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IN KAOLIN MEMBRANES

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The relative conductance at room temperature of a solution in kaolin membranes was studied as a function of the volume fraction of the membrane. The resistances of the membrane and of the solution were measured for various volume fractions, and the conductance of the membrane relative to the solution was calculated.

The relative conductance was linear with solid volume fraction over a range of volume fractions from 0.422 to 0.776. The equation was

$$K_m = 1.337 - 1.673f$$

where K_m is the ratio of the conductance of the membrane to the conductance of the solution, and f is the volume fraction of the membrane.

At volume fractions less than 0.5, the relative conductance was definitely greater than would be expected from an inert membrane.

The enhancement of conductance was attributed to surface conduction along the pores of the membrane.

THE ELECTRICAL CONDUCTANCE OF AQUEOUS SOLUTIONS
IN KAOLIN MEMBRANES

by

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THE ELECTRICAL CONDUCTANCE OF AQUEOUS SOLUTIONS IN KAOLIN MEMBRANES

INTRODUCTION

Porous bodies are often used to separate electrodes in batteries and some electrolysis cells. Since such separators affect the internal resistance of the system, it is of interest to determine the in situ conductance of the separator as a function of its physical parameters.

One material that may be formed into a variety of separators is kaolin. Kaolin may be fired to produce a wide range of volume fractions. Also, the ion-exchanging ability of kaolin might be expected to enhance its conductance over that of a completely inert separator.

One of the most widely used methods of studying the conductance of a membrane is to study its relative conductance. The relative conductance is the ratio of the conductance of a solution impregnated membrane to the conductance of the solution if it occupied the whole space of the membrane. In the petroleum and ceramic industries the reciprocal of the relative conductance is called the formation factor.

The object of this thesis was the study of the relative

conductance at room temperature of fired kaolin membranes impregnated with tap water. The study was made possible by the use of a conductance cell which could be used to measure both the conductance of the solution and the membrane.

The study was concerned with the development of equipment and techniques for attaining the following objective: A relationship between the relative conductance of a kaolin membrane and the volume fraction of the membrane. From this objective, it was desired to find whether or not the conductance of the membrane was enhanced over that of a completely inert membrane.

BACKGROUND

Kaolin is a clay. Seven minerals belong to the kaolin group: nacrite, dickite, kaolinite, anauxite, metahalloysite, halloysite, and allophane. The first three minerals have a theoretical composition of $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ while the rest are distinguished by having varying proportions of Al_2O_3 , SiO_2 , and H_2O . The formulas are not meant to imply that distinct Al_2O_3 , SiO_2 , H_2O molecules exist in the clay. The various minerals are distinguished by their crystal structures and temperatures of dehydration.

The firing of kaolin above 1000°C . develops resistance to deformation while retaining a large part of the pore space. According to H. Salmang (10) the porosity is composed of many types of pores. Micropores and coarser pores may be present in the clay particles, and fine and coarse pores or voids may be present between the particles. The situation is complicated by the fact that the pores may be open or closed depending upon whether or not they have been sealed. Although the micropores may be considered open when filled with air, they may be closed to water if the water does not fill them.

D. A. Holdridge and M. Francis (4) extracted water soluble

salts from clay by using distilled water. The amount of salt that could be extracted contained only about seven percent of the total of all absorbed ions.

G. W. Phelps (9) investigated the ion-exchange capacities of kaolin, montmorillonite, and illite clays. He found that the ion exchange capacity of kaolin was from three to 15 milliequivalents per 100 grams of dry clay. W. E. Worrall, R. W. Grimshaw, and A. L. Roberts (13) found that the ion-exchange capacity of kaolin varied with particle size. This result would be expected of surface phenomena.

Dispersions

Many authors have developed equations for the relative conductance of spheres, ellipsoids, and cylinders dispersed in a medium. The relative conductance (K_m) is defined as the ratio of the conductance of the mixture of solid and impregnating solution (k_m) to the conductance of the solution (k_c). The volume fraction (f) is defined as the ratio of the volume of the solids to the total volume of the mixture.

