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INVESTIGATION OF CHANGING DIELECTRIC PROPERTIES DURING DEHYDRATION OF SAWDUST MODIFIED CLAY COMPOSITIONS

[1] Viktor BÁNHIDI, [2] Balázs FÉNYI, [1] Gábor CSATÓ, [3] Norbert HEGMAN

[1] DEPARTMENT OF CERAMICS AND SILICATE ENGINEERING, UNIVERSITY OF MISKOLC
[2] RESEARCH INSTITUTE FOR TECHNICAL PHYSICS AND MATERIALS SCIENCE, HUNGARIAN ACADEMY OF SCIENCES
[3] INSTITUTE OF MATERIALS SCIENCE, UNIVERSITY OF MISKOLC, HUNGARY

ABSTRACT:
The dielectric properties of modified clays from the central northern region of Hungary have been investigated. A series of samples with varying sawdust / clay ratios were prepared and saturated with water. During the drying process (at room temperature) the loss of mass and the changes in the dielectric properties were measured periodically. The dielectric data was evaluated from the point of view of water content, sawdust content and relative weight loss. We have found that the dielectric values have logarithmic dependence on the mass loss values. Thus, it gives more sensitive indication of dehydration with higher accuracy than the usual measurement of weight loss.

KEYWORDS:
dehydration, dielectric properties, clay compositions, capacitive Schering bridge

1 INTRODUCTION

The water content of clay minerals and industrial raw materials is a very important technological parameter, it determines the technological time and energy need of comminution or milling, shape forming with extrusion, drying and firing [1]. The amount of adsorbed water and the swelling during water uptake is determined by the charge of clay layers and the ions on the free surface. The adsorption of water and other adsorbate materials is usually a stepwise process, and a hysteresis is observed during an adsorption-desorption cycle [2]. The dielectric properties of water depends on its ion content, viscosity and other electrochemical interactions, this leads to differences between the water within the clay and the water extracted from the clay during the technological processes. Clays and other aggregates contain water in different forms: water of crystallization, intercalated, adsorbed, capillary and free water [3,4]. The water of crystallization is a building part of the structure. It is difficult to remove without damaging the crystal structure. The intercalated water causes the clay to swell as it can be found between the silicate layers. The adsorbed water is fount on the surfaces of clay particles and it has a layered structure with a tightly and loosely bounded layer. Capillary water is found between the grains outside of the loosely bound adsorbed water layer. The water which can move relatively easily in a clay structure even if only driven by gravitation is the free water. In figure 1 we show the layered structure of waters around clay particles [3].

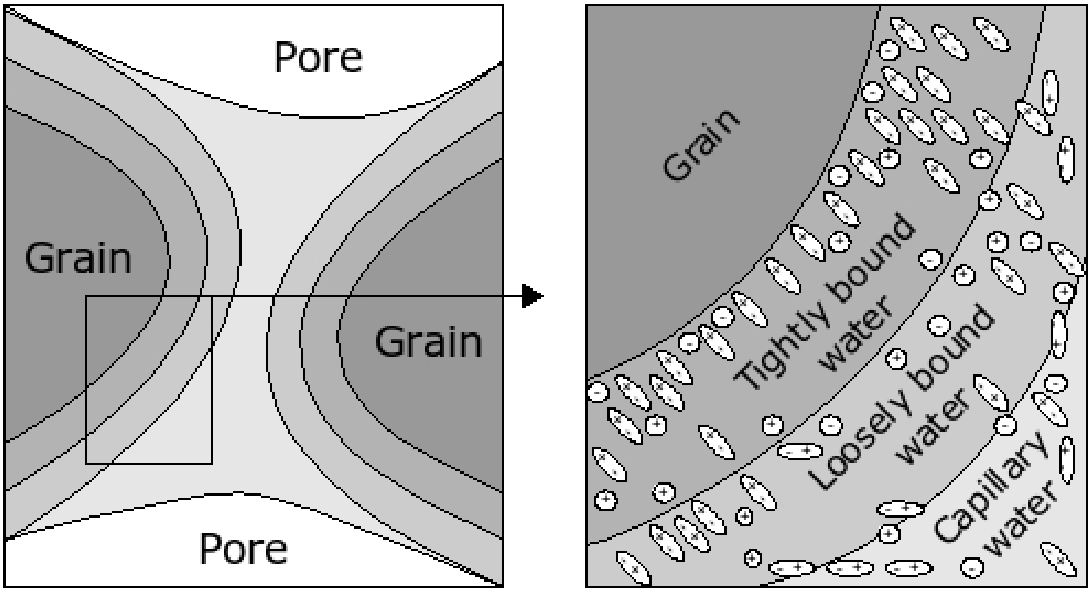

FIGURE 1. Structure of water found in clays [3]

The distribution of adsorbed water in the different water types as a function of the water content is very specific for different clay minerals. We used sawdust as modification material in one specific type of clay to produce samples for the determination of the effect in dielectric properties caused by the changing water conditions and the modified structure.

