

HYDRATION PROPERTIES OF POTASSIUM DEFICIENT CLAY MICAS

by

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ABSTRACT

A clay mineral that in its natural state expands to 15 Å with water and to 17 Å with ethylene glycol was treated with various concentrations of KCl. At the highest KCl concentration all the material was rendered nonexpanding. There was a threshold KCl concentration at which potassium ions were absorbed in sufficient quantities to prevent expansion of the clay in water. At concentrations less than the threshold the material is characterized by a random interlayer mixture of expanding and nonexpanding layers. The sequence produced with increasing KCl concentration is: expanding clay → inter-layer mixture → nonexpanding clay.

Solvation with ethylene glycol is more effective than solvation with water for much higher potassium ion population densities in the interlayer space. At potassium ion population densities intermediate between those at the concentration thresholds for water solvation and for ethylene glycol solvation, there are layers that will expand with glycol and not with water.

Low potassium ion population densities correspond to low surface charge densities of potassium saturated clays, and the clays expand like montmorillonite. The high potassium ion population densities correspond to high surface charge densities of potassium-saturated clays and illite and the clays do not expand. With intermediate potassium ion population densities corresponding to intermediate surface charge densities for potassium-saturated clays, the clays expand with ethylene glycol but not with water.

INTRODUCTION

Characterization of three-layer clay minerals traditionally has centered around their expansion properties. Until recently, it was thought that there were two types of three-layer clay minerals, those that expanded and those that did not expand. The expanding clay minerals, the montmorillonite group or montmorillonoids, were thought to have this ability to expand because of their low surface charge density which resulted from relatively little isomorphous substitution of Al^{3+} for Si^{4+} . The nonexpanding three-layer clay minerals, the illites, were thought of as resisting expansion because of a high surface charge density resulting from greater Al^{3+} for Si^{4+} isomorphism.

Walker (1958) has suggested that there is no clear two-fold classification of the micaceous clay minerals but instead that a complete gradation of surface charge density exists from montmorillonite to the highly charged three-layer silicates. With surface charge density being directly related to expansion properties, it must now be considered that there is a complete

variation in the ability of the three-layer clays to expand. A thorough examination of the process of expansion in three-layer clay minerals is necessary before any use of this property can be made for evaluating the extent of isomorphism.

Expansion in the clay minerals is an interaction between two forces. On the one hand, liquid molecules adsorbed onto the oxygen surface of the silicate layers require space between the layers and act, through their adsorption forces, as a lever to pry the layers apart. Their effectiveness in separating the silicate layers is resisted by binding forces exerted through whatever charged interlayer material is present. Expansion occurs when the adsorbed liquid molecules exert a separating force that exceeds the binding force acting through the interlayer material between the silicate layers. The layers remain unexpanded when the binding force exceeds the separating force.

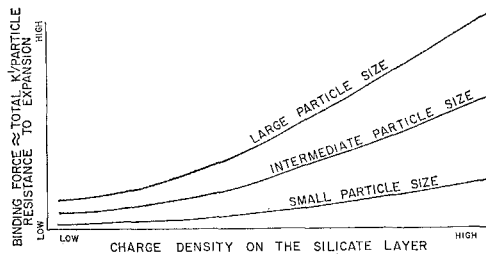


FIGURE 1.—A proposed relationship between resistance to expansion in three-layer minerals and charge density for varying particle size layers.

The binding force between silicate layers is a result of a coulombic attraction between the negatively charged silicate layer and the positively charged interlayer ions. If we assume that each negative charge on the silicate layer is neutralized by a singly charged interlayer cation, the binding force should be a function of the number of interlayer cations per layer. This number of interlayer cations would, in turn, be equal to the product of the charge per unit area of surface (charge density) and the areal extent of each particle. Figure 1 is a graph showing a possible relationship among these three variables as proposed by Jonas and Roberson (1960). The binding force is an increasing function of charge density. When charge density is low, the effect of particle size on the binding force is small. For silicate layers that are more highly charged, the particle size exerts a strong control over the binding force acting between two silicate layers.