J. C. Maxwell (6) considered the case of spheres dispersed in a medium, with each sphere acting as if it were alone in the medium. Hence, Maxwell's equation was expected to hold for only small volume fractions. In the case of nonconducting spheres, his relation between the relative conductance and the volume fraction was

$$K_m = \frac{2(1-f)}{2+f} \quad (1)$$

Many other significant equations are reviewed by R. E. Meredith (7). In all the treatments reviewed, the predicted values of the relative conductance have values equal to or less than the value predicted by the equation

$$K_m = (1-f) \quad (2)$$

provided that the solid was nonconducting.

Porous Media

D. Arguss, H. R. Karas, and V. L. Decker (1) considered the case of a porous body consisting of voids and interconnecting passages. They express the relative conductance as a function of the tortuosity (T) of the passages in a membrane and the effective volume fraction (f_e). Their equation is

$$K_m = T^{-2(1-f_e)} \quad (3)$$

Arguss, Karas, and Decker recognize two types of volume fractions: the actual volume fraction and the effective volume fraction. The actual volume fraction is defined as the ratio of the volume of the solid to the volume of the porous body. The effective volume fraction is defined as one minus the ratio of interconnecting channels and voids to the volume of the porous body.

The tortuosity is defined as the ratio of the actual length traveled by an ion in going from one face of a membrane to the other parallel face, to the actual distance between the parallel faces of the membrane. The distance to be traversed is not the same for all ions due to interconnecting passages within the membrane. Thus, the tortuosity is statistical in nature.

M. J. R. Wyllie, and M. B. Spangler (14) have noted that the tortuosity can be an order of magnitude greater for consolidated porous membranes than for compacted porous bodies. It is to be noted that the tortuosity should always be greater than one since the straight line distance between the parallel faces of a membrane should be the shortest distance which can be traversed by an ion.

J. E. Owen (8) has considered a model which consists of passages of square cross-section which pass through cubical void spaces. He defined a constriction factor as the ratio of the length of a side of a cubical void to the length of a side of the cross-section of the passage. He deduced that more than one combination of tortuosity and constriction factor could be used to calculate the same value for the relative conductance at a given volume fraction. This would indicate that there is no unique relation between the electrical and geometrical properties of a porous medium. Hence, the notion of tortuosity is in doubt.

Wyllie and Spangler (14) have investigated the effect of partial

saturation of a porous medium which had been initially saturated with a solution. The effect was to decrease the conductivity of the porous body. They defined a resistivity index as the ratio of the relative conductivity when the body was saturated to that of the body when it was unsaturated. They experimentally determined that the relation between the resistivity index (I) and the fraction saturation (S_w) was

$$I = S_w^{-m} \quad (4)$$

The exponent, m , was found to be independent of the absolute value of saturation but dependent upon the composition of the porous body.

G. E. Archie (2) has experimentally determined that the relation between the volume fraction and relative conductance is

$$K_m = (1 - f)^{+m} \quad (5)$$

The value of the exponent was found to range between 1.8 and 2.0 for sandstone.

J. W. Lorimer, E. I. Boterenbrood, and J. J. Hermans (5) investigated the conductance of viscose membranes. The viscose membrane was ion-selective and was impregnated by aqueous solutions containing various concentrations of potassium chloride. The relative conductance of the membrane increased with increasing salt concentration. At a concentration of 0.00107 equivalents per liter the relative conductance was 0.70 while increasing the concentration to 0.00497 equivalents per liter increased the relative conductance to 1.34. It is to be noted that a small addition of salt increased the

relative conductance enormously.

W. T. Grubb (3) investigated the conductivity (k_m) of an ion-selective membrane composed of a phenolic resin. He found that the conductance of the membrane was a strong function of the activity of the water (a_{H_2O}) in the membrane, namely

$$\log_{10} k_m = 0.0899 + (1.920) a_{H_2O} \quad (6)$$

when

$$.2 < a_{H_2O} < 1.0$$

N. Street (12) studied the surface conductance of kaolinite. Due to the existence of an electrical double layer at the solid-liquid interface of a particle, there exists a higher concentration of ions near the phase boundary than in the rest of the solution. The conductance due to the ions near the phase boundary is the surface conductance. Street studied the surface conductance of kaolinite suspensions in a calcium chloride solution over a range of volume fractions from 0.011 to 0.045. He found that the surface conduction enhanced the conductance of the suspension.

