

THE INFLUENCE OF PRESSURE ON THE ELECTRICAL RESISTIVITY OF CLAY-WATER SYSTEMS*

by

W. J. LANG†

University of Illinois

ABSTRACT

THE influence of pressure on the electrical resistivity of clay-water systems was investigated and found to reflect the abnormal nature of adsorbed water. The resistivity of montmorillonite-water systems varied with pressure in a manner similar to a dilute salt solution at pressures above 7000 psi. At pressures below this, abnormal pressure-resistivity relations resulted which were attributed to the presence of abnormal water associated with clay mineral surfaces. The pressure-induced breakdown of the abnormal water associated with montmorillonites was found to occur in abrupt stages as indicated by anomalies in the pressure-resistivity curves.

The anomalies indicated that layers of adsorbed water have differing degrees of structural bonding by which variations of the water-orientating ability of clay minerals may be compared. In general calcium montmorillonite was found to allow the most rigid bonding of the adsorbed water while sodium montmorillonite gave rise to the most extensive development of the abnormal water.

The abnormal water was found to re-form with some hysteresis effects when the pressure was released. An increase in temperature was found to decrease both the amount and the relative strength of the abnormal water.

INTRODUCTION

DURING the past ten years, the complex interaction of clay mineral surfaces with water has been under intensive investigation. Numerous individual investigations have provided evidence which indicates that the water adsorbed on clay mineral surfaces, particularly montmorillonites, has physical and thermodynamic properties that differ from those of normal water. Such differences were generally anticipated because of the theory of "rigid" or "oriented" water that has evolved during the past years as a result of the anomalous behavior of clay-water systems. The present work has been intended further to define differences between clay-adsorbed water and normal liquid water by resistivity and pressure techniques. The material

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† Presently with International Minerals and Chemicals Corp., Libertyville, Ill.

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LITERATURE

Of the more recent investigations, Oster and Low (1963) report that the entropy of water adsorbed on montmorillonite surfaces was lower than pure liquid water and that the more coherent water structure was primarily responsible for a greater activation energy for ion movement. Yamaguchi (1959), in a series of tests, related the development of the structural characteristics of adsorbed water to the strength and sensitivity of soils. The electrical resistivity and heat capacity of the adsorbed water were determined to be greater than that of normal water and closely related to the strength of the soils.

Although considerable experimental evidence has indicated that there is a substantial degree of structural arrangement within clay-adsorbed water, there has been very little evidence from which a sound model can be made interrelating the water structure with the clay surface and the exchangeable cations. A number of models have been proposed in which the *c*-axis of an open-structured ice-like water is parallel to the *c*-axis of the clay mineral (e.g. Hendricks and Jefferson, 1938; Macey, 1942; Barshad, 1949); however, more recently Anderson and Hoekstra (1965) have presented evidence that suggests that the *c*-axis of the adsorbed water may be perpendicular to the *c*-axis of the clay mineral.

An open-structured model of the abnormal adsorbed water has been supported by the density measurements of Anderson and Low (1958) in findings that the density of adsorbed water became less than that of pure water at close proximities to montmorillonite surfaces.

The present investigation was based on the postulate that if clay-adsorbed water has open-structured form and is less conductive than normal water, then pressure should induce a structural breakdown in the water which could be detected by resistivity measurements.

EXPERIMENTAL

Apparatus

In order to measure the influence of pressure on the resistivity of clay-water systems, a pressure chamber-resistivity cell was constructed. To produce interpretable results, it was necessary to control or hold constant any factors other than the structural rigidity of the adsorbed water that would significantly affect the resistivity of the system. The most important factor and most difficult to control was the prevention of water leakage from the system. The loss of water during compression would have affected the resistivity by (1) changing the ratio of water-to-clay and electrolyte, and

(2) changing the clay fabric which would alter the tortuosity of the path for the movement of the conducting ions.

