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PURIFICATION OF HALLOYSITE BY MAGNETIC SEPARATION

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Abstract: Rational use of mineral resources requires advanced separation methods in order to obtain high quality products. In this study chemical treatment with magnetic separation of halloysite from Dunino (Poland) is presented. Initial crushing, hydrochloric acid absorption treatment, sedimentation (settling) and polygradient magnetic separation in weak magnetic field were applied to separate aluminosilicates from iron and titanium oxides (impurities). The process allowed to obtain a product of approximately 98% purity of the aluminosilicate fraction (halloysite + kaolinite). The tailings from magnetic separation consisted of iron oxides, while the intermediate product consisted mainly of aluminosilicate and iron chlorides resulting from the HCl treatment. The obtained products can be used as a component of polymer nanocomposites, sorbents and in ceramics industry.

Keywords: *halloysite, magnetic separation, HCl treatment*

Introduction

Magnetic separation methods are available for application in various industries. Due to many benefits of magnetic methods of material treatment, the range of applications of this technique is enormous (Svoboda and Fujita, 2003). For a long time the magnetic techniques were widely used in raw material processing and in aluminosilicate industry (Brozek et al., 1991; Iannicelli et al., 1997).

Polygradient magnetic separation can be used for cleaning fine particles of minerals. The „Dunino” deposit of weathered basalt located in the western part of Poland consists mainly of halloysite and can be regarded as an interesting example of

mineral resource deposit. The raw material can be enriched aiming to obtain products containing aluminosilicates, iron and titanium oxides of different grades of purity. Mineralogical and chemical composition analyses of crushed particles showed that aluminosilicates dominate in smaller than 50 μm particle size fractions, while iron and titanium oxides have a higher concentration in the coarse particle size fraction (Makary et al., 1990). In order to commercialize raw minerals, the physical and chemical processes resulting in modification of morphology, separation of iron oxides and removal of other components from kaolinite and halloysite are of interest of many researchers (Ambikadevi and Lalithambika, 2000; Stechman, 2001; Pytlinski and Myjkowski, 2003; Zhang et al., 2012; Belkassa et al., 2013; Saklar and Yorukoglu, 2015).

In order to separate aluminosilicates from iron and titanium oxides a four stage physicochemical separation process can be applied consisting of initial crushing, hydrochloric acid absorption treatment, sedimentation (settling), and polygradient magnetic separation in weak magnetic field.

Magnetic properties of mineral depends on its chemical compounds. In general, magnetic separation is used to concentrate magnetic materials and to remove the magnetized particles from fluid streams. Separation is achieved by passing either the suspension or mixtures of particles through a non-homogeneous magnetic field (Meireles et al., 2010). As a result, this process leads to either retention or deflection of magnetizable particles. Thus, the presence of isomorphous elements, strongly magnetic (ferromagnetics) such as iron, nickel, cobalt and lanthanides can be given as an example. Therefore, these elements may change the properties of mineral from diamagnetic (in its pure form) to antiferromagnetic when containing impurities. Classification of minerals according to their magnetic properties differs in various publications due to this phenomena or magnetic separation methods applied (Ciesla, 2003; 2012; Moeser et al., 2004; 2010; Drzymala, 2007).

The presence of impurities in the raw mineral was used in this study to separate iron oxides from the raw material. Magnetic separation as a complimentary method of the Dunino halloysite deposit raw material cleaning was used in order to obtain high purity halloysite concentrate which can be used as a component of polymer nanocomposites, sorbents and in ceramics industry.

Materials and methods

Halloysite is a volcanic-derived mineral. It is a product of basalt weathering with the formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. The investigated halloysite was characterized by the specific layered-tubular and platy structure (Fig. 1). When dry, the mineral is very brittle and under very low loads it easily disintegrates into irregular crumbs. Similarly to other kaolinite minerals, it adsorbs water but unlike montmorillonite it does not increase its volume (swelling effect). After drying at the temperature above 60 $^\circ\text{C}$ halloysite loses water and its structure becomes similar to kaolinite with the

heterogeneous disordered structure. Due to the high content of iron oxides the raw material from Dunino deposit has a rusty-reddish color. The specific surface S_{BET} of dried material is equal to $60.8 \text{ m}^2/\text{g}$, pore volume $0.28 \text{ cm}^3/\text{g}$, and pore diameter of 12.2 nm as well as density range $2.4\text{-}2.8 \text{ g/cm}^3$. Halloysite as a layered aluminosilicates from kaolinite subgroup and it is an object of intensive basic and applicative research (Matusik, 2014). This mineral can be used for many innovative purposes (Lewicka, 2012) such as environmental protection (Sakiewicz et al., 2012), material engineering and nanotechnology (Hedicke-Hochstotter et al., 2009; Yuan et al., 2012; Zhang and Fu, 2012; Zhang and Yang, 2012).

