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PARTICLE SIZE DISTRIBUTION OF NANOSCALE ULEXITE MINERAL PREPARED BY BALL MILLING

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Abstract

Commercially available raw ulexite (U) minerals were milled up to 120 min by using a high-energy ball grinder for different initial feed sizes ($-75\ \mu\text{m}$ and $-3\ \text{mm}$), ball to powder ratios (5:1 and 10:1), ball sizes (1 mm and 5 mm), and process control agents (3% and 6%). Particle size distribution and morphology measurements of milled powders were carefully studied. In particle size analysis, the lowest d_{90} , d_{50} , d_{10} and d_{min} values were detected to be $17.547\ \mu\text{m}$, $1.732\ \mu\text{m}$, $283\ \text{nm}$ and $35\ \text{nm}$, respectively. Therefore, nanoscale in particle size for the ulexite mineral has been achieved. In addition, the smallest milling time was found as 30 min. Moreover, the best powder yield was determined to be 90.5%. In morphology analysis, the milled powders were observed to be more homogeneous than the initial feed size minerals. Besides, findings of morphology analysis were in agreement with that of particle size analysis. It was decided that optimized ball milling parameters are $-3\ \text{mm}$ for initial feed size; 10:1 for the ball to powder

ratio; 5 mm for ball size; 3% for process control agent. The results obtained from this work will be useful for nanoscale research and industrial applications of ulexite ($\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 5\text{B}_2\text{O}_3 \cdot 16\text{H}_2\text{O}$) material, which is boron mineral.

Keywords

Alexie, Ball Milling, Particle Size, Morphology, Optimization

1. Introduction

Boron is a very valuable element in terms of future technology. This element is found in ulexite, colemanite, tincal, pandermite and similar minerals in the nature as oxidized compound. Of these minerals, one of the most common reserves in the world is the ulexite (sodium-calcium-borate hydrate). Ulexite mineral has a very wide area which is used now and is considered for future use. These include the fabrication of glass, porcelain, leather, cosmetics and photographic chemicals, detergent materials, polymer, catalysts, steel, refractory materials, fertilizers, disinfectant, food preservative, textiles, nuclear fiberglass, insulators (Demirkiran, Bayrakçi, & Asin, 2013; Ipek & Sahan, 2013), hydrogen energy (NaBH_4) (Sert, Yildiran, & Toscal, 2012), superconducting material (MgB_2) (Vignolo et al., 2014), shielding material (Demir & Un, 2013), ultra-high temperature ceramic material (ZrB_2) (Guo, Hu, & Kagawa, 2011), asphalt concrete (Kutuk-Sert & Kutuk, 2013), cement concrete (Kutuk-Sert, 2016) and brick (Emrullahoglu Abi, 2014).

In recent years, many researchers from different countries have worked extensively on nanosized minerals. The cause is much better when their physical, structural, electrical, magnetic, and so on properties are compared to micronsized minerals (Canakci et al., 2014; Ashik & Daud, 2016).

There are many methods used to decrease the particle size of a mineral to nanoscale from micronscale. Among them, ball milling method is one of the popular ones especially in terms of cost (Alizadeh, Sharifianjazi, Haghshenasjazi, Aghakhani, & Rajabi, 2015). However, in this method, grinding parameters such as the milling time, ball to powder mass ratio (BPR), process control agent (PCA), size of the ball, initial feed size, size of the vial, rotation speed, atmosphere of mill are very important (Abdellahi, Bahmanpour, & Bahmanpour, 2014; Zhang, Zhu, & Wang, 2008).

Kutuk investigated that the particle size of the ulexite mineral was reduced to submicron (<1 μm) size using the ball milling method. In the first study, he measured the average particle size (d_{50}) of 8.846 μm and the smallest particle size (d_{min}) of 158 nm in the laser size analyzer (Kutuk & Kutuk-Sert, 2017). In new second study, he found a d_{50} value of 5.921 μm and a d_{min} value of 240 nm on the laser size analyzer (Kutuk, 2016). The d_{min} values in both studies are submicron scale but not nanoscale (<100 nm). Apart from these studies, no other work related to the nanosized particle size of the ulexite mineral was found in the literature. That is why the main goal of this manuscript is to reduce the particle size for ulexite minerals to a smaller size, i.e. nanosize.

2. Experimental Details

2.1 Materials

Commercial raw ulexite minerals were supplied to Eti Mine Works General Management's Bigadic Boron Mine Company (Eti Mine) in Turkey. These minerals which are 3.35 mm in sieve size (No. 6) (U-3 mm, coarse powder) and 75 μm in sieve size (No. 200) (U-75 μm , fine powder) with the standard of ASTM (the American Society for Testing and Materials) were used as starting materials in this study. Oxide compound analysis of these materials was performed by Eti Maden Company as listed in Table 1 (Eti Mine, 2014a, 2014b).

