Purification of Dunino halloysite by H_2SO_4 leaching and magnetic separation

Piotr Sakiewicz[1], and Marcin A. Lutynski[2,a]

[1]*Division of Nanocrystalline and Functional Materials and Sustainable Proecological Technologies Institute of Engineering Materials and Biomaterials, Silesian University of Technology, Konarskiego 18a, C44-100 Gliwice, Poland*
[2]*Institute of Mining, Faculty of Mining and Geology, Silesian University of Technology, Akademicka 2, C44-100 Gliwice, Poland*

Abstract. The article presents results of purification and comminution of raw halloysite from the Dunino deposit. The aim of the study was to clean halloysite from Dunino deposit with acid (H_2SO_4) leaching and to remove iron impurities in order to obtain fine grained fractions smaller than 20 µm, which can be used in future for manufacturing polymer-aluminosilicate composites. The proposed method, where nanotubes (HNT) and nanoplates (HNP) were separated, consisted of several simple stages including crushing, milling magnetic separation and sedimentation. A multi-stage process resulted in three products: heavy iron oxide fraction, HNP and HNT mixture (<20 um) and remaining intermediate product (mostly iron, titanium oxides and aluminosilicates >20µm).

1 Introduction

Halloysite is an interesting example of phyllosilicates. As a member of clay mineral group together with other aluminosilicates (e.g. montmorillonite, kaolinite) is often used in many applications [1, 2] e.g as a filler in natural or modified forms in nanocomposites [3, 4]. Halloysite is a two-layer mineral with chemical formula $Al_2Si_2O_5(OH)_4$, consisting of one tetrahedral sheet of silica (SiO_4) linked through oxygen atoms to one octahedral sheet of alumina octahedral (AlO_6). As a mineral it belongs to the kaolinite subgroup, which is represented by the same chemical formula $Al_2Si_2O_5(OH)_4 \cdot nH_2O$, where n is the number of water molecules that occupy the interlayer spaces of the clay aggregates. The value of n is zero for kaolinite and up to 4 for halloysite. The raw halloysite mineral contains a layer of water in its interlayer space which results in an increase in layer thickness up to 1.01 nm (called 10 Å halloysite). The interlayer water molecules can be removed by heating at elevated temperature. This process turns down the interlayer distance ranging from 0.715 nm up to 0.75 nm thickness (called 7Å halloysite) [2, 5]. However, after a dehydration process, the halloysite plates stay separated.

There are several variations of the crystal structure of halloysite, most common include either halloysite tubules or plates. Halloysite plates are composed of either one or more plates loosely joined together with the so-called "gallery", where different atoms, ions and molecules can be absorbed. Platy halloysite is ready for delamination, intercalation and exfoliation. Halloysite from the Dunino

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[a] Corresponding author: Marcin.Lutynski@polsl.pl

deposit is characterized by the specific platy and tubular structure. The octahedral external surface is built up from the hydroxyl groups with outstanding hydrogen and has a positive surface charge when the oxygen surface of the tetrahedral sheet is negatively charged, like montmorillonite. This platy structure gives the possibility and facilitates ability to activate both the surface tetrahedral and octahedral sheet [1-5].

In the raw material from natural deposits in countries like New Zealand and America halloysite has usually a tubular structure. The external surface of the halloysite nanotube is siloxane surface and internal alumina surface, active groups Al-OH are situated on the edges of the tube. In plates, a higher share of the active Al-OH edges occur, besides due to their spatial distribution they are more readily available. It should be recognized that the individual layers of the slats forming the wall of the tubes can participate, only to a small extent, in a variety of processes (intercalation, sorption, formation of various bonds, etc.). Halloysite from the Dunino deposit has a unique structure of mixed nanoplates and nanotubes which can be in certain cases its advantage. Another important factor in the reactivity of halloysite is the substitution occurring in the crystal structure where the most common are mineral substitutions of Al and Fe in the Si tetrahedra and Fe, Mg, Ti for Al in octahedra. These substitutions cause local imbalances of electric charges and create a number of so-called active sites capable of forming bonds with many different substances [1-5].