EXPERIMENTAL METHOD

The measurement of the relative conductance of a sintered membrane requires a means of measuring the resistance of the membrane and the resistance of the solution in the pores of the membrane. The solution used was tap water from which the air had been removed. In order to eliminate temperature effects, the resistance measurements of solution and of membrane were taken simultaneously in a special conductance cell.

The conductance cell is shown in cross-sectional and expanded views, in Figure 1. The apparatus depicted consisted of the following parts:

- (1) Three perforated copper electrodes.
- (2) A plastic spacer which formed a cell chamber for the measurement of the conductance of the solution. The spacer was $\frac{1}{4}$ inch thick.
- (3) A plastic spacer which formed a cell chamber for the measurement of the conductance of the membrane impregnated with solution. The spacer was $\frac{1}{4}$ inch thick and the same inside diameter as the other spacer.
- (4) Chambers on either side of the electrodes.

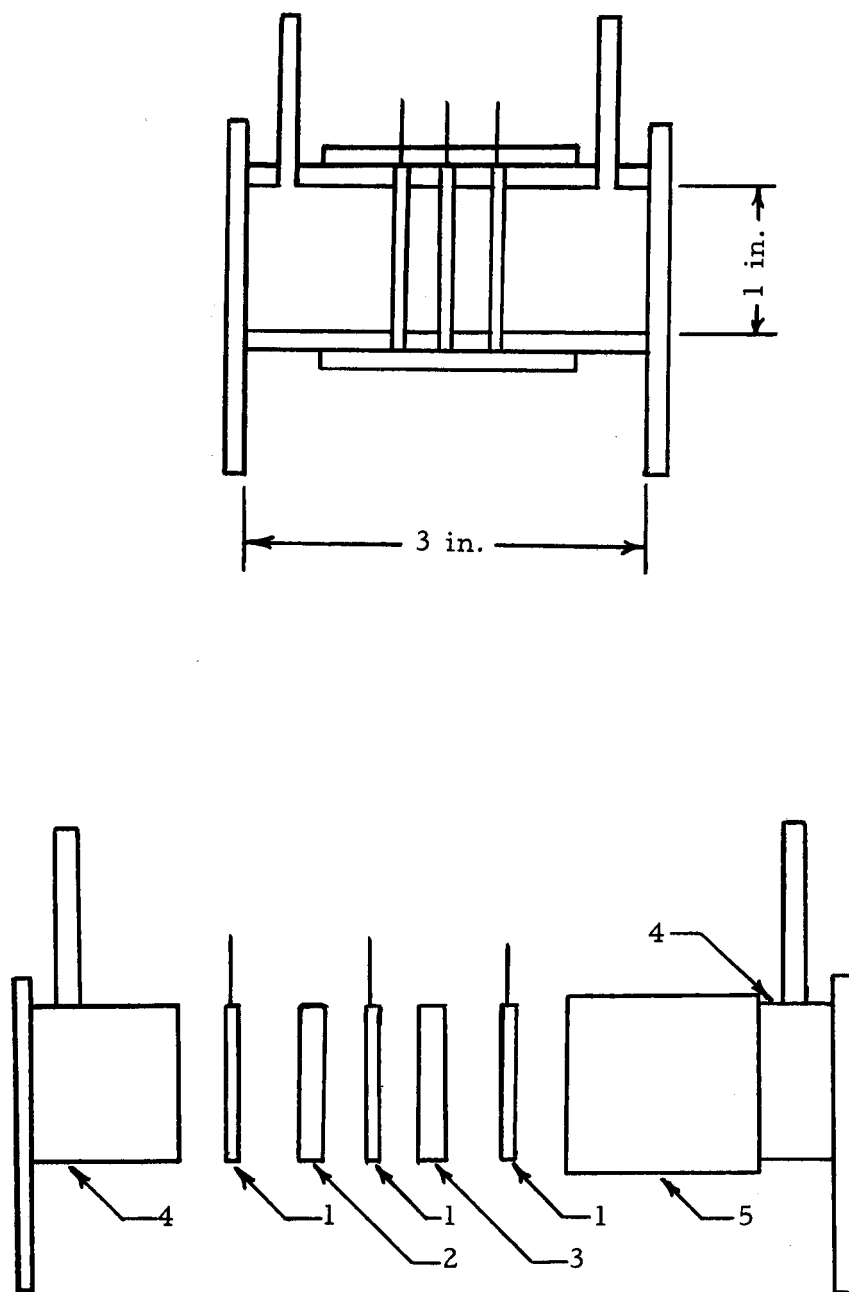


Figure 1. Cross-Sectional and Expanded View of Conductance Cell.

- (5) A plastic sleeve which held the assembly together.

All parts of the cell except the electrodes were made from Plexiglass. The electrodes were made from copper sheets.

If the ratio of the conductance of the membrane in one cell chamber to the conductance of the solution in the other cell chamber was to be the relative conductance, the two cell chambers had to have the same conductance when containing only solution. The conductance of the solution in the two cell chambers was experimentally found to be the same within three significant figures.

A schematic diagram of the A. C. bridge is presented in Figure

2. The apparatus depicted consisted of the following parts:

- (1) Three General Radio Company type 1432-M decade resistance boxes.
- (2) A capacitance box.
- (3) A General Radio Company type 1212-A null detector with a type 1203-B power supply.
- (4) A General Radio Company type 578-A transformer.
- (5) A General Radio Company type NO1210- C adjustable oscillator with a type 1203-B power supply.
- (6) A Radio Corporation of America type 160-B cathode ray oscilloscope.
- (7) A conductance cell.

