

## Selected properties of the halloysite as a component of Geosynthetic Clay Liners (GCL)

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### Materials

#### ABSTRACT

**Purpose:** The aim of this paper was to present some properties of halloysite and its applications as a component of Geosynthetic Clay Liners (GCL). The following article presents results of comparative tests of the influence of different factors on the halloysite and halloysite – bentonite mixture properties.

**Design/methodology/approach:** Many studies including SEM, XRD, FTIR, EDS, ICP and XRF have been made to examine the halloysite and halloysite – bentonite mixture properties.

**Findings:** Influence of the halloysite additive on characteristics of sealing GCL properties.

**Research limitations/implications:** Studies described in this work should help to improve composition and optimize parameters of sealing clay mixtures improving activities and functioning of GCL during a long period of time. Comparison of the effects of the halloysite additive on characteristics of sealing clay layers properties and the possibility of its application in this area.

**Practical implications:** Knowledge about changing of GCL properties during long time exploitation in landfills allows for selection of their main sealing parameters. The wrong choice of GCL parameters leads to multiplication of environmental costs and pollution of the area around storage place.

**Originality/value:** Halloysite shows high sorption properties in relation to toxic heavy metals (eg cadmium, lead) and solutions containing harmful hydrocarbons, eg benzene, as well as toxic gases (ammonia, hydrogen sulfide). They are in aqueous solutions, therefore, their capacity for migration through protective barriers sometimes pose a growing threat to the environment. Using halloysite as a component of GCL significantly reduced this problem. The halloysite additive to GCL reduces the vulnerability of the sealing barrier towards the influence of calcium ions improving quality and durability of mineral insulation.

**Keywords:** Geocomposite; Halloysite; Geosynthetic Clay Liners (GCL); Halloysite - bentonite mixture; Sodium - bentonite; Calcium - bentonite

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## 1. Introduction

A Geosynthetic Clay Liners are a geocomposite typically consisting of two layers of woven fabric filled with mineral material primarily used for the lining of landfills. It is a kind of geomembrane which usually incorporates a usually bentonite or other kind of clay, which is characterized by a very low hydraulic conductivity (symbolically represented as  $K$ ). The resulting lower permeability slows the rate of leakage out of the landfill. The issue of insulation and sealing of landfills as well as other locations where spills may occur that threaten the environment is widely known all around the world. All the sealing techniques which have been used so far reduce existing risks, but none of them is able to eliminate them completely. Extensive research conducted around the world led to the development of solutions that reduce significantly the risk of contamination of the environment. In recent 20 years Geosynthetic Clay Liners (also known as GCL) have gained wide acceptance.

An increasing emphasis on environmental issues poses a challenge for scientists to improve and optimize the properties of insulating and sealing landfills, and other places exposed to spills or leaks of environmentally hazardous substances. This problem is widely recognized all around the world and all the previously known techniques of sealing and insulation only reduce existing threats, but none of them is able to completely eliminate all actual and potential threats. Every year, billions of tons of waste of different composition are stored in the world. Extensive research conducted in many research centers around the world led to the development of solutions that significantly reduce the risk of contamination by hazardous substances. One of the solutions to reduce environmental risk is Geosynthetic Clay Liners filled with a layer of mineral granules, which are widely used and acclaimed in sealing technology [1,2].

GCL - Geosynthetic Clay Liners consist of geotextiles, between which there is a layer of mineral granules, until now usually bentonite [1], combined into a whole. Bentonite consisting mostly of montmorillonite. The advantages of the liners are mainly as follow: the ease and speed of application, high durability, resistance to climate factors, low permeability of the liquid and a huge ability of swelling and water absorption. Apart from these advantages, however, the GCL also have disadvantages because they are very prone to chemical reactions that over time cause deterioration of the insulating properties in the level dependant on the type of the affecting factors. Since in the typical exploitation conditions the geoliner is exposed to the environment with a very diverse chemical composition, they should therefore be characterized by high chemical resistance and low sensitivity to change their properties under the influence of leaching and mechanical interactions.

A number of research [1,3,4,7,8] allowed to assess the influence of the physicochemical factors on the properties of solutions used so far. These studies revealed inter alia that the changes in the insulating properties of the liners result from the reaction with chemical substances included in the leaching and depends on its type and concentration.

Works [9-13] have also revealed that the deterioration of the properties of the bentonite liners ensues from the decrease of their mechanical properties. The swelling ability causes the deterioration of the mechanical properties and concentration of

the re-dried granulate with numerous cracks in the insulation layer. Periodicity of this process leads to an almost total loss of insulating properties.

The landfills are filled throughout tens of years and, in principle, would retain their contaminants for a long time after their closure. During this time, consolidation of the stored components should be expected, and what often follows the change in the pH of the leachate, in many communal landfills.

Conducted in the paper [3] analysis of the variability of the leachate composition made in the landfill in Larissa confirms the regularity of that: during the first 5 years, the leachate pH usually changes from  $\text{pH} = 4-5$  to 7, and after the next 5 years it reaches  $\text{pH}$  of 8-10.

Sodium bentonite has been the most often used granulate which fills the GCL. However, the studies conducted in different countries where the liners with sodium bentonite were used clearly show that the typical composition of leachate containing Ca ions can cause dramatic changes in some important parameters of the liners in a short period of time. Then, a noticeable increase of hydraulic permeability takes place as well as the decrease of coefficient of expansion which deteriorates the ability to seal and "self-healing" of the holes and leaks [7]. In order to acquire sealing properties of sodium bentonite, the bentonite sealing layer needs preferentially clear water. Different cycles of drying and hydrating have a negative influence on the quality of sealing. After several such cycles hydraulic permeability is increased and the time needed to reach acceptable tightness can be extended up to several days [9].

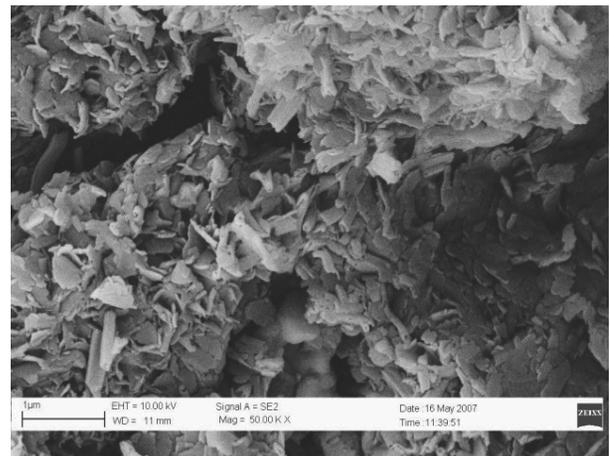


Fig. 1. The platy structure of halloysite from Dunino deposit (SEM)

The most important component of bentonite is montmorillonite. It has a fairly specific structure, weak interlayer binding and high ability to cation exchange process. It is responsible for susceptibility to swelling and shrinking. Water and exchangeable cations may easily penetrate and distribute its layers causing it to swell. Egloffstein in his studies [5] found that even the calcium content of 0.000025-0.015 mol in clear water may cause the conversion of sodium bentonite to the calcium one. This results from the fact that cations Na in sodium bentonite are easily displaced by multivalent cations such as Ca or Mg [6].

Unfortunately, this conversion significantly reduces the physicochemical properties of bentonite and makes it less useful in the described applications. The swelling property [1] of bentonite strictly depends on the pH of the environment, in which it is located and the course of history of wetting process. Even a relatively small amount of impurities may increase the permeability of  $10^5$  times. This means that the seal irretrievably loses its properties and does not fulfill its task. In the studies [7] it was observed that such a drastic deterioration can occur rapidly, especially in the case of interaction of Ca ions, after 200 days within a layer of sodium bentonite the concentration of Na stands only for 6% of the initial content.

This is also confirmed by the results of studies conducted in Germany [4]. It was observed that interaction of complex chemical composition of leachate, combined with the change of their pH may be particularly dangerous. As it is visible the main reason for deterioration of the seal layers are the above-mentioned properties of sodium bentonite. Instability of the chemical composition of typical operating conditions and sensitivity to the presence of ions, especially Ca, which are found in virtually any environment, as well as in engineering elements (eg, limestone is used for the construction of the drainage layer), result in the fact that after many years of its uncritical application more and more questions concerning the prospects for its use in normal conditions of landfills exploitation arise.

