

Application of GCLs in contact with leachates or chemical solutions

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ABSTRACT: The sealing ability of GCLs is as a result of its bentonite content. Bentonite is a type of clay with high water adsorption capacity, swelling volume and very low permeability. Furthermore bentonite is a very good ion exchanger. All these properties depend on the chemical reactive clay mineral montmorillonite, which is the main component of bentonite. The very finely grained montmorillonite has large electrically charged surfaces. Hence, exchangeable cations and water molecules are easily adsorbed by this clay mineral. After hydration and innercrystalline swelling the montmorillonite surfaces of sodium bentonites form electrical double layers around the clay particles which push the clay particles apart from each other. The effect of this behavior is a very high swelling capacity. The thickness of the double layers and therefore the swelling volume as well as the bentonite's permeability in GCLs depends on the electrolytic concentration of the pore water. The most important property of the bentonite in GCLs which is the very low permeability, can rapidly increase if a GCL is exposed to leachate or chemical solutions with high electrolytic contents, low pH-values or high concentrated organic components. This paper points out a number of simple investigations, which help to decide whether an effective GCL-seal is achievable under the given circumstances or if mitigative measures are necessary in order to attain the desired sealing properties..

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. GCLs 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.

The best known interaction is the ion exchange. As a result of this interaction a Na-bentonite which is highly capable of swelling can turn into a Ca-bentonite which is less capable of swelling. These interactions can have an influence on the function of the sealing layer (permeability). Under unfavorable conditions damages are possible.

First theoretical reflections and, in consequence, possibly simple test methods to verify them are necessary to clarify under which conditions unfavorable effects are to be expected, e. g. nature and threshold concentration of the chemical substances in the leachate, the reaction of the chemical substances, general conditions etc. The most important aspect is how high the threshold concentration is to be expected to set off the unfavorable effects.

Simple static and dynamic test methods in a measure cylinder resp. simple columnar percolation tests under certain stress conditions (additional load) are suggested instead of costly long-term percolation tests with natural and synthetic leachates or mineralogical and soil-physical test methods.

2 SUITABILITY TEST - BENTONITE PROPERTY TEST

2.1 Usual tests with bentonite used for GCLs

Usually, the following test methods are applied to check the suitability of a bentonite used as the sealing component of GCLs:

Table 1: Usual bentonite tests for GCLs

Water content (oven-drying at 105 °C [% by weight]) ≤ 15 % by weight
Swelling volume acc. to ASTM D 5890 (2 g/100 ml [cm ³] ≥ 25 cm ³)
Water adsorption capacity acc. to ENSLIN/NEFF (0.5 g/24 h [% by weight]) ≥ 600 % by weight
Methylene blue test (mg/g or in % of a standard bentonite)

The determination of the sedimentation volume acc. to HOFMANN (1975) is similar to the examination of the swelling volume acc. to ASTM D 5890: 1 g bentonite is suspended and dispersed in 90 ml of water and then flocculated with 10 ml of an ammonium chloride solution. The sedimentation volume, which develops after approx. 2 days, admits conclusions on the fineness of the deflocculation and thus on the montmorillonite content and the ionic occupancy. In the author's opinion, this test is more sensitive and expressive regarding the quality of the bentonite (especially the ionic distribution) than the determination of the swelling volume acc. to ASTM D 5890.

For a more detailed characterization of the bentonite, especially concerning its chemical long-term resistance, further tests should be carried out.

2.2 Intensive tests with bentonite

2.2.1 X-ray diffraction analysis - mineral constituents

The x-ray diffraction analysis (XRD) characterizes the mineral constituents of a bentonite. This consists mainly of montmorillonite. The x-ray diffraction analysis is not very suitable to determine the montmorillonite content of the bentonite (better: the methylene blue test), but it is very useful for the identification

and semi-quantitative analysis of the kind and quantity of the accompanying minerals of the montmorillonite. The most frequent accompanying minerals are: Quartz, calcite, dolomite, sanidine, albite, cristobalite, illite, kaolinite, chlorite, mixed-layer, zeolites, gypsum, bauxite minerals, pyrite.

