



## Electrokinetic monitoring of synthetic geoclay liners

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### Abstract

On-going work and preliminary results are presented from impedance spectroscopy investigations of sodium bentonite. The purpose of the work is to find out if alternating electric current measurements might be utilised for monitoring the conditions of synthetic geoclay liners. Theoretical analyses as well as preliminary results indicate that sufficient alteration in the signal might be obtained for variation in moisture content, salt content and location, as desired. The results also indicate that the impedance spectroscopy method is applicable for the understanding of the microstructural aspects of bentonite.

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### 1. Introduction

Synthetic clay membranes are currently used extensively in final covers for deposited waste. The membranes consist of two layers of geotextiles with high-quality bentonite in between. When moistened, the bentonite swells and forms an essentially impermeable gel, which protects the waste against percolating water. Albeit introduced in the form of man-made liners, the active component bentonite is a natural material, which has been stable in the environment for a very long time, frequently tens or hundreds of million years. Thus, there are good reasons to believe that the integrity of synthetic clay liners may be maintained for very long times.

Nonetheless, further assurance of appropriate functioning is desirable (Brundin et al., 2001). The mechanical integrity of a liner might be jeopardized if differential settlement takes place in the underlying waste. The chemical integrity might be affected by inappropriate chemical conditions (e.g., high pH in ashes or due to ammonia formation) and the physical form of the microstructure (and imperviousness) might be altered if the electrolyte content of the pore water is altered (e.g., through capillary suction).

Thus, it is desirable that the appropriate functioning is assured by monitoring. For synthetic geoliner consisting of sheets of polymer material, this can be achieved by applying arrays of electrical conductors above and below the liner with the respective directions perpendicular to each other. Reduction of resistance between any two liners indicates that there is a leak and that this leak exists in the vicinity of the

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crossing between the two conductors. This technique has not been applied to clay liners since they conduct electricity also when there is no leak. Thus, in the latter case, leaks will typically have to be detected through follow up on the drains. This method is very unspecific with regard to location, however. The need for a suitable monitoring system for clay liners has been recognised in the international literature (Koerner, 1996).

In order for a monitoring method to be feasible, it is necessary that measurements can be made at a large number of positions over a disposal site. One of the very few potential methods that would meet this requirement is impedance spectroscopy. Although the instrumentation is intermediate in degree of complexity, the sensors can probably be made in a very simple manner since they only consist of electrodes.

## 2. Purpose and scope

The purpose of the present work is to test the feasibility of impedance spectroscopy to monitoring of the condition of a synthetic clay membrane.

The scope of the work thus includes the testing of the sensitivity and selectivity of the signal detected to relevant parameters such as density, water content, salinity of the pore water, open gas-filled porosity, time and temperature. The scope also includes analysis of suitable electrode arrangements and selectivity with regard to different positions in a waste site cover.

This paper presents work in progress (Arevius, 2001). It is hoped by the present authors that this will promote discussion of impedance spectroscopy and montmorillonite microstructure issues at the workshop *Clay microstructure and its importance to soil behaviour* in October 2002 and also provide input for the continued work.

## 3. Impedance spectroscopy

In the presence of ideal resistors, capacitors and inductances, Ohm's formula can be generalised to:

$$I(\omega) = U(\omega)/Z(\omega) = U(\omega)/[Z'(\omega) + Z''(\omega)i] \quad (1)$$

Where  $U(\omega)$  = the voltage applied,  $Z(\omega)$  = the impedance,  $\omega$  = the angular frequency of the current (or voltage) and  $I(\omega)$  = the resulting current. Furthermore,  $i = (-1)^{1/2}$ ,  $Z'(\omega)$  is the real (resistive) part of the impedance and  $Z''(\omega)$  is the imaginary (usually capacitive) part of the impedance.

Useful quantities include:

$$\begin{aligned} |Z(\omega)| &= (Z'(\omega)^2 + Z''(\omega)^2)^{1/2} \text{ and } \tan \theta(\omega) \\ &= Z''(\omega)/Z'(\omega) \end{aligned} \quad (2)$$

where  $|Z(\omega)|$  = the magnitude of the impedance vector and  $\theta(\omega)$  = the phase angle.

