Multimineral multilayer clay liners for waste deposits
Etanchements argileux multimineral à plusieurs couches pour les décharges

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ABSTRACT: Clays are preferred as sealing materials for waste deposits because of their small permeability and ion sorption capacity. Yet different clays of different mineralogical composition possess different properties in respect to their long-term stability under waste barrier conditions. A sealing system which meets the requirements of low long-term permeability, high ion sorption capacity and long-term chemical stability should therefore not consist of only one kind of clay, but has to combine different minerals with different functions. In general, two different layers are necessary: an „active" layer which has to extract as many pollutants from the leachate as possible, and an „inactive" layer, which provides the long-term stability of the system. Different configurations of the two layers are possible. The active layer can be upgraded by adding substances of high ion sorption capacity.

RÉSUMÉ: Les argiles sont préférées comme matériaux d'étanchements à cause de leurs charactéristiques spécifiques (petite perméabilité, capacité de sorption). Pourtant des argiles différentes de composition minéralogique différente possèdent des propriétés différentes au niveau de la stabilité de longue durée dans des conditions de dépôt de déchets. Un système de l'étanchement qui satisfait à l'exigence de la perméabilité de longue durée, de la grande capacité de sorption et de la stabilité chimique doit être composé d'argiles différentes avec des fonctions différentes. En général, deux couches différentes s'imposent: une couche „active" qui extrait les polluants de l'eau d'infiltration, et une couche „inactive" qui garantit la stabilité de longue durée du système. Des configurations différentes sont possibles pour les deux couches. La couche active peut être améliorée par l'addition de substances de grande capacité de sorption.

1 INTRODUCTION

The deposition of waste requires an effective sealing system of the waste body to prevent the incorporation of contaminants into the groundwater. In general the sealing system has to meet three requirements:

1. A very low long-term permeability to minimize the amount of leachate migrating through the barrier.
2. A high ion sorption capacity to remove contaminants from the leachate.
3. A long-term stability even in respect to geological time periods.

Clay liners are preferred as sealing materials as they possess both small permeability and ion sorption capacity. Conventional barriers consisting of PEHD (Polyethylene High Density) liners with underlying mineral liners have a very small permeability. Yet the long term stability of the PEHD liner is uncertain. If the PEHD liner becomes permeable, the mineral liner is the only barrier left to retain contaminants from the groundwater.

As for the mineral liners, usually clays of the smectite group are used as they possess both high sorption capacities and low permeability. Additionally these clays (also known as montmorillonites or bentonites) are highly swellable due to a double H_20 layer in their interlayer space. High swelling capacity is usually identified with the self-healing ability of the sealing system. Yet smectitic mineral phases are not stable thermodynamically and in case of chemical attack of leachate (Weiss 1988). They show dissolution processes when treated with acids, loss of swelling capacity and plasticity upon absorbing heavy metal ions (Wagner 1988) as well as significant volume changes in contact with organic substances. In practice clay mineral alterations have been observed in smectitic barriers (Echle et al. 1988). Finally, the long-term stability of smectites under waste barrier conditions is not given.

Therefore clay materials such as kaolinitic clays are used increasingly. As clays of the kaolinite group have no swelling capacity due to the lack of exchangeable cations in their interlayer space they are very stable when exposed to chemical attack by the leachate. Kaolinitic clays, however, possess only small ion sorption capacity and extract only a small amount of contaminants from the leachate.

A sealing system which meets all the requirements mentioned above must therefore not consist of only one kind of clay, but has to combine different minerals with different functions.

In general two different layers are necessary: an "active" or „adsorption" layer consisting of highly reactive substances which has to extract as much pollutants as possible from the leachate, and second an "inactive" layer which does not react with leachate components and provides the long-term stability of the sealing system. Two different arrangements of active and inactive layer are possible. The active layer can be orientated towards the waste followed by the inactive layer which provides a long-term low permeability. Yet it is also possible to place the inactive layer towards the waste. Each of the two possibilities has already been executed.

