The relationships between the kinetic grinding parameters with interstitial fillings and the liberation degree of a chromite ore

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Abstract: In this study, the relationships between the liberation degree and the kinetic breakage parameters of a chromite ore obtained from the Burdur (Türkiye) were examined under the laboratory conditions. Firstly, liberation degrees for chromite particles were determined by the particle counting method in a metal microscope for 4 different size groups. Secondly, the breakage parameter of chromite ore which was dry ground with a ball mill was obtained using standard test methods. Additionally, the model parameters were also determined for the fractional interstitial fillings (U) of the chromite sample. Thirdly, the kinetic grinding parameters were compared with the liberation degree of the chromite sample. As a result of the tests, a very good correlation was obtained with R^2=0.998, and regression analysis in the grinding processing of the chromite ore was used to verify the validity of the relationship parameter of S_i that was produced. To these, it was found that interstitial fillings (U=0.6, 0.8, 1.0, and 1.2) have an effect on the grinding.

Keywords: grinding, ball mill, kinetic model, liberation degree, interstitial filling

1. Introduction

Chrome, one of the most used metals in the contemporary world, is essential in the creation of stainless steel. From saleable chromite ore, grades containing more than 40% Cr_2O_3 are desired. Before ore concentration, the most important aspects of mineral processing are the determination of liberation levels, the comminution process, and mineralogical features. Grinding is one of the most significant unit operations in mineral processing. It consumes up to 70% of the energy needed in a typical mineral processing plant and accounts for 3-4% of the electricity produced globally. There are numerous variables in the grinding process, some of which are challenging to comprehend (Deniz, 2011a; Deniz, 2020).

Liberation of valuable minerals from non-valuable (gangue) minerals is an essential step before physical or physicochemical separation processes. The usual technique of liberation involves crushing and grinding ore lumps to produce finer progenies, which is inherently wasteful in terms of energy (Veasey and Wills, 1991) and may also cause difficulties with pulp rheology during separation. Thus, research should be directed toward discovering strategies for weakening the particulate borders between ore minerals and gangue minerals in order to improve liberation by non-random (intergranular) particulate boundary rupture. In mineral processing, the most significant factors to consider are the degree of liberation, the comminution process, and the mineralogical features of the ore prior to the concentration (Deniz, 2022).

Process mineralogy data includes ore characterization and mineral liberation status. Ore samples are characterized according to the amount of mineral/metal they contain, metal behavior, mineral particulate sizes, structure texture properties, and mineral associations. These properties are used to determine the liberation states of minerals and the most appropriate enrichment method. For example, the structural and textural properties of minerals, such as the formation of particulate size, are the parameter that directly affects the degree of ease of the mineral extraction process and therefore the cost

of the process, and it is at least as important as knowing the amount of precious minerals or metals in the ore. The amount of minerals with different structure-texture characteristics can also be used to predict the performance and product characteristics of subsequent processes (Donskoi et al., 2007; Deniz, 2022).

Determining the liberation degrees of minerals will give an idea about the efficiency of separation in beneficiation. Similarly, it will make it clear whether leaks in the process are due to insufficient liberalization or improper separation conditions. The problem can be determined clearly with the mineralogical measurements to be made. By measuring the liberation of the samples taken from the flow branches in the facility, much more reliable design and optimization decisions can be made, and it will also be possible to monitor the long-term facility performance in this way (Deniz, 2022).

In recent years, the notion of analyzing grinding in ball mills by using the concepts of specific rates of breaking (S_i) and cumulative breakage functions ($B_{i,j}$) has garnered a significant amount of interest. Austin examined the benefits of using this methodology, and the scaling-up of laboratory tests to industrial mills has been the subject of conversation in several articles, the findings of which were compiled by Austin et al., (1984).

