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Review Article

An Overview of Halloysite Mineral

Emrah Durgut[a,*], Mustafa Çınar[b,**], Orhan Özdemir[c,***]

[a] *Çanakkale Onsekiz Mart University, Can Vocational School, Çanakkale, TÜRKİYE*
[b] *Çanakkale Onsekiz Mart University, Department of Mining Engineering, Faculty of Engineering, Çanakkale, TÜRKİYE*
[c] *İstanbul Technical University, Department of Mineral Processing Engineering, Faculty of Mines, İstanbul, TÜRKİYE*

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ABSTRACT

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 dickite, nacrite, and halloysite are rarer. Although halloysite is primarily used in ceramic production, application in other industries is increasing and gaining economic value due to its unique properties. The use of halloysite is determined by the degree of purity and the properties of the nano-sized tubular structure. Naturally obtained halloysite mineral has a key position in the field of nanotechnology due to its unique physicochemical properties originating from its tubular structure. Also, due to its low reserves in many parts of the world, halloysite is a more economical material for the sectors compared to artificially produced nanomaterials. Halloysite reserves known in Türkiye are located in the Çanakkale and Balıkesir regions. Although there are many useful studies on halloysite in different areas, additional studies are needed to understand the nano-sized properties of halloysite ore and to ensure its use that will provide maximum benefit. This study aimed to contribute to the studies on halloysite in terms of literature by compiling studies on the characterization of halloysite minerals, reserve information, physicochemical properties, enrichment methods, and usage areas.

Keywords: *Clay, Halloysite, Nanotechnology, Nanotube, Beneficiation.*

1. Introduction

Halloysite ($Al_2Si_2O_5(OH)_4$) is a clay mineral composed of aluminum, silicon, oxygen, and hydrogen elements as basic components. Halloysite is typically formed by hydrothermal weathering of aluminosilicate minerals and can be found together with dickite, kaolinite, montmorillonite, and other clay minerals (Murray, 2007). Halloysite was first studied as a tubular mineral by the Belgian geologist Omalius d'Halloy, and was given this name by Berthier (1826) in honor of the mineral's discoverer. Literature studies with the term halloysite in the title, abstract, or keyword started in the 1940s and the number of studies on the subject has increased considerably with the addition of the term halloysite nanotube (HNT) since the 2000s. This clearly shows the importance of the halloysite issue (Figure 1).

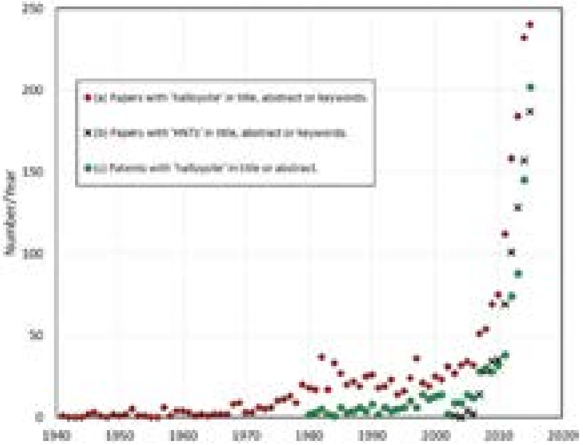

Figure 1: Number of publications on halloysite/halloysite nanotube by years (Churchman et al., 2016).

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[*] emrahdurgut@comu.edu.tr • https://orcid.org/0000-0002-4637-7087
[**]Corresponding author: mcinar@comu.edu.tr • https://orcid.org/0000-0001-9553-423X
[***]orhanozdemir@itu.edu.tr • https://orcid.org/0000-0002-4408-546X

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Halloysite mineral has been named halloysite, metahalloysite, hydrated halloysite, and endellite by different researchers due to its different morphological, structural and chemical properties (Ross and Kerr, 1934; Alexander et al., 1943; MacEwan, 1947; Churchman and Carr, 1975). Currently, halloysite mineral is classified as hydrated halloysite (basal spacing 10 Å) with chemical formula $Al_2Si_2O_5(OH)_4 \cdot 2H_2O$ and dehydrated halloysite (basal spacing 7 Å) with chemical formula $Al_2Si_2O_5(OH)_4$ according to basal XRD peaks (Brindley, 1961; Santos et al., 1965; Grim, 1968). Figure 2 shows the molecular and morphological representation of halloysite-7 Å mineral.