2 EXPERIMENTAL DETAILS

2.1 Material Preparation

The sample preparation was carried out in the laboratory of the Department of Ceramics and Silicate Engineering, University of Miskolc. The raw material was general purpose clay prepared for the brick industry from the mines of Solymár. The additive sawdust was dried and sifted to provide continuous quality to ensure the comparability of the clay compositions. Additive was mixed in to the dried clay powder in 0 (blank), 1, 3, 5 w%. Following the industrial processes, the powders were first mixed and homogenized in a lab size edge runner mill (pan mill). After the initial homogenization water was added to ensure the required plasticity of the material [5]. As shape forming uni-axial pneumatic wet pressing device was used with elastic polypropylene tool. The initial pressure was 1.5 bar to ensure the homogenous arrangement of the viscous material in the form, which was raised up to 3 bar at the end of the shaping cycle to produce compact samples for the measurements. To reduce the rate of dehydration of the prepared samples a climate controlled box was used.

2.2 Measurement Technique

A capacitive Schering bridge (shown in figure 2) was used to measure the dielectric properties of our clay compositions [6]. AC voltage bias was applied to the input of the bridge by a function generator.

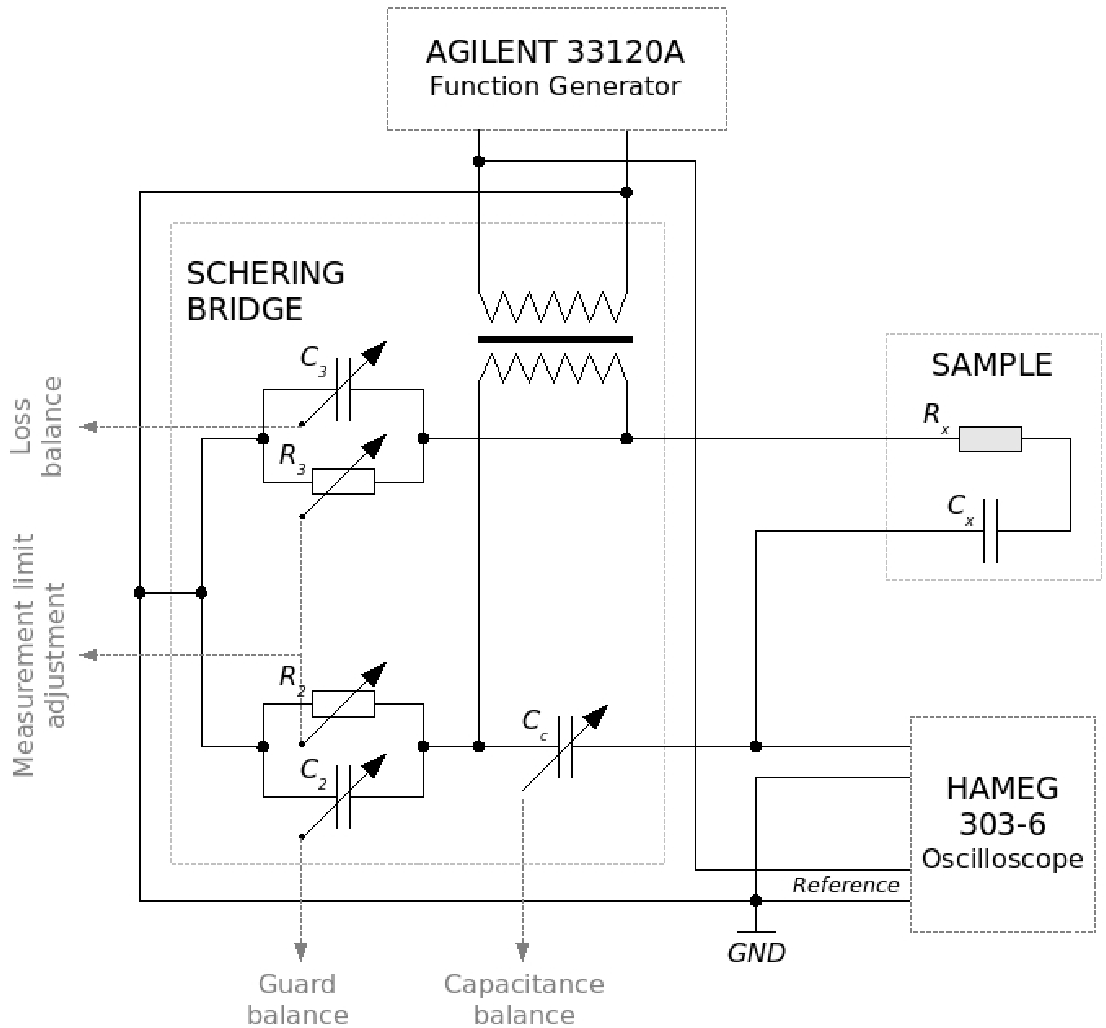

FIGURE 2. Schering bridge: Set up for dielectric measurements

