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PROMOTOR EKOLOGII

Brief description of the Halloysite from the "Dunino" mine

Halloysite is a 1:1 aluminosilicate clay mineral with the empirical formula $Al_2Si_2O_5(OH)_4$. Its main constituents are aluminium 20.90%), silicon 21.76%), and hydrogen (1.56%). Halloysite typically forms by hydrothermal alteration of alumino-silicate minerals. It belongs to the kaolinite mineral group. Halloysite deposits are rare in the world. Currently, there are only three known working Halloysite mines. The only site in Europe is the Haloysite Mine in DUNINO (South Poland).

Dunino Mine resources belong to the largest deposits in the world and are estimated around 10.000.000 tons. The site Dunino is homogenous, which ensures a stable quality for long term deliveries.

The owner of the Mine is the INTERMARK Company which deals with the processing of this mineral and R&D work.

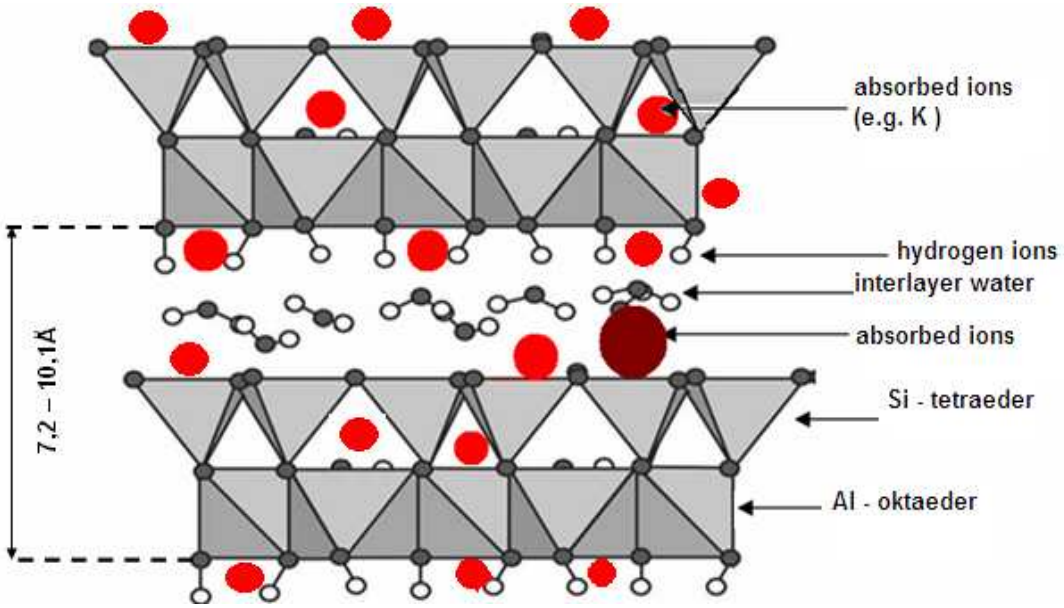

Fig.1 Structure of the halloysite

The raw mineral halloysite from the mine DUNINO consists of two main fractions:
a/ alumino-silicate fraction consisting mainly of halloysite (so called light fraction)
b/ ferro-titanous fraction (so called heavy fraction).

Both fractions are presented in a form of separated grains, they are not chemically bound (Fig. 2). First stage of mine material processing is the fractional separation for alumino-silicates fraction and heavy fraction.

