

## Bentonite as sealing material in geosynthetic clay liners

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GCL's consist of carrier geotextile on bottom and cover geotextile on top to focus the effective sealing material - the bentonite - inside. On contact with water, bentonites are swelling and close the pore spaces so that the permeability is very low. This extreme free swelling is bound to water with a low content of electrolytes. The effects of chemicals in leachates on the permeability of GCL's, regulations and limits of application are described as follows:

### 1. Introduction

Geosynthetic clay liners are used in various sealing measures as they are easily applicable. They are applied for the sealing of ponds, buildup basins, rainwater retention basins, storage spaces for water-endangering materials, roads and railway lines through water protection zones, surface cappings for mining spoilbanks, landfills and contaminated sites. GCL's can be applied without demur for sealing against clear rainwater. However, it is necessary to make detailed tests before applying them for sealing against contaminated leachates or other chemical solutions. It is necessary to know the structure and the properties of the sealing material bentonite - especially its main content, the clay mineral montmorillonite - to be able to assess the possible effects of chemicals on the sealing function.

There is a great range of chemicals and leachates which can come in contact with bentonite as sealing material. Therefore it is necessary to describe their electrical properties (charge, valency, polarity, dipol moment) to be able to assess possibly negative effects on the permeability. There also has to be considered marginal conditions as concentration, solubility in water of the chemicals, saturation state of the bentonite, loading etc.

### 2. Characteristics of bentonites

Bentonite is a soil, consisting mainly of three-layer clay minerals, capable of swelling, from the dioctahedral smectite group. The most widespread member of this group is the clay mineral montmorillonite, which is also the main constituent of bentonite. In addition, bentonite contains other accompanying minerals, such as quartz, cristobalite, feldspars, carbonates, mica and other clay minerals. High quality bentonite contain 60 - 90 % of montmorillonite by weight. For industrial applications and for their use in sealing applications, it has become usual, for the sake of simplicity, to talk of calcium bentonites, natural Na-bentonites and soda-activated bentonites, the so-called active bentonites. Bentonites occur largely as the product of weathering, through a chemical transformation from acid volcanic glass tufa (volcanic ashes) which have been deposited in the sea (Na-bentonites) or in fresh water (Ca-bentonites).

The exceptional soil physical, chemical and soil mechanical characteristics of montmorillonite, and therefore the bentonites, are based on the structure of the three-layer clay minerals of the smectite group. One montmorillonite crystal is made up of a series of tetrahedron-octahedron-

tetrahedron layers, which, because of the partially isomorphous exchange of  $\text{Si}^{4+}$  ions by  $\text{Al}^{3+}$  ions in the tetrahedron layers, and of  $\text{Al}^{3+}$  ions by, e.g.  $\text{Mg}^{2+}$  ions in the octahedron layer, possess a negative layer charge at the base areas of the clay minerals. The excess negative charge is balanced by the interlayer cations (principally  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ) which contain the T-O-T layers. The interlayer cations thus bond the single elementary layers into larger crystals of approx. 5 to 25 elementary layers.

On contact with water, the interlayer cations begin to hydrate. Depending on the amount of water, hydration with one, two and four water layers occur between the silicate layers. Assuming that the montmorillonite is completely dry, the layer separation, as a result of hydration, increases by stages, from 0.96 nm to approx. 1.23 nm, 1.52 nm and maximum 2.0 nm. This expansion of the interlayers by hydration of the interlayer cations is known as inner-crystalline swelling.

In the case of Ca-montmorillonite, the swelling process is confined to inner-crystalline swelling. This may double the montmorillonite's volume (MADSEN & MITCHELL 1989).

In the case of Na-montmorillonite, the inner-crystalline swelling in water or low-electrolyte solutions may change into so-called osmotic swelling, because of the further hydration of the  $\text{Na}^+$  ion, with further water layers being formed. In this process, the  $\text{Na}^+$  ions move from their central position in the interlayer to the layer surfaces, with which they form co-called electrical double layers which are mutually repellent. Compared with the inner-crystalline swelling, which results at the most in a doubling of the layer separation (from 0.91 to max. 2.0 nm), repulsion of the electric double layers works at greater distances and results in the silicate layers being partially separated from each other, with single silicate layers or fine layer parcels being formed.

The thickness of the electric double layer, which is approx. 100 nm (MADSEN & MITCHELL 1989, BUSCH & LUCKNER 1974), i.

