EXPANSION OF FRACTIONATED MONTMORIL-
LONITES UNDER VARIOUS RELATIVE HUMIDITIES*

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ABSTRACT

Distinction between the non-expanding three-layer clay minerals, illites, and the expanding three-layer clay minerals montmorillonites is accomplished by glycolation treatment. Distinction among the montmorillonites can be accomplished if the interlayer cation, type and amount of adsorbed liquid, and particle size are kept constant. With these variables constant, the expansion of montmorillonites can be correlated with particle size and/or charge on the tetrahedral layer.

Sodium saturated montmorillonite samples taken from 0–100 per cent relative humidity generally exhibit three hydration levels. Coarse fractions and fractions that possess high charge densities per unit area, compared to fine fractions and fractions that possess low charge densities per unit area, expand the most at low humidities and expand the least at high humidities. This is explained by cation or surface hydration and the strength of the bond between the layers. Introduction of potassium into the interlayer positions of the montmorillonite lattice decreases the ability of the silicate layers to expand. Examination of the diffraction patterns reveals that physical combinations of particles with different hydrations, interlayer mixtures of hydrates, and interlayer mixtures within the physical combinations have been produced.

INTRODUCTION

MONTMORILLONITES are three-layer clay minerals that are characterized by their expansion properties. This expansion brought about by treatment with ethylene glycol or some other strong adsorbing organic liquid is used to distinguish montmorillonites from the similar, non-expanding three-layer clay minerals, illites.

Differences in expansion, however, arise among members of each montmorillonite species. These differences are the result of charge density on the silicate layer, interlayer cation, adsorbed liquid and particle size. If the last three variables are kept constant by pre-treatment of the clay samples, then expansion can be correlated with charge density on the silicate layer. With charge density being directly related to chemical

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composition, expansion can be used as a tool to distinguish subtle differences in chemical composition between samples.

Charge Density

Walker (1958) suggested that the classification of the three-layer clay minerals is not clear because of the gradation from the high-charged silicate layers of the illites to the low-charged layers of montmorillonites. He concluded that the expansion of the clay structure is directly related to the surface charge on the silicate layer, and variation in the surface charge will affect the ability of the three-layer clay minerals to expand.

Figure 1 illustrates a generalization of Walker's proposal showing the gradation series from the high-charged illites through the intermediates
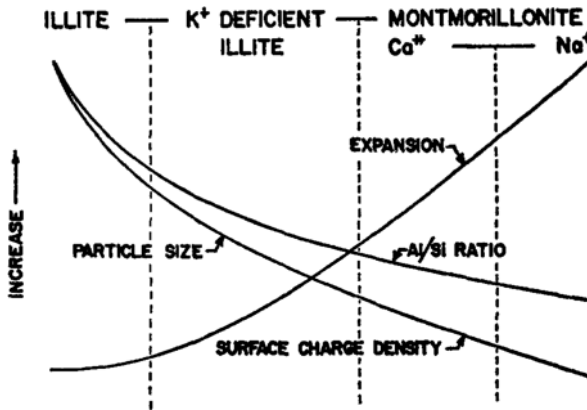

FIGURE 1.—Gradation series for the three-layer clay minerals showing the trend of particle size, expansion, aluminum/silicon ratio and surface charge density.

of the potassium-deficient illites, to the low-charged sodium montmorillonites. The trend of the aluminum/silicon ratio, particle size, and interlayer expansion is also given for the gradation series.

Foster (1954) stated that chemical changes through ion substitutions affect the charge on the silicate layers, causing a change in the expansion of the montmorillonite lattice. Isomorphous replacement of trivalent aluminum for quadrivalent silicon in the tetrahedral sheet gives rise to net residual charges on the silicate surface. In addition, replacement of the aluminum in the octahedral layer by magnesium or some other bivalent ion also causes a charge deficiency. This total charge deficiency is balanced by cations in the interlayer position.

