IMPROVEMENT OF SINTERING PROPERTIES OF HALLOYSIT-KAOLINITE MIXTURE LOW QUALITY CERAMIC RAW MATERIAL BY MECHANICAL DISPERSION AND WET MAGNETIC SEPARATION

Emrah DURGUT[1,2], Mustafa CINAR[3*], Mert TERZI[1], Ilgin KURSUN UNVER[1], Yıldız YILDIRIM[4], Feridun BOYLU[5], Orhan OZDEMİR[1*]

[1]Istanbul University-Cerrahpasa, Department of Mining Engineering, Faculty of Engineering, Buyukcekmece, Istanbul, TÜRKİYE
[2]Canakkale Onsekiz Mart University, Can Vocational School, Canakkale, TÜRKİYE
[3]Canakkale Onsekiz Mart University, Department of Mining Engineering, Faculty of Engineering, Canakkale, TÜRKİYE
[4]Kaleseramik Research and Development Center, Canakkale, TÜRKİYE
[5]Istanbul Technical University, Department of Mineral Processing Engineering, Maslak, Istanbul, TÜRKİYE

**Corresponding author: mcinar@comu.edu.tr and orhanozdemir@iuc.edu.tr*

A B S T R A C T

As in all sectors, there should be no disruptions in the supply chains to ensure the continuity of the need for quality kaolin group of clay minerals and production safety, which the ceramics industry needs. Therefore, countries turn to domestic raw material resources to meet the raw material needs of their sectors and conduct research for necessary improvements. In this study, in order to improve the sintering properties of a low-quality clay ore containing halloysite and kaolinite, it was aimed to obtain a low iron content product by reducing the high iron (3.9%) content of the ore by removing iron and titanium minerals with mechanical dispersion and wet magnetic separation processes to use in the ceramic industry.

XRD analysis revealed that the ore contained halloysite, kaolinite, and quartz minerals with diamagnetic properties, and goethite gangue minerals with paramagnetic properties. In this context, first of all, the ore suspension prepared at 35% pulp in solids ratio was mixed using a pilot scale mixer by adding 7.5 kg/ton sodium hexametaphosphate (SHMP), and then wet screened from a 212 µm sieve to remove iron-containing minerals that did not disperse and remained in coarse size fraction. As a result of mechanical dispersion and wet sieving, a product with a size of +212 µm with 26.4% Al_2O_3, 50.8% SiO_2 and 9.6% Fe_2O_3 content was obtained, while at -212 µm size a product with 31.3% Al_2O_3, 59.0% SiO_2 and 3.2% Fe_2O_3 containing a product was obtained.

Then, this sample was subjected to wet magnetic separation at 5750 Gauss magnetic field intensity with a wet high-intensity magnetic separator. The Al_2O_3, SiO_2 and Fe_2O_3 contents of the nonmagnetic product were found to be 31.7%, 51.5% and 2.3%, respectively. Fe_2O_3 removal efficiency was 30.2% for 5750 Gauss. Additionally, shrinkage/water absorption and *L-a-b* color values in sintering studies with nonmagnetic products were measured as 8.3% / 12.7% and 74.0-7.2-12.9, respectively, in wall tile conditions.

As a result, it was observed that the mechanical dispersion and wet magnetic separation process provide significant improvements in the color values of the material under wall tile sintering conditions.

Keywords: *Kaolinitic clay ore, mechanical dispersion, wet screening, wet magnetic separation, sintering in wall tile condition*

1. INTRODUCTION

Halloysite is a type of clay mineral found in the kaolin group together with kaolinite, dickite, and nacrite minerals. Kaolinite is the most common mineral in this group, while halloysite is rarer (Berthier, 1826; Carson and Kunze, 1970; Delvaux et al., 1992).

Kaolin group clay minerals are generally produced from quarries by open pit methods. Selective mining and separation may be necessary as there may be quality differences within the quarry. In this case, it is important to classify and stock the kaolin produced from the quarry with similar quality to meet the criteria related to the next enrichment or usage area. The ores found in nature contain impurities in their structures (Murray, 2006). In order to eliminate these impurities by mineral processing and enrichment methods, firstly, particle size liberation of the minerals should be ensured by size reduction methods. Grinding process is used to reduce the particle size of the minerals in the ore quickly. However, the grinding process degrades the tubular structure of the halloysite mineral and reduces the value of the product (Takahashi 1959a; Takahashi 1959b). On the other hand, since clay minerals have a plastic structure, they can be brought to their natural fine size by dispersion in an aqueous environment. At this stage, they are also separated from non-plastic, hard, and coarse-sized minerals according to particle size (Murray, 2007, Durgut et al., 2022a).

