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The Properties of Moulding Sand with Halloysite

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Abstract

Until now, the mould sand in general use in the foundry industry are based on bentonite, which resulted from the fact that a good recognition properties and phenomena associated with this material. Come to know and normalized content of montmorillonite and carbonates and their important role in the construction of bentonite, and mass properties of the participation of compressive strength or scatter. Halloysite is widely used in industry and beyond them. However, little is known about its use in the foundry in Poland and abroad. This article presents preliminary research conducted at the Foundry Department of Silesian University of Technology on this material. Will raise the question of the representation of this two materials, which contains information connected with history and formation of materials, their structure and chemical composition. In the research, the results of compressive strength tests in wet masses of quartz matrix, where as a binder is used halloysite and bentonite in different proportions.

Keywords: Halloysite, Bentonite, Moulding Sand

1. Introduction

To best characterize today's foundry would say that it is a developing and continually improve industry, which strive for develop better and more modern moulding materials and modern lines.

To live up to the increasing demand for castings were invented automatic processing lines, which are used in mass production. Their use greatly contributes to: increase productivity, reduce staff, increased safety (using the existing OSH), reduce energy consumption and reduce the cost of the finished product [1].

The lifetime of automatic molding line amount several years, should therefore not surprising that the foundries have machines of various types and different levels of technology. In the absence of investment in equipment is expected to receive the products of varying quality, and thus, the risk of defects in the finished product.

Automation in the previous period concerned the processes related mainly to the implementation of form, hence the early arrangements are known as automatic molding lines (ALF). Operations flooding liquid metal to the mould, core and shake-out took place on these lines out of automatic cycle. Currently offered solutions of automate lines practically all aspects of the implementation of the casting, it is therefore justified their name - automatic casting lines (ALO) [2].

However, not alone the technological level of the machinery used may contribute to modernizing and improving the foundry technology. Equally important, and perhaps more important, is the continuous development of new moulding materials.

Currently the most widely used molding material is quartz molding sand with bentonite binder. In Poland and abroad, numerous studies are conducted to improve its properties, which have a direct impact on the quality of the finished casting and technology design. The paper is an attempt to assess the suitability of halloysite for making moulds and/or foundry core in mainly used for automatic moulding line.

2. Characteristic of bentonite

At the beginning important is to consider what is currently used bentonite. Initially, this mineral was named "taylorite" from the name of William Taylor, who studied clay deposits in the United States. This name was used until a new division of deposits into separate groups. For the first time the name of bentonite was used in 1898, when the W.C. Knight discovered near Fort Benton (Wyoming) a new type of rock rich in clay minerals of montmorillonite group, accompanied by minor amounts of other clay minerals such as kaolinite and illite [3]. Bentonite is one of the sub-smectite (Fig. 1), whose main feature is unusual hygroscopicity resulting from a specific building block.

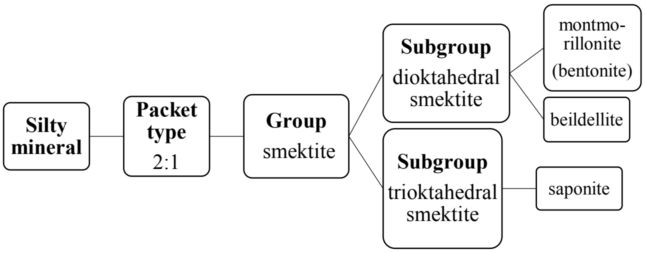

Fig. 1. Classification of bentonite by AIPEA (Association Internationale pour l'Etude des Argiles) [16]

As mentioned, the bentonite clay is a rock formed by transformations of volcanic glaze occurring in the sediments, such as pyroclastic tuffs and tuffites [4]. The main component of bentonite are minerals from the group of smectities, containing at least 75% montmorillonite [5]. Related of bentonite are bentonite clays (besides smectite contain a higher amount of other clay minerals) resulting from weathering of aluminosilicate rocks and sediment in the aquatic environment [4].

The largest deposits of this mineral can be found in: USA, Russia, Georgia, Romania, France, Serbia, Brazil, Germany, Czech Republic and Slovakia.

Polish deposits of this material are unfortunately very small and more frequently can meet a variety of bentonite clays, whose main component are unclay mineral. The country has identified the four bentonite deposits of minerals:

- bentonite's basalts detritus/decomposed rock of Lower Silesia,
- bentonite clays of the Upper Silesia,
- bentonite clays of the southern margin of the Holy Cross Mountains,
- bentonite clays of the Carpathian.