Particular attention of scientist is paid to the unique structure of halloysite nanotubes (HNT) and nanoplates (HNP) [2,4,6,7,8]. The presence of iron and titanium oxides e.g.: magnetite, magnesioferrite, ilmenite, hematite and goethite in raw material is the major problem impeding the use of halloysite in nanotechnology and polymer industry [8,9]. Due to the high content of iron oxides the raw material from the Dunino deposit has a rusty-reddish colour. Even low quantity of iron oxides may cause strong pigmentation in aluminosilicates [8] and change the properties and colour of polymers containing them. Many physical and chemical processes such as magnetic separation and acid leaching are commonly used in purification of aluminosilicates [8-18].
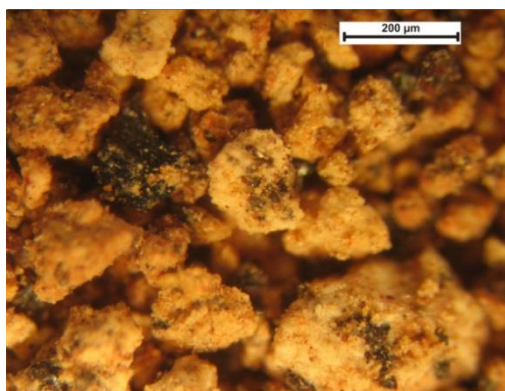

Figure 1. Structure of raw material after first milling. Impurities in the form of iron and titanium oxides are clearly visible.
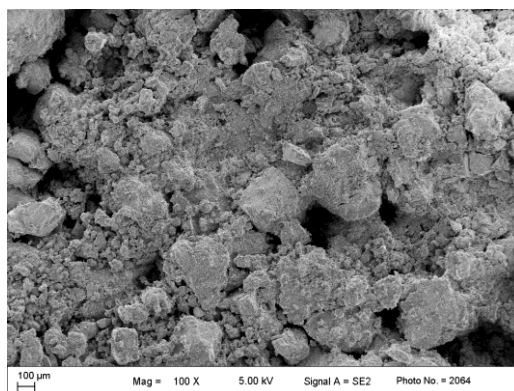

Figure 2. Structure of raw halloysite from the Dunino deposit after drying and crushing (SEM picture).

2 Experimental procedure and results

The previous work [9] allowed to purify raw material by HCl treatment and obtain a fraction consisting mainly of aluminosilicates with particle size smaller than 20 μm. The purification process developed earlier, however consisted of more than thirty stages and operations. To separate aluminosilicates from iron and titanium oxides by physicochemical separation the following operations were applied crushing, milling, filtration, drying, hydrochloric acid treatment,

sedimentation (settling), polygradient magnetic separation in strong (2T) magnetic field. The use of polygradient magnetic separation in the magnetic field was sufficient to separate heavy magnetic minerals (e.g. Fe_3O_4), which were difficult to remove with the use of other methods. In this research however, authors focused on optimization of the following stages of the process: crushing, milling magnetic separation and sedimentation and what's more, leaching in hydrochloric acid was replaced by sulfuric acid leaching in order to enhance the purification process.

The first stage of preparation involved drying the raw material at the temperature of 100 °C for one hour. The ball mill was used for crushing the raw material (Fig. 1). The structure of dried and crushed raw material was observed under the scanning electron microscope (Fig. 2). In the next stage the material was sieved below 1 mm. The particle size analysis were carried out to check the particle size distribution of the unified material. Histogram showing the particle size distributions of raw material after drying, crushing and sieving is shown in Fig. 3. A dried, crushed and sieved material was homogenized and the mass of 400 g was designated as a feed for further processing. The feed was immersed in 550 cm^3 of water, stirred and washed. The resulting slurry was ground in a ball mill with steel balls of 5 to 10 mm in diameter.
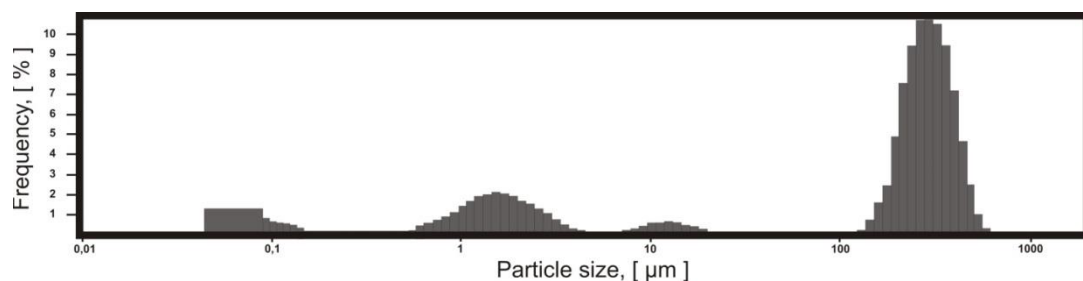

Figure 3. Histogram showing the particle size distributions of raw material after drying, crushing and sieving.