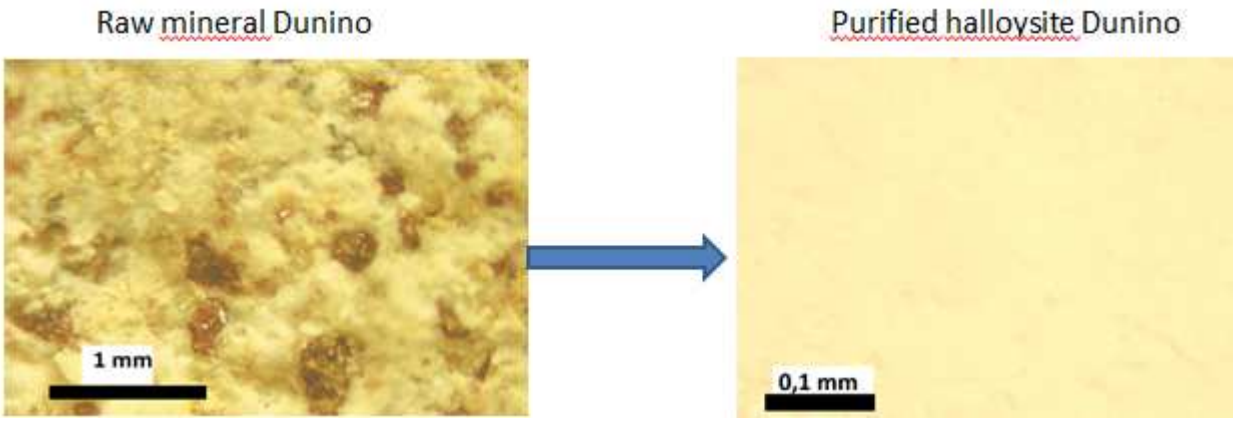

Fig. 2 Raw and purified halloysite from the site Dunino

The light fraction consists of halloysite nanaotubules, partially rolled nanoplatelets and disordered, mainly loosely dispersed platelets.
The separate grains have the dimension below 2-3 µm and are loosely aggregated (Fig. 3)
Their disaggregation is much easier in comparison with e.g. delamination of kaolinite or other minerals used as filler or carrier.
The platy shape of halloysite nanoparticle in comparison with the rolled tubular particle is characterized by significantly higher active specific surface area on both sides:

- tetrahedral silanol suface
- octahedral aluminol surface.

Many publications concerning different applications of halloysite reveal that for the forming of different types of bonds very importent is the octahedral side of the crystal. In the tubular halloysite this surface is rolled and the access to this surface in the inside of the nanotube is difficult if at all possible. Furthermore, the active area of the nanotubules is much smaller than in the case of the nanoplatelets.
The structure of the halloysite from the Mine Dunino is characterized by big numer of substitutions for Al and Si atoms. This results in electric unbalance of the planar surfaces and edges and large number of the active sites.

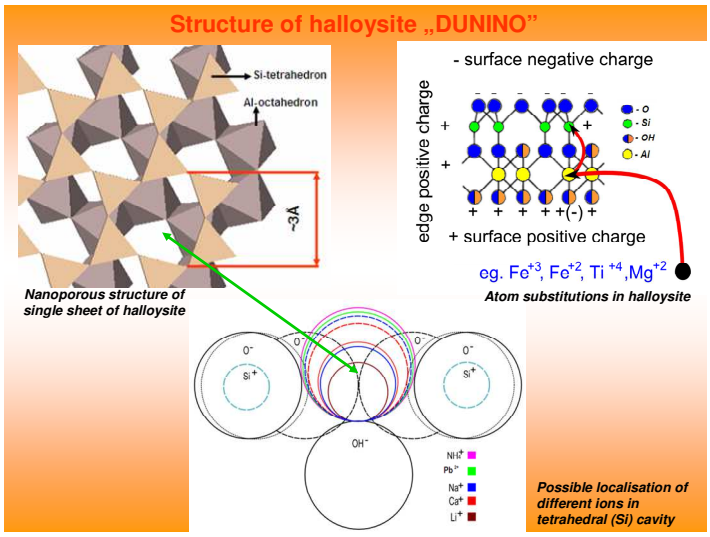

Fig.1 The cavities in the halloysite crystal and possible placement of absorbed ions in the tetrahedral cavity

Such features ensure high active specific surface area and cation exchange capability in comparison to other kaolinite-like minerals.
It is noteworthy that the mechanical properties of halloysite are several times higher than parameters of all plastics and metals and the small share of this additive ensures significant improvement of the plastics quality (E.G. Young modulus is ca 300 GPa)
A proper processing of halloysite can significantly improve its properties as a component of nanocomposites.

