Laboratorní a výpočetní metody

ELECTRIC CONDUCTIVITY OF WATER-SATURATED PORCELAIN MIXTURE

Part I. Method for Determining Electric Conductivity and its Dependence on Moisture content

Jiří Havrda, Eva Gregorová, František Oujiří

Department of Silicate Technology, Institute of Chemical Technology, Suchbátarova 5, 166 28 Prague 6

A method was worked out for determining the electric conductivity of water-saturated porcelain mixture in the course of electric resistance drying. On the basis of measuring the starting currents in bodies of various moisture contents, the electric conductivity of mixtures in open and isolated systems can be expressed for a given voltage. The conductivity was found to be independent of moisture content but was affected by the measuring temperature.

INTRODUCTION

A ceramic mixture in plastic state can be regarded as a water-saturated binary mixture of a solid (ceramic material) and a liquid phase (water and a dissolved electrolyte), free of any gaseous phase. The mixture is electrically conductive as a result of the presence of soluble salts. This characteristic is made use of in the manufacturing technology, particularly in the case of technical porcelain, in an operation called electric resistance drying which is based on generation of heat within the body volume by passage of electric current. The electric conductivity decreases sharply during transition from the water-saturated mixture (plastic state) to the unsaturated one (solid state), so that the electric resistance drying can only be utilized up to a certain content of the liquid phase. For this reason the electric resistance drying can be applied to drying ceramic mixture in plastic state [1]. Knowledge of the electrical properties of the ceramic mix is indispensable for a mathematical description of the process.

The existing empirical solution of electric resistance drying of ceramic bodies does not provide any explicit idea of the electrical properties of ceramic mixtures in plastic state. The basic question therefore is whether a ceramic mixture in plastic state behaves as a homogeneous or inhomogeneous conductor in an electric field. In the case of mathematical modelling it is thus necessary to establish the form of the constitutive equation for current density in the ceramic mix.

Determination of the constitutive equation of a ceramic mixture can be based on the assumption that the conductor consists of electroneutral particles and electrically charged ions. The flux of electric charges can then be regarded as a diffusion flux because a relative movement of ions with respect to neutral particles is involved. The thermodynamics of irreversible processes [2, 3] shows that this flux is generally evoked not only by the electric field potential, but also by the

concentration gradient and temperature. The constitutive equation of an inhomogeneous conductor has then the form

$$j = -\sigma \text{ grad } \varphi - L_1 \text{ grad } C - L_2 \text{ grad } T, \tag{1}$$

where the terms L_1 grad C and L_2 grad T represent the so-called diffusion-electric and thermoelectric phenomena respectively, while C is the concentration, L_1 is the diffusion-electric coefficient, L_2 is the thermoelectric coefficient and σ is electric conductivity which generally depends on potential.

On the assumption that the last two terms in equation (1) can be neglected one obtains a homogeneous conductor which obeys Ohm's law:

$$j = -\sigma \text{ grad } \varphi. \tag{2}$$

To decide whether the behaviour of this mixture in an electric field is described by equation (1) or (2) requires the significance of all the terms in equation (1) to be expressed, i.e. the respective coefficients and their dependence on the above variables to be determined.

The present study has the purpose to work out a method for determining the electric conductivity of water-saturated porcelain mixture and to express its dependence on moisture content.

METHOD FOR DETERMINING THE ELECTRIC CONDUCTIVITY OF A PORCELAIN MIX

Two procedures differing in experimental arrangement were suggested for the determination of electric conductivity of porcelain mixtures. In the first arrangement, the electric conductivity measurement was based on the conditions of an isolated system while those of an open system were created in the other, i.e. mass exchange with the environment was allowed.