Table 1: Oxide Compound Analyses of Initial Ulexite Minerals

Compound	Ulexite (wt.%)	
	-3 mm	-75 μm
B ₂ O ₃	25.50 \pm 1.50	37.00 \pm 1.00
CaO	21.00 \pm 3.00	19.00 max
SiO ₂	13.00 max	4.00 max
Na ₂ O	2.00 min	3.50 max
SO ₄	0.60 max	0.25 max
As	40 ppm max	40 ppm max
MgO		2.50 max
SrO		1.00 max
Al ₂ O ₃		0.25 max
Fe ₂ O ₃		0.04 max
Humidity		1.00 max

2.2 Milling process

U-3 mm and U-75 μm minerals were ground at a milling time of 7.5 min, 15 min, 30 min, 60 min and 120 min in a planetary high-energy ball grinder (Retsch, model 'PM 100'). Ball milling method was carried out at room temperature and air atmosphere by using a 250 ml zirconium oxide vial. Zirconium oxide balls were 1 mm and 5 mm in diameter. BPR was 5:1 and 10:1. Rotational speed of vial was 500 rpm. PCA type was methanol (Merck, 99.99% purity) and its amount was 3% and 6% of the mineral in weight. To avoid overheating of the vial during milling, the grinder was stopped each 15 min and later it was continued to work in opposite direction after a 5 min break.

For ease of understanding, the milling names are labeled as presented in Table 2. For example, U_10: 1 label was done instead of U_3m_10: 1_5m_3% (Powder name_Initial powder size_BPR_Ball size_PCA).

Table 2: Milling Labels

Milling name	Label
U_3m_5:1_5m_3%	U
U_3m_5:1_1m_3%	U_1 mm
U_3m_5:1_5m_6%	U_6%
U_75mc_5:1_5m_3%	U_75 mc
U_3m_10:1_5m_3%	U_10:1

2.3 Measurements

Particle size distributions of initial materials and milled powders were measured by using a laser scattering size analyzer (Malvern, model 'Mastersizer Hydro 2000 MU'). This analyzer averaged the size of them as soon as scanning each powder four times. Therefore, d_{90} , d_{50} , d_{10} and d_{min} values were detected respectively corresponding to 90%, 50%, 10% and min percent passing volume in the particle size distribution.

For powder yield, the powders were weighed on an electronic balance with a sensitivity of 0.01 g before and after milling (Dikomsan, model 'KD-TBC 600'). The yield was calculated from the following formula:

$$\text{Powder yield (\%)} = (\text{Final powder}/\text{Initial powder}) \times 100 \quad (1)$$

The photo of the U-3 mm initial material was taken using a digital camera (Samsung, model 'ES73'). Microstructure image of milled U₁₀: 1 powder was examined by a polarizing optical microscope (POM) (Olympus, model 'BX-51') having both a camera (Olympus, model 'DP72') and software (Stream Basic). Nanostructure images of the U₁₀:1 powder were investigated by a scanning electron microscope (SEM) (Jeol, model 'JSM-6610') after the U₁₀:1 powder had been coated with gold for good conductivity.

3. Results and Discussion

3.1 Laser Size Analysis

The d_{90} values of milled powders by milling time are shown in Figure 1. The best sample among the milled powders is U₁₀: 1 powder. The d_{90} values of U₁₀: 1 powder are 816.708 μm , 670.055 μm , 32.854 μm , 17.547 μm , 23.464 μm and 51.870 μm for milling time of 0 min, 7.5 min, 15 min, 30 min, 60 min and 120 min, respectively. According to these values, it was found that the d_{90} value dropped rapidly from 0 min to 30 min, but slowly increased from 30 min to 120 min. The increasing state can be attributed to the cold welding mechanism (Sivasankaran, Sivaprasad, Narayanasamy, & Iyer, 2010). More clearly, the powder particles are first disintegrated during the milling process since they are subjected to intensive plastic deformation. As the specific surface area (SSA) of the disintegrated particles increases, the particles recombine after a certain SSA value.

In addition, the smallest d_{90} value was detected with 17.547 μm at the milling time of 30 min.

Figure 2 presents d_{50} values of milled powders by milling time. The best sample among the milled powders is U₁₀: 1 powder. The d_{50} values of the U₁₀: 1 powder are 444.220 μm , 22.931 μm , 7.303 μm , 1.732 μm , 9.425 μm and 19.233 μm for the milling time of 0 min, 7.5 min, 15 min, 30 min, 60 min and 120 min, **in turn**. The behavior of these values is the same as that of d_{90} values.

Besides, the smallest d_{50} value measured in this study is 1.732 μm at the milling time of 30 min. In a similar study for the ulexite material in the literature, the d_{50} value was found to be 8.846 μm at a milling time of 30 min (Kutuk, 2016). Therefore, the optimum milling time

obtained from this study is in good agreement with the literature. However, the d_{50} value obtained from this study is better than the literature. This is because, most likely, is PCA. It is well known that PCA is a lubricant or surfactant (Suryanarayana, 2001).

As can be seen from Figure 3, the sample with the best d_{10} value among the milled powders belongs to U_10: 1 powder. The d_{10} values of this powder are 10.052 μm , 5.288 μm , 0.704 μm , 0.283 μm , 1.873 μm and 3.391 μm for the milling time of 0 min, 7.5 min, 15 min, 30 min, 60 min and 120 min, respectively. The smallest d_{10} value was determined to be 0.283 μm at the milling time of 30 min. This value is remarkable because it is on the submicron scale.

As can be seen from Figure 4, the best sample among the milled powders belongs to the U_10: 1 powder. The d_{min} values of this powder are 1905 nm, 275 nm, 35 nm, 363 nm and 363 nm for the milling time of 0 min, 7.5 min, 15 min, 30 min, 60 min and 120 min, **in turn**. The behavior of these values is the same as that of d_{10} values.

