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MECHANICAL ACTIVATION OF LIZARDITE BY DRY GRINDING FOR ENHANCED MINERAL CARBONATION

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Abstract

Mechanical activation of Ca/Mg silicates by grinding is a pre-treatment of some mineral carbonization processes. In this study, the mechanical activation of lizardite ore from a chromite beneficiation plant waste by grinding in a stirred media mill was studied. For grinding studies, grinding times of 10-20-30 min and stirring speeds of 600-800-1000-1200 rpm were the parameters investigated, while the ball charge rate was 60% and the ore charge rate was kept constant at 40%. This way, the effects of grinding time and stirring speed on particle size distribution and energy consumption were investigated. At the end of the grinding studies, the stirring speed was determined as 1200 rpm, and the grinding time was 10 min for the finer particle size distribution (d_{10}: 2,7 µm, d_{50}: 13,6 µm, d_{90}: 57.6 µm) with less energy consumption (130.4 kWh/ton). FT-IR analyses proved that the samples were dehydroxylated by the milling process. As a result, according to the analysis performed after grinding, it can be said that the finer product obtained can be used in mineral carbonation processes.

Keywords

Lizardite, Serpentine, Grinding, Mechanical Activation, Stirred Media Mill

1. Introduction

The mineral carbonation technique prevents the emission of CO_2 gas, formed due to various industrial processes, into the atmosphere by chemically binding to calcium and magnesium silicates (Li & Hitch, 2018). Three different techniques are used in mineral carbonation and these are thermal activation, chemical activation, and mechanical activation. In these three methods, silicate minerals' crystal structures deteriorate, increasing the carbonation rate (Haug et al., 2010; Azdarpour et al., 2015; Aminu et al., 2017;). Mechanical activation is a grinding process that is performed to decrease particle size and enlarge the surface area of minerals. Grinding causes the removal of hydroxyls (dehydroxylation) of hydrated minerals, and so yields a highly disordered crystal structure. This is the recently favored process for magnesium silicates to produce disordered crystalline structures for mineral carbonation uses (Alex et al., 2016). Olivine and serpentine group minerals are the most appropriate Ca/Mg silicate mineral raw materials for CO_2 mineral carbonation, as they are abundant in nature and bind relatively more CO_2 per unit mass (Goff et al., 2000). Lizardite, the most common mineral of the serpentine group, is a trioctahedral phyllosilicate type mineral and has the general chemical formula of $Mg_3Si_2O_5(OH)_4$. Layered (1:1) and hydrated lizardite minerals generally contain 12.1-13.5% H_2O, 41.0-42.1% SiO_2, and 38.3-40.9% MgO in their crystal structure (Dlugogorski & Balucan, 2014; Çiftçi et al., 2021). The carbonation process of magnesium silicates can be determined by reactions (1) and (2), respectively.

$$Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2 \quad (1)$$

$$Mg_3Si_2O_5OH_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O \quad (2)$$

Studies on the mechanical activation of serpentine minerals such as lizardite by grinding to be used in the mineral carbonation are limited (Nelson, 2004; Li & Hitch, 2018). This study investigated the mechanical activation of lizardite mineral, produced as a chromite ore beneficiation plant waste, by a stirred media mill. The effects of stirring speed and grinding time on particle size distribution and energy consumption were investigated in detail.

2. Materials and Methods

2.1 Materials

The lizardite ore used in this study was taken from the waste site of OGELMAN Mining Companys' chromite ore beneficiation facility in Harmancık/BURSA.

2.2 Methods

2.2.1 Characterization studies

Before the mineralogical and chemical analysis, the sample was dried at 105ºC for 24 h and ground in a ring mill for 2 min. Mineralogical analysis was performed using a Shimadzu XRD-6000 instrument to determine the mineral compositions of the sample. The elemental composition of the sample was determined by chemical analysis using a Rigaku ZSX Primus II XRF spectrometer. Particle size analyses were performed using a Malvern Mastersizer 2000 instrument (Çiftçi et al., 2020).

2.2.2 Grinding studies

The procedure of our previous study was followed for grinding experiments (Çiftçi & Özçatal, 2021). A vertical stirred media mill with an effective volume of 1 L was used for the grinding experiments. A pin-type shaft was used as the stirrer, and yttrium-stabilized zirconium oxide balls (3 mm: 598 g, 5 mm: 1967 g, total volume: 530 mL) were used as the grinder media. Before grinding, the sample was dried at 100ºC for 24 h. After the balls and sample were added to the mill chamber, the mill cooling water was turned on, and the stirring process was started. The energy consumed in the grinding experiments was recorded with an electricity meter attached to the circuit. The operating parameters of each grinding experiment are summarized in Table 2.1.