It is also useful to relate data recorded to resistors and capacitors. The impedance of an ideal resistor is simply the resistance (usually denoted  $R$ ). The impedance of a capacitor is given by:

$$Z(\omega) = -i/\omega C \quad (3)$$

where  $C$  = the (equivalent) capacitance.

It is frequently attempted to interpret experimental data in terms of resistors and capacitors. Thus, a resistor in series with a capacitor in parallel with another resistor, see Fig. 1a, gives rise to a  $-Z''$  vs.  $Z'$  relation illustrated in Fig. 1b. The frequency increases with decreasing resistance  $Z'$ . Plots of experimental data in accordance with Fig. 1b are called *Nyquist plots*.

In macroscopic electrolytes, polarisation is usually incomplete due to the relative slowness of diffusion processes. The polarisation increases with decreasing

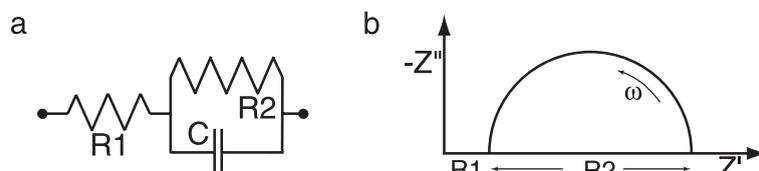


Fig. 1. The equivalent circuit in (a) gives rise to the  $Z''$  vs.  $Z'$  relation illustrated in (b).

frequency and often there is a linear relation between  $Z'$  and  $Z''$ . Such impedances are called *Warburg impedances*.

#### 4. Clay microstructure

The active mineral in bentonite is montmorillonite which is a smectite type of clay mineral. The silicate layer in montmorillonite comprises three sublayers of silicate–aluminate and has a high negative charge. This charge is balanced by counterions of primarily sodium and calcium which reside at or near the surface of the layer. Sodium is the dominating counterion in the qualities used for bentonite liners.

The individual layers stack on top of each other to form primary particles. The ratio between the largest and smallest dimension of such a particle is typically 100:1. When primary particles are dispersed in water, the counterions dissociate and form a diffuse charged layer in the water near the particle. This water is stagnant and does not move relative to the particle even if the dispersion is stirred. The mobility of the counterions (by diffusion) may well be similar to that in solution, or even higher because of the generally more extensive hydration of the ions in bulk solution.

In the case of sodium montmorillonite and fresh water, a similar dissociation takes place also between the individual silicate layers. By this process, the distance between individual layers can amount to the equivalence of many sheets of water molecules with maintained long-range order.<sup>1</sup>

Under constrained conditions, this tendency to accumulate water between the layers gives rise to a swelling referred to as *osmotic swelling*. In cases where the distance between the layers corresponds to only a couple of layers of water molecules, another mechanism of swelling takes place, which is called *crystalline swelling*. The latter takes place in fresh as well as saline water.

The association pattern in a bentonite slurry is complex, involving flocculation (cardhouse pattern)–deflocculation as well as dispersion–aggregation

(stacked pattern), depending on type of counterion and salinity. It is important to consider that one pattern, once developed, might not necessarily change swiftly to another. This applies also to the porosity situation.

It can be expected that oxonium and hydroxide ions in the water will distribute in accordance with the principle of anion exclusion together with the law of mass action. As a result, the water in the diffusive layer will be more acidic and the pore water more alkaline than the average of all water. Also, there will be higher average concentrations of oxonium and hydroxide ions as a result of these effects. It should be noted that the mobility of oxonium and hydroxide ions may be an order of magnitude higher than that of other ions. This high mobility in combination with the just mentioned “enhanced” dissociation may imply that conduction’s through motion of protons could—in some cases—be more efficient than conduction through motion of heavier cations.

It should be recognised that that which in ordinary chemical language is referred to as diffusion or motion of oxonium and hydroxide ions actually involves only motion of protons along hydrogen bonds in combination with 180° reorientation of water around its two-fold symmetry axis. Thus, physical transfer of protons take place at a high rate but that of oxygen at a much slower rate involving the diffusion of entire water molecules.

