ($Na_2B_{10}O_{16}$) olduğunu gösterdi.

Anahtar Kelimeler: Üleksit, karbon dioksit, sodyum pentaborat, Taguchi metodu.

1. INTRODUCTION

The boron is one of the most important natural sources of Turkey. Turkey holds %73 of the world boron reserves in addition to the ore deposits of colemanite, tincal and ulexite. In Turkey, boric acid and borax hydrate are produced. Boron components have significant role in today's ultimate technologies and are notably consumed in areas in Europe and Northern America. Ever-increasing level of use and utilization in diverse fields have futher increased the importance of boron. Today, boron components plays great role in our daily life. Additionally, mankind have used boron for thousands of years without realizing it.

In some countries boric acid is produced by dissolving ulexite with sulphuric acid. Also, studies on

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kinetic, optimization and mechanism of dissolution of ulexite in various acids have been performed. The dissolution kinetic of ulexite with mineral acids like H_2SO_4, H_3PO_4, with organic acids like acetic acid and acidic gases has been elaborated,[1-5] In addition, dissolution kinetics of ulexite mineral in some different solutions were subject to the studies.[6-8] However, any process study that encompasses the direct production of sodium pentaborate from ulexite has been encountered so far.

Increasing uses of fossil fuels in the world causes fluctuations of CO_2. However existing natural mechanisms remain inadequate to eliminate these emissions. In the end, this circumstance gives rise to the global warming and climate change.[9] Carbondioxide is a gas produced by the animals in the course of the respiration through putrefaction of the biomass and benefitted by the plants during the photosynthesis. Although carbondioxide constitutes solely 0.04% of the atmosphere, it is actually one of the most important greenhouse gases. Uses of fossil fuels have been shown to be the causes of the increased concentration of carbondioxide in the atmosphere, which is believed to result in the global warming. Therefore, CO_2 emission has become a considerable environment problem. Natural balance mechanisms to dispose CO_2 emissions in the world fall short and this situation causes global warming and desertification. Hence, methods and measures to decrease the CO_2 emission should be developed. Besides, Europe and global society has made a commitment of decreased carbon future as an aim that should be achieved until the mid-century. In 2009, the European Council set a goal to reduce EU-wide greenhouse gases emission until 2050, which was around 80%-95% in the 1990s.[10]

Some countries and international organizations take diverse measures and develop various methods in order to reduce CO_2 emission. One of those methods is to withhold the CO_2 by natural rocks. [11] Many studies have been carried out regarding the retention of the CO_2. However, in the most of these studies, acquired products subsequent to the CO_2 retention process are unvaluable; [11-14] dissolution kinetic of the lizardite - which was partly de-hydroxided with the CO_2 under unstable conditions - was examined in 30-120 °C warmth and 0,1-2 bar partial pressure conditions and a model based on surface complex formation to define specific dissiolution velocities was developed.[15]

In this study, sodiumpentaborate, which is an important boron product, has been obtained through using ulexite ore in CO_2 retention. Sodium pentaborate is a crucial boron compound that is used in several fields particularly agriculture and yet has no production in our country. In existing patents, this compound is obtained from boric acid and borax.[16] In the present study, the optimization of dissolution of ulexite with pure CO_2 in aqueous medium and under pressure is scrutinized. Consequently, CO_2 is held in the form of Ca and $CaCO_3$ within the ulexite, and sodium pentaborate is obtained by the crystalization of the attained dissolution after concentrated.

2. MATERIALS AND METHODS

2.1. Procurement and preparation of the materials

For the study, the ulexite which was obtained from Bigadiç, Balıkesir and its XRD is given in the Figure 1 was used. 40.49% B_2O_3, 16.6% CaO, 5.59% Na_2O, 33.81% H_2O, 1.33% MgO, 0.03% Al_2O_3, 0.02% Fe_2O_3, 2.11% SiO_2 and 0.02% SO_4^{2-} were found in the chemical analysis. The samples were milled with a laboratory type grinder. The milled sample was sieved to -250,-180,-150, -125, -75 ve -45 µm with standard sieves. The CO_2 gas used in the experiments has 99.9% purity grade and procured from the Linde Company.

