One-step method for measuring the effect of humidity on powder resistivity

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Abstract—**Relation between powder resistivity and humidity is typically measured in several steps. When a standard resistivity cell is used, this procedure may take weeks. We present a method for measuring powder resistivity as a function of moisture using a one-step process. System consisted of two parallel electrodes immersed in powder. High voltage electrode was a uniform square but the ground electrode consisted of two parts: a narrow current electrode connected to an electrometer and a guard electrode surrounding the current electrode. Relative humidity surrounding the particles was measured at the height of current electrode. Relative humidity of ambient air was rapidly increased from 5 RH% to 100 RH% and both current and humidity within the powder were recorded as diffusion of moisture took place. System was modeled using computer simulations. As an example, resistivities of three different lactose, wheat flour and quartz are presented. Resistivity was found to decrease several orders of magnitude between 10 RH% and 90 RH%. As powder was dried, significant hysteresis was observed. Since a small change in humidity results in very large change in resistivity, system could be used to study surface sensitive phenomena such as surface amorphicity and surface chemistry.**

I. INTRODUCTION

Volume resistivity of a powder is an important parameter in many processes which involve powder handling and processing. During various operations, such as transport, mixing and filling, particles contact different surfaces and as a result, powders acquire charge due to triboelectric charging [1,2]. If the rate of charge build-up in the system is higher than charge migration away from the powder, the net charge of the powder containing volume will increase. This is especially true in situations where large amounts of powders are collected to silos, flexible intermediate bulk containers (FIBCs) and such. High charge density might result in strong electric fields, particle adhesion and even dust explosion and fires [3]. In many cases, the triboelectrification is hard to control. However, charging can be reduced and charge decay can be increased, for example, with addition of humidity [4,5,6].

Resistivity is naturally related to the rate of charge decay. More conducting powders provide a route for the excess charge to flow to the ground more quickly than highly in-

sulating powders. Resistivity is also strong function of surrounding relative humidity; high humidity reduces the resistivity due to adsorbed conducting water layer on the particle surfaces [7]. Thus, by increasing the humidity, charge relaxation can be enhanced.

Traditionally, the relation between resistivity and humidity has been measured in several steps. Dry powder is placed in a resistivity cell, voltage is applied between the electrodes and the current is recorded. From the recorded voltage and current, resistance can be calculated using Ohm's law. For the calculation of resistivity of the material, dimensions of the cell need to be known. The volume of standard resistivity cell is roughly 0.5 liters. Electrodes are circular, placed vertically and their radius is 25 mm. Spacing between the electrodes is 5 mm and the electrodes are aligned parallel to each other [8]. Next, the humidity of surrounding air is increased to a certain value, typical increase being approximately 10 – 15 RH%. Water molecules will then diffuse into the powder bed. Depending on the powder properties, particle size and the height of the powder bed, the diffusion will last for a certain time. For many powders, the time needed for the system to reach equilibrium can be several days. The equilibrium has been reached when the current signal has reached a steady state. Then again humidity is increased in a stepwise manner. So, measurement of the whole range of interest can take weeks. It should be pointed out that in theory the required time can be decreased if pretreated samples were used. In other words, samples with different initial moisture content are used. However, the volume resistivity measurement is very sensitive to powder packing between the electrodes [9]. It is practically impossible to pack the powder in reproducible manner. Small variations in particle orientations and powder density result in large variations in measured resistivity. For example, if the cell is tapped during the measurement, particles rearrange, density of powder increases and measured current increases. Reproducibility between different measurements can be improved by applying a constant force between the electrodes, but this method has not been used in the present study [9]. Thus, for accurate measurements, same sample should be used throughout the applied moisture range.

In the present study, authors have developed a one-step method for measuring the powder resistivity as a function of moisture. The system consists of a novel electrode arrangement and simultaneous measurement of humidity within the powder bed. Instead of increasing humidity in steps, humidity was instantly raised from approximately 5 RH% to 100 RH%. Presented system suffers from very high hysteresis and therefore the results are not readily comparable with steady state method. However, method can also be used to study adsorption processes at air-solid interface since the resistivity is such a strong function of humidity.