The effects discussed above are in agreement with experimental results and analyses made by Slade et al. (1987).

#### 5. Potential dielectric properties

Pore water existing between primary particles may contain ions which conduct electric current. From such portions, a Warburg behaviour might be expected at low frequencies.

The expected electric behaviour near and between the silicate sheets is illustrated in Fig. 2 and is also explained in the text below.

Water between silicate layers as well as water near the surfaces of the primary particles contain positive counterions. In the case of fresh pore water, these are the only ionic conductors available. In the case of saline water, the water near the surfaces is deficient

<sup>1</sup> As evidenced by X-ray crystallography and reflexions from planes defined by the *c*-direction (normal to the silicate layers).

## POLARISATION IN BENTONITE - "ARTIST'S IMPRESSION"

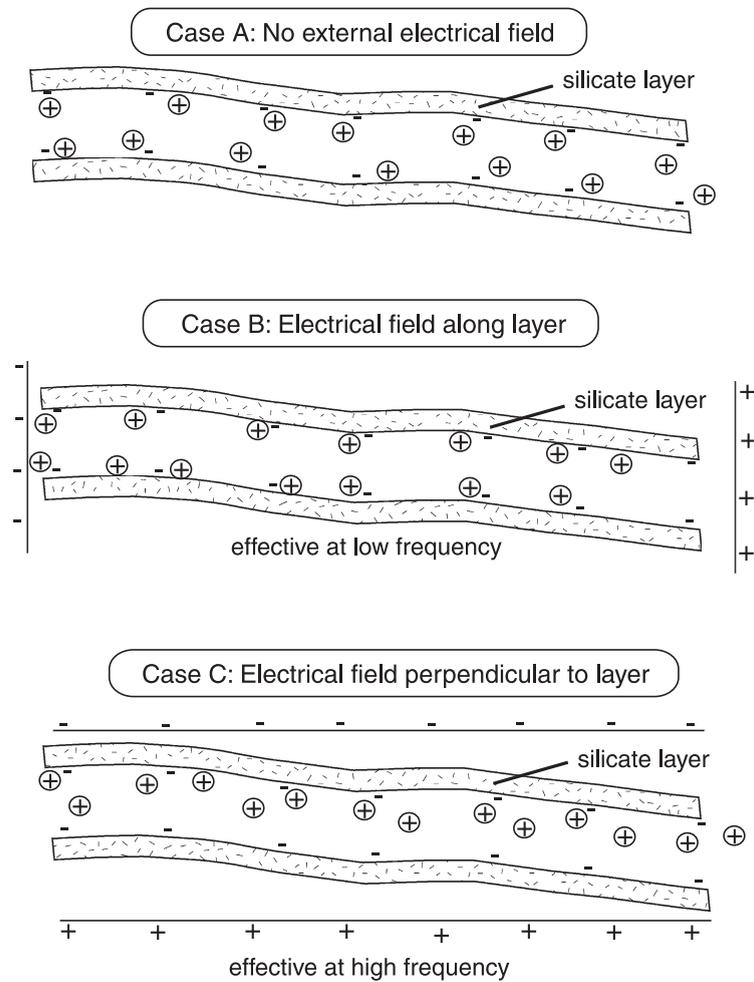


Fig. 2. The expected electric behaviour between the silicate sheets.

with regard to negative ions (ionic exclusion). Electric field gradients acting along the silicate sheets cause motion of these ions together with associated polarisation. Also in this case is a Warburg behaviour expected. It should be noticed, however, that the associated distances—the diameters of the primary grains—may well be smaller than that in an electrolyte.<sup>2</sup> Therefore, the Warburg behaviour may actually

<sup>2</sup> I.e., an electrolyte in a typical electrochemical experiment with a distance between the electrodes which by far exceeds the dimensions in the plane of a clay particle.

show similarity to the Nyquist plot situation, especially if recordings are made at very low frequencies.

The interactions mentioned so far involve diffusion over comparatively large distances and are therefore expected to be observable at lower frequencies.