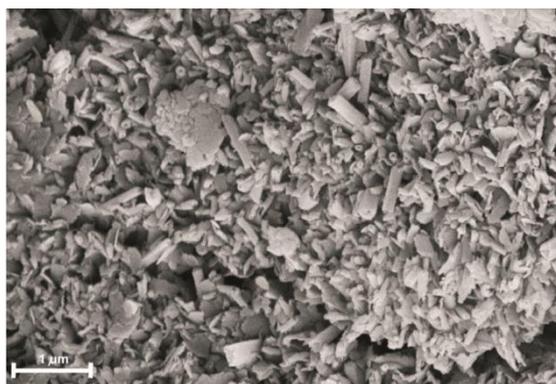


Fig. 1. SEM photo of layered-tubular structure of raw halloysite from Dunino deposit

The samples from Dunino deposit were analyzed with the use of X-ray diffraction (XRD) (Fig. 2). Minerals found in the raw material of Dunino deposit are shown in Table 1.

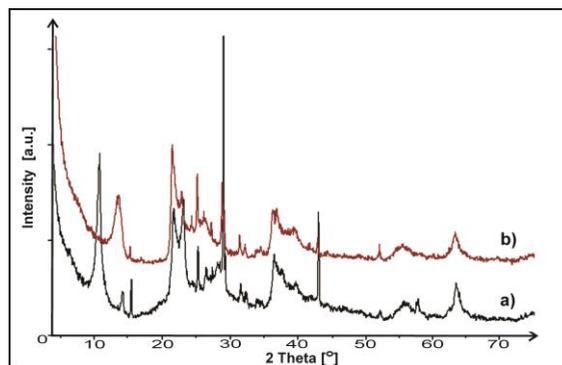


Fig. 2. X-ray diffraction patterns of a) raw halloysite 1 nm and b) halloysite 0.7 nm after drying

Table 1. Mineralogical composition of the Dunino deposit

Mineral	Chemical formula	Oxide based formula
Halloysite	$\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8 \cdot 2\text{H}_2\text{O}$	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$
Kaolinite	$\text{Al}[\text{Si}_4\text{O}_{10}] \cdot (\text{OH})_{10}$	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
Magnetite	$\text{Fe}^{+2}\text{Fe}^{+3}\text{O}_4$	$\text{FeO} \cdot \text{Fe}_2\text{O}_3$
Magnesioferrite	$\text{MgFe}_2^{+3}\text{O}_4$	$\text{MgO} \cdot \text{Fe}_2\text{O}_3$
Ilmenite	FeTiO_3	$\text{FeO} \cdot \text{TiO}_2$
Geikielite	MgTiO_3	$\text{MgO} \cdot \text{TiO}_2$
Crandallite	$\text{CaAl}_3\text{H}[(\text{PO}_4)_2 \cdot (\text{OH})_6]$	$2\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$
Goyazite	$\text{SrAl}_3\text{H}[(\text{PO}_4)_2 \cdot (\text{OH})_6]$	$2\text{SrO} \cdot 3\text{Al}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$
Gorceixite	$\text{BaAl}_3\text{H}[(\text{PO}_4)_2 \cdot (\text{OH})_6]$	$2\text{BaO} \cdot 3\text{Al}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$
Hematite	Fe_2O_3	$\text{FeO} \cdot \text{Fe}_2\text{O}_3$

The initial separation process of minerals in the raw material from the Dunino deposit was done with the use of acid absorption treatment using dry HCl. The obtained homogeneous fluid was separated when settled due to the density difference. As the final step of upgrading a polygradient wet magnetic separator was used. It was the most efficient for fine particle size separation ($<1 \mu\text{m}$). In this case, the magnetic separator dealt with the finest fractions of raw material consisting mainly of iron oxides, for instance magnetite. A custom made matrix magnetic separator was equipped with cylindrical neodymium magnets as a filtration medium. In all experiments the applied magnetic flux was 2 T.

Resulting products were identified with optical modular microscope SteREO Discovery ZEISS. The surface morphology of samples was analyzed with a scanning electron microscope Zeiss Supra 35 equipped with EDS for the chemical composition analysis. In order to enhance the quality of photos some of samples were coated with a thin layer of gold.