Hayer [9], Hewitt and Daniel [10] dealt with further studies concerning cycles of drying and hydrating of liners, Kraus [11] dealt with freezing and defrosting and La Gatta and all [12] dealt with distortion caused by land subsidence. In all of these studies, the tendency of the bentonite layer to cracking and creation of leaks was observed. Multiple cycles of drying and wetting, freezing and thawing showed that the layer of bentonite tend to rupture and formation of cracks. It was also found that the ability to "self-healing" strictly depends on the thickness of the layer and the pressure of the above storage materials. In the study conducted by Benson [13], correlation between wetting and drying processes and the process of ion exchange of sodium ions to calcium ions was found.

Analysis of the above findings prompted the authors to consider the possibility of improving the characteristics of the seals by applying other kinds of minerals. An analysis of the literature shows that a new type of material should also work on a modified physical principle of operation. The optimum layer should keep the tightness regardless the state of its hydration and chemical composition of the liquid influencing it. It also should be flexible to a degree that allows for compensation for any distortion. The ideal type of seal would seal tile with microplate moving in relation to one and tightly adherent to one another. If, additionally, between the microplates there will be a flexible pug layer meets the exploitation requirements of most landfills.

The authors of the paper therefore decided to examine the opportunities created by the combination of two minerals, corresponding to the adopted assumptions. A certain confirmation of the assumptions are also the results of work [14] confirming that bentonite-kaolin mixtures in many cases behave better than the bentonite itself. Since halloysite belongs to a related group of minerals, it was decided to conduct a series of studies with the aim of answering the question whether the bentonite-halloysite may be used for sealing purposes in ground and water building.

A composition of a sealing layer should be characterized by low sensitivity to chemical processes and stability of physicochemical properties, at least in the range pH = 2 to pH = 10. It should preserve the ability of sodium bentonite to self-sealing of the landfills damages which so often occurs in municipal landfills. A new type of seal shall meet the economic criteria, and be easily accessible and easy to use.

After analyzing the characteristics of many minerals, calcium bentonite and halloysite were selected for the studies. In favour of the choice of calcium bentonite speaks its frequent occurrence in many parts of the world and good results of the experiments with this mineral in the seals. It is successfully used for the production of GCL by Huesker company [4]. On the other hand, the use of halloysite was supported by the results of the studies conducted in the conditions corresponding to the ones frequently occurring in landfills, where the insulating layer is subjected to relatively high pressures coming from waste.

## 2. Material

Calcium bentonite occurs much more frequently than sodium bentonite and is much cheaper and less sensitive to chemical effects. The disadvantage is a lower swelling ability, which reduces its susceptibility to "self-healing" of created leaks. The fact, however, that it may serve as an insulating layer, even in difficult circumstances, is proved by already mentioned GCL containing only calcium bentonite [4]. Due to the current regulations in force in most EU countries, it is required that the GCL contain a swelling component, therefore for the tests was used calcium bentonite partially activated by sodium carbonate to the extent that it fulfills the requirements previously applicable standards.

For the study the halloysite was used as a sealing component. It originated from the "Dunino" deposit located in Lower Silesia (this is one of some currently exploited deposits of this mineral in the world). Dunino deposit contains at least 10 million tons of a homogeneous raw material as open pit mine. Halloysite extracted from this deposit is a product of basalt weathering. The microscopic view of the material used for the research shows the Fig. 1. It is characterized by high chemical resistance to acids and bases under normal environmental conditions. As Choma-Moryl's [15] research has shown, halloysite may be used for many purposes in the environment protection e.g. for the manufacturing of coagulants for municipal and industrial wastewater treatment, rehabilitation of industrial degraded areas, landfills manufacturing of absorbents, catalysts and filler for nanocomposites.

Another advantage of halloysite is increasing ability of microplates to close which goes together with pressure increase which results in increase of the coefficient of permeability under load  $k = 4.8 \cdot 10^{-12}$  m/s, and so is better than for both types of bentonite. The Helios-Rybicka's [16] studies show an interesting halloysite property. Namely, it can absorb large amounts of heavy metals, and in this respect it is comparable to the zeolite. This feature can be of big importance considering the sealing of landfills where the risk of ground water contamination is very high.

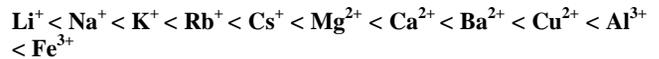
GCL have been used in civil engineering for sealing and insulating purposes for more than 20 years. The time allowed careful examination of their behavior and capabilities under a variety of conditions. It has been discovered that the leachate from the environment has, in many cases, an adverse impact affecting the quality of the sealing. The main reason for this was the ion exchange that took place in the clay layer and was caused by certain components of leachate. In that geo-chemical environment an ion exchange of sodium-bentonite into calcium-bentonite can occur within a period of approximately 1-3 years, which results in an increased hydraulic conductivity, where they should withstand decades or even hundreds of years [17-20]. In the case of usually used Na-bentonite GCLs, this means that the ion exchange of Na-cations for multivalent cations (e.g. Ca) should be avoided or minimized. In his work, Jo [21,22] stated that the replacing of Na-cations by other monovalent K- cations does not cause a negative effect in hydraulic conductivity of bentonite. The monovalent ions retention in the clay liner and prevention of their exchange by multivalent ions achieved by means of halloysite could help to maintain the sealing properties of the liner for a longer time in comparison to the traditional liners.

Halloysite is a two-layer mineral, characterized by its affinity to the monovalent cations. Those cations can act as an "anchor" for the inner-sphere and interlayer cation-water complexes. Because halloysite plates easily dispersed and delamination in water, much easier than montmorillonite does. Both minerals with different surface properties can form a new kind of interlayer space which can be resistant to the multivalent cations activity.

It is widely known that the exposure of traditional Na-bentonite GCLs to inorganic solutions rich in multivalent cations can result in a significant degradation of sealing properties of GCL.

Montmorillonite is a substantial component of all bentonites. The structural unit of montmorillonite is a layer consisting of two inward-pointing tetrahedral sheets with a central alumina octahedral sheet. The layers are continuous in the planar directions but the bonds between layers are weak and have great cleavage allowing water and other molecules to enter between the layers and thus causing expansion. The external silica sheets reveal a linkage of the silicon atoms with the oxygen that forms a network with "holes" in the center. The shape of the hole can be hexagonal or pseudo-trigonal, depending on the number and the kind of elements substituted for Al in octahedrons and Si in tetrahedrons and on the number of octahedrons filled with Al or other elements [23-25]. The number and location of the substitutions in both sheets have significant influence on clay properties. There are several kinds of bentonites (depending on the cation type between the layers, e.g. Na, K, Ca, Mg, Li) characterized by different properties. There are usually different types of cations and anions together in between the layers and they influence the properties of clay. The basal distance between one layer and another is typically above 0,9 nm and can reach a few nanometers depending on the interlayer ions, their concentration and water saturation [26,27,28]. The capacity of cationic replaceability depends mainly on the valence, hydrated and nonhydrated ion size, the concentration of ions and, to significant extent, on the properties of clay basal and edge surfaces. As generally reported in the geochemistry and fundamental soil mineralogy literature, higher valence cations

replace lower valence cations and smaller hydrated cations or larger ionic radius cations replace larger hydrated cations or smaller ionic radius cations of the same valence that are present in the exchangeable sites [29,30,31]. In general, the replaceability sequence presents as follows:



An exception to the above replaceability pattern is possible when cations of lower replacing power exist in very high concentrations in solution relative to high replacing power cations [29]. Bentonite clay, when used in a field as a hydraulic barrier, comes in contact with various inorganic chemicals which can affect the performance of bentonite clay and reduce its permeability. It has been reported that  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions, often present in municipal solid waste (MSW) and incinerator ash, can be detrimental to the bentonite if permeated over extended periods of time [31-35].