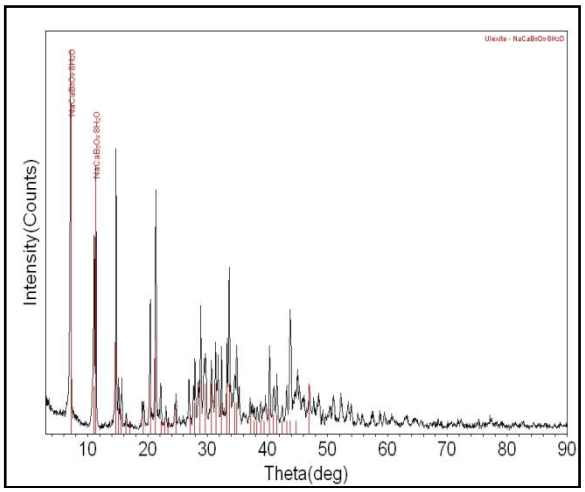

Figure 1. XRD pattern of the used ulexite.

Moreover, water-dissolving B_2O_3, acid-dissolving B_2O_3 and humidity analyses for the solid wastes acquired by the experiment as well as B_2O_3, CaO and MgO analyses for the solutions were conducted. Also, B_2O_3, CaO and MgO analyses were carried out in solid products from solutions. ICP appliance was used for the CaO and MgO analyses. Humidity analyses were carried out gravimetrically while B_2O_3 analyses were volumetrically performed.

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2.2. Parameters used in the experiments and their levels

The parameters used in the tests and their levels are specified according to the previously conducted pre-tests and these parameters are determined as solid-liquid ratio, pressure, particle size, temperature and time. Parameters and their levels are shown in the Table 1.

Table 1. Parameters used in experiments and their values

Parameters		Parameter Levels			
		1	2	3	4
A	Solid/Liquid Ratio (g/300 g)	75	99	120	150
B	Pressure (bar)	5	10	15	20
C	Temperature (°C)	80	90	100	110
D	Time (min)	20	40	60	90
E	Particle size (μm)	-150	-125	-75	-45

2.3. Experiment design and its analysis

Along with the present study, it was aimed to determine the optimum conditions for the dissolution of ulexite with CO_2 in gas under pressure. Parameters used in the studies which were conducted with ulexite samples and CO_2 gas under pressure were pressure, temperature, solid to liquid ratio, stirring speed and time. The fistly, it was planned to examine four different level of each parameter and thereby L_{16} (4^5) Taguchi factorial fractional experiment design plan was used.[17]

2.4. Implementing dissolution experiments

During the tests, after adding 300 g water and adequate amount of ore into the reactor, the cover of the reactor was closed. Afterward, desired pressure was achieved by transferring CO_2 into the reactor through CO_2 cylinder. The reactor content was heated until the convenient temperature was reached. In the end of the test duration, the reactor was cooled, its cover was opened, solid and liquid constituents were seperated by filtrating the reactor's contents. Solid waste was weighed as wet and dry and humidity content of the wet waste was detected. Later, B_2O_3 ratios that passed into the solution were calculated by means of the B_2O_3 analyses, which could be dissolved in both water and acid, carried out on the solid waste. Additionally, XRD of the solid waste was taken. Liquid part was also weighed, its density was detected and B_2O_3, CaO, MgO analyses were carried out. The reactor seen in the Figure 2, had 1 liter volume and made of stainless steel. Its operating pressure and temperature could be controlled.

Figure 2. Experiment system used in the studies under pressure.

2.5. Crystallization studies

Sodium pentaborate is extracted from the solutions that were acquired in the end of the dissolution studies. In these studies, two methods were used:

In the first method, sodium pentaborate is acquired by drying the solution obtained from the high temperature and pressure reactor in a spray drier. In this study, a spray drier, Yamato ADL311 model was used. In the other alternative, the density of the solution was brought to 1250 kg m^{-3} by evaporating and then it re-cooled down to 25°C so that the crystallization was actualized. B_2O_3, Na_2O, MgO and CaO analyses made for the solid producs obtained in both methods besides the XRDs of the samples were obtained.

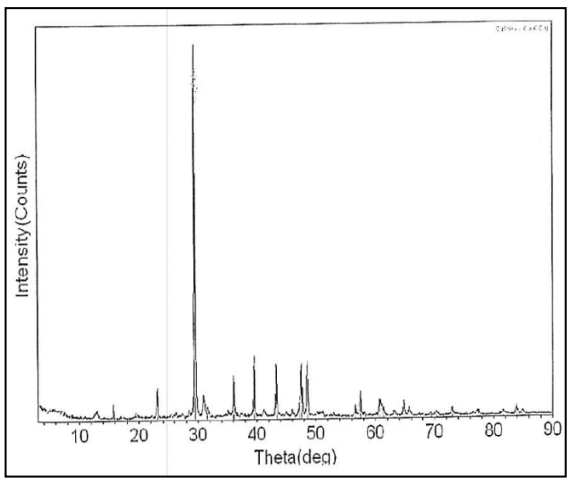

Figure 3. XRD of the solid obtained from dissolving ulexite with pure CO_2 in aqueous medium under pressure.