Natural clay minerals are important raw materials for the ceramic industry. Clay minerals are widely used as raw materials for construction industries such as ceramic tile and brick (Singh, 2022). The properties of clay that contribute to the ceramic industry are chemical composition, strength before and after firing, thermal properties, phases formed during sintering, and refractoriness (Ngun et al., 2011; Tarhan and Tarhan, 2019). These properties are provided by optimizing clay minerals in the ceramic industry. Türkiye's ceramic industry imports the quality kaolin needed from abroad. As in all sectors, to ensure the continuity of the raw material requirement and production safety of the ceramics industry, there should be no disruptions in the supply chains (Fiederling-Kapteinat, 2004). However, the pandemic in the world and the conflicts between countries cause troubles to this chain nowadays (O'Driscoll, 2022). Therefore, countries turn to domestic raw material resources to meet the raw material needs and conduct research for necessary improvements. Since the Turkish ceramics industry has difficulties in meeting the quality of kaolin raw material imported from abroad, it has turned to domestic resources and rearranged ceramic recipes accordingly.

This study aimed to develop an enrichment process, which includes mechanical dispersion and wet magnetic separation methods, for the production of high-quality clay for the ceramic industry from low-quality halloysite ore, which is an important raw material source for the ceramic industry.

2. MATERIAL AND METHODS

2.1. Material

For the experimental studies, the sample taken from the halloysite source in the Kızıldam village of Yenice district of Çanakkale province was first passed through a jaw crusher and brought to a particle size of -10 mm. Afterward, the sample was homogenized, and the chemical analysis of the sample was performed, and the results are presented in Table 1. Moreover, the moisture content measured by drying the sample at 105°C for 4 hours was determined as 9.4%.

Table 1. Chemical analysis of raw halloysite sample

*LOI	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	Na_2O	K_2O
12.0	50.9	29.7	0.7	3.9	0.2	0.4	0.2	1.1

**LOI: loss on ignition*

As seen from Table 1, TiO_2, Fe_2O_3, CaO, MgO, Na_2O, and K_2O were detected in the sample, apart from the halloysite content chemically. In addition to them, in the qualitative mineralogical analysis (XRD) of the sample, the presence of quartz, kaolinite, halloysite, gibbsite, and goethite minerals was determined (Figure 1).