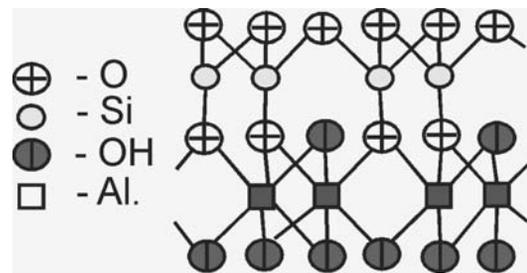


Fig. 2. Structural unit of halloysite [44]

Further adsorption of monovalent cations by the negatively charged interlayer and external surfaces causes the formation of the electrical "double layer" in between the mutually repellant surfaces which results in separation of single platelets. As the osmotic swelling is only caused by the hydration of monovalent (namely, Na<sup>+</sup>) ions, presence of highly concentrated polyvalent cations will inevitably negate the formation of a dispersed clay microstructure and will cause the staggered formation of aggregated clay caused by the reduction in the thickness of double layer diffusion [36]. The swelling of the sealing clay layer is a very important parameter due to its "self-healing" features. Montes [37] has studied the behavior of the commercial MX80 bentonite when saturated with different kinds of cations. The same water content in the interlayer space caused the biggest swelling of Na and K saturated bentonite when the divalent Ca and Mg-cations produced a significantly smaller swelling. The swelling is determined by the cation-water inner-sphere complexes "anchored" at the hexagonal (or ditrigonal) hole of the tetragonal sheet of the clay surface and the outer-sphere complexes lying near to surface [38]. The volume of the interlayer water and number of complexes in the interlayer space depends mainly on the type of the interlayer cations or their composition. The bigger number of monovalent cations always ensures a better swelling. For this reason, it is very important to retain the "good" monovalent cations in the interlayer space to the maximum extent possible.

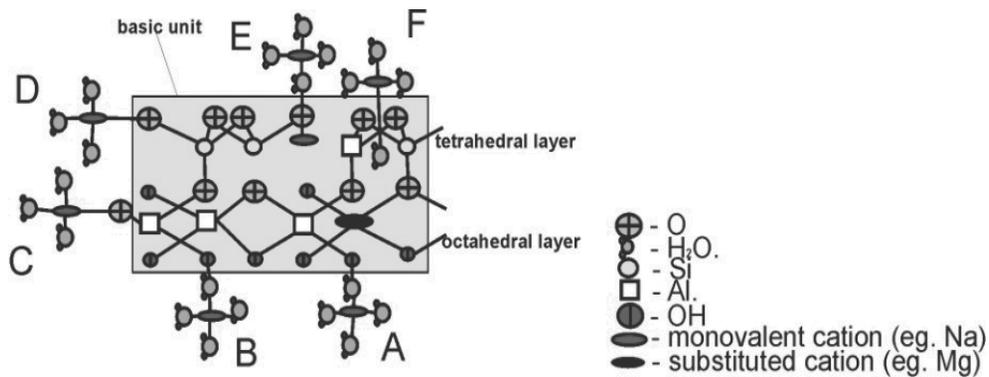


Fig. 3. Various possibilities of cations connecting with the halloysite clay layer [44]

Halloysite has many applications [39,40]. As a mineral, it belongs to the kaolinite subgroup which is represented by the same chemical formula  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$ , 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 halloysite mineral contains a layer of water in its interlayer space which results in an increase in layer thickness up to  $10.1 \text{ \AA}$  [23,41]. The interlayer water molecules of halloysite can easily and irreversibly be removed by a slight increase in the temperature which in turn results in formation of the  $7 \text{ \AA}$  halloysite characterized by the interlayer distance ranging from  $7.15 \text{ \AA}$  up to  $7.5 \text{ \AA}$ . However, after a dehydration process, the halloysite platelets stay separated. The structural unit of halloysite consists of two sheets: Si-tetrahedra and Al-octahedra. 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, usually and like with montmorillonite, negatively charged (Fig. 2).

The surface charge can be radically changed by cation substitution. In opposition to kaolinite, the single halloysite plates are not joined together; there is usually a bigger distance between the layers than the one in kaolinite which stems from the presence of either water or different cations. In kaolinite the layers are held together by strong hydrogen bonds between the oxygen from the tetrahedral layer and hydrogen from the octahedral hydroxyl group. Halloysite, in opposition to kaolinite, is characterized by the great number of substitutions of Al atoms in octahedral layer for divalent atoms (usually Mg or Fe), trivalent Fe or four-valent Ti. Furthermore, Si in the tetrahedral sheet is often replaced by Al [41,42]. This substitution effects change the local microstructure creating new possibilities for different bonds on both sides of a single layer, which is not possible with montmorillonite. The basic dimensions of adjacent tetrahedrons and octahedrons vary [42]. With montmorillonite or kaolinite the differences are compensated by the rotation of tetrahedrons. This rotation provokes the change of shape of hexagonal oxygen "hole" into a pseudotrigonal "cavity". The change influences the type and strength of the bonds of the cavity with adjacent ions and the possibility of them being trapped in the cavity. The substitution of Al for example, Fe in the octahedron results in an elongation of the octahedra which causes the shape of the hole between the tetrahedra to remain hexagonal. Also, this substitution influences

the maintaining of platy shape of the platelet [42]. Singh [43] reports that the hexagonal shape of this hole can also be an effect of the presence of water being strongly bonded inside the hole. This hole has an ability to connect e.g. Na or K-cation and form a stable inner-sphere complex. Many authors confirmed that halloysite sheet surface readily connects with the monovalent cations when divalent cations such as Ca and Mg do not form the bonds directly with the surface [43-46].

Some of the possible bonds between the halloysite basal and edge surface and adjacent water-cation complexes presents Fig.3. Individual ingredients from the cations connecting with the halloysite clay layer:

- The water particle is connected to the hydroxyl group surface on the octahedral side with the hydrogen bond in place where an Al-cation is substituted by another cation (eg.  $\text{Mg}^{+2}$ ). This replacement makes the bond stronger than regular Al-octahedra. Water molecule is a part of an interlamellar complex which is formed by a cation and which may have different configuration. For example with a Na-cation it can have the coordination number = 6, so an octahedral complex structure will be formed.
- The water particle is connected to the hydroxyl group surface on the Al-octahedral side with the hydrogen bond. This bond is weaker than the one described in case A.
- An unbalanced edge Al-cation joins the complex by means of an oxygen or hydroxyl group. This complex can be connected with the next complex.
- As in the C case, the cation-complex is joined, but this time through an oxygen atom or a hydroxyl group to an unbalanced Si-cation.
- A cation is trapped in the pseudo-trigonal or hexagonal cavity on the Si-layer side. The strength of this placement is greater than the strength resulting from the hydration. In such situation the water molecule joins the cation and so forms the new configuration including the outer-sphere cation complex.
- In this case a water molecule is strongly placed in the cavity. When the strength resulting from the hydration is weaker than the strength holding molecule in a cavity, the cation joins the molecule and forms a combined inner and outer sphere complex. This bond type is typical for the cations with small energy of hydration (e.g. Na and K).

There are also other possibilities of complex forming, depending on the substitution in both the tetrahedral and the octahedral layer, pH and ion concentration. It should be noted that halloysite, in comparison with montmorillonite, offers more possibilities to connect the cations, especially the monovalent ones. The reason for this being its different construction, including the shape of cavity which in case of halloysite is more conducive for the monovalent cations.

#### ***The differences and similarities between montmorillonite and halloysite***

Despite the similarity of the octahedral and tetrahedral sheets of the montmorillonite and halloysite, both minerals have different features. The main differences are mentioned below.

A single particle of montmorillonite has the Si-tetrahedral sheet on both basal sides. Six of adjacent Si- tetrahedra form a pseudotrigonal cavity with oxygen atoms as corners caused by the tetrahedrons rotation. Halloysite has a Si-tetrahedral sheet on one side and a Al-octahedral sheet on the other. The oxygen atoms of halloysite tetrahedra form a regular 6-fold hexagonal structure. This structure remains intact even after dehydration which suggests that either the "hole" water remains within the structure or that the rotation is blocked by physical forces [41,42]. The hexagonal shape of the hole can remain intact also due to the activity of Fe - cations substituted for Al in the octahedra. This difference influences cation activity which can be incorporated to the cavity or has better conditions to close near the sheet surface and form an inner-sphere complex .