Also, the smallest d_{min} value was measured at 30 min milling time. In general, the optimum milling time was decided as 30 min because of the fact that the milling time for all of the d_{90} , d_{50} , d_{10} and d_{min} values of the U_10: 1 powder is 30 min.

Finally, the smallest d_{min} value was detected as 35 nm. So far, the smallest particle size measured in similar studies in the literature is 158 nm and this value is on the submicron scale (Kutuk, 2016). From this perspective, it was found that nanoparticles were successfully obtained in the milled powder of ulexite mineral through this study.

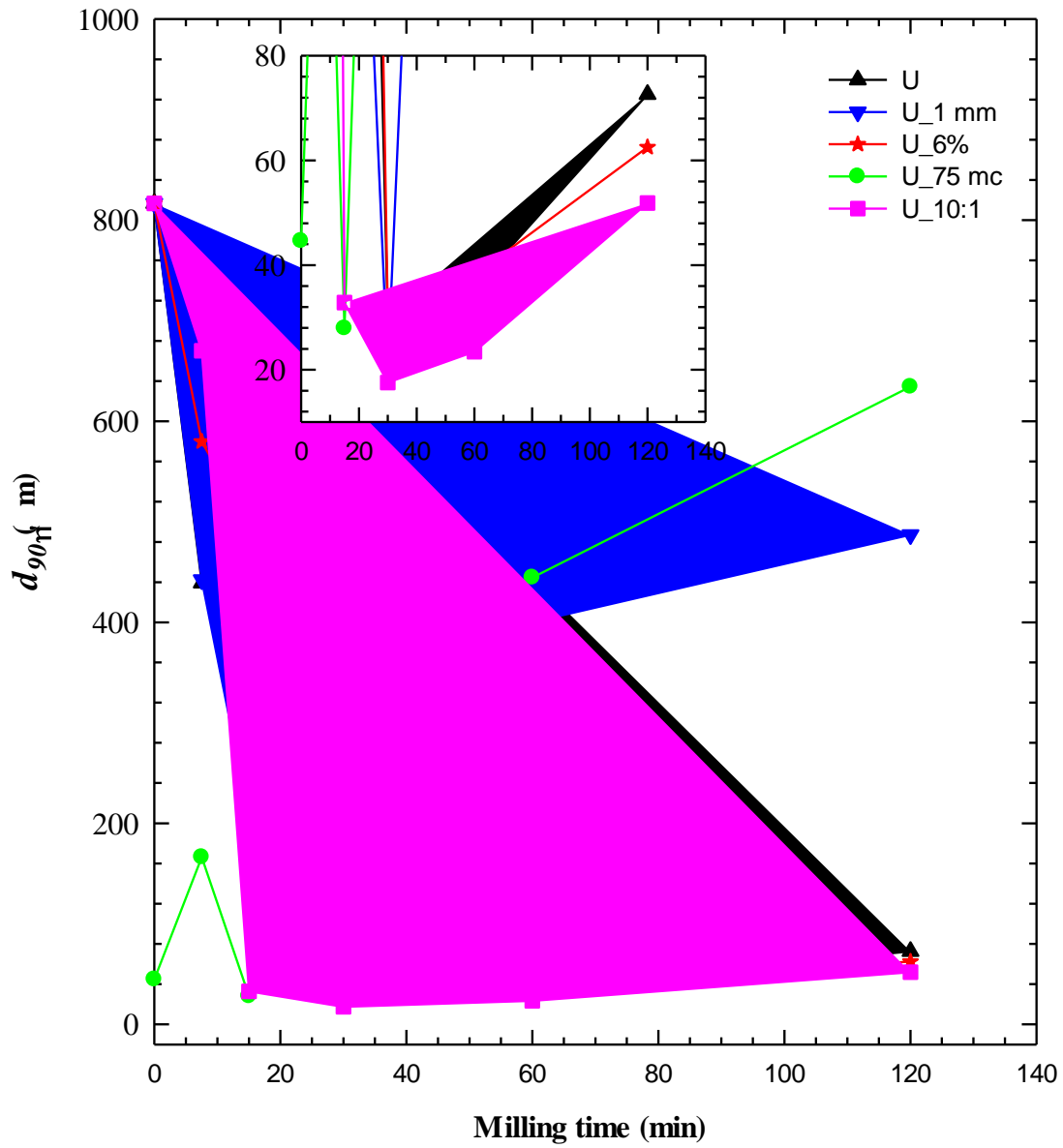


Figure 1: The change of d_{90} value by the milling time. The inner figure is magnification for $<d_{90}= 80 \mu\text{m}$

