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Effect of Blunging/Dispersion Parameters on Separation of Halloysite Nanotubes from Gangue Minerals

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Abstract: Clay minerals need to be dispersed with blungers before their utilization in the related industries due to their plastic properties, and size reduction is carried out in a wet medium. Clay minerals also contain impurities such as nonplastic materials in their structure. Mechanical dispersion parameters are important in the separation of clay group minerals (halloysite and kaolinite) from their typical non-clayey gangue minerals (quartz and goethite). In this study, the removal of impurities from halloysite ore obtained from Kızıldam, Turkey, was examined in terms of mechanical dispersion parameters, namely, feed size, blunging time and speed, pulp concentration, pulp temperature, and the aging process. The effect of these parameters on halloysite dispersion was determined by particle size, chemical, and mineralogical analysis, and optical and scanning electron microscope images. The results obtained from the studies of the mechanical dispersing and particle size distribution of the products indicated that the optimum dispersion parameters were determined as −10 mm feed size, 8 h, and 1000 rpm blunging time, and speed, 35% pulp concentration at 25 °C pulp temperature. Under these optimum conditions, a 72.3% amount of −38 µm clay product containing 35.6% of halloysite, 46.5% of kaolinite, 12.0% quartz, 1.9% goethite, 0.9% gibbsite, and 3.2% other minerals were obtained from the halloysite ore, having 30.5% of halloysite, 43.4% of kaolinite, 19.1% quartz, 2.9% goethite, 1.4% gibbsite, and 2.7% other minerals. In this study, it was understood that feed size, pulp concentration, blunging time, and speed were important parameters, while pulp temperature and the aging process had no significant effect on the mechanical dispersion of Kızıldam halloysite. In addition, impurities such as quartz and iron-bearing minerals were separated from the ore by blunging and sieving.

Keywords: halloysite; kaolinite; mechanical dispersion; blunging; purification; clay minerals

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1. Introduction

Kaolin mineral structure, which contains kaolinite, dickite, nacrite, and halloysite minerals, is formed by the repetition of a tetrahedral layer and an octahedral layer. The oxygen at all ends of silica tetrahedrons is in the same direction, so that the oxygen and/or hydroxyls, which may be present to balance loads, are shared by silicones in the tetrahedral layer and aluminum in the octahedral layer. While kaolinite mineral has the chemical formula of $Si_4Al_4O_{10}(OH)_8$, whose unit structure of Si_4O_6 comes from the silica tetrahedron layer and the unit structure of $Al_4O_4(OH)_8$ comes from the alumina octahedron layer [1,2], the ideal formula for halloysite is $Si_2Al_2O_5(OH)_4.nH_2O$, and the mineral is named 7Å and

10Å in the literature, depending on the n molecule water [3–5]. The n value is 0 for 7Å halloysite, and it reaches 2 in 10Å halloysite [6]. Therefore, chemical analysis of halloysite mineral with 7Å basal layer is the same as kaolinite mineral, however, halloysite 10Å mineral contains 2 moles more water [7,8]. As the molecular water content of the halloysite mineral increases, the basal opening between layers is enlarged (Figure 1).

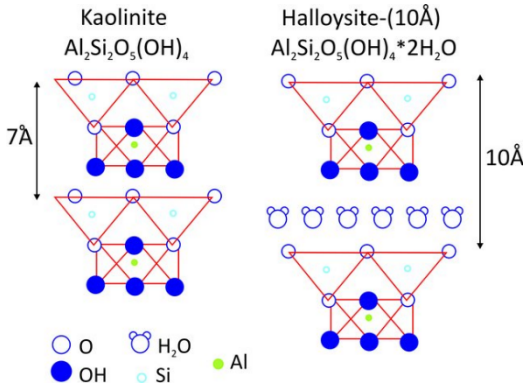


Figure 1. Demonstration of kaolinite and halloysite 10Å minerals [9].

Kaolin group minerals can be classified according to their usage areas, mineralogical composition, or physical characteristics [10]. Halloysite is primarily used in ceramic production as well as paper, paint, plastics, and other industrial branches. The commercial value of halloysite is determined by its whiteness, purity, particle size distribution, and sintering behavior in the ceramic industry, and the market size is increasing continuously. There are many halloysite deposits in the world, but most of the pure reserves are found in New Zealand and can be sold without purification. Commercial halloysite reserves in Turkey are formed by hydrothermal alteration in the Balıkesir and Canakkale provinces [11]. Besides, high-quality kaolin clays are used in mullite production, therefore low-quality kaolin clays need to be purified with ore dressing and beneficiation methods.

Halloysite deposits have impurities such as quartz, muscovite, limonite, anatase, illite, iron minerals, and some organic substances that negatively affect the quality of the raw material. Many studies have been carried out to investigate the removal of impurities in an economical way. The halloysite purification begins with the detection of impurities by eye within the mine site and removal by triage process in terms of color difference. Coarse-grained impurities are removed by using screens, hydro cyclones, and magnetic separators, while fine-grained impurities require special methods to be applied, such as centrifugation, flotation, and leaching [12–15]. Halloysite ore must be dispersed in terms of particle size reduction because the grinding process damages the halloysite form by breaking nanotubes, which causes forming finer particles of gangue. Therefore, it will be difficult separating these finer particles from clay minerals is difficult [16]. The dispersing process is carried out by adding water and dispersants in blungers and the dispersion parameters must be optimal in terms of separating clay minerals, which are fine-sized in natural form as compared to the non-plastic minerals. After the dispersion process is completed, the coarse-sized (>44 μm) impurities are removed using hydro cyclones or sieves and classified according to the particle size [17].

The structure of clay minerals and the factors related to mechanical blunging are significant factors in the dispersion process. The aggregated stability of clay suspensions is affected by soil organic carbon, clay minerals, Fe, and Al oxides that behave as binding agents, which are related to clay mineral structure [18–20]. Besides parameters that are related to suspension conditioning, blunging mechanics and dispersant type are the controllable factors for the dispersion process.

In traditional ceramic tile body production, raw kaolin is milled with other raw materials and sieved to finer particle size [21]. In the milling operation, coarse-sized impurities are ground along with kaolin minerals and are included in the ceramic body

slip. These impurities cause defects on the surface of tiles that lower production quality. This study aimed to determine the dispersion characteristics of the Kızıldam halloysite ore with a mechanical blunger and obtain the optimum conditions for removing impurities from the halloysite ore. For this purpose, the effect of several mechanical parameters such as blunging speed and time, pulp concentration, temperature, and aging on the dispersion properties of the halloysite sample was investigated in detail. Then, the products obtained at the optimum conditions were determined with the chemical and mineralogical analyses, as well as optical microscopy and SEM studies. It is thought that the information obtained from this study will help produce the ore with a higher content of kaolinite and halloysite, which can be used in the ceramic industry.

2. Materials and Methods

2.1. Materials

The raw halloysite ore used in this study was obtained from Kızıldam village, Yenice district of Çanakkale province, Turkey. The ore was initially crushed using a laboratory-type jaw crusher and reduced to −10 mm particle size. Subsequently, the crushed sample was classified by sieving and dried in the laboratory oven at 60 °C until the constant weight was obtained, and the moisture content was determined as 9.4%.

Finally, chemical and mineralogical analyses of the sample were carried out with Axios Max model X-ray Spectrophotometer device (XRF, PANalytical, Almelo, The Netherlands)and X'pert Pro MPD X-ray Diffractometer (XRD, PANalytical, Almelo, The Netherlands) between 3–70°, 2θ, respectively. Rietveld method was used to determine the quantitative XRD results. Duplicate analysis was done for each sample, and the average values were taken into account.