The amount of powder in a mill relative to the amount of media is usually defined as: "The fractional powder filling is the fraction of the voids of the mill bed, and the porosity of the bed is assumed to be 0.4 for a ball bed." This defines that the amount of solids in the active breakage regions will depend on the interstitial filling (U). (Shoji et al., 1982; Deniz and Onur, 2002; Deniz, 2011a). Shoji et al. (1982) and other researchers stated that the interstitial filling fraction of U = 0.8-1.1 is an accepted powder-to-ball load ratio to achieve grinding in a ball mill.

In this study, firstly, thin sections of a chromite ore sample were made in order to investigate the bonding and liberation between the rock minerals, the mineralogical properties between the chromite mineral and the gangue minerals olivine and serpentines, and the crack microstructure at fracture was investigated. Thereafter, studies were done with four mono-size fractions ranging from 2.36 mm to 0.106 mm generated. Next, the parameters of S_i equations were derived from the size distributions at various grinding times, and the model parameters (S_i, a_T and α) were compared with the liberation degree of the chromite sample. During a regression analysis of the chromite sample, the validity of the generated S_i connection parameter was established via correlation. Finally, the effect of the interstitial filling (U) on the breakage parameters (S_i and α) was investigated.

2.   Materials and methods

2.1. Materials

In this study, a chromite ore taken from the Burdur region in Türkiye was used as a feed material. The results of the chemical analysis of this chromite ore in Panalytical brand, Zetium model XRF device are presented in Table 1.

Table 1. Chemical compositions of the chromite ore by *XRF*

Components	SiO$_2$	Cr$_2$O$_3$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	Na$_2$O	K$_2$O	CaO	LOI*
%	13.28	32.82	14.05	21.90	17.68	0.26	0.01	0.01	4.01

LOI: Loss on ignition

Chromite, serpentine as a gangue mineral, serpentine group minerals (chrysotile and lizardite), and olivine were found as a result of chemical and mineralogical analysis. Chemical analysis showed that the average Cr$_2$O$_3$ content was 32.82% and Cr/Fe ratio was found to be 1.49. This result tells us that the ore is not podiform, that is, it is a stratiform type mineralization. Therefore, it shows that the ore can be used in the chemical sector rather than the iron-steel sector.

2.2.   Methods

2.2.1. Mineralogical analysis

Thin sections of the samples were made from lump samples. Then, the mineralogical texture of chromite mineral and gangue mineral was examined in these samples.

Fig. 1. shows that dunite rock is formed by the serpentinization of peridotite. There are occasional olivine minerals in the rock. However, in these olivines, very little serpentine mineral was formed both the mineral boundaries and the fractures formed in their bodies. Chromium minerals are mostly roundish, sometimes angular. They are very slightly broken. Chromium can also be found in very small, medium, and large sizes. Where it is found, serpentinization is also overdeveloped. The chromite ore contains almost 25–35% of chromite, 45–50% of serpentine, and 15–20% of olivine.
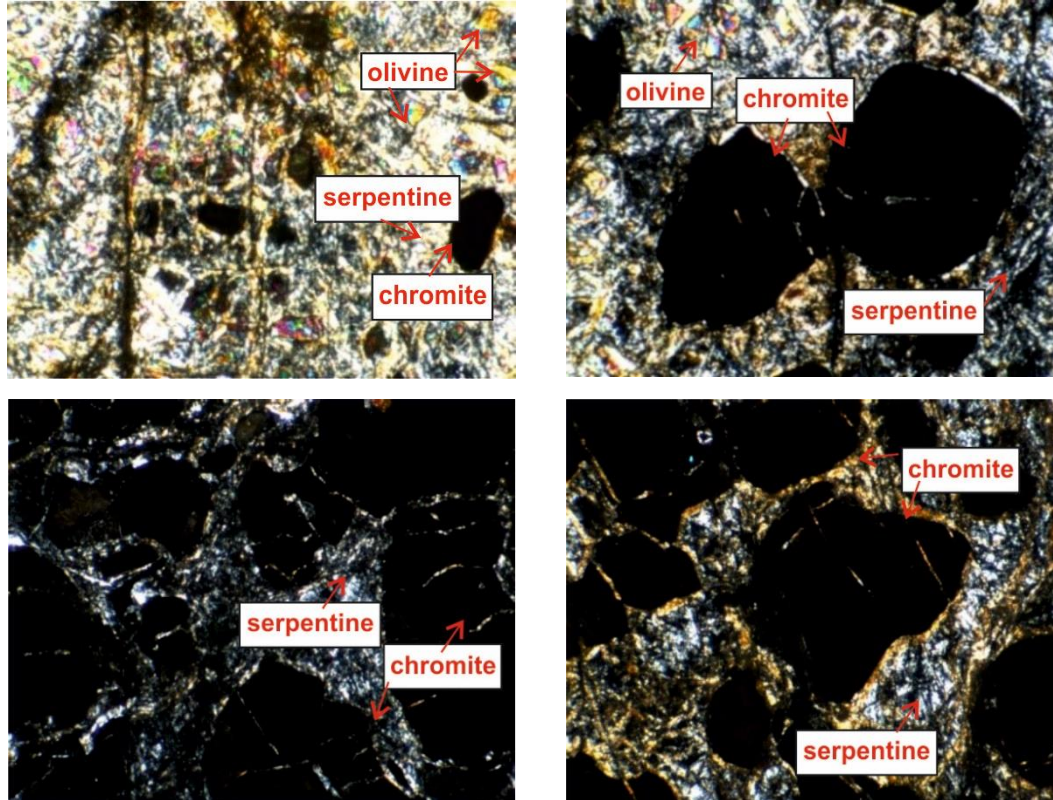