To simplify the problem, the theoretical principles of the two methods may be based on one-dimensional transmission of electric current through a planarly bounded body. In the case of an isothermal process free of concentration changes, i.e. grad $C = 0$ and grad $T = 0$, equation (1) acquires the form

$$j = -\sigma \, d\varphi/dx, \tag{3}$$

where x is the ordinate in the transmission direction, and for $d\varphi$ it holds that

$$U = \int_A^B d\varphi, \tag{4}$$

where U is the electric voltage. In order to evaluate σ from equation (2), the method must permit the voltage applied to a body L in length and with a sectional area of S, and current I with a current density j to be measured. For the current density j it holds that

$$I = \int_0^S j \, dS. \tag{5}$$

The experimental conditions are more complex in the case of the open system. However, the basic arrangement is the same as in the previous case. The only difference is that in this arrangement the moisture is exchanged with the environment, which results in the formation of moisture fields in the body and thus in the

creation of a moisture gradient in the body. This is why all the data on the moisture dependence of electric conductivity have to be related to the body axis where grad $C = 0$. To obtain information on concentration changes it appears advantageous to introduce a quasistationary state, i.e. one for which it holds that

$$T(x) = \text{const.}, \quad C(x) = f(x), \quad \mathrm{d}\bar{C}/\mathrm{d}t = -h/A, \tag{6}$$

where h is the volume flux of moisture and $\bar{C}$ is the mean moisture content, and A is one half of the body thickness. In this state a time-independent concentration profile in the body has already fully developed and the concentration changes in the body are then determined by weight losses due to the evaporated liquid. For this reason, equation (6) can be applied to any arbitrary point in the body, and the following equation holds for moisture calculation at the body axis:

$$C_s = C_{0s} - h\,t/A, \tag{7}$$

where C_s is the actual concentration at the body center, and C_{0s} is the moisture content at the body center at quasistationary state.

The experimental arrangement of both methods is shown in Fig. 1. The system consisting of body *1* and supply electrodes *2* (carbon-filled rubber with fibrous aluminium) is supplied with adjustable constant alternating voltage from transformer *6*; the voltage is indicated by a voltmeter. Another voltmeter measures the voltage on the body proper. The current passing throught the body is recorded by an ammeter. The temperature field in the body is measured by copper-konstantan thermocouples *5*. The adjustable moisture proofing *3* and thermal insulation *4*, and placing the insulated body on balance *7* in a laboratory recycling drying oven *8* with adjustable temperature, relative humidity and air flow rate allowed an either isolated or open system to be created in the body and losses in weight to be determin-
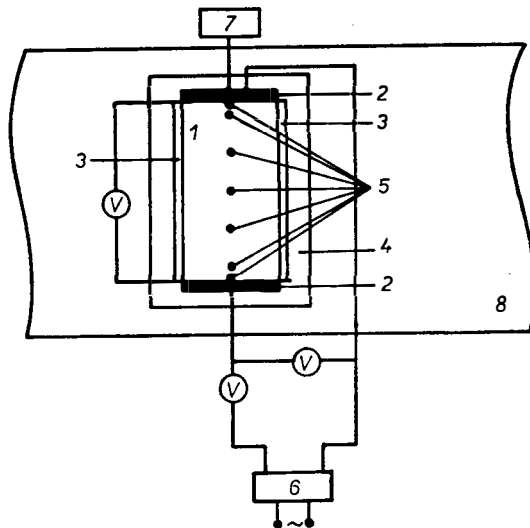

Fig. 1. Schematic diagram of the apparatus; 1 — body, 2 — electrodes, 3 — moisture proofing, 4 — thermal insulation, 5 — thermocouples, 6 — transformer, 7 — balance, 8 — laboratory recycling drying oven.

ed; the data was used to calculate the value of surface moisture flux for the quasi-stationary state. The C_{0s} value can be calculated from the moisture profile established by cutting the body into slices.