Table 2.1 *Operational Parameters of the Grinding Experiments*

Experiment no	1	2	3	4	5	6	7	8	9	10	11	12
Stirring speed (rpm)	600	600	600	800	800	800	1000	1000	1000	1200	1200	1200
Grinding time (min)	10	20	30	10	20	30	10	20	30	10	20	30

(Source: Authors' Own Illustration)

3. Results and Discussion

The chemical analysis results of the sample used in the grinding studies are given in Table 3.1. Accordingly, it was determined that the sample consisted mainly of Si and Mg elements and

showed a high rate of loss on ignition (15%). The obtained data showed that the sample was a serpentine group mineral. The exact mineralogical composition was determined by XRD analysis.

Table 3.1 *Chemical Composition of the Lizardite Sample*

Component	SiO_2	Al_2O_3	Fe_2O_3	MgO	CrO	CaO	SO_3	LOI
Content, wt.%	32.22	0.73	7.10	39.3	0.97	0.84	0.18	14.94

LOI: loss on ignition.

(Source: Authors' Own Illustration)

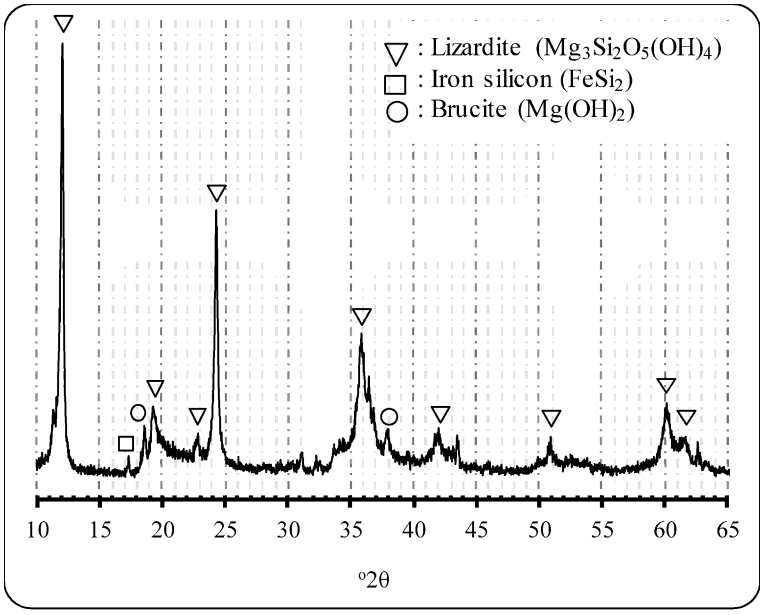


Figure 1: *XRD Pattern of the Lizardite Sample*

(Source: authors' own illustration)

The XRD pattern of the sample (Figure 1) showed that all of the materials representing the sample content had a certain crystal structure. Additionally, it was determined that the sample mainly consisted of lizardite minerals and the presence of small amounts of brucite and iron silicon.

Stirring speed and grinding time are the most effective working parameters in grinding processes with stirred media mills. The results of the grinding experiments were evaluated with the particle size distribution curves of the ground samples obtained. All comparative graphs were drawn to evaluate the obtained data accurately (Figures 2 and 3). The grinding chamber experiences a heightened level of energy and strength due to the stirring speed, resulting in an increased probability of the grinding media impacting and wearing down the particles. As the stirring speed continues to rise, the stress intensity inside the mill chamber progressively amplifies,

substantially affecting the interaction between the grinding media and the material to be ground (Altun et al., 2012; Hasan et al., 2017; Çiftçi & Özçatal, 2021).