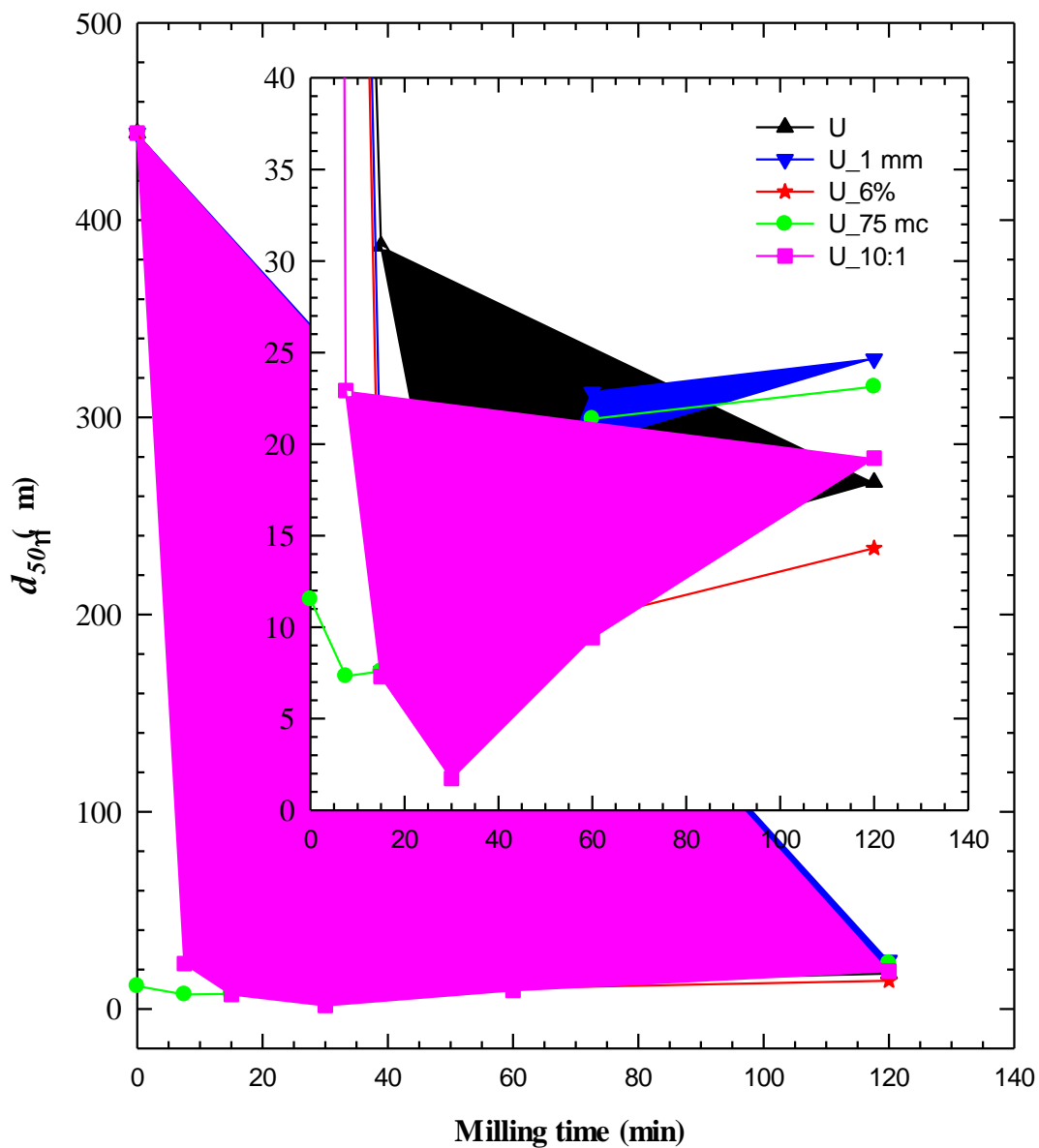


Figure 2: The change of d_{50} value by the milling time. The inner figure is magnification for $<d_{50}= 40 \mu\text{m}$.