Fig. 1. Views of the texture of chromite and gangue minerals from thin sections of the chromite ore

2.2.2. Determination of the specific rate of breakage (S_i)

As with the definition of a chemical reactor, it is vital to have a thorough understanding of the first-order grinding hypothesis while conducting laboratory-scale grinding studies. The first-order the expression indicates that the reaction proceeds unabated in all reactors. There are second-, third-, and fourth-order response rates if the reaction slows down (Austin, 1972; Austin and Bagga, 1981; Austin et al., 1984).

To better understand the first-order state of grinding in a ball mill, when a W-weighted sample is placed, the particle size distribution of the sample in the mill is defined as $\sqrt{2}$ or $\sqrt[4]{2}$, respectively, in the size range of 1, 2, 3,…n.

If the upper dimension range is fed to the mill, at $t=0$, $w_1(0) = 1$. When this sample is ground at increasing time intervals such as t = 1, 2, 4, 8, ... min, if the amount $w_1(t)$ remaining above a fixed sieve size decreases linearly to lower dimensions, the material is crushed in accordance with the first-order grinding hypothesis. This break is expressed as follows (Austin et al., 1984):

$$\frac{-dw_1}{dt} = S_1 w_1(t) \tag{1}$$

Dimension 1 disappearance rate is proportional to $w_1(t)$ with W. From here, the rate of disappearance of dimension 1 in the time interval dt; and if S_1 is constant during the grinding process, that is, the breakage is first order, then;

$$\log(w_1(t)) - \log(w_1(0)) = \frac{-S_1 t}{2.3} \tag{2}$$

Many researchers have developed techniques for the measurement of S_i and $b_{i,j}$ values in laboratory ball mills. Using a specific sieving range, S_i values vary with particle size (Austin et al., 1984). A summary of their pertinent conclusions is as follows;

$$S_i = a_T \left({}^{X_i}/_{X_0} \right)^{\alpha} Q_i \tag{3}$$

where X_0 is the standard size (1 mm), X_i (mm) is the top size of class i, a_T and α are the model parameters, and Q_i is the correction factor for greater particles and is calculated by Eq. (4) (Austin, 1972):

$$Q_i = \frac{1}{1 + (x_i/\mu)^{\Lambda}}, \Lambda \geq 0 \tag{4}$$

where μ and Λ are the correction factors (Austin et al., 1984). Austin et al. (1984) have evolved methods for measuring S_i in laboratory ball mills. The following is an overview of their relevant findings.