The excitation signal from the generator trigger output was connected to an oscilloscope as a reference, which displayed the bridge signal as null detector. The sample a serially connected capacitive (C_x) and resistive (R_x) element was put in between the plates of the measuring capacitor, which's stray capacity could be eliminated by the proper and careful tuning capacitor (C_3) of the bridge while the measuring capacitor was empty. The suitable adjustment of capacitors (C_c and C_2) and resistors (R_2/R_3 ratio) gave the zero signal output of the bridge in amplitude and phase respectively, measured by the oscilloscope. If the bridge is balanced equation 1 is satisfied.

$$\left(\frac{1}{j\omega C_x}+R_x\right)\cdot\left(\frac{R_2}{1+j\omega C_2 R_2}\right)=\frac{1}{j\omega C_c}\cdot\frac{R_3}{1+j\omega C_3 R_3} \quad (1)$$

Evaluating equation 1 for both real and imaginary parts, one can obtain the unknown capacity and its loss tangent (tg δ= $\omega C_x R_x$ in serial set up).

$$C_x=\frac{R_2}{R_3}C_c \text{ and } tg\delta=\omega R_2 C_2 \quad (2)$$

The measured ratio of the test capacity C_x with and without materials between the test plates gives the relative dielectric permittivity of the material compositions our work was focused on.

3 RESULTS

During the drying process we have periodically executed weight and dielectric permittivity measurements on each prepared compositions to follow the dehydration. The results are represented in figure 3. measured at a fixed frequency of 9 kHz. The data points gathered from different sawdust contents and dehydration level can be easily fitted by a logarithmic function relative to the mass or weight loss. In our measurement we did not see a significant effect of the sawdust content on the common characteristics of the graph but a change in the steepness of the lines could be determined with decreasing amounts of sawdust.