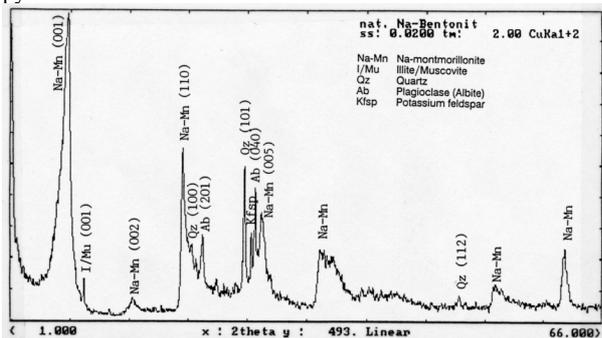


Fig. 1: X-ray diffraction analysis, powder preparation of sodium-bentonite

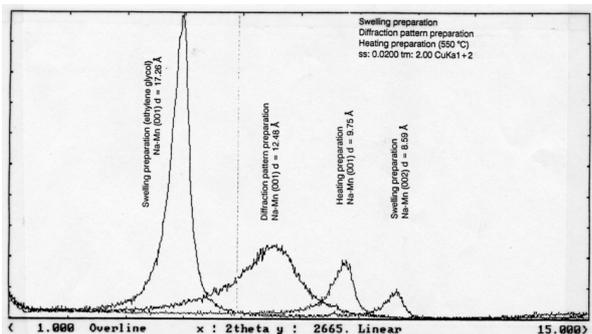


Fig. 2: X-ray diffraction analysis, pattern, swelling and heating preparation of sodium-bentonite

Evaluation of the results:

The kind and quantity of the accompanying minerals of the montmorillonite are a criterion for the quality of the bentonite. Water-soluble compounds or accompanying minerals as mainly calcium hydroxides, gypsum, calcite (dolomite), which mainly emit Ca^{2+} , are principally disadvantageous for the long-term maintenance of the sodium occupancy of the bentonite which is responsible for substantial properties of the bentonite. Na-activated calcium bentonites have to be specially mentioned, since the calcium, which is exchanged during the activating process, remains in the system and is present in a particularly easily soluble form (calcium re-exchange). Therefore, the calcite content of a bentonite as well is a criterion for its quality.

2.2.2 Cation exchange capacity - ionic distribution in the bentonite

The cation exchange capacity (CEC) of a bentonite is, like the methylene blue value, a measure for the montmorillonite content. The cation exchange capacity can be approximately calculated as well by the methylene blue adsorption. 1 mol methylene blue has 319.5 g. A (usual) solution of 5 g methylene blue/litre has a concentration of 0.015649 mmol/ml or mval/l. The CEC results from multiplying the MB consumption in ml with the concentration:

$$\text{MB consumption [ml]} \cdot \text{concentration [mval/ml]} \cdot 100 = \text{CEC [mval/100 g]}$$

The determination of the cation exchange capacity acc. to MEHLICH (1948), for instance, gives more precise results, but it is much more time-consuming. The ionic distribution (Na^+ , Ca^{2+} , Mg^{2+} , K^+ , Fe^{2+} , Al^{3+}), however, is decisive for the quality of the sodium bentonite (swelling capacity, water adsorption, k-value). It can be best determined by exchange with an alcoholic ammonium sulfocyanate solution (MÜLLER-VONMOOS 1982).

