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Application of grinding kinetics analysis of inorganic powders by a stirred ball mill

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Abstract−The need for ultra fine particles has been increasing in the preparation field of raw powders such as fine ceramics and high functional products. A series of wet grinding experiments were carried out on inorganic powders such as calcite, pyrophyllite and talc by a stirred ball mill. The grinding rate constant K' in the equation of grinding kinetics was examined based on the grinding kinetics analysis as the same type of function of a previous paper on a vertical type planetary ball mill. The experimental particle size distribution of the ground products was obtained in various grinding conditions. The grinding rate constants K and K′ were expressed by empirical equation involving experimental conditions by a stirred ball mill. The empirical equation on the grinding rate constant was expressed in terms of a function involving the ball diameter of grinding balls, the median diameter of feed material, and Bond's work index of material, in the experimental conditions. The values of empirical constants C_1 and C_2 were 21.13 and 0.0109 on K, while C_1 and C_2 were 120.99 and 0.0192 on K′, respectively. And the particle size distribution of ground products of each test material for a given grinding time was found to be expressing the selection function (the specific rate of breakage) which was obtained from the grinding kinetics analysis. In this study, the grinding rate change on calcite and pyrophyllite was similar at the same experimental operation condition. However, in the case of talc, it was observed that the grinding rate was not increased compared with other samples.

Key words: Ultra Fine Grinding, Stirred Ball Mill, Grinding Kinetics, Selection Function, Grinding Rate Constant

INTRODUCTION

Importance of ultra-fine grinding in the submicron range has increased recently in connection with the development of new functional materials such as new ceramics and electronic materials in various industrial fields [1-3]. Grinding to submicron range by a stirred ball mill has been achieved commercially in many cases [4-6]. For the ultra fine grindings, use of stirred media mills increases steadily due to its advantages. Because of the easy operation, simple construction, high grinding rate and low energy consumption compared with the other fine grinding machines, stirred ball mills have received more and more attention in recent year [7]. In the stirred media mill, a large number of grinding balls are rotated by stirrer and screw in a vessel. The breakage occurs mainly by impact of the media. Thus the grinding ability was increased as the power intensity to grind effectively to finer sizes. Zheng et al. [5] showed that stirred media mills are used in numerous industries because of their high energy efficiency, fine and ultrafine grinding ability, and reduced contamination. The grinding rate constant is a very important factor needed to estimate a grinding process [8]. The description of grinding kinetics by the population balance model was first proposed by Reid [8] and has been accepted now widely [9]. In the final analysis of particle size distribution to find the grinding characteristics, the primary goal of mathematical modeling is to provide a practical tool for scale-up, design, simulation, control and optimization of industrial grinding circuits with an acceptable degree of precision and with least possible expenditure of cost and time [9,10]. Many investigators have analyzed grinding kinetics for individual grinding equipment and have shown good agreement between calculated and experimental results [11-13]. In the previous work, we investigated the grinding kinetics analysis to fine grinding characteristics of some inorganic materials such as calcite, pyrophyllite, and talc using a composite grinding media by a planetary ball mill [3] and proposed the regression equation for grinding rate constant. In addition, the grinding kinetics of various grinding mills has been studied to find the grinding mechanism through particle size distribution [11-13]. In this study, for examining with the ultrafine grinding mechanism, a series of experimental investigations using inorganic powders by the stirred media mill was performed under various experimental conditions [14,15]. Tanaka's approximate solution based on the grinding kinetics was applied to the ground data of this experiment [16,17]. So, the grinding rate constant K′ was examined as a function of the ball diameter of grinding balls, feed size and Bond's work index. In addition, it was investigated that the grinding rate constant K′ might be regressed by an experimental equation. The particle size distribution of the ground products of each test material for a given grinding time was found to be expressing the selection function (the specific rate of breakage), which was obtained from the grinding kinetics analysis.

