MICROWAVE METHOD FOR STUDYING THE POROUS STRUCTURE OF WATER-SATURATED DIELECTRIC MATERIALS

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A method is described for determining the porosity of water-saturated dielectric materials on the basis of the anomalous microwave dispersion of water. A study of the porous structure of kaolin, clay, a ceramic, and silica gel is reported.

The microwave loss in a moist dielectric material is sensitive to the moisture content [1, 2], because of the anomalous microwave dispersion of water (in the liquid phase). In the phase-transition region, at negative Celsius temperatures, the dielectric properties of water change abruptly, and the microwave energy loss is reduced by 2-3 orders of magnitude [3]. Since there is a stable relationship between the melting temperature of ice and the capillary radius [4], this loss change can be exploited to study the porous structure of moist dielectric materials [5].

If we adopt a model consisting of a layer of water and dry material for the moist material, and if we express the microwave loss in decibels [6], then the loss is related to the porosity in a first approximation by the following equation (the sample is assumed plane-parallel and infinite, the wave is assumed plane, and the reflection loss is neglected):

$$N = 8.686\alpha x \frac{V_{\mathrm{w}}\gamma_{\mathrm{tv}}}{m_{\mathrm{tv}}} = 8.686\alpha x \frac{V_{\mathrm{w}}}{V_{\mathrm{tv}}} = 8.686\alpha x \Pi \ (\mathrm{dB}), \tag{1}$$

where $\Pi = V_{\mathrm{w}}/V_{\mathrm{tv}}$ is the porosity, V_{w} is the volume of the open pores (equal to the water volume at complete saturation) in the material, V_{tv} is the total volume of the sample, $\alpha = (2\pi/\lambda)\sqrt{(\varepsilon'/2)\sqrt{1+\tan^2}-1}$ is the attenuation constant, and x is the thickness of the sample.

We can find an equation describing the microwave loss in a moist material within which phase transitions of water occur by assuming that the loss in crystallized ice is on the same order as that in the dry skeleton of the material and if we assume that the attenuation constant α in the liquid phase does not change at negative Celsius temperatures. Under these conditions the crystallization of water, accompanied by a reduction of the amount of liquid water, leads to a reduction of the effective porosity and thus of the microwave loss.

At a negative Celsius temperature T the loss N_T is given by an equation like (1):

$$N_T = 8.686\alpha x \Pi_{\mathrm{eff}}, \tag{2}$$

where

$$\Pi_{\mathrm{eff}} = \frac{V_T}{V_{\mathrm{tv}}} = \frac{V_T}{V_{\mathrm{w}}}\Pi; \tag{3}$$

and V_T is the volume of liquid water at the given temperature.

Using (3) we can rewrite (2) as

$$N_T = 8.686\alpha x \Pi \frac{V_T}{V_{\mathrm{w}}}. \tag{4}$$

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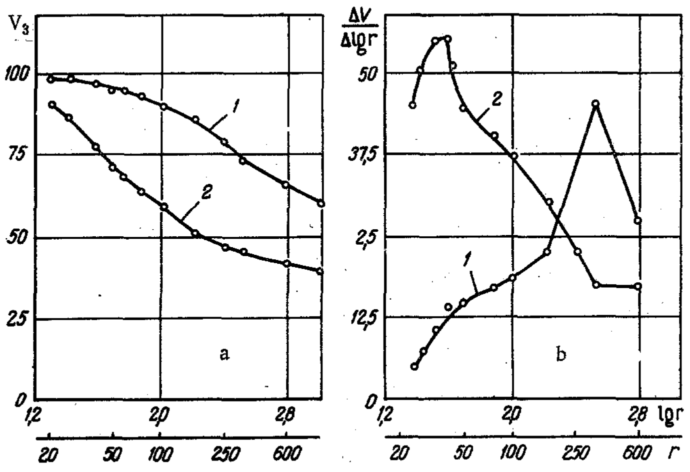

Fig. 1. Integral (a) and differential (b) distributions of pores with respect to radius in clay (2) and kaolin (1). Here V is in % and r is in Å.

Accordingly, the loss turns out to depend on V_T/V_W if α, x, and Π are constant.

From Eqs. (4) and (1) we find

$$\frac{N_T}{N}=\frac{V_T}{V_W}. \tag{5}$$

Using the experimental temperature dependence of the microwave loss in a sample we can calculate the ratio V_T/V_W (the fraction of the pore volume filled with liquid water, expressed as a percentage of the total pore volume) or V_3, the fraction of the pore volume filled with ice at the given temperature T (expressed as a percentage of the total pore volume). Equation (3) is used to calculate the effective porosity at temperature T (expressed as a percentage or in cubic centimeters per gram); alternatively, if we multiply V_3 by Π, we can find the volume of ice-filled pores as a fraction of the total sample volume.

Using the data of [4] and the experimental $V_3(T)$ dependence we can calculate the function $V_3(r)$ or $V_3(\log r)$; a plot of either of these functions represents the integral pore distribution with respect to radius.

A laboratory microwave apparatus designed and constructed for corresponding experiments is described in [7]. The measurement procedure is described in [8]. The samples selected for these experiments are of materials having a broad range of pore dimensions: molded kaolin and clay, ceramics fired at various temperatures, and fine pore commercial silica gel.