As seen from the chemical analysis of the sample presented in Table 1, the contents of SiO_2, Al_2O_3, and Fe_2O_3 of the sample were 50.9%, 29.7%, and 3.9%, respectively.

Table 1. Chemical analysis of raw Kızıldam halloysite ore.

Compound	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	Na_2O	K_2O	LOI
Content (%)	50.9	29.7	0.7	3.9	0.2	0.4	0.2	1.1	12.0

LOI: Loss on ignition.

Additionally, the mineralogical analysis of the sample shown in Figure 2 indicated that the sample contained 43.4% kaolinite and 30.5% halloysite, along with gangue minerals of 19.1% quartz and 2.9% goethite.

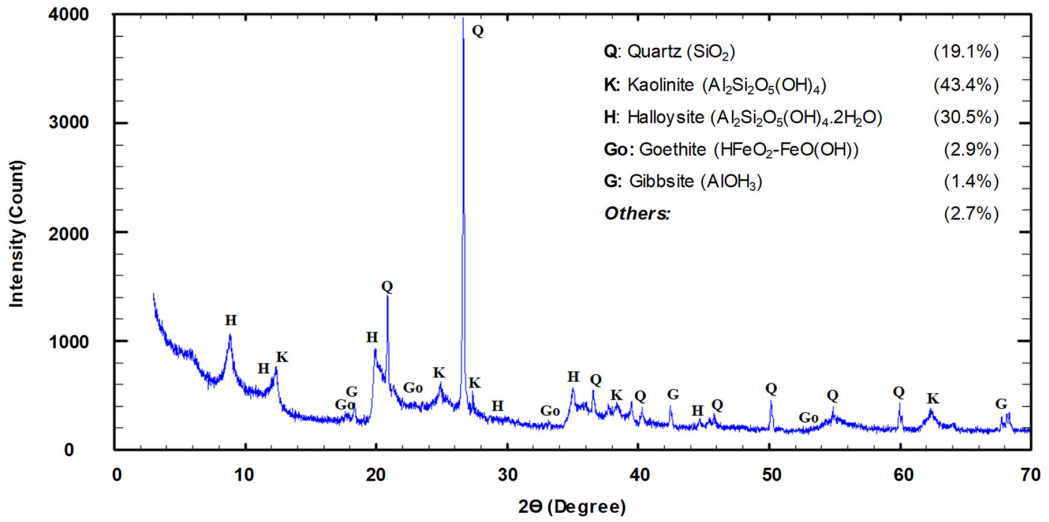


Figure 2. XRD result of raw Kızıldam halloysite ore.

2.2. Methods

An overhead mixer was used for the mechanical dispersion (blunging) studies in which plastic clay minerals were liberated from non-plastic hard minerals without changing their sizes. Normally, blunger is used in the ceramics industry for this purpose. For this reason, that mixer was used as a blunger to adjust the industrial conditions in the laboratory.

Viscosity measurements of samples were performed with an NDJ-1 viscometer and the optical imaging studies were executed with a Soif Bk-Pol Trinocular microscope. pH and temperature measurements of the pulps were carried out with an Isolab pH meter. Scanning electron microscope (SEM) images were taken with the JSM-7100F model (JEOL, Tokyo, Japan) and the EDX spectrums were measured using the X-Max model detector. In order to increase the conductivity of the samples, $8 \cdot 10^{-1}$ mbar/Pa vacuum was applied and gold-palladium (80–20%) coating was performed by applying a voltage of 10 mA.

Within the scope of halloysite dispersion studies with mechanical force, the halloysite ore feed size (−10, −5, −2 mm), blunging speed (500, 1000, 1500 rpm), and time (0, 1, 2, 4, 8, 16, 32 h), aging (1, 2, 4 days), pulp concentration (20%, 35%, 50%), and pulp temperature (25 °C and 50 °C) parameters were investigated in terms of particle size distribution and chemical composition of the resulting products.

In the case of dispersion studies at 50 °C pulp temperature, a Sci-LOGEX magnetic stirrer/heater was used to keep the pulp temperature constant. Before each test, a pre-test was made, and the temperature of the pulp was measured with a thermometer if the temperature was constant at the desired value or not.

In the experimental studies, the halloysite suspension was dispersed in tap water which had a pH of 7.4 at 25.4 °C and the dispersed suspension was sieved using 38, 75, 150, 250, 500, and 1000 µm sieves. The sieved materials were dried at 60 °C and weighed to determine the final particle size distribution of the products. Since clay minerals would become dispersed and in fine particle size, the clay content in −38 µm particle size was determined according to the change in Al_2O_3 ratios obtained from XRF analyses. Figure 3 shows the flowsheet of the experimental study.

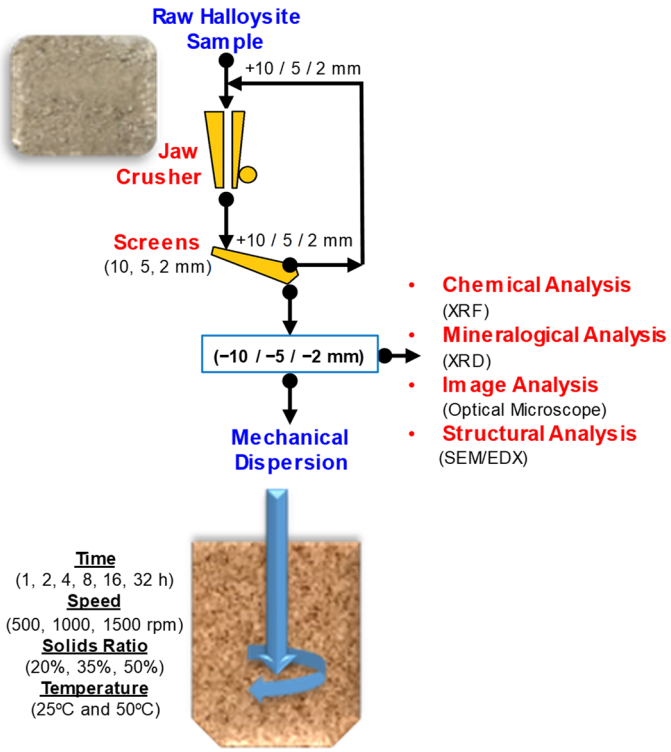


Figure 3. Flowsheet of the study.

3. Results

3.1. Effects of Feed Size and Blunging Time on Dispersion

Grinding is the most preferred method of reducing the particle size of the particles, especially in hard and non-plastic ores. However, clay minerals can be gained by dispersing in mechanical mixers in an aqueous environment because they are plastic materials and are naturally fine-sized [17]. Therefore, it can be considered that clay minerals are easy to separate from associated gangue minerals through size classification methods and are not recommended to be milled, since ground gangue minerals deteriorate the effective separation. Eliminating milling and applying disintegration of clayey minerals in the water will result in ultrafine clayey minerals leaving the gangue minerals at coarse sizes. In addition, a tubular form of halloysite mineral is affected negatively during dry and wet grinding, causing a devaluation of the product [16,22].

It is well-known that the specific gravity of both halloysite and quartz are so close to each other that it prevents the separation of those based on gravity. Thus, the difference in particle size of those minerals was planned as a parameter for effective separation. Clayey minerals have originally fine sizes when disintegrated in water and quartz, and need comminution to reach down to finer sizes similar to clays. To prevent the elimination of particle size difference on separation feed, we planned to keep size at coarse sizes to eliminate the size reduction of quartz during blunging. For this reason, the effect of feed size on the dispersion behavior of the halloysite sample was investigated with different feed-sized samples (−10 mm, −5 mm, and −2 mm) to determine the relationship between the feeding size and the change in the quality of the sample after the blunging process in terms of coarser and finer feeding sizes. The suspensions prepared at 35% pulp concentration were dispersed using an overhead mixer as a function of blunging time. The results of the PSD test of the products seen in Figure 4 showed that the amount of fine fraction increased with increasing the time for each feed size, which indicated that the clay minerals dispersed successfully during the blunging.

