Physicochem. Probl. Miner. Process., 61(3), 2025, 203225

http://www.journalssystem.com/ppmp

Physicochemical Problems of Mineral Processing

ISSN 1643-1049
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Fine-size separation of halloysite, kaolinite, and quartz minerals as binary systems using dispersion and sedimentation methods

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Abstract: Clay minerals are mainly composed of aluminum hydrosilicates. In some minerals, aluminum is completely or partially replaced by Fe or Mg. Alkaline minerals or alkali metals are present as major constituents of clay minerals. While some clay sources may contain a single clay mineral, they often contain different minerals such as quartz, calcite, feldspar, pyrite, etc. as impurities. They also contain organic matter and water-soluble salts. Halloysite is a clay mineral belonging to the kaolinite group and USA Environmental Protection Agency (EPA 4A) declared it as an innocuous/adaptable material to human health and the environment. Halloysite ore deposits are mainly found together with kaolinite and quartz minerals, but can also be found as a pure source. The degree of purity of halloysite ore determines the industrial area where it will be used and therefore its economic value. Since clay minerals are naturally composed of fine particles, it is necessary to disperse the clay particles in suspension to separate halloysite and kaolinite minerals. In addition, there are also fine-grained quartz minerals, and to recover pure halloysite minerals, it is necessary to determine their properties in the fine size fraction. In this study, the dispersion properties of halloysite, kaolinite, and quartz minerals in the presence of sodium silicate (*SS*), sodium tripolyphosphate (*STPP*), and sodium hexametaphosphate (*SHMP*) dispersants in fine-size fraction (-38 µm) were researched by particle size measurements and mineral separation properties were investigated by sedimentation experiments at different acidic, neutral, alkaline pH values. In dispersion experiments, the d_{90} values of halloysite, kaolinite, and quartz minerals were 74.0, 50.7, and 61.3 µm without any dispersant addition, and such values decreased to 54.7, 26.3, and 57.1 µm as *SHMP* increased to 10 kg/ton, respectively. d_{50} and d_{10} values showed a significant change for halloysite, while no important change was observed for kaolinite and halloysite. *SHMP* had the most effect on the particle size change in the dispersants especially on halloysite minerals. The least effect on particle size change was observed in the quartz sample with dispersant addition. The sedimentation experiments aimed to investigate the effects of pH on halloysite, kaolinite, and quartz recoveries in binary systems as settled products. Kaolinite settled more at acidic pH and halloysite at basic pH. There was no pH-dependent change in the settling behavior for halloysite and quartz. In the quartz-kaolinite system, quartz mineral settled more than kaolinite for all pH values. The settling experiments showed the importance of morphological differences between tubular halloysite and lamellar kaolinite minerals.

Keywords: halloysite, kaolinite, quartz, sedimentation, dispersion, dispersant

1. Introduction

Metallic ores, mineral fuels, natural stones, and industrial raw materials are used in agriculture, ceramics, glass, refractories, metallurgy, construction sectors, and electrical/electronic industries by forming significant elements of daily lives (Allaby, 2013; Adekunle et al., 2015; Hamdi et al., 2018; Balde

DOI: 10.37190/ppmp/203225

et al., 2021). Nowadays, various mineral processing and beneficiation methods need to be applied to raw materials due to the deficiency of pure sources (Murray, 1976; Mukherjee, 2011). Therefore, the researchers have studied to separate minerals from each other for using them efficiently in related industries. Besides, fine-sized characteristics of minerals need to be understood owing to the development of nanotechnology (Zhou and Keeling, 2013; Ma et al., 2024).

Size reduction/classification and beneficiation methods are used in dry and wet mediums according to the mineral liberation size and technology. Mineral processing and beneficiation methods are crucial for the evaluation of minerals in nanotechnology (Takahashi, 1957; Takahashi, 1959). Shear force is effective for the separation of plastic and non-plastic minerals in aqueous media. For this reason, mixers are used to achieve particle size liberation and reduction of such minerals. The grinding method is also preferred for particle size reduction and liberation, but mixing in aqueous media is more meaningful, especially since grinding negatively affects the usage properties of plastic clay minerals in the field of nanotechnology (Wilson, 2007). The clay minerals have different effects on rheological properties during the industrial production steps (Khaydapova et al., 2015). Therefore, it is important to determine the rheological properties of clays used in wet systems. The rheological properties of clays depend on many parameters such as the solids ratio, chemical and mineralogical composition, particle shape and size distribution, dispersant type and dosage, pH, temperature, organic content, non-clay minerals, etc. (Chang et al., 1993; Maxwell and Dinger, 2008; Shoaib et al., 2022). Inorganic or organic additives, which can be named as dispersants, binders, and plasticizers, are added to the clay-water suspension to get a suspension with high solids ratio by affecting rheological behaviour. Sodium carbonate, sodium silicate, tetrasodium pyrophosphate, sodium tripolyphosphate, sodium polyacrylate, and sodium citrate are well-known dispersants. Binder additives are microcrystalline cellulose, ammonium alginate, and methylcellulose. Plasticizer additives are ethylene glycol, and glycerol (Tadros, 2005). Dispersion is the process by which solid colloidal particles move away from each other in the pulp such that they remain in suspension by repulsive electrostatic motion caused by the dispersant. Therefore, dispersants increase the fluidity of the suspension and reduce the apparent viscosity in aqueous suspensions (Landrou et al., 2018).