Bentonite can be defined as hydrated aluminum silicate with three-layer package, consisting of two silicone oxygen layers and the separation alumino oxygen layer (Fig. 2).

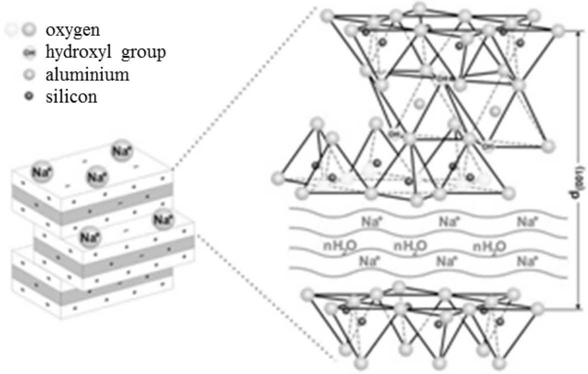

Fig. 2. Package building of montmorillonite [6]

The general structural formula of bentonite [6]:

$$mMg[Si_4O_{10}](OH)_2p(Al_2\ Fe^{III})_2[Si_4O_{10}](OH)_2nH_2O \tag{1}$$

the proportion m:p=0,8÷0,9.
The formula of montmorillonite:

$$Al_2O_3{\cdot}4SiO_2{\cdot}3H_2O{\cdot}nH_2O \tag{2}$$

Equation (2) shows the theoretically pure montmorillonite with the chemical composition: 48÷56% SiO_2, 11÷22% Al_2O_3, 5% or more of Fe_2O_3, 4 to 9% MgO, 0.8÷3.5% and more CaO, 12÷24% H_2O and such chemicals as K_2O and Na_2O which lower the refractoriness [7].

Chemical composition (2) naturally occurring montmorillonites are quite different. Result is the possibility of isomorphic substitution of silicon network where Si^{4+} ions can be replaced by Al^{3+} ions and changes aluminooxygen network and where Al^{3+} ions can be replaced by Mg^{2+}, Li^{3+} or others ions. As a result of described changes may arrive to reduce the attractive forces between the elementary packets, which may contribute to the growth of grains, which is caused by absorption of water molecules between the packages. Dimensions of montmorillonite network are 0.96÷2.14 nm and mainly depend on the thickness of the layer of water.

Depending on the cations present in the clay, there are two types of bentonites:

- sodium bentonites,
- calcium bentonites (or calcium-magnesium).

Among mention frequently is used calcium bentonite due to properties like the greater the potential for absorption of water, less sensitive to moisture and better resistance to high temperatures. Comparison of properties of both materials are shown in Table 1.

Table 1.
Comparison of properties of calcium and sodium bentonite [8]

Characteristics of bentonite	Sodium	Calcium
water absorption according to Enslin	large	small
ability to swell	very large	small
heat resistance	bigger	smaller
casting properties	good	weak
rheological properties	good	weak
waterproofing	good	medium
the ability to create a thixotropic gel	large	small

Chemical composition of bentonite is dependent on the deposit of material. Table 2 shows the sample locations of deposits in the world.

Table 2.
Chemical composition of bentonite in different regions of the world [9÷12]

The location deposit of halloysite	Poland	Germany	Slovakia	Serbia	Brasil
	Chemical composition [%]				
SiO_2	56.65	49.85	65.92	57.51	52.78
Al_2O_3	16.00	16.23	13.58	17.13	27.39
Fe_2O_3	2.11	6.80	2.08	7.67	6.35
MgO	4.73	3.18	7.15	2.35	1.96
CaO	1.63	3.19	2.29	1.81	0.46
Na_2O	2.65	2.63	1.43	0.75	-
K_2O	0.80	0.52	1.66	1.18	0.56
TiO_2	0.11	0.70	-	-	0.79
P_2O_5	0.034	0.150	-	-	-

3. Characteristic oh halloysite

This mineral is named by a Belgian geologist Omalius d'Halloy, who first discovered the deposits of this material in 1826. Haloizyt belongs to the sub-group of kaolinite clay minerals (Fig. 3). The main feature that distinguishes it from other materials, affecting its property, is the "tubular" construction of crystal grains, and ease of chemical processing.

