

ELECTRICAL RESISTANCE MEASUREMENTS OF KAOLINITE AND SERPENTINE POWDERS DURING DEHYDROXYLATION*

by

M. NAKAHIRA

Pennsylvania State University, University Park, Pa., U.S.A.

ABSTRACT

Direct current resistance measurements were made of kaolinite and serpentine powders to follow the changes in resistances during their dehydroxylation processes in air. The resistance of kaolinite remained almost constant during the dehydroxylation, whereas that of serpentine showed a rapid decrease. The formation of distorted lattice sites where the charge carriers are scattered under an electric field was assumed in the former case. On the other hand, the result in the latter case was interpreted in terms of an increasing cation mobility.

INTRODUCTION

LITTLE work has been done so far on the electrical properties of clay mineral powders in relation to their thermal decomposition and transformation processes. Freund (1960) attempted to follow the change in the electrical resistance of metakaolin to the subsequent phases over a temperature range 700 to 1300°C. More recently, Toussaint (1961) and Fripiat and Toussaint (1963) have studied the dehydroxylation process of kaolinite by measuring the change in a.c. conductivities in vacuum as well as under various water vapour pressures, together with parallel infrared observations; they have put forward a concept of proton delocalization to explain their experimental results.

The present author has attempted to obtain experimental information concerning the d.c. conductivities of kaolinite and serpentine with the main object of seeing whether a suspected difference in the dehydroxylation behaviors of these minerals might be followed by electrical resistance measurements. Difficulties inherent in making d.c. measurements on powder specimens have been encountered, however, in interpreting the experimental data. No attempts are made, therefore, to draw quantitative

*Contribution No. 63-57, College of Mineral Industries, The Pennsylvania State University, University Park, Pa.

conclusions from the present experiments. Efforts were made to observe the resistance behaviors of specimens as the dehydroxylation proceeded.

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EXPERIMENTAL

A kaolinite from Georgia was used which contained small amounts of chlorite. Serpentine powders, less than 200 mesh particle size, were obtained

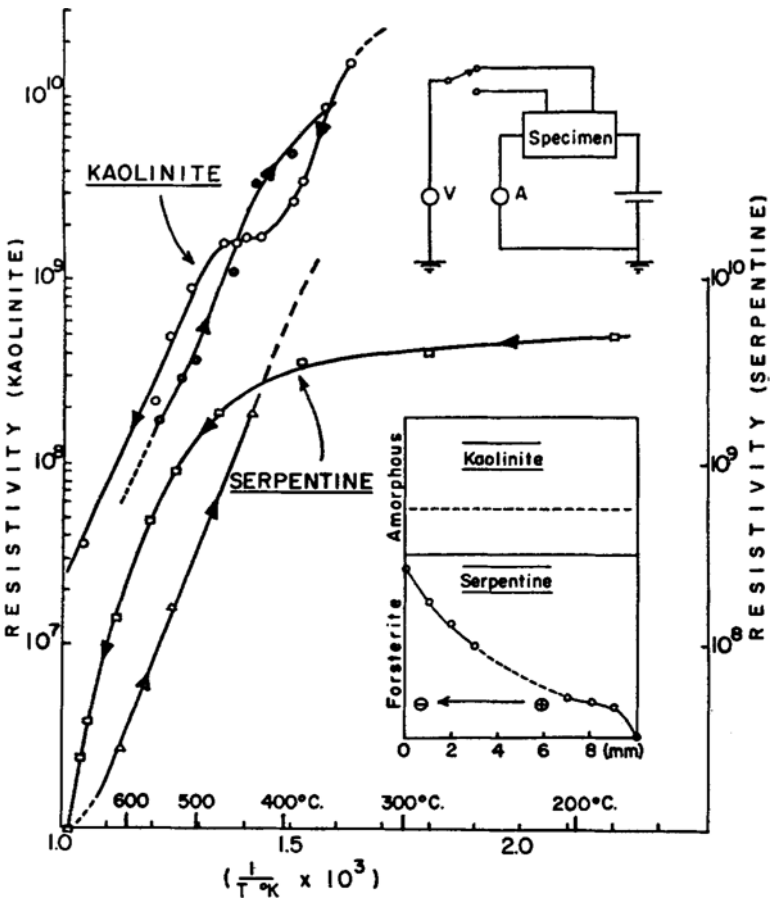


FIGURE 1.—Block diagram of the measuring circuit, resistivity curves of kaolinite and serpentine, and products after dehydroxylation. $\text{Log}_{10} R$ for kaolinite is shown on the left ordinate; for serpentine on the right.

from a massive serpentine from Quebec Province, Canada, which showed no impurities by X-ray diffraction.

Clay powders were wet with a few drops of acetone and small cylindrical pellets, about 10 mm in length and 9 mm in diameter, were made in a pellet mold by applying hand pressures. They were dried thoroughly at 160°C for 24 hr. This procedure made the specimens hard enough for the subsequent measurements.