The tendency of the silicate layers of a montmorillonite to expand in the

presence of a liquid is restricted by a binding force exerted by the charge on the silicate layers and the type of cations that are present between the layers. The binding force is an increasing function of the charge density. When the charge density is low, the binding force is small for comparable particle sizes, and when the silicate layers are more highly charged the binding force between the layers is strong (Jonas, 1960).

Interlayer Cation

Of the natural cations found in the interlayer position of the montmorillonite lattice, all are known to exhibit different binding strengths with the silicate layer. In order to compare the expansion of montmorillonites, and thus attempt to relate expansion to charge density, it is necessary to base exchange the clays so that the cation in the interlayer position is of one type. Sodium was chosen in this experiment because it forms a weak bond with the silicate surface. This may be the result of its ionic radius, dissociation and/or hydration characteristics. The monovalent character of the sodium ion is useful for it permits an even distribution of neutralizing cations on the charged silicate surfaces.

Potassium is another useful cation because of its strong attraction for the silicate surface. Weaver (1958) has shown that some expanding three-layer clays, at first classified as montmorillonites, exchanged their interlayer cations for potassium, contracted to an illite spacing of 10 angstroms and resisted expansion with water or other strong adsorbing liquids.

Based on Weaver's work it can be reasoned that montmorillonites possessing a high surface charge density should contact in interlayer spacing with replacement of the exchangeable cations by potassium. Furthermore, with a higher potassium concentration or surface charge, a greater percentage of the clay layers would be expected to contract.

Interlayer Liquid

Another variable to be considered when observing the expansion of a montmorillonite is the type and amount of liquid used to expand the silicate layers.

In general, the expansion of a montmorillonite can be thought of as a tug-of-war between the binding force exerted by the charged surfaces through interlayer cations, and the adsorption forces of the liquid molecules that penetrate between the silicate layers. The adsorption force of the liquid or its effectiveness in the separation of the silicate layers is governed by its molecular configuration (size) and its chemical compatibility for either the silicate surface or the interlayer cation.

The fluids commonly used in examining the expansion of montmorillonites are water, usually as the vapor at 50 per cent H_2O relative humidity (RH), ethylene glycol and glycerol. Of these three, water excels because

it possesses a low adsorbing force and because this force can be controlled by regulating the relative humidity about the sample while X-ray diffraction is recorded.

Particle Size

In this study of the expansion of montmorillonites, reasons have been presented for controlling two variables, (1) interlayer cation and (2) adsorbed liquid. Another variable that should be considered is particle size.

Figure 2 illustrates the distribution of particle size versus weight per cent for a Texas and Wyoming bentonite. Both bentonites are used commercially in drilling muds. Both exhibit distinctively different hydrate volumes in
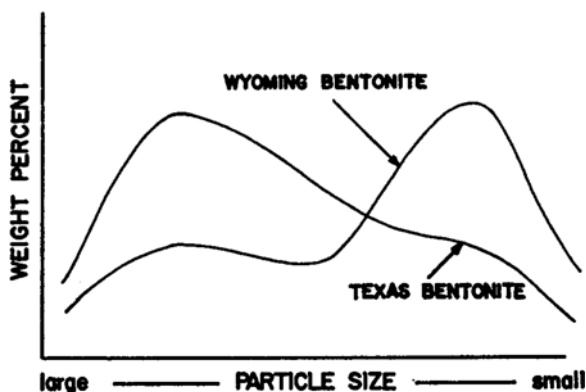

FIGURE 2.—Plot of weight per cent versus particle size for a Wyoming and Texas bentonite.

water and differ in rheological properties of their muds. Although the two bentonites are converted to the sodium variety by base exchange, it can be observed from the generalized plot that the Wyoming bentonite has a greater percentage of material in the fine particle size range. This then accounts for the superior rheological and base exchange properties of the Wyoming-type bentonites.

Two questions that arise when considering particle size are:

1. If there is no difference in chemical composition for various particle sizes, would they all be expected to expand to the same degree ?
2. If there is a change in chemical composition with a variation of particle sizes, how does this effect expansion?