EXPERIMENT

Calcite ($CaCO_3$, S500, mean diameter x_{50}=6.42 μm, density ρ=

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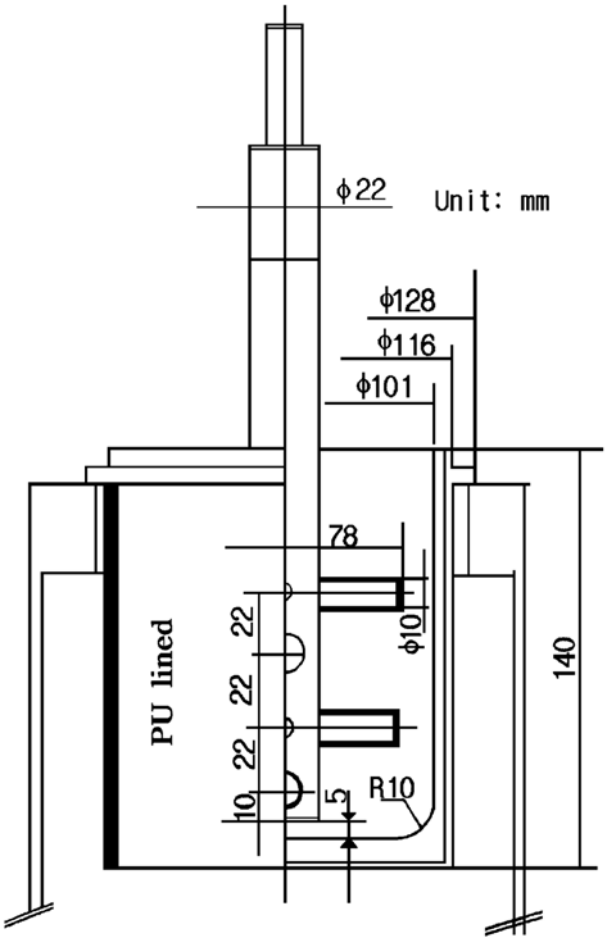

Fig. 1. Dimensions and shape of grinding mill pot of experimental stirred ball mill.

2,720 kg m^{-3}, specific surface area S_{w0}=1,420 m^2 kg^{-1}), talc (TS-1000, x_{50}=10.48 μm, ρ=2,740 kg m^{-3}, S_{w0}=0.570 m^2 kg^{-1}) and pyrophyllite (PLW, x_{50}=4.07 μm, ρ=2,730 kg m^{-3}, S_{w0}=1,490 m^2 kg^{-1}) were used as grinding materials. Grinding tests were conducted in a vertical stirred media mill following the previous work [15]. Fig. 1 illustrates the dimensions of grinding chamber and the shape of a laboratory-scale stirrer. The net effective volume of the milling chamber was 0.95 *l*. Alumina balls with 99.9% purity (Nikkato Co., Ltd. Japan, ρ=3,630 kg m^{-3}) having the diameter ϕ=1.0 mm, ϕ=2.0 mm, ϕ=3.0 mm were used for grinding. The particle size distribution of ground samples was analyzed by a technique based on laser diffraction and scattering using Mastersizer Microplus (Malvern Co., Ltd. UK), with which ultra-sonic homogenizer, US-300T (Nihonseiki Kaisha, Ltd. Japan), was used as a dispersion device. In the ball mill, a stirrer was rotated at a constant gap of 5 mm from the bottom of the grinding chamber. Total charged weights of the grinding balls were fixed at 1.38 kg, giving the ball filling ratio J=0.7 and the weight percent of the slurry concentration was fixed at 60 wt%. A grinding experiment was done with a batch process in which samples were taken from the pot at the determined grinding time interval. The particle size distribution of the samples was measured without any dispersion agent. Instead, prior to the measurement of particle size distribution, the homogenizer was used for the dispersion of particles for 90 seconds. At the end of each test, all the grinding media and ground samples were removed from the mill, and the media were separated from the ground products by sieving. A series of experiments were carried out to investigate the effect of experimental parameters such as stirrer speed, ball size, ball filling ratio and slurry concentration on the particle size distribution of the products at different grinding time. The grinding consumption power was recorded on-line every 2 minutes within the first 30 minutes, then every 5 minutes afterwards.