The sorption layer should consist of minerals such as smectites. Additionally these smectitic clays can be upgraded with reactive mineral phases which form stable compounds with the leachate components (e.g. heavy metals). The inactive layer should consist of kaolinitic clays or clays that have been upgraded with kaolinite.

2 CLAY MINERALS IN MINERAL BARRIER SYSTEMS

Clay minerals like smectites and kaolinites are alumosilicates. Their properties are caused by their mineralogical structure and their small grain size. Generally they are characterized by their large specific surface, their ability to adsorb ions and their low permeability. The principal structural units of clay minerals are two-dimensional arrays of silicon-oxygen tetraedra and two-dimensional arrays of aluminium- or magnesium-oxygen-hydroxyl octaedra. The succession of tetrahedral and octrahedral

Table 1. Material properties of the layer types.

Layer	Dominant mineral type	dominant properties
active	smectite group	highly swellable high sorption capacity low permeability
inactive	kaolinite group	long term stability thermodynamically resistant

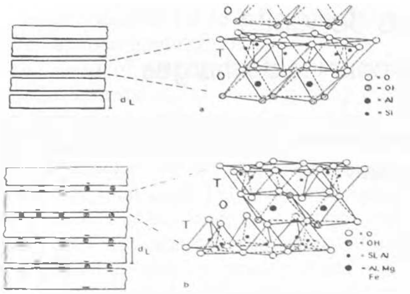

Figure 1: Three-dimensional description of the sheet structure of 1:1 clay minerals (a) and of 2:1 clay minerals (b); T = tetrahedric sheet, O = octahedric sheet, d_L = basal spacing. From: Jasmund & Lagaly (1993)

sheets determines the kind of clay minerals. 1:1 layer minerals are formed by a regular succession of tetrahedral (T) and octahedral (O) sheets (TOTOTO.....), while 2:1 layer minerals are characterized by silicate sheets of the form TOT TOT TOT..... (see figure 1)

Prototypes of the 1:1 layer clay minerals are minerals of the kaolinite group and of the 2 : 1 layer clay minerals are the minerals of the smectite (montmorillonite) and illite groups. Besides these groups there are also mixed-layer minerals of more complicated structure which are characterized by a more or less random succession of the tetrahedral and octahedral structural units.

3 TRANSPORT AND RETARDATION PROCESSES IN CLAY BARRIERS

In general the contaminant transport through clay barriers is controlled by three parameters: convection, diffusion and sorption.

Convection is characterized by hydraulic conductivity k and hydraulic gradient i. For small values of i the convective part of contaminant transport is near the diffusive transport (Gray & Weber 1984).

Diffusive transport is based upon a concentration gradient. The diffusion coefficient depends on the medium properties (charge capacity, cation exchange capacity) and the properties of the diffusing particles (ion radius, valence, solution pH) (Czurda 1994).

Adsorption takes place at the negatively charged silicate surfaces of the clay minerals, the negatively charges interlayer surfaces and the positively charged edges.

Sorption depends of the amount of the available surface and of the form of the diffusive double layer which forms at the negatively charged clay surface to compensate charge. As the surface of the clays of the smectite group is very high (400 - 800 m²/g), their sorption capacity in respect to polar contaminants (e.g. heavy metals) is also very high. Yet they are not able to retent organic contaminants. The surface charge can be affected by the chemical reactions of the leachate components (Bradl 1995).

4 ADMIXTURES FOR THE CLAY BARRIER

To increase the sorption capacity of the active layer the clay material can be upgraded with different substances which are described in the following.