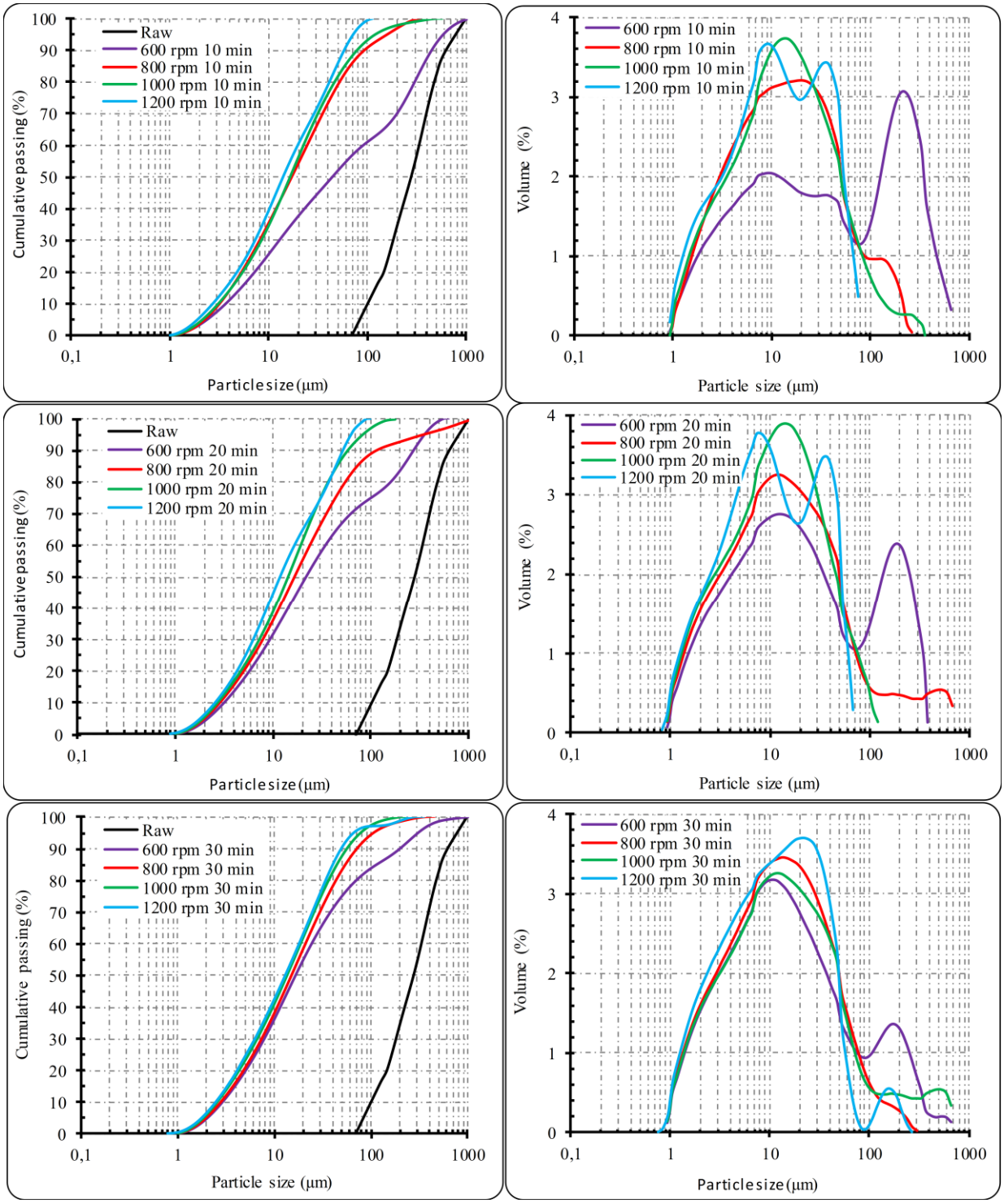


Figure 2: *Particle Size Distributions of the Ground Products as a Function of Stirring Speed (Source: Authors' Own Illustration)*