If one assumes the bentonites to be fairly homogeneous in chemical composition irrespective of particle size, all fractions would be expected to expand the same. However, Jonas and Roberson (1960) point out that

coarse particles will retard expansion because of the large flake area which furnishes sites for a large number of interlayer ions. When there are large numbers of interlayer cations, regardless of their density per unit area, they retard expansion. With the selective cation removal at the edges of small particles, there is a possible reduction of ion density. Thus, one would expect finer particles to expand more than coarse ones.

The sedimentary montmorillonites, on the other hand, would be expected to exhibit differences in chemical composition because of the possibility of separate modes of origin and environmental changes prior to their deposition. With changes in chemical composition the sedimentary montmorillonites should express greater differences in expansion with particle size than the bentonites.

In order to control the variable of particle size distribution in the examination of montmorillonites, it is necessary to separate the clay samples into various size fractions, compare each of the size fractions, and compare like-size fractions from other samples.

DESCRIPTION OF SAMPLES

Two sets of samples were selected for the study of the expansion of fractionated montmorillonites. These included four API bentonites and a Wyoming bentonite (Table 1).

TABLE 1.—SAMPLE LOCATION, API NUMBER AND TETRAHEDRAL AL/SI RATIO

Location	API No.	Tetrahedral Al/Si Ratio
Lorena, Miss.	20	0.0391
Burns, Miss.	21	0.117
Chambers, Ariz.	23	0.0178
Otay, Calif.	24	0.0025
Wyoming	—	—

The purpose for the selection of the API samples was to obtain a comparison among different calcium-type bentonites. The Wyoming bentonite was chosen in order to study the degree of expansion of several particle sizes within one particular sodium bentonite.

Calculation of the aluminum/silicon ratio in the tetrahedral layer from the formulae given in the API Research Project No. 49 shows that the order of increasing ratio for the samples is No. 24, No. 23, No. 20, and No. 21 (Table 1). This order of increasing aluminum content in the tetrahedral layer also indicates an increase in the surface charge on the silicate

layer, and thus a decrease in expansion. Although the clays had been fractionated it is believed that these ratios will be expressed by differences in expansion for either the coarse or fine fractions.

SAMPLE PREPARATION

The API samples were converted from predominately calcium montmorillonites to sodium varieties by treatment with sodium chloride solutions. Washing was accomplished by centrifugation and dialyzing. The clays were then fractionated into two size ranges: coarse—2 to 0.1 microns, and fine—less than 0.1 micron.

The Wyoming bentonite had been fractionated, prior to cation treatment, by means of a Sharples centrifuge. Of the fractions obtained, four were chosen for study; A, 2–1 micron; B, 0.4–0.3 micron; C, 0.15–0.05 micron; and D, less than 0.05 micron. The fractions were subsequently treated with sodium chloride solutions for the conversion of the interlayer cation to sodium. Washing was carried out in the same manner as the API samples.

Base exchange measurements of all fractions indicated some increase in the base exchange capacity with a decrease in particle size. This is explained by the increasing edge/area ratio with a decrease in particle size. This factor makes it imposible to correlate base exchange measurements with charge density on the silicate layer. Base exchange measurements made after the sodium chloride treatments showed that sodium was present as the interlayer cation in all of the samples. No other cations could be detected.

The sodium-converted samples were treated with different normality potassium chloride solutions. Oriented slides were made for each of the treated samples.

Prior to diffraction, each sample was allowed to reach equilibrium with a certain relative humidity in a dessicator. The slides were then quickly transferred to the humidity chamber mounted on the X-ray sample holder. In order to eliminate the possibility of spacing changes occurring during the transfer, time was again allowed for the sample to reach equilibrium with the relative humidity in the same holder before the diffraction was recorded.

EXPERIMENTAL PROCEDURES

Humidity Control

The control of the relative humidity on the samples reported is similar to the method used by Gillery (1959). The constant humidity of the air is accomplished by passing compressed air through saturated salt solutions whose vapor pressure corresponds to a certain per cent relative humidity.