The material was washed and the density of the resulting slurry was $d = 1.35$ g/cm^3. The next stage of the experiment was chemical processing where 50 ml of H_2SO_4 was added to the slurry. After 90 min of leaching and mixing in reactor at 90 °C, the coarse material was washed out. The filter cake was washed with water and filtrated. The resulting material was subjected to magnetic separation in order to separate magnetite from nonmagnetic fraction. Detailed description of the experimental procedure is shown in Fig. 4.

Since the coarse fraction had still slightly reddish colour it was cleaned by slow magnetic separation one more time. A matrix magnetic separator was equipped with cylindrical neodymium magnets as a filtration medium. In all experiments the polygradient magnetic separation in magnetic field was used. The applied magnetic flux was 2 T. The magnetic fraction concentrate was marked as the sample no. 1.Consequently the slurry was settled out and the particle size fraction below 20 μm was separated in a sedimentation column. The obtained homogeneous fluid was separated when settled due to the density difference, in which ferruginous minerals of high specific density, are separated from the layered aluminosilicates. The resulting product consisting of light aluminosilicates fraction mostly HNT and HNP was marked as the sample no. 2. The particle size analysis of this fraction was done to check the particle size distribution of this material. Fig. 5 shows the histogram showing the particle size distributions of sample no. 2.

The resulting material was filtrated, dried and subjected to microscope analysis (Fig. 6). The remaining mixture of iron, titanium oxides and aluminosilicates over > 20 μm in particle size was marked as the sample no. 3. Consequently, the pre-thickened material was subjected to dehydration in a filter. The sample intended for the study was a mixture of magnetite, hematite and goethite crystals of size above 20 μm and other phases such as dispersed micro crystallites of halloysite with particle sizes ranging from a few to several μm and irregular aggregates of particle sizes 20 - 1000 μm (Fig.6). The results of physicochemical treatment of raw material from the Dunino deposit are shown in Table 1.
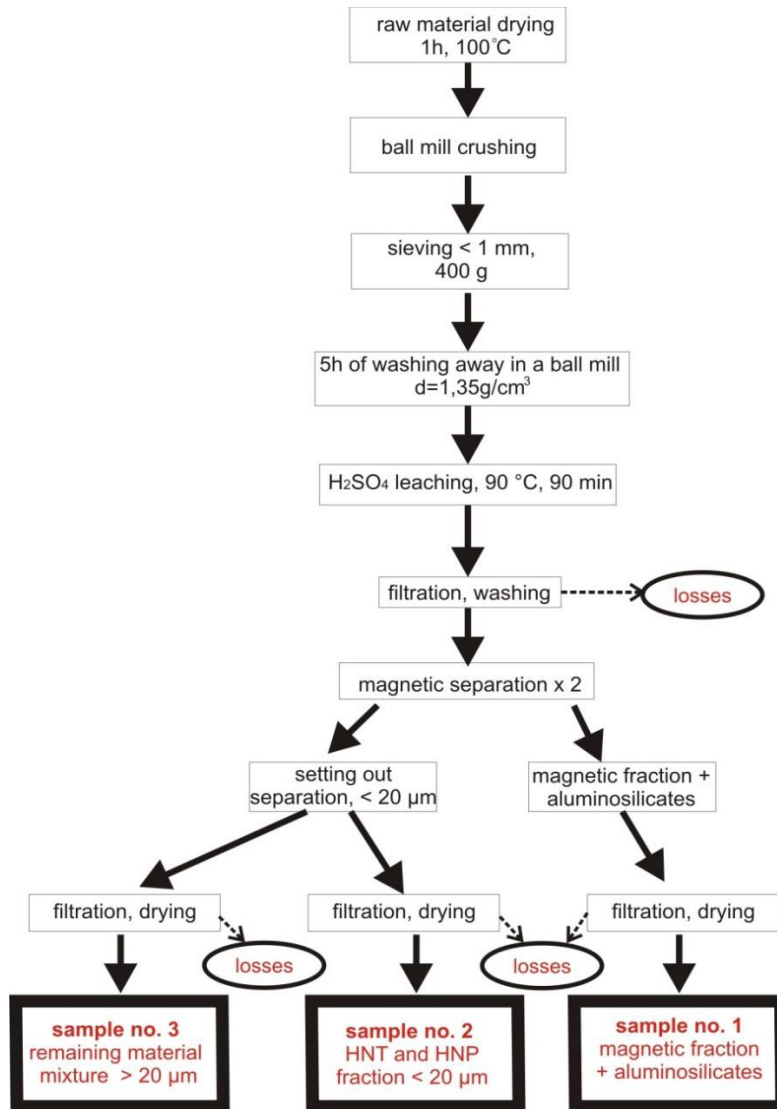
Figure 4. Detailed diagram of purification procedure of halloysite by H_2SO_4 leaching, magnetic separation and sedimentation.
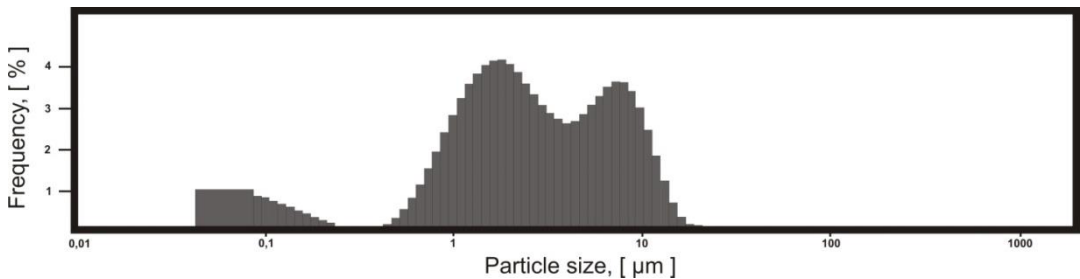