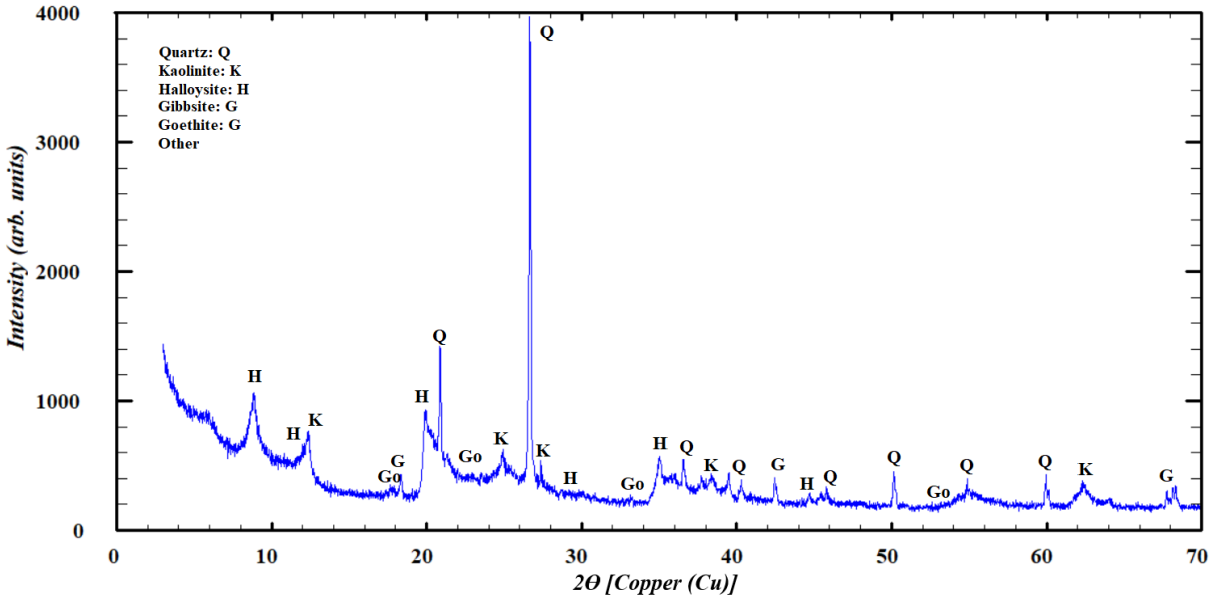


Figure 1. Mineralogical analysis of raw halloysite sample

2.2. Method

In the mechanical dispersion process, the halloysite ore crushed to -10 mm size was prepared with 0.75% sodium hexametaphosphate (SHMP) as a dispersant in proportion to the dry raw material amount, and water at 35% pulp in solids ratio, mixed in the mechanical blunger at 500 rpm for 4 hours. Next, the dispersed pulp was sieved through sieves with an aperture of 0.212 mm. Then, the -0.212 mm-sized pulp was subjected to magnetic separation using the Carpco wet magnetic separator at 5750 Gauss at a feeding speed of 1 lt/min. Finally, the chemical analyses for the nonmagnetic and magnetic products were carried out.

In the wet grinding process, halloysite ore crushed to -10 mm size was ground in a laboratory-type jet mill by adding pure water with 7.5 kg/ton SHMP at 35% pulp in solids ratio compared to the dry raw material amount. The dry matter balance on the sieve was taken as the particle size control of the raw materials to be sintered. The particle size of the sample was studied as +63 µm for wall tile firing conditions as 2%. The raw material sample was prepared by wet grinding for sintering tests. The mechanical dispersion and wet grinding samples were prepared as described above and the sintering process was carried out.

After the samples to be used in sintering were prepared as suspension, they were passed through a 150 µm sieve and dried in an oven at 105ºC for 4 hours. The dried pulp was ground using agate and mortar, and granules were obtained by humidifying at 6%. The granules were shaped in a circular form of 5×5 cm in a hand press at a specific pressure of 325 kg/cm^2 for wall tile conditions. The pressed 5×5 cm tablets were dried in an oven at 105ºC for 4 hours and then fired in wall tile conditions.

3. RESULTS AND DISCUSSION

3.1. Mechanical Dispersion Experiments

Halloysite ore was subjected to a pilot-scale mechanical dispersion process following the flow chart shown in Figure 2. The dispersion process was prepared by using 8 kg of ore in -10 mm size and 30 lt of tap water at 35% pulp in solids ratio in a plastic can, by adding 7.5 kg/ton SHMP dispersant. The suspension was blunged at natural pH at 500 rpm for 4 hours. As seen in Figure 2, the -0.212 mm particle size fraction comprised 31.3% of Al_2O_3, 50.9% of SiO_2 and 3.2% of Fe_2O_3, while the +0.212 mm particle size fraction consisted of 24.6% of Al_2O_3, 50.8% of SiO_2 and 9.6% of Fe_2O_3.