The success of the process was evaluated based on the amount of −38 μm size fraction of blunged materials (Figure 5). As seen in Figure 5, the amount of −38 μm material increased with the increase in blunging time. On the other hand, the amount of −38 μm material increased with the coarser feeding size for the same blunging period. Thus, it was determined that the clay minerals, which are plastic, passed to the finer size more quickly with mechanical dispersion that was made in the feed size of −10 mm. In addition, at the end of the 8 h of blunging time, the material amounts of −38 μm size for −10 mm, −5 mm, and −2 mm feed sizes were determined as 72.3%, 70.7%, and 66.3%, respectively (Figure 5).

Additionally, the contents of SiO_2, Al_2O_3, and Fe_2O_3 of −38 μm size samples for each feed size were determined and presented in Figure 6a–c, respectively. Particularly, the investigation of the Al_2O_3 change in −38 μm particle size aimed to determine the conditions in which the clay minerals were most concentrated. Previous studies on similar samples taken from the same region have determined that the halloysite, kaolinite, and alunite minerals were found as Al_2O_3 sources in the ore [11,23]. Theoretically, the Al_2O_3 content of halloysite and kaolinite is 39.5%. This indicated an increase in the clay mineral content of the ore containing Al_2O_3, which was 29.7% in raw ore. The highest Al_2O_3 content was determined as 32.9% under the conditions of −10 mm feed size at 8 h of blunging time (Figure 6b).

Murray (2006) [17] defined the size of +44 μm as a coarse-sized group after blunging kaolin ore in an aqueous environment, stating that the group consisted of quartz sand, mica, and heavy minerals. In Figure 6a, the change of SiO_2 content in the −38 μm size fraction at the end of the blunging process was given. As the suspension was sieved in the aqueous medium without mechanical blunging (0 h), high SiO_2 content was thought to be caused by the quartz mineral under 38 μm of particle size. As the blunging time increased, the SiO_2 content in the samples decreased irregularly for up to 8 h, and then began to increase slowly. This increase indicates that after 8 h of blunging, coarse-grained quartz minerals in the ore began to crumble due to the effect of friction force. Additionally, the lowest SiO_2

and Fe_2O_3 were 48.7% and 2.7%, respectively (Figure 6a–c). Additionally, 8 h was chosen as an optimum blunging time.

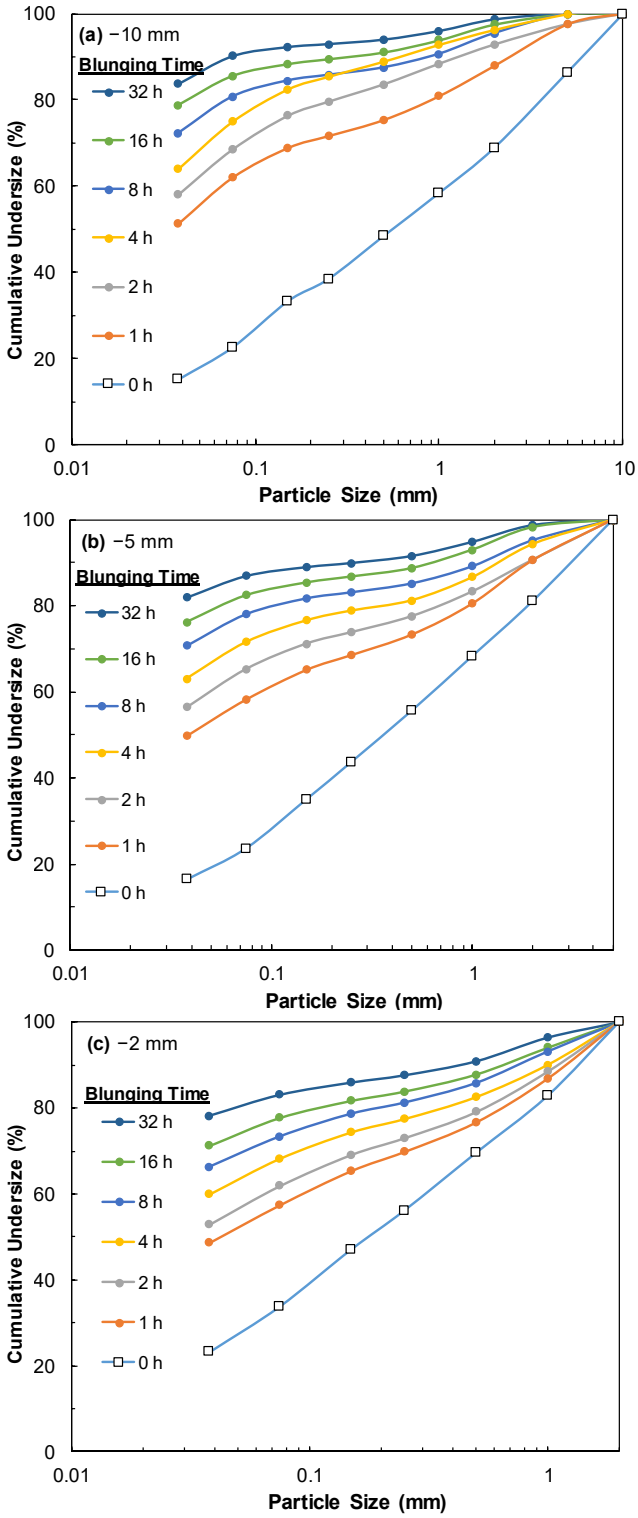


Figure 4. Particle size distribution of halloysite products as a function of blunging time at different feed sizes (−10 mm, −5 mm, and −2 mm) (1000 rpm blunging speed and 35% pulp concentration at room temperature, 25 °C, no aging).

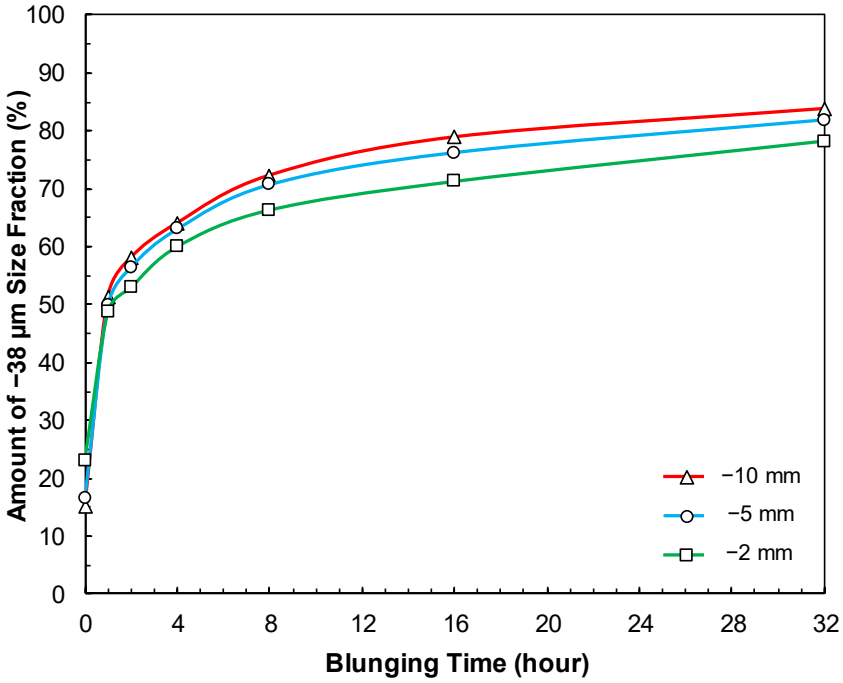


Figure 5. The amount of −38 μm size fraction products according to feed size and blunging time (1000 rpm blunging speed and 35% pulp concentration at room temperature, 25 °C, no aging).