The octahedral Al-sheet in montmorillonite is covered with the external Si-tetrahedral sheet. This Al- sheet has only one free hydroxyl group which does not have the possibility to affect the interlayer ions directly. It can only act in combination with the tetrahedron. When using halloysite, this sheet forms the surface of the basic unit. Every Al-atom is connected to three external hydroxyl groups and one inner hydroxyl group that can be found on the tetrahedral sheet. This groups are very active in forming different bonds within wide pH area (Fig. 3).

The surface charge of the octahedral sheet on the basal surface resulting from the hydroxyl group is usually positive. There is a negative charge on one side of halloysite and a positive one on the other as opposed to montmorillonite which has a negative charge on both basal surfaces.

The influence of atom substitution in the octahedron (eg. Mg for Al) is significantly stronger in halloysite than in montmorillonite. The negative charge in the octahedron creates stronger influence on the adjacent ions in the interlayer space directly on the octahedral side.

The number of atom substitutions is higher in halloysite than in montmorillonite. In halloysite they cause a unique change in the structure resulting in layer separation which in other minerals from the kaolinite group are strongly bound together. The typical substitutions are :

- a) for Al in octahedron: Mg, Fe, Cu, Zn, Mn, Ni , Cr, Li and also  $Ti^{+4}$ ,
- b) for Si tetrahedron: Al.

The single halloysite layer easily absorbs water and delaminates in opposition to e.g. kaolinite where delamination requires much more energy.

Halloysite in opposition to montmorillonite swells in water to a minimal degree only. Single platelets are loosely dispersed in water and act as carriers for other ions.

Halloysite is characterized by a great affinity to the monovalent cations: Ka, Na Li, Cs. This affinity is significantly higher than in case of multivalent cations such as Ca and Mg.

Wada [43] stated that when halloysite is saturated by Ca-ions - Ca 90% of Ca- ions can be displaced by Na-ions, which is a basic difference between halloysite and montmorillonite.

It is interesting that the characteristics of most of the minerals depend on so many factors, such as the content of impurities and atom substitutions. In practice, it is difficult to find two identical layer-minerals characterized by identical properties. The same applies to halloysite and montmorillonite. All known halloysite and montmorillonite difference when it comes to their typical properties depend on the site and processing method. Special attention must also be paid to different types of atom bonds which play a significant role in the relation of mineral to the adjacent atoms and compounds. In standard conditions the covalent, ionic, hydrogen and van der Waals bonds play the main role. Even small differences in such elements as distance of the atoms, type of the substituted ion and the shape of the cavity can play a significant role, shaping the sorption properties of the basal and edge surfaces of mineral layer. Apart from the above mentioned differences, halloysite and montmorillonite have a common property. It's their capability of delamination and dispersion of the particles in the water. Under the influence of water particles of montmorillonite separate from each other. The reason here is the hydration of interlayer atom (normally Na, Ca or K) resulting in swelling of bentonite. This reaction takes place quite differently in halloysite. The single lamellae of this mineral are already separated from each other in raw state. As a rule, there is one or more particles of water and an interlayer atom placed between the adjacent lamellae. The type of this atoms depends on the conditions of the halloysite formation. These are typically the monovalent atoms. Under regular conditions there are unsaturated  $O^-$ ,  $OH^-$  anions or metal cations ( $Si^+$ ,  $Al^+$  or substituted, e.g.  $Mg^+$ ) on the edges of the lamellae of both minerals. These ions create the possibility for the hydrogen or ionic bonds of water molecules.

The attraction force between the adjacent basal surfaces of the lamellae is very week. With montmorillonite, it is mainly caused by repulsion of the negatively charged tetrahedral surfaces. There is much greater possibility of halloysite forming different bonds with other ions than it is with montmorillonite. One of the important reasons for this is a greater number of substituted cations both in octahedral and in tetrahedral sheets. The substitution process in the octahedral sheet is simpler because of easier access of the cations to the octahedron which has indirect contact with the adjacent cation. With montmorillonite, before a cation can approach the octahedron, it must first pass through the Si-tetrahedron which is very difficult. One can suppose that during the replacement the balance of the acting bonds is disturbed and the Al-ion removed from the octahedron has more chances to replace the Si-ion in the tetrahedron. This new situation radically changes the activity of all bonds existing in both layers. The significantly greater negative charge starts to play the main role in forming of the new situation. The cations have better conditions to connect to the halloysite surface and to

form the so called inner - sphere surface complex. As stated by Yariv and Shoval [47] the cations can also form bonds with the octahedral and tetrahedral sheet using a water molecule. An ion (e.g.  $\text{Na}^+$ ) located in hexagonal hole in the tetrahedral sheet or near to this hole creates another possibility of water intercalation. The average diameter of this "hole" is ca 0.26 nm [41]. When the size of an ion is smaller it could be placed in this "hole" if other strengths allow, but the bigger ions always lie above the layer surface [24,26]. All those ions strongly interact with tetrahedral charge sites (oxygen ions) forming so-called inner-sphere surface complex. The configuration of water molecules is different in the inner-sphere surface complex and the outer-sphere surface complex laying in the interlayer space. When both complexes meet, a disorder in the water region (a disorder with distorted H-bonds) may occur and the water network may be oriented in any possible direction [24]. The characteristics of absorbed water on the clay surfaces reveals the competition between interlayer cations for intercalated water molecules. It is not only the basal spaces that play a role in forming new space structures of intercalated clay. The edge spaces also play a significant role and that differs in halloysite and montmorillonite. The edge charge may change from (+1) to (-3) [23] depending on pH of the solution. The equilibrium position of the cations near the surface of a layer cannot be calculated without taking into account the hydration energy. This energy orients the cation in the direction of the interlayer water and hinders its tendency to penetrate the hexagonal or ditrigonal hole in the lamellae. The hydration may also have a positive effect by holding a cation near the surface of clay. It is so in case when the water molecule is located in the hole and bound there by different bonds depending on the cation substituted in the octahedron or tetrahedron and other surrounding ions or the shape of the hole - hexagonal or trigonal [24,41]. The water particle is then strongly associated with a cation which can additionally be connected with other water particles from the interlamellar space. This complex, strongly bonded with the surface of lamellae, can act as an "anchor" for other complexes of different cations associated with water molecules in different configurations. The combination of surface properties of both minerals could produce some new interesting characteristics of such a mixture.

### 3. Experiment procedure

The aim of the studies was to investigate the sorption capacity of cadmium, phosphorus and the behavior of the mixture of halloysite and montmorillonite under the influence of different monovalent and divalent Ca-cations in comparison to the only montmorillonite layer. Cadmium is one of the most present heavy metals in landfill leachate, phosphorus is responsible for the eutrophication of lakes and rivers. Halloysite has a special affinity to the monovalent cations. The presence of these ions in the montmorillonite ensures its high swelling, which is a very important feature in its application in different sealing liner systems (municipal landfills etc). These ions (especially Na) are in normal conditions easily replaced in montmorillonite by the multivalent ions like Ca contained in the leachate from landfills. It results in significant increase in the sealing permeability. Because the halloysite is not very sensitive to the presence of the

multivalent cations it would be interesting to test the behavior of the mixture of both minerals in the presence of the different ions. Halloysite can act in the mixture as a monovalent cation carrier and can prevent their exchangeability. When the surfaces of both lamellae come to contact and one of them is strongly holding the monovalent cation, it creates good conditions for creation of a new complexes between both surfaces. The exchange of the monovalent cations should be reduced. Such mixture should retain its properties over a long period of time in typical field conditions. Fig. 4 presents different variants of the surface contact of the lamellae of both minerals. Only one combination (tetrahedral Si-minus-to-tetrahedral Si-minus) reminds the situation when only montmorillonite is present in the sealing layer. Other variants create the possibility of many new bonds.

