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## EFFECT OF HEAT TREATMENT ON BREAKAGE RATE FUNCTION OF ULEXITE

**Halil IPEK, Haydar SAHAN**

Osmangazi University, Engineering Faculty, Mining Engineering Department, Eskisehir, Turkey  
hipek@ogu.edu.tr, Tel : +90 2222393750, Fax: +90 222 239 36 13

**Abstract:** The kinetics of batch grinding and heat treated of ulexite using different size fractions (–3350+2360, –2360+1700, –1700+1180, 1180+850, –850+600, –600+425, –425+300, –300+212 and –212+150 micrometers) was determined using a standard Bond ball mill. It was found that breakage of ulexite follows the first order behavior for all feed sizes with the correlation coefficients equal to approximately 98%. The dry grinding of the single-sized fraction and heat treatment of ulexite showed that heat treatment samples were ground much faster than the original ulexite samples.

**Keywords:** *ulexite, grinding, ball milling, breakage rate function, heat treatment, micro wave*

### Introduction

About 70% of world's known boron reserves are in Turkey. A great portion of Turkish commercially recoverable boron reserves are colemanite, ulexite and tincal. Ulexite has a triclinic crystal structure with a chemical formula of  $\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$  (hydrated sodium calcium borate). It has many important uses such as in the production of glass, agriculture goods, textiles, nuclear fiberglass, and insulators in the cellulose industry (Mobbs, 2010)

Size reduction of minerals by grinding is widely used in the preparation of raw materials for the manufacturing. As it is known that a significant amount of energy which is used in grinding, turns into heat and cannot be efficiently used in grinding. It is possible to obtain more effective grinding by setting up more effective grinding systems which consumes less energy (Bozkurt and Ozgur, 2007, Ipek and Goktepe, 2011).

The design and scaling-up of ball mills are important issues in the size reduction process. Therefore, various models are used for predicting the behavior of large industrial-scale mills. An analysis of grinding in ball mills uses the concepts of selection and cumulative breakage distribution functions. The selection function (specific rate of

breakage) is defined as the fraction by weight of particles of a given size  $i$  which are selected and broken per unit time of grinding. This value varies with size and is denoted  $S_i$ . The cumulative breakage distribution function,  $B_{ij}$ , is defined as the fraction by weight of breakage products from size  $j$  which falls below size  $i$ , where  $i \leq j$  (Austin and Bagga, 1981; Austin et al., 1984).

When ulexite is subjected to heat treatment, internal thermal reactions occur. First, mineral loses its crystallization water followed either by the production of amorphous material or recrystallization into new phases. According to Sener et al. (2000) ulexite does not decrepitate. Instead, it only exfoliates due to gradual removing of water vapor and the structure becomes amorphous with numerous microcracks and interstices. This product is weak and can be easily ground to powder (Sener et al, 2000).

The objective of this study is to analyze the effect of heat treatment of ulexite on its breakage rate function.

## Theoretical background

Austin and Bagga (1981) analyzed the variation of specific rates of breakage during batch grinding of several materials to fine sizes. They found that the normal region could be defined by the first-order breakage:

$$\text{Rate of breakage of size } 1 = S_1 w_1(t) W, \quad (1)$$

where  $S_1$  is the specific rate of breakage of feed size 1 material, and  $w_1(t)$  is the mass fraction of the total charge,  $W$ , at time  $t$  of grinding.

Assuming that  $S_1$  does not change with time due to the first order breakage process, this equation integrates to

$$\log [w_1(t)] = \log[w_1(0)] - S_1 t/2.3. \quad (2)$$

Plotting experimental values of  $w_1(t)$  versus  $t$  using log-linear scales enables to determine the  $S_i$  values for the top size interval of material being tested. The equation for the variation of the specific rate of breakage  $S_i$  with particle size is

$$S_i = a_T x_i^\alpha. \quad (3)$$

If  $S_i$  passes through a maximum at a certain size

$$S_i = a_T (x_i/x_1)^\alpha Q_i \quad (4)$$

$$Q_i = [1/(1+(x_i/\mu)^\lambda)] \quad (5)$$

where  $x_i$  is the upper limit of the size interval indexed by  $i$ .  $x_1$  is 1 mm,  $a_T$  and  $\alpha$  are model parameters that depend on the properties of the material and the grinding conditions while  $Q_i$  is a correction factor. According to Austin et al. (1981, 1984) the specific rate of breakage varies with particle size. While  $Q_i$  assumes the value of 1 for

fine size particles, it becomes smaller with increasing size.  $\mu$  is the particle size at which the correction factor is 0.5 and  $A$  is a positive number which show how rapidly the rates of breakage fall as size increase and the higher  $A$  values show that the more rapidly the values decrease.