The vessel, Fig. 1, was constructed and found to be absolutely leakproof up to 40,000 psi in all but a few instances. It was constructed from a No. 303 grade stainless steel rod, 8 in. long and 4 in. in diameter. The rod was bored

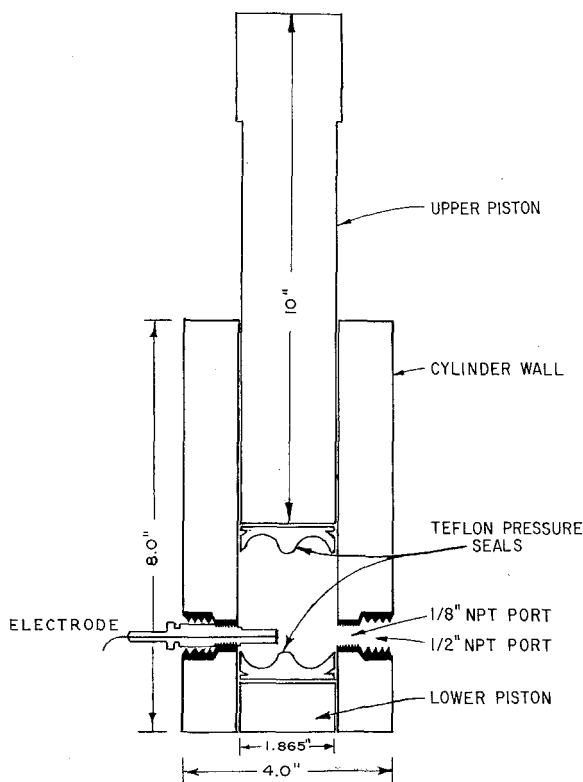


FIG. 1. Diagram of pressure-resistivity cell.

to make a cylinder with an inside diameter of 1.865 in. after the cylinder walls were polished. Pistons for both ends of the cylinder were machined from stainless steel and pressure seals were constructed from Teflon. The pressure seals were cut in the form of discs which had a cup-shaped face so that with increasing pressure the Teflon would press more tightly against the cylinder walls and maintain a high-pressure seal. The system was designed for uniaxial compression with the bottom piston remaining fixed relative to the cylinder and the top piston being movable during compression.

The electrical connections were made by drilling $\frac{1}{8}$ in. N.P.T. holes through

the cylinder walls for connection with Conax* high pressure insulated electrical connectors. The connectors were used for connection with the electrodes and also as pressure fitting for a ceramic insulated, sheathed thermocouple. The electrodes were platinum discs, 0.70 cm in diameter, which were soldered to the lead wires of sufficient length to give an 0.60 cm separation. The remaining portions of the lead wires were insulated and strengthened by thick coating of epoxy cement.

The resistivity measurements were made at an alternating current frequency of 1000 cycles with a General Radio Type 650-A Impedance Bridge and Type 650-P Oscillator-Amplifier. The instrument provides an accuracy to within 1% and a sensitivity in the order of a fraction of a per cent.

The hydraulic press used for the compression was a Riehle Model FA-300 with a capacity of 300,000 lb. The applied force that was used to calculate the internal pressure could be controlled and measured to an accuracy of 0.1%.

Temperature measurements during compression were made with an iron-constantan thermocouple and a Leeds and Northrup potentiometer with an ice-point reference junction.

Calibrations of Measurements

The cell constant of the pressure-resistivity cell was determined to be approximately 0.36. A comparison was made of the resistance of several electrolyte solutions of varying concentration in the pressure chamber with the resistance values of these solutions determined by a cell with a known constant.

In order to relate the pressure in the chamber to the applied load, it was necessary to take into account the friction of the pressure seals. For this purpose, the compression chamber was filled with a hydraulic fluid, and a Bourdon-type pressure gauge was connected to one of the $\frac{1}{2}$ in. N.P.T. enlarged portions of the electrode ports. During the compression of this fluid, it was found that gauge pressure became constant after a few seconds for any given load and that there was a linear relationship of 0.350 psi per pound of applied load. The point deviation from linear was no greater than 1% at pressures above 1000 psi but reached a maximum deviation of 10% at 500 psi, the lowest value on the pressure gauge. This relationship is assumed to be the same for the compression of the clay-water systems and the error in the same order of magnitude. The pressure values of less than 1000 psi reported in this paper are considered to be substantially in error with respect to the absolute value but still useful for comparative purposes. The true pressures in the range below 1000 psi would be higher than those reported.

Sample Preparation and Testing Procedure

The clay samples selected for testing were obtained from the collection of the Geology Department of the University of Illinois. Represented are two

* Conax Corporation, Buffalo, New York.

types of calcium montmorillonite, Cheto and Aberdeen, a Wyoming sodium montmorillonite, and a kaolinite from Redwood Falls, Minnesota. The montmorillonites are not homoionic and reference to either sodium or calcium type means only that these cations dominate the exchange positions. Further information including chemical analysis of these general montmorillonite types may be obtained from Grim and Kulbicki (1961).