An XRD phase analysis of samples was conducted with the use of XRD 7 diffractometer Seifert-FPM. The applied emission was Co K-alpha with Fe filter. The X-ray tube parameters were 35 kV/25mA. The scattering angle for phase analysis 2θ was in the range from 4 to 100° . The measurements were done in steps of $0.04^\circ 2\theta$ every 2 s per step.

Experimental procedure

Detailed description of the experimental procedure is shown in Fig. 3. The first stage of preparation involved drying the raw material at temperature of 60°C and crushing it into the particle size below 10 mm. Hence, the 1.0 nm halloysite structure transformed into 0.7 nm halloysite (Fig. 2) (Joussein et al., 2006). In the next stage the feed was ground for 20 minutes in a ball mill. A dried and crushed material (Fig. 4) was homogenized and the mass of 400 g was designated as a feed for further

processing. The feed was immersed in 550 cm³ of water, stirred and washed. The resulting slurry was ground in a ball mill with steel balls of 1 to 5 mm in diameter. Washing of the material was conducted for 4 hours and the density of the resulting slurry was $d = 135 \text{ g/cm}^3$.

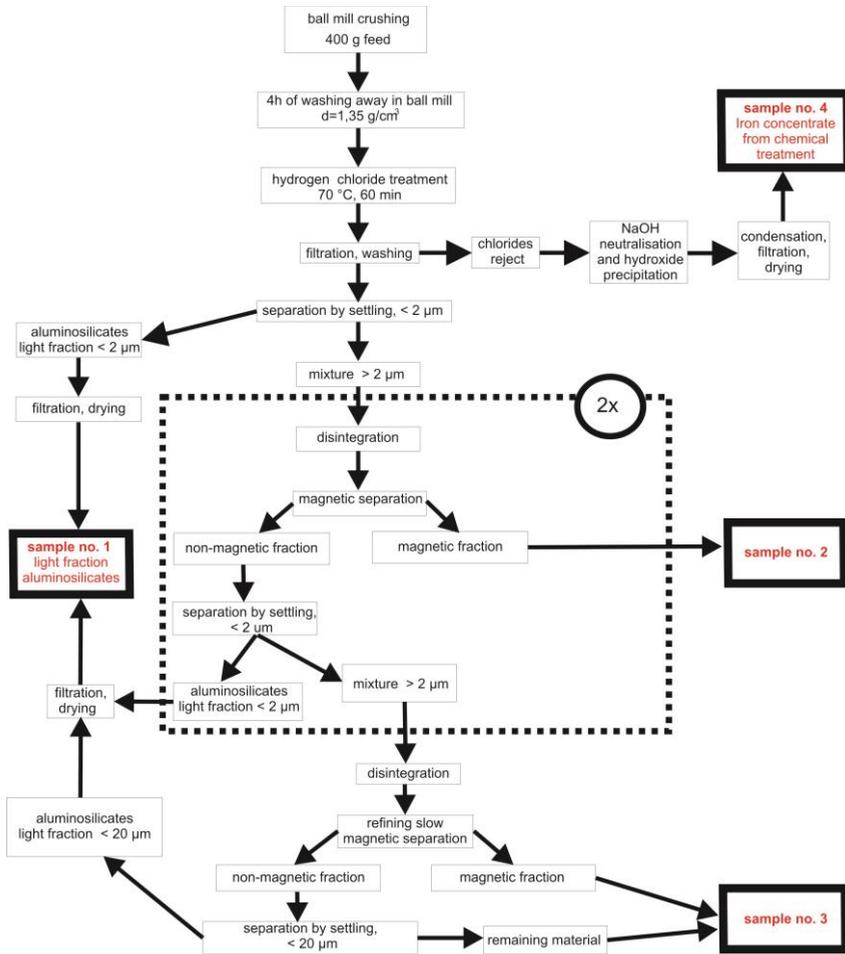


Fig. 3. Detailed diagram of Dunino halloysite deposit raw material cleaning procedure on the laboratory scale (sample number explained in the text)

The next stage of the experiment was chemical processing where the slurry was subjected to absorption of 60 g (approximately 40 dm³) of dry HCl. In order to enhance the absorption rate the slurry was agitated for 60 minutes at the temperature of 70 °C. The purpose of this process was to dissolve iron oxides, particularly hematite, which has relatively weak paramagnetic properties. HCl also played a role of a surfactant to facilitate the process of washing and segregation of minerals. The reaction mixture was separated from the chloride solution and the excess HCl was

removed by repeated stripping with water (Fig. 5). Consequently the slurry was settled out and the particle size fraction below $2\ \mu\text{m}$ was separated in a sedimentation column. The resulting material was filtrated, dried and subjected to the microscope analysis (Fig. 6). After each stage of crushing and sedimentation the light fraction was separated by sedimentation. A resulting product consisting of light aluminosilicates along with non-magnetic product (reject) was marked as the sample no. 1 (Fig. 6).