Jonas and Roberson (1960) have explored the dependence of expansion properties on particle size. Their experiment was designed to hold constant three of the four variables that control expansion. They hoped to eliminate charge density on the silicate layer as a variable by comparing only samples of a single clay mineral that had been variously treated in the laboratory. It

was assumed that the silicate layers were not altered in composition by the mild chemical treatments used and therefore were not changed in charge density. The interlayer ion was kept from varying by saturating all the samples with potassium ions before expansion properties were measured. Because expansion properties among the variously treated samples were compared with only one solvating liquid, the effects of nonuniform adsorption forces were avoided. The fourth variable, particle size, was controlled by grinding and gravitation size fractionation. It was found that particles of high surface charge density could expand whenever they occurred in small enough particle size.

It is proposed here to consider the dependence of expansion properties on the character of the interlayer ion. Particle size cannot be held constant, but by using in the experiment a single sample each portion of which will have a uniform particle size distribution, it is hoped that the effect of particle size distribution on expansion can be recognized. From other studies, it is thought that the sample contains a narrow particle size range.

Although nonexpanding micas with sodium and calcium interlayer ions are known, the only nonexpanding natural micaceous clay minerals contain potassium as interlayer ions. In some clays potassium can occur as the only interlayer ion and still not interfere with expansion. In the literature are numerous references to expanding three-layer clay minerals which will exchange potassium, contract to a 10 Å spacing, and resist expansion with water and ethylene glycol (Weaver, 1958; Walker, 1950). It can be concluded that for these clays a stronger binding force between silicate layers can be made through potassium than through sodium or calcium. The clay silicate layers that will resist expansion when saturated with potassium have a high charge density. The low charge density silicate layers continue to expand even when saturated with potassium.

If no variation in charge density existed among the layers of a natural clay sample, it would be expected that potassium as it became available to the layers would spread uniformly over all the layer surfaces. The layers of equal size would then have a uniform resistance to expansion. When sufficient potassium became available through which a minimum binding force could be established, the layers would all be nonexpanding.

It must be realized that to acquire a given total number of potassium ions (and therefore a given binding force), a smaller potassium ion population density would be needed by large particles than would be necessary for small particles. Large particles therefore would resist the expansion forces of a given solvent with one potassium ion population density while smaller particles would not.

Variation in the attraction of solvating molecules to the silicate layer surfaces has been suggested for treated clays (Johns and Tettenhorst, 1959). A series of solvents acting on surfaces having varying potassium ion populations (caused either by variation in layer charge density or layer areal extent), and hence varying interlayer binding forces, would solvate different propor-

tions of these surfaces. Those highly attracted solvent molecules would be adsorbed on relatively greater proportions of the surfaces, including some with high potassium ion populations. Those solvents whose molecules are attracted to the silicate layer surface by a somewhat lower force would be adsorbed on only those surfaces having lower potassium ion populations. It could be reasoned, therefore, that expansion is *not* a property that a clay layer either has or does not have but rather one which the clay layer may exhibit with one solvent and not with another or with one degree of potassium ion saturation and not with another.

The clay described here is especially well adapted for a study of the relation between potassium content and expansion. In its natural state the clay is completely expanding and produces a basal periodicity of 15.5 Å in equilibrium with 50 percent relative humidity (RH). When treated with a 1 N solution of potassium chloride, it is rendered completely nonexpanding with a periodicity of 10 Å. Weaver (1958) has published diffraction curves of this clay as Womble shale which demonstrates these properties. In addition to the expanding clay the sample contains a small quantity of illite and kaolinite or chlorite, or both.

EXPERIMENTAL TECHNIQUE

The raw sample was ground lightly to aid disaggregation and then suspended in distilled water; no dispersing agent was used. The $<2\mu$ fraction was removed from the suspension by centrifugation (Hathaway, 1956) and was used in all subsequent operations. The base exchange capacity is 70 meq/100 g.

Thirty-five ml of the $<2\mu$ suspension containing 0.116 g dry weight of the sample was mixed with varying proportions of 0.05 N KCl standard solution and distilled water to obtain clay-KCl-water mixtures whose total volumes were 50 ml each, and whose resultant initial KCl concentrations were 0.02 N, 0.01 N, 0.002 N, and 0.001 N, respectively. The clay was allowed to age at room temperature in these KCl solutions for a minimum of 72 hr with occasional stirring. The 0.02 N and the 0.01 N suspensions finally were allowed to settle naturally and the clear solution was decanted. The clay was washed three times with distilled water to remove the excess salts. The 0.004 N, 0.002 N, and 0.001 N solutions would settle neither naturally nor with centrifugation; these three solutions were not washed. At no time before the oriented aggregate slides were made were any of the samples allowed to dry. The clay samples were resuspended in distilled water to a total volume of 50 ml, and two oriented aggregate slides of each sample were made using the same volume of suspension on each slide.