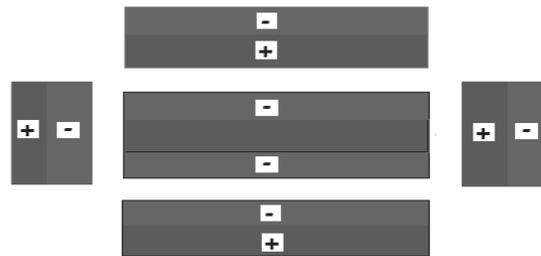


Fig. 4. Some possible configurations between the montmorillonite and halloysite particles (2-layer halloysite, 3-layer - montmorillonite) [44]

Based on former investigations a mixture consisting of 75% Na-saturated bentonite and 25% of halloysite was chosen for the tests. The bentonite was a Na-activated bentonite and a processed halloysite from the Halloysite Mine "Dunino" (Poland) were used. The processed halloysite consists of loose platelets with the planar dimensions below  $1\mu\text{m}$  with thickness in dry state below ca 25 nm and limited number of nanotubules. It is easily dispersible in water which causes delamination of grain into the thin platelets. This ensures a high active surface area. In this respect, both minerals are similar. The tests conditions are partially based on the real field conditions. Normally the insulating and sealing clay layer is saturated with neutral water or directly with a leachate containing the solutions of different salts and another substances. They are able to replace the "good" Na-ions for the "bad" Ca-ions in a short period of time. The halloysite should slow the process down or inhibit it. The ion exchange results in the change of the chemical composition of the clay, the interlayer distances and the change of the frequencies of bonds IR radiation. These three combined methods were chosen for the investigation of the samples. IR absorption spectra of the samples were recorded using a FTIR spectrophotometer GENESIS Series ATI Mattson with the KBr tablet. XRD spectra were recorded by means of RTG diffractometer type XRD 7 Seifert-FPM with the  $\text{Co K}\alpha$  source and Fe filter. Chemical composition of the samples was tested by means of spectrometer TRIDENT XM4 produced by EDAX and XRF method by means of Rigaku ZSX-Primus spectrometer. Optical observations and pictures were taken with the use of high resolution SEM microscope SUPRA 35 produced by ZEISS.

Leachate from MSW landfills typically has high values for the "bad" Ca-cation - strength in typical MSW leachates rarely exceeds 0.1 M concentration [48,49,50]. Also, the temperature of an ion exposure does not exceed the level of 30-50°C. For the durability characteristics of the mixture, there is not only the question of what is the influence of tested solution, but also a question of what durable changes it caused in the mixture. It is known that the prehydration of the sealing layer with demineralized water significantly delays process of ion exchange. However, this process is still forth-going and at a certain point in time it reaches the saturation level causing remarkable deterioration of the sealing parameters. In order to shorten the saturation time, the dry tested samples were stirred directly with the salt solutions. The 10g mixture of both minerals was stirred for 20 minutes with 1 liter of 0.1M solution of NaCl, KCl or CaCl<sub>2</sub> respectively at the temperature of 50°C. Then the suspension was left for one week. The treated mixture was next centrifuged. Centrifugation ensures high efficiency of separation which cannot be achieved by filtering alone. After that the precipitated mixture was thoroughly stirred and washed out with demineralized and deionized water at the 50°C temperature. Next step was the saturation with other salt.

The typical order of saturation was as follows:

NaCl → washing out → CaCl<sub>2</sub> → washing out  
or  
CaCl<sub>2</sub> → washing out → NaCl → washing out

A- sample mixed with deionized and demineralized water was also prepared for comparison purposes. The changes in the structure of composition which remained after saturation and washing out with water should result in the changes of XRD, FTIR parameter and chemical composition. The samples were marked as follows:

B- bentonite, H- halloysite, HB - tested mixture consisting of 75% of bentonite and 25% of halloysite, NaX - sample saturated with NaCl and dried at 50°C, Na - sample saturated with NaCl and washed out, NaCa - sample Na saturated with CaCl<sub>2</sub> and washed out, CaX - sample saturated with CaCl<sub>2</sub> and dried at 50°C, Ca - sample saturated with CaCl<sub>2</sub> and washed out, CaNa - the sample Ca saturated with NaCl and washed out, K - sample saturated with KCl and washed out, KCa - sample K saturated with CaCl<sub>2</sub> and washed out.

The research program included also the impact of the wetting/drying cycle on the structure and the state of the sealing layer on the bottom of container of which the test sample of sealing mixture was placed between two layers of geotextiles. The construction of the sample was similar to the one of a liner and the thickness of the sealing layer corresponded to the liners with surface density of 5 kg/m<sup>2</sup> - typical for most currently produced GCLs. Studies on the impact of the wetting/drying cycle consisted in saturating samples with water and then drying them to a moisture content of W = 20%. The cycle was repeated five times. The tests were made to commercial sodium bentonite and 75% calcium bentonite + 25% halloysite (Figs. 5).

The study of Cd content was determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP), Phosphorus concentration was determined using the colorimetric method. The sorption test was performed according to apparatus

from Fig. 6. Comparative study of cadmium concentration was made before and after penetration of liquid solution through the 2 cm halloysite and bentonite layer (HB).

## 4. Results and discussion

Bentonite-halloysite mixture containing 25% of halloysite showed that the samples containing halloysite and with 5 cycles of wetting and drying in the presence of water of pH = 7 are characterized by:

- halloysite-bentonite mixture has much less tendency to the formation of cracks after drying;
- halloysite-bentonite mixture is characterized by reduced contractility;
- halloysite-bentonite mixture is quicker to achieve tightness after the drying cycle, because the surface of the cracks is smaller by about 80% and existing cracks are disappearing faster than in the case of pure sodium bentonite.

These features are of a big significance for the functional properties of the liners. They mean that the impact of a possible dryness of the liner on the amount of leakage in case of application of the mixture will be smaller, and the layer will recover faster to the initial tightness parameters (Fig. 5a and 5b).

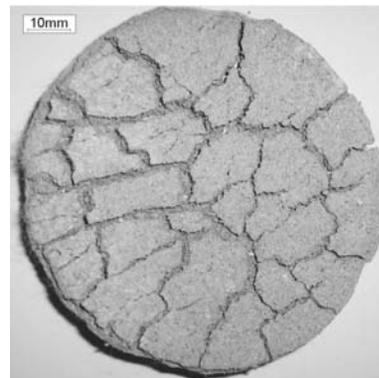


Fig. 5a. The sample of commercial sodium bentonite after 5 wetting/drying cycles

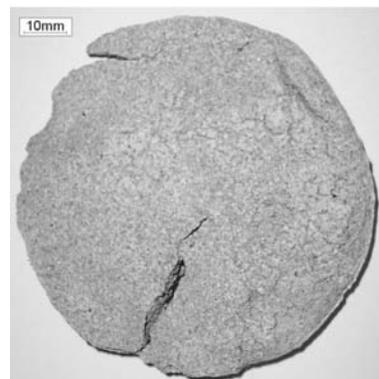


Fig. 5b. The sample containing 75% calcium bentonite + 25%, halloysite after 5 wetting /drying cycles

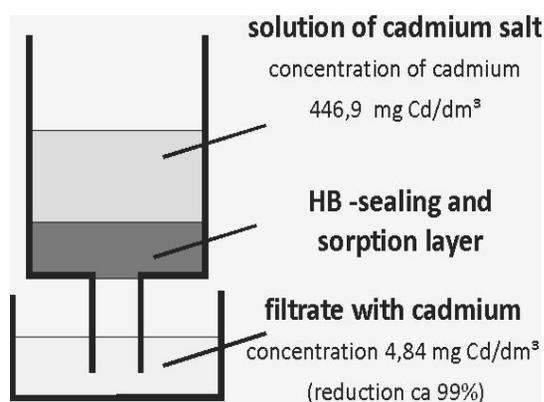


Fig. 6. Scheme of stand for the sorption test

In the Fig. 7 presents the content of the elements Na, Mg, K and Ca in the tested samples is presented. These elements were chosen because of their decisive role in determining the sealing quality. After the stirring of the HB sample with the NaCl-solution and a following washing with deionized and demineralized water, a slight reduction of Na and K was observed. The reduction of Mg and Ca was higher. This change was probably caused by the washing out of the solvated salts of these elements. The followed saturation of the sample with the solution of  $\text{CaCl}_2$  caused only small changes in the composition and the level of Na decreased only by ca 25%. This means that only a part of Na, probably from the montmorillonite interlayer space, was changed by Ca. The cations located near the layer surface remained in their positions which has a positive influence over the quality of the sealing. The comparison of the Ca and CaNa samples shows that the level of Na-ions lowered in the first sample ca 25% which can be caused by the washing out of interlayer Na-complexes by Ca-solution from the interlayer space of the not delaminated montmorillonite platelets. The Na-inner-sphere complexes and complexes lying near the basal or edge surfaces of halloysite platelets remained unwashed. In the sample CaNa the Ca-cations are largely replaced by Na-cations. Their level was even higher than in HB sample which can indicate that more new complexes formed there than there where they were to be found initially.