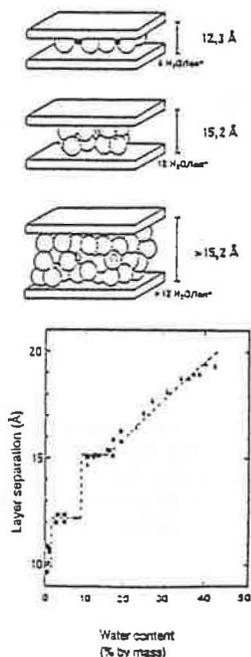


Fig. 1: Hydration levels and changes in the layer separation, related to water content

e., the effectiveness of the repelling forces, is dependent on the valency of the ions, the index of pH of the pore solution, the concentration of the electrolytes and the dielectric constant for the pore solution (MADSEN & MITCHELL 1989).

The swelling pressures resulting from the repelling forces (approx. 2 MN/m<sup>2</sup>) are considerably lower than in the case of inner-crystalline swelling.

The 2nd water layer is approx. 100 MN/m<sup>2</sup>, 3rd and 4th water layers are approx. 27 MN/m<sup>2</sup> (MADSEN & MITCHELL 1989). The swelling volume (free swelling) resulting from the inner-crystalline swelling (Ca-bentonite) is approximately two or four times as much; the swelling volume of Na-bentonite (inner-crystalline + osmotic swelling) is approximately 8 to 15 times as much. In the case of swelling under load, the extend of swelling ( $dh/h_0$ ) is considerably less, and varies with applied loads in a range of 20 to 100 kN/m<sup>2</sup>, from approx. 40 to 20 % for Na-bentonite (AGK 1988/89)

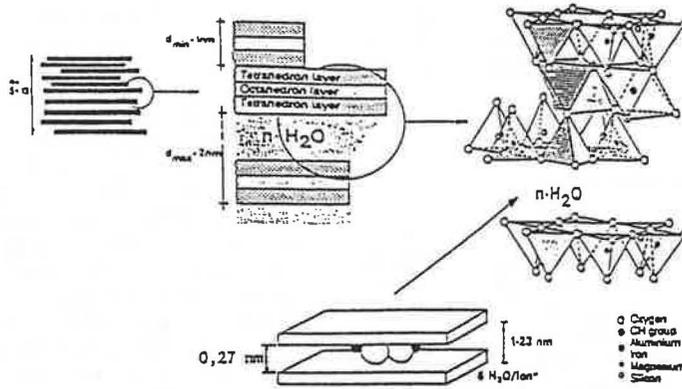


Fig. 2: Structure and form of the three layer clay mineral montmorillonite (Grim & Güven 1978, Kohler & Martiani 1984)

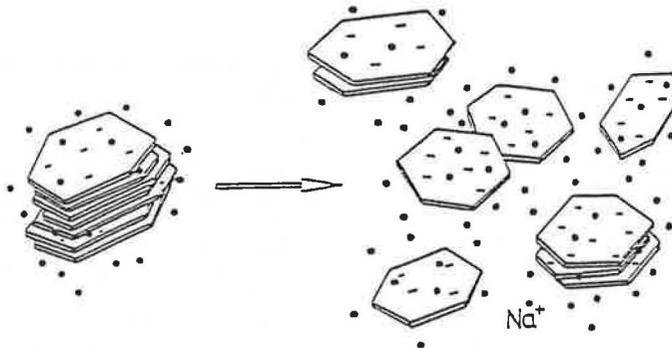


Table 1. Characteristics of the clay mineral montmorillonite (Weiss 1988, Scheffer & Schachschabel 1992, Jasmund & Lagaly 1993)

Individual layer thickness [nm]	0.91
Diameter of layers [nm]	30 - 300
Most common number of layers [-]	25 - 80
Specific surface [m <sup>2</sup> ]	600 - 800
CeC (mval/100g)	30 - 120

Fig. 3: Decomposition of sodium smectite crystals into individual silicate layers (Jasmund & Lagaly 1993)

### 3. Interactions of chemicals and their diluted solutions with bentonite

Apart from the properties of the bentonite, the properties of the leachate (soil solution or chemicals in a diluted, hydrous solution) play a decisive role. In the following, the most important groups of substances and their interactions with bentonite and as simple methods of identification as possible will be described. Limits of application as well will be recommended as far as possible.