Because the preparations of the various potassium concentration treatments were not uniform, the exact concentration of potassium ions on the clay surfaces is not known. It is certain, however, that the preparations resulted in a series of samples of increasing potassium content with correspondingly decreasing calcium content.

Two x-ray diffraction patterns of each sample were made: one after equilibrating with 50 percent RH at 25°C for 24 hr, the other after equilibrating with ethylene glycol vapor at 60°C for 24 hr.

It was assumed that the original clay suspensions were uniform for all samples. The 7 Å diffraction feature in the samples was used as a natural, internal standard. Instead of comparing peak heights on one pattern to like peak heights on another pattern, the ratio of peak heights of the three-layer clay diffraction to the peak heights of the 7 Å line on the same pattern was compared to like ratios on other patterns. In this way, slight differences in oriented aggregate slide preparation (thickness, degree of orientation, etc.) were minimized. Under the conditions of these experiments, it was assumed that these ratios, based upon peak heights as determined directly from the x-ray diffraction patterns, are proportional to the quantity of material present.

RESULTS

Figure 2 shows the variation in relative peak heights of the several diffraction features attributed to the three-layer clay in the samples as a function of the amounts of potassium introduced in the preparation process. The original sample contained a small amount of mica diffracting at 10 Å. The curves of relative 10 Å peak heights begin at a value near 2 for the sample before potassium treatment instead of beginning at zero. This mica is considered to be an inert contaminant which does not vary in amount from one sample treatment to another. All increases over 2 in relative peak height of the 10 Å diffraction are considered to be the result of a contribution from expanding three-layer clay that has been collapsed by the potassium addition.

For samples that have been equilibrated with 50 percent RH, the relative peak height of the 10 Å diffraction, Curve D, increases slowly for low concentration KCl treatments. This increase indicates that only a small proportion of the expanding layers have exchanged enough potassium to develop an interlayer binding force sufficiently strong to resist the expansion forces of water vapor at 50 percent RH. This gradual increase in the proportion of layers that resist expansion continues through the 0.002 N KCl treatment.

The 0.004 N KCl treatment produces a very large increase in the relative peak height of the 10 Å diffraction, corresponding to the acquisition by a large proportion of layers of more than the critical number of interlayer potassium ions necessary to develop a binding force strong enough to resist water expansion.

Through the same suite of samples, with increasing potassium composition the increase in relative 10 Å diffraction peak height follows a different path when the samples are glycol saturated (Curve E). The gradual rise begins from the relative intensity value near 2 and reaches a maximum at a much higher concentration KCl treatment than for the 50 percent RH series. At the 0.01 N KCl treatment, where resistance to expansion against water vapor has been developed by essentially all the layers, the resistance

to expansion against ethylene glycol vapor has been developed by only a portion of the layers. Many of the layers still are expanded by the glycol and give diffraction at 17 Å.