Both Na and Ca levels were found to be reduced in K-sample. The reduction of Na stems from the known capability of K to locate in hexagonal cavity of the tetrahedral layer where it is able to replace Na-ions. The following saturation with Ca-solution resulted in just a small reduction of the Na and Mg content. The level of potassium returned to its original value which can indicate that this element remained in its position in hexagonal cavities or near to the lamellae layer.

The FTIR infrared spectroscopy method is used to describing the kind and place of a particle interaction with adjacent atoms and molecules. IR absorption can help to determine the place and the bond character when the chemical composition or XRD patterns are similar. The FTIR bands of halloysite and montmorillonite are described in literature [52-55]. Some characteristic points of IR absorption in the unit structure of both minerals presents Fig. 8. The IR spectra for the H, B, HB samples and certain spectra differences for the HB, Na and NaCa samples.

There are visible differences in the band area  $f_1 = 3695$  and  $f_2 = 3620 \text{ cm}^{-1}$ . The band  $f_1$  is ascribed to the external hydroxyl group of halloysite and does not occur in montmorillonite. The band  $f_2$  is ascribed to internal hydroxyl group and occurs in both minerals. With halloysite, it has the wave number of  $3621.66 \text{ cm}^{-1}$  while it is  $3617.80 \text{ cm}^{-1}$  with montmorillonite, which indicates that the strength acting on this group differs in both minerals. There are also significant differences to be found in other bands showing the differences of acting strengths of similar groups in both minerals. The differences can greatly influence the behavior of the interlayer ions and particles. Fig. 9 shows the influence of different cations on the transmittance of HB samples, Na and Ca in the bands  $f_1$ ,  $f_2$  and the band  $f = 3420 \text{ cm}^{-1}$  ascribed to the interlayer water. The transmittance in  $f_1$  area decreased which possibly indicates that despite the washing out of a part of internal hydroxyl groups it is still engaged in creating different bonds which results in shifting the frequency to  $3621.66 \text{ cm}^{-1}$  for the sample Na and  $3619.73 \text{ cm}^{-1}$  for the sample NaCa. The disappearance of the band  $690 \text{ cm}^{-1}$  and the reduction of the peak  $795 \text{ cm}^{-1}$  (both attributed to the Al-OH groups) were observable in the process. These changes, according to the Yariv and Shoval works [56], are caused by those groups being involved with different complexes. The comparison of the bands intensities and their shifting confirm that all hydroxyl groups of halloysite are engaged in forming different bonds with the interlayer cations. Small differences between Na and NaCa samples confirm that influence of Ca-cations on the existing bonds is relatively insignificant. There are remarkable differences in the band  $3420 \text{ cm}^{-1}$  that show that the quantity of absorbed interlayer water in the Ca sample is relatively smaller than in case of the HB sample. This fact indicates that the tested mixture limits the quantity of the adsorbed water at the presence of Ca-cations which does not correspond with the test carried out for montmorillonite alone [57].

The absorbance in the bands  $1040$ ,  $530$  and  $470 \text{ cm}^{-1}$  typical for Si-O bonds is very intensive and confirms the strong activity of those groups in different configurations with the interlayer ions and complexes for both minerals.

The comparison of XRD patterns in different samples is presented in Fig. 9. The patterns were compared with the ones published for halloysite and montmorillonite [38,41,55,56,57,58]. The samples were tested in a dried state and so offered only a partial answer to the question of the influence of any solution or salt suspension. One can distinguish the bands  $d(001)$  of  $13-15 \text{ \AA}$ ,  $10 \text{ \AA}$  and  $7 \text{ \AA}$  (area ca  $8^\circ, 10^\circ$  and  $14^\circ$  of  $2 \text{ Theta}$  respectively) resulting from the main components of mixture (bentonite partially saturated, dry and halloysite). The results show that in every case there is a visible change of the main  $d(001)$  reflection between  $13$  and  $15 \text{ \AA}$  and shifting from the area  $10 \text{ \AA}$  to the area  $13-15 \text{ \AA}$  resulting from the saturation of the bentonite. The following peaks show not only the  $d_{hk}(02)$  and further reflection but also the main reflections of other HB mixture components.

The difference in both patterns between the HB and Ca samples is relatively small which means that the influence of the Ca-cations on the insulation of HB layer behavior is insignificant. The  $d(001)$  distances in the Ca-montmorillonites are usually higher than  $15 \text{ \AA}$ . For Na and K samples the shape of both patterns is similar which could indicate that the influence of both cations is also similar and durable. The oblate shape of the peak

d(001) areas results from the differences in the interlayer distance. It can be caused by the presence of different concentration of different cations and their form in the inner-sphere complexes. These complexes and the complexes at the edges of lamellae can be present also after the intensive washing out of the samples. Their stable and strong bonding on the basal and edge surfaces of lamellae forms favorable conditions for the formation of even more new interlayer complexes connected. A strong inner complex based on the monovalent cation can act as an "anchor" on the surface of clay, which, to a great extent, is resistant to activity of other ions

There are no significant visible differences between the presented state of the platelets. In the picture, it is not possible to distinguish clearly the platelets of both minerals after the process of mixing and drying. It is possible only by performing the EDS

test under the SEM microscope. The thorough mixing ensures the obtaining of optimal retention of monovalent cations. There are visible traces of precipitated dried salts on the surface of unwashed NaX and CaX samples, which also cause different peaks in the XRD patterns (Fig. 10). The pictures show that neither direct influence of salts on the lamellae nor the washing out cause any agglomeration when bentonite is exposed to the calcium salts (Figs. 11-12), which has already been stated by other authors [19,59].

The results showed that the filtrate after passing through a 2 cm layer of halloysite and bentonite mixtures are characterized by a significant decrease of cadmium and phosphorus concentration reaching 90-99%. Comparable decrease in the concentration was achieved in the Al, Fe, Cr, Ni content. A detailed list of these studies will be described in the next publication.