THEORETICAL BACKGROUND

The particle size distribution of the final ground products represents the most important property of the final products. When the grinding rate in a batch-grinding test is examined in terms of materials balance, two basic functions are used: the selection function indicates the fracture probability of particle, and the breakage function shows the size distribution of fractured particles. Defining the selection function, S(x, t) and the breakage function, B(γ, x), a dynamic mass-size balance is taken as follows [3], where agglomeration of fine particle is negligible, as

$$\frac{\partial^2 D(x,t)}{\partial t \partial x} = -\frac{\partial D(x,t)}{\partial x} S(x,t) + \int_x^{x_m} \frac{\partial D(\gamma,t)}{\partial \gamma} S(\gamma,t) \frac{\partial B(\gamma,x)}{\partial x} d\gamma \quad (1)$$

where D(x, t) is the cumulative undersize of particles, t the time, x the particle size, and γ the size of single particle to be broken, and x_m the maximum particle size present. Assuming S(x, t)=Kx^n, and B(γ, x)=$(x/\gamma)^m$ for grinding kinetics of Tanaka [16-18], wherein K is the grinding rate constant, m and n are the exponents, respectively, and R(x, t) is the cumulative oversize:

Kinetics of grinding plays an important role in discussing the particle size distribution in the lapse of the time. Cumulative oversize of ground particle corresponding to the particle size y at the grinding time t, R(x, t), is expressed as

$$R(x,t) = R(x,0)\exp(-Kx^n t) \quad \text{for } m=n \quad (2)$$

$$R(x,t) = R(x,0)\exp[-(\mu K x^n t)^\nu] \quad \text{for } m \neq n \quad (3)$$

where m and n are empirical constants, K is merely a constant of the mathematical model, but should be interpreted in the future in relation to the physical meaning of the grinding process and x is particle size. Eq. (2) can be rewritten in the form of Eq. (3) to obtain the values of parameters through a regression analysis:

$$R(x,t) \approx R(x,0)\exp(-K' x^{n'} t^\nu) \quad \text{for } m \neq n \quad (4)$$

where K′ and n′ are defined as $(\mu K)^\nu$ and $n\nu$, respectively.

The values of K′, n′ and ν are parameters to estimate the particle size distribution of ground materials. If the values in Eq. (2) are known accurately, we can estimate the particle size distribution of ground products at each grinding time.

To obtain the grinding rate constant K′ and exponents n′ and n, Eq. (3) is covered as the following [3]:

$$\ln\left[-\ln\frac{R(x,t)}{R(x,0)}\right] = \ln K' t^\nu + n' \ln x \quad (5)$$

$$\ln K' t^\nu = \ln K' + \nu \ln t \quad (6)$$

The grinding rate constant K′ and exponents n′ and ν can be obtained

by regression analysis of the experimental data of particle size distribution to Eqs. (5) and (6). Within the experimental data of the grinding rate constant, K (in $\mu m^{-n} min^{-1}$) in Eq. (2), or K′ (in $mm^{-n'} min^{-1}$) in Eq. (4) was expressed by an empirical equation involving

Table 1. Summary of analysis result of the grinding rate equation on each experimental condition