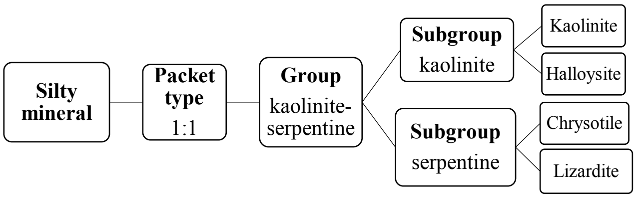

Fig. 3. Classification of halloysite by AIPEA (Association Internationale pour l'Etude des Argiles) [16]

Halloysite deposits are the result of surface weathering of volcanic rocks (basalts), but the most efficiently process occurs in humid and hot climates.

The deposits of this mineral can be found in the USA, China, New Zealand, Greece, Macedonia, Algeria, Poland and Slovakia. At the moment there are three active mines of halloysite: in the USA (about 1 million tons), New Zealand (about 3 million tonnes) and Poland (about 10 million tons).

Halloysite can be defined as hydrated aluminum silicate with monoclinic geometry. In contrast to distinct from kaolinite, which is very similar, it is distinguished morphology of crystals present in the form of tubes, resulting from the rolled plates. The size of these tubes depends mainly on creation of reserves and ranges from 500÷1100 nm long and 15÷50 nm inner diameter (Fig. 4) [13].

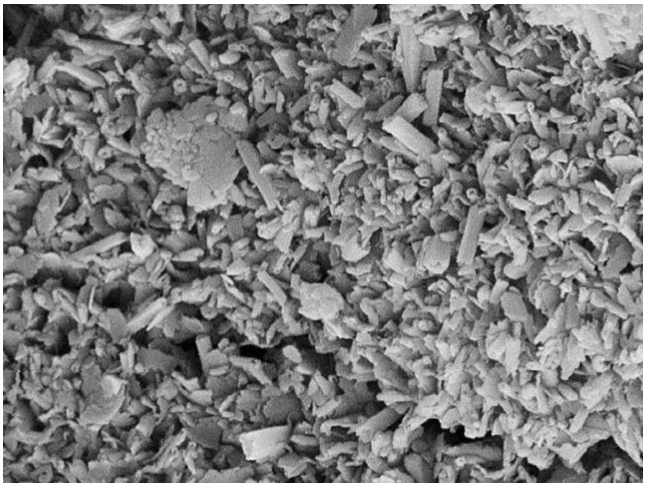

Fig. 4. Microscope picture of halloysite [14]

This mineral has two variations. The first is hydrated halloysite (10 Å) (chemical formula $Al_2Si_2O_5(OH)_4{\cdot}2H_2O$), in which the interlayer space of the water molecules are located and halloysite (7 Å) ($Al_2Si_2O_5(OH)_4$), which his dehydrate variation [15]. In both varieties can be distinguished:

- tetrahedron - small silicon cation centered around him four oxygen anions, which form tetrahedral layer (at the base of the tetrahedron are oxygens, which are common to neighboring tetrahedron, creating, in the ideal case, the ring of hexagonal symmetry) (Fig. 5) [16].

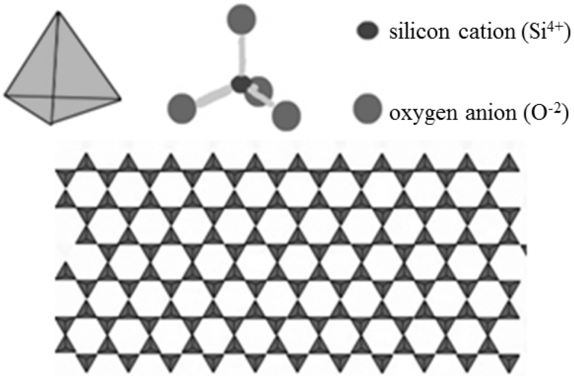

Fig. 5. Schematic tetrahedrons and tetrahedral layers [16]

- octahedron – in his center is a metal cation (usually aluminum) centered around each other six oxygen anions and hydroxyl groups, forming a layer of octahedral (each anion is common to the neighboring octahedrons) (Fig. 6) [16].