## Materials and experimental methods

### Material

The -125+25 mm size fraction of ulexite washed concentrate, obtained from Etibank Mining Co., was used. The density of ulexite, measured with a pycnometer, was 1.95 g/cm<sup>3</sup> basing on seven measurements and Moh's hardness of ulexite, measured by a hardness pen, was 1. All samples were rewashed to separate from clay minerals and then they were crushed below 5 mm. Approximately a 100 kg cleaned sample was crushed with a jaw crusher and classified into nine different mono sized fractions for kinetic tests. The chemical analyses of these test material are given in Table 1.

Table 1. Chemical composition of investigated ulexite sample

B <sub>2</sub> O <sub>3</sub> (%)	SiO <sub>2</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	CaO (%)	MgO (%)	Na <sub>2</sub> O (%)	SO <sub>3</sub> (%)	SO <sub>4</sub> (%)
38.1	3.1	0.05	0.02	16.5	1.4	3.9	0.02	0.02

### Grinding Tests

In order to determine the breakage rate function, one size fraction technique was used (Austin et al., 1984). In this technique, nine different mono sized fractions which are -3350+2360, -2360+1700, -1700+1180, -1180+850, -850+600, -600+425, -425+300, -300+212 and -212+150 micrometers were prepared. In each case, the mill was loaded in such a way that 100% of the interstitial void volume of the ball charge was filled with the mono-sized material at the beginning of the experiments. This load was 2263 g and it was calculated with the following formulas (Sahan, 2010):

$$N_c = \frac{42.3}{\sqrt{D-d}}$$

$$J = \left( \frac{\text{mass of balls/ball density}}{\text{mill volume}} \right) \times \frac{1.0}{0.6}$$

$$f_c = \left( \frac{\text{mass of powder/powder density}}{\text{mill volume}} \right) \times \frac{1.0}{0.6}$$

$$U = \frac{f_c}{0.4J}$$

The characteristics of the Bond mill used in grinding tests and test conditions are outlined in Table 2.

Table 2. Mill characteristics and test conditions

Mill	Diameter, D, cm	30.5				
	Length, L, cm	30.5				
	Volume, V, cm <sup>3</sup>	22272				
	Speed, rpm	70				
	Critical speed, N <sub>c</sub>	86.55				
Media charge	Diameter, d, mm	38.10	31.75	24.50	19.05	12.70
	Number	43	67	10	71	94
	Total mass, g	22603				
	Specific gravity g/cm <sup>3</sup>	7.79				
	Fractional ball filling, J	0.22				
Material charge	Fractional powder filling, f <sub>c</sub>	0,09				
	Powder-ball loading ratio, U	1,00				

## Results and discussion

### Determination of specific rate of breakage

In order to determine the breakage rate parameters of original and heat treated ulexite samples, which were classified into eight different mono-size fraction, were ground dry for 0.25, 0.5, 1, 2, 3, 4, and 5 minutes separately. The heat treatment process was performed at 400 °C and 600 °C for 30 minutes in a Lenton brand furnace and also at 850 W for 10 minutes in a Siemens brand household microwave oven. The mono-sized samples were entered to the furnace after the furnace reached the target temperature of 400 °C and 600 °C. The mono-sized samples were entered into the microwave after the microwave worked for 5 minutes at 850W. The feed sample weight was 275 g for all heat treatment tests because of the capacities of the furnace and the microwave oven. Average weight losses were 15.00%, 30.06%, 10.24%, and ranging between 14.40–15.80, 29.15–30.94, 9.24–11.09 for 400 °C, 600 °C and 850 W respectively. Average weight losses of all feed sizes are shown in Fig. 1.