It was seen that −10 mm of feed size was enough to disperse suspension in terms of particle size as compared to −5 mm and −2 mm feed sizes, and there was no need for unnecessary crushing for better dispersion. It was also seen that −10 mm of feed size led to an increase in −38 μm particle size quantity and Al_2O_3 content, along with blunging time. The probable reason for this situation was the free particles in the liquid environment which caused a lower viscosity, and bigger particles in the −10 mm feed size acted as grinding media, thus the dispersion and particle size reduction were effective.

3.2. Effect of Blunging Speed on Dispersion

The blunging speed was changed to 500 rpm, 1000 rpm, and 1500 rpm, while the other parameters were arranged and kept constant at −10 mm of feed size, 8 h of blunging time, and 35% pulp concentration. The effect of blunging speed on dispersion was examined in terms of the amount and chemical analysis of the −38 μm size fraction of the products (Figure 7).

As shown in Figure 7a, the amount of materials that were sieved −38 μm after the dispersion process in 500–1000–1500 rpm blunging speeds was found to be 63.6%, 72.3%, and 76.2%, respectively. Additionally, while Al_2O_3 content with a blunging speed of −38 μm at 1000 rpm was 32.8%, Al_2O_3 content of −38 μm was determined as 31.7% and 31.5%, respectively, at 500 rpm and 1500 rpm blunging speeds (Figure 7b). As seen from Figure 7a, the blunging speed at 500 rpm was not enough for the dispersion of clay minerals and the Al_2O_3 value was lower compared to 1000 rpm. At 1500 rpm blunging speed, SiO_2 and Fe_2O_3 contents increased from 48.5% to 49.2% and 2.7% to 3.9%, respectively, and Al_2O_3 decreased from 32.8% to 31.5% as compared to 1000 rpm. This indicated that as the blunging speed increases, the content of hard minerals in −38 μm size fraction as quartz and iron-bearing minerals were simultaneously comminuted together with clay minerals and passed to −38 μm size fraction. Additionally, 1000 rpm was chosen as an optimum blunging speed.

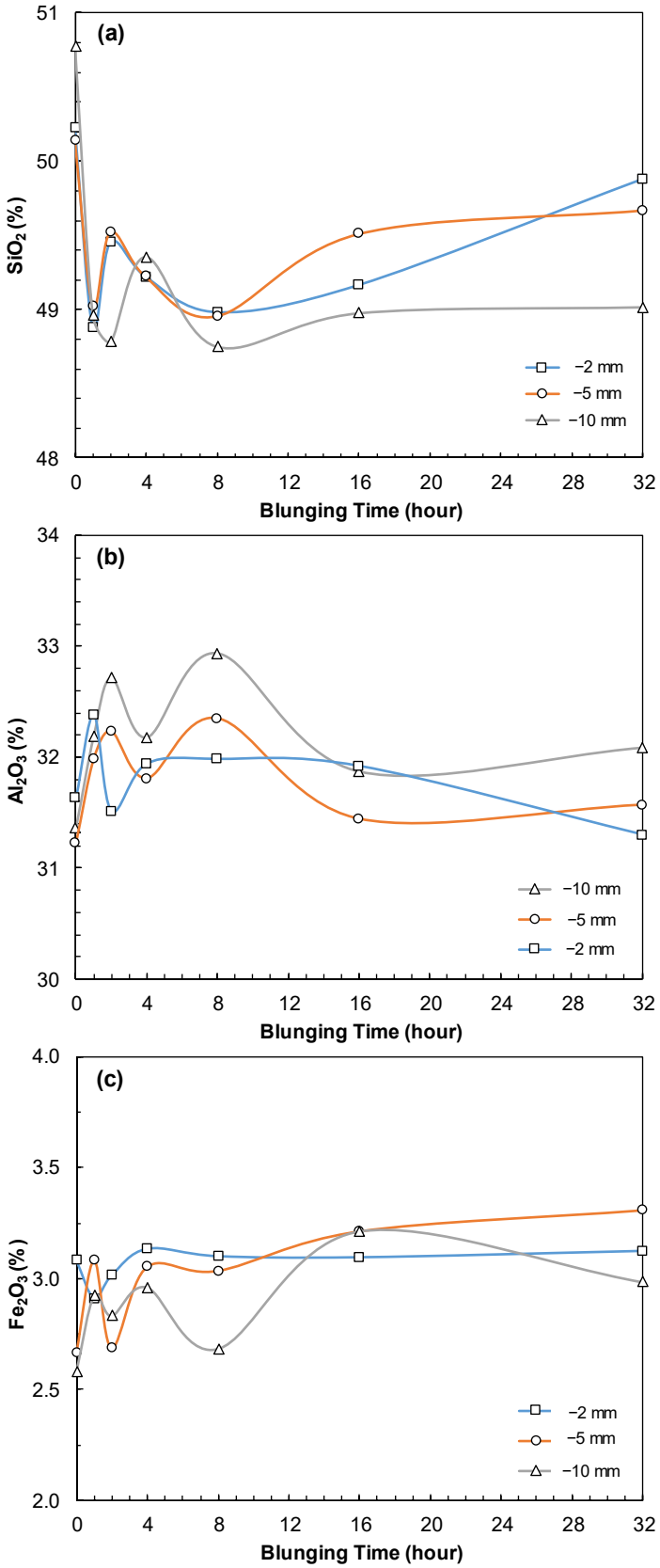


Figure 6. (**a**) SiO_2, (**b**) Al_2O_3, and (**c**) Fe_2O_3 contents of −38 µm size fraction as a function of blunging time (1000 rpm blunging speed and 35% pulp concentration at room temperature, 25 °C, no aging).