Table 2 displays the typical configurations for grinding in a laboratory mill. In order to calculate the particular rate of breakage, four mono-size fractions (-2.36+1.70, -1.70+0.850, -0.850+0.425, and -0.425+ 0.106 mm) were produced and processed batch-wise in a laboratory ball mill. Prior to conducting the final product size analysis, each sample was removed from the mill and dry-sieved.

Table 2. Ball mill characteristics and test conditions

Mill	Length, L (mm)	200			
	Diameter, D (mm)	200			
	Volume (cm³)	6283			
	Critical, Nc (rpm)[a]	102			
	Operational	77			
Media (Balls)	Diameter, d (mm)	30			
	Specific Gravity	7.80			
	Quality	Alloy steel			
	Assumed Porosity (%)	40			
	Ball-Filling Volume Fraction, J[b]	0.30			
Material	Specific Gravity	4.47			
	Powder-Filling Volume Fraction, f_c[c]	0.072	0.096	0.120	0.144
	Interstitial Filling, U[d]	0.6	0.8	1.0	1.2

[a] Calculated from $N_c = 42.3/\sqrt{D \cdot d}$ (D, d in meters)
[b] Calculated from $J = \left(\frac{mass\ of\ balls/ball\ density}{mill\ volume} \right) \times \frac{1.0}{0.6}$
[c] Calculated from $f_c = \left(\frac{mass\ of\ powder/formal\ bulk\ density}{mill\ volume} \right)$
[d] Calculated from $U = \frac{f_c}{0.4J}$

For productive grinding in industrial applications, the interstitial filling rate of the mill is chosen to be between 0.8 and 1.1 (Shoji et al., 1982; Austin et al., 1984; Deniz, 2011a). The U value of 1.0 was chosen as the interstitial filling rate for the liberation degree in this investigation.

3. Results and discussion

3.2. Determination of liberalization degree

It is the easiest method to determine the degree of particle liberation, and it is based on the examination of the crushed and ground ore sample under a microscope for each size after sieve analysis. The sample was crushed down to a size of -2.36 mm, and then the crushed sample was classified into (-2.36+1.7 mm, -1.7+0.850 mm, -0.850+0.425 mm, -0.425+0.106 mm size fraction). A certain amount of the particle with high representativeness was taken from the classified materials and washed separately for each size. It ensures that the surface is clean by removing foreign materials such as dust. As a result, maintaining a clean surface while counting is critical for achieving accurate results. The dried samples were placed on the glass slide in certain quantities separately for each size (Fig. 2).

It was concluded that the net results were obtained from the particle counting process based on a certain number of particles (a minimum number of 1000 particles). The particle counting process was started on the prepared slides. During the counting process, several photographs were taken with a professional camera (Canon EOS) and with a microscope (James Swift-stereo zoom microscope). The results are given in Table 3.
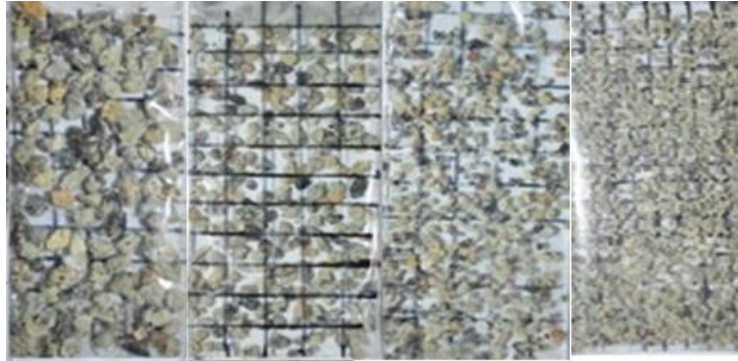

Fig. 2. The views at the microscope of the samples prepared to determine the degree of liberation of the chromite ore by grain counting