Halloysite is commonly found in association with fine-grained kaolinite and quartz minerals in its natural deposits. Although the separation of halloysite from kaolinite and quartz is not well-documented in the literature, it is known that halloysite, kaolinite, and quartz exhibit different sedimentation behaviors at varying pH levels (Durgut et al., 2022). Halloysite used in ceramic bodies is generally utilized in its raw form as extracted from the deposit, and the impurities inherent in its structure can lead to quality defects. Therefore, it is necessary to remove impurities from the halloysite (Abdelilah et al., 2018). On the other hand, halloysite ore can be further purified to obtain halloysite nanotubes (HNTs) (Weiner et al., 2006; Abbasi, 2018). Due to their nanotubular morphology and the presence of chemically distinct inner and outer surfaces, halloysites are considered high-value raw materials for the production of advanced technological materials in various industries (Zhang et al., 2016). Today, understanding the fine structures of clay minerals is becoming increasingly important for the production of nanotechnological materials. Clay minerals have recently started to be used in the field of nanotechnology with various next-generation analysis methods and the unexplored properties of nano clay minerals have encouraged researchers to work on this subject. In this study, the effects of sodium silicate (*SS*), sodium tripolyphosphate (*STPP*), and sodium hexametaphosphate (*SHMP*) addition on halloysite, kaolinite, and quartz particle size distribution in aqueous medium by mechanical dispersion. Besides, the beneficiation of minerals was evaluated according to the loss of ignition values in the binary system by sedimentation method in fine-size (-38 μm).

2. Materials and methods

2.1. Materials

Dispersion and sedimentation behaviors were determined by using pure halloysite and quartz (Türkiye) and kaolinite samples (Ukraine) in an aqueous medium. Initially, the mineralogical composition was verified using X-ray Diffraction (XRD) analysis with an X'Pert Pro MPD X-ray Diffractometer (PANalytical, The Netherlands) over a scanning range (2θ) of 3-80° and a step size (2θ) of 0.0263° with a Cu radiation source. Quantitative XRD results were obtained through the Rietveld

refinement method. The halloysite sample was composed of metahalloysite and halloysite that had 7 and 10 Å of basal clearance, respectively (Fig. 1a). Besides kaolinite (Fig. 1b) and quartz (Fig. 1c) samples were formed as pure minerals.