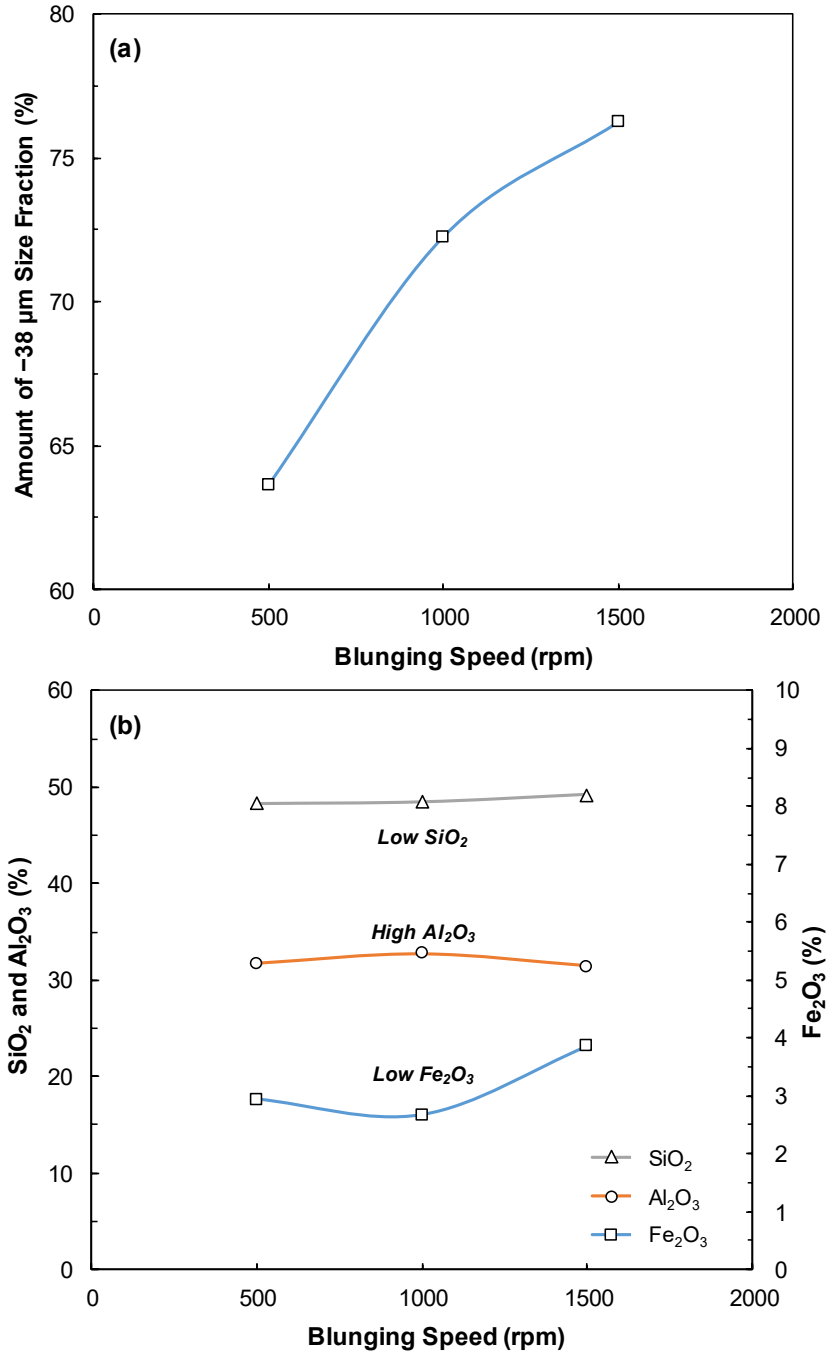


Figure 7. (**a**) The amount and (**b**) Al_2O_3, SiO_2, and Fe_2O_3 contents of −38 µm size fraction as a function of blunging speed (Feed size −10 mm, 35% pulp concentration at room temperature, 25 °C, no aging).

3.3. Effect of the Pulp Concentration on Dispersion

Halloysite ore was agitated through the conditions of −10 mm feed size, 1000 rpm blunging speed during 8 h at 20, 35, and 50% pulp concentrations. The amounts of −38 µm sized material were determined as 63.1%, 72.3%, and 74.9% for the pulp concentrations of 20, 35, and 50%, respectively (Figure 8a). The Al_2O_3-SiO_2 contents of −38 µm sized material obtained from experiments that were done in the conditions 20%, 35%, 50% of pulp concentrations were determined as 31.8%−49.5%, 32.8%−48.5%, 31.5%−49.8%, respectively (Figure 8b). In reality, there is a 1% of Al_2O_3 and SiO_2 content difference among pulp concentrations in the chemical analyses, which indicates a nearly 2.5% of clay mineral content difference for the mineralogical content of the samples.

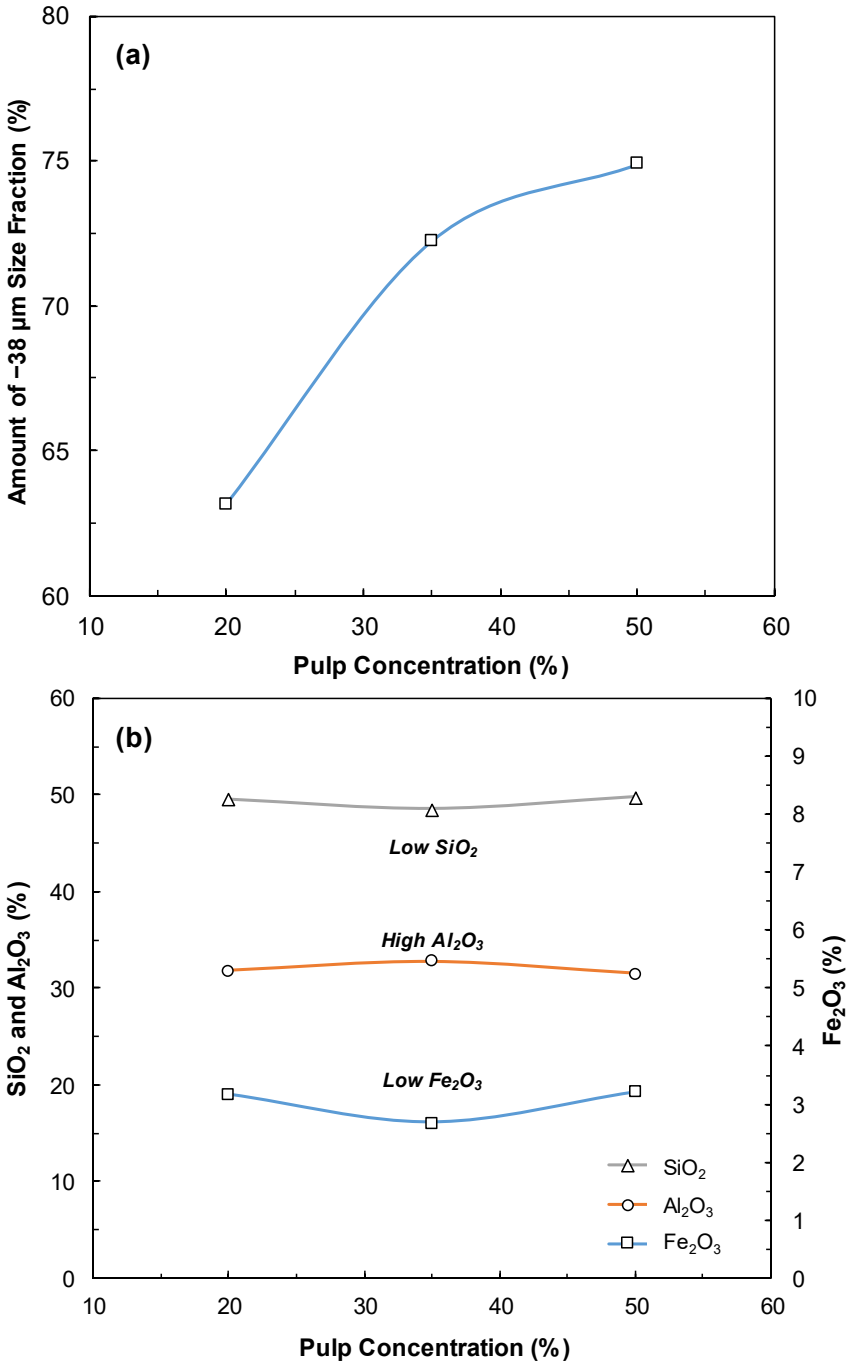


Figure 8. (**a**) The amount and (**b**) Al_2O_3, SiO_2, and Fe_2O_3 contents of −38 µm size fraction as a function of pulp concentration (Feed size −10 mm, blunging speed 1000 rpm, at room temperature 25 °C, no aging).

Following blunging at 35 and 50% pulp concentrations, the amount of the −38 µm materials remained close to each other and lower at 20% pulp concentration. This is explained by the fact that at 20% pulp concentration, the friction does not occur sufficiently, and the nonswelling clay particles remain agglomerated because the particles come into contact with each other less. The increase in the pulp concentration of pulp results in higher viscosity since water molecules are too close to enter clay particles, and Van der Waals bonds between the particles are high [24]. Therefore, the increase in plastic viscosity leads to high particle packing. The plastic viscosity raises with compact particle–particle interaction and a high pulp concentration for halloysite. The shape of the halloysite affects the flow

characteristics of the slip. The short lath-shaped halloysites show higher plastic viscosity compared to the long tubular and spheroidal-shaped ones [25]. Yield stress also increases parallel with inter-particle contact, which is a result of the high pulp concentration [26].