At high frequencies, polarisation in a direction perpendicular to the silicate layers may dominate the interaction. In this way, much of the conduction along the previously mentioned paths might be short-circuited. The frequency behaviour can be expected to depend on the distance between the layers and the extent of the diffuse layers. Again, it is the diffusion

(now in a direction perpendicular to the flat clay particle) that can be expected to be limiting in time.

It is conceivable that open and gas-filled porosity might have a considerable influence on the interactions. Since the primary particles are very flat, shrink-

age of them might give rise to pore patterns that resemble open fractures. These will be good insulators and also not very good capacitors, and consequently, it might be expected that the current prefers to go elsewhere.

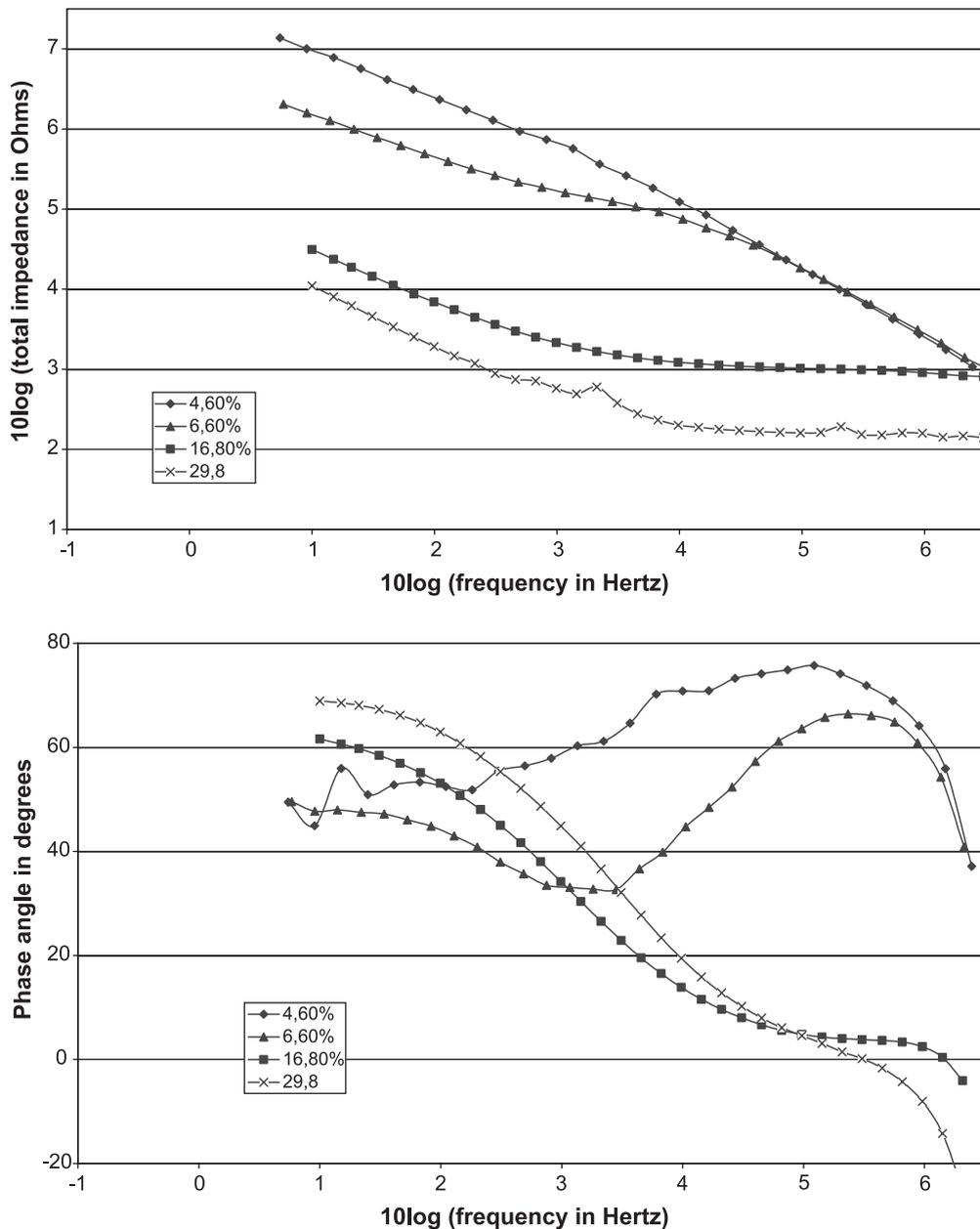


Fig. 3. Impedance spectra for different moisture content (water ratio) in highly compacted sodium bentonite (Volclay MX-80). No salt added.