In preparation for testing, the clays were dried and ground to pass a 180-mesh sieve. Degassed distilled water was added to 120 g of clay in a plastic bag while under vacuum in a desiccator. Sufficient water was added to the clays to make them plastic and easily workable. The samples were then removed from the desiccator and kneaded thoroughly in the plastic bag for 20–30 min to obtain a uniform mixture of clay and water. Before placing the clay paste into the compression chamber, the inside cylinder walls were sprayed with several coats of Fluoro Glide,* a Teflon-like dry film lubricant to reduce friction of the pressure seals, prevent sticking of the clay paste to the cylinder walls and to provide an electrical insulation. The clay pastes were placed in the cylinder and the pistons were forced together until any air trapped during the loading was driven out and the clay was just beginning to extrude through the electrode ports. The electrodes were then inserted and secured.

Resistance measurements were made during the compression when the resistance became constant at a static load. This generally required only 10 to 15 sec. The measurements were taken during the compression cycle except in one test where measurements were taken both during the compression and decompression. The rate of compression and decompression when tested was about 100 psi per minute.

The pressure-resistivity testing was done at room temperature except for one test at an elevated temperature. In this case, the pressure chamber and sample were heated to 45°C and placed in a styrofoam container with expanded vermiculite packing for the complete period of testing.

RESULTS AND DISCUSSION

Preliminary pressure-resistivity testing was carried to a maximum pressure of 38,700 psi. Several abnormalities were observed in the pressure influence on resistivity at pressures below 10,000 psi, and thus most of the observations were confined to lower pressure ranges. In a clay-water system where the type of conductance is primarily electrolytic, it would be expected that the influence of pressure on the electrical resistivity would be indeed similar to that of a comparable electrolytic solution. This was not found to be the case as may be seen in Fig. 2. The curve of the dilute NaCl solution was plotted from the data of Körber (1909) in which only the relative resistance of the solution under pressure and at atmospheric pressures are given. The resistance values have been transposed to convenient resistivity values for the purpose

* Chemplast, Inc., East Newark, New Jersey.