As shown in Figure 8, similar particle size distribution characteristics at 35% and 50% pulp concentrations indicated that the clay minerals had reached saturation in terms of the amount of water required for dispersion. In industrial terms, although it is thought that the amount of energy required to reach the same particle size distribution will decrease in the blunging process as the pulp concentration increases, on the other hand, low viscosity is also preferred for the transmission and sieving process of the pulps.

3.4. Effect of the Pulp Temperature on Dispersion

In industrial practice, the flow resistance or viscosity of the pulp is reduced with high temperature, allowing it to reach increased capacities in the preparation process, while the amount of unit energy required for blunging the product decreases. In order to test the effect of the pulp temperature on blunging, which is defined as the amount of −38 µm sized material, some blunging tests in different pulp temperatures were carried out. The pulp temperature was increased to 50 °C from room temperature of 25 °C and the other parameters such as feed size (−10 mm), blunging time (at 1000 rpm), and the pulp concentrations (at 35%), were kept constant. The change in particle size is illustrated in Figure 9. When the pulp temperature increased from 25 °C to 50 °C, no significant difference was observed in the amount of −38 µm sized material.

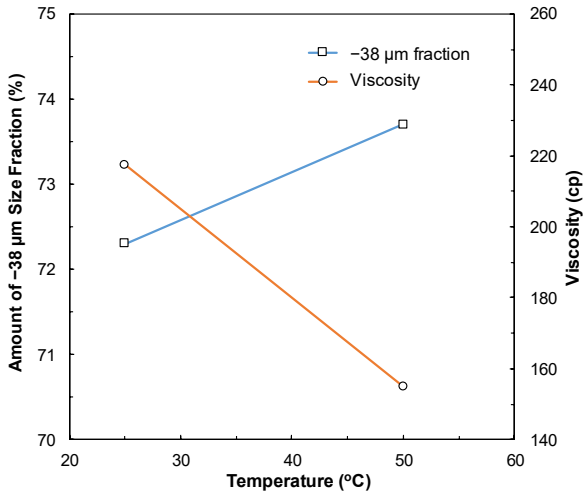


Figure 9. The change in the −38 µm sized material amount as a function of temperature (Feed size −10 mm, 35% pulp concentration, blunging speed 1000 rpm, no aging).

Temperature increment disrupts the face-to-edge form of clay particles, thus inter-particle forces and yield stress are reduced. However, viscosity shows a slight decrement [27,28]. Since the difference in pulp viscosity for the operational pulp temperatures of 25 °C to 50 °C for 1–2–4–8 h of blunging times did not allow the grains to move sufficiently apart from each other, no significant change was observed in the amount of −38 µm size fraction, although the viscosity of the pulp will be lower with rising pulp temperature.

3.5. Effect of the Aging Process on Dispersion

The aging process is used in the industry to improve the pulp rheology, homogenization, and dispersion of clay minerals. To examine the effect of aging on particle size, the ore was agitated for 8 h at a blunging speed of 1000 rpm after aging in water for 1, 2, and 4 days at 35% pulp concentration and sieved at 38 µm. As shown in Figure 10, it was understood that the aging process had no significant effect on particle size. [29] showed that the aging behavior of suspensions varies with dispersant type and kaolin/bonding

clay ratio in their study of low and high plastic clay mixtures. The 2-layered kaolin group shows low swelling characteristics compared to 3- and 4-layered clay groups [30].

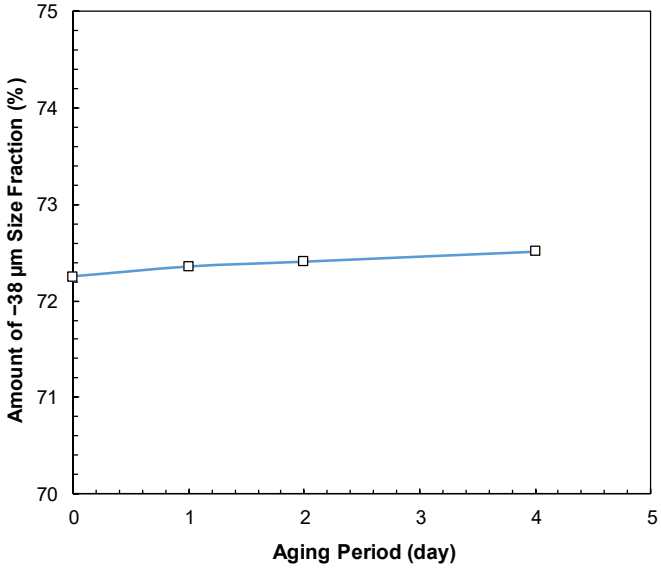


Figure 10. Change in material amounts of −38 µm sized material depending as a function of aging time (Feed size −10 mm, 35% pulp concentration, blunging speed 1000 rpm, at room temperature 25 °C).

On the other hand, the acidic nature of the clay ore causes calcium carbonate dissolution. As a result, divalent cation in the clay suspension increases while interparticle repulsion decreases [31]. In an acidic medium, kaolinite layers are in the form of the face (−charged) and edge (+charged) shaped, thus yield stress and viscosity are high [28]. Meanwhile, the pH of the suspension of Kızıldam halloysite changed from 4.5 to 4.3 for 20 and 50% of pulp concentrations.

It was observed that the 1–2–4 days aging process applied to Kızıldam Halloysite ore in room conditions had no significant effect on the particle size distribution of the ore. The fact that the aging process does not have a significant effect on the dispersion behavior was attributed to the non-swelling characteristic of the 2-layered type of kaolinite and halloysite minerals, and the acidic nature of Kızıldam halloysite ore could be one of the reasons for agglomerated form.

3.6. Characterization of the Products Obtained as a Result of Optimum Mechanical Blunging Parameters

In mechanical dispersion experiments of halloysite ore, the optimum conditions were gained as feed size of −10 mm, blunging time of 8 h, blunging speed of 1000 rpm, 35% of pulp concentration, 25 °C (room temperature), and no aging process. As a result of these experiments, chemical analyses were carried out after determining the amounts of particle size groups obtained from the experiments to examine the chemical change.

In Figure 11, SiO_2, Al_2O_3, LOI, and Fe_2O_3 contents of the particle size groups of the products from the test under optimum mechanical dispersion conditions were illustrated. As expected, the increase in Al_2O_3 indicated that clay minerals were concentrated in −38 µm. The increase in SiO_2 in the group of −500 + 250 µm indicated that quartz minerals were more present in this size fraction. On the other hand, the increase in iron content in parallel with the particle size indicated that the iron minerals were concentrated in coarser size groups.