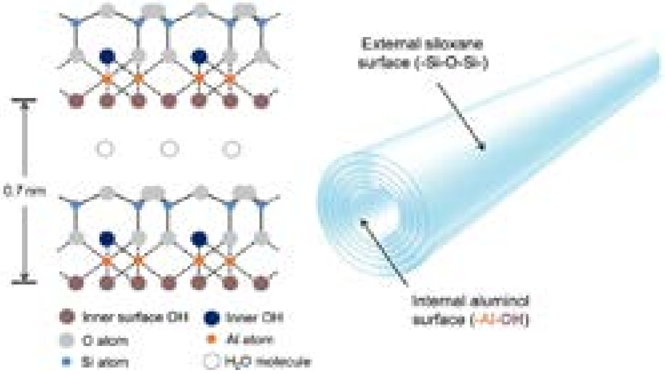

Figure 2: Molecular and morphological representation of halloysite-7 Å.

2. Characterization of halloysite mineral

Because dehydrated halloysite (7 Å) have the same chemical composition as kaolinite and give the same XRD peaks in mineralogical analysis, they must be characterized by intercalation method and/or SEM images to be separated from each other (Churchman et al., 1984; Robertson and Eggleton, 1991). In the intercalation method, dehydrated halloysite (7 Å) is brought to a hydrated (10 Å) state by various processes, and thus, it can be distinguished from kaolinite mineral due to the different basal XRD peaks (Figure 3).

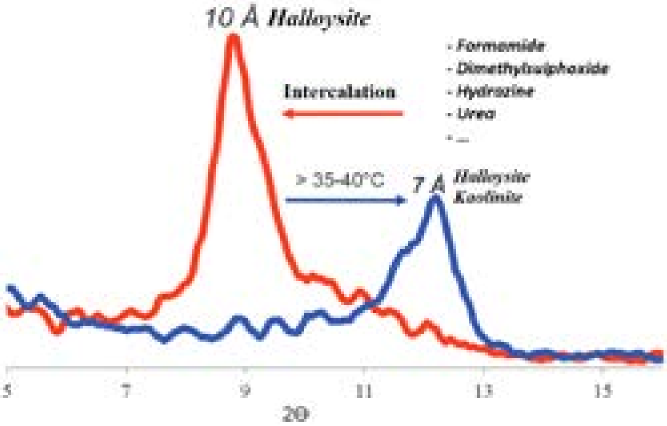

Figure 3: XRD patterns of kaolinite, halloysite-7Å and halloysite-10Å (Saklar et al., 2012a).

Intercalation of halloysite with organic compounds and salts has been studied extensively in the literature (Churchman and Theng, 1984; Frost and Kristof, 1997; Hillier and Ryan, 2002; Franco and Ruiz Cruz, 2004). After grinding halloysite-7Å with potassium acetate, the basal spacing value can be increased to 10 Å by intercalation of water and ethylene glycol. This situation does not change the basal spacing in kaolinite and dickite (Miller and Keller, 1963). Similar results obtained when hydrazine, water, and glycerol were used (Range et al., 1969). In intercalation studies with $K_3C_6H_5O_7$ (citrate), KCOOH (formate), KOCN (cyanate), KSCN (thiocyanate), and KNO_2 (nitrite) with mono, divalent, and trivalent cations, it was observed that these salts tend to intercalate between the halloysite layers. It has also been determined that halloysite intercalates with salts of monovalent (K^+, NH_4^+, Rb^+, and Cs^+) cations (Carr et al., 1978). Even if concentrated solutions are required, low solubility of silver and thallium salts in water do not allow forming compounds for efficient intercalation. In an aqueous clay suspension, halloysite interlayer regions are relatively water-repellent in contrast to the outer surface-water interface and therefore do not tend to form strong ionic species associated with water. Therefore, it can be said that the intercalation phenomenon will only be possible by cations, which have low bonding energy with water (Carr et al., 1978). It is known that the viscosity of aqueous salt solution is related to the ability of the ions to combine with water. The tendency of ions to disrupt structure is related to their electrical field strengths. Low field strength means high disrupting ability. This refers to the size and valence properties of the ions. The smaller the size, the lower the force, thus meaning lower electrical field strength. The intercalation behavior of cations is closely related to the fluidity of saline solutions. Relatively hydrophobic cations (disrupting the water structure) intercalate the water-repellent zones in halloysite-water systems. Experimental studies have shown that the tendency of very large ($Cr_2O_7^{-2}$ and $Ce(NO_3)_6^{-2}$) and highly charged (AsO_4^{-3}, $S_2O_5^{-2}$, $S_2O_3^{-2}$) anions to intercalate the interlayer spaces is quite limited. Data in studies on halloysite support that salt molecules do not completely replace water molecules in the formation of interlayer compounds and this is related to the type of salt used (Wada, 1961; Carr et al., 1978).