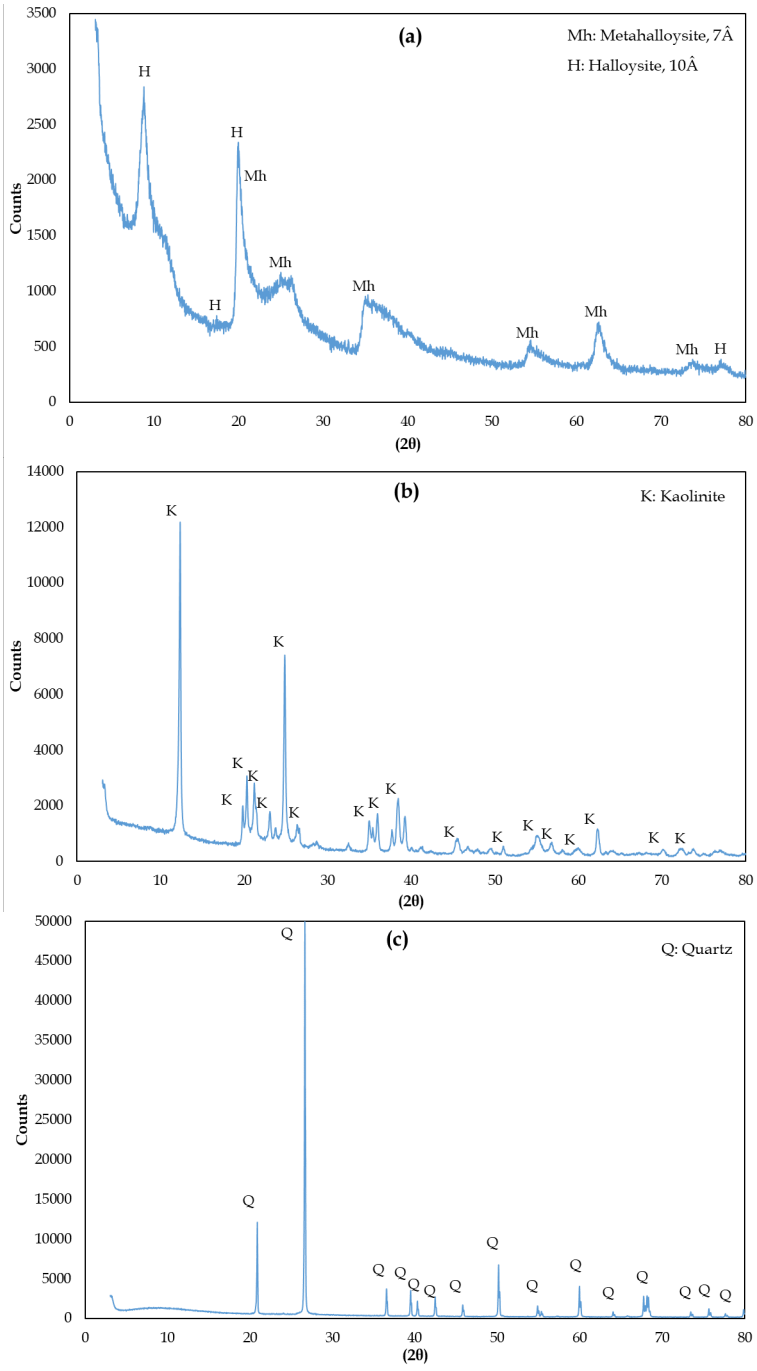


Fig. 1. The XRD patterns of pure (a) halloysite, (b) kaolinite, and (c) quartz samples

The halloysite used in the sedimentation experiments was obtained through mechanical dispersion at 600 rpm for 4.5 hours with a 20% solids ratio in the pulp. The kaolin used in the sedimentation experiments was prepared by mechanical dispersion at 600 rpm for 30 min with a 20% solids ratio in the pulp. Halloysite and kaolin as plastic clay minerals and quartz as non-plastic mineral were used in experimental studies. Plastic clay minerals were dispersed to reach -38 µm particle size by mechanical dispersion in an aqueous medium. However, different conditions were applied due to unlike dispersion behaviors of halloysite and kaolin samples. Besides, the quartz samples were firstly ground to -38 µm in the dry medium due to their non-plastic character using a Union Process HD-01 model stirred mill

with a 750 cm^3 capacity, then subjected to sedimentation experiments. The quartz was fed into the mill along with ceramic grinding media, which occupied 80% of the mill volume, ensuring that the quartz filled 10% of the total mill volume. The grinding process was conducted at 1000 rpm for 20 min. Following the mechanical dispersion process, the samples were sieved to obtain -38 µm particles to use the same particle size in sedimentation experiments. However, quartz was used directly as it reached the desired particle size after grinding. The particle size distributions of pure sample suspensions were determined with a laser diffraction analyzer (Mastersizer 2000, Malvern, UK) by taking with a 2 cm^3 Pasteur pipette after the suspensions prepared at 5% solids ratio were mixed and homogenized in a magnetic stirrer for 5 min (Fig. 2).

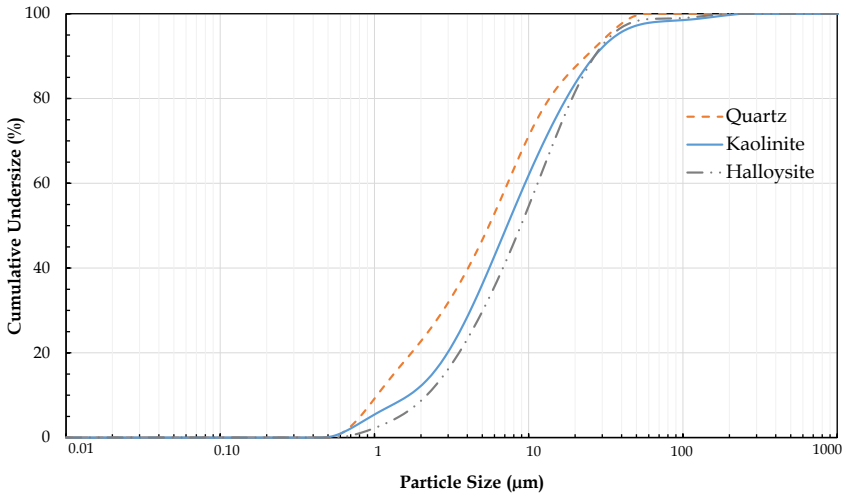


Fig. 2. Particle size distribution analysis of pure samples used in the sedimentation experiments

The particle size distribution curves of the samples used in the sedimentation experiments are presented in Fig. 2. While d_{10}, d_{50}, and d_{90} values of the samples were determined as 2.18, 8.90, 26.72 µm, for halloysite, these values were 1.67, 7.24, 26.70 µm, and 1.04, 5.52, 23.58 µm for kaolinite, and quartz, respectively.

2.2. Methods

2.2.1. Dispersion experiments

Dispersion experiments were carried out with sodium silicate (*SS*) with a molecular weight of 184.04 g/mol and a density of 1.526 g/cm^3 obtained from Zag Industrial Chemicals (Türkiye), sodium tripolyphosphate (*STPP*) with 94% purity obtained from TEKKIM Chemical Company (Türkiye), and extra pure sodium hexametaphosphate (*SHMP*) with a total phosphate content of 65-70% obtained from ZAG Chemical Company (Türkiye) to see the particle size change of halloysite, kaolinite, and quartz suspensions. 2.5 - 5 - 10 kg/ton of dispersants were used in dispersion experiments for 30 min of mixing duration at 20% solids ratio in a magnetic stirrer operated at 600 rpm mixing speed. Then, dispersed suspensions were sieved through a 74 µm aperture sieve, and particle size distributions were analyzed with the laser diffraction analyzer. The experimental flowsheet for the dispersion experiments is shown in Fig. 3.