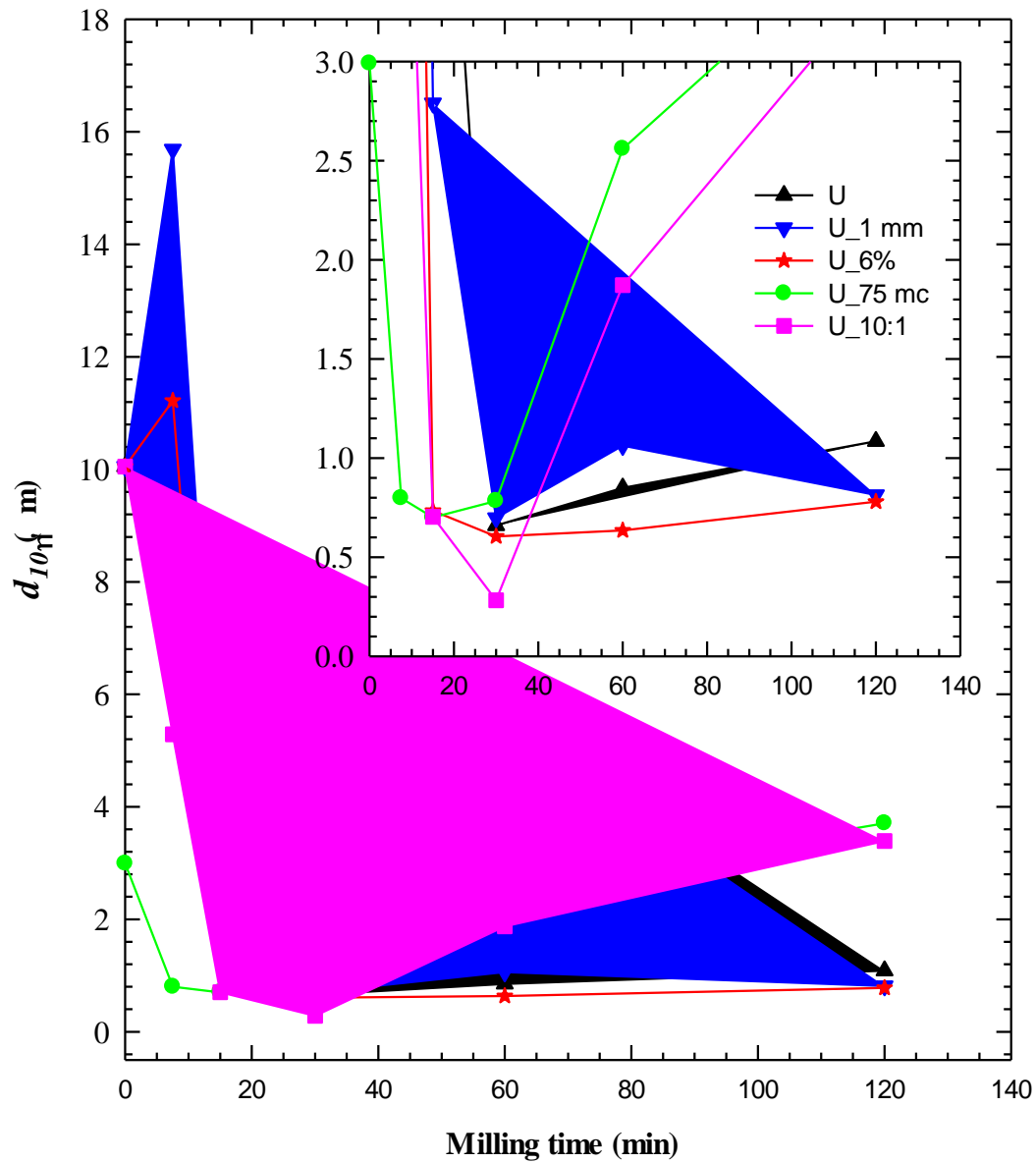


Figure 3: The change of d_{10} value by the milling time. The inner figure is magnification for $<d_{10} = 3.0 \mu\text{m}$.

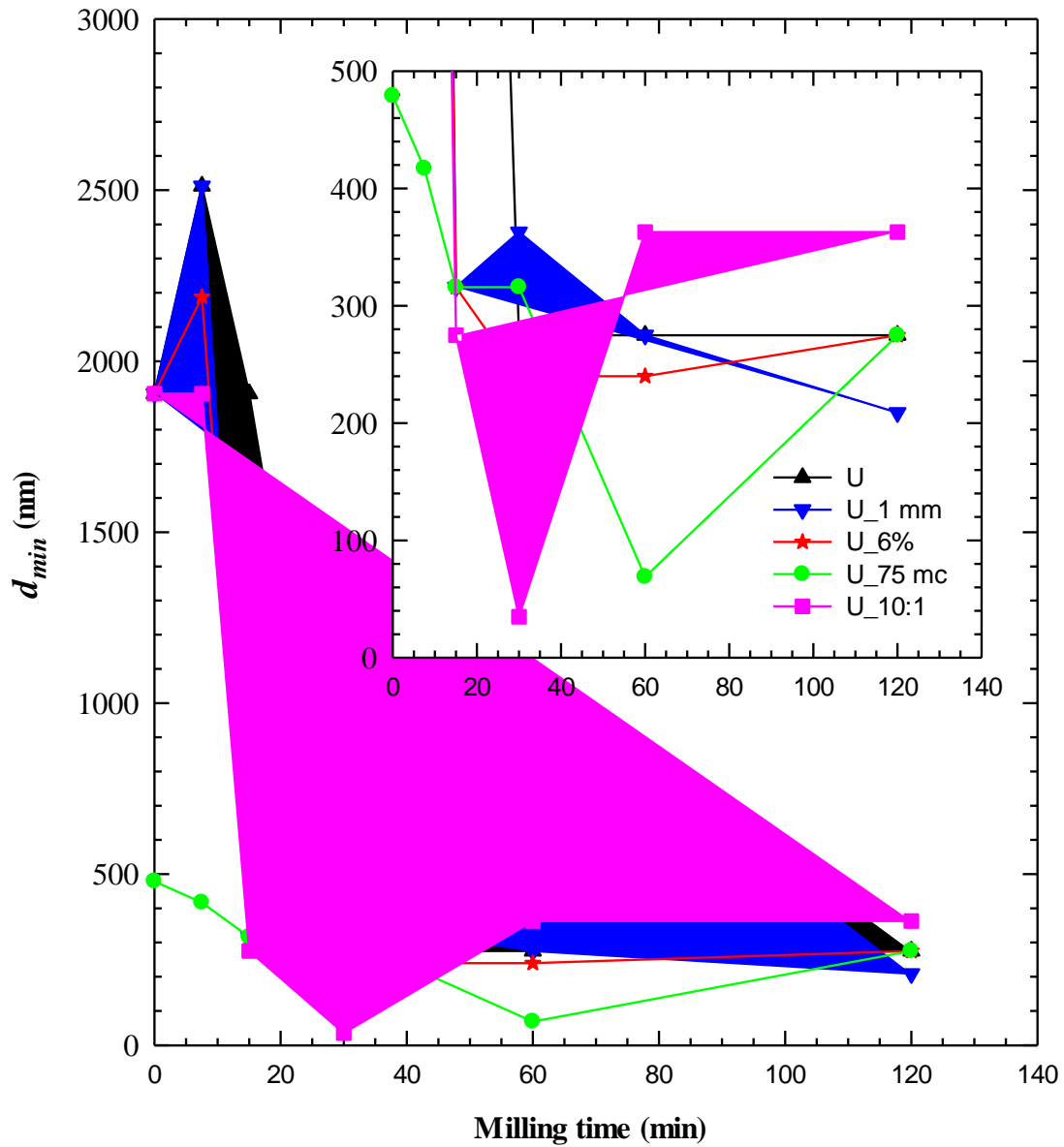


Figure 4: The change of d_{min} value by the milling time. The inner figure is magnification for $<d_{min} = 500$ nm.