System was modeled using COMSOL Multiphysics software (COMSOL, Inc., USA).

II. Materials and methods

A. *Description of one-step process*

Theoretically, it could be possible to measure the humidity dependence of resistivity using a standard resistivity cell with circular electrodes in one-step process. One can measure humidity at the bottom of the powder bed simultaneously with resistance across the electrodes. When humidity is instantly raised to a high and constant value, diffusion of moisture starts to take place. During the measurement, both humidity and resistance

data are recorded as a function time. From the humidity data, diffusion coefficient could be calculated using Fick's second law. This information can then be used to calculate humidity at any location between the electrodes at any time. There will be a humidity gradient between the electrodes and thus resistivity between the electrodes will vary in both time and space. Circular electrodes can be considered as a set of separate electrodes with varying cross sectional area and different resistance placed in parallel. So, by combing diffusion equations with geometrical and electrical equations, it could be possible to calculate the resistivity as a function of humidity. However, there are some setbacks. Firstly, the equations turn out to be very difficult to solve and numerical methods could prove more useful than analytical. Secondly, calculations are based on diffusion coefficient which is not a constant but it varies with humidity and hygroscopic properties of powder [10]. Thirdly and more importantly, current between the electrodes is not restricted to the volume between the electrodes alone. In fact, when there is a large resistivity gradient, electric current will find its easiest way to travel from electrode to another and this path extends to the regions above the electrodes. Thus, current density in the system is a complicated function of geometry, electric field, humidity gradient, diffusion, etc.

First approach to tackle the problems mentioned above is to simplify the problem. Since the diffusion equation does not provide reliable information about the humidity between the electrodes, humidity can be measured directly at the electrode location, not at the bottom of the powder bed. With this setup, one important variable in the calculations can be neglected. Also, instead of using relatively large circular electrodes, narrow rectangular electrodes can be used. Then, it can be assumed that humidity is constant inside the volume between the electrodes. When narrow electrodes are used, the problem of current "leaking" to the areas of higher conductivity is emphasized. However, this problem can be overcome by adding additional guard electrodes which homogenize the electric field in the region of interest. Now, the current which flows at more humid and more conductive regions of the resistivity cell flows to the grounded guard electrode and will not be recorded by the current meter.

In this study, dry atmosphere was obtained by purging the chamber with dry air (less than 1 RH%). Resistivity and humidity inside the powder were monitored and when the signals reached a steady-state, humidity of surrounding air was instantly increased to approximately 100 RH% by placing a water containing petri dish into the chamber. Measurement was finished when humidity at the electrode location was more than 90 RH%. For most powders, required time was approximately 10 hours but for flour even 20 days was not enough (Table 1).

B. Materials

The main objective of this work is to present a measurement method. Thus, any powder sample which does not dissolve in high humidities could be used. We have studied three different grades of lactose α-monohydrate; Capsulac 60, Prosmalac 40 and Tablettose 70 (Meggle, Germany), which differ especially in particle size. Particle size was quite large in all these samples, and as a result, diffusion of moisture was also quite rapid. Common wheat flour (Ravintoraisio Oy, Finland) with small particle size and higher absorption was also used and this sample showed much slower diffusion compared to the lactose. Also, Quartz powder (Merck, Germany) was used to include an in-

organic powder which does not absorb moisture. Particle sizes were measured as an aerosol using laser diffraction (Helos H2370, Sympatec GmbH, Germany). Selected particle properties are presented in Table 1. Specific surface areas (SSA) were also measured using gas adsorption technique (TriStar, Micromeritics, USA) and SEM images were also acquired (Fig.1.). Tablettose 70 had highest SSA which was due to highly agglomerated structure as shown in Fig. 1. Prior to measurements, samples were stored in desiccator which contained silica gel. Samples were used as received; no sieving or other handling was performed.