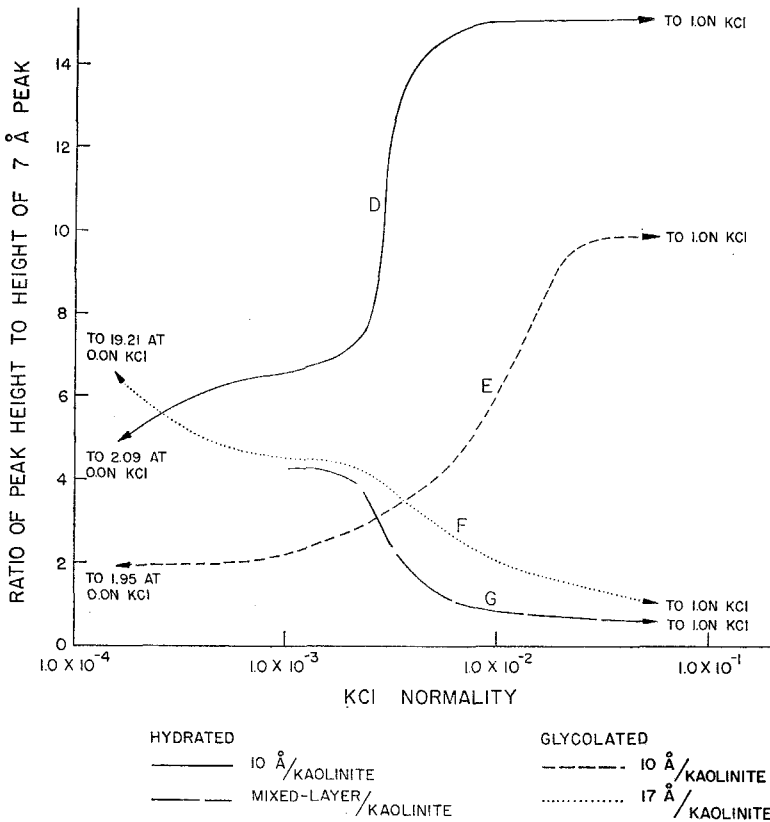


FIGURE 2.—Relative peak heights of the various diffraction features from a potassium-treated three-layer clay as a function of concentration of the potassium.

Figure 3 depicts the diffraction patterns which illustrate most clearly that clay layers can be expanded with ethylene glycol when they are not expanded with water vapor at 50 percent R.H. Curves A and B are diffraction traces for the sample treated with 0.01 N KCl. Curve A shows no evidence of layers that have been expanded with water vapor. The same sample exposed to ethylene glycol vapor has a considerable diffraction at 17 Å. All of the layers that expanded with the glycol treatment were not expanded with water. Those same layers when supplied with more potassium, as in the sample shown in Curve C (treated with 1 N KCl), can resist expansion with ethylene glycol.

This shows that higher concentration KCl treatments yield greater potassium ion population densities even after the layers have enough potassium to resist expansion with water. This greater potassium ion population density allows the layers to resist expansion with a stronger binding force, which ultimately exceeds that necessary to prevent expansion with glycol.

The other curves on Fig. 2 show the relative amount of diffraction given by the remainder of the sample that is not diffracting at 10\AA . Of course, at low concentration KCl treatments the bulk of the three-layer clay mineral diffracts at 15\AA when hydrated and expands to 17\AA with glycol treatment. Curve F shows the gradual decrease in relative peak height of the 17\AA diffraction as the concentration of the KCl treatment increases. This function is essentially inverse to that of Curve E and shows an inflection at about the same concentration KCl treatment.

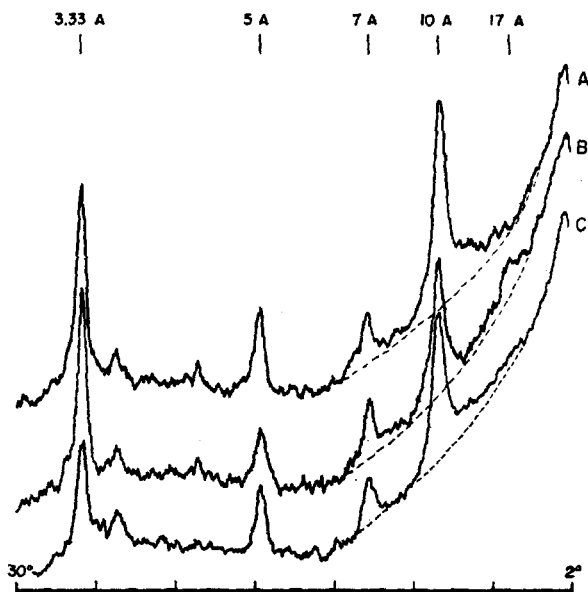


FIGURE 3.—Diffraction patterns for Womble shale. (A) 0.01 N KCl treatment, 50 percent RH; (B) 0.01 N KCl treatment, ethylene glycol; (C) 1.0 N KCl treatment, ethylene glycol.