After the heat treatment, the samples were resized. The mono-sized feed samples consisted of approximately 96% in the top size interval ( $w_2(0) = 0.04$ ). Test charge of the mono-sized feed samples were 2263 g, as mentioned above, and were constant during all the grinding tests.

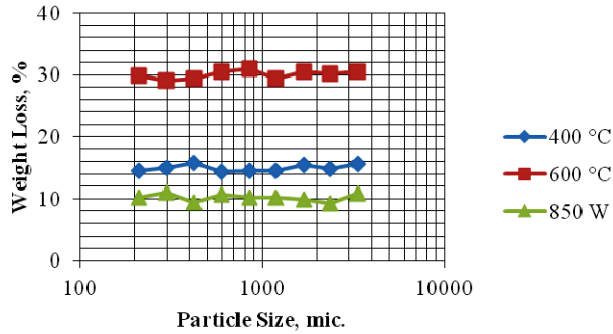


Fig. 1. Average weight losses versus all feed sizes

Figures 2-4 show the initial grinding results of ulexite plotted as first order process for the eight different mono-sized fractions. It can be seen that the breakage process follows the first order behavior for all the feed sizes. The values of correlation coefficient are listed in Table 3. The  $S_i$  values are determined from the average slopes of plots (Fig. 2–4) represented mathematically by Eq. 2.

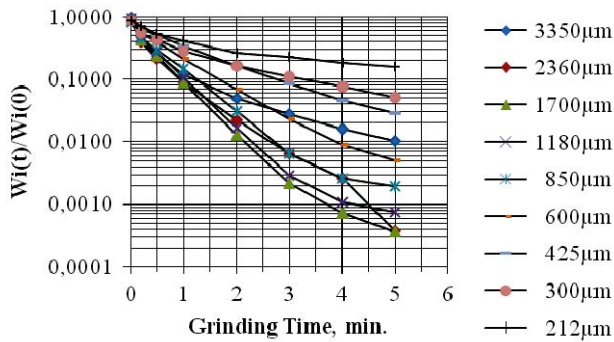


Fig. 2. First order plot for dry grinding of different feed sizes of ulexite

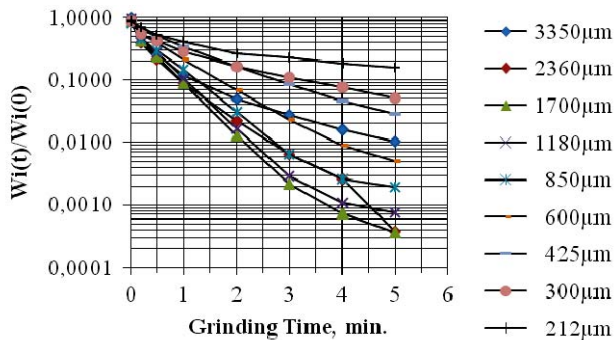


Fig. 3. First order plot for dry grinding of different feed sizes heat treated ulexite at 400 °C for 30 minutes in a furnace

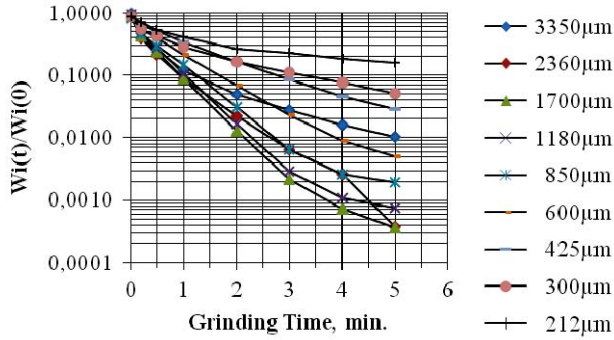


Fig. 4. First order plot for dry grinding of different feed sizes of heat treated at 600 °C ulexite for 30 minutes in furnace