#### 3.1 Acids

Acids increase the electrolyte concentration (reduce the electrical double layer and thus the swelling volume), exchange part of the Na<sup>+</sup> ions by H<sup>+</sup> ions, dissolve calcite partly or completely and thus release Ca<sup>2+</sup> for the ion exchange. Highly concentrated mineral acids (pH < 1) attack the grid of the clay minerals and release Al, Mg and Fe.

The pH-value of acidic solutions which are in constant contact with bentonite should amount to  $\text{pH} > 3$  or, even better,  $> 5$ .

### 3.2 Alkaline solutions

Alkaline solutions (e.g. NaOH) first work like a deflocculation agent (edge charge negative!) and - up to approx.  $\text{pH} = 11$  (and depending of the type of cation) - have hardly any effect on the bentonite or even reduce its permeability. Highly concentrated alkaline solutions, however, attack the grid of the clay mineral and release  $\text{SiO}_2$  and Al.

The pH-value of alkaline solutions which are in constant contact with bentonite should amount to  $\text{pH} < 13$  or, even better,  $< 11$ .

### 3.3 Interactions with dissolved inorganic components

#### 3.3.1 Electrolyte contents - Ionic concentration

The concentration of the electrolytic solution, this means the ionic concentration of the hydrous solution, effects the thickness of the electrical double layer of the montmorillonite particles (reciprocal repulsion of the particles) and thus the swelling capacity of the montmorillonite. The thickness of the double layer is the highest in water with a very low electrolytic concentration and it decreases when the ionic concentration increases. The coagulation concentration of a Na bentonite in suspension can be taken as a reference value to assess the range of (low) electrolytic concentration where no negative effects caused by hydrous (electrolytic) solutions have to be feared. For monovalent cations it ranges between 25 and 150 mmol/l, for bivalent cations between 0.5 and 2 mmol/l and for trivalent cations between 0.01 and 0.1 mmol/l (JASMUND & LAGALY, 1993). In practical applications of GCLs, however, these concentrations are often exceeded. Moreover it has to be taken into account that these data relate to closed systems and that GCLs are used in open systems (increase or decrease in ions possible). However, this may be tolerated within relatively wide ranges of concentration, if the following marginal conditions are taken into account.

#### 3.3.1.1 Water hardness

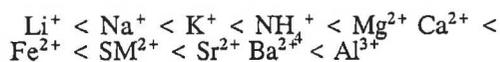
The water hardness is a common parameter for natural ground, surface and drinking waters and gives important hints regarding the electrolyte content (contents of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) and the ion exchange equilibriums. The definition of water hardness differs from country to country. One German degree of hardness  $1^\circ \text{Gh} = 7.14 \text{ mg/l}$  or  $0.179 \text{ mmol/l}$  or  $0.358 \text{ mval calcium}$ . One American degree of hardness  $1^\circ \text{Ah} = 1 \text{ mg/l CaCO}_3 = 0.4 \text{ mg/l Ca} = 0.01 \text{ mmol/l} = 0.02 \text{ mval/l calcium}$ . It is better to state the data in hardness equivalents (mval/l), since this considers the quantity of dissolved substances and its valency. Thus the hardness equivalents of other analyzed cations and anions can be calculated.

#### 3.3.1.2 Control parameter electrical conductivity

The electrical conductivity is a control parameter easily to be determined to assess the leachate components in ion form. A relatively precise relation exists between the conductivity in  $\mu\text{S/cm}$  and the concentration of the solution in mval/l ( $100 \mu\text{S/cm} \approx 1 \text{ mval/l}$ ). For nearly pure water this relation is valid with an accuracy of  $\pm 5 \%$ , for water with an ionic concentration of 1-10 mval with an accuracy of  $\pm 15 \%$  (DAVIS & DE WIEST 1967). The multiplication of the conductivity with the factor 0.725 results in the approximate residue on evaporation at  $25^\circ \text{C}$ .

#### 3.3.2 Ion exchange

For Na bentonites the montmorillonite crystals have exchangeably bound mainly  $\text{Na}^+$  ions on their outer surfaces and in the interlayers to form a charge equalization to their negatively charged base surfaces. The exchange force of the cations increases within an elemental period with increasing valency (valency effect) and within the same group of elements with increasing ion radius.