The membranes were prepared from Baker and Adamson Code

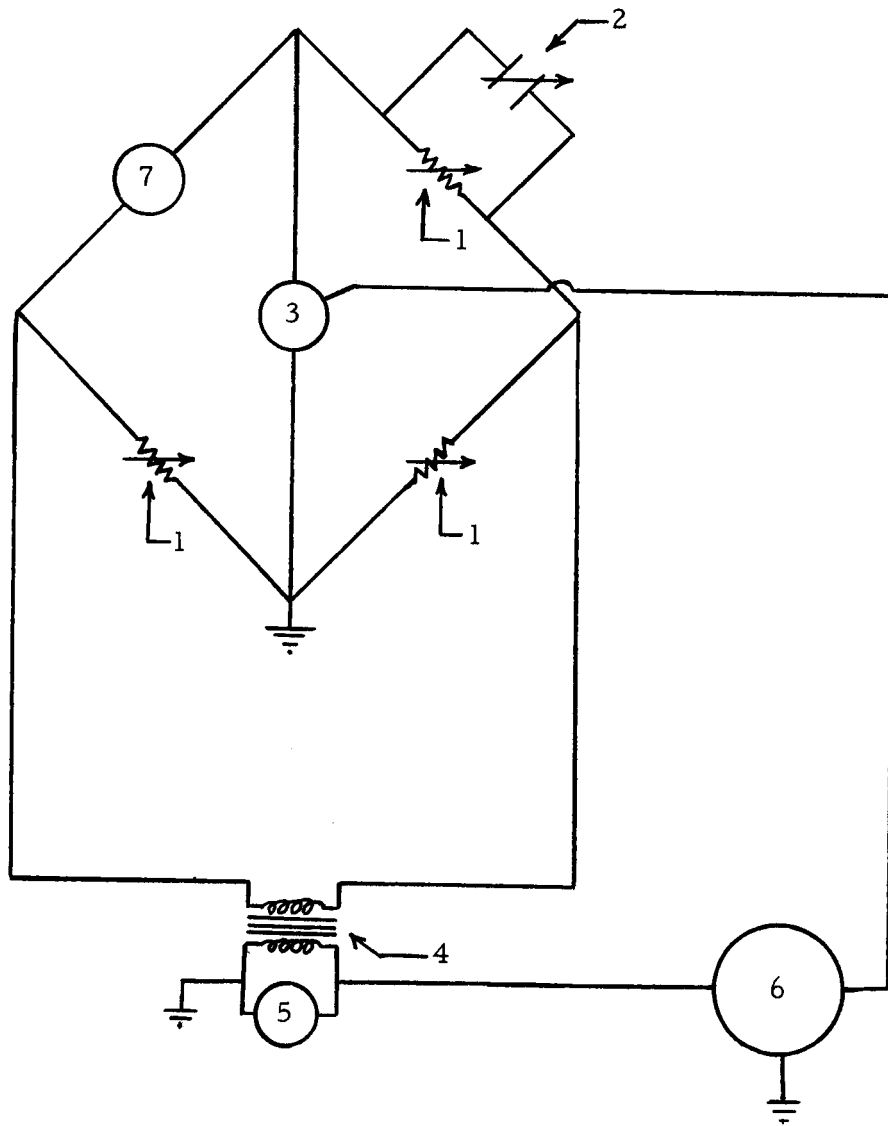


Figure 2. A. C. Bridge Circuit Schematic.

1814 kaolin powder. The finished membranes were cylindrical with a thickness of $\frac{1}{4}$ inch and had a diameter varying between $\frac{13}{16}$ and one inch. The membranes were prepared by first sintering kaolin powder for two hours at 800°C . The sintering dehydrated the powder and caused the powder to become coarser.

Before the sintered kaolin could be pressed into membranes, water had to be added to the kaolin so that a mixture containing eight percent water was formed. The water acted as a lubricant during pressing. A one inch inside diameter cylindrical steel die was used to form the membranes. During pressing, the pressure on the face of the piston in the die was 900 psi. The membranes were then dried and fired.

The porosity of a membrane is dependent upon the firing temperature and upon the duration of firing. The porosity decreases with both increasing temperature and increasing duration of firing. The conditions under which the membranes were fired in a Pereco Model LB80-104 electric furnace during this experiment are presented in Table 1. As can be seen in Table 1, the volume fraction increased as the firing temperature increased.

The porosity of the membranes was measured by their absorption of water. A fired membrane was allowed to absorb water from the air until it reached constant weight. The dimensions of the membrane were measured with a caliper, and the volume of the membrane

was calculated. The membrane was immersed in water for one day and was then placed in boiling water for 15 minutes in order to expel all of the air in the membrane. The water impregnated membrane was then weighed and the amount of water absorbed obtained by difference. The void fraction was then obtained by dividing the weight of absorbed water by the density of water and by the volume of the membrane. The volume fraction was obtained by subtracting the void fraction from one.

Table I. Firing of Kaolin

Volume Fraction	Firing Temperature, °C	Duration of Firing, hr
.422	1000	10.4
.469	1100	22.2
.599	1200	10.5
.676	1290	10.5
.776	1400	10.5

Conductance measurements were made three times for each membrane. The conductance cell was disassembled and reassembled between each measurement. The spacers and sleeve were sealed in place by the use of "Lubriseal" stopcock grease. The conductance of the grease was negligible.

Each measurement consisted of measuring the resistance of the

cell containing solution and the resistance of the cell containing the solution impregnated membrane. The measurements were repeated until the resistances were constant over a period of 30 minutes. The resistance was measured by the A. C. bridge previously described.

The relative conductance was found by calculating the ratio of the resistance of the solution to the resistance of the membrane. The average value of the relative conductance for the three measurements was used. The maximum deviation of the relative conductance from the average value was 0.006 which amounted to 3.1 percent of the average value.

THEORY AND DISCUSSION OF RESULTS

The simplest model of a porous medium consists of a bundle of straight parallel capillaries of uniform diameter (d) as shown in Figure 3. Such a simplified model has been used by A. E. Scheidegger (11) for the flow of fluids through porous media. The solid material is nonconducting.