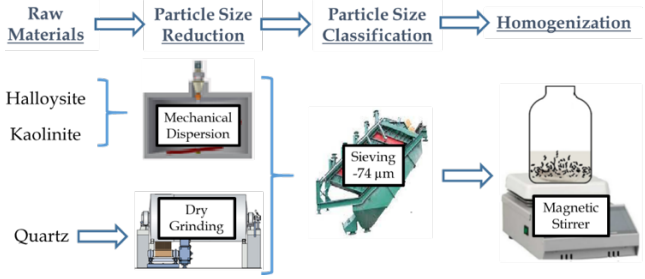
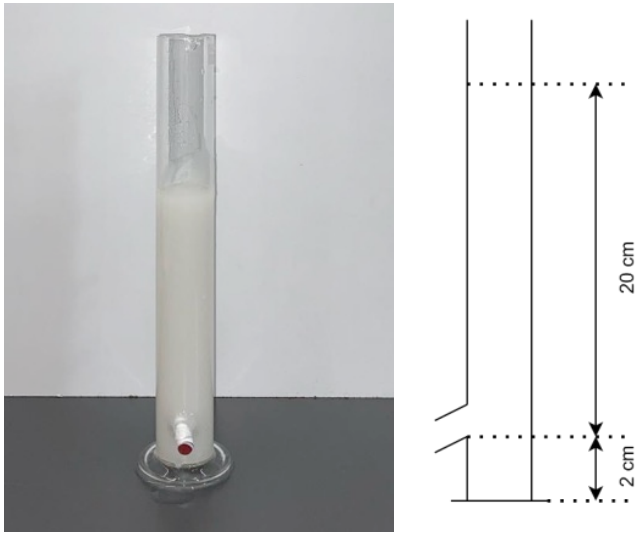


Fig. 3. Experimental flowsheet for dispersion experiments

2.2.2. Sedimentation experiments

Sedimentation experiments were conducted using suspensions prepared with pure samples that were dispersed and brought to a fine particle size of -38 μm. The experiments were performed with binary suspensions of halloysite-kaolinite, halloysite-quartz, and kaolinite-quartz mixtures. The mixtures were prepared at 1:1 ratio and homogenized by stirring at 600 rpm for 5 min using a magnetic stirrer. The pulp pH was adjusted using oxalic acid dihydrate as acid and potassium hydroxide as alkaline to the desired value between 3-11. The natural pH values of halloysite, kaolinite, and quartz suspensions were measured as 3.6, 6.2, and 6.5, respectively, using a pH meter (AB23PH-F, Ohaus, Switzerland). Extra pure oxalic acid dihydrate (99.5% purity, TEKKIM Chemical Company Türkiye) and analytical-grade potassium hydroxide (85% purity, molecular weight: 56.11 g/mol, TEKKIM Chemical Company Türkiye) were used to examine the sedimentation behavior of halloysite, kaolinite, and quartz minerals, respectively. A 5-min stirring process was applied for homogenization, and then the suspensions were transferred to the sedimentation cell seen in Fig. 4 for 30 min of the sedimentation process. After 30 min, the valve located 2 cm above the bottom of the tube was opened to collect the suspended product, while the settled product remaining below the valve level was collected separately using wash water. A photo of the sedimentation cell and a schematic representation of the sedimentation cell used in the experiment are shown in Fig. 4.



(a) (b)

Fig. 4. (a) The view and (b) the schematic representation of the sedimentation cell

2.2.3. Loss on ignition (*LOI*) analysis

The composition of the products obtained from the sedimentation experiments was determined according to differences in the loss on ignition, which was a characteristic property of the pure minerals. For the loss on ignition analysis, the samples were placed in porcelain crucibles and dried at 60°C in an oven. After drying, the samples were transferred to a muffle furnace and heated at 850°C for 3 hours. At the end of the 3 hours, the furnace was turned off and allowed to cool down gradually. The products were then weighed, and the loss on ignition values was calculated according to Eq. 1 where m_b and m_a explained the masses before and after the heating process, correspondingly.

$$\%\mathrm{LOI} = \frac{m_b - m_a}{m_b} \times 100 \quad (1)$$

Loss on ignition values for halloysite 7 Å, halloysite 10 Å, and kaolinite minerals were 14.0%, 24.5%, and 14.0% in theory due to chemical-bonded water content, accordingly. In this study, *LOI* values for the halloysite and kaolinite samples used were determined to be 18.29% and 13.75%, respectively. 18.29% of *LOI* content showed that the halloysite sample was a mixture of 7 Å and 10 Å together. Besides, there was no *LOI* content for pure quartz and the difference in *LOI* could make the mineral content calculation via *LOI* in a binary system. Loss on ignition analyses were performed in triplicate

for each sample, and the average values were used. The compositions of the products obtained from the sedimentation experiments were determined using Eqs. 2 and 3:

$$(100 - LOI_{s1}) \ * \ m_{s1} + (100 - LOI_{s2}) \ * m_{s2} = (100 - LOI_p) \ * m_p \quad (2)$$