Sample	Ball (mm)	t (min)	$K't^{n'}$	$\ln(K't^{n'})(mm^{-n'})$	n′ (-)	R^2 (%)	K′
Calcite	1	7.5	0.0781	−2.5496	1.096	99.41	0.0078
		15	0.1764	−1.7350	1.026	99.43	
		30	0.2898	−1.2386	1.226	99.29	
		60	0.6098	−0.4946	1.289	99.27	
		mean			1.159		
	3	7.5	0.2227	−1.5019	1.004	99.77	0.0464
		15	0.4117	−0.8875	0.967	99.86	
		30	0.5898	−0.5280	1.299	99.46	
		60	1.1020	0.0971	1.176	98.86	
		mean			1.112		
	5	7.5	0.1868	−1.6777	0.817	99.82	0.0606
		15	0.2924	−1.2296	0.907	99.50	
		30	0.4866	−0.7203	0.912	99.66	
		60	0.6750	−0.3930	1.146	99.43	
		mean			0.945		
Pyrophyllite	1	7.5	0.0627	−2.7696	0.973	98.17	0.0225
		15	0.0723	−2.6265	1.297	99.93	
		30	0.1020	−2.2828	1.312	99.88	
		60	0.1475	−1.9139	1.254	99.79	
		mean			1.209		
	3	7.5	0.0626	−2.7710	0.973	98.17	0.0184
		15	0.0644	−2.7431	1.342	99.92	
		30	0.0920	−2.3862	1.391	99.87	
		60	0.1475	−1.9139	1.254	99.79	
		mean			1.240		
	5	7.5	0.0936	−2.3687	0.872	97.18	0.0363
		15	0.0759	−2.5783	1.114	99.56	
		30	0.1187	−2.1312	1.008	98.96	
		60	0.1631	−1.8134	1.136	99.88	
		mean			1.033		
Talc	1	7.5	0.0067	−5.0045	1.240	99.64	0.0002
		15	0.0069	−4.9777	1.314	99.62	
		30	0.0072	−4.9335	1.457	99.86	
		60	0.0266	−3.6272	1.162	99.72	
		mean			1.293		
	3	7.5	0.0045	−5.3944	1.136	99.87	0.0018
		15	0.0061	−5.1023	1.228	99.83	
		30	0.0077	−4.8700	1.262	99.62	
		60	0.0110	−4.5062	1.389	99.84	
		mean			1.254		
	5	7.5	0.0035	−5.6470	1.048	97.89	0.0011
		15	0.0071	−4.9426	1.081	99.08	
		30	0.0102	−4.5824	1.123	99.41	
		60	0.0162	−4.1246	1.100	99.04	
		mean			1.088		

the ball diameter of grinding balls, d_B (in mm), the median diameter of feed material, x_{mo} (in μm), and Bond's work index of material, W_i (in kWh/t) involved in the experimental conditions as follows:

$$K \text{ or } K' = \frac{c_1}{(W_i x_{mo})^2}\left(\frac{x_{mo}}{d_B}\right)\exp\left[-c_2\left(\frac{W_i x_{mo}}{d_B}\right)\right] \quad (7)$$

This empirical equation was derived from dimensional analysis of various factors including experimental conditions [3,16-18].

RESULTS AND DISCUSSION

The values of grinding rate constants K and K′, the exponents, n, n′ and ν can be obtained by using the same procedure of regression analysis shown in Table 1 such as in the previous paper.

At first, the exponents n′ and ln(K′t′) are obtained from regression analysis using Eq. (4), then the grinding rate constant K′ and exponent ν are obtained from the subsequent regression analysis using Eq. (5). Here, in this paper the dimension of and K′ is $\mu m^{-n'} \cdot min^{-\nu}$. The results are summarized in Table 2 together with the determined coefficient R^2 of each statistical run.

For d_B=1.0 mm, it was confirmed that the particle size distribution of the ground products calculated by Eq. (1) using the value of parameters of grinding kinetics in Table 2 was in good agreement with the experimental data. The validity of Eq. (4) has been confirmed with a determined coefficient of 99.2% or above for calcite, 81.35% or above for pyrophyllite, and 85.63% or above for talc within this experimental ranges. It was considered that the value of the exponent of particle size n′ in the selection function and the exponent of grinding time ν in the breakage function are not varied with the various ball sizes of grinding ball, and they are constants dependent on the physical properties of feed material.

Fig. 2 shows a comparison of the particle size distribution of particles calculated by the value of parameters of grinding kinetics and that of experimental data in various grinding balls. It is considered that the results show a good agreement and the simulation of parameter size distribution could be used for the sake of design and analysis for grinding process.

It is important to derive an empirical equation for the grinding rate constant K′ expressed by parameters involving experimental parameters. The grinding rate constant K′ can be regarded as a definite function of the various parameters involved. This might make it possible to regulate the size distribution of product by adjusting the operating variables of the mills. This suggests a possible contribution of the operating variables of a mill to the rate constant K′ which controls the particle size distribution of ground products [17].

