Evolution of AC conductivity of wet illitic clay during drying

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Abstract. The evolution of the AC electrical conductivity during drying as well as the relationship between sample volume and moisture of green illite samples were investigated. The samples were prepared from illitic clay (80 mass % illite, 4 mass % montmorillonite, 12 mass % quartz and 4 mass % of orthoclase) and distilled water with initial moisture content 36 mass % and were freely dried in air. Conductivity was measured by the volt-ampere method with AC power supply of 5 V in the frequency range from 50 Hz to 10 kHz. The AC conductivity steeply increased with increasing moisture, up to 15 mass %. At higher values of the moisture, the AC conductivity was high and almost constant. The volume of samples increased with increasing moisture when the moisture was higher than 8 mass %. Below this value, the dimensions of samples do not significantly change. The dependence of the relative volume change on moisture is presented in a form of the Bigot’s curve.

Keywords: Illite, Electrical AC conductivity, Bigot’s curve, Drying.

1. Introduction
Illitic clay is very often used for manufacturing ceramic products by the “wet technology” in which ceramic body is shaped from a wet plastic mass. Therefore, the wet body consists of a porous solid skeleton and the water in pores and on crystallite surfaces. Water content can reach from 20 to 35 mass %. The illitic clay body expands due to adsorption of water molecules between individual clay crystals when the water content increases. The illite structure is built from an octahedral sheet located between two tetrahedral sheets forming a triple layer (figure 1). Ions K+ are located between these triple layers, and in addition to them, water molecules can be also present here. To remove these water molecules, the sample must be heated up to 300 - 350 °C [1]. The surface of illite is formed from the tetrahedron layer with hexagonal patterns with hollows in their centers (figure 1) in which adsorbed polar water molecules are bound [2]. Large-radius K+ ions are also present on the illite surface [3]. Water in clay body is commonly classified as 1) hygroscopic water, 2) capillary water and 3) free water [4].

The hygroscopic water is created from some layers: the first is extremely well-arranged monomolecular water layer directly and tightly bound to the electrically charged surface defects. The second layer (~1.3 nm in the case of illite [2]) is created from well-arranged water molecules. This layer gradually transforms to loosely bound adsorbed water; the thickness of this water layer is 2 – 6 nm [4]. The hygroscopic water is in equilibrium with the air humidity, i.e. the amount of the
Hygroscopic water in clay body is dependent on air temperature and pressure [4,5]. The hygroscopic water cannot be removed at room temperature [6].

The next progressively thickening water layer, so-called capillary water, covers the hygroscopic water. The capillary water is a part of the wet plastic mass that is prepared from illite powder and water, i.e. this water is introduced into the illite body during the technological process. The capillary water is held by surface forces in small pores, micropores, and capillaries. Molecules of capillary water are free and mobile. Due to this reason, it evaporates easily at room temperature. The capillary water separates the clay crystals, so its removal leads to a contraction of the clay body. Its amount is proportional to the porosity, i.e. the greater surface area the bigger amount of the hygroscopic water.

![Figure 1. Structure of illite according to [7]](image)

Electrical measurements are a useful, non-destructive tool for characterizing porous clays. The electrical conductivity of wet clay has two components - a volume conductivity and surface conductivity [8,9]. The volume conductivity of the wet clay results from conduction through the water occupying the pores. This conductivity is proportional to the amount of the hygroscopic and capillary water. The surface conduction occurs at the water-crystal interface. It represents the conduction in the hygroscopic water layer (which is the nearest to the crystal surface) and a conduction mechanism operating directly on the particle surface, probably associated with proton migration [10]. Mobile monovalent cations can easily move along surfaces of plate-like clay crystals and this movement results in electrical conduction under the applied electrical field [8,11].

The low-frequency AC electrical field may be used to study the conductivity of clays because polarization and relaxation processes typically affect responses at frequencies below 100 kHz [12]. Measurements at 1 kHz are reported in [9].

It should be pointed out that electrical properties of clays are still relatively unknown and published experimental data are limited. The articles published on the AC conductivity mostly investigate the effect of water content on this conductivity. Results for clays from three different sources show that the electrical resistivity of clay is low when the content of the water exceeds 15 – 20 mass %. As the clay becomes dryer, its resistivity increases considerably. Dependencies of the electrical conductivity on the moisture content can be met more often in works devoted to the study of soil [13,14]. In [15], the authors report on the relation between the electrical properties and the microstructure of clays.
The aim of this contribution is an experimental study of the AC electrical conductivity and shrinkage of the illitic clay during its drying. The AC conductivity was measured at different frequencies.

2. Experimental

Samples were made from illitic clay supplied by the mine in Füzéradvány, Hungary. The clay consists of 80 mass % of illite, 4 mass % of montmorillonite, 12 mass % of quartz and 4 mass % of orthoclase. The chemical composition of the clay is in Table 1.

| SiO₂ | Al₂O₃ | Fe₂O₃ | TiO₂ | CaO | MgO | K₂O | Na₂O | L.O.I. |
|------|-------|-------|------|-----|-----|-----|------|-------|
| 58.0 | 24.0  | 0.6   | 0.05 | 0.38| 1.70| 7.85| 0.10 | 7.3   |

Samples of dimensions 50×50×8 mm were made from the plastic mass obtained from 64 mass % of clay powder and 36 mass % of distilled water.

The relative amount of the water \( w \) in the sample was measured using the digital balance Kern EW with a sensitivity of 0.01 g. The relative moisture was calculated as

\[
\frac{w}{d} = \frac{m(w) - m_d}{m_d}, \tag{1}
\]

where \( m(w) \) is the actual sample mass during drying and \( m_d \) is the mass of the dry sample after heating at 120 °C for 2 h.

