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Influence of relative humidity on electrical properties of α-Al_2O_3 powders: Resistivity and electrochemical impedance spectroscopy

François Favre [a], Frédéric Villieras [a,*], Yann Duval [a], Edward McRae [b], Christophe Rapin [b]

[a] *Laboratoire Environnement et Minéralurgie, UMR INPL-CNRS 7569, Ecole Nationale Supérieure de Géologie, Centre de Recherche François Fiessinger, 15 avenue du Charmois, B.P. 40, 54501 Vandoeuvre-lès-Nancy cedex, France*
[b] *Laboratoire de Chimie du Solide Minéral, UMR CNRS 7555, Université Henri Poincaré–Nancy 1, B.P. 239, 54506 Vandoeuvre-lès-Nancy cedex, France*

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Abstract

The influence of humidity on the electrical properties of α-Al_2O_3 powders has been investigated using adsorption isotherms, DC resistivity, and electrochemical impedance spectroscopy. Samples of two α-Al_2O_3 particle sizes were examined, both individually and mixed together. The results show that the grain-bed resistivity decreases with humidity, whereas the grain capacitance is almost constant. The resistivity difference between the two particle sizes is of several orders of magnitude, while the capacitance values are not very different. These results are interpreted in terms of the layer-by-layer growth of water adsorbed on the grain surfaces. The first, more tightly bound adsorbed layer does not provoke the same effects as those layers adsorbed at higher relative humidity.

Keywords: α-Al_2O_3; Impedance spectroscopy; Electrical resistivity; Porous media

1. Introduction

Among the range of today's available geophysical tools, electrical measurements are very useful for investigating soil and ground without digging [1,2]. Indeed, in soil science, only noninvasive methods allow the investigation of an entire soil surface or volume without its total destruction, since digging disturbs the ground water flow paths. The use of such methods, however, requires understanding the relationship between the nature of the soil and the data collected from the exploration [3]. So laboratory experiments on excavation samples are needed to establish and understand these correlations.

Electrical resistivity or conductivity are those parameters of materials in general that span a range of magnitudes greater than that of any other; indeed, between the resistivity of a good metal and that of a good insulator at room temperature, there are almost 25 orders of magnitude [4]. In a geophysics environment, these parameters are influenced by two factors: (i) the saturation and salinity of the water in this porous media, and (ii) the value of the specific surface area, which is related to the clay and fine-particle content.

Much research has recently concentrated on studying the dielectric and electrical properties of such liquid-containing porous media. Studies have focused, for instance, on the electrical conductivity, which is related to the electrochemical interactions at the solid–liquid interface [5]. The current study will deal with such effects on the electrical properties of Al_2O_3 powders with the aim of understanding the strong interaction between the solid and water, in the case of a high-resistance material.

Three parameters are studied. The water isotherms give information on the specific surface area of the grains and on the water organization on the grain surfaces. Direct current (DC) and alternative current (AC) resistivity measurements are used to determine the charge transport. Finally, AC ca-

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[*] Corresponding author. Fax: +(33)383-59-62-55.
E-mail address: frederic.villieras@ensg.inpl-nancy.fr (F. Villieras).

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pacitance will furnish complementary information on the charge accumulation.

2. Experimental

2.1. Materials

The materials used in this work are two monodisperse powders of α-Al_2O_3 provided by Pechiney (France). The grains contain a few silica impurities. The particle sizes were determined by a laser measurement system (Mastersizer, Malvern). The first powder presents a 320-µm mean diameter and a 270-µm mode and will be further referred to as AL1. The second possesses an 80-µm mean diameter and a 70-µm mode and will be designated AL2.

2.2. Macroscopic experimental investigation of water adsorption

Adsorption measurements were carried out in order to determine the quantity of water adsorbed on the solid surfaces as a function of relative pressure. Experiments were performed with a continuous gravimetric apparatus built around a MK2–M5 CI Electronics Ltd. symmetric microbalance. Pressures were measured using Druck 0–10^3 and 0–10^5 Pa absolute pressure sensors. The pressure accuracy was 0.02% of the read pressure. Water vapor was supplied from a source kept at 41 °C, through a Grandville–Philips leak valve, at a slow flow rate to ensure quasi-equilibrium conditions at all times [6]. The adsorption isotherms, i.e., the mass adsorbed at 30 °C versus quasi-equilibrium pressure, were directly recorded by a computer in the range 10^{-1}–10^5 Pa.

Sample masses were 1.7 and 1.4 g for AL1 and AL2, respectively. Sample outgassing was performed directly in the adsorption device for 18 h at 383 K under a secondary vacuum of 1×10^{-5} Pa.

In the case of AL1, the high relative pressure part of the isotherm was somewhat inaccurate due to the low specific surface area of the sample. In order to check for possible capillary condensation, additional information was obtained by equilibrating 50 g of sample with water vapor in a closed chamber. Sample weight (accuracy 0.5 mg) was recorded several times as a function of relative pressure. Adsorbed amounts were normalized (positive offset) to ensure continuity with the adsorption isotherm obtained with the microbalance.

2.3. DC resistivity measurement

Zero-frequency four-point electrical resistivity measurements were realized in a cell provided with two steel cylinders as electrodes (supported on a frit and embedded in a Pyrex glass tube). A Keithley 6617A electrometer with a built-in source was used; it allowed determining currents as low as a few nA. Measurements were taken with a voltage of 500 V. A sample of 2.0 g was put between the electrodes, corresponding to a cell level of about 1.8 mm for AL1 and 1.5 mm for AL2. The influence of the relative humidity was established by putting the cell into an enclosed box connected to a “wet air generator.”

2.4. EIS measurement

Electrochemical impedance spectroscopy (EIS) allows determining the impedance as a function of the frequency for complex electrochemical systems, in which the DC resistivity is often very high. From these measurements, one can determine the contribution of the resistive and capacitive components of the overall total impedance. The measurements were made with an EGG 5210 frequency analyzer interfaced with the EGG m398 software. The potential amplitude was set to 50 mV and the frequency range was 100 kHz to 10 mHz with five measurements per decade. The same cell as for the DC measurements was used for the EIS measurements.

The cell was put into a bag with a beaker filled with water at different temperatures. The relative humidity was measured with a hygrometer. When equilibrium was reached, the EIS measurement began.

Experiments were performed with 2-g samples. In a second phase, mixtures of the two powders were studied. Mixtures were made with 2 g of AL1 and increasing quantities of AL2. The added AL2 quantities varied from 0 to 1.8 g. These samples will be further designated by the ratio $T = \text{mass(AL2)}/\text{mass(AL1} + \text{AL2)}$.

For AL1 or AL2 alone, the relative humidity varied from 25 to 80%. For mixture samples, measurements were realized for three humidity ranges RH1, RH2, and RH3 (Table 1).

EIS results are represented in Nyquist plots. The resistance R was derived from the low-frequency intersection of a semicircle fit on the complex impedance plane with the real complex axis. The resistivity ρ was calculated from the resistance R by

$$\rho = RS/d \ [\Omega\,\mathrm{m}],$$

where S is the sample face surface area (m^2) and d its thickness (m).

Analysis of EIS data takes into account two observations. The first is that a vertical line fit in a Nyquist plot corresponds to a purely capacitive system. The second is that in the presence of more than one semicircle, each can be modelled by an RC circuit. The resistance R is determined as

Table 1
Relative humidity ranges

Name	Mean (%)	Std deviation (%)
RH1	30	4
RH2	50	7
RH3	70	5