Because halloysite has a tubular structure, electron microscopy is a fundamental method to distinguish it from other kaolin group minerals and to investigate such materials. The development of Scanning Electron Microscopy (SEM) method has enabled new findings about halloysite, while the use of Transmission Electron Microscopy (TEM) method has made it possible to obtain information about the structure of halloysite that has never been obtained. With SEM analysis, the information on the halloysite tubular structure, and the length and width of the tubes can be obtained, while more detailed information such as individual lumen lengths and diameters of the tubes can be obtained with TEM analysis. Halloysite minerals can be observed circular or cylindrical in TEM analysis (Figure 4).

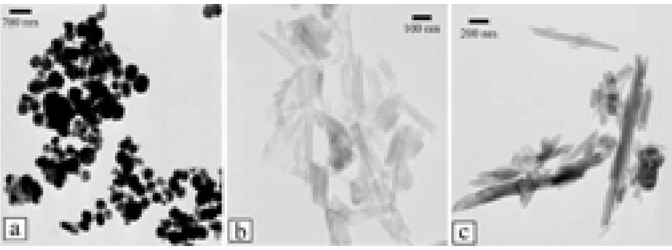

Figure 4: TEM images of three basic morphologies of New Zealand halloysite: (a)circular (Opotiki); (b)short tubes (Te Puke); (c)long tubes (Matauri Bay) (Joussein et al., 2005).

Considering the tubular structure, halloysite shows two types of structures "cylindrical" and "prismatic or polygonal" (Dixon and Mckee, 1974; Kogure et al., 2013). Ultra-high-resolution SEM imaging demonstrated the polygonization of halloysite tubes with multiple crystal surfaces (Figure 5).

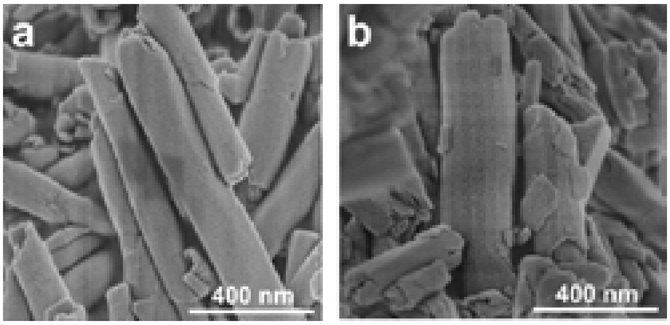

Figure 5: Ultra high-resolution images a)Cylindrical tubes b)Prismatic tube images with thin sections on tube surfaces (Kogure, 2016).

Physicochemical properties such as cation exchange capacity, specific surface area, and pore volume vary according to the environmental conditions in which the halloysite is formed. Morphological differences between the halloysite and the impurities are the factors that have the most obvious effects on the formation of specific surface area and internal pore diameter. The fact is that inner and outer surfaces have different chemical compositions that affect the surface charge at different pHs (Durgut et al., 2022a). The presence of water in the interlayer space reduces the bonding with neighboring layers. All these factors determine the use of halloysite in new areas such as nanocarriers, nano molds, and nanofillers.

Cation exchange capacity varies according to the types of clay minerals in the halloysite ores. The cation exchange is seen in the defective crystal corners, in the form of displacement in the lattice, and as the replacement of hydroxyl ions on the surface with hydrogen. According to studies in the literature, the cation exchange capacity of halloysite reaches up to 60 cmol/kg (Kunze and Bradley, 1963; Norrish, 1995; Takahashi et al., 2001; Hart et al., 2002; Joussein et al., 2007). The cation exchange capacity of halloysite decreases due to natural or artificial drying processes (Grim, 1968). Therefore, cation exchange capacities of hydrated halloysites are higher than dehydrated halloysites. In addition, halloysite has a higher cation exchange capacity than kaolinite minerals due to the structural arrangement in hydrogen bonds, the presence of negative charges, and different hydration statuses (Wilson, 2004). In addition, the cation exchange capacity of halloysite is affected by purity, particle size, and morphology. As the Al^{3+} in the octahedral layer is replaced by Fe^{2+}, the Al content decreases and the Fe content increases, and thus the cation exchange capacity of halloysite increases (Singh and Gilkes, 1992). As the particle size decreases, the cation exchange capacity of halloysite increases due to the increased edge-surface interaction (Delvaux et al., 1992; Chorover and Sposito, 1995; Wu et al., 2013). The presence of soluble salts in the pores of tubular halloysites causes a higher cation exchange capacity than halloysites in other structures (Ma and Eggleton, 1999).