The sample shrinkage was measured with the linear dial indicator with a resolution of 0.01 mm. The sample and linear indicator were placed on the balance (figure 2). The sample was put on supports to have a free access to the air from all sides of the sample.

The electrical resistance was measured with A-V method. The RC oscillator Hameg 8030-6 with AC voltmeter Hameg 8012 served as the voltage source and multimeter Fluke 289 served as AC ammeter. The AC conductivity was measured at frequencies 50, 200, 500, 1000, 5000 and 10000 Hz. We used two kanthal wires (Φ 0.3 mm) as electrodes. From the measured resistance \( R \), thickness of sample \( b \), radius of electrodes \( r \) and distance between the electrodes \( a \), the clay conductivity can be calculated from the formula [16]

\[
\sigma = \frac{1}{\pi R b} \ln \left( \frac{a}{2r} + \sqrt{\frac{a^2}{4r^2} - 1} \right). \tag{2}
\]

Equation (2) is valid for an infinite plane, but the area of the sample is 50×50 mm. As found in [16], if the side of the sample exceeds 6\( a \), the sample can be considered as infinite. Since \( a = 4 \) mm, this condition is fulfilled.

3. Results and discussion

The relationship between the relative moisture of the investigated clay sample and its contraction during drying, so called Bigot’s curve, is depicted on figure 3. The initial mass fraction of the water in the sample is ~34 mass %. As the sample becomes dryer, its dimensions decrease down to the critical moisture. After reaching the critical moisture, which is ~13 mass %, the sample dimensions stay constant, in spite of the continuing drying. The linear contraction of the sample at the critical moisture is ~13 mass %.
The initial volume of the sample is $2 \times 10^4 \text{ mm}^3$ and its volume at the critical moisture is $1.32 \times 10^4 \text{ mm}^3$, i.e. the relative volume reduction is 34 %.

The results of electrical measurements in which the relationships between the AC conductivity, measured at frequencies 50, 200, 500, 1000, 5000 and 10000 Hz, and the relative moisture calculated from equation (1) are shown in figure 4. As explained above, the water in the investigated sample occurs in two layers. The first layer, hygroscopic adsorption water, is bound to the crystal surface with electrostatic forces. The second layer is the capillary water introduced into the sample during technology.

**Figure 2.** The scheme of the measurement unit. RCO – RC oscillator with V-meter, A-m – ammeter, DI – dial indicator

| Balance |
|---------|
| Sample |
| RCO     |
| A-m     |

**Figure 3.** Relationship between the relative linear contraction and relative moisture

At the moisture $w > 15 \text{ mass } \%$, the capillary water is responsible for a good electrical conductivity. The conductivity very slightly decreases as the sample loses the capillary water from the initial moisture 34 mass % down to its critical value ~15 mass %. This behavior of the conductivity is a consequence of thinning the capillary water layers during drying. The only exception is the frequency 50 Hz at which a very flat maximum at $w \approx 25 \text{ mass } \%$ is observed.

When the moisture content reaches the critical value, the AC conductivity is mainly determined by the capillary water, the content of which relatively rapidly decreases. Since a resistivity of the illite
crystals is high, the current through illite crystals is negligible compared to the current through water layers. Since the thickness of the hygroscopic layer is very low and constant at room temperature, the conductivity of this layer can be considered as constant. As a consequence, the AC conductivity is mainly influenced by a rapid decrease of the capillary water.

Figure 4. Relationships between AC conductivity and moisture measured at different frequencies

The frequency dependence of the AC conductivity for $w = \text{const}$ can be obtained from figure 4. Such example is given for $w = 20$ mass % in figure 5. The relationship can be divided into two parts: 1) where the conductivity increases rapidly with the frequency (from 50 Hz to 1 kHz) and 2) where the conductivity changes slowly (from 1 kHz to 10 kHz). The moisture 20 mass % is relatively high and water layers continuously cover illite crystals; consequently, capillary water is the main environment for the AC current.

Figure 5. Frequency dependence of AC conductivity for $w = 20$ mass %

In water layers, the self-ionization of capillary water $\text{H}_2\text{O} + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^-$ and the reaction $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$ occur. The created $\text{H}^+$ ions are very mobile charge carriers. The $\text{OH}^-$ ions have dipole moments and can contribute not only to the electrical transport but also to the orientation relaxation. $\text{H}^+$ ions can also contribute to the relaxation by a localized hopping. This implies that complex picture
of the ionic conductivity must be expected. A small contribution of K\textsuperscript{+} ions (as they are components of illite) to the AC conductivity is also possible.

During drying, the majority of capillary water disappears from pores and crystal surfaces, the critical moisture is reached. The AC conductivity steeply decreases for \( w < 13 \) mass \% for each frequency used in figure 4. Only hygroscopic water is present. Its molecules are relatively well oriented and the relative permittivity of this layer is about 80 [4].

4. Conclusions

The evolution of the AC conductivity during drying at different frequencies (between 50 Hz and 10 kHz) was monitored. To better understand the drying process, the contraction of the sample was also recorded. It was found, that:

- The contraction exhibits an approximately linear dependence on the moisture reduction until the critical moisture content is reached. Below the critical moisture content (15 mass \%) the sample dimensions remain almost constant.
- The AC conductivity is relatively high above 15 mass \% of the moisture content. Below this value, the conductivity steeply decreases as a result of the removal of the capillary water and decrease in the intercrystalline distances.
- At higher frequencies, the AC conductivity is higher and at the moisture content above 15 mass \% it does not significantly depend on the moisture content.
- AC conductivity is built up of two mechanisms (according to frequency dependences) – bound water rotation combined with protonic jumps and grain conduction.
- The first mechanism predominates in the whole studied frequency range, at room temperature.

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