3.3. Determination of the specific rate of breakage

The first-order plots of four feed sizes of chromite ore for U=0.1 are shown in Fig. 3a. The findings showed that often occur in accordance with the first-order relation, with S_i values derived from the incline of the straight line depicting the first-order plots. The slope of the straight line of first-order plots was used to calculate the S_i for each mono-size fraction for U=1.0 (Fig.3b and Table 3).
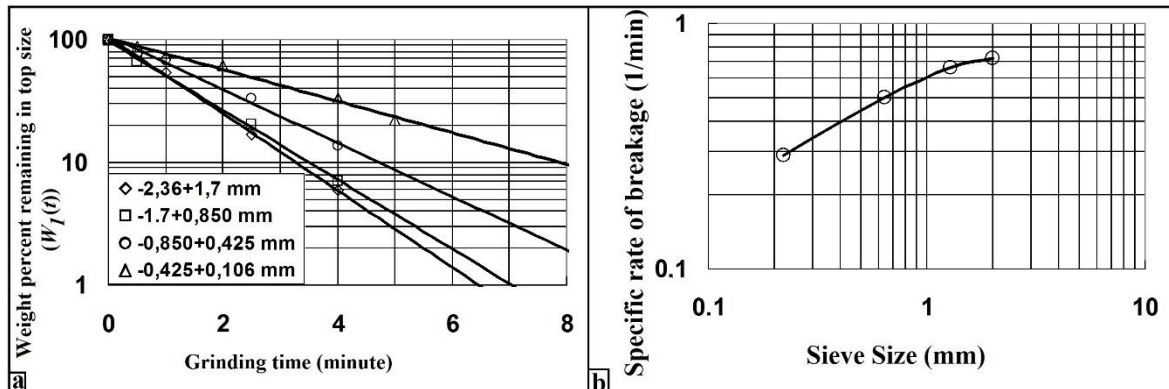

Fig. 3. First-order plots (a) and the specific rate of breakage (b) for U=1.00

Table 3. Relationship between liberation degree (%) with mean sieve size and the specific rates of breakage

Sieve Size (mm)	Mean Sieve Size (mm)	Liberation Degree (%)	S_i(1/min)
-2.36 +1.70	2.030	49.56	0.72
-1.70 +0.850	1.275	67.57	0.66
-0.85 +0.425	0.638	77.04	0.50
-0.425 +0.106	0.266	80.00	0.29

The S_i values of the four different interstitial fillings (U) tested depending on the size are shown in Fig. 4. As the feed size increased, the S_i and a_T values also increased, that is, it broke very quickly below the original particle size. From the experimentally obtained a_T values (Table 4), it was seen that the grinding was much more effective for U=1.0 among all sieve size fractions for the chromite ore than for

other interstitial filling values. As a result, the similar results were obtained with the data obtained from other researchers (Deniz and Onur, 2002; Ipek, 2006; Deniz, 2011a; Deniz, 2011b).
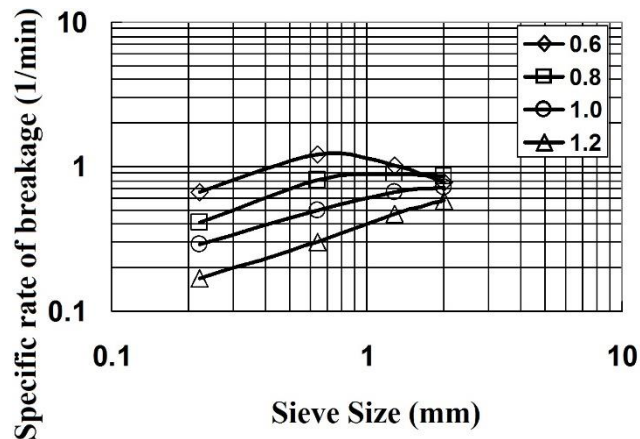