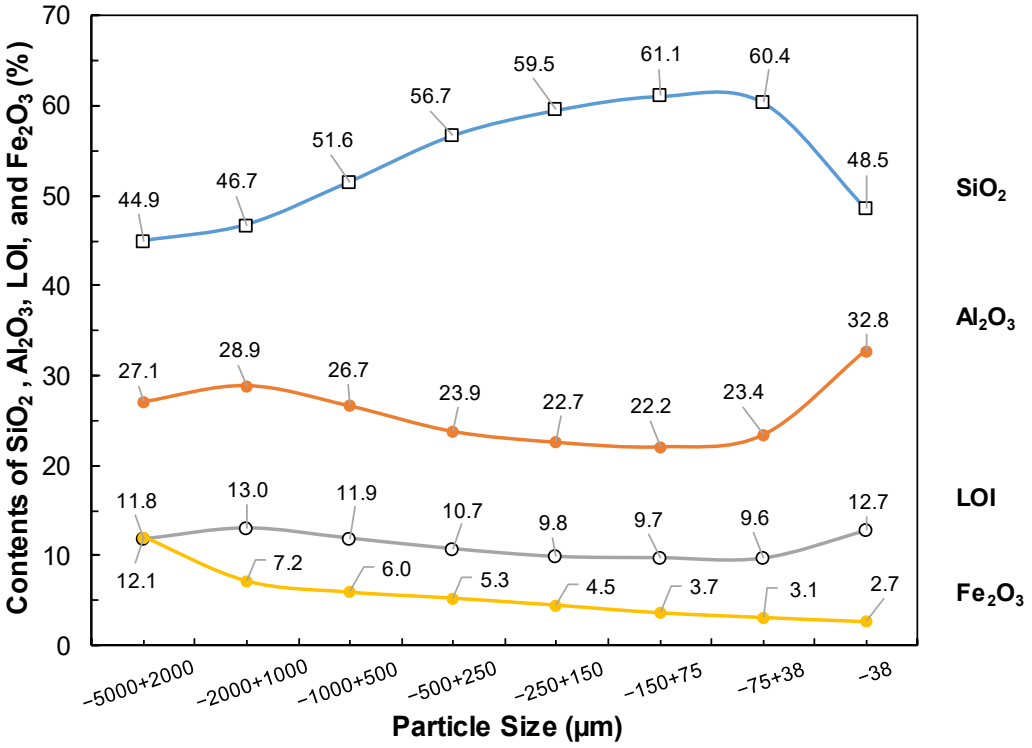


Figure 11. The change of SiO_2, Al_2O_3, LOI, and Fe_2O_3 contents of particle size groups in optimum mechanical dispersion conditions (Feed size −10 mm, 35% pulp concentration, blunging speed 1000 rpm, at room temperature 25 °C, no aging).

As obtained from the microscope images of particle size ranges, angular particles were seen in the samples without being subjected to the dispersing process, and it was seen that these angular particles turned into sub-angular grains within the mechanical dispersion. This indicated that the parts on the edges of the particles crumbled to the finer particle size with the dispersion process. In the mechanical dispersion experiments, the maximum Al_2O_3 content was reached in the −38 µm particle size, especially during the 8-h dispersion period, which was considered a finding to the increase in the content of kaolinite + halloysite in the ore. Optical microscope images taken before and after dispersion also showed that these irregular parts were relatively softer clay-type minerals and had moved to a finer size with the dispersion (Figure 12).

The optical images of −38 µm-sized materials could not be taken due to the difficulty encountered in the homogenous spreading of the agglomerated and very fine particles in this fraction, therefore SEM images were taken to characterize the type of clay minerals, tubular halloysite, and layered kaolinite structures were confirmed by SEM imaging. From the SEM images, it was measured that the widths of the tubes range between 78–150 nm and the lengths between 280–919 nm. It was also seen that the tubular halloysite minerals were agglomerated (Figure 13).

Figure 14 also shows that the amounts of kaolinite, halloysite, quartz, gibbsite, and goethite minerals obtained from the test under optimum conditions were 46.4%, 35.6% 12.0%, 0.9%, and 1.9%, respectively, for the size fraction of −38 µm. The results indicated that the contents of quartz, gibbsite, and goethite in the ore were reduced by mechanical blunging and screening.

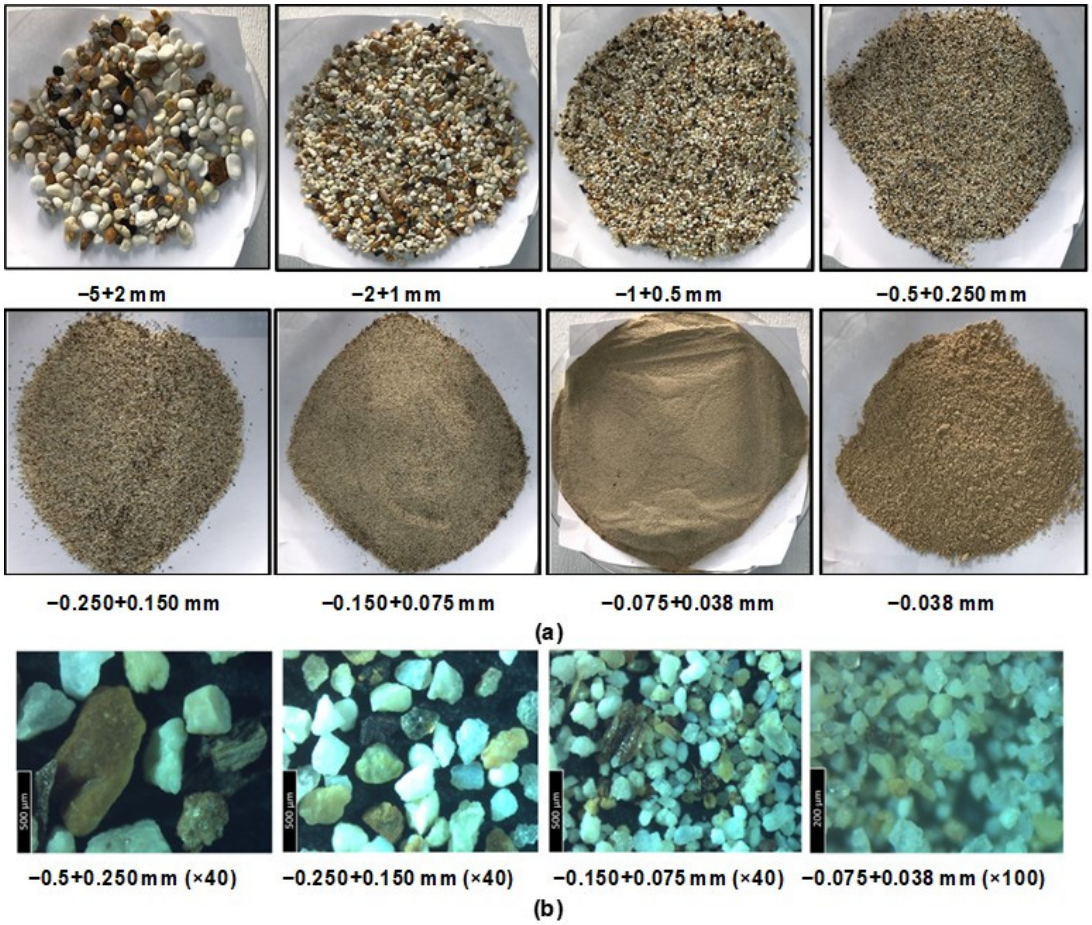


Figure 12. (**a**) Photographs of products as a function of particle size (**b**) Optical microscope images of the products at low particle sizes under optimum conditions (Feed size −10 mm, 35% pulp concentration, blunging speed 1000 rpm, at room temperature 25 °C, no aging).