The specific surface area value of halloysite also depends on purity, particle size, and acid-base treatment. Pasbakhsh et al. (2013) measured the specific surface area and porosity values of halloysites from different regions. It was observed that the highest pore volume was in nanotubes with cylindrical lumen, low impurity, and smooth thin walls. In addition, studies have shown that halloysite mineral has higher specific surface area values than kaolinite (Joussein et al., 2005).

3. Halloysite reserves, market and prices

Halloysite is found in various regions around the world. Halloysite sources are generally found near kaolinite deposits, but they can also be seen in altered rocks in the form of veins (Ece and Schroeder, 2007; Garcia de Oliveira et al., 2007).

The Matauri Bay halloysite source in the Northland of New Zealand is located next to the rhyolite rock. This source consists of approximately 50% halloysite and 50% quartz, cristobalite, and a small amount of feldspar. The Matauri Bay halloysite has a heterogeneously distributed tubular structure up to 3 mm in length and plated kaolinite. These resources have been produced at an annual rate of approximately 80000 tons since 1969. The mineral processing plant capacity produces 25000 tons/year and the lifetime of the quarry is planned to be more than 50 years. Since ore with high whiteness is obtained from this facility, it is exported to more than 20 countries, especially for use in the production of high-quality ceramic products (porcelain, fine porcelain, technical ceramics, etc.). Although Matauri Bay is the most well-known source of halloysite in New Zealand, there are also small reserves in Te Puke and Opotiki regions (Keeling, 2015; Joussein, 2016).

Halloysite deposits in the United States of America (USA) are located in the state of Utah. Approximately 1.2 million tons of halloysite have been produced in the past from the Eureka Dragon ore deposit in the Tintic mining area in Juab County. Halloysite particles have a morphology consisting of small tubes with inner diameters ranging from 5 nm to 30 nm and lengths between 50-1500 nm. The mineral contents in the samples taken from the region consist of 84% halloysite, 8% kaolinite, and other minerals (quartz, gypsum, sulfate/phosphate minerals). 501200 tons of reserve containing 64% halloysite has been calculated by means of the newly received drilling data at the Dragon mine site. Pure halloysite and a by-product with high iron content that can be used in the pigment industry are obtained from the mineral processing plant (Boden et al., 2012; Joussein, 2016).

Halloysite ore found at the Dunino mine in Lower Silesia, Poland, was formed from the weathering of basalt. Halloysite is produced by Intermark/Kopalnia Haloizytu Dunino, founded in 1998, by open pit mining near Krotoszyce in the Legnica region. The mineral deposit consists of over 10 million tons of various raw materials with homogeneous distribution. The bed thickness of the halloysite reserve, which is around 500000 tons, reaches up to 20 m in height. Dunino ore bed consists of a mixture of nanotubes and nanosheets containing 80% halloysite mineral. There are also small and homogeneously distributed iron and titanium oxides as impurities (Clarke, 2008; Keeling, 2015).

The two halloysite deposits in Türkiye were located along the contact between metamorphic rocks of the Triassic Karakaya Complex and lower Miocene volcanics (Genç, 1998). The Karakaya Complex basically consisted of Permian aged limestone masses and also contained phyllite and schist. There was a lower Miocene aged volcanogenic pile consisting of andesitic pyroclastic/lava on the basement rocks. It also contained tertiary aged granitic intrusions cutting the Karakaya Complex and andesitic pyroclastics. There was an occurrence of halloysite in the volcanogenic pile, formed in relation to limestone, with a width of approximately 45-50 m, a length of 125-130 m and a depth of approximately 12-15 m in the north-south direction. There were also limestone blocks of different sizes in the occurrence. In addition to halloysite minerals in the region, there were also minerals such as kaolinite, smectite, illite, alunite, jacobsite, pyrochroite, hematite, goethite and birnessite. It was thought that halloysitization occurred as a result of hydrothermal solutions of magmatic origin rising along faults and affecting andesitic pyroclastic. It was thought that one of the most important factors in the formation of halloysite was the limestone that regulated the pH of the environment (Laçin and Yeniyol, 2006). Kaolinite and halloysite quarries belonging to Esan Eczacıbaşı are located in Balıkesir and Çanakkale regions in Türkiye. Halloysite resources found here are considered important because they are quite pure. It is known that there are 50000 tons of halloysite reserves in the region (Ece et al., 2008). While the diameters of halloysite tubes in Tabanköy vary between 40-50 nm, their lengths can reach up to 1500 nm (Demir and Altaş, 2017).