Fig. 4. The specific rates of breakage for four different fractional interstitial fillings (U)

Table 4. Typical specific rate of breakage parameters for four different fractional interstitial fillings (U)

f_c	U	a_T	α	μ	Λ
0.072	0.60	1.22	0.575	2.08	3.65
0.096	0.80	0.89	0.638	2.71	3.34
0.120	1.00	0.60	0.510	3.26	4.03
0.144	1.20	0.39	0.532	3.94	5.85

3.3 Verification of the correlations between the liberation degree and the breaking characteristics of chromite ore

In this study, a computer simulation software package program (IBM *SPSS* 22) applies the least-square method was used to generate the linear regression. The regression function, the liberation degree (%) of the chromite ore was introduced as a dependent variable, and mean sieve size (mm), and the S_i (1/min) as independent variables. The coefficients of the independent variable were estimated using the *SPSS* program from the experimental results. To analyze the accuracy of the multiple linear regressions, the estimated values of the degree of liberation of the chromite ore were plotted against the experimental values, as seen in Fig. 5b. Also, it was seen from Fig. 5 that the degree of liberation (%) of the chromite ore obtained as a result of comminution was in the very good correlation (R^2=0.998) depending on the specific rate of breakage and mean sieve size).

The values of the specific rate of breakage and mean sieve size over a linear relationship with liberation degree can be stated as follows:

$$\text{Liberation Degree (\%)} = 76.581 + 34{,}556 * S_i - 24.455 * \text{Mean Sieve Size} \qquad R^2 = 0.998 \qquad (5)$$

Fig. 5b shows the 3D relationship between the degree of liberation (%) and the other two variables (the specific rate of breakage (S_i) and mean sieve size). Obviously, the degree of liberation of the chromite ore is most affected when the mean sieve size (mm) changes, while it is less affected by the specific fracture rate (S_i).

3.4. The relationships between the relative absolute rate of breakage ($f_c S_i$) and interstitial filling (U)

Shoji et al. (1982) stated that the resultant of the parameters of f_c (powder filling) and S_i is proportional to the mill capacity of the product, which is called the "*relative absolute rate of breakage*". By evaluating $f_c S_i$ against U, we get the highest capacity for the mill. It is concluded that $U = 0.6$ to 1.1 is the optimum filling condition for maximum breakage rates at all powder loads (Shoji et al., 1982).
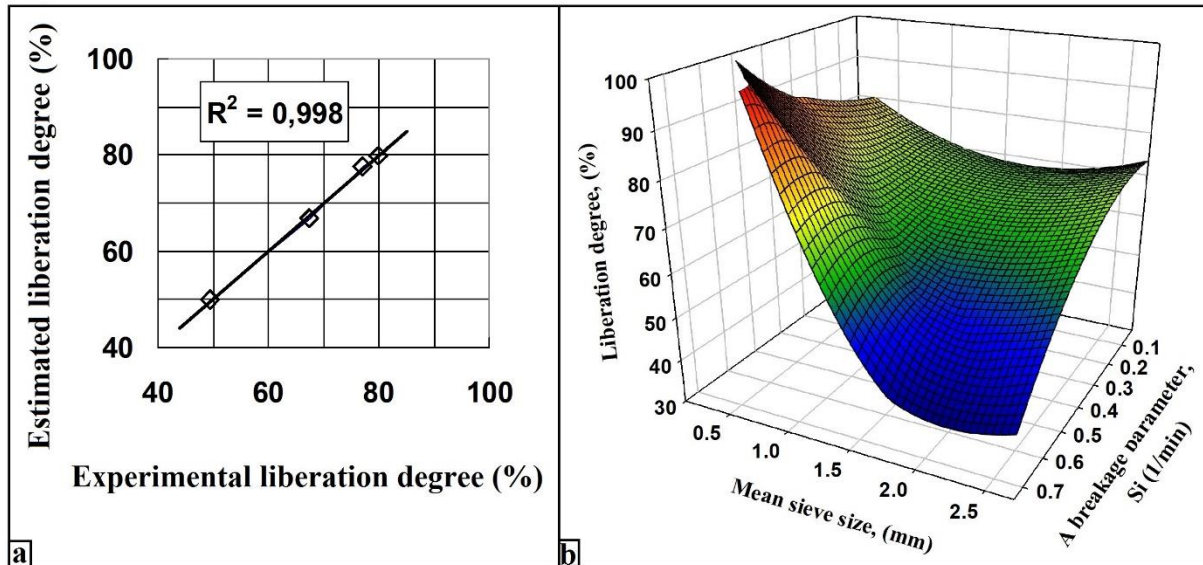
Fig. 5. Comparison of the estimated values and the experimental values (a), variation as a 3D graph of the degree of liberation with the specific rates of breakage and the mean sieve size for the chromite ore (b)