3.2 Powder Yield Analysis

Figure 5 (a) shows the graph of powder mass according to the milling name. The maximum powder loss is 13.9 g for U_75 mc powder, while the minimum powder loss is 1.8 g for U_10: 1 powder.

Figure 5 (b) displays the graph of powder yield according to the milling name. Worst powder yield is 63.4% for U_75 mc powder, whereas the best powder yield is 90.5% for U_10: 1 powder. The reason for the lower yield percentage for U_75 mc powder is that the powder layered by accumulating in the bottom of the vial. This layering was thought to be because the SSA is larger if the initial size of the powder particle was fine powder. Results of measurement performed by using the laser size analyzer indicate that the SSA value is $0.07 \text{ m}^2/\text{g}$ for the U-3 mm material and $0.41 \text{ m}^2/\text{g}$ for the U_75 mc material (unmilled).

The reason for the high yield percentage for U_10: 1 powder can be attributed to the low mass of powder due to BPR. Thus, the force / energy value transmitted by the balls to the powder particles becomes higher.

In the literature, the best powder yield for a milled ulexite U_5 m powder with submicron particle size was determined as 89% (Kutuk, 2016). In this study, that of the milled ulexite U_10: 1 powder was found as 90.5%. Therefore, 1.5% better results were obtained.