DOI: 10.32571/ijct.467098 **E-ISSN:2602-277X**

3. FINDINGS

3.1. Dissolving ulexite with pure CO_2 in aqueous medium under pressure

The parameters used in the tests were solid/liquid ratio (A), pressure (B), temperature (C), time (D) and particle size (E). Experimantal data regarding the B_2O_3 ratios which passed into the solution by the end of the dissolution process are given in the Table 2. As can be seen on the table, all dissolution values exceeded 95%. On the other hand, the XRD of the solid waste obtained by filtration of the reaction mixture was also given in the Figure 3. Figure 3 exhibits that $CaCO_3$ occurred during the dissolving process.

Table 2. B_2O_3 ratios passed into the solution in dissolving the ulexite with pure CO_2 in aqueous medium and under pressure

Test No	Parameters					1. Series Experiment %	2. Series Experiment %	Ave-rage
	A	B	C	D	E			
1	1	1	1	1	1	99.8	98.93	99.3
2	1	2	2	2	2	98.87	98.96	98.9
3	1	3	3	3	3	98.83	98.80	98.8
4	1	4	4	4	4	99.43	99.24	99.3
5	2	1	2	3	4	99.35	98.81	99.0
6	2	2	1	4	3	99.05	99.00	99.0
7	2	3	4	1	2	99.12	99.03	99.0
8	2	4	3	2	1	99.31	98.28	98.8
9	3	1	3	4	2	98.38	97.63	98.0
10	3	2	4	3	1	99.08	98.31	98.7
11	3	3	1	2	4	98.62	99.19	98.9
12	3	4	2	1	3	97.90	97.58	97.7
13	4	1	4	2	3	95.08	96.94	96.0
14	4	2	3	1	4	96.75	99.15	97.9
15	4	3	2	4	1	98.74	98.79	98.7
16	4	4	1	3	2	99.39	98.97	99.1

4. RESULTS

4.1. Experimental results of ulexite dissolved with CO_2 under Pressure

4.1.1 Observed and estimated dissolved B_2O_3 amounts

It is seen that the levels of the parameters that maximize the performance statistics are, B_3, C_1, D_3 ve E_1. Using these values of the parameters, estimated values are calculated and in order to determine the confidence interval and the adequacy of the model, two verifications experiments are conducted. The experimental results and the additional studies conducted under the optimum conditions with different parameter levels are presented in Table 3. The amount of B_2O_3 passing into the solution is estimated as 100% and measured as 97.45% at the optimum conditions.

Table 3. Estimated and observed amounts of %B_2O_3 passing into the solution

Parameters	Value	Level
Solid/liquid ratio (g/500 g)	75	1	1
Pressure, bar	15	3	3
Temperature, ℃	80	1	1
Time, min	60	3	3
Particle size, µm	-150	1	1
Observed B_2O_3 (mean value of 2 experiments) (%)	97.45		
Estimated value B_2O_3, (%)	100		
Confidence interval	100±8		

Table 4. Chemical analysis of the product from spray drier

Components, %			Impurities, ppm			
B_2O_3	Na_2O	H_2O	CaO	MgO	CO_3^{2-}	SiO_2
66.63	12.02	20.93	263	107	135	180

4.2. Crystallization of sodium pentaborate with the obtained solutions

In this study, the solutions obtained under pressure with CO_2 along with the solutions obtained under atmospheric pressure are used. These studies are conducted in two ways.

4.2.1. Drying of the solutions with Spray Drier

71 g of dry content out of 640 g solution is obtained in the studies conducted with 170℃ inlet and 10℃ outlet at constant flow rate in the spray drier. The chemical and XRD analysis of the dry content is given in Table 4 and Figure 4, respectively. Table 5 shows CaO, MgO, CO_3^{2-}

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and SiO_2 impurity contents are 263, 107, 135, 180 ppm, respectively. In addition to this, XRD analysis in Figure 4 shows that the product has lost its crystal structure. The 66.63% content of B_2O_3 shows that approximately 4 moles of water in $Na_2B_{10}O_{16}.10H_2O$ is separated by the heating effect and creates an amorphous structure in $Na_2B_{10}O_{16}.6H_2O$.