Shoji et al. (1982) found U = 0.83 as the maximum value for mill capacity, while Tangsathitkulchai (2003) found U= 1. Ipek (2006) found that the highest mill capacity for K-feldspar is at U=1.25, while Deniz and Onur (2002) found U = 0.4 for the pumice sample. In addition, Deniz (2011a) found about U= 1.5-2.0 for the gypsum sample, while Deniz (2017) found that the optimum value of U for the highest mill capacity for natural amorphous silica was above 166.7% ($U \geq 1.667$). On the other hand, Deniz (2011b) found that a maximum of U for the diatomite sample was 1.31 for up to 0.300 mm fractional particle size. However, the optimum value for under 0.300 mm fractional size was U>1.61.

Plotted against $f_c S_i$ versus U for chromite ore (Fig. 6), and as a result of the graphical representation, different results were found with the results from some investigators (Shoji et al., 1982; Deniz and Onur, 2002; Tangsathitkulchai, 2003; Ipek, 2006; Deniz, 2011a; Deniz, 2017). From our results, it was observed that the relationship between the increase in U value and the relative absolute rate of breakage ($f_c S_i$) varies depending on the particle size. It has been determined that while high U values (U=1.0-1.2) contribute to the mill capacity in large sizes, low U values (U=0.6) contribute to fine sizes. This is a similar result to our data as stated by Deniz (2011b). The biggest reason is the weak bond structures of the chromium and the side-rock in coarse particle sizes. Since there was sufficient freedom for fine sizes between the chromite mineral and its gangue minerals such as olivine and serpentine, the specific rates of breakage slowed down with increasing single-grain strength. As a result, it has been determined that the optimum U value for the highest mill capacity varies according to the particle size.
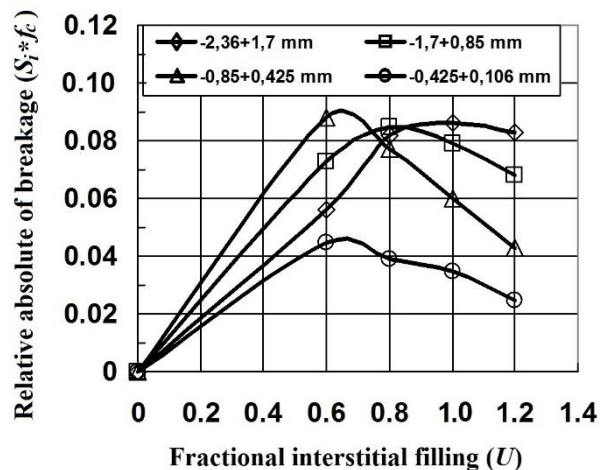

Fig. 6. Variation of the fractional interstitial filling (U) and the relative absolute of breakage ($S_i f_c$)

3.5. The relationships between the first-order breakage constant (αU) and the interstitial filling (U)

LeHouillier et al. (1977) said that a low U-value appears to be more efficient for grinding the fine particles i.e. α is lower than normal, and excessive grinding of the fine particles occurs. Thus, grinding would produce a proportionally finer and narrower size distribution.