As this sequence, which is called "iyotrope sequence", shows, the  $\text{Na}^+$  ion is situated very far on the side of the ions with a low exchange force. It is thus preferably

exchanged by all cations on its right side having a higher electric charge (valency) and an increasing ion radius. With the normally bivalent heavy metals ( $SM^{2+}$ ) principally the same rules apply as for the other ions. For cations of higher valency the exchange equilibriums towards  $Na^+$  ions are situated so far on the right side of the sequence that even comparably low concentrations are sufficient to exchange the  $Na^+$  to a large extent. To evaluate the effects of the dissociated ions more precisely the individual components of the solution have to be determined for higher conductivities. A particularity is the so-called specific adsorption of the cations  $K^+$  and  $NH_4^+$  which - due to their size and shape - fit very well into the hollows of the hexagonal indentations of the oxygens of the base surfaces of the montmorillonite crystal. When  $Na^+$  is nearly fully exchanged by  $K^+$  or  $NH_4^+$  this may lead to a nearly irreversible contraction of the interlayers.

### 3.4 Interactions with organic components

Highly concentrated, non-polar organic liquids with a low dielectric constant (petrol, fuel, chlorinated hydrocarbons etc.) diffuse at longer contact with swollen bentonites into the diffuse electrical double layers of the montmorillonite particles and compact them (comparable: high electrolyte contents). This leads to a shrinkage of the clay and - when the load is missing - to crackings. Bentonites do not swell in contact with these liquids. The use of dry GCLs for sealing purposes against such liquids has no effect at all! Bentonite saturated with water is at first absolutely impermeable against such non-polar liquids. The polar water in the pore space of the clay is the better moistening phase and prevents at first the non-polar liquids from penetrating. Depending on the marginal conditions (water saturation, bentonite quantity, load), this effect, however, only lasts some hours up to several days. Non-polar organic liquids are only slightly soluble in water (g - mg/l). Hydrous solutions of these liquids thus have no effect on the bentonite. When polar organic liquids (e. g. methanol, ethanol, phenol, acetone, ethylenic glycol etc.) are highly concentrated (> 70 %) (MADSEN & MITCHELL, 1989) they have a compacting

effect on the electrical double layer and thus unfavourably influence the swelling volume. Diluted solutions (e. g. < 5 - 10 %) are usually harmless.

Organic cations (cationic tensides, e. g. alkyl ammonium) are very well integrated by the montmorillonite into the interlayers. When highly concentrated this may cause the bentonite to shrink.

### 4. Instructions for the application of GCLs in contact with leachates or chemical solutions

When the water is assumed to contain certain components, GCLs should not be installed without prior testing. The following list shall help to prevent failures. The observance of simple application instructions (see section 5.1) makes it possible to extend the limits of application to a relatively large degree.

No limitation of applications:

- For waters with low electrolyte content (soft water) having conductivities < approx. 250 S/cm or approx. 8° Gh or 143° Ah. Here the coagulation concentration (flocculation concentration) of a Na-montmorillonite (1.2 mmol to 1.7 mmol/l (48-68 mg/l)  $Ca^{2+}$  SCHEFFLER & SCHACHTSCHNABEL, 1992) serves as a guidance. With Na-bentonites the coagulation concentration for  $Na^+$  is increased approx. by the factor 10. If the waters additionally contain mainly  $Na^+$  ions, no problems with the ion exchange have to be expected even on a long-term basis.
- For hydrous solutions with low electrolyte content (see above) of unpolar organic liquids (petrol, fuel, highly volatile halogenated hydrocarbons etc.), since the slight solubility of these substances in water exclude relevant concentrations.

No applications of GCLs!

- No application for permanent sealing purposes against concentrated, non-polar organic liquids with a low dielectric constant

(petrol, chlorinated hydrocarbons, xylol, ethanol etc.). Exceptions are only possible when the GCL is saturated with water and when the contact remains short. Permeability tests with GCLs saturated with water and diesel oil carried out over a period of 3 months showed no increase in the permeability coefficient (NAUE FASERTECHNIK, 1991).

- No application for permanent sealing purposes against acid with pH-values < 3 and alkaline solutions with pH-values > 13.