The humidified air is then transferred to an air-tight plastic box mounted over the sample holder of the X-ray machine. The windows of the humidity chamber are made of thin polyethylene plastic which allows the passage of the X-rays without any appreciable interference or loss of intensity.

X-ray Diffraction

Although in this study, the first order basal (001) spacing could be recorded from the oriented slides, only the second and third orders were considered of sufficient quality for interpretation. The reason for this is that the first order of the basal reflection, the most intense diffraction maximum of montmorillonites, occurs in the narrow range of 4 to 8 degrees 2θ (Cu Ka radiation). Application of the Bragg formula, $N\lambda = 2d \sin \theta$, reveals that a small shift in the basal spacing is not easily recognized within this range. The second and third order of the basal reflection, occurring within the range of 10 to 20 degrees 2θ, is more suitable for interpretation. When the Bragg formula is applied in this 2θ range it is evident that a small change in the basal spacing results in a large change in 2θ. With the need of measuring small changes in the basal spacing, diffraction patterns cover the range of 10 to 20 degrees.

RESULTS AND CONCLUSIONS

X-ray diffraction patterns taken of all the samples show an increase in hydration of the silicate layers with an increase from 0 to 100 per cent in the relative humidity. Within the 10 to 20° range of 2θ, the following orders of the basal spacing occur:

Code No.	Basal Spacing
0	2nd order of the zero-layer hydrate (4.9 Å)
1	2nd order of the one-layer hydrate (6.3 Å)
2	3rd order of the two-layer hydrate (5.1 Å)
3	3rd order of the three-layer hydrate (6.1 Å)
3*	4th order of the three-layer hydrate (4.6 Å)

Examination of the diffraction patterns of the API fine fractions indicates that the three levels of hydration have been reached (Fig. 3). At 0 per cent RH all of the samples are of the zero-layer hydrate (approximately 10 Å). Sample No. 20 varies slightly with a spacing of 10.2 Å. At 10 per cent RH all the samples are hydrated the same in that they exhibit a low intensity maximum with a spacing between the zero-layer and one-layer hydrate.

At 20 per cent RH the basal spacing of the clays are approximately 6.3 Å and the diffraction maxima are of high intensity, suggesting that a one-layer hydrate is stable. From 40 to 80 per cent RH the samples differ slightly, but for all, hydration of the lattice is increasing from the
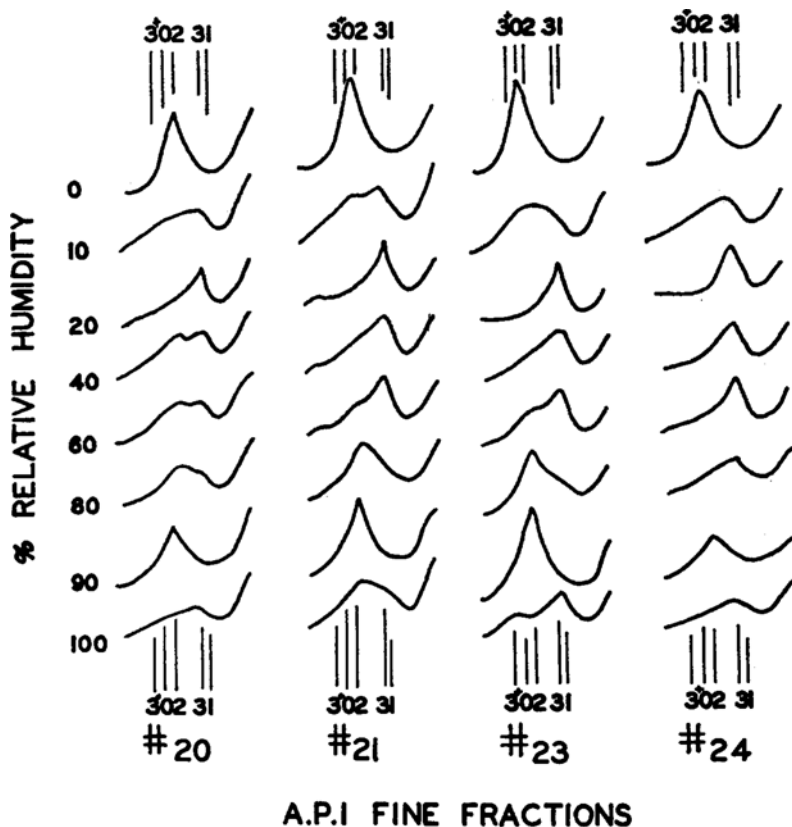
FIGURE 3.—X-ray diffractometer traces of API fine fractions (0.1 microns) taken from 0 to 100 per cent relative humidity.