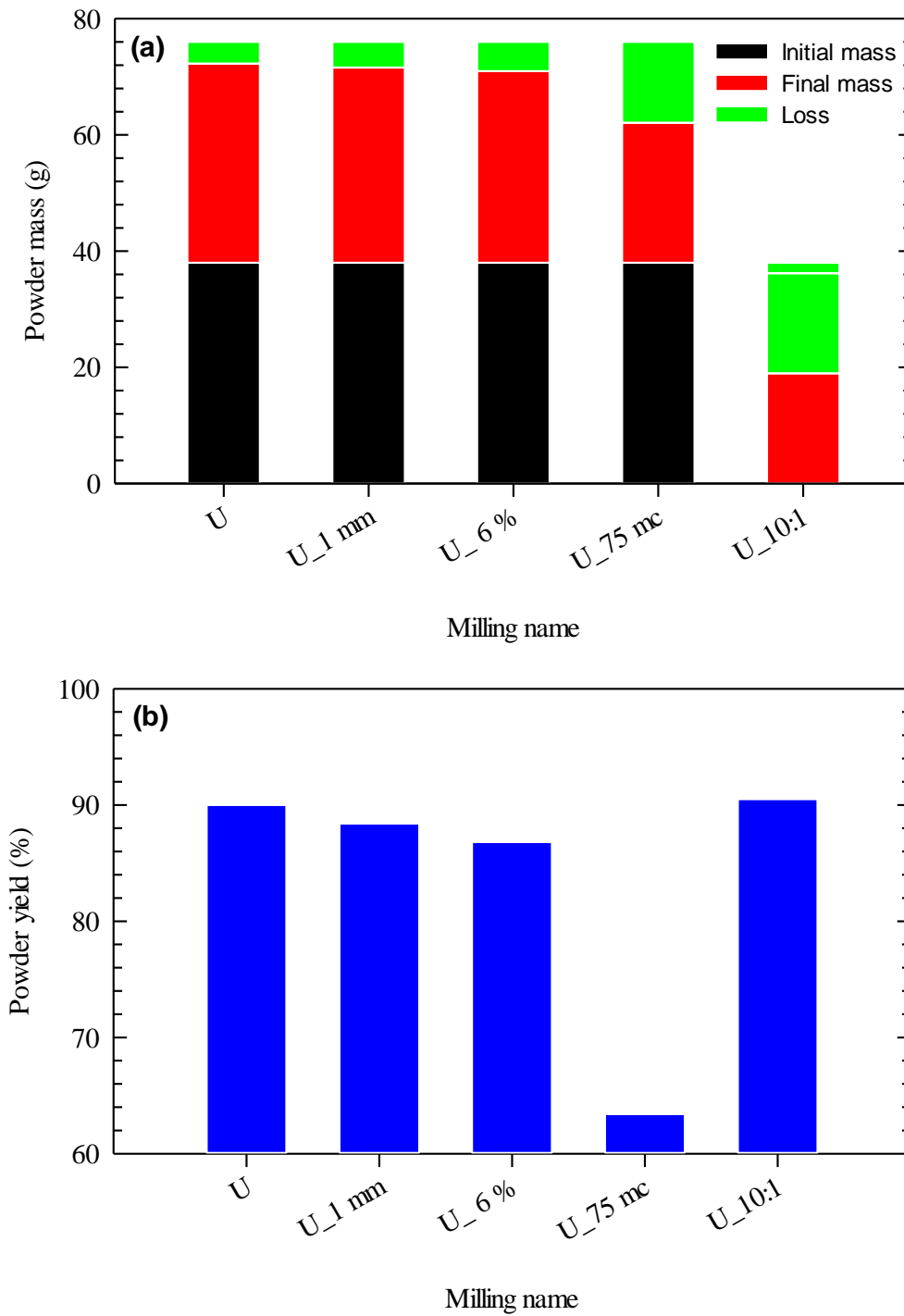


Figure 5: (a) Powder mass graph and (b) powder yield graph

3.3 POM and SEM Analyses

The photograph of the U-3 mm material on the millimeter paper is as shown in Figure 6 (a). A particle size of this material has a minority of less than 10 mm to 3 mm and a majority of less than 3 mm. That is, the particle size of the U-3 mm material is too large and its particle size distribution range is very broad. With this result, laser scattering size analyzer results ($d_{90}=816.708 \mu\text{m}$ and $d_{50}=444.220 \mu\text{m}$) support each other.

The POM image under x40 magnification for 30 min milling time of U_10: 1 powder appears to be presented in Figure 6 (b). As a result of milling process, it was found that the particle size of the material fell below $50 \mu\text{m}$, that is, it became powder. In addition, it was determined that the powder color changed into a single color (white) and that the agglomerating occurred. This result is in agreement with the result of a similar study of a milled ulexite mineral in the literature (Kutuk, 2016).

Figure 7 (a) indicates the SEM image of U_10: 1 powder for 30 min milling time under x500 magnification. It was observed that the powder particles agglomerated and the particle size changed from $20 \mu\text{m}$ to $<1 \mu\text{m}$. By milling the ulexite mineral, it was concluded that the particle size was much smaller and the particle shape had a smoother geometry. However, it was determined that the homogeneity of the powder improved as the particle size distribution range narrowed. These findings are in good agreement with the findings of the ball milling method for other materials in the literature (Kutuk-Sert, 2016; Varol & Canakci, 2013).

Figure 7 (b) presents a SEM image of U_10: 1 powder for 30 min milling time under x30k magnification. Under very high magnification, it was determined that the smallest powder particle size was below 100 nm. Namely, the particle size of the powder was observed at the nanoscale. The measurement result obtained from here confirms that from the laser size analysis.