Limited application - Tests and/or assessment required

- For hard groundwaters ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ), waters containing iron and leachates with high electrolytic concentrations. For conductivities > 1000  $\mu\text{S}/\text{cm}$  mainly the cations  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$  should be determined. If bivalent cations (range of hardness > 5-10 mval = 14-28° Gh and 250-500° Ah) are predominant, the application conditions should be limited (see below).
- For highly concentrated pure solutions containing  $\text{K}^+$  and  $\text{NH}_4^+$  (e. g. > 10 mval/l) the application conditions should be limited (see below) due to the specific interaction between these ions and montmorillonite.
- For heavy metal solutions of higher concentration. Here, the pH-value has to be observed above all. Most heavy metals are only slightly soluble in the spectrum of pH > 5.5 and < 11. Solutions up to a cumulative concentration of approx. 3 mval/l with simultaneously low concentrations of other bi- or trivalent cations seem to be harmless.

- For hydrous solutions with polar organic liquids (e. g. methanol, ethanol, phenol, acetone, ethylenic glycol etc.) in high concentrations, e. g. > 10 % - < 70 % (see also MADSEN & MITCHELL, 1989).

- For leachates with higher concentrations of organic cations (cationic tensides, e. g. diammonium dodecan, alkyl ammonium, plant-protective agents such like Paraquat, Diquat), since these cations are very well integrated into the interlayers by the montmorillonite which may cause the montmorillonite to shrink.

4.1 Application guidelines for the use of GCLs with leachates and chemical solutions

- a) Pre-swelling with water of low electrolyte content

With high electrolyte concentrations, particularly with high concentrations of bivalent cations, a pre-swelling of the GCL should be carried out using water with a low electrolyte content. The innercrystalline swelling of the montmorillonite (expansion of the interlayer space from  $\pm 1.23$  to 2.0 nm) caused by the hydration of the interlayer cations is to a large extent independent on the electrolyte content of the ion solution. Contrary to this, the so-called osmotic swelling of the  $\text{Na}^+$  montmorillonites which starts directly after completion of the innercrystalline swelling (expansion of the medium interlayer space from  $\pm 2.0$  to  $\pm 12-15$  nm) is depending on the concentration difference (osmotic pressure) between the highly concentrated inner solution (concentration of  $\text{Na}^+$  ions approx. 100-2000 mval/l) and the outer solution. If the electrolyte content of the outer solution is too high, an osmotic swelling will not take place (e. g. with sea water with approx. 600 mval of dissolved cations). Once the swelling of the bentonite is completed, its water binding property is

able to keep the adsorbed water. With other cations than  $\text{Na}^+$  an evitable, premature ion exchange is already occurring at water adsorption. 1 g bentonite has a CEC of  $\pm 0.7$  mval/g. With, e. g., 10 mval/l dissolved bivalent cations approx. 0.02 mval =  $\pm 3\%$   $\text{Na}^+$  ions are exchanged against bivalent ions already at water adsorption (GCL  $\pm 200\%$  by weight).

#### b) Thickness of the soil covering

When the soil covering is only small (e. g. < 30 cm) the use of GCLs, particularly under limited application conditions, is not recommended. In such cases the GCLs should be covered with at least 1 m of soil.

This has positive effects in many respects:

- = > The permittivity is slightly lower with a higher covering than with a low covering.
- = > When higher electrolyte contents or ion exchange processes over long time periods have caused the swollen bentonite to shrink, structural transformations are suppressed and the shrinkage is compensated without cracks by the consolidation of the bentonite layer.
- = > Disturbances of the structure caused by nearly complete desiccation (development of aggregates/crumbs) and frost (ice needles or lenses) are prevented or dampened to a large extent.

Due to the one-sided position of the ion exchange equilibria between the monovalent  $\text{Na}^+$  ions and the bivalent ions in favour of the bivalent ions and the simultaneous predominance of bivalent ions (usually calcium) in natural leachates, it is but a function of time and mass balance (concentration in the soil solution, ionic distribution of the bentonite, quantity of percolating water  $\{i, \nu\}$  and the diffusion) that the  $\text{Na}^+$  bentonite is converted into a  $\text{Ca}^{2+}$  bentonite. However, this has hardly any relevant effect on the permeability as long as the covering is sufficiently thick

(consolidation) and disturbances of the microstructure caused by frost and complete desiccation are prevented. Due to the finer microstructure of  $\text{Na}^+$  bentonites compared to  $\text{Ca}^{2+}$  bentonites (partly delamination of the booksheets into individual lamellas or thinner booksheets) after a first swelling in water with low electrolyte content, the use of primary Na-bentonites is reasonable, even if finally an ion equilibrium which corresponds to the geochemical environmental conditions will develop.

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