TABLE 1. MEAN PARTICLE SIZES AND SPECIFIC SURFACE AREAS OF USED POWDERS. ALSO, TIME PERIOD IN WHICH HUMIDITY GREW FROM 10 RH% TO 85 RH% SD.

	Particle size d50 (d10-d90) [μm] (n=3)	Specific surface area [m^2/g] (SD, n=2)	Time from 10 RH% to 85 RH% [min] (SD, n=3)
Wheat flour	81.4 (15.7 – 198.2)	0.2122 (0.0011)	> 30 000
Tablettose 70	203.2 (92.3 – 376.0)	0.3480 (0.0010)	823 (177)
Capsulac 60	274.0 (163.4 – 403.0)	0.0780 (0.0010)	636 (145)
Quartz	278.2 (156.0 – 451.6)	0.0328 (0.0002)	420 (60)
Prismalac 40	512.5 (232.5 – 873.9)	0.0795 (0.0005)	396 (32)
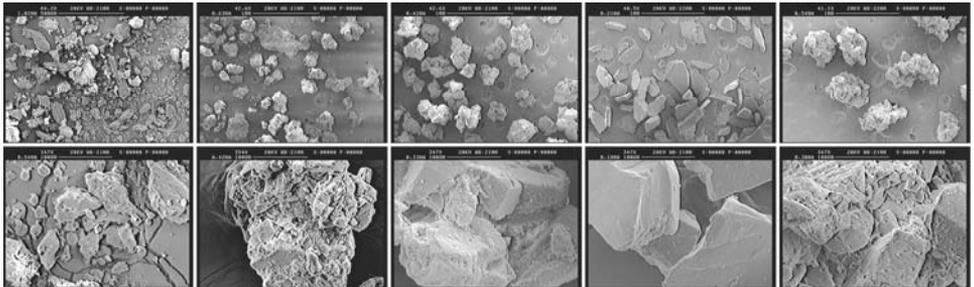
Fig.1. SEM images from left to right: Wheat flour, Tablettose 70, Capsulac 60, Quartz, Prismalac 40

C. Resistivity cell

A new resistivity cell was designed and manufactured at the central workshop of the University of Turku. Schematic image of the device is presented in Figure 2. The device consisted of square cell made of acrylic. Width of the cell was 80 mm and height 80 mm. Two copper electrodes were placed parallel to each other. Electrode which was connected to predefined potential (1000 volts) was square and its width and height were 50 mm. Another electrode was made of two parts: grounded guard plate (height 50 mm and width 50 mm) surrounding a current electrode which was separated from the guard electrode by 1 mm thick insulator. Height of the current electrode was 5 mm and width 30 mm and it was connected to an electrometer (Keithley 6517A, Keithley Instruments Inc.). Electrometer was set to measure resistance across the electrodes. Separation between the electrodes was set to 4 mm, and the center of the electrode was 40 mm from the bottom of the cell. Cell constant K of the resistivity cell was 0.0375 m. Thus, resistivity ρ was calculated from resistance R as $\rho = KR$.
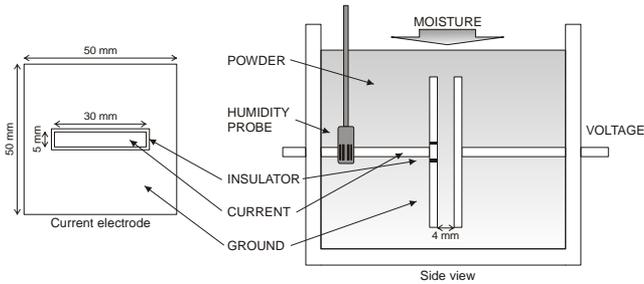
Fig. 2. Schematic diagram of the measurement system