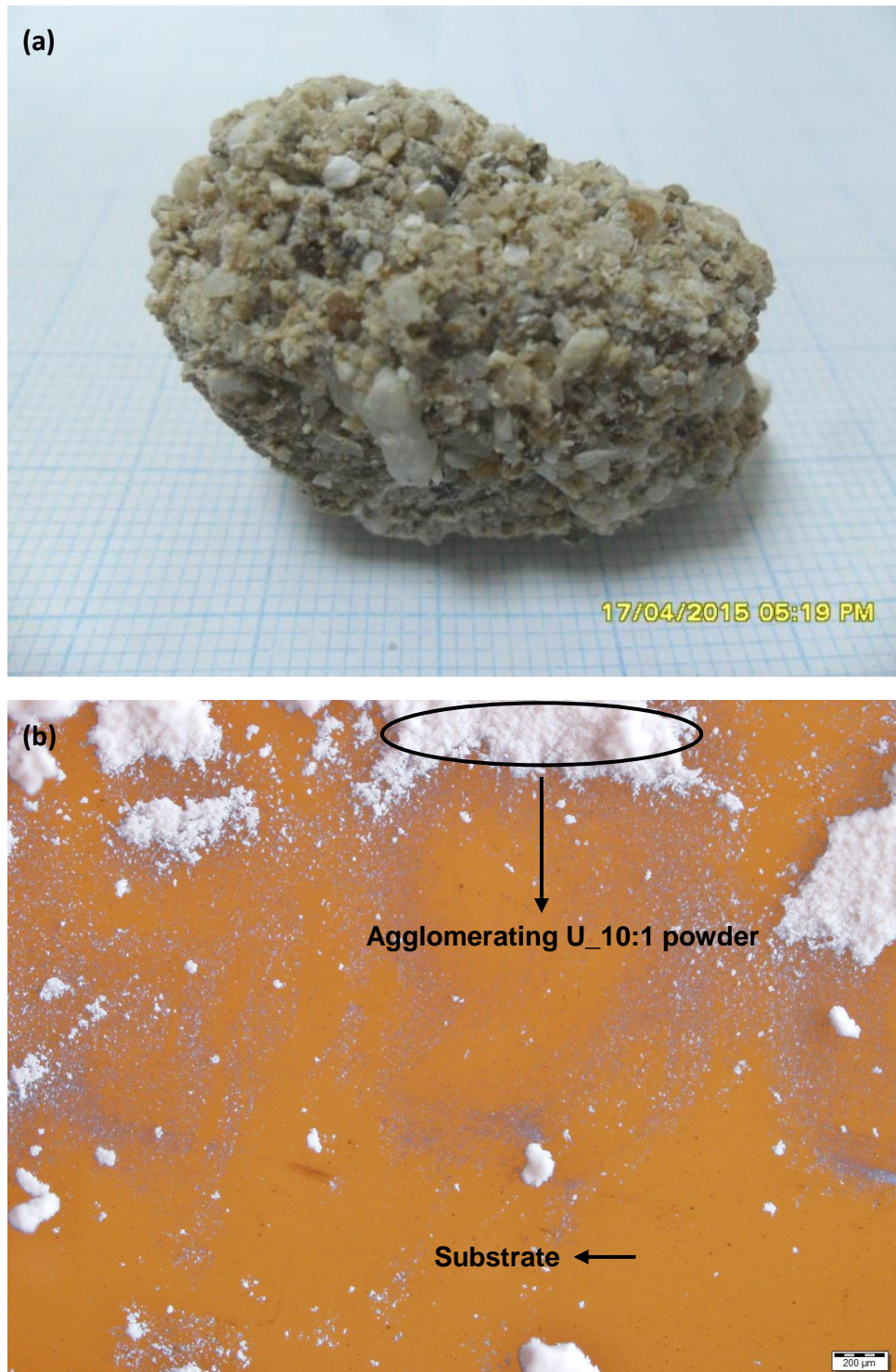


Figure 6: (a) Photo of U-3 mm initial material (b) POM image of the milled U₁₀: 1 powder under x40. The white color shows the U₁₀: 1 powder and the orange color shows the substrate.

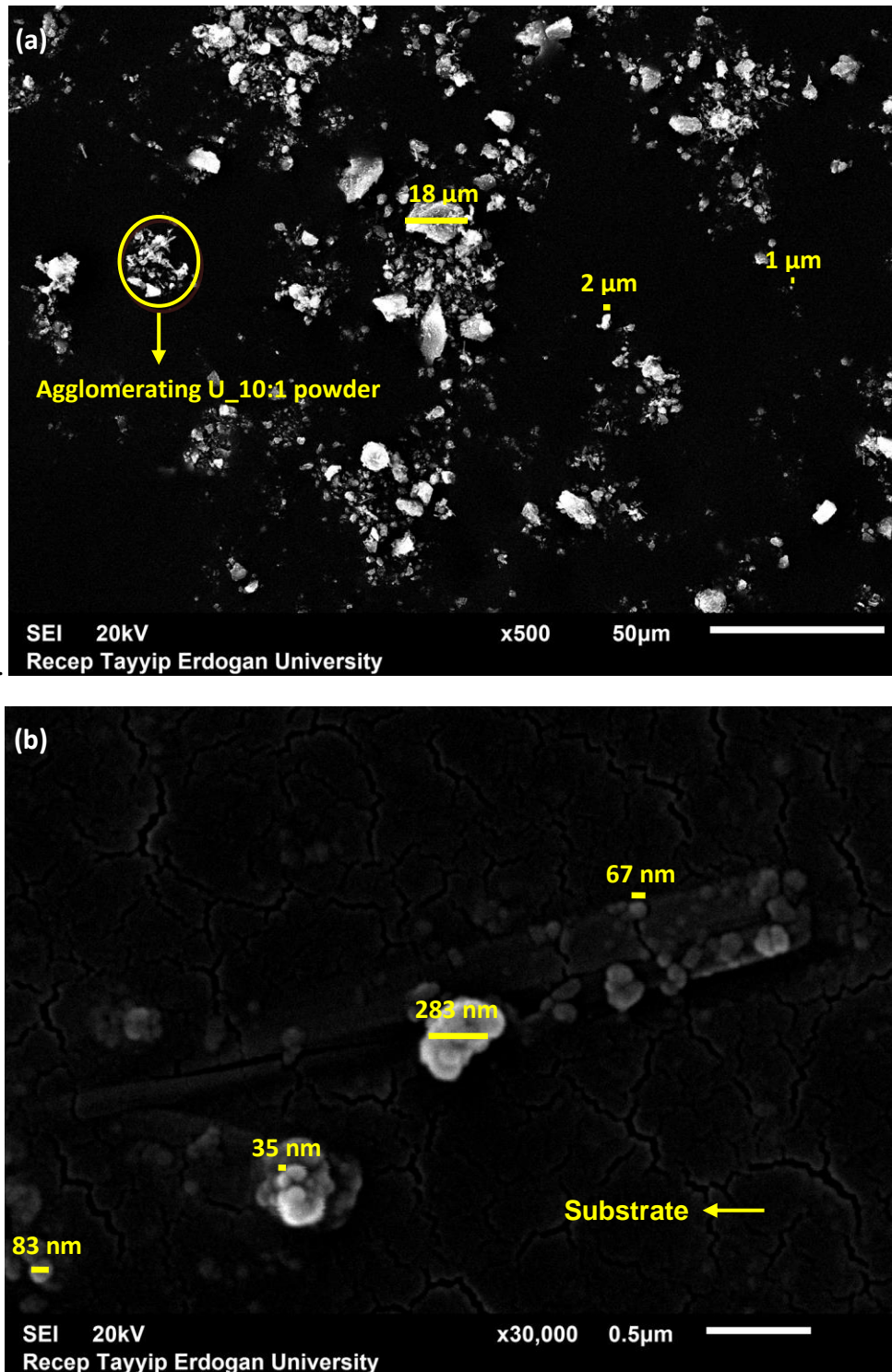


Figure 7: SEM images of the U_{10:1} powder: (a) x500 (b) x30k

4. Conclusion

The important conclusions can be summarized as follows:

- The smallest d_{50} value belongs to the U_10: 1 powder with 1.732 μm value. This showed that the BPR value in the milling parameters is more important than the values of the ball size, PCA and initial size.
- The smallest particle size was measured as 35 nm. Thus, the nanosized particle of the ulexite mineral was obtained.

For nanotechnology in future researches, the smallest d_{50} value may be detected below 1 μm when the milling parameters are considered.

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