$$m_p = m_h + m_k \quad (3)$$

In Eqs. 2 and 3, LOI_{s1} and LOI_{s2} represented the loss on ignition (%) values of the 1st and 2nd samples in the mixture, respectively. Additionally, LOI_p indicated the total loss on ignition (%) of the sediment product. The amount of the 1st and 2nd minerals in the sediment product (g) was denoted by m_{s1} and m_{s2}, respectively. Furthermore, the total amount of the sediment product (g) was represented by the symbol m_p. *LOI* values were used to determine the mineral amounts in binary systems and mineral recovery in the sediment, which was gained as a result of sedimentation experiments, was calculated according to Eq. 4:

$$\text{Recovery (\%)} = \frac{M_s x A_s}{M_f x A_f} x100 \quad (4)$$

where, M_s referred to the related mineral content of the sediment (%), A_s denoted the amount of the sediment (%), M_f represented the related mineral content of the feed, and A_f indicated the amount of the feed.

3. Results and discussion

3.1. Dispersion experiments

Dispersion results of pure samples were interpreted with dispersant effect and particle size distribution. Therefore, the particle size distribution was measured after the dispersion process in the presence of different dispersants.

The d_{10}, d_{50}, and d_{90} values of pure halloysite sample obtained from the dispersion processes at various *SS*, *STPP*, and *SHMP* dosages (2.5, 5, and 10 kg/ton) are shown in Fig. 5. d_{90}, d_{50}, and d_{10} values of pure halloysite sample were 74.0, 27.8, and 3.2 µm, respectively in the absence of dispersants. d_{90}, d_{50}, d_{10} values were analyzed as 63.8, 19.6, 2.6 µm, 57.5, 16.5, 2.7 µm, and 54.7, 15.8, 2.3 µm in the presence of *SS*, *STPP* and *SHMP* at 10 kg/ton, respectively. The surface charge of halloysite particles is negative above pH 3 in terms of zeta potential and the negativity increases as the pH becomes more basic (Durgut et al., 2022). However, the edges of halloysite tubes are thought to be positively charged as in the kaolinite mineral. Therefore, halloysite nanotubes agglomerate over a wide range in aqueous suspensions. In this study, dispersants increased the positive edge charge to larger values and caused the halloysite tubes to disperse away from each other, which was seen from the particle size reduction with dispersant dosage increment. However, although the surface charge of the halloysite was negative at its natural pH value of 4.2, it was closer to the point of zero charge (PZC), so the particle dispersion was not as much as the kaolinite mineral due to the natural pH 6.2 (Fig. 6).

The d_{10}, d_{50}, and d_{90} values of the products obtained by dispersing pure kaolinite samples at various dispersant dosages (2.5, 5, and 10 kg/ton) are presented in Fig. 6. d_{90}, d_{50}, and d_{10} values of pure kaolinite sample were 50.7, 8.7, and 1.6 µm in the absence of dispersants. d_{90}, d_{50}, d_{10} values were analyzed as 34.3, 9.3, 2.1 µm, 36.0, 9.4, 2.0 µm, and 26.3, 7.9, 1.4 µm in the presence of *SS*, *STPP*, and *SHMP* at 10 kg/ton, respectively. Theoretically, kaolinite particles have negatively charged surfaces and positively charged edges in terms of physicochemical properties. For this reason, negatively charged surfaces and positively charged edges attract each other electrically, forming a network structure and agglomeration in aqueous suspensions. The zeta potential of kaolinite becomes more negative as the pH increases from acidic to basic values due to the increase in negative ions in the environment and the particles push each other away (Durgut et al., 2022). In this study, the negative ion concentration originated from *SS*, *STPP*, and *SHMP* in the suspension supported kaolinite particles dispersion. Therefore, particle size distribution was reduced with dispersant addition as a result of the dispersion of the kaolinite network structures.

The d_{10}, d_{50}, and d_{90} values of the products obtained by dispersing quartz sample at different dispersant dosages (2.5 - 5 - 10 kg/ton) are given in Fig. 7. d_{90}, d_{50}, and d_{10} values of pure quartz samples were 61.3, 21.8, and 2.7 µm without dispersant addition. d_{90}, d_{50}, d_{10} values were analyzed as 58.1, 20.7,

2.7 µm, 63.5, 23.7, 2.9 µm, and 57.1, 20.5, 2.6 µm in the presence of *SS*, *STPP*, and *SHMP* at 10 kg/ton, respectively. The surface charge of quartz was determined to be negative in aqueous suspensions containing anionic dispersants and this negative value was found to be even more negative depending on the dispersant dosage (Durgut et al., 2022). In the case of 20% solids ratio in the pulp, the use of dispersant showed no significant effect on the particle size distribution since the quartz particles were already far enough apart.