Table 2: Characteristic ionic distribution of a high-quality sodium bentonite with a CEC of approx. 60 - 100 mval/100 g

Na	Ca	Mg	K	Fe	Al
60-90 %	5-25 %	3-15 %	0.1-0.8 %	< 0.5 %	< 0.5 %

Evaluation of the results:

The methylene blue adsorption already characterizes the montmorillonite content with sufficient exactness. Therefore, the determination of the CEC is usually unnecessary, as for sodium-bentonites it can be approximately calculated from the MB value. However, the ionic distribution at the bentonite is of some importance for the quality determining properties. The usual test methods, water adsorption capacity acc. to ENSLIN/NEFF and swelling capacity acc. to ASTM D 5890, reflect the ionic distribution only up to certain limits. If the Na portion of a sodium bentonite ranges above ± 40 %, these test methods normally do not show any significant differences to a high-quality sodium-bentonite with, for instance, a sodium portion of 85 %. This high-quality bentonite, however, has a higher "buffering capacity" against the ion exchange with mainly bivalent cations.

2.2.3 Calcium carbonate content

The determination of the calcite/dolomite content can be done semi-quantitatively by using the XRD method. The gasometrical determination acc. to SCHEIBLER or DIN 18129 is more precise, the carbon water analysis¹¹ (CWA), however, is even better. A differentiation of the total carbonate content in calcite/dolomite or siderite can be made by XRD.

Evaluation of the results:

The calcium (dolomite) content of a bentonite is of special importance to check the chemical

resistance in an acid environment. 1 % by weight of calcite contains a calcium potential of approx. 20 mval/100 g Ca^{2+} (1 % by weight of gypsum = 11.6 mval Ca^{2+} , 1 % by weight of dolomite = 10.6 mval Ca^{2+} and 6.5 mval Mg^{2+}). This amounts to approx. $\frac{1}{4}$ of the cation exchange capacity and in contact with acidic leachates in particular it is sufficient to initiate an extent re-exchange of Ca. In water free of carbonic acid calcite dissolves up to a concentration of 14 mg/l (0.7 mval/l), in water containing CO_2 this concentration is correspondingly higher (up to 850 mg/l at CO_2 saturation). Gypsum dissolves in concentrations up to 600 mg/l.

2.2.4 Water-soluble salts in bentonite

Some bentonites, e.g. from arid regions, contain soluble minerals or salts, which start to dissolve as ions when in contact with water. These ions may - up to a certain degree - unfavorably change by ion exchange the ionic distribution in the interlayers. To check the existence of water-soluble ions in bentonite, a 5 % suspension with de-ionized water is produced and conductivity, pH-value and the ions Na^+ , Ca^{2+} , Mg^{2+} , K^+ , Fe^{2+} , Al^{3+} are determined. This method is usually also suited to distinguish natural sodium bentonites and Na-activated calcium-bentonites. The pH-value and the conductivity as well as the contents of Na and Ca ions of the suspension are clearly higher with sodium-activated calcium bentonites than with natural sodium bentonites (surplus soda and exchanged calcium which remains in the system). To obtain a realistic survey of the soluble cations, a repeated washing with de-ionized water (cascade tests) and a following analysis of the wash with a back calculation in mval/100 g is normally required. It is reasonable to countercheck the determined cations via the conductivity.

Evaluation of the results:

¹¹ Heating up of the sample to 1000 °C in a nitrogen atmosphere, measuring of the CO_2 , which escapes in a gaseous form, by using the infrared analyzer, stoichiometrical back-calculation to CaCO_3 .

With natural sodium bentonites (Wyoming bentonites), the quantity of mainly Na^+ and Ca^{2+} ions, which has been released by washing with de-ionized water, is usually neglectably small. With bentonites from arid regions there are occasionally considerable quantities of soluble salts of the soil. With Na-activated Ca-bentonites the quantity of the exchanged calcium remaining in the system may be so large that it is sufficient to wash it twice with de-ionized water to cause an extent re-exchange of the Na-activated calcium bentonite into a calcium bentonite (GOLDE 1994).

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^+ ions by H^+ ions, dissolve calcite partly or completely and thus release Ca^{2+} for the ion exchange. Highly concentrated mineral acids ($\text{pH} < 1$) 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 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/. 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.