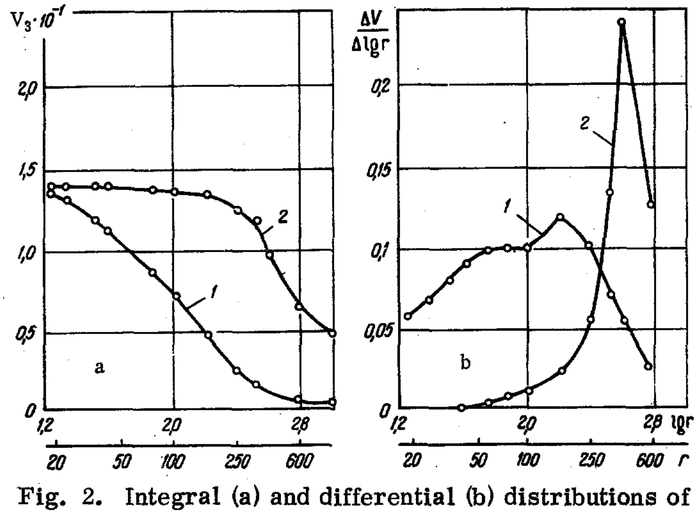

Fig. 2. Integral (a) and differential (b) distributions of pores with respect to radius in a ceramic. 1) Fired at 973°K; 2) 1273°K. Here V is in cm^3/g and r is in Å.

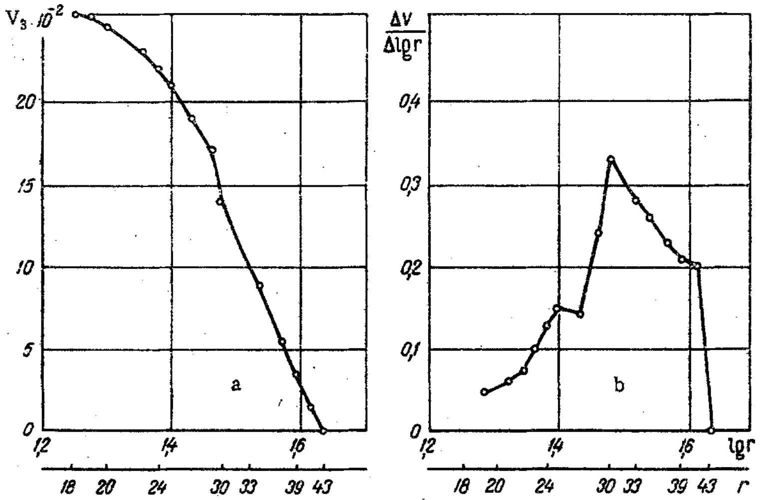

Fig. 3. Integral (a) and differential (b) distributions of pores with respect to radius in fine-pore silica gel. Here V is in cm^3/g and r is in Å.

The measured microwave loss in a sample is used to calculate the effective porosity and the volume of pores in which the water is in the solid phase at a given negative Celsius temperature; integral and differential pore distributions with respect to radius are constructed. Figures 1-3 show the integral distributions in clay and kaolin (Fig. 1), the ceramic (Fig. 2), and silica gel (Fig. 3), along with the corresponding differential distributions. We see that the integral distributions for the various materials differ in shape and breadth. The peaks of the differential curves are not at the same position for the different materials. While the first peak on the distribution for the moist micaceous clay (curve 2) occurs at $3 \cdot 10^{-7}$-$4 \cdot 10^{-7}$ cm, that for kaolin, which has a coarser dispersion, occurs at $2.5 \cdot 10^{-6}$ cm. A ceramic fired at a relatively low temperature (curve 1; 973°K) has a wide range of pore dimensions. Most of the pores have dimensions approximately equal to those of sorbent pores. The peak occurs at $2 \cdot 10^{-6}$ cm. There are an insignificant number of pores with radii $6 \cdot 10^{-6}$ cm. The ceramic fired at 1273°K, on the other hand, has no pores smaller than $4 \cdot 10^{-7}$ cm and very few in the range $4 \cdot 10^{-7}$-$2 \cdot 10^{-6}$ cm; the first peak of the distribution occurs at $4 \cdot 10^{-6}$ cm. Although this method does not permit a quantitative determination of the number of larger pores, the nature of the distributions for the samples fired at 1273°K implies that such pores exist.

The distributions for silica gel are particularly interesting: we see from Fig. 3a and 3b that there are no pores larger than $4.3 \cdot 10^{-7}$ cm in this sample, and the peak of the distribution is at $3 \cdot 10^{-7}$ cm. These results agree satisfactorily with the technical specifications for this type of silica gel.

Lacking the necessary apparatus we were not able to carry out comparative tests by other methods (e.g., by the BET method) and were thus unable to fully evaluate this method from the metrological standpoint. Nevertheless, analysis of the measurements shows that the total error consists primarily of the error in measuring the microwave loss, which is ± 0.65 dB for prolonged measurements and ± 0.25 dB for brief measurements, and the error due to the rms error in the determination of the melting temperature corresponding to a given capillary radius. The curve plotted from the data of [4] yields this value within ± 15%.

This method has the obvious advantages that it is nondestructive and does not require contact with the sample; it is also simple, uses readily available apparatus (standard microwave-measurement equipment can be used), and is highly sensitive. It can thus be hoped that new applications of this method will be found.

NOTATION

N is the microwave loss in a material containing (liquid) water at 273°K;
x is the thickness of the layer of moist material;
α is the attenuation constant of the medium;
λ is the microwave wavelength;

ε' is the real part of the complex dielectric constant;
$\tan\delta$ is the loss tangent;
V_w is the volume of open pores in the material;
V_{tv} is the volume of the sample of moist material;
Π is the porosity;
T is the temperature of the material (°K);
N_T is the loss at a negative Celsius temperature T;
Π_{eff} is the effective porosity;
V_3 is the volume of pores filled with ice at temperature T;
γ_{tv} is the density of the moist material;
r is the pore radius.

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