4.1 Organophilic Bentonites

Organophilic bentonites are bentonites where the inorganic interlayer cations have been substituted by organic cations like DMDO (dimethyl-dioctadecyl-ammonium) or OBDM (octadecyl-benzyl-dimethyl-ammonium). The distance between the layers increases by this substitution and the surfaces properties of the clay minerals change. The originally hydrophilic surface becomes hydrophobic and is able to adsorb organic contaminants. The mechanism is described by Schall & Simmler-Hübenthal (1994).

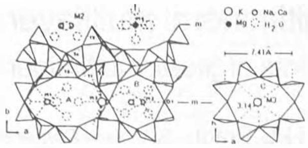

Figure 2: Molecular structure of a zeolithe (Klinoptiolithe) after Czurda (1994)

4.2 Zeolithes

Zeolithes are alumosilicates of the general formula $M_{2/z} \cdot Al_2O_3 \cdot x\ SiO_2 \cdot y\ H_2O$, where M is a metal ion of valence z. The mineralogical structure is shown in figure 2.

The characteristic molecular feature of a zeolithe is a three-dimensional channel system. The sieving effect is caused by the different pore size.

4.3 Activated Carbon

Activated carbon consists of carbon structures of very small graphite crystalls and amorphous carbon with porous structure. Activated carbon has a very large specific surface (500 - 1500 m²/g) and is therefore able to adsorb especially organic contaminants very effectively.

4.4 Inorganic Oxides

Oxides and hydroxides of Aluminium, iron and manganese are also able to adsorb contaminants, especially heavy metals. E.g. goethite (α-FeOOH) and hematite (α-Fe_2O_3) form very small crystalls (10-100 nm) and have a very large specific surface of 300 - 500 m²/g. As oxides and hydroxides possess variable surface charges only, they contribute to the cation exchange by proton dissociation of M-OH and M-OH_2 groups

5 EXPERIENCES WITH MULTIMINERAL MULTI-LAYER CLAY LINERS

As already mentioned above, two different philosophies can be developed in respect to the concept of the multimineral barrier. Kohler (1990) recommends to place the upper, kaolinitic layer above the lower bentonitic layer to protect the more sensitive bentonite by the chemically stable kaolinite.
In contrary, Wagner (1991) and Czurda(1994) propose a double mineral sealing, where the upper layer absorbs contaminants from the waste body and the lower liner provides the long-term stability of the system. The upper „active" layer is upgraded by organophilic bentonites or other substances with increased sorption capacity.

Each of the two sealing systems has already been executed. The industrial waste dump Flotzgrün has been equipped with a multimineral sealing below the CONTREP-system (Koch 1995). Four layers with 0,25 m thickness respectively have been executed, whereby the upper two layers consist of kaolinitic clay and the lower two layers consist of smectitic clay.

The sealing system of the waste deposit Erbenschwang, Bavaria, has been designed according to theoretical contaminant transport calculations. As reference substances chloride and heavy metals have been taken into consideration. The sealing system consists of 0,5 bentonite dry mixture, 0,5 m kaolinitic clay where the pore volume has been sealed by hydrosilicate and 0,15 m protective layer of kaolinitic gravel sand (Langhagen 1995). In 1991 about 2,5 m sealing of the waste deposit Wipperoda, Thuringia have been executed as multimineral sealing (Koch 1993). In contrary to the two examples mentioned above the adsorption layer of 0,5 m bentonitic clay is orientated towards the waste body.

The execution of those sealings is usually accomplished by the use of mixed-in-plant procedures in a mobile or semi-mobile mixing plant. The clay material is upgraded with the additives,

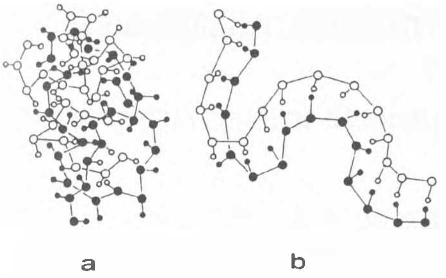

Figure 3: Two models for the structure of symplexes: 3a: Scrambled egg structure according to Michaels (1965); 3b. Ladder model according to Philipp et al. (1982)]

homogenized and then used. The requirements in respect to thickness, compaction and water content can be met easily with this procedure.