one-layer to the two-layer hydrate. It is only at 90 per cent RH that the two-layer hydrate is fully developed as indicated by the sharp high-intensity diffraction maxima. At 100 per cent RH the three-layer hydrate is beginning to be developed with samples No. 20, No. 23, and No. 24 possessing a spacing of approximately 18 Å. Sample No. 21 exhibits what appears to be a double diffraction maximum with the highest intensity in the two-layer hydrate region and the lower intensity maximum in the three-layer hydrate region. This, then, suggests that sample No. 21 has expanded less under 100 per cent RH than the other samples.

The diffraction patterns of the API coarse fractions indicate that two hydration levels along with a suggestion of a third (three-layer hydrate) have been obtained (Fig. 4). Data is not available for the coarse fraction of sample No. 24.
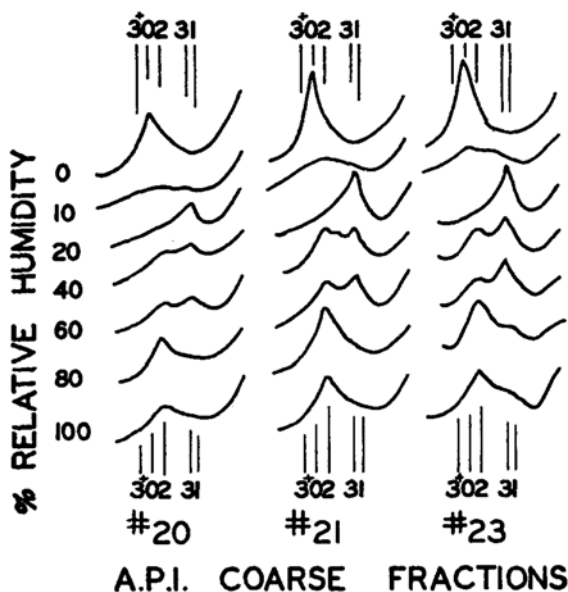
FIGURE 4.—X-ray diffractometer traces of API coarse fractions (2–0.1 micron) taken from 0 to 100 per cent relative humidity.

At 0 per cent RH all of the coarse fractions are of the zero-layer hydrate (10 Å). The one-layer hydrate has become fully developed at 20 per cent RH, with the two-layer hydrate being gradually developed at 40 per cent RH, and reaching stability conditions at 80 per cent RH. At 100 per cent RH the two-layer hydrate is still present but somewhat lower in intensity compared to the 80 per cent RH peak, indicating perhaps an increase in expansion. An interesting point of observation made when comparing the coarse fractions was that all the diffraction patterns were similar at the same relative humidities.

Examination of the diffraction patterns of the Wyoming fractions indicates again that three hydration levels have been obtained (Fig. 5). At 0 per cent RH all of the fractions are of the zero-layer hydrate with a second order spacing of around 4.8 Å. At 20 per cent RH fractions C and D possess a diffraction maximum at 4.8 Å with a shallow slope toward the one-layer hydrate (6.1 Å). Fractions A and B, on the other hand, expand to a higher hydration level as shown by the high intensity of the diffraction maxima in the one-layer hydration position (6.1 Å).