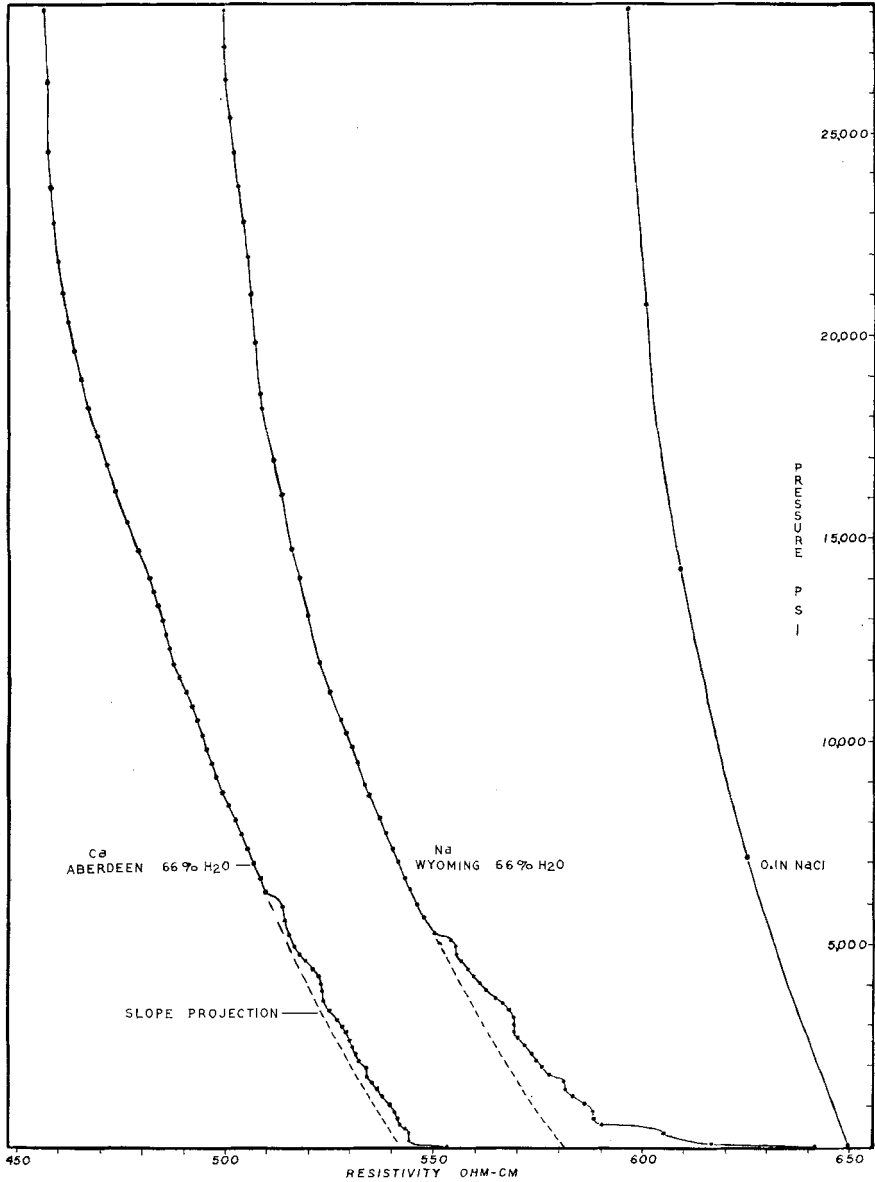


FIG. 2. Pressure influence on the resistivity of a dilute electrolyte and montmorillonite-water systems. Data for the 0.1N NaCl curve were adapted from Körber (1909).

of comparing the slopes of the curves. The general configuration of the dilute electrolyte curve shows that the effect of pressure is to decrease the resistance at a rate becoming less at higher pressures. The explanation of this, according to Bridgman (1931, p. 362), is that the mobility of the ions is enhanced by reduction of the viscosity of the solution. This effect is reported to occur at pressures up to about 30,000 psi, then there is a leveling off. A reverse effect is reported to take place at higher pressures. The clay-water systems behaved similar to the dilute electrolytic solutions only at pressures greater than 7000 psi. A downward projection of these slopes shows that there is an abrupt deviation toward higher resistivity values. Low (1961) elaborates upon the investigations which have been made and the evidence that clay-adsorbed water has a higher than normal viscosity. He also relates a greater activation energy for ion movement in clay-adsorbed water to the viscosity in essentially the same way that Bridgman has related the resistivity of dilute electrolytes to the viscosity of water during compression. It therefore seems logical to attribute the abnormally large pressure influence on resistivity in the lower portion of the curves to a pressure-induced breakdown of a viscous and more highly ordered adsorbed water. With all other factors held constant or nearly so, it is concluded that the water must have greater structural characteristics in the lower pressure range, and that it is broken down by compression and becomes like normal liquid water at higher pressures. This is in agreement with the finding of Yamaguchi (1959) and Oster and Low (1963) that clay-adsorbed water has higher resistivity than normal liquid water. This interpretation is in agreement with the open-structured, quasi-crystalline concept of adsorbed water, since if this water were more dense than normal liquid water, compression would have favored the existence of the more dense phase and probably induced further growth. In such case, an increase in pressure would be expected to produce an increase in resistivity.

From a closer inspection of the montmorillonite-water curves and a comparison with a well-crystallized kaolinite, Fig. 3, it is apparent that there is little if any interaction of the kaolinite and water. The anomalous behavior of the pressure influence on the resistivity of the montmorillonite-water systems would either seem to indicate that the structural breakdown of the adsorbed water undergoes stages of transformation or that particular water layers of differing degrees of structural rigidity are broken down at different pressures. The writer favors the latter interpretation on the basis that it better fits existing theory and evidence that the structural rigidity of adsorbed water diminishes with distance from clay surfaces. The pressure at which an anomaly occurs would therefore reflect the relative strength of bonding of water layers, the ones at the highest pressures presumably representing water layer closest to the clay surface. At the low pressures, particularly in the case of the sodium montmorillonite where the magnitude of the resistivity changes are large, there are possibly smaller anomalies within the larger resistivity shifts which cannot be defined without greater control.