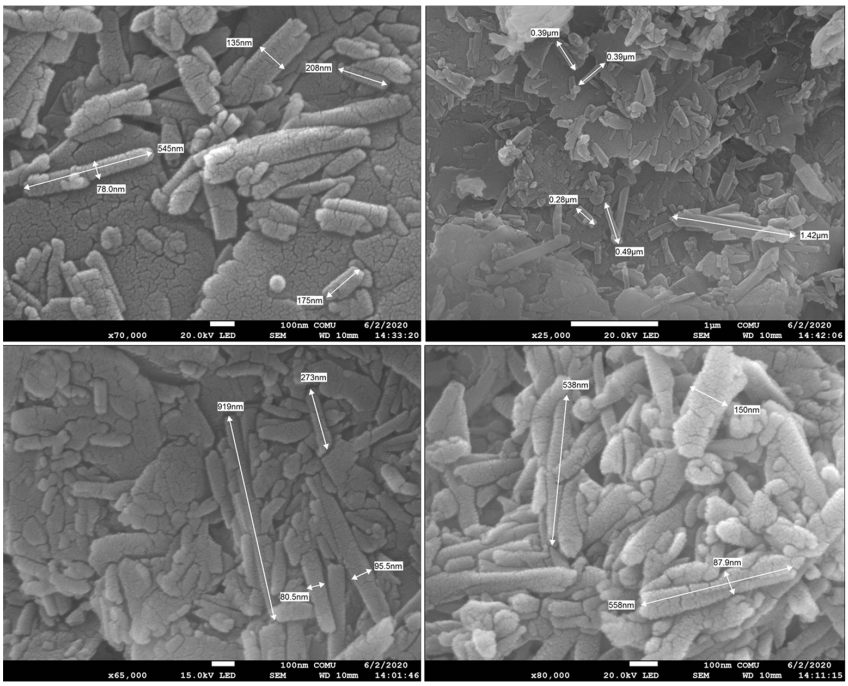


Figure 13. SEM Images of −38 µm sized material under optimum dispersion conditions.

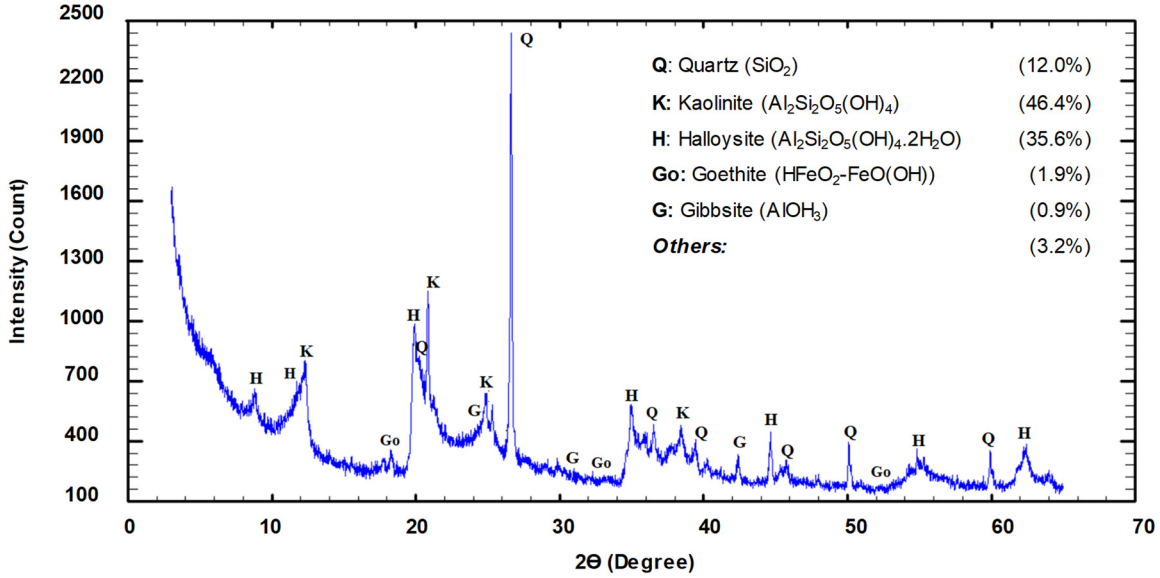


Figure 14. Quantitative mineralogical analysis of −38 μm sized halloysite ore under optimum conditions.

4. Discussion

The pure kaolin group clay minerals are one of the most important raw materials for producing different kinds of ceramic bodies. The ceramic market demands pure raw materials to manufacture ceramic products with high brightness color value. Notably, iron and titanium-bearing minerals in the raw materials result in darker body color and quality defects on the surface of the products.

The particle size reduction of the kaolin group clay minerals is performed with a traditional grinding method by ball mills in the ceramic industry, and grinding is an expensive operation compared to the blunging method besides impurities such as iron-bearing and quartz minerals, which are in coarse particle size and hard materials, are ground, blended into the body composition by grinding, and cause quality problems in the product. For this reason, this study was a pre-enrichment study to obtain the optimum or best conditions in the production of samples for the ceramic industry in terms of high Al_2O_3 contents and low SiO_2-Fe_2O_3 contents of the samples. In this context, the optimal or best conditions were determined according to maximum Al_2O_3 and minimum SiO_2-Fe_2O_3 contents that were gained from mechanical dispersion parameters as −38 μm sized material. In this regard, the effect of material feeding particle size, blunging speed and time, pulp concentration, pulp temperature, and aging on the dispersion properties of the halloysite sample was investigated in detail. It was understood that mechanical parameters had an important impact on the dispersion process in terms of chemical and mineralogical structure.

5. Conclusions

In this study, the effect of mechanical dispersion behaviors on the removal of the nonclayey minerals, such as quartz and goethite from halloysite ore, was investigated in detail. The parameters of feed size, blunging time and speed, pulp concentration, temperature, and the aging process were subjected to investigation.

The results indicated that the optimum (best) conditions for the dispersion of the halloysite sample were −10 mm of feed size, 8 h of blunging time, 1000 rpm of blunging speed, and 35% of pulp concentration conditions, 25 °C, and no aging was determined as the optimum mechanical dispersion parameters. Within the scope of mechanical dispersion studies of Kızıldam halloysite ore, it was determined that the amount of material that has moved to a finer size increases parallel to blunging speed, and after a certain value, quartz and iron-bearing minerals were in finer particle size under the influence of friction force.

Overall, 72.3% of −38 μm sized material was gained without the aging process. In the 1–2–4 days of the aging process, the −38 μm sized material was obtained as 72.4% to–72.5%, respectively. Additionally, 1:1 layered clay minerals do not swell much because of low ion adsorption capacity in the aqueous medium compared to the 2:1 and 3:1 layered clays. It was seen that 1:1 layered type clay mineral is the main reason that the wetting process showed no effect on the dispersion. The Al_2O_3-SiO_2 contents of −38 μm sized materials that were gained in the conditions 20%, 35%, 50% of pulp concentrations were consequently determined as 31.8–49.5%, 32.8–48.5%, and 31.5–49.8%. Particles could not come into contact with pulp concentration decrement, and after a certain value, it was seen that clay particles could not be dispersed enough. For 8 h blunging time, the 38 μm sized materials were changed from 72,3% to 73.7% with temperature increase from 25 °C to 50 °C. It was determined that the difference in viscosity caused by the temperature increase from 25 °C to 50 °C was not sufficient enough to disperse the pulp.

The test under the optimum operational parameters indicates that 72.3% amount of material with 32.8% Al_2O_3 content was obtained in −38 μm particle size. It was displayed that the angular particles turned into subangular grains with mechanical dispersion in the optical images. Quantitative XRD analyses showed that this particle size fraction consisted of 46.4% of kaolinite and 35.6% of halloysite minerals. The Fe_2O_3 content of the raw Kızıldam halloysite ore was reduced from 3.9% to 2.7 with a mechanical dispersion process such as a pretreatment method. This material can be used to improve the color properties of ceramic body or can be applied to magnetic separation, flotation, and leaching methods for further treatment to gain high-quality ceramic raw material. Besides, it was clear that the minerals were liberated in the optical microscope images in the +38 μm, and the Fe_2O_3 content was increased with particle size increment. The liberated iron-bearing minerals could be removed efficiently from the halloysite with magnetic separation methods in coarse particle size. In conclusion, feed size and blunging time were more effective parameters over blunging speed, pulp concentration, pulp temperature, and aging for mechanical blunging of Kızıldam halloysite clay.

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