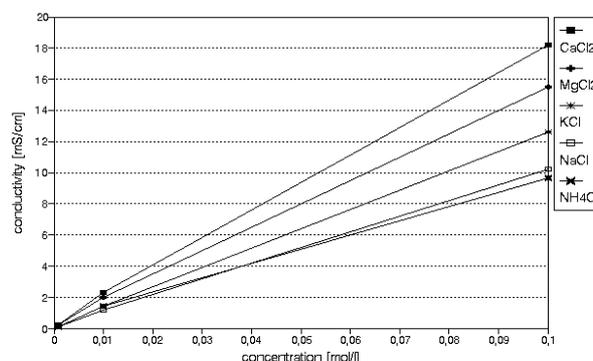
3.3.1.1 Water hardness

The water hardness is a common parameter for natural ground, surface and drinking waters and gives important hints regarding the electrolyte content (contents of Ca^{2+} and 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 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°C .

conductivity of chemical solutions with different concentrations



conductivity of chemical solutions with different concentrations

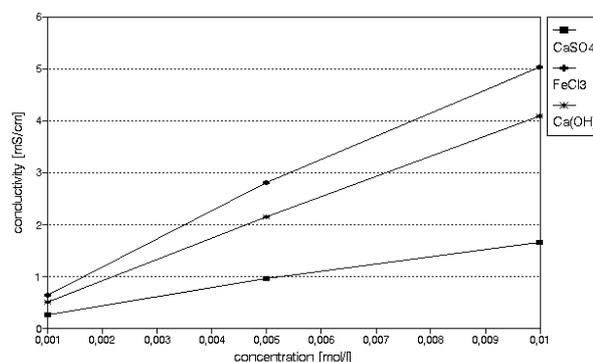


Fig. 3 and 4: Relation between normality and conductivity of the solution

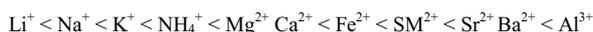
Tab. 3: Reference values for dissolved components (residue on evaporation, conductivity, equivalent concentration, in the main Davis & De Wiest 1966, Hötting 1989).

	Residue on evaporation [mg/l]	Conductivity [$\mu\text{S/cm}$]	Concentration (eq) [mval/l]
distilled water	< 3.6	< 5	0.05
rainwater	3-20	5-30	0.05-0.3
fresh water	20-1000	30-2000	0.3-20
brackish water	1000-10000	2000-45000	20-450
mineral water	7250-14500	10000-20000	100-200
saltwater	10000-100000	13800-138000	138-1380

	Residue on evaporation [mg/l]	Conductivity [$\mu\text{S}/\text{cm}$]	Concentration (eq) [mval/l]
sea water	35000	45000-55000	600
landfill leachates	300-50000	2000-100000	20-1000
water from oil fields	72500	> 100000	> 10000
brine	> 100000	> 138000	> 13800

3.3.2 Ion exchange

For Na bentonites the montmorillonite crystals have exchangeably bound mainly 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 "lyotrope sequence", shows, the 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 equilibria 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 ($\mu\text{g} - \text{mg}/\text{l}$). 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 %) 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 SIMPLE TEST METHODS TO VALIDATE THE INTERACTIONS BETWEEN DILUTED CHEMICALS AND BENTONITE

4.1 Swelling volume at free-swelling

To assess the effects of leachates on the long-term permeability on GCLs simple swelling tests can be carried out using original leachates, artificially produced soil solutions (eluates) or synthetic leachates. For the purpose of this paper swelling tests were carried out with 2 g/100 ml natural Na-bentonite (Wyoming), several active bentonites and calcium bentonite. The swelling tests were carried out with the salts NaCl , KCl , NH_4Cl , CaCl_2 , MgCl_2 , $\text{FeCl}_2 \cdot 4 \text{H}_2\text{O}$, the polar organic substances methanol, acetone, phenol in various concentrations (0.01, 0.05 and 0.1 mol/l or 5, 15 and 30 % solutions). 2 g bentonite on the bottom of the measuring cylinder approximately correspond to a GCL mass per unit area of $3 \text{ kg}/\text{m}^2$. The solutions were carefully filled in. This was to simulate the unilateral contact of a dry bentonite layer with leachate.