In comparison of the sodium and calcium montmorillonite curves, the

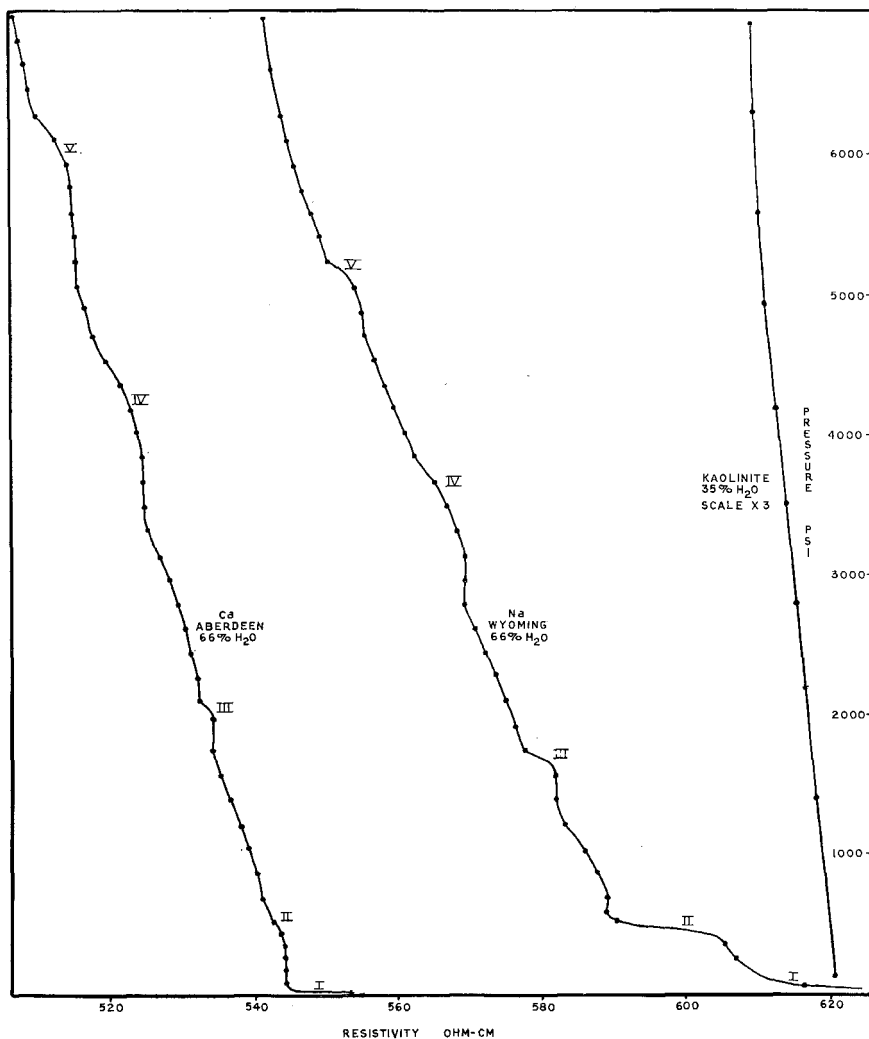


FIG. 3. Comparison of pressure-resistivity curves of Na-montmorillonite (Wyoming), Ca-montmorillonite (Aberdeen), and kaolinite. Roman numerals identify anomalies.

interpretation of the anomalies suggests that the first few molecular layers of water on calcium montmorillonite are more strongly held than those of sodium montmorillonite but that the latter permits more extensive growth of structural water at distances further from the clay surfaces. This is in agreement with conclusions of Grim (1962, p. 66), based on a comparison of the plastic behavior of the two montmorillonite types.

Minor differences in the location, configuration and separation of anomalies IV and V in the two clays may provide a clue for the elucidation of the nature of the interaction between the two cations and the quasi-crystalline water.

The general slope of the pressure-resistivity curves of the montmorillonites in the low pressure ranges can be explained by the existence of water with an abnormal degree of ordering. The configuration of the anomalies, however, requires additional consideration. If the anomalies indicate a phase transition from more ordered water to less ordered water, then it would be expected that there would be a decrease in resistivity at the beginning of the anomalies rather than a period where the resistivity remains relatively constant. A possible explanation of this is that at the pressure at which the anomaly begins, a slight cooling occurs as a result of the absorption of heat that would accompany the increase in entropy. The effect of such cooling would be to increase the resistivity or in this case counteract the reduction in resistivity associated with the pressure increase.

Thermal Relationships

The effect of temperature on the resistivity of clay-adsorbed water has been investigated by Anderson and Low (1958) and Yamaguchi (1959). These authors present evidence that the structural characteristics of the adsorbed water diminish with an increase in temperature. In order to examine the effect of a substantial temperature increase on the pressure-resistivity relationship of a clay-water system, a duplicate sample of the Wyoming clay was prepared and tested at an elevated temperature of 45°C. Figure 4 shows, in addition to the general trend of the resistivity to lower values, that the temperature increase has caused a steepening of the slope of the curve or a lessening of the pressure influence on the resistivity. This is exactly what would be expected if the ordering of the adsorbed water was substantially reduced by the temperature increase and therefore became less susceptible to pressure breakdown. The anomalies are reduced in magnitude and occur at lower pressure intervals and thus further indicate a less rigid water structure.