Let us consider only the n capillaries which pass through the medium. The conductance of the porous body due to the bulk solution will then be given by the conductance of n parallel resistors each of resistivity, r , length, l , and cross-sectional area, A . The conductance is

$$k_m = \frac{nA}{rl}.$$

If the bulk solution had occupied the whole space of the membrane of cross-sectional area, A' , the conductance would be given by

$$k_c = \frac{A'}{rl}.$$

Letting K' represent the ratio of k_m to k_c , we obtain

$$K' = \frac{nAl}{A'l}.$$

But

nAl = effective volume of the pores,

and

$A'l$ = volume of the membrane.

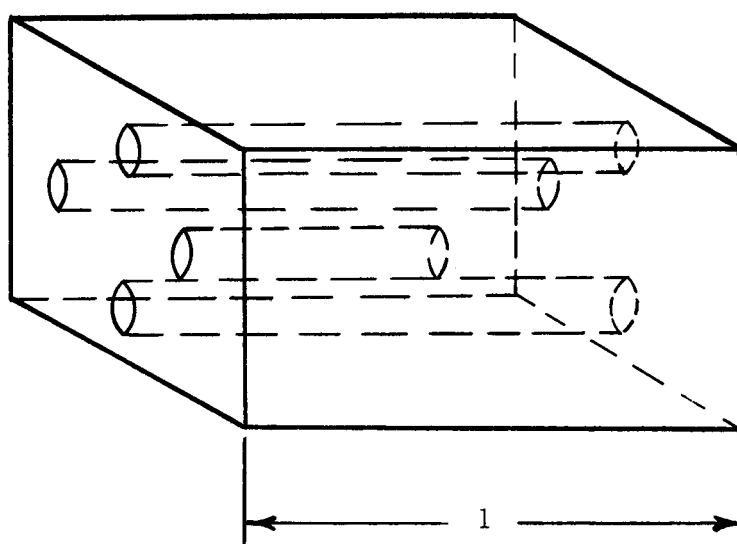


Figure 3. Proposed Model of Membrane.

Since the effective volume fraction (f_e) is defined as one minus the ratio of the effective volume of the pores to the volume of the membrane,

$$(1 - f_e) = \frac{nAl}{A'l},$$

and
$$K' = (1 - f_e). \quad (7)$$

Now, assume that there also exists a significant surface conduction along the surface of the capillaries and that the relative conductance due to surface conduction (K'') is proportional to the surface area of the pores. Since the surface area is proportional to the number of capillaries, and the volume of the pores is proportional to the number of pores, the relative conductance is proportional to one minus the effective volume fraction. Let the constant of proportionality be denoted by B ; then

$$K'' = B(1 - f_e). \quad (8)$$

Since both the surface conduction and the bulk conduction are occurring throughout the whole length of each capillary, the conduction must be in parallel. The equation for parallel conductances is

$$K_m = K' + K''.$$

Therefore,

$$K_m = (1 + B)(1 - f_e). \quad (9)$$

In order to use the actual volume fraction (f), a correction factor (y) is defined by

$$y = \frac{f}{e}. \quad (10)$$

Substituting Equation 10 into Equation 9, the following linear equation is obtained:

$$K_m = (1 + B)(1 - yf). \quad (11)$$

This model is not meant to be a rigorous description of the membrane, but it is presented as a simplified explanation for a straight line relationship with a slope less than minus one between the volume fraction and the relative conductivity. A rigorous treatment would have to consider tortuosity and constriction factors as well as volume fraction. Also, the implied assumption that the effect of varying the volume fraction is only to vary the number of pores is unrealistic. Actually the diameters of the pores may change as well as the number of pores, the tortuosity, and the constriction factor. For these reasons, the simple idea of surface conduction as presented above would not be expected to be true.

The kaolin membranes which were used were nonconducting. This fact was determined by drying a membrane and letting it equilibrate with the moisture in the air. After equilibrating, the membrane was placed between two electrodes in the conductance cell, and its resistance was measured. The resistance was found to be on the order of 2×10^7 ohms. Since the resistance of the solution impregnated membrane was on the order of 10^3 ohms, the kaolin was

considered to have been nonconducting.