Resistivity cell was surrounded by a sealed and grounded metallic chamber which acted as a Faraday cage and also enabled the humidity of surrounding air to be kept constant. Humidity inside the powder at the same height than the current electrode was measured by placing a probe (HMP37E, Vaisala) into the resistivity cell. The probe immersed in powder was separated from the powder with a fine steel mesh which did not add significant barrier for the water molecules. The probe was shielded with a tape so that an opening of 5 mm (same as the height of current electrode) allowed water molecules to interact with the probe. Thus, it was believed that the probe measured accurately the relative humidity of the atmosphere surrounding the particles. Another probe (HMP35E, Vaisala) measured the ambient humidity inside the metallic chamber. The probes were controlled with HMI38-instrument (Vaisala).

Measured resistance and both humidities were recorded using virtual instrument written with LabVIEW and a PC.

D. Simulations

Model of the resistivity cell was designed with COMSOL Multiphysics –software. Simulations were used to assess the amount of current density between the electrodes and in the regions above the electrodes when a humidity gradient was present.

III. RESULTS

A. Simulations

Simulations were used to assess the path of current density through the powder when diffusion of moisture generates a conductivity gradient between the electrodes. Two different cases were examined. In the first case, heights of both electrodes were 5 mm and widths 30 mm. Electrodes were placed horizontally. In the second case, square electrodes (50 x 50 mm) and a guard electrode were used as described earlier. Diffusion coefficient was $D = 10^{-7}$ m^2s^{-1} and potential difference between the electrodes was $V = 50V$. In the simulation, conductivity as a function of humidity was estimated by fitting exponential decay curve to experimental data. Conductivity as a function of humidity does not follow exponential function precisely, but adequately for estimating current flow through the system. Figure 3a&b show simulated humidity and electrical conductivity profiles from the bottom of the cell to the top of powder layer. Graphs are plotted in selected time intervals from 0 s to 100000 s and are valid for both electrode geometries. As Figure 3a

shows, humidity within the powder was zero at t = 0s and rapidly increased to 100 RH% at the top of the powder (80 mm). As time passes, humidity diffuses into the cell. This causes an increase in the conductivity, as shown in the logarithmic scale in Figure 3b.
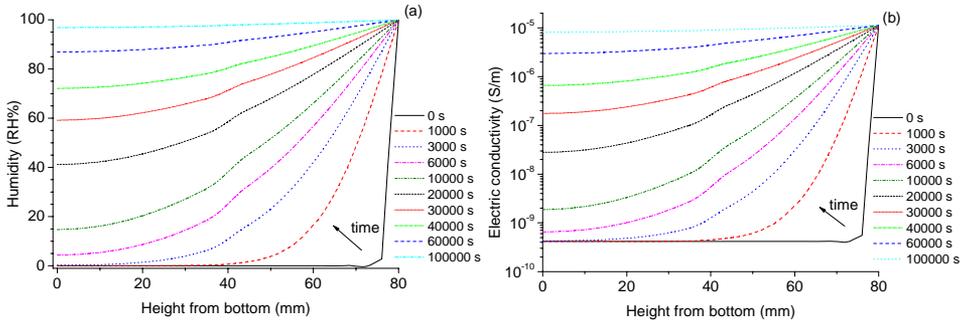
Fig. 3. Simulated humidity (a) and electrical conductivity (b) as a function of height from the bottom of the resistivity cell

Figure 4a shows current density at selected time intervals as a function of height from the bottom of the resistivity cell which had narrow electrodes. It can be seen that the current density was higher above the electrode which located at 40 mm from the bottom. As the diffusion continued, humidity gradient became smaller and the curves were more symmetrical.