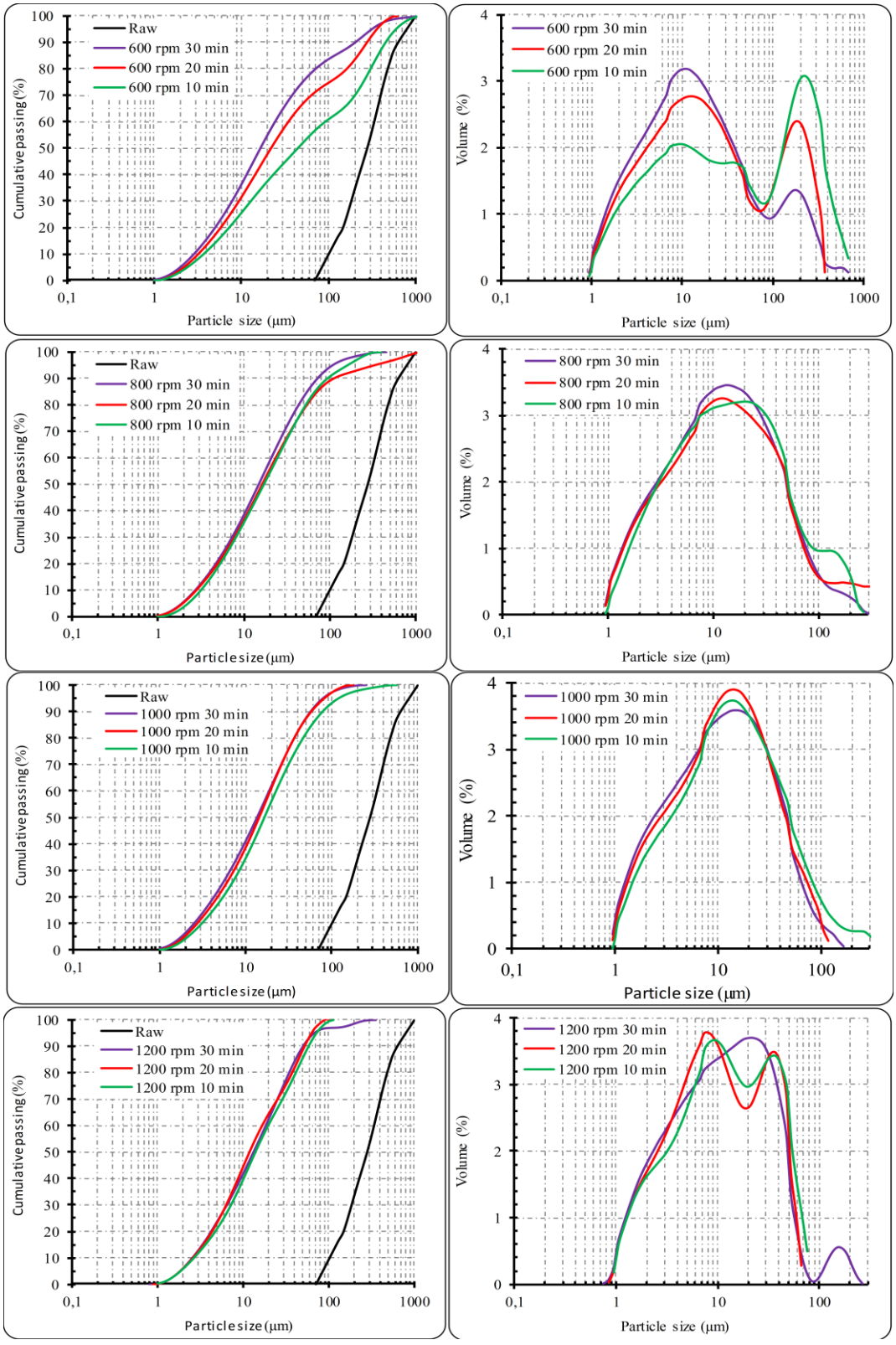


Figure 3: *Particle Size Distributions of the Ground Products as a Function of Grinding Time*

(Source: Authors' Own Illustration)

Figure 2 shows the effects of stirring speed on particle size distribution at constant grinding times. Accordingly, increasing the stirring speed at the fixed grinding times resulted in smaller particle sizes. While the difference between the particle size distributions obtained at different stirring speeds was sharper at low grinding times, such as 10 min, it was determined that the difference was much less when increasing the grinding time to 30 min. The most striking result in Figure 2 was that the particle size distribution at 600 rpm remained much larger in all grinding times compared to other stirring speeds. The result of the curves in Figure 2(right) was that most of the samples were grouped in 2 or 3 different particle sizes, showing a heterogeneous particle size distribution.