Comparison of Calcium Montmorillonites

In comparison of the Cheto and Aberdeen clays, Fig. 5, there is a distinct similarity of the curves, as would be expected, since both clays have a similar calcium to sodium ratio. There are, however, minor differences which may be related to a variation in the distribution of the exchangeable cations or minor structural differences in the clay lattices.

The test with the Cheto clay is the only test in which resistivity measurements were taken during gradual decompression. A hysteresis effect appears in the occurrence of the anomalies which suggests that the structural redevelopment of the innermost water layer does not occur alone but simultaneously with the second layer at a lower pressure. The lowest two anomalies

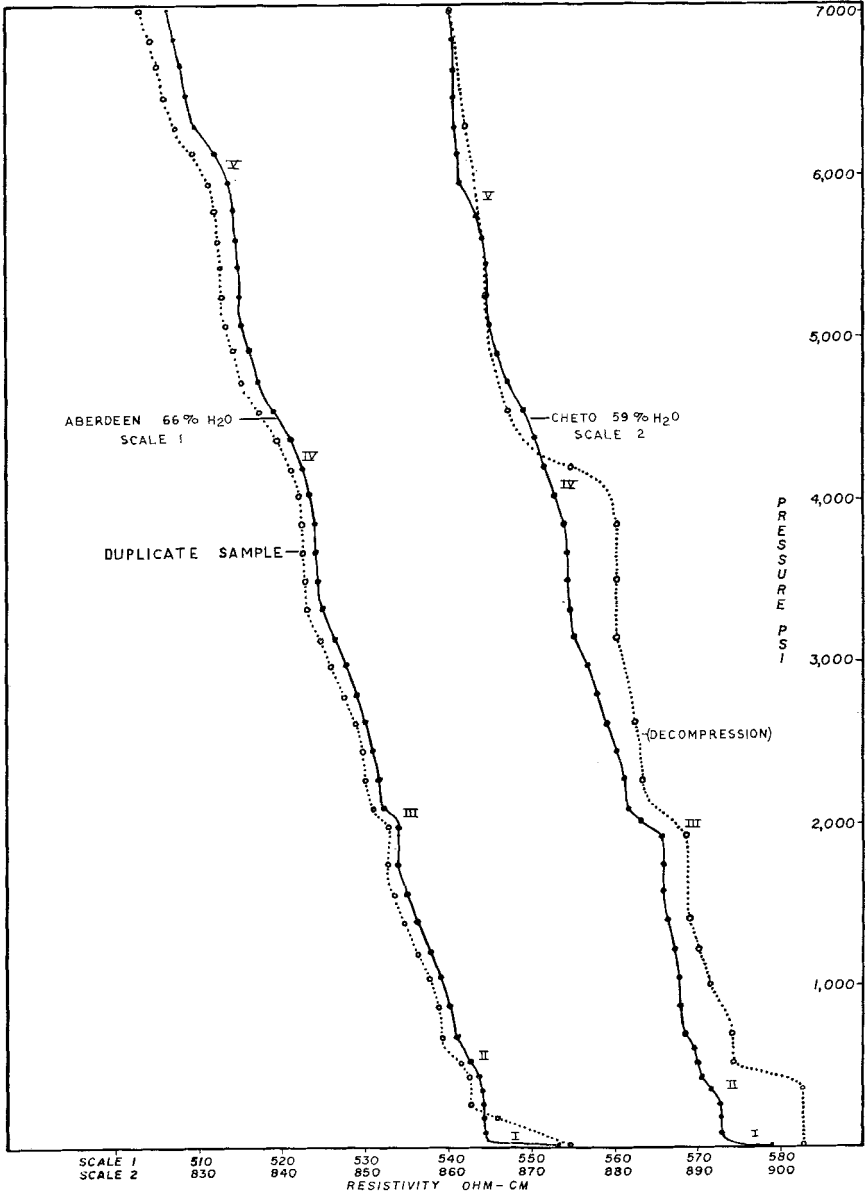


FIG. 4. Comparison of pressure-resistivity curves of Ca-montmorillonites, Aberdeen and Cheto.