The electric conductivity measurements were carried out on bodies 30 mm × × 30 mm × 60 mm in size with moisture content C over the interval $C \in \langle 0.3414$ m³m⁻³; 0.4281 m³m⁻³⟩ prepared from a porcelain mix with an elevated content of α — Al_2O_3 at a constant content of soluble salts, at 294.15 K and at 318 K in the case of the other experimental arrangement. Following preparation and moisture proofing, the bodies were kept in a water-saturated medium for 48 hours to achieve a homogeneous moisture and temperature distribution throughout the body volume. In view of the heat generated in the body by the passing current, to maintain the initial isothermal state and keep the same temperature in all of the experiments with the isolated system, only the starting current I_s was measured, i.e. that measured after switching the body into the electric circuit at time $t = 0$ and at a constant voltage on the body. For each moisture content, the starting current was always measured on five bodies. For the calculation from equation (3) one has to know the unidirectional potential of the electric field or voltage in the body. The measuring procedure is illustrated by Fig. 2. Probes B1 — B6, placed axially over the body length, measured the relationship $U = U(x)$ with respect to the reference probe B0, as shown in Fig. 3. The losses in the electrodes and in the electric circuit were calculated from the relationship and found to amount to 25 percent of the total voltage of 46 V. The voltage on a body $L = 6 \times 10^{-2}$ m in length was therefore 34.5 V, to which corresponds the electric field potential $d\varphi/dx = 575$ V/m.
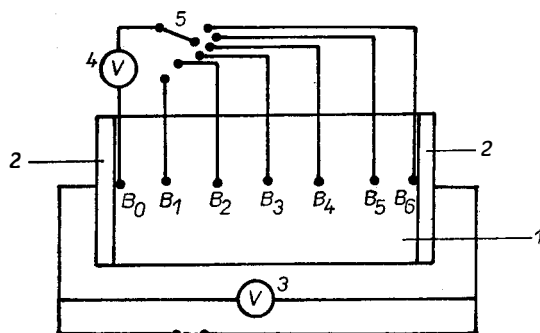

Fig. 2. Schematic diagram of electric potential measurement on the body: 1 — body, 2 — electrodes, 3 — voltmeter, 5 — switch.
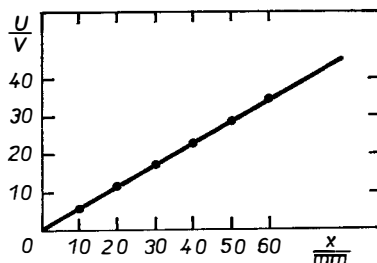

Fig. 3. The $U = U(x)$ dependence on the body.

In the case of the open system, the experimental measurements were supplement-·
ed with the time dependence of the electric current, surface moisture flux and
moisture content at the body center. These relationships are plotted in Fig. 4.
The temperature field in the body was measured with thermocouples in the quasi-
stationary state. At a mean body temperature of 318 K, the difference between
the body center and surface amounted to 0.1 K, which corresponds to a temperature
gradient of $dT/dx = 7$ K m^{-1}. This value was neglected and ₁the system was
regarded as an isothermal one.

DISCUSSION OF RESULTS

The mean values of the starting current and the calculated electric conductivi-
ties of bodies with various moisture contents according to equation (3) for the
experimental arrangement representing the isolated system are listed in Table I.
The results indicate that a change in the moisture content of the body over the
interval of volume moisture content of $C \in \langle 0.344$ m³m^{-3}; 0.4282 m³m$^{-3}\rangle$ does
not lead to any change in the electric conductivity of a water-saturated ceramic
mix, and can therefore be considered constant. Its mean value was $(0,164 \pm 0.004)$
Sm^{-1} at 294.15 K. The dispersion of the values measured is associated above all
with the reproducibility of preparing bodies of identical length and the possible
occurrence of contact resistance between the body and the electrodes.