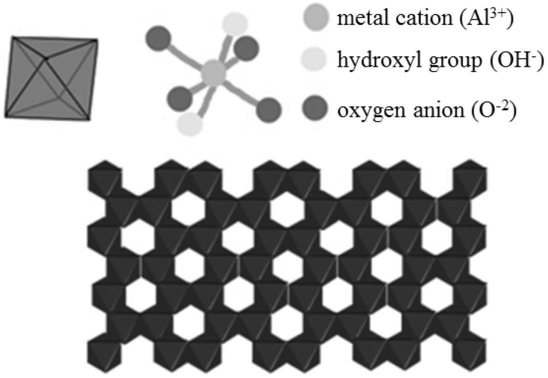

Fig. 6. Schematic octahedron and octahedrons layers [16]

Halloysite (10Å) (Fig. 7) turns out to be a quite unstable material, because at room temperature, and maintaining adequate moisture it can go in the variation of (7Å). Occurring between packages of mineral water has been divided into two types [15]:

- „hole water" – located in trigonal voids, probably forming hydrogen bonds with the oxide tetrahedron layer, strongly associated with mineral,
- „associated water" – weakly associated with the mineral forms a mobile layer.

Important is that the water associated type is present only in halloysite (7Å), while in halloysite (10Å) can be present both types of water.

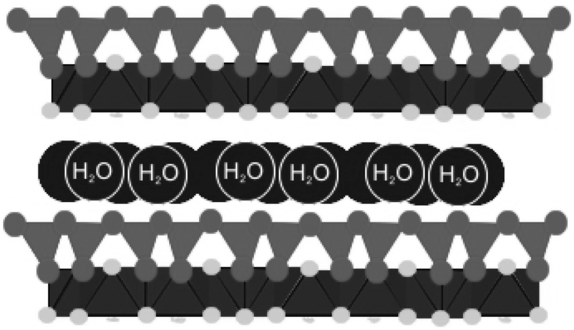

Fig.7. The structure of halloysite packet (10Å) [16]

The chemical composition depends on the formation of the deposit and the climate which prevails in the area (Table 3).

Table 3.
The chemical composition of halloysite in various regions of the world [17, 18]

The location deposit of halloysite	Poland	New Zealand	China
	Chemical composition [%]		
SiO_2	34.00	50.40	40.47
Al_2O_3	26.40	35.50	39.95
Fe_2O_3	26.00	0.25	0.43
MgO	0.60	0.00	0.03
CaO	1.30	0.00	0.76
Na_2O	0.10	0.20	0.05
K_2O	0.10	-	0.12
TiO_2	4.00	0.1	0.05
P_2O_5	-	-	0.15

4. The range and results of studies

The aim of this study is analyze the compressive strength of the masses where the bentonite and halloysite is used as a binder. Standard mass of bentonite halloysite was made according to *PN-85/H-11003 Foundry molding materials. Bentonite Foundry.* Determination of compressive strength in wet mass R_c^w was performed in accordance with *PN-H-11 073: 1983 Foundry molding materials. Measurement of strength.*

In the research was used the following materials and equipment:

- Quartz sand, medium in the main fraction 0.20/0.315/0.16; halloysite PJF from Dunino mine with reduce iron (about 5%);
- bentonite Mikrogel, not activated, fraction of 0.045 mm;
- laboratory roll mixer;
- laboratory manual standard rammer LU-1;
- universal device for testing mechanical properties of moulding mass, LRu type.

Stages of preparation of molding sand:

- measurement of the number of components,
- mixing the ingredients for about 2 min,
- gradually adding a measured amount of water during the work of mixer,
- mixing the ingredients for about 6 min,
- aeration of moulding sand.

After mixing the ingredients was formed a cylindrical shaped weighing 160 g with a laboratory standard rammer LU-1. Executed/Performed seven series of measurements of compressive strength at hourly intervals, and one measurement of the next day (24 hours after the first measurement)

4.1. The results of the standard masses

Standard mass for both bentonite and halloysite was performed according to standard *PN-85/H-11003 Foundry molding materials. Bentonite Foundry.* The composition of the two masses are shown in Table 4, and the results in Figure 8.