The experimental relative conductance and volume fraction values are presented in Table II and Figure 4. Each point plotted in Figure 4 is the average value of three measurements as listed in Table II. As can be seen from Figure 4, the data could be fitted by means of a straight line within a range of volume fractions from 0.422 to 0.776. The equation of the line obtained by the method of least squares is

$$K_m = 1.335 - (1.673)f. \quad (12)$$

If this equation is put in the same form as the equation predicted by the simplified model, the result is

$$K_m = (1 + 0.335)[1 - (1.253)f]. \quad (13)$$

By comparing Equation 13 with Equation 11 for the simplified model, it may be readily seen that the constant of proportionality for the surface conductance term had the value 0.335 while the void volume correction factor had the value 1.253. This meant that 25.1 percent of the relative conductance could be interpreted to be due to surface conduction. Also, the effective volume fraction was 125.3 percent of the actual volume fraction, or 20.3 percent of the capillary pores were closed. It must be emphasized that the above interpretations are true only insofar as the model is true.

One of the most striking things about the experimental data is

Table II. Experimental Data

Membrane	Individual f	Individual K _m	Average f	Average K _m
1	.424	.626	.422	.626
	.422	.631		
	.422	.621		
2	.469	.550	.469	.550
	.469	.548		
	.469	.553		
3	.616	.334	.599	.336
	.599	.338		
	.599	.335		
4	.676	.197	.676	.195
	.676	.189		
	.676	.199		
5	.776	.0478	.776	.0470
	.776	.0465		
	.776	.0467		
6*	.611	.320	.610	.322
	.610	.321		
	.610	.325		

* These values were for the water-washed membrane.