It can be concluded from the dispersion experiments that dispersion mechanisms of halloysite, kaolinite, and quartz minerals were investigated by measuring the particle size using *SS*, *STPP*, and *SHMP* dispersants that introduce anions into the medium. As seen from the particle size changes in Figs. 5, 6, and 7, halloysite and kaolinite samples were more affected than quartz samples with the dispersant dosage increment. The negative electrical charge given by the dispersants to the suspensions caused the edge charges of the clay minerals to be negative. The negative surface and edge charges caused the clay minerals to be dispersed from the agglomerated state and therefore a decrease in particle size was observed. Since the surface charge of quartz minerals was already negative, the negatively charged ion introduced by the dispersant caused the surface of quartz particles to become even more negative, but the change in particle size reduction was not as much as in clay minerals due to its morphological structure.

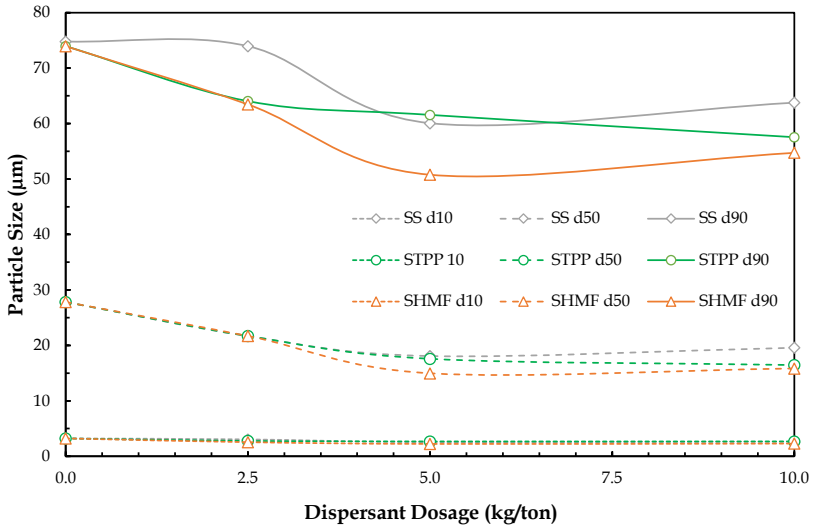


Fig. 5. d_{10}, d_{50}, and d_{90} values of the products obtained by dispersing pure halloysite sample as a function of dispersant dosage

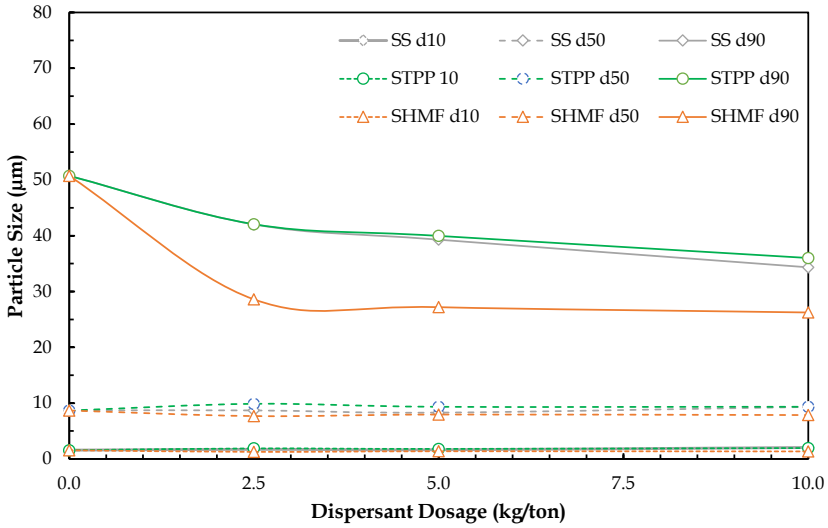


Fig. 6. d_{10}, d_{50}, d_{90} values of the products obtained by dispersing pure kaolinite sample as a function of dispersant dosage

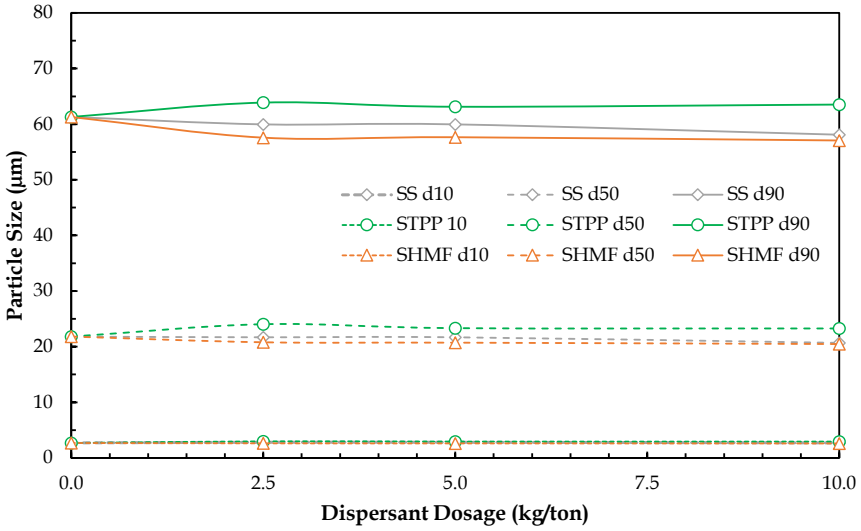


Fig. 7. d_{10}, d_{50}, d_{90} values of the products obtained by dispersing pure quartz sample as a function of dispersant dosage