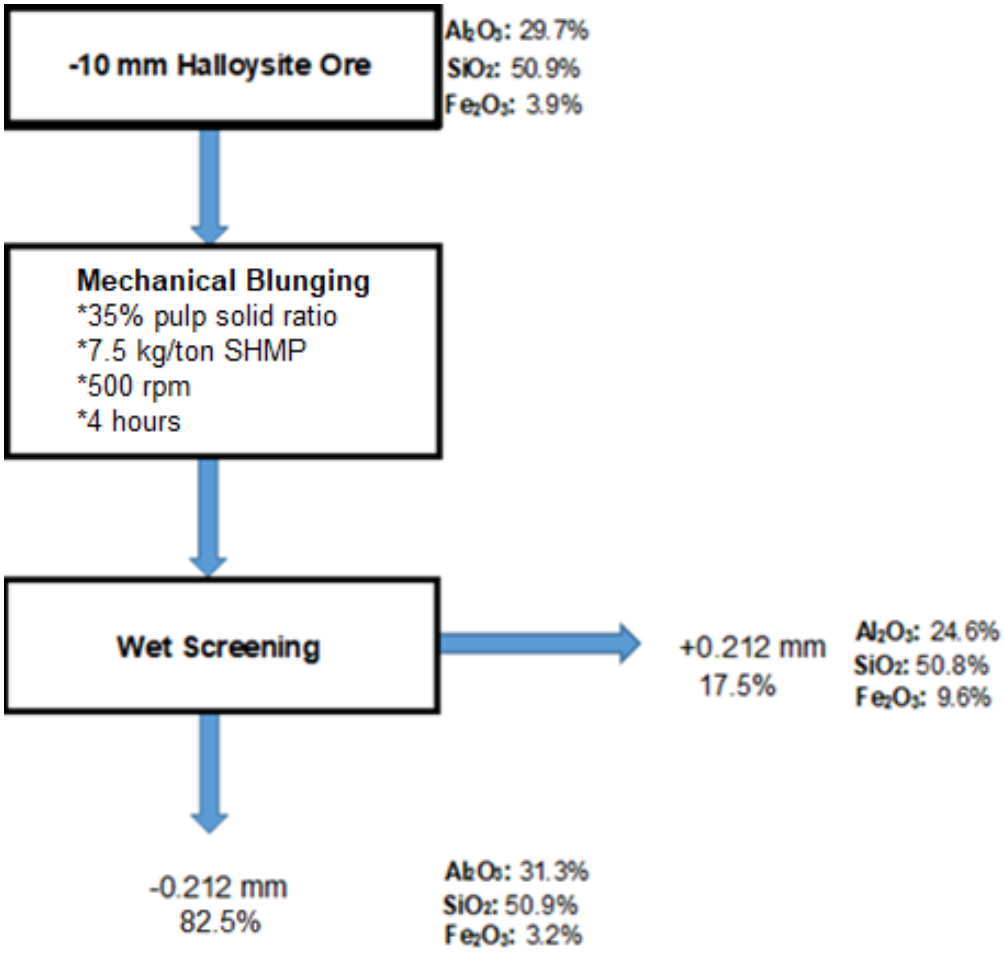


Figure 2. Chemical analysis of size groups obtained after dispersion and wet screening

3.2. Wet Magnetic Separation Experiments

To remove the fine magnetic minerals from the Kızıldam halloysite ore, the wet magnetic separation was applied with a Carpco separator to the suspension in the -0.212 mm size group obtained after the mechanical dispersion. The flow chart applied in the wet magnetic separation process and the results obtained are shown in Figure 3.

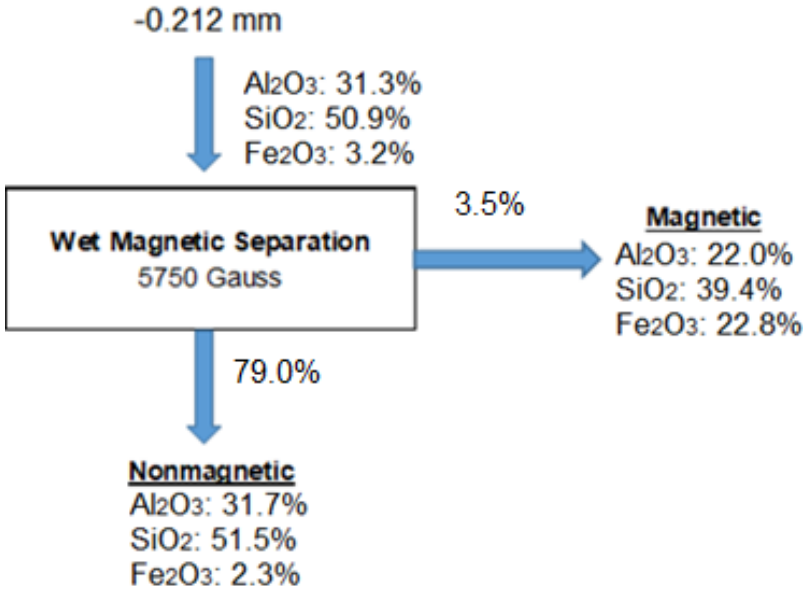


Figure 3. Flow chart of wet magnetic separation applied to -0.212 mm size group after mechanical dispersion

As a result of the wet magnetic separation experiment performed by applying 5750 Gauss, it was observed that Al_2O_3 (31.7%), SiO_2 (51.5%) and Fe_2O_3 (2.3%) contents in the nonmagnetic product remained, while Al_2O_3, SiO_2 and Fe_2O_3% contents of the magnetic product were determined as 22.0, 39.4 and 22.8%, respectively. Additionally, the presence of goethite mineral in the nonmagnetic product could be a reason why the Fe_2O_3 content in the nonmagnetic material cannot be lowered below a certain value in wet magnetic separation at the magnetic field intensities applied in the study (Maher, 1998).