Table I

Electric conductivity of a water-saturated porcelain mixture
with various moisture contents

C m³ m⁻³	I_s mA	σ Sm⁻¹
0.3444	83.6 ± 0.1	0.162
0.3580	85.0 ± 0.1	0.164
0.3695	86.5 ± 0.2	0.167
0.3851	85.0 ± 0.1	0.164
0.3965	85.0 ± 0.1	0.164
0.4282	86.5 ± 0.1	0.167

For the case of the experimental arrangement meeting the conditions of an open
system, the time dependence of mix electric conductivity is plotted in Fig. 4. The
results of measuring the electrical properties of a system exchanging moisture with
the environment indicate that in a quasistationary state, when the body tempe-
rature is constant, the electric conductivity also remains constant when the
body moisture content decreases. However, the value of the electric conducti-
vity is affected by the body temperature.

The independence of electric conductivity of a water saturated porcelain mixture
of its moisture content, established in the present study, can be used to suplemente
the hypothesis by Shumilin [4] on the possible autocontrol of electric resistance
drying within the body volume resulting from differences in local moisture content
and thus in electric conductivity. As indicated by the results of the present study,
if a ceramic mixture conforms to the requirements of a binary mixture, i.e. is

J. Havrda, E. Gregorová, F. Oujiři:

saturated with water or an electrolyte with uniformly distributed concentration of soluble salts, the autocontrol of the process cannot become effective as the electric. conductivity is independent of moisture content. The autocontrol may take place in systems comprising simultaneously water-saturated and water-unsaturated regions, as a result of their different electric conductivities.
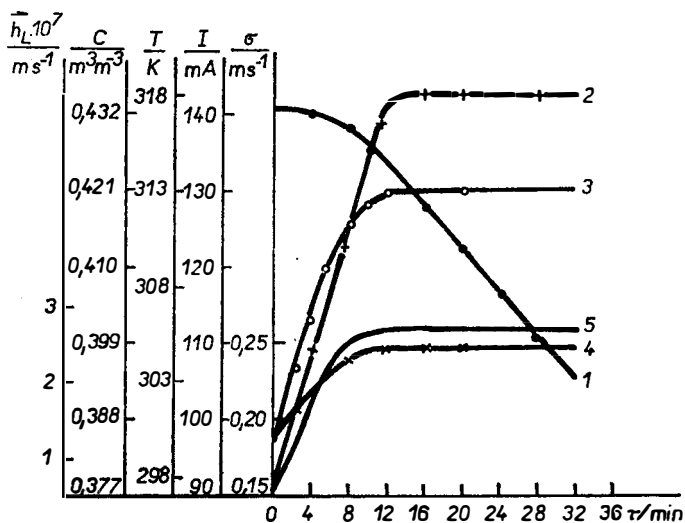

Fig. 4. The time dependence of moisture content — 1, temperature — 2, current — 3, electric conductivity σ — 4 and volume flux of moisture content **h** *— 5.*

References

[1] Lykov A. V.: *The Theory of Drying* (in Russian), Energia, Moscow 1968.
[2] De Groot S. R., Mazur P.: *Nonequilibrium Thermodynamics*, North-Holland, Amsterdam 1962.
[3] Sedov L. I.: *The Mechanics of Continuous Media* (in Russian), Nauka, Moscow 1976.
[4] Shumilin A. A.: *The Drying of Refractories* (in Russian), Metallurgizdat, Moscow 1952.

ELEKTRICKÁ VODIVOST VODOU NASYCENÉ PORCELÁNOVÉ SMĚSI

Část I. Metoda stanovení specifické elektrické vodivosti směsi a její závislosti na vlhkosti

Jiří Havrda, Eva Gregorová, František Oujiři

Katedra technologie silikátů, Vysoká škola chemicko-technologická, 166 28 Praha 6

Cílem práce je vypracovat postup stanovení specifické elektrické vodivosti binární keramické směsi v plastickém stavu a vyjádřit její závislost na vlhkosti. Je vypracována metoda pro izolovaný a otevřený systém, při které je přenos proudu jednosměrný. Jejím základem je stanovení proudu v tělese při známém napětí za definovaných vlhkostních, teplotních a koncentračních podmínek. V izolovaném systému byl pro daná napětí vzhledem k zachování izotermního stavu měřen pouze startovací proud v tělesech o různé vlhkosti. Pro oba systémy jsou vyjádřeny specifické elektrické vodivosti směsi. Výsledkem je zjištění, že specifická elektrická vodivost není funkcí vlhkosti.