swelling capacity <Wyoming-bentonite> with different chemical solutions

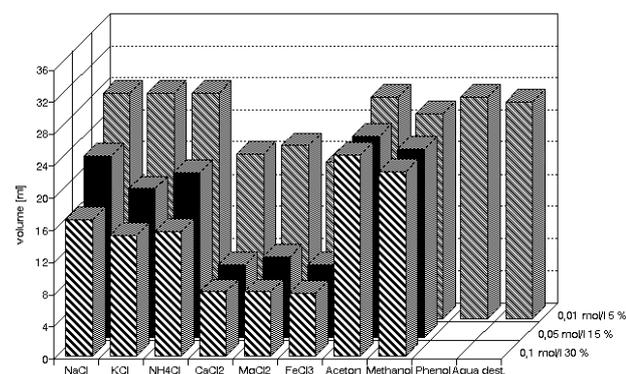


Fig. 5: Swelling volume of a sodium-bentonite with different diluted solutions of various concentrations

Evaluation of the results:

These simple swelling tests give a first impression about whether it has to be feared that the contact with leachates unfavourably effects the swelling volume and about the relevant ranges of concentration. It has to be mentioned that this system is closed, i. e. that no washing-out of ions (e. g. Na^+) or increase in ions will take place. The CEC of the 2 g of bentonite amounted to approx. 1.4 mval (CEC \pm 70 mval/100 g). The equivalent quantity of substances dissolved in water amounted to 1 mval up to 20 mval, this is 1 to 15 times the CEC of the bentonite. It has to be stated that low concentrations (5 % solutions) of acetone, methanol and phenol and the monovalent salt solutions NaCl , KCl and NH_4Cl (10 mmol/l) have a small effect. The bivalent salt solutions CaCl_2 , MgCl_2 and FeCl_2 already lead to a considerable reduction of the swelling capacity. The increase in the concentrations of the salt solutions by the factor 5 to 0.05 mmol/l shows a clear effect with all salts, whereas with methanol and phenol only their 30 % solutions lead to clear reductions of the swelling capacity.

4.2 Water adsorption acc. to ENSLIN/NEFF

Apart from the determination of the swelling capacity, the determination of the water adsorption capacity using the ENSLIN/NEFF apparatus (DIN 18132) is another simple method to examine the effects of leachates on the quality of bentonite. The water adsorption of the dry bentonite reacts very sensitively on the dissolved water components. The water adsorption with 0.1 mol CaCl_2 compared to de-ionized water is shown as an example. Since the handling is more difficult (the chemical solutions

have to be filled into the ENSLIN apparatus without developing bubbles) the free swelling has to be preferred to this test.

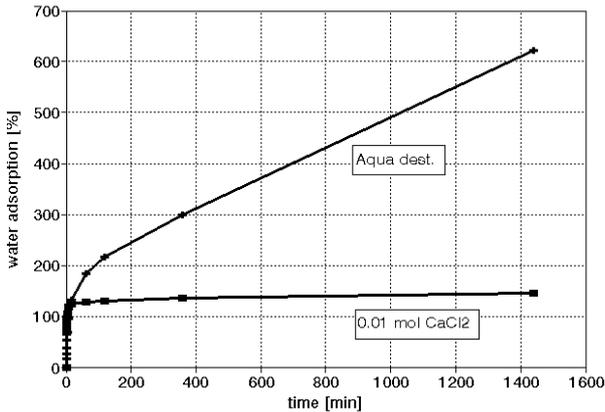


Fig. 6: Water adsorption acc. to ENSLIN/NEFF (DIN 18132) with de-ionized water and 0.1 mol CaCl₂

4.3 Permeability tests with original leachate, soil eluates and synthetic leachates

If reliable (quantitative) results regarding the permeability behaviour of GCLs towards leachates are required which exceed theoretical reflections or the a. m. qualitative tests, it is, in the present state of experience, still necessary to carry out permeability tests under practice oriented conditions using original leachates, soil eluates or synthetic leachates.