Shoji et al. (1982) showed that at α values lower than the normal value, it occurs between 0.2-0.3 in U. As noted by LeHouillier et al. (1977), it shows more reasonable to assume a continuous variation between α and U, but this is not stated with the powder filling of our data. Our study showed (Fig. 7) that U has a more effect on the first-order breakage constant (α).

Fig. 7 shows the effects of replacing the interstitial fillings (U) in the mill. It turns out that the results fit the optimal interstitial filling at U = 1.0.
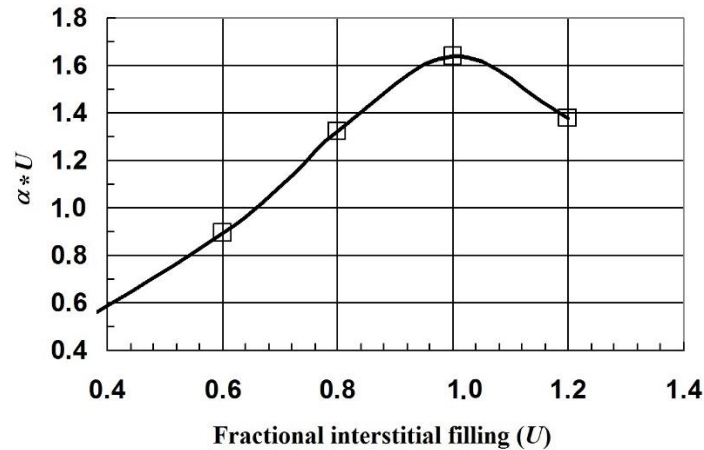

Fig. 7. Variation of the fractional interstitial filling (U) with the specific rate of breakage parameter (αU)

A low fractional interstitial filling (U=0.6) gives a small specific rate of breakage (S_i). As the U value increased from 0.6 to 1.0, that is, as the amount of powder increased, the collision spaces between the balls were filled, resulting in a higher specific rate of breakage. When the effective area between the balls was filled with powder, S_i reached a maximum value (U = 1.0). Adding more powder into the mill (1.0 < U > 1.2) increases the mill hold-up, but does not increase the specific rates of breakage as the collision zones are already saturated. Finally, overfilling the mill with powder (U < 1.2) caused collisions to be neutralized by powder cushioning, and the specific rates of breakage were reduced. This study has shown that U =1.0 was the optimum filling condition for the maximum breakage rates.

4. Conclusions

The operation of an ore preparation process varies according to the liberation status of valuable and gangue minerals in the ore. With the fractional process mineralogy study, the behavior of free and attached minerals can be monitored in all flow branches in the process, and therefore information about the performance of that process or equipment can be obtained. The data obtained based on particle size should be expressed with appropriate tables and graphics describing the process.

In general, it is understood that grinding kinetic parameters may vary depending on the sample. Therefore, it seems that product sieve size distributions and energy must be predicted using the grinding kinetics for each material.

It is designed according to the degree of liberation in mineral processing plants. In this context, the relationship between the degrees of liberation with the specific rate of breakage and the average sieve size values was provided. Also, the liberation degree of chromite ore is most affected when the mean sieve size (mm) changes, on the other hand, while less affected by the specific rate of breakage (S_i). The R^2 values of the linear regression equation developed to estimate the degree of liberation of the chromite ore were found to be 0.998.

By evaluating $f_c S_i$ against U, we get the highest capacity for the mill. In this study, it has been determined that the optimum U value of chromite ore for the highest mill capacity varies depending on

the particle size. Due to the weakness of the chromite mineral used in the experiments in the contact zones with other gangue minerals (olivine and serpentine), it was found that the U=1.0 effective ratio was found to be high because it is a material that can be easily ground in large sizes compared to single-type mineral containing materials such as quartz, diatomite, gypsum, etc.

Since the model parameters are obtained differently for the sieve size groups in the same sample, it is necessary to investigate different samples.

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