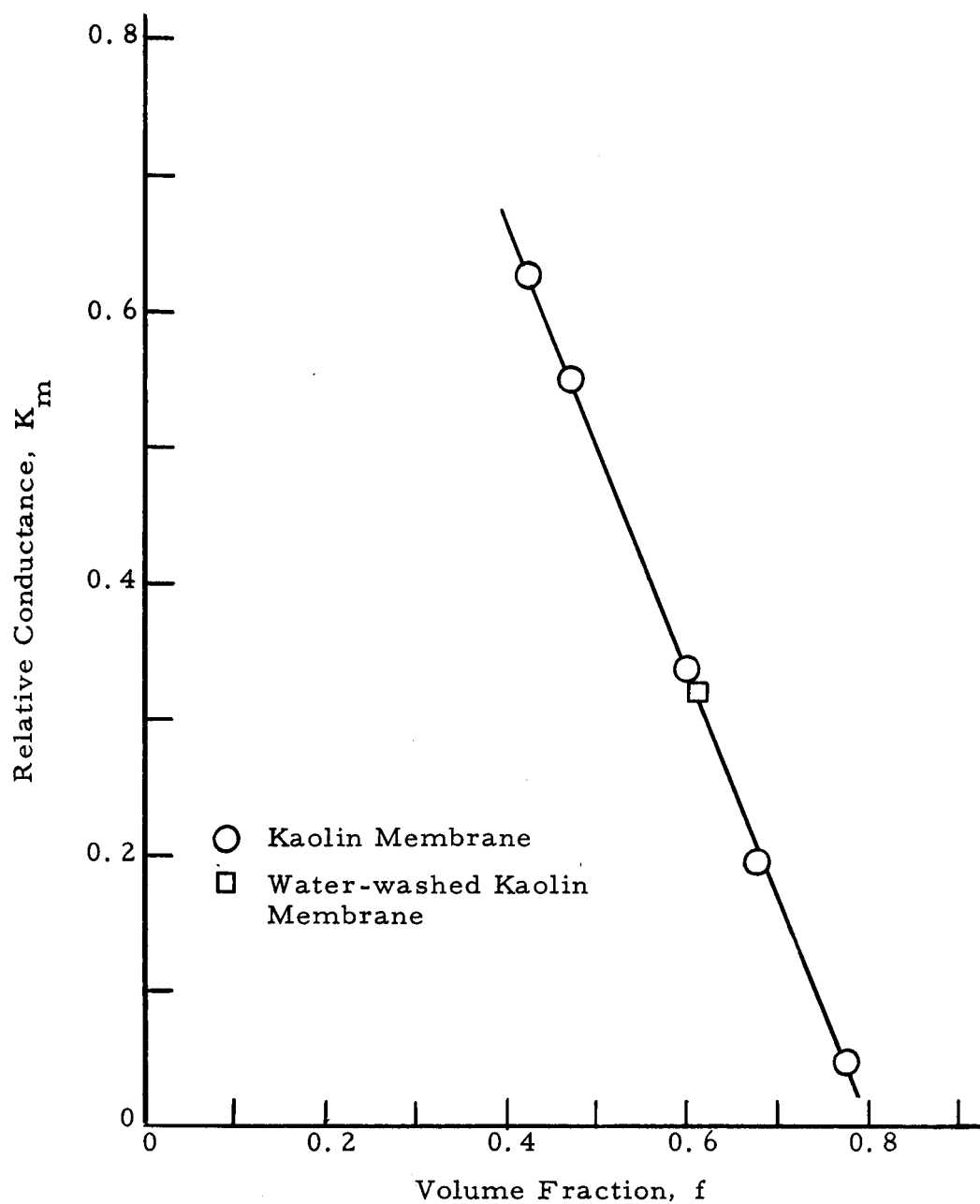


Figure 4. Relative Conductance of Kaolin Membranes.

that the relative conductance was higher than would be predicted from the equation

$$K_m = (1 - f_e) \quad (14)$$

provided 20.3 percent of the capillary pores were closed. For true volume fractions less than 0.5, the observed relative conductance was higher than predicted by Equation 14 even if no pores were closed. This can be most readily seen by looking at Equation 13. As was pointed out in the section on Background, the equations for beds of ordered spheres, ellipsoids, and cylinders all predict values of relative conductance below that predicted by Equation 14. Equation 3 for porous media also predicts a relative conductivity below that predicted for Equation 14. The reason for this is that the tortuosity should be greater than or equal to one. It can be seen that pure conduction through the solution in the pores can not alone account for the large values of relative conductance observed. The above reasoning leads one to the conclusion that either surface conductance or some other closely related phenomenon was responsible for the increased conductance observed in the experiment. The observation of surface conductance in kaolinite suspensions by Street (12) supports the hypothesis of surface conductance in kaolin membranes.

An experiment was performed to determine if soluble salts in the kaolin membrane had any effects on the relative conductance of the membrane. Sintered kaolin was leached by water until the