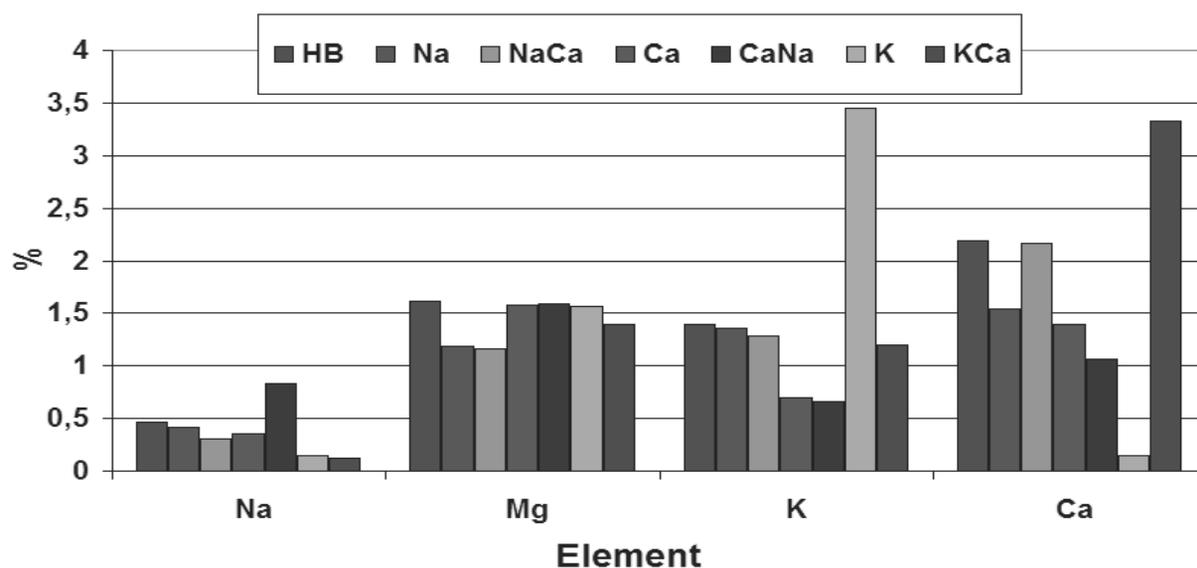


Fig. 7. Content of Na, Mg, K and Ca in the samples

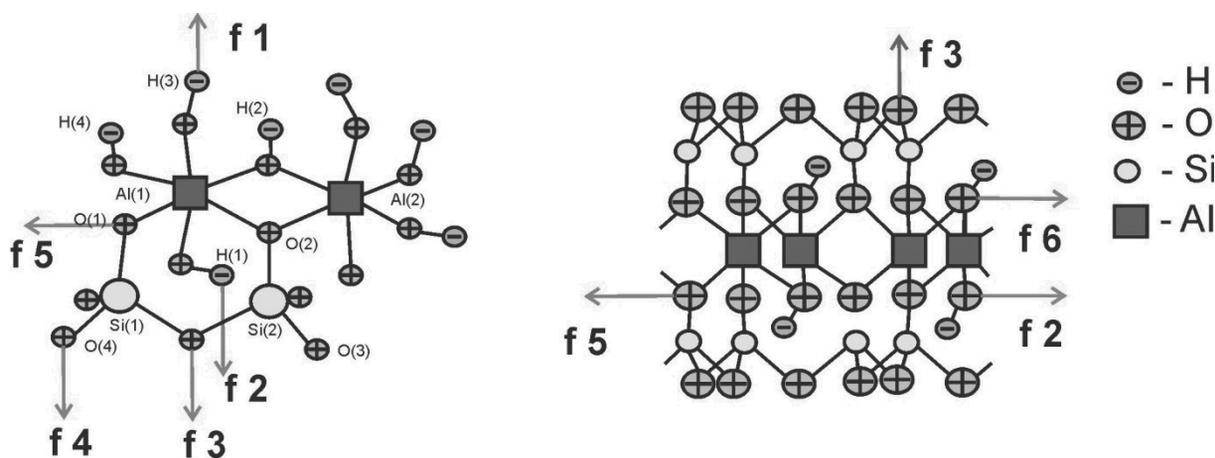


Fig. 8. Selected IR absorption points in the molecule structure (left -halloysite, right -montmorillonite) (bands:f1-3695 $\text{cm}^{-1}$ , f2 - 3620  $\text{cm}^{-1}$ , f3-1040  $\text{cm}^{-1}$ , f4-1115  $\text{cm}^{-1}$ , f5-540  $\text{cm}^{-1}$ , f6 - 920  $\text{cm}^{-1}$ )

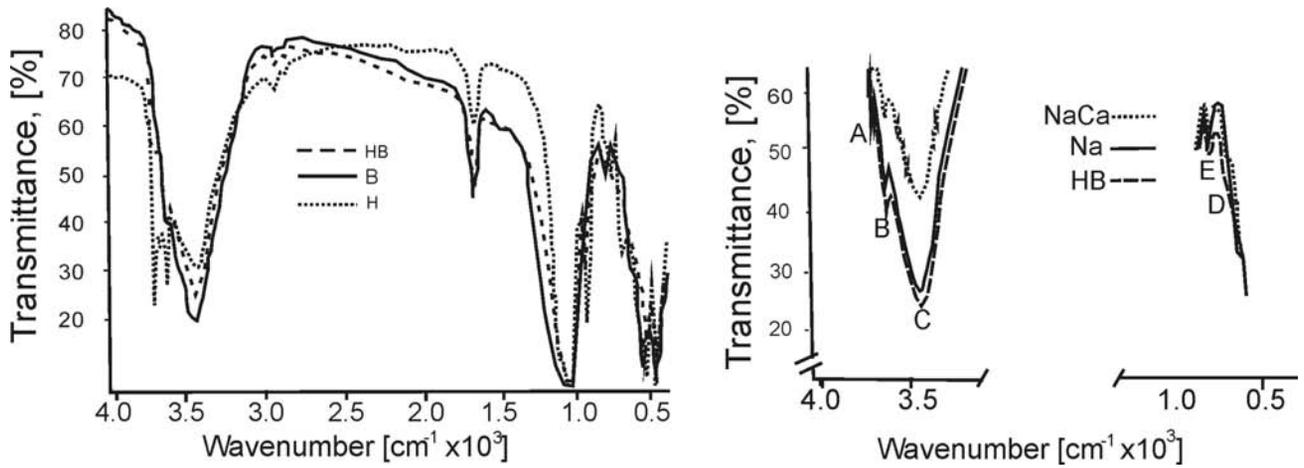


Fig. 9. FTIR spectra of the HB mixture (HB), bentonite (B) and halloysite (H) /left figure/ and of the NaCa, Na, HB samples /right figure/

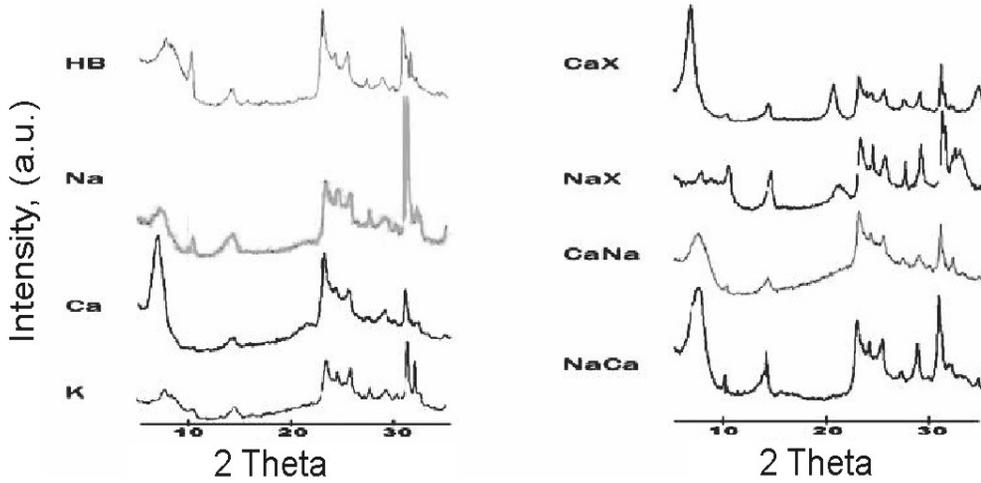


Fig. 10. XRD spectra of the samples

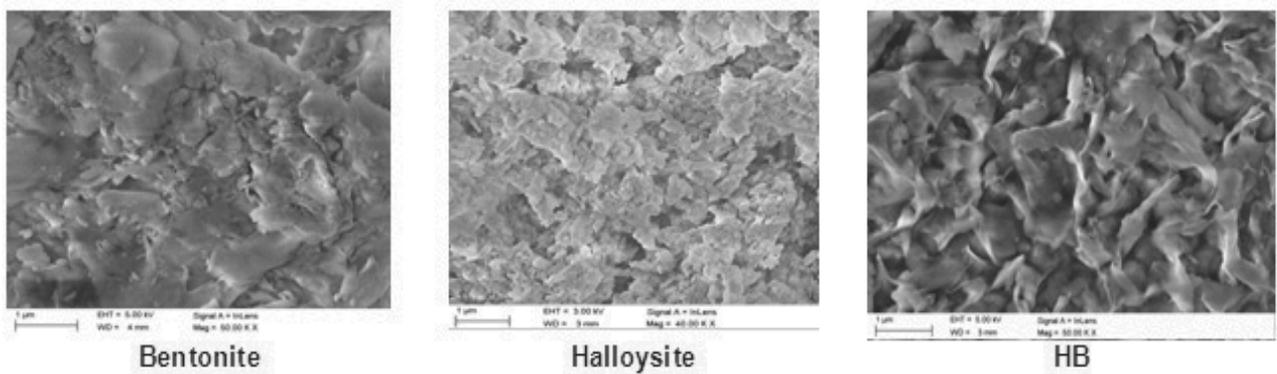


Fig. 11. Microscopic view of the dried samples of bentonite, halloysite and HB mixture (SEM)