Fig. 3 shows the plot of experimental data and the regression line drawn by the relationship between $K(d_B/x_{mo})(W_i x_{mo})^2$, $K'(d_B/x_{mo})(W_i x_{mo})^2$ and $(W_i x_{mo}/d_B)$. The slope and the intercept of the regression line were obtained by the least squares method.

In this experiment, the values of the empirical constants c_1 and c_2 on Eq. (4) were 21.13 and 0.0109 on K, and were 120.99 and 0.0192 on K′ within the experimental range, respectively. The determined coefficients R^2 of regression relationship were 51.17% on K, 84.94% on K′ for all the experimental data. By omitting the datum at d_B=3.0 mm, the value of R^2 could be increased up to 92.39% for K′. These data indicated much better fit to the non-linear Eq. (2) compared to the linear Eq. (2). In Eq. (2) of the case of m=n, the effect of grinding time was not included so that the regression coefficient of Eq. (2) on K is low. However, in Eq. (4) for m≠n the regression coefficient on K′ was increased by including the grinding time effect.

Fig. 4 shows the variation of a specific rate of breakage versus

Table 2. Summary of parameters of grinding rate equation for grinding ball size with test materials

Mill	Material	d_B [mm]	Eq. (1)		Eq. (3)			
			K [$\mu m^{-n} min^{-1}$]	n [-]	K′ [$\mu m^{-n} min^{-1}$]	n′ [-]	ν [-]	R^2 [%]
Planetary ball mill	Calcite	1	0.0708	0.907	0.1990	0.907	0.624	96.69
		3	0.1188	1.120	0.3340	1.120	0.820	98.64
		5	0.0846	1.540	0.2380	1.540	0.837	98.36
	Pyrophyllite	1	0.0199	1.330	0.0561	1.330	0.357	87.74
		3	0.0169	1.240	0.0475	1.240	1.140	99.20
		5	0.0231	0.830	0.0651	0.830	0.832	90.23
	Talc	1	0.0052	1.070	0.0147	1.070	0.643	90.87
		3	0.0033	1.160	0.0094	1.160	1.580	99.73
		5	0.0038	0.860	0.0107	0.860	0.926	98.30
Stirred ball mill	Calcite	1	0.0105	1.159	0.0078	1.159	1.093	99.20
		3	0.0238	1.112	0.0464	1.112	0.770	99.08
		5	0.0180	0.945	0.0606	0.945	0.594	99.03
	Pyrophyllite	1	0.0048	1.209	0.0225	1.129	0.456	98.15
		3	0.0045	1.240	0.0184	1.240	0.499	93.65
		5	0.0061	1.033	0.0363	1.033	0.358	81.35
	Talc	1	0.0005	1.293	0.0002	1.293	1.153	85.63
		3	0.0004	1.254	0.0018	1.254	0.433	99.13
		5	0.0004	1.088	0.0011	1.088	0.658	99.13