Figure 3 shows the effects of grinding time on the particle size distribution at constant stirring speeds. According to the results obtained from these comparative curves, it was determined that the grinding time had a significant effect on the particle size distribution at low grinding speeds (600 and 800 rpm). At the same time, it could have been more effective at high stirring speeds, especially at 1200 rpm. In Figure 3, after grinding at 1200 rpm for 30 min, the particle size distribution mostly remained below 100 µm, while a small portion of the sample showed a secondary size distribution above 100 µm. This result was not observed in 10 min and 20 min of grinding under the same conditions. As the grinding time increases under normal conditions, the particle size is expected to decrease more. However, the emergence of such a situation can be attributed to the agglomeration of the particles that have passed to very fine sizes due to increasing the grinding time more than necessary. In addition to the Van der Waals forces, the agglomeration is also caused by the binding effect of the water produced by dehydroxylation due to grinding for such materials.

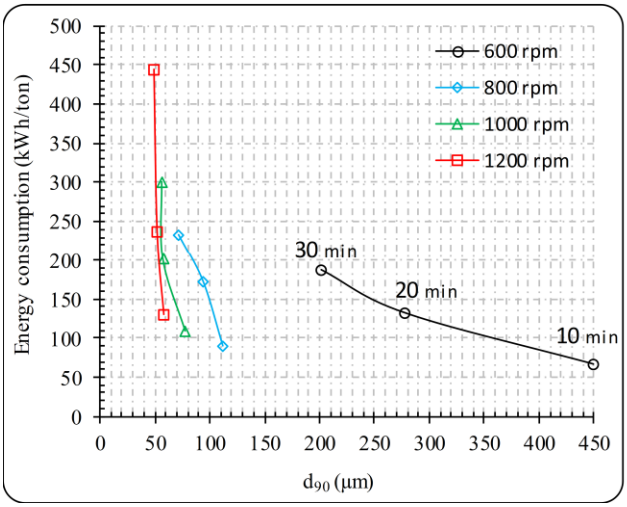
The d_{10}, d_{50}, and d_{90} values of the grain size distributions obtained at the end of milling are also summarized in Table 3.2. As an example, the d_{50} value of a sample (such as 600 rpm 10 min) indicates that 50% of the sample size is below that value (44.16 µm). As seen in this table, it was determined that the grinding time was very effective at low stirring speeds, and the stirring speed was very effective at low grinding times. For example, grinding time did not seriously affect d_{90} values in grinding at 1200 rpm. However, while the d_{90} value was 449.2 µm at 600 rpm milling for 10 min, the d_{90} value decreased significantly to 202.2 µm when grinding was extended to 30 min. In this respect, it has been proven that grinding at high stirring speeds in stirred media mills yields finer-sized products and saves time.

Table 3.2 *Particle Size Distributions of All Ground Products*

Stirring speed (rpm)	Grinding time (min)	d_{10} (µm)	d_{50} (µm)	d_{90} (µm)
Raw	Raw	100.00	270.00	600.00
600	10	3.66	44.16	449.23
	20	3.19	21.93	277.81
	30	2.90	16.60	202.17
800	10	3.18	17.14	111.18
	20	2.86	16.46	93.44
	30	2.77	14.94	71.30
1000	10	3.08	16.36	77.59
	20	2.71	14.24	57.74
	30	2.54	13.54	56.76
1200	10	2.68	13.85	57.58
	20	2.60	11.94	52.37
	30	2.52	13.16	49.92

(Source: Authors' Own Illustration)

The stress intensities are heightened by progressively increasing the stirring speed, consequently boosting the grinding speed. This effect is primarily attributed to the increased probability of particle collisions with the grinding media. Additionally, as the stirring speed rises further, the kinetic energy of the grinding media also rises, leading to its transfer to the particles and facilitating the process of particle breakage.



Stirring speed (rpm)	Grinding time (min)	d_{90} (µm)	Energy consumption (kW/ton)
600 rpm	10	449.2	67.8
	20	277.8	132.1
	30	202.2	187.8
800 rpm	10	111.2	90.4
	20	93.4	172.1
	30	71.3	232.9
1000 rpm	10	77.6	109.5
	20	57.7	201.7
	30	56.8	300.8
1200 rpm	10	57.6	130.4
	20	52.4	238.2
	30	49.9	443.3

Figure 4: *Energy Consumption of All Grinding Experiments*

(Source: Authors' Own Illustration)

Energy consumption is another point to be considered while evaluating the product obtained in grinding processes with particle size distributions. While determining the optimum operating parameters, energy consumption should be assessed in terms of cost. The electrical energy values consumed in all grinding trials are given in Figure 4. Accordingly, the connection between

grinding time and energy consumption in the mill has been reaffirmed, showcasing a linear association. The same situation was observed for the energy consumption depending on the stirring speed. It was determined that as the stirring speed increased, the energy consumption increased proportionally. Notably, when the mill attains meta-steady state dynamics, the power consumption stabilizes and remains consistent, as evidenced in other studies (Santosh et al., 2020; Çiftçi & Özçatal, 2021). This pattern has been observed in other investigations as well (Toraman & Katırcıoğlu, 2011; Toraman, 2013; Hacıfazlıoğlu & Korkmaz, 2020; Çiftçi & Özçatal, 2021).