Current flowing to current meter was calculated for both electrode geometries and the results are presented in Figure 4b. When there was no significant humidity gradient across the powder, that is at the very beginning and in the end of diffusion period, the current was approximately 300 % higher in narrow electrode geometry than in the guard plate geometry. Difference is emphasized at t = 5000 s when the humidity gradient is strong; difference was 775 %. This clearly demonstrates that significant amount of current is passing through more humid areas outside the volume between the electrodes. When resistivity as a function of humidity is finally calculated and plotted (Fig. 5.), differences between electrode configurations can easily be observed. Figure 5 shows that error in resistivity is almost one order of magnitude if guard plate is not used.
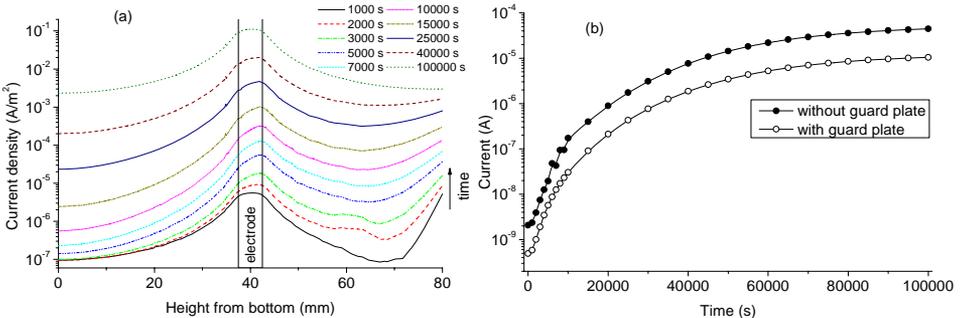
Fig. 4. Simulated current density as a function of height from the bottom of resistivity cell (a). Current flow to electrometer for both electrode geometries as a function of time (b)
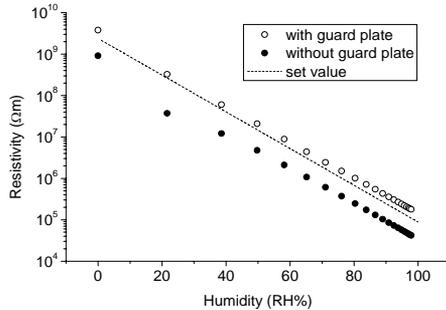
Fig. 5. Simulated resistivity as a function of humidity. Dotted line shows the predefined value

B. Experiments

Figure 6 shows measured resistivities of three lactose samples, wheat flour and quartz as a function of relative humidity inside the powder. Due to the sensitivity of measurement setup and very small currents, resistivities above 10^{13} Ωm have to be considered quite unreliable. In many cases, when the humidity of the powder was less than 10 RH%, current through the powder was very small (picoamperes). Increasing humidity by inserting the petri dish caused significant noise to the beginning of the signal. Thus, only data collected above 10 RH% is reported.

It can be seen that the resistivity decreased several orders of magnitude with increasing humidity. Presented curves also show differences in shape. For example, resistivity of Prismalac was high below the humidity of 35 RH% but lactose curves were quite similar at higher humidities. Resistivity change in quartz was smallest due to hydrophobic nature and wheat flour was most conductive. Differences in the shapes of the curves can arise from the different moisture adsorption (and absorption) properties of the samples. Unfortunately, when adsorption isotherms were measured for each sample, it was found out that adsorption was below detection limits of the instrument in the humidity range from 0 RH% to 90 RH%. Wheat flour was an exception, weight increase was 18.7 % at 90.2 RH%.
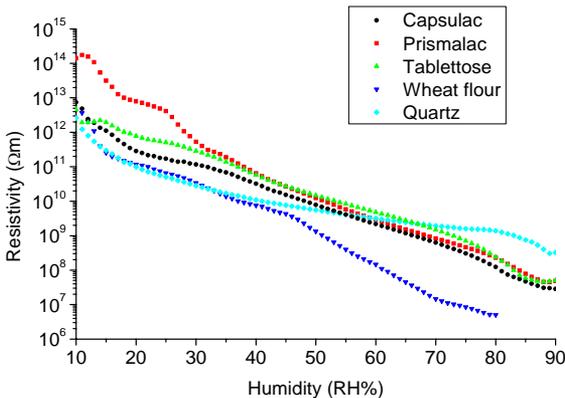
Fig. 6. Resistivities of three different lactoses, flour and quartz as relative humidity was increased