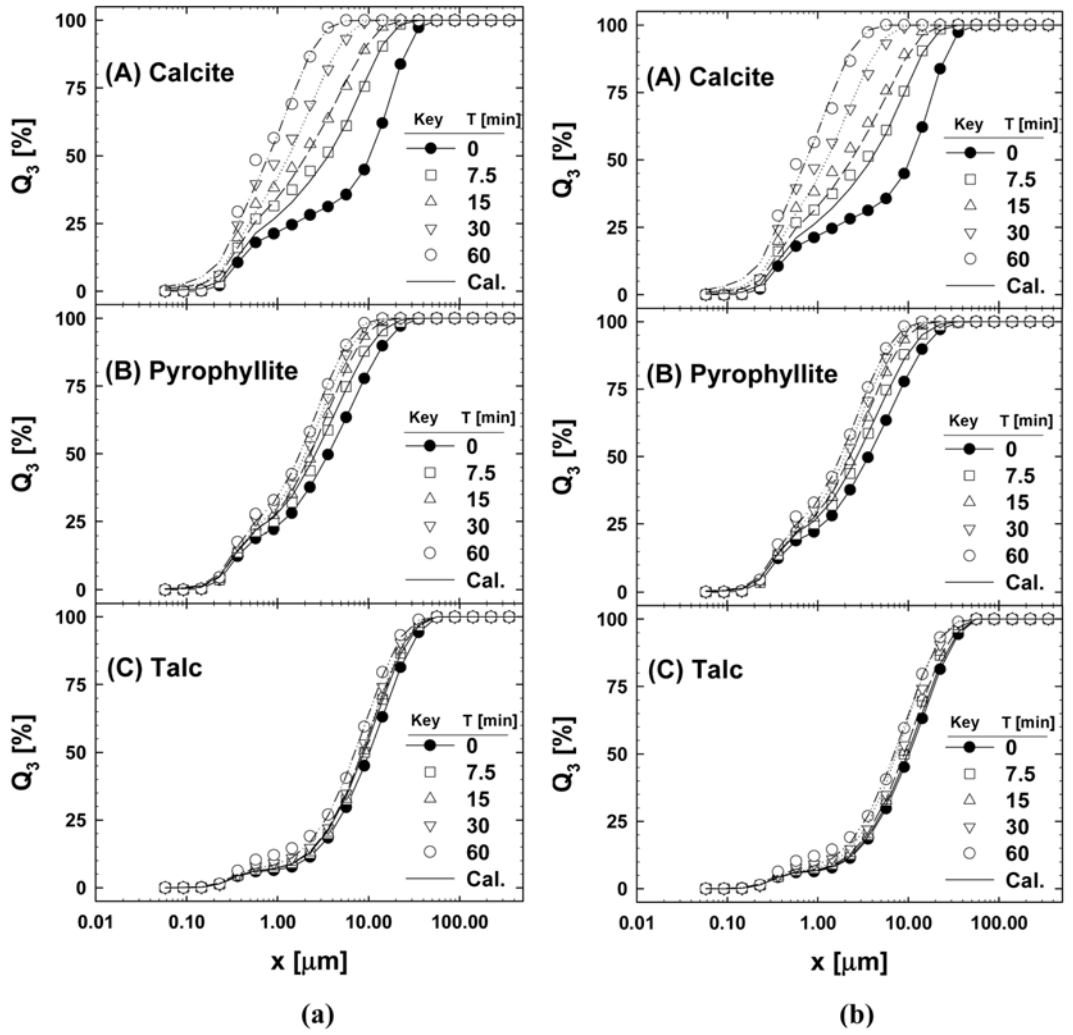

Fig. 2. Comparison of cumulative undersize percent of particle size, calculated by parameter of grinding rate equation with that of experimental data in case of grinding media of 1 mm. Value of m and n: (a) m=n, (b) m≠n.

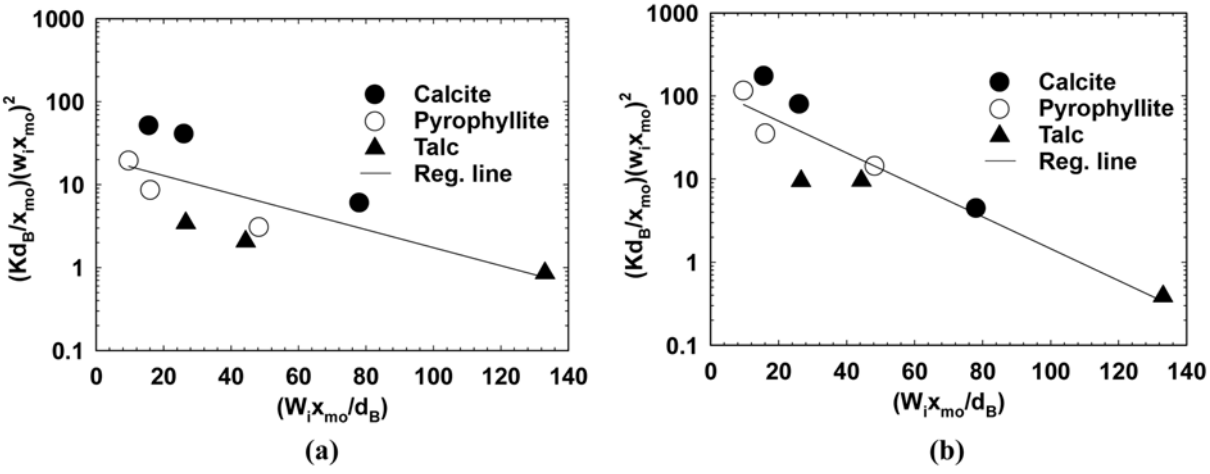

Fig. 3. The plot of experimental data for an empirical equation of grinding rate constant. Value of m and n: (a) m=n, (b) m≠n.