Fig. 4. SEM photo of a raw halloysite from Dunino deposit after milling and 20 minutes of drying

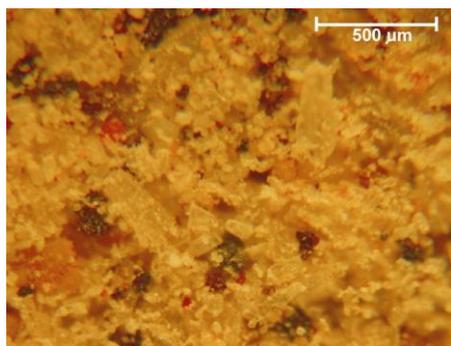


Fig. 5. Morphology of halloysite after washing and milling

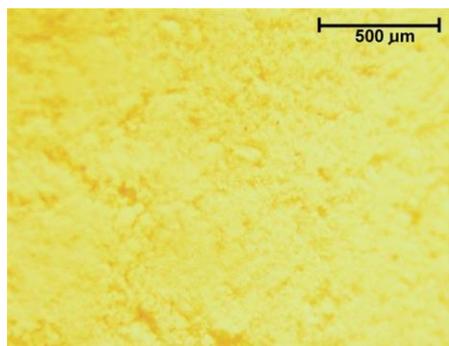


Fig. 6. Morphology of sample no. 1 after dry HCl treatment and sedimentation separation

The coarse material ($>2\ \mu\text{m}$) was subjected to wet milling and magnetic separation twice in order to separate magnetite from nonmagnetic fraction. The concentrate (magnetic fraction) was marked as the sample no. 2 (Fig. 7). The non-magnetic material was again separated by settling to fine fraction ($<2\ \mu\text{m}$) and coarse fraction ($>2\ \mu\text{m}$). Since the coarse fraction had a reddish color it was suspected that the cleaning was insufficiently efficient and the material was cleaned by slow magnetic separation. The non-magnetic fraction ($<20\ \mu\text{m}$) from this process was dried and added to sample no. 1 and was marked as the light aluminosilicates fraction. Finally, the pinkish-violet colored magnetic fraction from slow magnetic separation was the sample no. 3. The reject from HCl treatment was neutralized with NaOH resulting in

hydroxides precipitation. The material was concentrated, filtered and dried (sample no. 4).

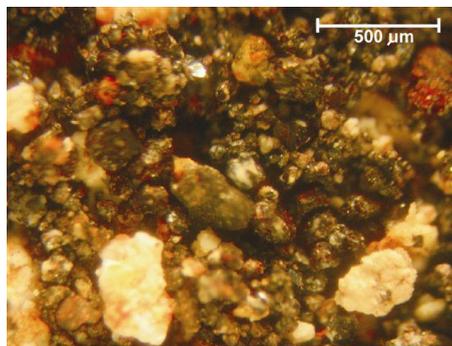


Fig. 7. Morphology of sample no. 2 – HCl treatment, settling and magnetic separation (magnetic fraction)

Results and discussion

Separation products were subjected to analyses with X-ray diffraction, SEM and optical microscope. Table 2 summarizes results and products of physicochemical treatment of raw material from Dunino deposit.

Table 2. Results of physicochemical treatment of raw material from the Dunino deposit

Sample no.	Processes applied	Yield [g]	Yield [%]
1	HCl treatment, settling out (float), magnetic separation, „light” non-magnetic aluminosilicate, < 20 μm	147.2	36.8
2	HCl treatment, settling out (sink), magnetic separation magnetic fraction, > 2 μm	41.6	10.4
3	HCl treatment, settling out (sink), repeatable slow magnetic separation magnetic fraction, > 2 μm	20.4	5.1
4	Precipitated hydroxides after HCl treatment Iron concentrate	160.0	40.0
	Losses	30.8	7.7

X-ray diffraction was used to determine the mineralogical composition of resulting products. Crystallochemical formulas of occurring minerals were recalculated into oxide-based formulas and the hypothetical content of occurring oxides in minerals was determined. Hence, a quantitative composition of the resulting products is presented in Table 3.