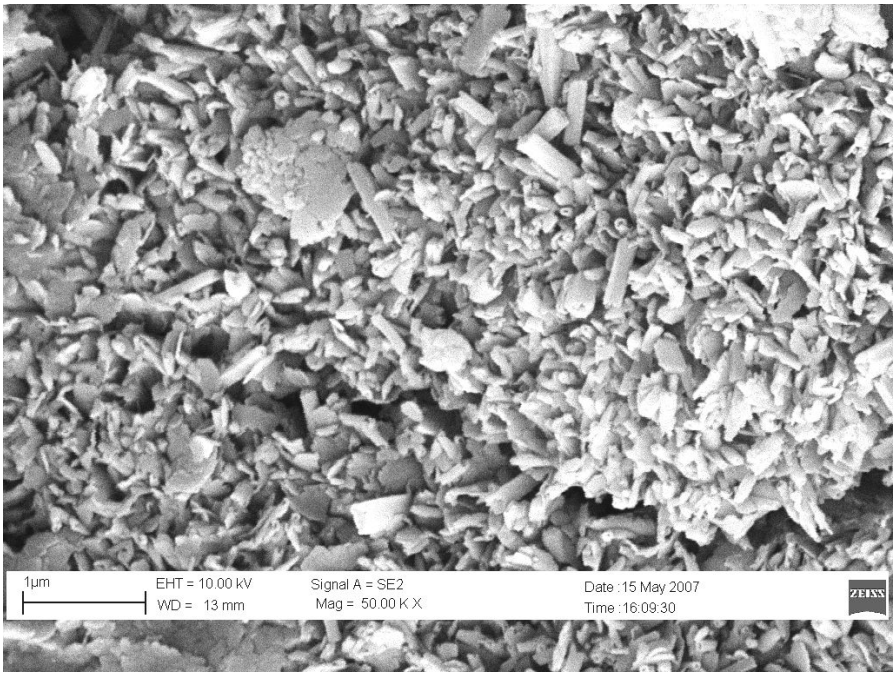

Fig. 3 Microscopic view of raw halloysite from the Mine DUNINO (Poland).
There are visible single nanotubules and nanoplatelets.

Halloysite nanoparticles have many advantages in comparison to e.g. carbon nanotubules such as:
- high thermal resistance,
- high durability,
- high electrical resistance (practically non electro-conductive).

The experience of many research works shows that the halloysite nanoparticles can be successfully used in nanocomposites characterised by high thermal resistance and high durability in different industry branches. They may also be used as a carrier for medicines, cosmetics and special paints in different applications.
Halloysite nanoparticles are not yet produced in Europe. The technology enabling their manufacturing from halloysite delivered from the mine DUNINO could ensure not only the quantity of nanoparticles needed for European purposes but also the quantity for export outside EU.
The own European mineral nanoparticles could bring a new impact for many industrial branches and research units.
The heavy iron-titanous fraction can be used as catalysts and as a pigment and paint component for different paints (especially anticorrosive paints). They are characterized by high specific surface area as sulphur-free components and therefore their quality is very high and area of their application could be very wide.
All of them can have remarkable impact on the reduction to EU countries of following minerals or mineral derived products:

- mineral nanoparticles
  The halloysite nanoparticles can be used as a filler for nanocomposites, carrier in pharmaceuticals and cosmetics, in agrochemical industry as carrier for controlled release of herbicides and pesticides.
- mineral fillers for polymers, composites, paints used in automotive and aerospace industry
- as an animal feed additive improving the fodder quality and reducing the mycotoxins
- as the efficient filter bed for air filtration in hatcheries and animal breeding farms, landfills etc.
- as a product for the insects control (e.g. red mite control in egg laying hens farms)
- catalyst in organic synthesis and reduction or ketonization of aliphatic and fatty acids.
  As such catalyst it can be used e.g. for biofuels manufacturing ensuring their quality and improving their combustion.
  The demand for such catalyst is still growing.