However, magnetic material obtained at 5750 Gauss had the highest Fe_2O_3 (22.8%). As a result of the mineralogical analysis for the magnetic product, it consisted of 19.7% quartz, 21.5% goethite, 29.6% kaolinite, 25.1% halloysite, and 4.1% other minerals.

3.3. Sintering Studies

Sintering conditions for wall tile (max. sintering temperature 1145°C, sintering duration 49 min.) were applied to the samples and the properties of sintered specimens are presented in Table 2.

Table 2. Properties of sintered specimens in wall tile conditions

Conditions / Samples		**Unit**	**Raw halloysite**	**After mechanical dispersion (-0.212 mm)**	**Non-magnetic**
WALL TILE	Specific pressure	kg/cm^2	325		
	Max. sintering temperature	˚C	1145		
	Sintering duration	min.	49		
	Shrinkage	%	7.8	5.5	8.3
	Water absorption	%	10.5	17.0	12.7
	Color	L	62.6	72.7	74.0
		a	9.8	8.2	7.2
		b	12.1	10.4	12.9

In the raw material sintering studies carried out under wall tile conditions, the shrinkage and water absorption values of the raw halloysite ore were found to be 7.8% and 10.5%, respectively. The shrinkage values of the mechanical dispersion (-0.212 mm) and nonmagnetic samples were determined as 5.5% and 8.3% while the water absorption values were obtained as 17.0% and 12.7%, respectively.

L-a-b values of the raw halloysite ore, after mechanical dispersion (-0.212 mm), and nonmagnetic samples were obtained as 62.6, 72.7, 74.0; 9.8, 8.2, 7.2*;* 12,1, 10.4, 12.9, respectively in the wall tile sintering conditions (Figure 4).

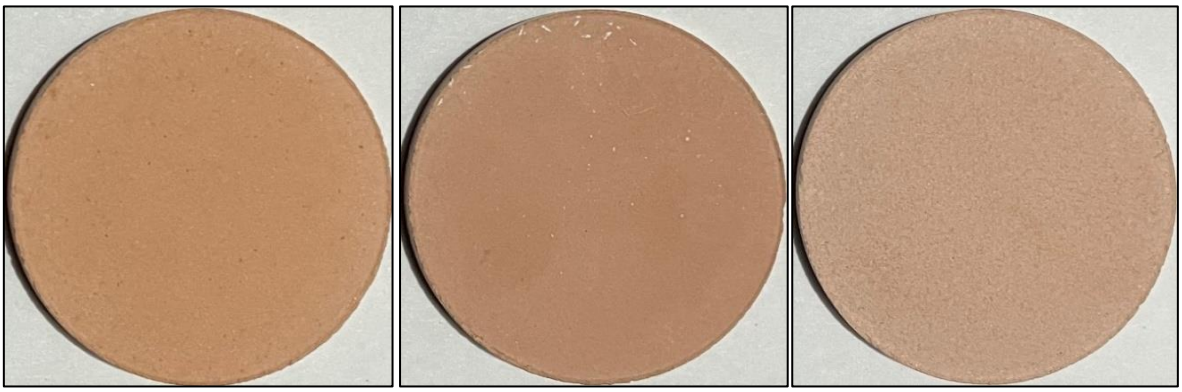


Figure 4. Sintered images of the raw halloysite, after mechanical dispersion and non-magnetic products in the wall tile conditions (from left to right)

4. CONCLUSION

In the mineralogical analysis of halloysite ore, it was observed that it consisted of halloysite, kaolinite, quartz, gibbsite, and goethite minerals. It was analyzed that the iron content increased in coarser particle size (+0.212 mm) fraction that was gained with the mechanical dispersion experiments. These results indicated that the ferrous impurities in the ore were relatively hard and in coarser size compared to other minerals. With wet grinding, these ferrous minerals were ground into a fine size. This situation reduced the whiteness of the product in the sintering phase of ceramic bodies, causing difficulties in the production of products where the white color was desired and in obtaining the desired color on the surface of glazed products (Durgut et al., 2022b). As a result of the wet magnetic separation experiment, the Fe_2O_3 content of the nonmagnetic product was decreased to 2.3% from 3.2%. In this study, it was observed that the clay mineral content of halloysite ore was increased, and the color after firing was improved in ceramic body studies by applying mechanical dispersion and wet magnetic separation.

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