the particle size of various samples for experimental conditions of the rotation speed. The result of the selection function calculated was a log-log plot of S against the particle size for several inorganic powders which show a linear relationship. The selection function is a specific rate of breakage. It was increased with the increase of the particle size and was changed with experimental conditions

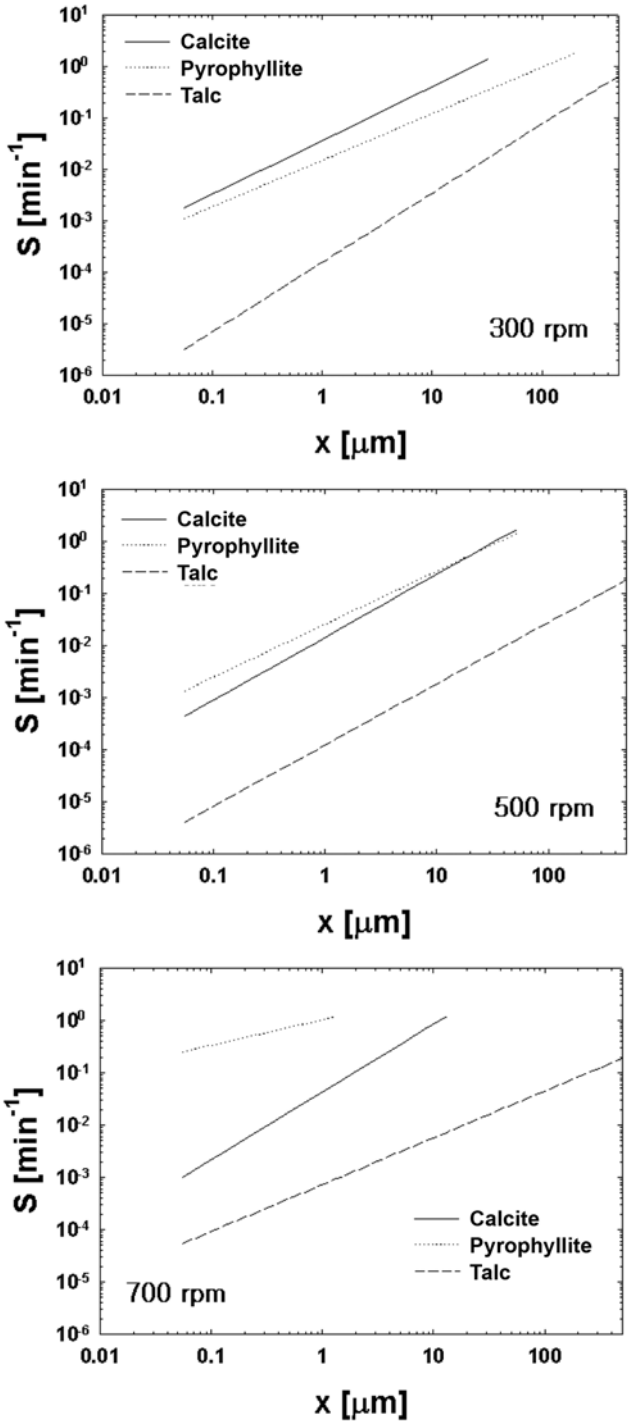

Fig. 4. Relationship between particle size and selection function on various samples for experimental conditions.