Obr. 1. Schéma aparatury; 1 — těleso, 2 — elektrody, 3 — vlhkostní izolace, 4 — tepelná izolace, 5 — termočlánky, 6 — transformátor, 7 — váhy, 8 — laboratorní cirkulační sušárna.
Obr. 2. Schéma měření elektrického potenciálu na tělese; 1 — těleso, 2 — elektrody, 3 — voltmetr, 5 — přepínač.
Obr. 3. Závislost U = U(x) na tělese.
Obr. 4. Závislost vlhkosti — 1, teploty — 2, proudu — 3, specifické elektrické vodivosti σ — 4 a objemového toku vlhkosti h — 5 na čase.

ЭЛЕКТРОПРОВОДНОСТЬ НАСЫЩЕННОЙ ВОДОЙ ФАРФОРОВОЙ СМЕСИ; I.

Метод определения удельной электропроводности и ее зависимость от влажности

Иржи Гаврда, Эва Грегорова, Франтишек Оуиржи

Кафедра технологии силикатов Химико-технологического института, 166 28 Прага 6

Целью предлагаемой работы является разработка метода определения удельной электропроводности бинарной керамической смеси в пластическом состоянии и определение ее зависимости от влажности. Был разработан метод для изолированной и открытой системы, при которой перенос тока протекает в одном направлении. Его основой является определение электрического тока в теле при известном напряжении и установленных условиях влажности, температуры и концентрации. Чтобы не нарушать изотермическое состояние, измеряли в изолированной системе при заданных напряжениях только начальный ток в телах с разной влажностью. Для обеих систем установлены удельные электропроводности смеси. Результатом работы является то, что удельная электропроводность не является функцией влажности.

Рис. 1. Схема аппаратуры; 1 — тело, 2 — электроды, 3 — изоляция влажности, 4 — термоизоляция, 5 — термоэлементы, 6 — трансформатор, 7 — весы, 8 — лабораторная циркуляционная сушилка.
Рис. 2. Схема измерения электрического потенциала на теле; 1 — тело, 2 — электроды, 3 — вольтметр, 5 — переключатель.
Рис. 3. Зависимость U = U(x) на теле.
Рис. 4. Зависимость: 1 — влажности, 2 — температуры, 3 — тока, 4 — удельной электропроводности σ, 5 — объемного тока влажности h от времени.

CENTRUM PRO VÝZKUM SUPRAVODIVÝCH MATERIÁLŮ VE FRANCII.

Koncem r. 1988 bude uvedeno do provozu výzkumné centrum pro supravodivé materiály ve francouzském Caen. Centrum, podobné institucím v americkém Houstonu a japonském Tokiu, bude stát místní úřady 6 mil Ffr (1,04 mil $) a bude spravováno Národním ústředím pro vědecký výzkum (CNRS) a firmami Rhone-Poulenc a Compagnie Générale d'Electricité (CGE). Francouzská vláda bude přispívat 75 % na provozní náklady, které budou činit 15 mil Ffr ročně.

(European Chem. News, 1988, 6. 6., 14)

Doušková

VÝROBA VZÁCNÝCH ZEMIN V JAPONSKU.

Firma Nippon Rare Earth, joint-venture francouzské Rhone-Poulenc a japonské Sumitomo Metal Mining, začne koncem r. 1988 vyrábět prvky vzácných zemin pro potřeby Japonska. Japonsko je zatím zcela závislé na importu vzácných zemin, které se začínají ve zvýšené míře používat v keramice pro elektroniku a pro výrobu supravodičů. Nová rafinérie firmy v Niihama bude vyrábět 15 prvků včetně samaria, ceru a neodymu.

(Electronic Chem. News 3, 1988, č. 15, 4)

Doušková