3.2. Sedimentation experiments

Fig. 8 illustrates the recovery and content of the sediment product settled at different pH levels in the halloysite-kaolinite binary system. The halloysite was beneficiated with 22.9% recovery at pH 3 and recovery increased as the pH raised to 11. The halloysite content was initially 44.0%, and then showed a slight decrease to 40.6% at pH 6.5 before increasing again at higher pH levels. The recovery of kaolinite was approximately 40% at low pH levels, exhibiting a slight decrease as pH increased, followed by a subsequent rise at higher pH levels. The kaolinite content started at ~60% at low pH levels, reached a maximum in the intermediate pH range, and then declined as pH continued to increase. In this context, high-purity halloysite could be obtained with high recovery under alkaline pH conditions.

Fig. 9 illustrates the recovery and composition values of the sediment product settled at different pH levels in the halloysite-quartz binary system. The recovery of halloysite started at approximately 93.6% at pH: 3, increased slightly at pH: 6.5 to 94.8%, and then decreased significantly at pH: 11 to 38.6. Although the recovery of quartz followed a similar trend, its decline at pH 11 was less pronounced compared to halloysite. The halloysite content exhibited relatively minor fluctuations with changing pH but tended to decrease at higher pH levels. Conversely, the quartz content showed a slight increasing trend as the pH increased.

Fig. 10 illustrates the recovery and composition values of the sediment product settled at different pH levels in the kaolinite-quartz binary system. The recovery of kaolinite started at 40.4% at low pH: 3, reaching its maximum at pH 6.5, and then decreased significantly at pH: 11. The recovery of quartz began at a lower value in the low pH range, attained its peak at pH 6.5, and subsequently exhibited a declining trend. While the kaolinite content remained relatively stable with varying pH, it tended to decrease at higher pH levels. In contrast, the quartz content gradually increased as the pH level increased.

It can be concluded from the sedimentation experiments of binary systems that halloysite-kaolinite system, kaolinite concentrated more than halloysite at acidic pH, and richer halloysite content was formed when pH reached 11 in the sediment. In the previous study, it was observed that the surface charge of the halloysite mineral turned from negative to positive when the pH reached 3 (Durgut et al., 2022). At this pH, the zeta potential of kaolinite was closer to the zero point of charge, it formed agglomerates by getting closer to each other and thus settled more than halloysite. In the halloysite-quartz system, there was no significant difference in terms of recovery, but the quartz content was higher than the halloysite mineral at all pH levels. This was explained by the slower settling of halloysite agglomerates compared to quartz particles. In the kaolinite-quartz system, quartz recovery was higher than kaolinite at all pHs. At acidic pH (3), the zeta potential of kaolinite was closer to the zero point of

charge so the kaolinite agglomerates settled more. As the pH moved to the basic medium kaolinite minerals separated into lamellar form, thus quartz minerals concentrated in sediment.

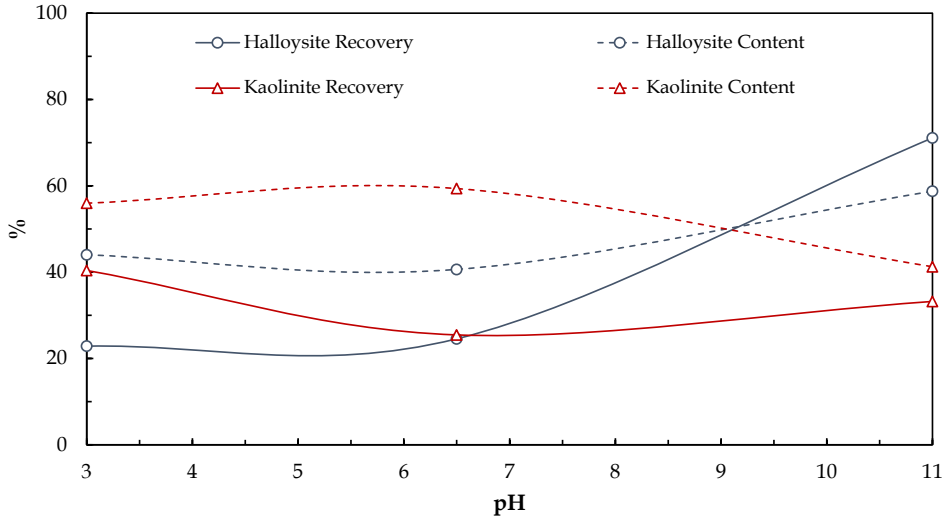


Fig. 8. Recovery and composition values of the halloysite-kaolinite binary system