6 EXECUTION AND QUALITY ASSURANCE

At the planning state design parameters have to be developed. Planning standards have to be defined and checked during execution under working conditions.

Besides traditional soil mechanical testing methods there are only few methods for testing the physicochemical behavior of clays. A new method which has been introduced into geotechnical work by Kliesch (1989) is suggested here: the socalled PET (Polyelectrolyte Titration). The interaction between clay minerals and fluid phase can be determined by this method. The principle of PET is explained shortly in 6.1.

6.1 Polyelectrolyte Titration (PET)

PET is a testing method to quantify the reaction of a clayey suspension with a defined amount of known polyelectrolytes. Polyelectrolytes are macromolecules with dissociative groups like e.g. -COOH and $-SO_3H$ (anionic) or $-NH_2$, $-N(R_3)^+ X^-$ (cationic) (Krause et al. 1984). The polyelectrolytes which can be used are the cationic polydimethyldiallylammoniumchloride (CATFLOC) or the anionic potassiumpolyvinylphosphate (KPVS).

The principle of polyelectrolyte titration is based upon the reaction of a large number of ionic polymers of opposite charge (polycations resp. polyanions) while forming complexes (socalled symplexes), which have a molar ratio of almost unity. Figures 3a and 3b show two possible models for the structure of such symplexes.

The quasi stoechiometric reaction of numerous solved ionic polymers allows the titration of the turning point. The colloidal particles in the suspension are partly adsorbed at the piston and cylinder wall of the socalled streaming current detector (SCD) (figure 4). A laminar current is induced by the piston movement which causes a shearing force of the diffuse double layer of the clay minerals. The shearing of the diffuse double layers induces an electric flux, which can be probed by the electrodes, rectified and read at an microamperemeter. The kind of surface charge is shown by the lightning of a red or green light. The amperage is a characteristic measure for the charge density. By adding the respective polyelectrolyte (anionic or cationic) the induced current is compensated. The amount of polyelectrolyte consumed is the measured parameter for the charge density of the clay suspension. If the specific surface of the clay is known, the active net charge of the clay can be calculated (Bradl 1995). PET is very sensitive towards changes of the input data by producing quick and reliable results. Moreover, handling is easy and can be executed without problems on site.

6.2 Application

First of all PET can be used for defining design parameters according to the selection of clay materials, contaminants and admixtures. With the help of thermodynamical calculations (Kliesch 1990, 1994) and traditional soil mechanical testing methods planning standards can be developed in order to set up the quality assurance plan. Under mixed-in-plant conditions PET can be integrated in the automatically testing procedure during execution under work conditions (quality assurance). If unexpected contaminants become evident PET can be easily used to find out the possible danger of a potential sealing damage.

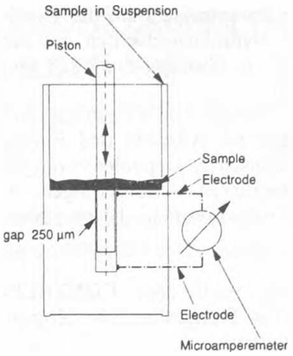

Figure 4: Principle of the SCD apparatus

7 CONCLUSIONS

The addition of mineral phases with a large surface and high ion sorption capacity such as smectite minerals can be recommended to increase the sorption capacity of the sorption layer. The thickness of the sorption layer should be designed in such a way that its sorption potential is higher than the elution potential of the waste body. According to German standards (TA Abfall), the thickness of the mineral layer must not remain under 1.5 m. The concept of the multimineral multilayer clay liner allows the reduction of the thickness and therefore of costs without reducing the retention capacity and the impermeability of the system. With the help of PET design parameters, planning standards and the quality assurance during execution of clay liners can be easily accomplished.

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