Figure 5. Histogram showing the particle size distributions in sample no. 2 (aluminosilicates HNT and HNP mixture < 20 μm).
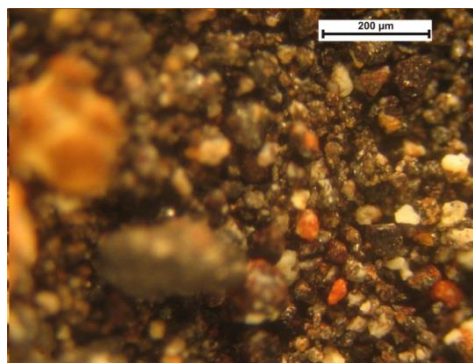
Figure 6. Iron concentrate + aluminosilicates after H_2SO_4 treatment and double magnetic separation (mainly iron oxides).
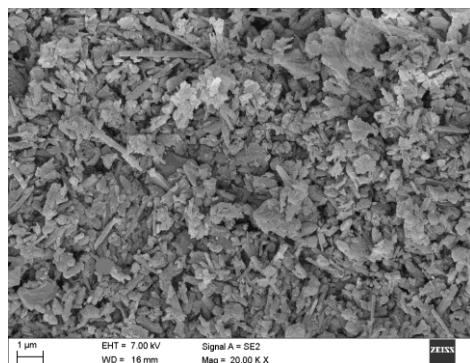

Figure 7. The structure of „light" non-magnetic fraction of halloysite after H_2SO_4 treatment, settling out (float) (magnetic separation aluminosilicate, < 20 µm).

The procedure described above proved that iron oxides can be removed from halloysite by chemical leaching without either deformation of the crystalline structure or changes in the particle morphology. Scanning electron microscope observations (Fig. 7) confirm that light fraction sample consisted mainly of halloysite nanotubes (HNT) and nanoplates (HNP).

Table 1. Results of physicochemical treatment of raw material from "Dunino" deposit.

Sample no.	Processes applied	Yield [g]	Yield [%]
1	Iron concentrate + aluminosilicates after H_2SO_4 treatment and double magnetic separation	65	16.25
2	HNT and HNP mixture < 20 µm	101	25.25
3	Remaining material mixture > 20 µm	210	52.5
	Losses	24	6

3 Summary and conclusions

The aim of this work was to obtain fine-grained fraction of halloysite particles consisting of nanotubes (HNT) and nanoplates (HNP). Physicochemical processing consisting of acid leaching treatment using H_2SO_4, sedimentation and magnetic separation gave promising results. The proposed method where nanotubes (HNT) and nanoplates (HNP) were separated, consisted of several simple stages and can be easily scaled up to the industrial scale. The main advantage of this method was that the impurities in the form of iron and titanium oxides, which were present in the Dunino deposit, were removed efficiently and with small amount of loses (6% on average). The first and second stage of the process, drying and milling, helped to purify the light aluminosilicate fraction, and therefore the recovery in magnetic separation was much more efficient than in the previously developed method [9]. The most desirable product of this method was light fraction of aluminosilicate (< 20 µm) consisting mainly of halloysite nanotubes (HNT) and halloysite nanoplates (HNP) which can be used for the manufacturing of e.g. polymer - aluminosilicate composites. The average yield of this fraction was 25.25%.The yield of mixed fraction (> 20 µm) of aluminosilicate and the rest of the iron and titanium oxides was on

average 52.5%. Although this fraction was not of high quality yet it can be used for manufacturing of high quality sorbents. The yield of heavy iron oxides fraction separated during magnetic separation was 16.25% on average and although it appears as a reject it can be utilized e.g. for manufacturing of pigments.

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