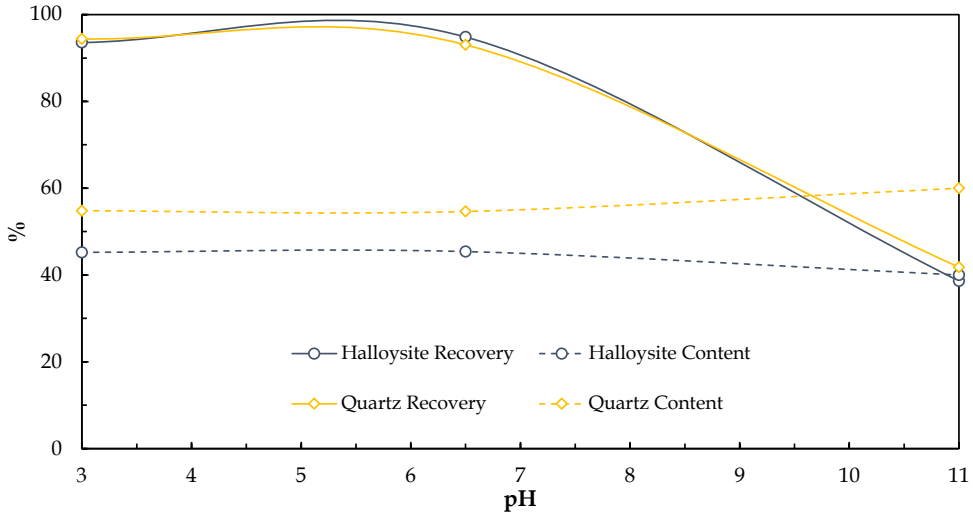


Fig. 9. Recovery and composition values of the halloysite-quartz binary system

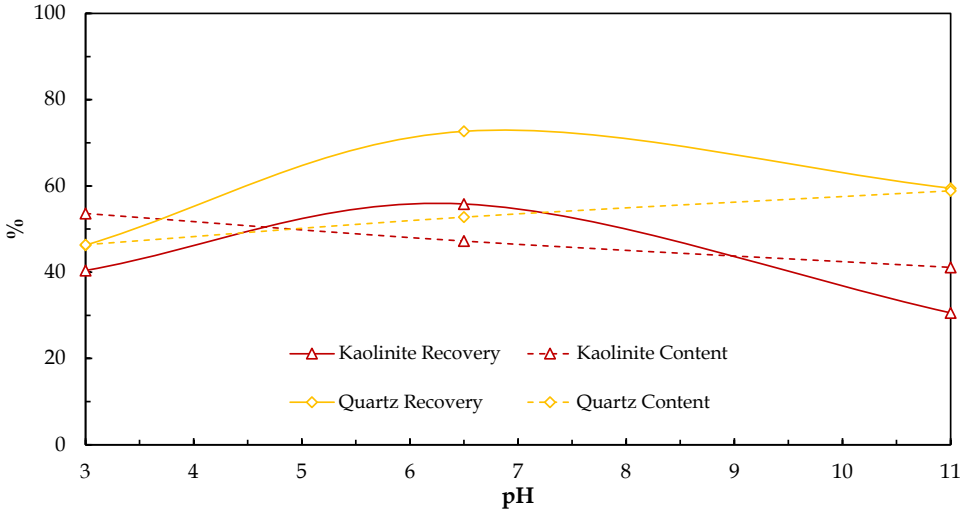


Fig. 10. Recovery and composition values of kaolinite-quartz binary system

4. Conclusions

In this study, firstly, the particle size changes of halloysite, kaolinite, and quartz minerals in aqueous media using different dispersants were investigated by the mechanical dispersion method. Then, sedimentation experiments were carried out by mixing such minerals in aqueous medium as binary groups and the mechanisms of fine particle size (-38 μm) separation were researched. In the dispersion experiments, a significant decrease in d_{90} values was observed with increasing dosage in all dispersants used for halloysite and kaolinite samples, while a partial decrease was observed in d_{50} values. d_{10} values did not change significantly. In quartz minerals, the addition of dispersant did not affect the particle size, and d_{10}, d_{50}, and d_{90} values remained almost unchanged. It was observed that there was no significant change after 5 kg/ton dosage in all dispersants used for halloysite and kaolinite minerals with dispersant addition. Halloysite and kaolinite mineral particles that belonged to the clay group, changed from agglomerated to dispersed form in the presence of dispersants, thus particle size change was observed more than in quartz minerals. The agglomeration of clay minerals was due to the different electrical charges in particle surface/edge properties, these differences were eliminated with positive ion addition by means of dispersants. As a result, the surface/edge of clay mineral particles had the same electrical charge (+), thus moved away from each other and particle dispersion occurred. In this context, the optimum dispersant dosage was determined as 5 kg/ton. Besides, it was understood that *SHMP* produced finer-sized products compared to *SS* and *STPP* at the same dosage. In conclusion, it was understood that *SHMP* was a stronger dispersant than *STPP* and *SS*. In the sedimentation studies of quartz minerals with halloysite and kaolinite separately, halloysite and quartz showed similar properties, while kaolinite settled more slowly in this system. This was due to the difference in the shape of tubular halloysite and lamellar kaolinite minerals. In the kaolinite-halloysite system, kaolinite settled faster at acidic pH because the point of zero charge was approached more closely at acidic pH level, while halloysite settled faster at basic pH value because of the higher surface/edge electrical charge difference.

Acknowledgments

The authors would like to express their sincere thanks and appreciation to the Office of Scientific Research Projects of Istanbul Technical University for the financial support (Project no: MAB-2023-44800).

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