## 6. Experimental results

The purpose of the experiments carried out so far has been to find out if variations in the signal can

be identified for changes in water content and salinity, and work is presently underway to determine the quantitative relations. Also, impedance measurements have been carried out in which a

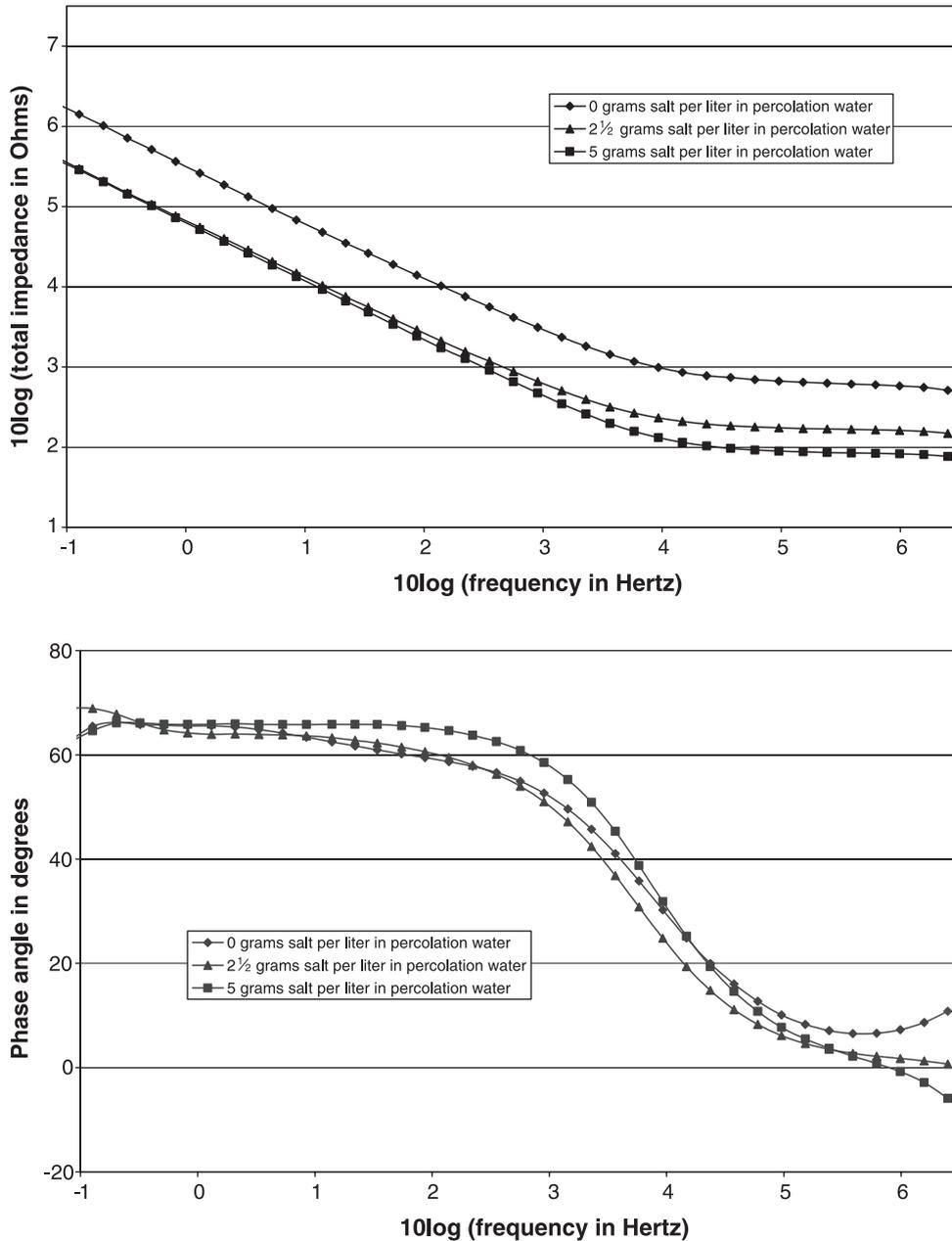


Fig. 4. Impedance spectra for a moisture content (water ratio) around 30% in dried sodium bentonite (Volclay MX-80) filter residue obtained after percolation with water having different contents of dissolved sodium chloride.