Under 40 per cent RH fraction D has expanded to a combination of a two-layer and a one-layer hydrate. Fractions A, B, and C at 40 per cent RH have also expanded to the combination of a two-layer and one-layer hydrate. The intensity of the one-layer hydrate, however, is greater than that for fraction D.
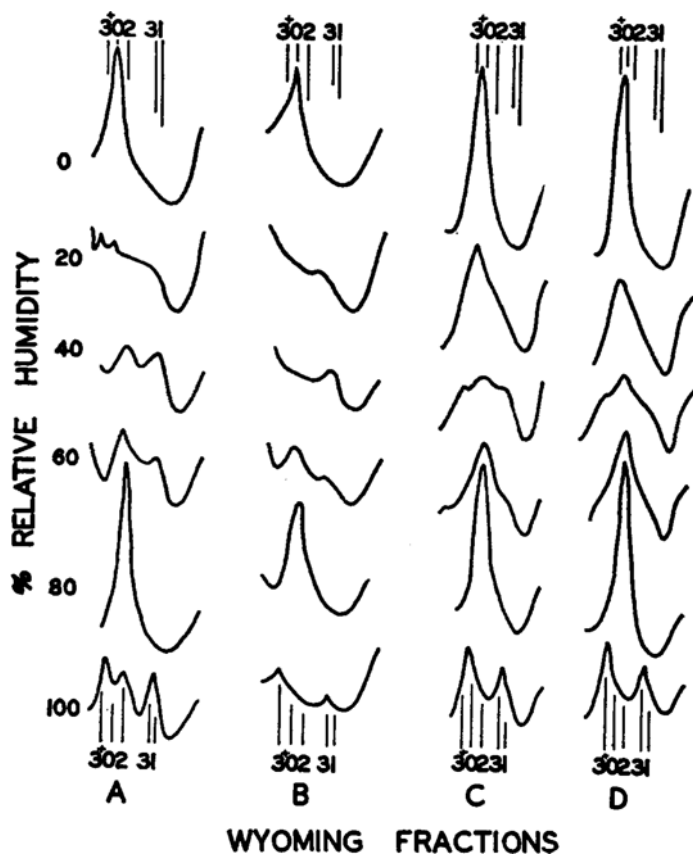
FIGURE 5.—X-ray diffractometer traces of Wyoming fractions; A, 2–1 micron; B, 0.4–0.3 micron; C, 0.15–0.05 micron; and D less than 0.05 micron; taken from 0 to 100 per cent relative humidity.

At 60 per cent RH all of the fractions have increased in hydration but still contain the combination of the one- and two-layer hydrates. At 80 per cent RH all of the fractions have high intensities for the two-layer hydration level (5.1 Å) indicating that the clays are stable with two layers of water at this relative humidity.

Under 100 per cent RH fractions B, C, and D have all expanded to a three-layer hydrate with well-developed third and fourth orders (6.1 and 4.6 Å). Fraction A, on the other hand, possesses two hydration levels as indicated by the presence of the third order of the two-layer hydrate, and by the third and fourth orders of the three-layer hydrate (6.1 and 4.6 Å). This then indicates that at 100 per cent RH, A, the most coarse fraction

studied, will not attain the hydration level of the finer fractions (B, C, and D).

When the calculated basal spacing (A) is plotted against the per cent relative humidity for each of the sodium treated API fine fractions, the curves (Fig. 6) reveal that sample No. 24 in the 20 to 80 per cent RH range expands less when compared to the rest of the samples. Sample No. 20 expands the most within this humidity range while samples No. 21 and No. 23 fall in between these two extremes. At 100 per cent RH all of the samples except No. 21 have expanded to the same degree, three layers of water.
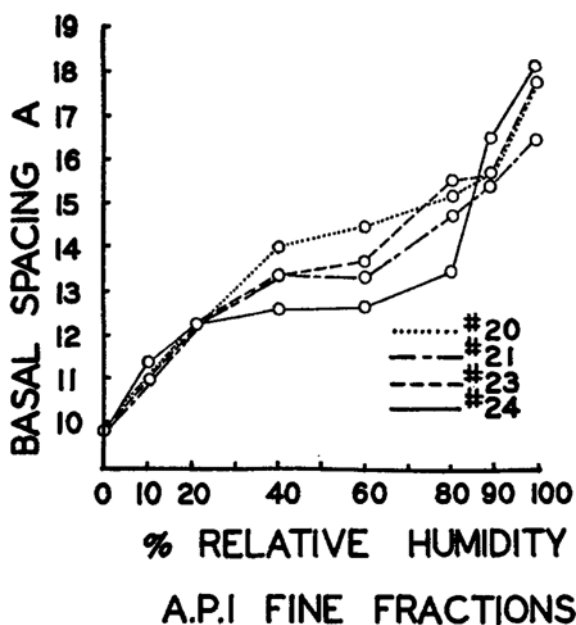