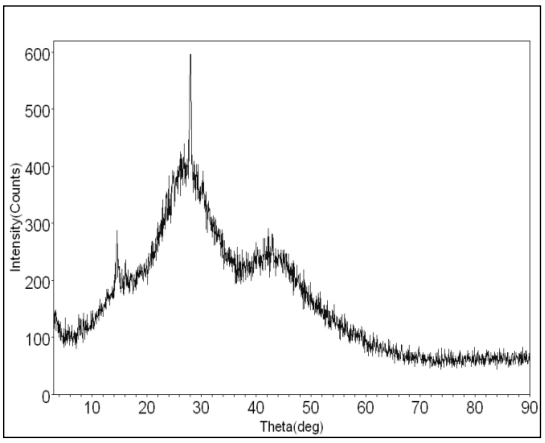

Figure 4. XRD pattern of the solid product from spray drier for the dissolution of ulexite with CO_2 under pressure in aqueous medium.

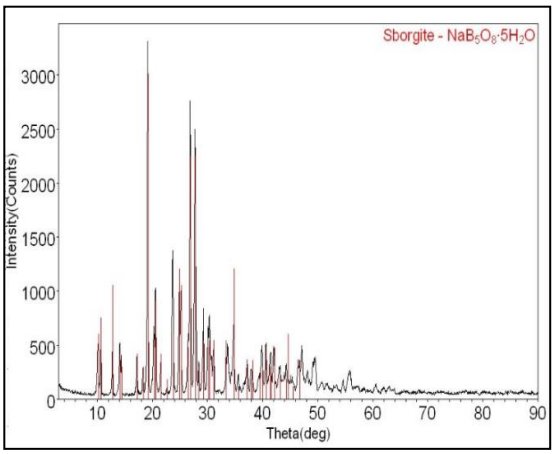

Figure 5. XRD pattern of the solid product from evaporation and then crystallization.

4.2.2. Evaporation of the solutions and crystallization from concentrated solution

In this study, 600 g of solution with 1.10 g ml^{-1} density obtained with CO_2 under pressure is concentrated to 1.25 g ml^{-1} and then cooled down to crystallize and the crystal solution suspension is filtered from the solution and dried.

The chemical and XRD analysis of the obtained dry content is given in Table 5 and Figure 5, respectively. Table 5 shows that CaO, MgO, CO_3^{-2} and SiO_2 impurity contents are 185, 38, 114, 150 ppm, respectively. Figure 5 shows that all of the formed crystals are sodium pentaborate decahydrate. The impurity content here is lower than the ones obtained in the spray drier.

Table 5. Chemical analysis of the crystals from evaporation and then crystallization

Components, %			**Impurities, ppm**			
B_2O_3	Na_2O	H_2O	CaO	MgO	CO_3^{2-}	SiO_2
58.19	10.31	29.98	185	38	114	150

In this study, the solubility optimization and for original ulexite ore samples with different particle sizes under pressure using pure CO_2 and the production of sodium pentaborate are investigated and the following results are obtained.

The reaction between ulexite and CO_2 in the aqueous medium, which forming sodium pentaborate is as follows:

$$Na_2O.2CaO.5B_2O_3.16H_2O + 2CO_2 \rightarrow Na_2B_{10}O_{16}.10H_2O + 2CaCO_3 + 6H_2O$$

The studies in the aqueous medium under pressure result in 99% solubility. This shows that the optimum conditions to dissolve ulexite ore under pressure in aqueous medium and to produce sodium pentaborate decahydrate or other pentaborate hydrates are 75 g ulexite / 300 g water for solid / liquid ratio, 15 bars for pressure, 80 °C for temperature, 60 minutes for the time and -150 µm for the particle size. The spray drying of the solutions obtained by dissolving ulexite resulted in an amorphous sodium pentaborate in the form of $Na_2B_{10}O_{16}.6H_2O$, concentration of the solution at 90 °C and cooling down to 25°C resulted in sodium pentaborate decahydrate in the form of $Na_2B_{10}O_{16}.10H_2O$.

ACKNOWLEDGEMENTS

Authors thank to Çankırı Karatekin University for continuous motivation.

Conflict of interest

Authors declare that there is no a conflict of interest with any person, institute and company, etc.

DOI: 10.32571/ijct.467098 **E-ISSN:2602-277X**

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