such as the property of raw material and type of the grinding mill. The intensity of the impact of the grinding balls decreases in proportion to their mass, and a change in property of the ground material, such as the crystalline structure, can be facilitated by using higher impact energy of the grinding balls. This means that the change in the crystal structure of raw materials that can be achieved is limited by the impact energy required to fracture the particles and the number of contact points. This is primarily dependent upon the grinding ball diameter and the ball's density. More recent research has demonstrated that, for large particle sizes, the straight-line relationship no longer holds, and the pattern of decrease is typical. The falling off of the grinding rate is due to two factors: the larger particles are not readily nipped between the balls, and they tend to be cushioned by a layer of fine particles [19]. The fine particles were ground effectively by small impact energy; however, the coarse particles were ground only by a partial impact that went over the particle solidity with added impact energy. In this experiment, the phenomenon of a decreased grinding rate did not appear because the raw materials were very fine and the ball size and ball density were relatively big. The grinding rate change of calcite and pyrophyllite was similar for the same conditions. But, in the case of talc, it was observed that the grinding rate was not increased compared with other samples. In the raw materials' size range of this experiment, the grinding rate of pyrophyllite and calcite powder was increased compared with the talc powder.

Calcite is a carbonate mineral which has rhombohedral (trigonal) crystal shape. This mineral can be easily ground because of its well developed cleavages that are parallel to the crystal face. Both pyrophyllite and talc belong to phyllosilicate mineral, having 2 : 1 layer structure. The two minerals, however, differ in their nature of octahedral sites. Pyrophyllite is a dioctahedral clay mineral, whereas talc is a trioctahedral clay mineral. Pyrophyllite shows a structure having 1/3 of its octahedral sites empty because trivalent Al^{+3} occupy only two out of every three octahedral sites. Talc, however, shows a stable structure having no empty octahedral site because divalent Mg^{+2} occupy all three octahedral sites. Due to the structural difference between the two minerals, it is considered that pyrophyllite having empty octahedral sites can be more easily ground [14].

CONCLUSIONS

A series of wet grinding experiments using inorganic powders by a stirred ball mill were carried out. The grinding rate constants K and K′, selection function and breakage function were fit to the data of the particle size distribution obtained from the stirred ball mill.

The empirical equation on the grinding rate constant K in $\mu m^{-n} \cdot min^{-1}$ or K′ in $\mu m^{-n'} \cdot min^{-\nu}$ was expressed in terms of a function involving the ball diameter of grinding balls, d_B in mm the median diameter of feed material x_{mo} in μm, and Bond's work index of material, W_i in kWh/t in the experimental conditions as follows:

$$\text{K or K}' = \frac{c_1}{(W_i x_{mo})^2}\left(\frac{x_{mo}}{d_B}\right)\exp\left[-c_2\left(\frac{W_i x_{mo}}{d_B}\right)\right]$$

where the values of empirical constants, c_1 and c_2 were 21.13 and 0.0109 on K, while c_1 and c_2 were 120.99 and 0.0192 on K′, respectively.

The grinding rate change on calcite and pyrophyllite was similar at the same conditions. In the case of talc, it was observed that the grinding rate was not increased compared with other samples. In the raw materials' size range of this experiment, the grinding rate of pyrophyllite and calcite powder was increased compared with talc powder. The difference of results was shown according to crystal structural properties of minerals. It is confirmed that the grinding rate increased with the increase of the mill rotation speed.

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NOMENCLATURE

$B(\gamma, x)$: breakage function of grinding
c : empirical constant
d_B : ball diameter [mm]
K : grinding rate constant [$\mu m^{-n} min^{-1}$]
K' : $=(\mu K)^{\nu}$
J : filling ratio of ball [-]
m : empirical constant
n : empirical constant
n' : $=n\nu$
Q_3 : cumulative undersize percent based on weight [%]
R(x, t) : cumulative oversize of particle at grinding time t [-]
R^2 : determined coefficient [%]
S(x, t) : selection function of grinding
t : grinding time [min]
W_i : Bond's work index [kWh/t]
x : particle size [mm]
x_{50} : median diameter of particles [mm]
x_{mo} : median diameter of feed material [mm]
γ : particle size to be crushed [mm]
μ : empirical constant
ν : empirical constant

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