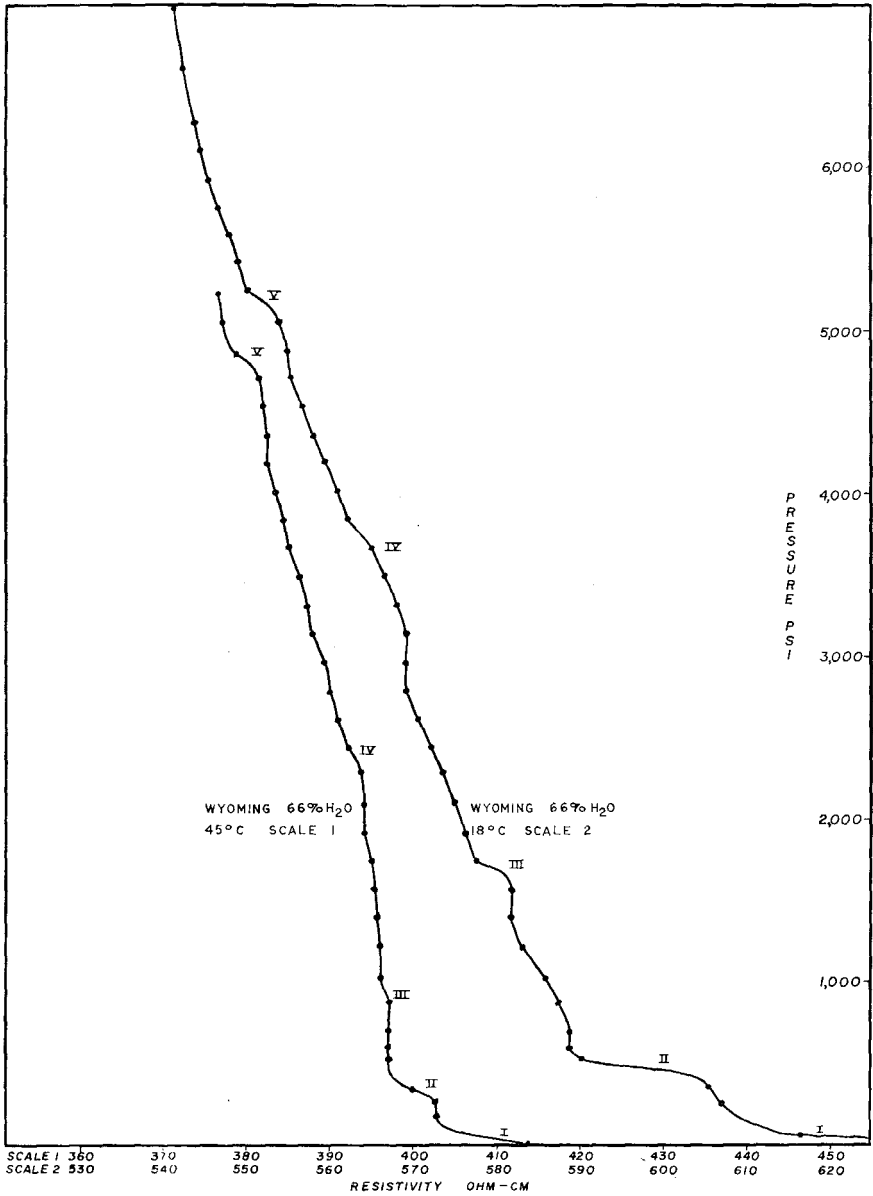


FIG. 5. The effect of temperature on the pressure-resistivity curve of Na-montmorillonite.

appear to have magnified, and suggest an improved water structure. A possible explanation is that when melted during compression the water could become more uniformly distributed with respect to the clay surfaces and then be in a better position to find the appropriate structural site upon decompression.

A similar effect in relation to the redevelopment of oriented water has been noted by Hiller (1964). His investigation of bentonite suspension indicated that a transition from gel to sol state occurred gradually during compression to 560 kg/cm² (about 8000 psi) and that the gel structure reformed with some time lag during decompression.

Reliability of Data

The interpretation of the resistivity data obtained requires that the clay fabric remained unchanged throughout the pressure testing. The clay and water, after thorough kneading, would have had a random fabric at the beginning of the testing. In order to determine that the fabric was not altered during the testing, cubes with 2.0 cm dimensions were cut from the center of each sample. The resistance was measured across the three axes and the samples were found to be electrically isotropic. This is further substantiated by the fact that the pressure-resistivity curve plotted for the decompression of the Cheto clay closely approached the compression curve.