Table 4.
Components of the standard masses

Component	Quantity	Participation in the mass [%]
Quartz sand	8 kg	93.00 %
Binder	0.6 kg	7.00 %
Water	0.3 l	3.50 %

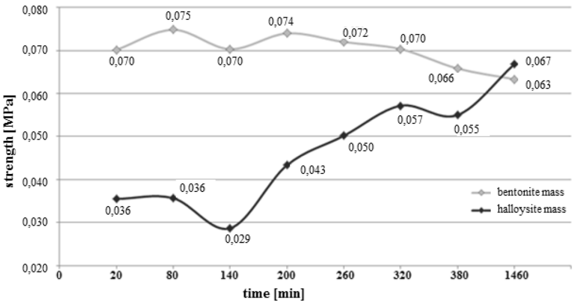

Fig. 8. The average value of compressive strength of the standard masses as a function of time

4.2. The results of the masses with increased participation of the binder

The following series of results was changed the increase in the share of the binder by weight maintaining the same amount of water that the *PN-85/H-1100* standard.

Table 5.
Components of the masses with increased participation of the binder

Component	Quantity	Participation in the mass [%]
Quartz sand	8 kg	86.96 %
Spoiwo	1.2 kg	13.04 %
Woda	0.3 l	3.26 %

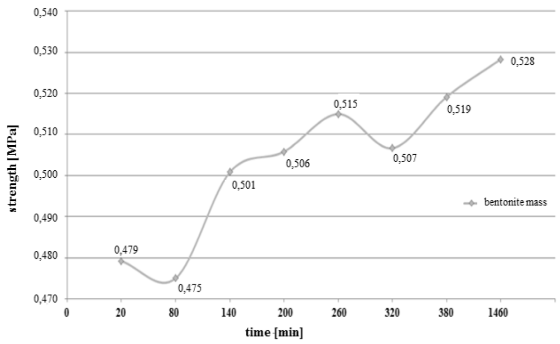

Fig. 9. The average value of compressive strength of mass increased participation of the binder as a function of time

Research of halloysite cannot be achieved due to large of tenderness what prevented the execution of relevant samples. Supposedly water contented was too small, what cause that it was unable to build the packages of octa- and ektrahedrons, making it impossible to obtain adequate bonding.

4.3. The results for the masses with a higher content of binder and water

In the third series of tests increased both participation of the binder and the water in relation to the standard mass. The shares of these components increased respectively from 7% to 13% and from 3.5% to 5.43%.

Table 6.
Components of the masses with increased participation of the binder and water

Component	Quantity	Participation in the mass [%]
Quartz sand	8 kg	86.96 %
Binder	1.2 kg	13.04 %
Water	0.5 l	5.43 %

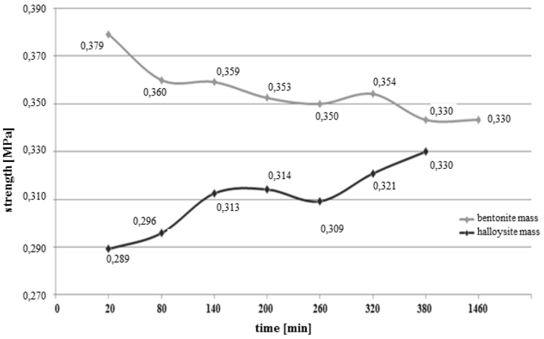

Fig. 10. The average value of compressive strength of mass increased participation of the binder and water as a function of time

5. Conclusions

Based on conducted studies following conclusions have been formulated:

- In the standard masses can be observed that the strength of bentonite mass as a decreases function of time reflecting the decline in the strength of the border of the binder-matrix, the inverse tendency can be observed in a halloysite mass, whose strength increases, it can be also seen that after 24 the strength of the two masses are comparable (0.063÷0.067 MPa).
- Mass, where halloysite was increased (maintaining the same amount of water, as the standard masses, although it was properly mixed in a roll mixer, it was not properly connected to each other, and therefore it was not suitable to conduct research (at run-time samples mass was disintegrated); resulted in increased content of bentonite upward trend in the compressive strength of mass.
- For both masses with increased participation of the binder was noted a similar trend as the standard mass, ie. strength of halloysite mass increases with the time and the strength bentonite mass – decreases; after 24 hours these values reach a similar level of the order of 0.33 ÷ 0.34 MPa.
- For the mass, where increased participation of the binder or binder and water increased the value of compressive strength by up to one order of magnitude compared to the standard mass.
- The comparable results advisable is to explore other technological properties of the masses of halloysite including linear changes in form, scatter and durability in a wetly area.
- By dint of the lack of effect of swelling of the binder and moisture due to increased strength as a function of time potential destiny of the masses of halloysite are strong, stiff and wet moulds for ductile iron and ADI casting.

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