To be considered:

- simulation of the correct load (flexible wall permeameter)
- simulation of the fixed condition of the GCL (see also draft permeability cell)

To limit the test duration it is reasonable to use

- higher hydraulic gradients
- higher concentrations (synthetic leachates) as quick-motion effects.

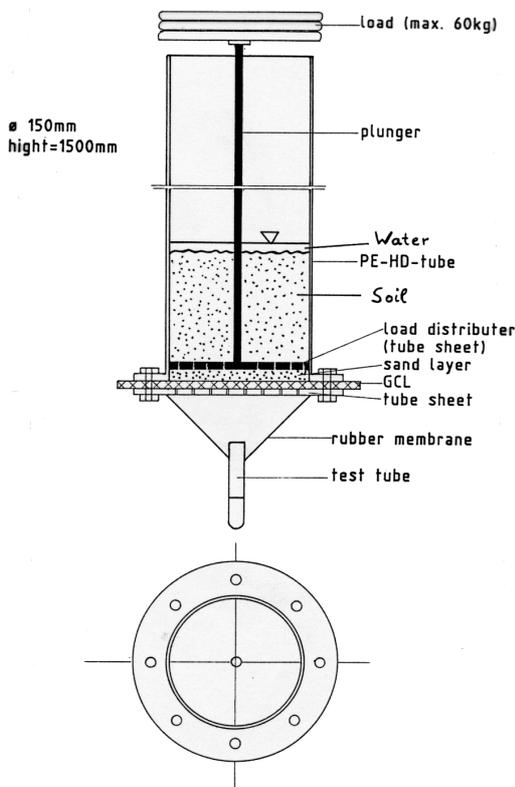


Fig. 7 Simple permeameter cell for permeability test with different loads

It is important that final balanced conditions are achieved within the test period. The determination of reference parameters of the test liquids and the percolate is therefore required. The test is carried out until pH-value, conductivity, sodium content and special leachate components in the test liquids and the percolate have approximately the same concentration over a longer period of time. If the permeability does not change or hardly changes at the loads chosen as test conditions, it can be assumed that this will also be the case under installation conditions. This is limited by the fact that in shallow installations (covering < 1 m) desiccation and frost present additional strains for the GCL. If the behaviour towards the covering soil is to be tested, this covering soil can be filled into the test cell which is then filled up with, e. g., rainwater. It has to be observed that the load is applied correctly.

5 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 µS/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) Ca²⁺ (SCHEFFER & SCHACHTSCHABEL 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.
- 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 (Ca²⁺, Mg²⁺), waters containing iron and leachates with high electrolytic concentrations. For conductivities > 1000 µS/cm mainly the cations Ca²⁺, Mg²⁺, Fe²⁺ 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 K⁺ and NH₄⁺ (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. di-ammonium 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.

5.1 Application guidelines for the use of GCLs with leachates and chemical solutions of higher concentration

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 ± 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 Na^+ montmorillonites which starts directly after completion of the innercrystalline swelling (expansion of the medium interlayer space from ± 2.0 to $\pm 12-15$ nm) is depending on the concentration difference (osmotic pressure) between the highly concentrated inner solution (concentration of 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 Na^+ an evitable, premature ion exchange is already occurring at water adsorption. 1 g bentonite has a CEC of ± 0.7 mval/g. With, e. g., 10 mval/l dissolved bivalent cations approx. 0.02 mval = $\pm 3\%$ 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. 15-30 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 equilibriums between the monovalent Na^+ ions and the bivalent ions in favour of the bivalent ions and the simultaneous predomination 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 $\{i, \text{Psi}\}$ and the diffusion) that the Na^+ -bentonite is converted into a 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 Na^+ bentonites compared to 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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