As a result, considering the data in Table 2, it was determined that grinding operations in stirred media mills were more appropriate at high stirring speeds and low grinding times. In this way, it has been proven that the product milled to much finer sizes is obtained with less energy consumption. Considering these results in this study, it was determined that the most suitable grinding conditions were 1200 rpm stirring speed and 10 min grinding time.

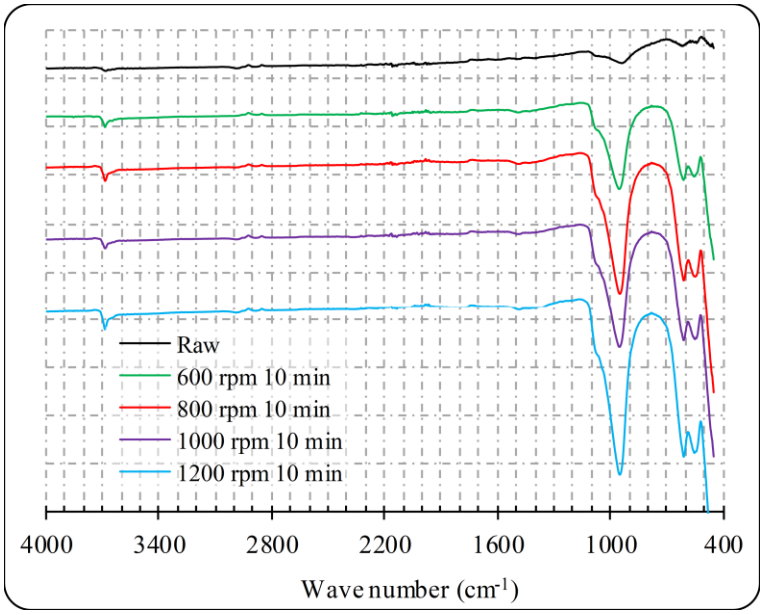


Figure 5: *FT-IR Spectrums of Some Ground Products*

(Source: Authors' Own Illustration)

FT-IR spectra are given in Figure 5 to examine the changes in the functional groups in the structure of the ground samples. After mechanical activation, the positions of the bands remain almost the same, but they become stronger and clearer. This outcome can be understood by referring to Rayleigh's equation, which establishes a connection between the scattering of light and the size of the particles. Essentially, the phenomenon can be explained by the fact that larger particles scatter light more effectively (Li & Hitch, 2018). In addition, OH stretching, which is more pronounced

at a wavenumber of 3680 cm^{-1} due to dehydroxylation by grinding, is attributed to the structural hydroxide groups of the milled samples.

4. Conclusion

Mechanical activation is a grinding process for magnesium silicates to produce disordered crystalline structures for mineral carbonation uses. A chromite plant waste sample was subjected to dry grinding experiments using a pin-type vertical stirred media mill for mechanical activation. Two operational parameters, grinding time and stirring speed, were investigated for optimum grinding while keeping the material and ball charge constant. Characterization studies revealed that the raw sample predominantly consists of lizardite.

It was concluded that stirred media mills could effectively dry grind lizardites into ultrafine particle sizes. Additionally, it was determined that the optimum grinding conditions in stirred media mills were low grinding time (≤10 min) and high stirring speed (≥120 rpm). In this way, it was seen that a finer-sized product was obtained with lower energy consumption. By utilizing specific operational parameters (60% ball charge, 40% material charge, 1200 rpm stirring speed, and 10 min grinding time), a ground lizardite product with a d_{90} value of approximately 57.6 µm was achieved. The selected operational parameters resulted in an energy consumption of 130.4 kWh/ton during the grinding process.

In future research, mill ball and material charge rates can be examined in detail for grinding. Thus, a product with a finer size and less energy cost can be obtained. Apart from these, benefits can be achieved in terms of particle size and energy consumption by making changes in the stirrer pin design.

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