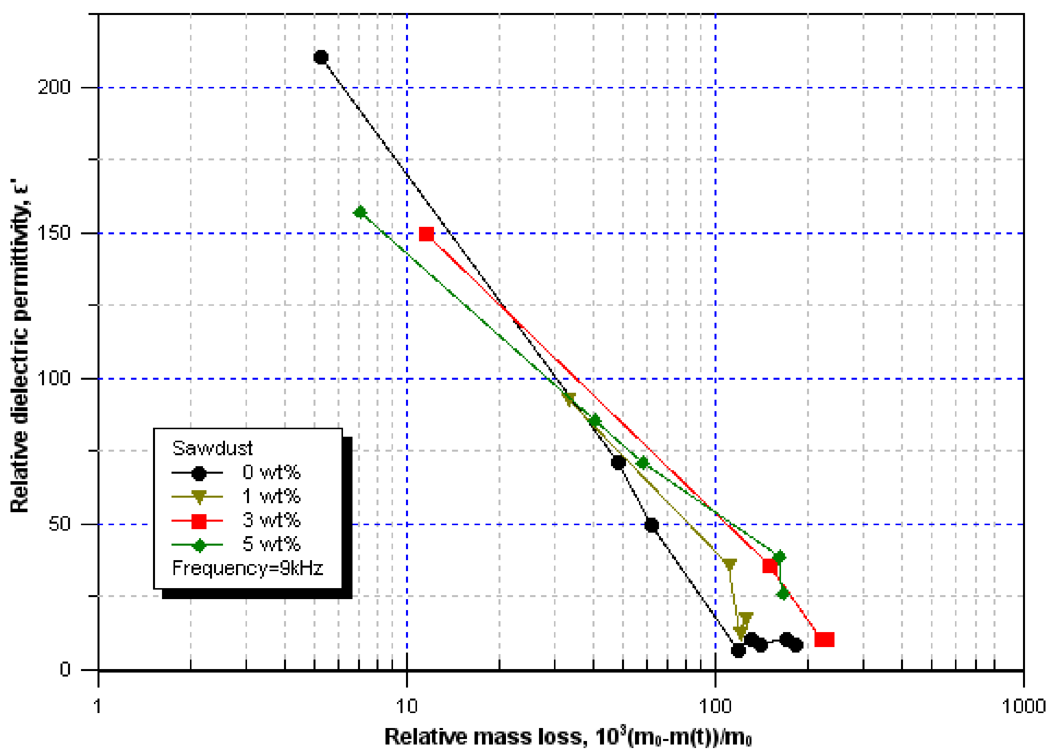

FIGURE 3. Changing the dielectric properties of different sawdust added samples during dehydration, measured at 9 kHz

The following figure (figure 4), shows the same logarithmic dependences but these are displayed for the different measuring frequencies. We have found that the slope of the curves are fairly constant, there is only a slight shift as the permittivity decreases with increasing the measuring frequency. The logarithmic dependence found in figure 3 and 4 with the right calibration for the examined material could be used as a quick and accurate, non-destructive method to determine the humidity in the product. A similar application is described by Bogena and co workers in their recent publication in the Journal of Hydrology [7].

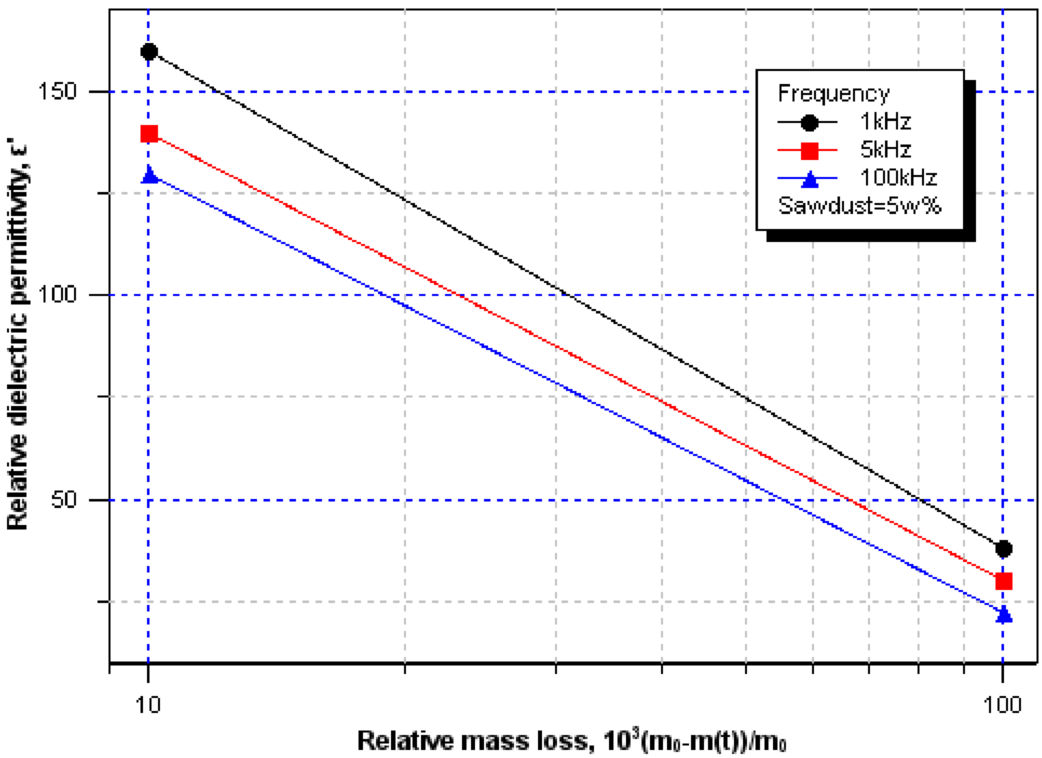

FIGURE 4. Changing the dielectric properties measured at different excitation frequencies during dehydration, sawdust content 5w%