For samples that were hydrated at 50 percent RH, the low concentration KCl treatments produced some diffraction intermediate between 15\AA and 10\AA which was considered to be from an interlayer mixture. The relative abundance of this diffraction reached a maximum near the critical concentration for the KCl treatment and diminished as all the layers became non-expanding at high concentration KCl treatments. Variation in abundance of this mixed layer diffraction is shown by Curve G as a function of the

concentration of KCl treatment. The process by which the expanding three-layer clay is rendered nonexpanding by potassium treatment appears to be conversion first to an interlayer mixture of expanding and nonexpanding layers and finally to the nonexpanding form.

DISCUSSION

Assuming that the surface charge density is uniform for all the particles in the sample studied, the data on expansion properties can be used to indicate relative crystallite size distribution. Those layers that have collected a sufficient number of potassium ions at low concentration KCl treatments to form an interlayer binding force strong enough to resist hydration at 50 percent RH would have to have a considerable areal extent. Those that required more nearly complete saturation of the surface charge, which would produce a greater potassium ion population density obtainable at higher concentration KCl treatments, to develop the necessary binding force would be smaller in areal extent.

Curve D of Fig. 2 is actually a cumulative curve of layers that have surpassed the necessary binding force to resist hydration at 50 percent RH. The curve is characterized by a sharp inflection at which most of the layers were converted from expanding to nonexpanding over a small KCl concentration interval (therefore a small potassium ion population density interval). This, in turn, would suggest that most of the layers had similar areal extents. The layers with larger areas would have already collapsed to 10Å at lower concentration KCl treatments; this was only a small portion of the sample. Those layers with smaller areas would have continued to expand until supplied with more potassium ions; very little of the sample acted in this way. In the authors' opinion, the implied particle size distribution is a reasonable one. Only a series of similar experiments performed on a carefully fractionated sample could definitely demonstrate that the sharp inflection in Curve D is truly an indication of uniform particle size.

For this clay, the binding force developed between layers through potassium ions is much greater than that through other ions. If the binding force developed through other ions is neglected, the expansion forces can be considered to be controlled only by the potassium that is introduced in interlayer positions. Those samples treated with low concentration KCl solutions and which developed only low potassium ion population densities could be compared with three-layer clays having low surface charge densities that had been saturated with potassium. The same potassium ion population density would be developed by the silicate layer of low charge density when the surface charges were completely satisfied by potassium ions. Likewise, the samples treated with higher concentration KCl solutions should have similar potassium ion population densities and therefore similar expansion properties to three-layer clay minerals with higher surface charge density.

Within the limitations imposed by these assumptions, the series of samples treated with varying KCl concentrations simulates a series of three-layer

clay minerals with varying surface charge density and uniform particle size. This series is divided by expansion properties into three categories. The low effective charge density samples (those treated with low concentration KCl solutions) expand with water and with ethylene glycol and would correspond to montmorillonite. The effective high charge density samples (those treated with high concentration KCl solutions) do not expand with either water or ethylene glycol and would correspond to illite. The material with intermediate effective charge density will expand with ethylene glycol and not with water and suggests itself as a third category of three-layer clay minerals.

Ethylene glycol and water are examples of strong and weak solvating agents, respectively. Curves similar to D and E of Fig. 2 could be drawn for other liquids. Walker (1958) already has suggested that glycerol is somewhat stronger than water but not as strong as ethylene glycol in its solvating properties for clay. The curve for glycerol in Fig. 2 would have an inflection at an effective surface charge density above that for water and below that for ethylene glycol. A family of such curves could be drawn for the various solvating agents. By means of such a series, the third category of three-layer clay minerals (not illite and not montmorillonite) could be again subdivided into many more units, thus demonstrating the continuity of surface charge density.

SUMMARY

The resistance to expansion that is developed by three-layer clay minerals is a function of the number of ions through which a binding force can be established. The number of interlayer ions is a function of the product of surface charge density and particle areal extent. The effect of areal extent on the expansion of the three-layer clay minerals has been studied by Jonas and Roberson (1960), and the effect of surface charge density on a sample of uniform particle size is studied herein. A sample is prepared in a series of known relative potassium deficiencies and is used to simulate a series of surface charge densities.

The low charge density preparations exhibited swelling properties identical with montmorillonite; the high charge density preparations resembled illite in their swelling properties; and the intermediate charge density preparations would not expand with water at 50 percent RH but would expand readily with ethylene glycol.

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