A resistance cell was constructed with a fused silica framework and with platinum electrodes pressed against the specimen. To measure the resistance of the specimen, two potential probes were pressed tightly on the specimen as shown schematically in Fig. 1, in which a block diagram of the measuring circuit is given. A Keithley 610R electrometer and a General Radio 1230-A type electrometer were used to measure the potentials of the probes and the current through the specimen, respectively. A stable d.c. voltage of 30 V was applied to the electrodes from a Kepco SM-160-2MX power supply. The resistivity of the specimen was calculated from the probe spacing, the potential difference between the probes, the current through the specimen, and the geometry of the specimen. It was assumed that the resistance of the specimen was of ohmic character.

When the temperature reached a predetermined value, the specimen was held at that temperature for at least 10 hr to attain thermal equilibrium. This was necessary also to avoid the effect of water liberated from the specimen. The voltage was then applied for a certain length of time to measure the resistance, and if a current decay was observed the reading was taken after the current had become steady. The time required to reach a steady state was variable, ranging from about 30 min to more than an hour. A decay of this kind was observed frequently with serpentine specimens. A heating and a cooling cycle were carried out for each run. The results are given in terms of \log_{10} (resistivity) versus inverse absolute temperature on the left hand side of Fig. 1.

To examine the specimen after complete dehydroxylation, another line of experiments was conducted. The specimen, when completely dehydroxylated, was kept at constant high temperature with 30 V applied on the electrodes for 4 hr. It was then taken out of the furnace and sliced layer by layer for X-ray examination. The phases formed were not measured quantitatively; only a qualitative result is given on the right-hand side of Fig. 1.

RESULTS

On heating kaolinite, the $\log R-1/T$ curve indicates three different stages of the process. The first stage extends to 430°C and a decrease in resistivity is observed as the temperature is raised. The second stage, between 430°C and 490°C, corresponds to the dehydroxylation process and

the resistivity now remains almost constant. Upon completion of dehydroxylation, the third stage again exhibits a sharp decrease of resistivity. The cooling curve of the same specimen lacks this second stage, as shown in Fig. 1.

A heating curve for serpentine is represented by two steps. The first one continues to about 450°C and a slow decrease in resistivity is observed throughout this range. Then the resistivity starts to decrease very rapidly as the temperature is raised above 500°C. The cooling curve is almost straight down to about 400°C. At about 350°C, a very high resistance of the specimen made it almost impossible to make reasonable measurements.

A few remarks should be made concerning the behavior of the current passing through the specimen. With kaolinite specimens little current decay with time was observed until the temperature reached about 700°C. On the other hand, the serpentine specimens always showed a decay at each temperature above 450°C.

The second line of experiments as described in the previous section showed that, with a kaolinite specimen held at 550°C for 4 hr under an applied d.c. field, no crystalline material was observed. In contrast to this case, forsterite was found to form increasingly towards the negative side of the serpentine specimen held at 650°C.

DISCUSSION

With the present experiments, little can be said about the conduction mechanisms for kaolinite and serpentine. The data obtained should be discussed in terms of particle contact phenomena or surface properties of particles.

The present results for kaolinite are largely consistent with those of Fripiat and Toussaint (1963), except that in the second stage they found a small increase of resistivity with rising temperature whereas in the present experiments the resistivity remains largely constant. Also, their dehydroxylation temperature was somewhat lower than in the present work. Probably these differences arise from the lower ambient pressures in their experiments. On the basis of their data, they concluded that the conduction in the first and second stages arises from a proton delocalization process; and consequently the increase in resistivity in the second stage (dehydroxylation) was considered to be due to the loss of protons as water molecules. The theory implies an electrolysis process under an electric field.

An alternative explanation, however, is possible. As dehydroxylation proceeds, an increasing number of distorted lattice sites may be produced, at least on the surface of the particles, as a result of loss of oxygens from the crystal lattice. These sites may scatter the charge carriers, whatever they may be, resulting in an increase of resistance of the specimen. In the

present experiments, the measured resistances can be regarded as arising mainly from surface-surface contacts. No sintering was observed. The surface distortion may have caused an increase of resistance.

The resistivity-temperature variation of serpentine differs from that of kaolinite in that a rapid decrease occurs in the stage of dehydroxylation. In the line of thought described above this may indicate that the dehydroxylation of serpentine proceeds in a relatively orderly way as compared with that of kaolinite and distorted lattice sites are not necessarily formed. What causes the rapid decrease in resistance is still open to question. It might arise partly from an increase in the cation mobility during the dehydroxylation. If the cation mobility increases, it will contribute to the total conductivity and so decrease the resistance of the entire system. The current decay observed with time may be a sign of space-charge build-up caused by the migration of cations. Unless the migrating cations are discharged freely at the negative electrode and supplied spontaneously from the other electrode, the resulting space-charge build-up in the specimen will impede the current (see von Hippel, 1959). With kaolinite, little decay was observed.

CONCLUSION

Little has been proved in the present experiments. However, the results show the possibility of a new approach to the problem of dehydroxylation, and, therefore, are presented in the hope that further experimental work will be undertaken.

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