The gathered results can also be evaluated as a function of the adsorbed amount of water. This is shown in figure 5. We can see a sharp rise at around 25% of adsorbed water which is a good agreement with results found in the scientific literature [2,3,8-10]. This behavior is attributed to the appearance of free water in the capillary channels after the interlayer spaces are saturated. More detailed and sensitive measurements show [3] that fine steps also can appear at low water content which is caused by the water penetration into the different adsorbed layers with different interaction strengths.

The sawdust in our compositions acts as an inner water reservoir governing the water balance within the mineral material. Higher concentration of sawdust (3, 5%) causes smaller step to appear in the dielectric permittivity at around 13% of adsorbed water, and shifts the great rise to higher water contents. This is caused by the more hygroscopic nature of the sawdust compared to the clay, thus, it will pick up water more quickly that the clay itself and the hydration of the laminar structure will only occur after the saturation of the sawdust is almost completed. This is why we only see the saturation of the lamellar layers at a higher total water content level. Investigations at other measuring frequencies show the same effect related to the sawdust concentration, so there is no limitation in the applicable frequency range from the side of the measurement; the limiting factor might more likely be the capability of the used device.

After the drying process the samples were fired as required by the technology. We repeated the examinations of dielectric permittivity on the finished products, the comparative results (as function of sawdust content) are shown in figure 5. It is expected that during the high temperature treatment the original sawdust content was converted into porosity and residual matter.

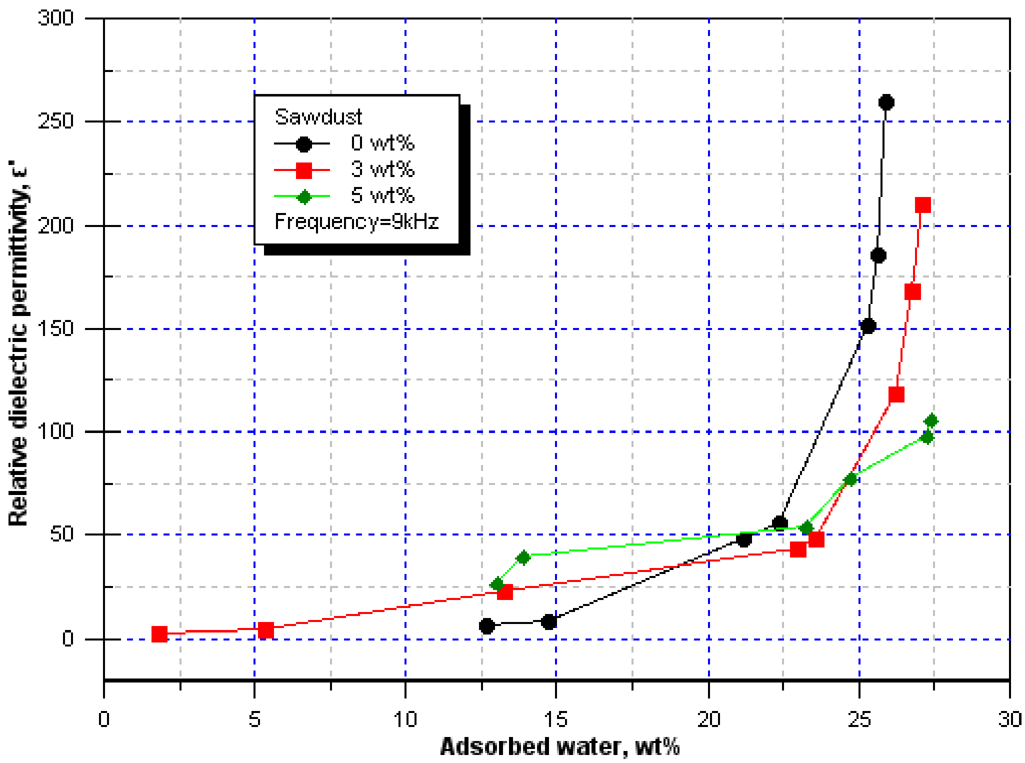

FIGURE 5. Relative dielectric permittivity as function of adsorbed water content measured at 9 kHz

With the increase of the porosity the dielectric permittivity is expected to decrease as less and less material is measured. This is shown in figure 6 at the highest measuring frequency (100 kHz). An interesting anomaly found at the lower frequencies as a local maximum appears between 1 and 2%. The frequency dependence of the relative dielectric permittivity is quite pronounced in case of the fired product. To find the answers for these anomalous behavior further studies on simplified materials is proposed.