conductance of the water was constant for different washings. The kaolin was then fired. The measured volume fraction and relative conductance were 0.610 and 0.322 respectively. As shown in Figure 4, the relative conductance agreed with the value predicted by Equation 12. The water-soluble salts had no apparent effect upon the relative conductance of the membranes since the salts had been leached out of the pores before measurements were taken.

CONCLUSIONS

- 1) Within a range of solid volume fractions from 0.422 to 0.776, the relative conductance of kaolin membranes could be represented by a linear function of the volume fraction of the membrane

$$K_m = 1.335 - 1.673f.$$

- 2) The resistance of a dry kaolin membrane which had been allowed to equilibrate with the moisture in the air was sufficiently high to consider the conductance of the kaolin as being zero.
- 3) The relative conductance of a water-washed kaolin membrane agreed with the value predicted by the equation

$$K_m = 1.335 - 1.673f.$$

- 4) The magnitude of the observed relative conductances of kaolin membranes indicated that surface conduction is a significant factor in the mechanism of conductance.

NOMENCLATURE

<u>Symbol</u>	<u>Definition</u>
$a_{\text{H}_2\text{O}}$	Activity of the water in the membrane
A	Cross-sectional area of capillary pore
A'	Cross-sectional area of membrane
B	Constant of proportionality for surface conductance
d	Diameter of a capillary pore
f	Volume fraction of membrane
f_e	Effective volume fraction
I	Resistivity index
k_m	Conductance of membrane
k_c	Conductance of solution
K_m	Relative conductance of membrane
K'	Relative conductance of membrane due to solution conductance alone in the membrane
K''	Relative conductance of membrane due to surface conduction in the membrane
l	Length of capillary pores
m	An exponent
S_w	Fraction saturation
T	Tortuosity

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