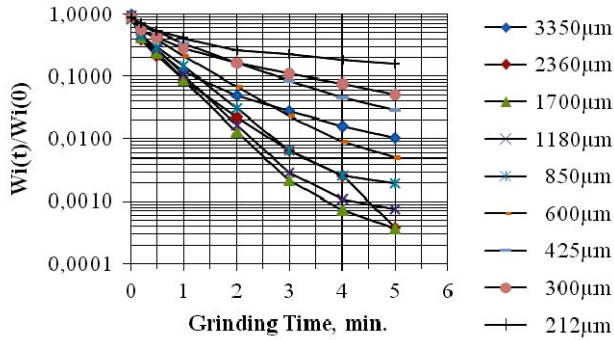


Fig. 5. First order plot for dry grinding of different feed sizes of 850 W heat treated ulexite for 10 minutes in microwave

Table 3. Values of correlation of the first order plots for dry grinding of ulexite samples

Feed Size microns	Original	400 °C	600 °C	850 W
-3350+2360	0,9901	0,9837	0,9893	0,9865
-2360+1700	0,9991	0,9778	0,9908	0,9700
-1700+1180	0,9969	0,9852	0,9926	0,9938
-1180+850	0,9952	0,9913	0,9928	0,9945
-850+600	0,9864	0,9917	0,9962	0,9931
-600+425	0,9884	0,9899	0,9621	0,9883
-425+300	0,9955	0,9716	0,9719	0,9831
-300+212	0,9975	0,9770	0,9770	0,9780
-212+150	0,9992	0,9018	0,9771	0,9559

As shown in the charts above, the heat treated samples were broken very fast, up to 2 minutes of grinding. After that, a slowing down effect was observed. Therefore,

the  $S_i$  values of the heat treated ulexite were determined for two minutes of grinding while the grinding time of the original sample was 5 minutes.

Figure 6 shows that the variation of the specific rate of the breakage with the feed sizes. It is clearly seen there that the values increase sharply until 1700 micrometers and then they sharply decrease for 400 °C heat treatment and 850 W microwaved ulexite samples. Also the values increase sharply until 2360 micrometers and then decrease sharply for 600 °C while the  $S_i$  values increase sharply for 1180 micrometers and then smoothly decrease for original ulexite sample. This was due to the inefficiency of the largest particle sizes that were not nipped properly in the mill. The variations of the  $S_i$  values with the particle sizes were fitted with Eqs 4 and 5. The specific rate of breakage parameters  $a_T$ ,  $\alpha$ ,  $\mu$  and  $\Lambda$  depend on the properties of the material. As can be seen in Table 4, the grinding conditions were calculated by non-linear regression techniques.

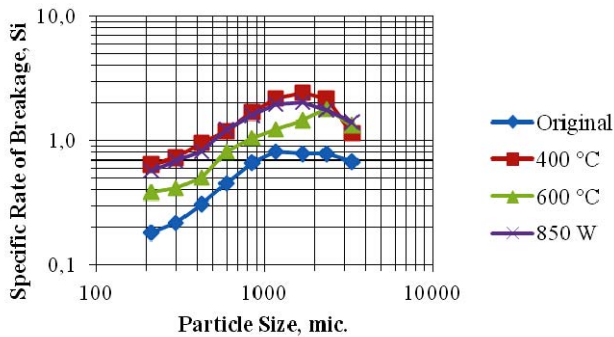


Fig. 6. Variation of  $S_i$  values of original and heat treated samples of ulexite with particle size

Table 4. Specific rate of breakage parameters

	$\alpha T$	$\alpha$	$\mu$	$\Lambda$
Original	0.72	0.92	2.42	2.62
400 °C	1.90	0.79	2.55	4.34
600 °C	1.13	0.77	3.26	3.99
850 W	1.75	0.76	2.55	3.03

## Conclusion

The grinding of ulexite samples obeys the first order breakage kinetics for all feed sizes both for the original and heat treated ulexite. Dry grinding of the single-sized fraction of ulexite and heat treated ulexite showed that heat treated samples were ground much faster than the original ulexite samples. Contrary to expectations, the breakage rate of the 600 °C heat treated ulexite sample is slower than that of 400 °C and 850 W heat treated ulexite samples. The  $a_T$  parameters show this situation clearly. As mentioned in the Sener (2000) study, ulexite samples recrystallize at 600 °C.

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