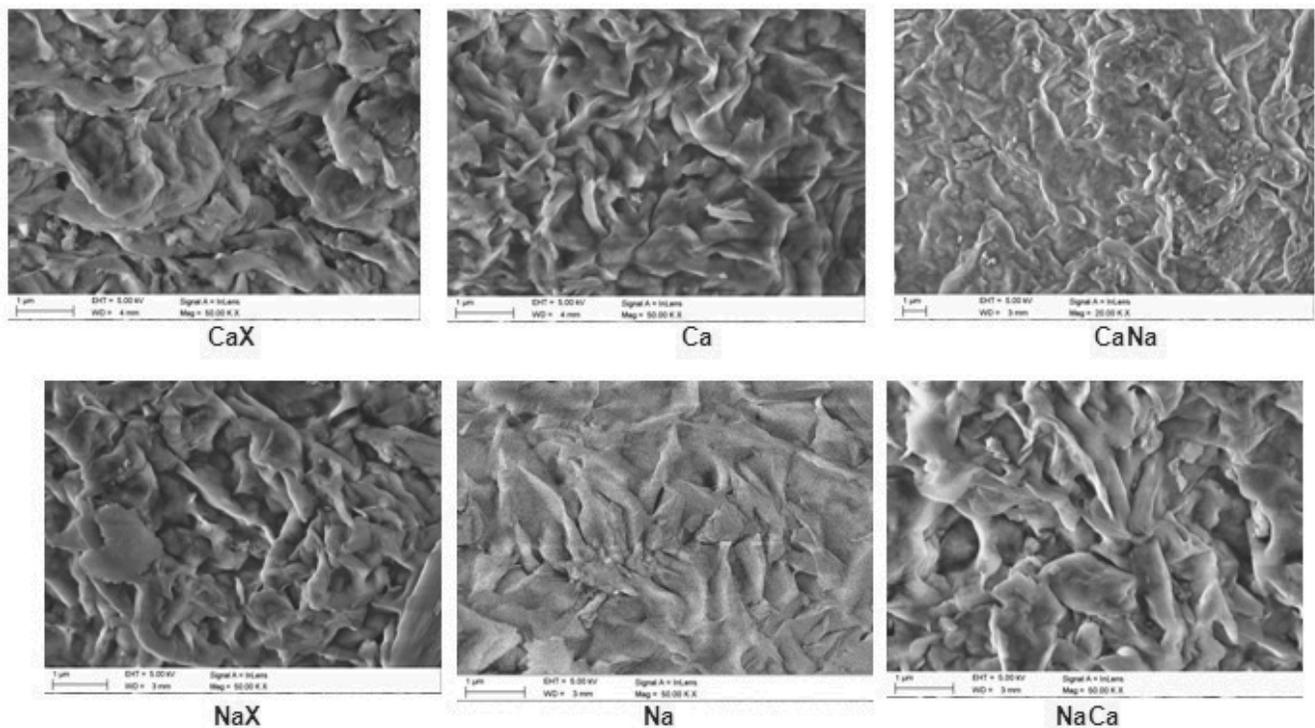


Fig. 12. Microscopic image of the dried samples (SEM)

## 5. Conclusions

One of the problems of waste disposal is 100% isolation of landfills. It is not possible to stop, retain and clean all the leachate generated in landfills. Hazardous leachate come mainly from the mixing of rain water with harmful substances formed from landfilled waste created in physico - chemical reaction.

The use of leachate drainage system allows only a partial minimization of uncontrolled leaching of hazardous substances. Filling up the landfills lasts several years and because of the dynamic processes occurring during this time the use of GCL is one of the best but not perfect solution.

Because of construction, location and different natural hydraulic permeability of GCL leaks into the natural environment will always occur.

It is estimated that each year, beyond the control, from each hectare of landfill leak hundreds of cubic meters, carrying with them difficult to identify and environmentally hazardous chemicals including inter alia heavy metals and phosphorus causing eutrophication of lakes and rivers.

Until now process of technical approval of GCL and research standards concerning isolation and sealing landfills allowing for use distilled water at pH 7. But it does not reflect actual conditions and the composition of the leachate. For this reason it is important to reduce the scale of the risk of contamination and stop the substances in the insulating layer.

Optimizing the composition of the insulating layer allows for minimizing number of uncontrolled leachate, and hold a large part of hazardous substances. Halloysite addition to the insulating layers can reduce the permeability of the heavy metals. For example cadmium which is one of the most dangerous due to its high toxicity to the human body.

As opposed to montmorillonite, halloysite shows a strong affinity to the monovalent cations, such as K, Li, Cs and Na, and is in practice quite insensitive to multivalent cation activity. However, both minerals have a feature in common - both easily delaminate in water and solutions of different salts. The mixture of finely dispersed lamellae of both minerals can combine the positive features of both minerals and retain the monovalent cations in a new type of interlayer space between the surfaces of halloysite and montmorillonite. These cations form the inner-sphere, outer-sphere and water-cation complexes, and these complexes are primarily responsible for good swelling and good self-healing properties of the Na-bentonite. The properties of the tested HB mixture were measured by means of complementary methods - XRD, EDS, FTIR, and the samples were observed under the SEM - microscope.

All test results confirm that the HB mixture is characterized by the following properties:

1. It retains the monovalent cations and retards the exchange of those cations for multivalent ones.
2. Retaining the monovalent cations and cation complexes, all surfaces of the halloysite particle, both basal and the edges, are active.

3. The addition of halloysite can prevent the agglomeration of bentonite platelets, which was found to be a main reason for swelling characteristics decreased as well as the increase in water permeability properties.

The expected results may be achieved only when the area of the surface contact for both minerals is large enough. This condition can be met by intensive mixing to produce small delaminated particles. The XRD method and the microscopic images show that the average planar dimensions of the lamellae of both minerals do not exceed 1-2  $\mu\text{m}$  with the thickness about 20-30 nm. This could indicate that the delamination process could progress more intensively. Only the maximal delamination of both minerals ensures the high extent of retention of monovalent cations. Not delaminated lamellae of montmorillonite retain all their properties, including their high affinity to the multivalent cations. In the samples tested, only a small part of the basal surfaces of both lamellae came to contact with each other and could connect the "good" monovalent ions.

Further studies carried out on the issue should help evaluate the concepts and help to optimize the parameters of the sealing clay mixture for a variety of applications. The behavior and functioning of the sealing layer during a long period of divalent cations presence is another subject for further research.

The conducted studies confirmed the possibility of replacing the sodium bentonite in the GCLs with a mixture containing halloysite and partly activated calcium bentonite.

The study of five-cycle wetting/drying revealed:

- halloysite-bentonite has much less tendency to the formation of cracks in the dried samples than sodium bentonite;
- halloysite-bentonite mixture is characterized by a lower tendency to shrinkability.

Little tendency to consolidation and cracking of dried material combined with a favorable ability to swell and "self-healing" justifies the use of halloysite-bentonite layers as an alternative to the conventional solutions.

The ability of halloysite to absorb heavy metals like cadmium and phosphorus may reduce the risk of contamination of ground water by the landfill leachate.

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