Table 3. Quantitative XRD analysis of the samples

Sample no.	Hematite group	Ferromagnetic group	Aluminosilicates halloysite + kaolinite	Crandallite group	Others
1	-	-	97.41%	1.40%	1.19%
2	-	16.85%	80.10%	1.50%	1.55%
3	2.20%	4.18%	89.60%	2.88%	1.14%
4	29.45%	-	-	25.67%	44.88%

The main product of separation, marked as the sample No.1 with yield of 36.8%, consisted mainly of halloysite and kaolinite of almost 98% purity. The major impurities were crandallite group minerals, an aluminous hydroxy phosphates which are not prone to magnetic separation and are difficult to solute in acids. Other separation products i.e. samples no. 2 and 3 were also consisting mainly of aluminosilicates, yet with larger content of ferromagnetic group and hematite group in sample no. 3. However, in this case the total yield of samples no. 2 and 3 was only 15.5%. The tailings consisted of iron oxides and crandallite group. Since aluminosilicates were not detected in tailings (sample no. 4) the process can be regarded as efficient.

Additionally, X-ray diffraction patterns of fine aluminosilicate fraction (sample 1) were analysed and it occurred that only 0.7 nm halloysite is present. It can be suspected the 1.0 nm halloysite transformed into 0.7 nm halloyiste while drying (Fig. 1) and HCl treatment. SEM (Fig. 9) and optical microscope (Fig. 6) observations confirm the tubular-plate structure of white aluminosilicate fraction.

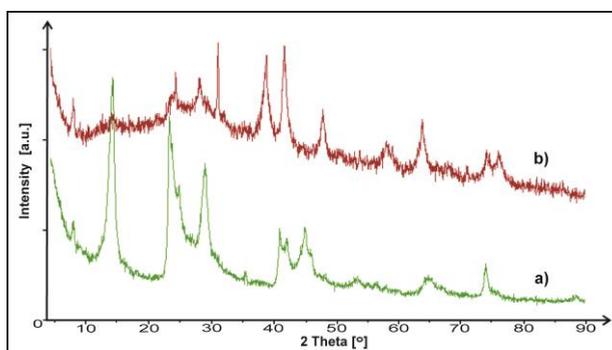


Fig. 8. X-ray diffraction patterns of a) sample no. 1 and b) sample no. 2

The XRD of sample no. 2 (Fig. 8), which consisted mostly of heavy products such as iron oxides, indicated also kaolinitic peak 0.717 nm and kaolinite/smectite structure which can also be an unstructured halloysite 0.7 nm. Nevertheless, in sample no. 2 the dominant minerals were hematite, magnetite and to low extent, aluminosilicates.

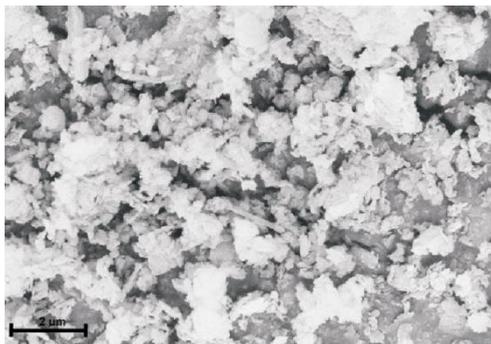


Fig. 9. SEM morphology of sample no. 1 – HCl treatment, magnetic separation and first stage settling

Although the proposed method of halloysite upgrading is composed of several stages, it can be easily up-scaled to an industrial scale. The main advantage of it is that the impurities in the form of iron oxides, which are present in the Dunino deposit, are removed efficiently and with negligible amount of losses.

Conclusions

The physicochemical process combined with magnetic separation applied for upgrading raw halloysite from the Dunino deposit in Poland gave promising results and the following products were obtained: (i) light aluminosilicate fraction consisting mainly of halloysite; (ii) heavy iron oxides – reject from magnetic separation and (iii) intermediate product consisting mainly of aluminosilicate and iron chlorides resulting from HCl treatment.

The polygradient magnetic separation in the weak magnetic field used in the study allowed to separate heavy magnetic minerals (e.g. Fe_3O_4) which were difficult to remove with the use of other methods. The main product, i.e. purified aluminosilicate, where the dominant mineral is halloysite, can be purified in other processes to be used for polymer composites, ceramics manufacturing or as a high quality sorbent. Further research should be focused on the first stage of the process, that is milling, where the light aluminosilicate fraction is liberated, and therefore recovery in magnetic separation can be higher.

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