In China, there are kaolin deposits consisting of a mixture of plated kaolinite and tubular halloysite. Longyan reserves in the Fujian Region are halloysite deposits with low iron and titanium content formed by the kaolinitization of granites. On the other hand, there are also important resources in Dafang, Qingxi, Zunyi, and Shijin in the Guizhou District. Dafang halloysite consists of tubular fine particles with very low iron and titanium contents. However, the ore beds in this region were formed in the form of small veins. While the annual production amount of Longyan District is 50000 tons, this value is 2000 tons in Gouzhiu District (Wilson, 2004).

In the Eucla Basin region of South Australia, near Playa Lake, there are halloysite reserves with a purity of 95% and a very regular morphology up to a tube length of 1500 nm. There are halloysite deposits with thin and long veins in Jarrahdale in the north and Patch Clay in the west of Australia (Joussein, 2016).

In the Thung Yai region of South Thailand, there are deposits containing approximately 70% halloysite, consisting of microtubes with pores and sheets 80-200 nm in diameter and 450-500 nm in length. Quartz and anatase can be seen as impurities in these deposits. In addition, in the Ranong and Narathiwat regions of Southern Thailand, there are ore beds containing 70% tubular halloysite and kaolinite as co-minerals, quartz, mica, and potassium feldspar as trace minerals (Bordeepong et al., 2012).

Large sources of halloysite are known to exist in Japan (Sudo and Takahashi, 1955; Saigusa et al., 1978) and South Korea (Jeong, 1998; Khan and Kim, 1991). There are tubular halloysite sources with low iron and titanium contents in Brazil (Wilson et al., 2006). Halloysite deposits are found in the southwest of the Rio Negro region in Argentina (Cravero et al., 2012). Table 1 shows the chemical, mineralogical, morphological, and physical properties of halloysites from some important countries around the world.

Table 1: Chemical, mineralogical, and physical properties of halloysites in the world (Joussein, 2016).

Country	New Zealand	USA	New Zealand	Australia	China	Poland	Türkiye
Name	Matauri Bay	Dragon Mine	Te Puke	Camel Lake	Longyan	Dunino processed	Turkish
SiO_2	50.40	43.50	44.82	44.96	48.00	43.30	46.00
Al_2O_3	35.50	38.80	36.70	37.57	38.00	34.50	37.01
Fe_2O_3	0.25	0.33	3.40	1.21	0.29	2.60	0.70
MgO	trace	0.12	0.01	0.19	0.30	0.08	0.45
Na_2O	trace	0.07	0.01	0.09	0.10	0.19	0.10
K_2O	trace	0.07	0.05	0.31	1.71	0.05	0.30
CaO	trace	0.26	0.01	0.28	0.16	0.26	0.15
TiO_2	0.05	0.02	0.37	0.15	0.02	1.18	0.30
MnO	0.01	0.01	0.01	0.01	trace	trace	trace
P_2O_5	0.06	0.83	0.02	0.01	unknown	0.05	unknown
SO_3	0.06	0.26	0.02	0.63	unknown	unknown	unknown
LOI	13.80	15.70	14.66	14.53	12.40	15.39	15.00
Halloysite (%)	96	84	98	95	79 (Hal/Kaol)	70-80	95
Accessory minerals	quartz cristobalite anatase	kaolinite quartz gibbsite alunite	quartz cristobalite anatase	quartz alunite anatase Fe oxides	mica minerals quartz anatase	quartz anatase	quartz alunite anatase feldspar
Morphology	Tube/platy	Tube	Blocky and short tubes	Tube	Tube/platy	Tube/platy	Tube
CEC ($cmol_c$/kg)	2.5	2.1	5.2	18.8	unknown	9.1	4.2
BET (m^2/g)	22.1	57.3	33.31	74.6	unknown	unknown	72.2

The quarry sales prices were 27.5 TL/ton for kaolin and 808.5 TL/ton for halloysite in 2019 (General Directorate of Mining and Petroleum Affairs, 2019). Here, the price difference for the mineral with the same chemical structure explains the importance of halloysite. On the other hand, the price of halloysite ore of purity to be used in plastics, polymers, and medicine reaches up to AU$5000/ton (Andromeda Metals, 2019). Thus, it is seen that the price of beneficiated halloysite ore, has increased significantly. When halloysite nanotubes are considered as an alternative material to carbon nanotubes, they appear to be biologically harmless. It is also known that the price of halloysite nanotubes (US$4/kg) is quite economical compared to carbon nanotubes (US$500/kg) (Bordeepong et al., 2011).