During the measurements it was noticed that as powders were again dried by flushing the chamber with dry air, resistivity increased rapidly in the beginning of the drying cycle and reached a steady state at relative high humidities. In other words, very large hysteresis was observed. As an example, hysteresis loops of three cycles of quartz are presented in Figure 7a. From the hysteresis it follows that the recorded resistivity data is not comparable with resistivities measured using steady state method.
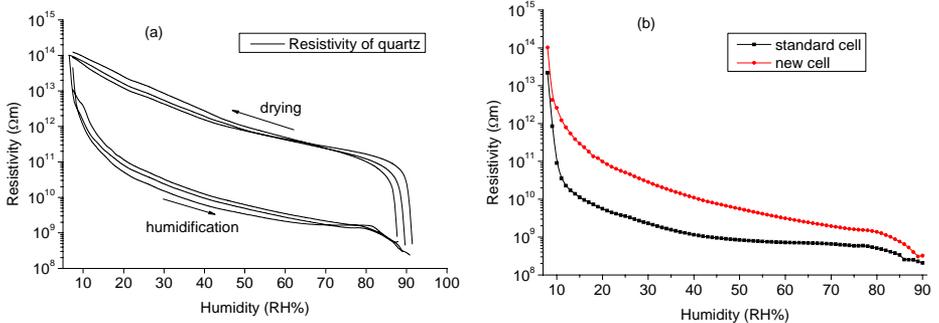
Fig. 7. Hysteresis of resistivity of quartz (a) and comparison of quartz resistivity in standard cell and new resistivity cell

Comparison between the standard cell and the presented method was also performed. In this study, resistivity of quartz was also measured using a standard cell. Humidity was recorded at the height of electrode center. Figure 7b shows a behavior which could be expected. At low humidity, values of resistivities were quite similar. Standard cell showed lower resistivity which could be due to non-uniform field at the electrode edges. In other words, some current passed through the powder in regions outside the volume between the electrodes. As humidity of surrounding air was changed to 100 RH%, current increased very rapidly due to diffused humidity and increased conductivity of powder between the top parts of circular electrodes. Resistivity difference was highest at 12 RH% (3400%) but it decreased with increasing humidity and at 89 RH% resistivity with new cell was only 34% higher than the one measured with standard cell. This difference may be due to different particle packing between the electrodes but more likely due to non-uniform electric field of standard cell.

IV. DISCUSSION

Computer simulations show that the developed electrode arrangement could be used to study the change in resistivity as diffusion of moisture takes place. By placing a grounded guard electrode around the current electrode, the electric field becomes uniform and stray currents which flow through more conducting areas at the upper area of the cell will not be recorded. As a result, presented resistivity cell will show higher resistivities compared to standard cell.

Significant hysteresis was observed when the sample was successively humidified and dried. It is assumed that as diffusion of humidity begins, water molecules are rapidly adsorbed on the surfaces of particles which provide a path for the current to flow and thus reduce the surface resistivity. Depending on the material, water molecules may then ab-

sorb deeper into the material which results in reduced bulk resistivity. When humidity is decreased, adsorbed water molecules quickly desorb into free space between the particles and surface resistivity decreases. Absorbed water molecules diffuse out from the particles more slowly and desorb as they reach the particle surface and thus bulk resistivity is increased.

Since resistivity is very sensitive to the amount of adsorbed moisture, this measurement method could be utilized in studies concerning various surface processes. For example, small surface amorphicity is very difficult to quantify. However, amorphous layer of only few atomic layers is much more reactive that crystalline and will absorb more moisture [11]. Accurate measurement of resistivity as a function of humidity could provide a method for studying adsorption and recrystallization processes. In future, measurements will be performed with materials, which undergo phase transformation as a function of moisture.

V. ACKNOWLEDGEMENTS

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