The resistivity of electrolytic solutions is particularly sensitive to temperature variations. It was therefore necessary to determine the magnitude of temperature increase that accompanied the compression of the clay-water systems. Separate compression tests were run on the montmorillonite-water systems in which the temperature was measured by a thermocouple penetrating 1½ in. into the sample. A temperature increase in the order of 0.9° to 1.4°C was found to occur during compression to 8000 psi and about twice this amount at 16,000 psi. The instrumentation and thermocouple employed were only sensitive to detect temperature variations of about 0.5°C and greater. No indication was observed of a slight cooling as was postulated in the previous section; however, such thermal reactions would not be expected to be within the sensitivity of the measurements. The temperature variations that were observed, however, could be expected to contribute to the slope of the pressure-resistivity curves by producing a resistivity variation of about 2.49% per degree centigrade change according to Jackson (1964, p. 231). However, since an equivalent temperature rise was observed during compression from 0 to 8000 psi and from 8000 to 16,000 psi, this could not account for differences in the character of the pressure-resistivity curves within the two ranges.

A factor that would contribute somewhat to the resistivity decrease with increasing pressure would be the increasing concentration of ions per unit volume with the compression of the solvent. This effect, although probably slight, would tend to be more pronounced in the portion of the clay-water curves representing the destruction of the open-structured, more compressible,

adsorbed water. It would therefore tend to accentuate the differences in the pressure-resistivity characteristics of clay-adsorbed water and normal liquid water.

Another factor that must be considered as a potential source of error in the experimental results is the possibility of significant variations in the cell constant during compression. Undoubtedly, some variation did occur during compression as a result of changing of the cell dimensions and compression of the Teflon seals. The effects of the shortening of the cell length would be minimized as a result of having the electrodes positioned as remote as possible from the movable piston. The amount of compression of the Teflon seals and its effect on the cell constant could not be determined but it is not considered to have significantly altered the results. Hamann (1957, p. 122) reports a change in the cell constant of a cell comprised entirely of Teflon with platinum electrodes of only about 6% at 12,000 atm (176,400 psi) and a major contribution to this error results from a 2% contractual phase change in the Teflon at 5000 atm. Since the cell used in the present investigation had Teflon only as pressure seals and the testing pressures never approached 5000 atm, significant changes in the cell constant from Teflon compression would not be expected. The lack of variation in the pressure-resistivity curve of kaolinite (Fig. 3) provides a reasonable assurance that the cell constant was not noticeably altered within the pressure ranges of these tests.

A possible error in the resistivity measurements could have resulted from small amounts of air being trapped at the electrode-clay paste contact. Although precautions were taken to avoid this it is likely that small amounts of air remained. Any such error could be significant only in the very low pressure range because the air would have become dissolved within the first few hundred psi of applied pressure. It is also unlikely that such a phenomenon could account for the differences in the first two anomalies of the heated and unheated Wyoming montmorillonite, the calcium montmorillonite pastes and the absence of the anomalies in the kaolinite paste.

The most significant factor supporting the reliability of the experimental results is the fact that the pressure-resistivity curve could be reproduced with reasonable accuracy for a given duplicate sample (Fig. 4).

SUMMARY AND CONCLUSIONS

The pressure-resistivity investigation of clay-water systems has provided further evidence of the abnormal state of water adsorbed on the surface of montmorillonites. The abnormally large pressure influence on the resistivity of clay-water systems at pressures below 7000 psi compared to that of comparable dilute electrolytes is interpreted to reflect the presence of water of a quasi-crystalline state. Anomalies in the pressure-resistivity curves are believed to be caused by a structural breakdown of particular water layers and appear to provide a means by which orienting characteristics of different

clays may be compared and studied. As other authors have indicated, there is strong evidence that the rigidity and amount of clay-adsorbed water decreases substantially at elevated temperatures. There was evidence that the water structure, collapsed by pressure, re-forms when the pressure is released.

The results of this investigation are considered to have bearing upon the sedimentation and loss of water of clay sediments during compaction since hydrostatic load or weight of overburden may affect the clay-water interaction. From an engineering standpoint, the effect of pressure and temperature should be considered a factor in determining the strength and sensitivity of soils as well as shearing forces. In a similar manner, the loading of continental shelf sediments by continuous deposition could cause a melting of the clay-adsorbed water, a reduction in strength and give rise to turbidity currents without a sudden triggering mechanism.

The effect of pressure upon montmorillonitic reservoir rocks could be to alter the size and strength of hydration envelopes surrounding clay particles and therefore alter the reservoir permeability.

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