The worldwide halloysite market was 29.1 million US$ in 2017. It is estimated that this figure will reach 50.21 million US$ in 2025. Figure 6 shows the distribution of the halloysite market in the USA by the area of use.

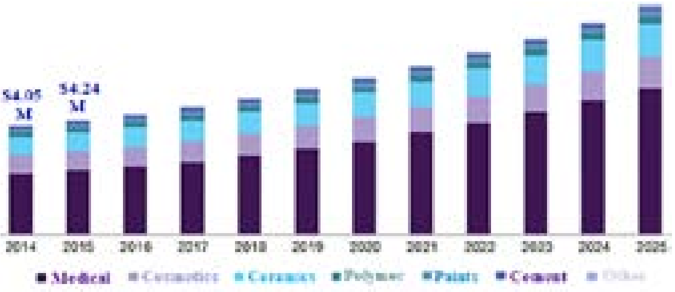

Figure 6: Halloysite market in the USA by the area of use between 2014-2025 (https://www.grandviewresearch.com/industry-analysis/halloysite-market).

4. Uses and beneficiation methods of halloysite

There are some decisive criteria for the use of halloysite, and these criteria vary according to the area of use. Uygun (1999) stated that the chemical and mineralogical properties sought in halloysites exported to England should have a minimum of 35% Al_2O_3, a maximum of 0.7% Fe_2O_3, a maximum of 1.2% SO_3 and a minimum of 92% halloysite, a maximum of 5% quartz, and a maximum of 3% alunite contents.

The beneficiation methods of halloysite is similar to kaolinite beneficiation methods. However, grinding of halloysite causes changes in the nano-sized tubular structure and negatively affects the product properties (Takahashi, 1957). When the halloysite is ground, it gradually turns into an irregular structure and XRD peak intensities weaken, that is, the peak intensity that determines halloysite-10 Å decreases with grinding. As the grinding duration progresses, mullite crystals grow. On the other hand, the density decreases and reaches a constant value. This constant value is close to the density of silica-alumina gel or allophane. While the milled halloysite sample from the electron microscope images has a tubular structure at the beginning of the grinding process, fine crystals with sharp corners are obtained as the grinding progresses, the fine crystals later come together and the particle size increases, and finally irregular spherical particles are formed. As a result, the particle size increases irregularly with agglomeration, resulting in a silica gel-like structure (Takahashi, 1959a). In wet grinding of halloysite, unit layers are rolled over each other due to the tubular structure compared to dry grinding, and therefore it becomes difficult to form cleavage in wet grinding. While the density of halloysite increases gradually at first, it tends to decrease after reaching a certain value. In wet grinding, the corners of the layered kaolinite crystals begin to curl and turn into a tubular structure similar to halloysite. In the halloysite, different structures with broken tubular, layered, and rectangular shapes were observed. This shows that wet milling causes crushing rather than cutting force (Takahashi, 1959b). As a result, cracking and crushing effects were observed more in dry grinding, while weak cleavage effects were observed for kaolinite and weak crushing effects for halloysite in wet grinding.

After the industrially quarried halloysite ore is brought to the mineral processing facility, it is mixed in large pools and dispersed, and size separation is made with hydrocyclones to separate the coarse-sized minerals. Important impurity source minerals in halloysite and kaolinite deposits are goethite and muscovite. They may also contain quartz, feldspar, gibbsite, smectite group clay minerals, and anatase. Very fine-sized impurities in the structure are defined chemically by EDX analysis, and exact mineral types cannot be determined. Iron oxide/hydroxide minerals, which are in the form of extremely fine-sized submicron particles, may be trapped between clay minerals or adhered on halloysite tubes-kaolinite plates. Because the grinding process disrupts the structure of halloysite nanotubes, dispersing it into a fine size by mechanical dispersion in the aqueous medium ensures that the nano-tubes are less damaged than grinding and that the hard impurities remain large without grinding and are separated from the halloysite by particle size separation methods (Durgut et al., 2022b).