  Because all products of halloysite processing are products needed on market- halloysite is practically "zero wastes" mineral.

The halloysite from the mine Dunino can be delivered in following forms:

1) raw halloysite
2) dried and ground
3) calcined
4) activated halloysite
5) upgraded - white halloysite

The chemical composition of basic offered products is contained in Tab. 1

No	Description	Components [%]				Colour	Remarks
		Al	Si	Fe	Ti		
1	HW	21±1	23±1	1,5±0,5	1,2±0,5	white	Processed halloysite with platy and tubular structure, Fe and Ti mainly in substitution form for Al and Si
2	FL	23±1	25±1	5±1	0,8±0,5	light beige	Natural halloysite with reduced Fe and Ti quantity
3	HD	19±1	20±1	12±1	1,5±0,5	dark beige	Natural raw mineral
4	FC	12±1	13±1	32±2	5,4±1	dark grey (brich red calcined)	Raw mineral with high Fe- and Ti-oxides content

Tab. 1 Chemical composition of Mineral Dunino based products

Application of Mineral DUNINO based products :

1) Raw halloysite

for further processing for eg.:

- fillers for paper and plastics and nanocomposites
- coagulants for wastewater treatment,
- paint components and dyes,
- fodder additives,
- various sorbents for wide applications
- medicines and cosmetics,
- removal of big disaster spills (chemicals, oils etc.) and reduction of environmental effects of such spills.

2) Dried and ground halloysite

Dried and ground halloysite can be used as :

- fodder additive,
- component of long term acting fertilizer (controlled release of plant nutrients),
- additive for biomass combustion,
- air filter bed chemical processing and in animal breeding farms,
- component of various paints (anticorrossive, antibacterial and antifungal, paints for interior and exterior surfaces etc.),
- component for cosmetics,
- immobilizer for heavy metals (eg. wastewater, rivers, remediation of contaminated soil etc.)
- Halodrob – a product for insecticide control (e.g. red mite, bed bugs, alphitobius diaperinus)

3) Calcined halloysite

Calcined halloysite is an excellent absorber for:

- all kinds of spills (oil, acidic and basic spills),
- gas and air filter (eg. filter for biogas),
    - water filter

4) Activated halloysite

Acidic and basic activation causes an increase of sorption capacity of gases and liquids, increases significantly the specific surface area and porosity.

Activated sorbents can be used for the same purposes as the calcined. Their use ensures a longer activity of the filter and higher efficiency for the spill removal.

This sorbent is also extremely effective for the immobilization of heavy metals in water and wastewater.

Activated halloysite is used also as a catalysts.

5) Purified halloysite (white halloysite)

Purified halloysite can be used as:

- component of medicines and cosmetics (as carrier of slow release substances, absorber of gases and liquids)
- component of nanocomposites,
- filler for paper industry and plastics,
- component of paints.

6) Other halloysite derived products

We offer also other halloysite derived products:

- coagulants for wastewater treatment,
- pigments for paints, especially for anticorrosive paints
- friction materials (hard iron containing grains 0-1 mm from the raw material processing).

Possibilities of co-operation

INTERMARK offers the following possibilities of co-operation:

a) delivery of a/m goods,
b) participation in research programs (eg. medicines, nanocomposites),
c) common investments projects,
d) sharing of processing licenses with ensuring of the delivery of the basic material

Final remarks

INTERMARK has developed more than 10 different technologies for the manufacturing of various advanced products. In this area we co-operate with many Polish and European research institutes.

We are ready to co-operate with partners in the field of application of already manufactured products, as well as in the field of new technological solutions.

We are also interested in the co-operation in the area of further purification and processsing of our mineral. Our experienced specialists are ready to share their knowledge and experience.

For further information and proposals, please do not hesitate to contact us.

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