clay liner is placed between crossed arrays of electrodes.

In the first series of experiments mentioned above, pieces of highly compacted bentonite were kept in desiccators, whose atmospheres were kept at constant relative humidity by using saturated salt solutions. The results are shown in Fig. 3.

In another experiment, bentonite was contacted with water solutions of different salinity whereafter the dispersion was filtered using vacuum. Variations were obtained with salinity content and with time.

The material obtained in this experiment was partially dried. Spectra for these materials are shown in Fig. 4. As expected, the impedance is considerably higher for this more porous material as compared to the compacted material in Fig. 3.

It is interesting to note that the salinity effect is limited. Partially, this is due to the fact that salts are precipitated. Furthermore, the pore water might not contribute very much to the spectra if it occurs in the form of occlusions. Also, a high salinity gives rise to stacked patterns with small distances between the silicate sheets as well as the primary particles. It is

conceivable that ions are less mobile in this situation. It is also possible that protons contribute to the conduction in the low salinity cases, cf. the discussion above.

Some of the spectra show positive values of  $Z''$  (which means that the reactance is inductive rather than capacitive). Based on some analysis of this in the literature (Rubinstein and Zaltzman, 1999), the present authors are inclined to relate this to the anion exclusion effect. Since the species present in liquid are mainly positive ions, electric–mechanical couplings may take place resulting in an effect, which is similar to that of a coil.

Impedance measurements on a bentonite mat have been carried out using crossed electrodes and the result is shown in Fig. 5. Analysis of spectra for pairs of electrodes above and below the clay liner have indicated that differences in moisture content at different intersections can readily be identified. It thus seems possible to localise variations in the spectra to specific parts of the liner and thus in a practical case to identify where for example leaks in a liner may occur.

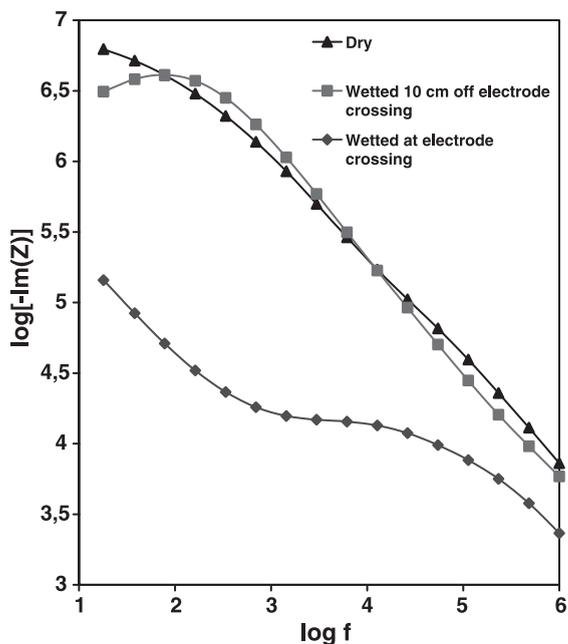


Fig. 5. Impedance measurements on a bentonite mat using crossed electrodes, cf. text.

## 7. Conclusions

The conclusions so far are as follows:

- The total impedance depends on moisture content as well as on salinity of the pore water
- The impedance generally decreases with increasing moisture content, especially at low frequencies
- The ratio between the impedance at low and at high frequency might be utilised in order to obtain a qualitative measure of the moisture content
- Alterations in a clay liner might be localised using crossed electrodes
- The impedance spectroscopy method is applicable for the understanding of the microstructural aspects of bentonite

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