Magnetic minerals such as hematite, magnetite, and biotite are removed by magnetic separators with proper field strengths. In order to further purify the halloysite ore, the iron content is reduced to a very low level by leaching methods using organic and inorganic acids. Saklar et al. (2012b) reported that as a result of high-field intensity wet magnetic separation experiments of halloysite ores in Çanakkale and Balıkesir regions, the magnetic separation is not efficient because the hydraulic drag force is more effective on fine-sized particles and higher magnetic field strength is needed. Solvent type and temperature are very important in removing impurities by leaching from the halloysite. There is no effective separation at low temperatures (25°C), hence leaching can be performed efficiently at higher temperatures (80°C). It is known from the literature that oxalic acid is a good solvent for removing ferrous impurities in the structure of clays (Ambikadevi and Lalithambika, 2000; Baba et al., 2015). Because some alumina may also dissolve from the clay surface at high acid concentrations, the structure of halloysite should be carefully examined (Belkassa et al., 2013; Saklar and Yörükoğlu, 2015). Leaching and wet magnetic separation can be used together to efficiently purify halloysite in the fine-sized fractions (Sakiewicz and Lutynski, 2016; Sakiewicz et al., 2016).

Fine quartz particles in clay ores are removed by flotation (Bidwell, 1970). Fatty acids and cationic collectors can be used in halloysite flotation. In halloysite flotation with sodium oleate, a low basic pH (8.2) is more efficient than a high basic pH (12.5). In this case, the pH of the environment increases the interaction of collector and the mineral surfaces by converting the aluminum hydroxides into aluminates, thus increasing the flotation performance. Sodium ions from collectors are firmly adsorbed on the surfaces in flotation studies. In order to remove these ions from the surfaces, the samples must be thoroughly washed (Uvarov and Vovk, 1971). While sodium fluosilicate, aluminum sulfate, and dextrin have a depressant effect on halloysite minerals, there is no such effect for sodium silicate (Yapa, 1993).

Halloysite is more conductive under a voltage of 10000 volts for electrostatic separation operations. However, the liberation size of the mineral should be above 0.1 mm (Yapa, 1993).

Alkaline treatment, ultrasonication, and centrifugation methods can be used to improve the dispersion properties of halloysite nanotubes in suspensions, to remove impurities by preventing agglomeration, and to separate nanotubes into separate size fractions. Surface modification with organosilane compounds and amine salts has positive effects on the dispersion of halloysite tubes (Abbasi, 2018). Kaolin group clay minerals are generally enriched efficiently in aqueous media. The flowchart of a typical process applied in the enrichment of such minerals in aqueous media is given in Figure 7.