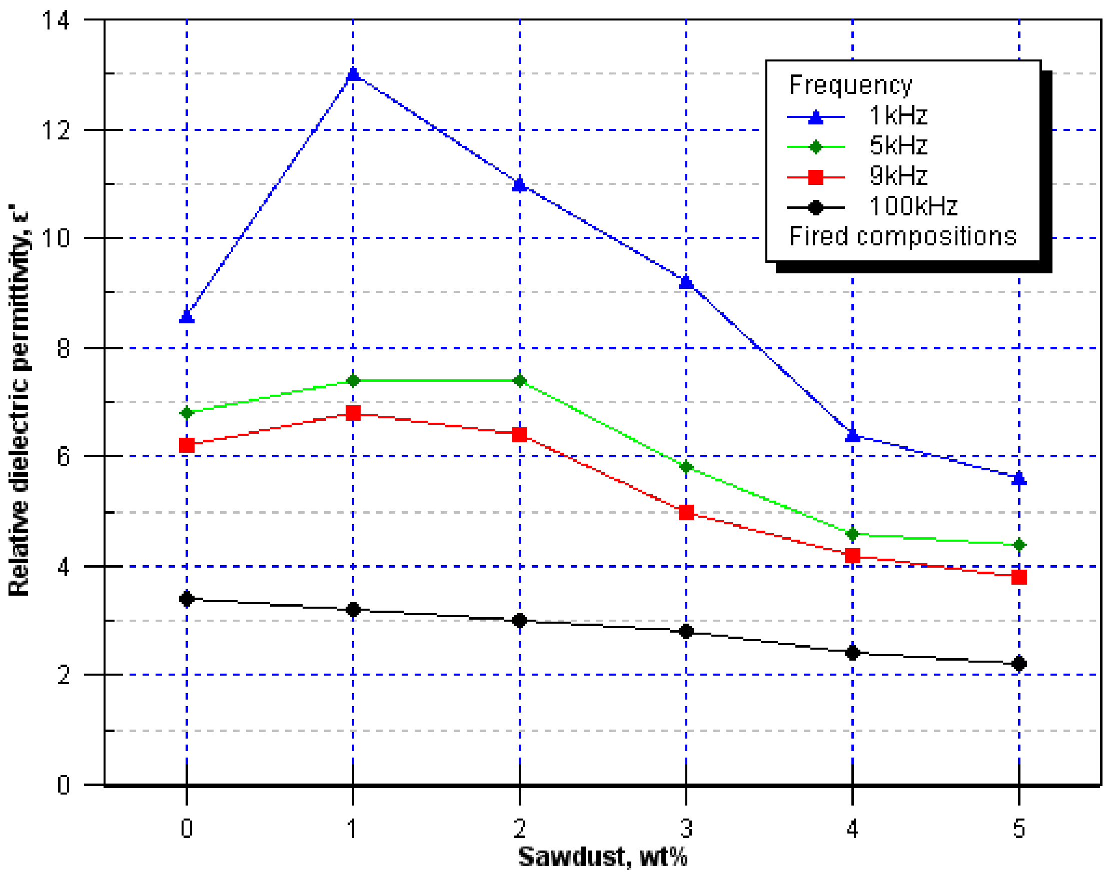

FIGURE 6. Relative dielectric permittivity of fired clay compositions as function of original sawdust concentrations

4. CONCLUSIONS

During this work we have measured the dielectric properties of several clay based compositions as their water content changed during the drying process. We found that the method of measuring dielectric properties is a very sensitive way to follow the dehydration and describe the mechanism of water adsorption and desorption is mineral clays. The technique is more accurate and with higher sensitivity than measuring the weight loss, and shows applicability for quick, non-destructive industrial measurements. The additive sawdust has a great effect on the water uptake of the clay, and the balance of the different types of adsorbed waters within the structure even at low concentrations. The fired samples show the expected behavior at high frequencies. The explanation of the anomaly found at lower additive concentrations at low frequencies requires further studies.

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