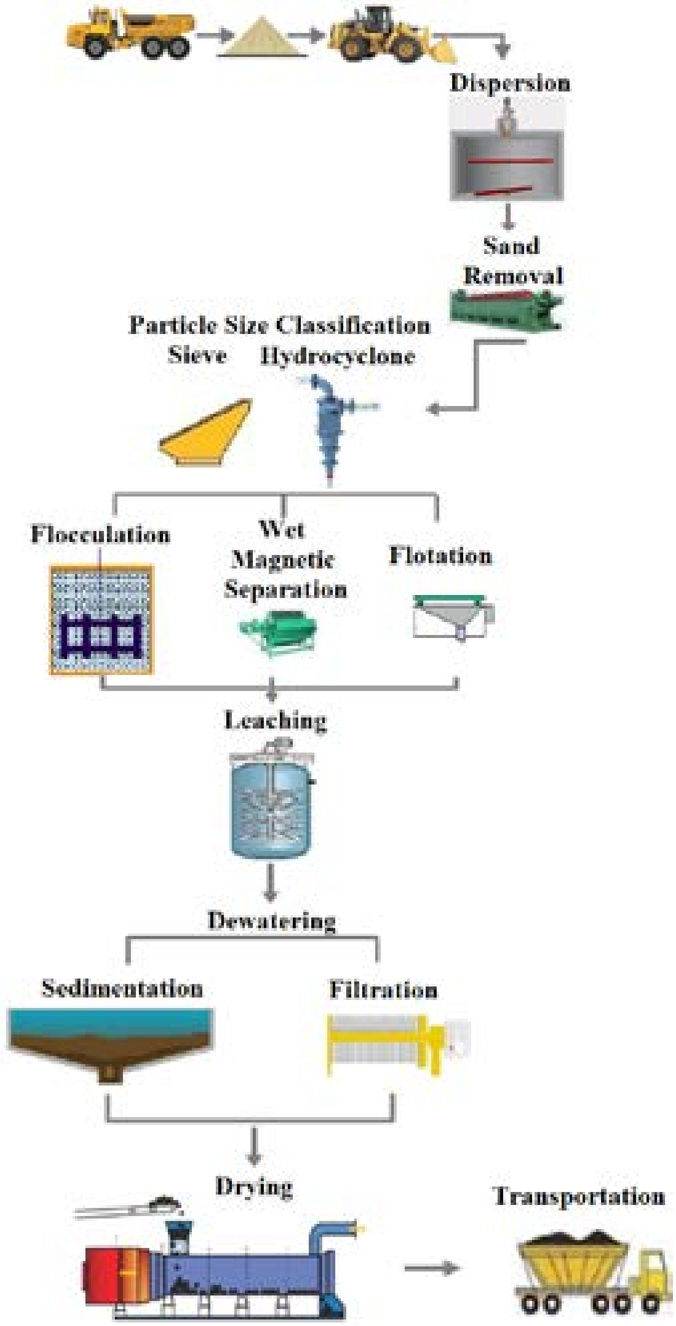

Figure 7: Flowchart of a typical wet kaolin clay mineral processing and enrichment.

If additional particle size separation is required after enrichment, hydrocyclone is used again, and then filter press or rotary filters are used to remove moisture (Murray, 2006). In this way, the halloysite can remain in a hydrated (10 Å) form. If spray dryers are used during drying, halloysite turns into a dehydrated (7 Å) form due to the appeared high temperature. It has been reported in the literature that the hydrated (10 Å) structure turns into a dehydrated (7 Å) structure by losing the water between the layers within 50-150°C (Joussein et al., 2006; Saklar et al., 2012a; Başara and Saklar, 2015). The process of removing the water depending on the desired structure is important at this point.

Halloysite is classified as a harmless and biocompatible nanomaterial in nature according to the Environmental Protection Agency (EPA 4A). Halloysite is a fine-sized ore with a large surface area and excellent dispersion in the matrix. It also has a high cation exchange capacity. There is a growing interest in using halloysite in various applications such as clay-polymer nanocomposites, catalysis, and adsorption. This unique nano-clay mineral is preferred in such applications due to its one-dimensional tubular structure and properties that can be changed by modification of the inner/outer surfaces. Therefore, tubular clay minerals are used as advanced functional materials. Drug-active substances are also adsorbed on halloysite surfaces. As such, it provides homogeneity, gives consistent release rates, and prevents overdose. Compared to organic carriers, halloysite-based drug delivery systems are long-lasting and non-toxic even at high drug dosages. This gives a powerful healing effect. Halloysite reduces the cost of surface-active materials due to its adsorption feature on the surface. Thanks to this feature, it can be used in cream, powder, gel, spray, and lotion forms. On the other hand, reusability is another important feature of halloysite.

5. Conclusions and recommendations

Natural halloysite is a low-cost industrial mineral that can be used in the production of functional materials such as nano-sized carriers. Halloysite has long been used in the production of porcelain, kitchen, and bathroom ceramics due to the properties such as whiteness and translucency that it brings to the product after sintering due to its low iron and titanium contents. In addition, due to fine particle size, it is also used in areas such as suspension-supporting agents in glaze applications. Purified halloysite nanotubes are coated with metallic and other additives and gain various electrical, chemical, and physical properties. Halloysite is used as a filling material in rubber production, and when used in polymers and cement, it improves the mechanical properties of the material. The choice of halloysite in these areas is determined by the lumen volume, shape, and size. As the tube length-to-diameter ratio of halloysite increases, technical characteristics such as strength, durability, active ingredient loading/release capacity of cement, polymer, and drug improves. Halloysite nanotubes add more strength to this structure when compared to other clay minerals that are frequently used in polymer nanocomposites. Halloysite is used in cosmetics, home and personal care materials, pesticides, medical products, and similar fields based on the principle of adsorption of active ingredients on the surfaces of nanotubes and the controlled release of these components. Understanding of the physicochemical properties of halloysite is important in terms of adding more value to the areas where it is used. How the surface and structural modification of halloysite affects the cation exchange capacity and dispersion behavior, and the details of the chemical processes on the transformations in the tubular structure of halloysite need to be studied in detail. As a result, the value of halloysite deposits in Türkiye is increasing day by day in terms of both direct raw material export and production of high-quality products. For this reason, studies on the development of processes for more efficient production of high-quality materials obtained from halloysite deposits with beneficiation operations within the scope of zero waste in proper areas gain importance for the future. The rapid increase in the number of scientific studies and publications on this material from the past to the present confirms this situation.

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