FIGURE 6.—Basal spacing (angstroms) versus per cent relative humidity for API coarse fractions.

Correlation between the expansion of the API fine fractions and the calculated aluminum/silicon ratios suggests a discrepancy in the data when it is applied to the hypothesis that clays with a low aluminum/silicon ratio should expand the most. However, if one considers that the clays with a high surface charge will possess more neutralizing cations between the silicate layers, then a reasonable explanation can be obtained. Because of the high number of cations for the higher charged clays the attractive force for the water molecules, due to the hydration of the cations or the silicate surface, will be greater. Thus, at low humidities the high charged

clays will hydrate more than the low-charged clays; the low-charged clays not expanding because of the low attraction for the water molecules due to low charge density and insufficient number of cations. At higher humidities, however, the opposite effect occurs. The high-charged clays will resist expansion because of the strong binding force between the silicate layers, whereas the low-charged clays expand easily because of the low binding force between the layers and the fact that the hydration force is greater (higher humidity).

No conclusions can be drawn from the study of the calculated basal spacing versus the per cent relative humidity for the API coarse fractions other than that all of the samples expand to the same degree for a given relative humidity (Fig. 7). It should be noted that the fine fractions hydrated to three layers of water at 100 per cent RH whereas the coarse fractions did not. This supports the idea that there is a charge density decrease with a particle size decrease.
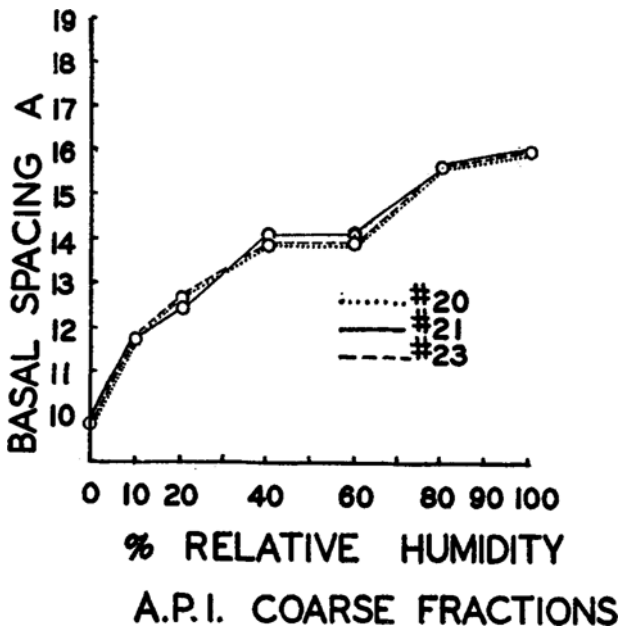

FIGURE 7.—Basal spacing (angstroms) versus per cent relative humidity for API coarse fractions.

Examination of the basal spacing versus the per cent relative humidity for the Wyoming fractions (Fig. 8) indicates that at low relative humidities the coarse fractions (A and B) expand to a higher degree than the fine fractions (C and D). In the middle relative humidity range fraction D and

possibly C have expanded to a higher degree than A and B. Finally, at 100 per cent RH it becomes more evident that the order of increasing expansion is from the coarse to the fine particle sizes.
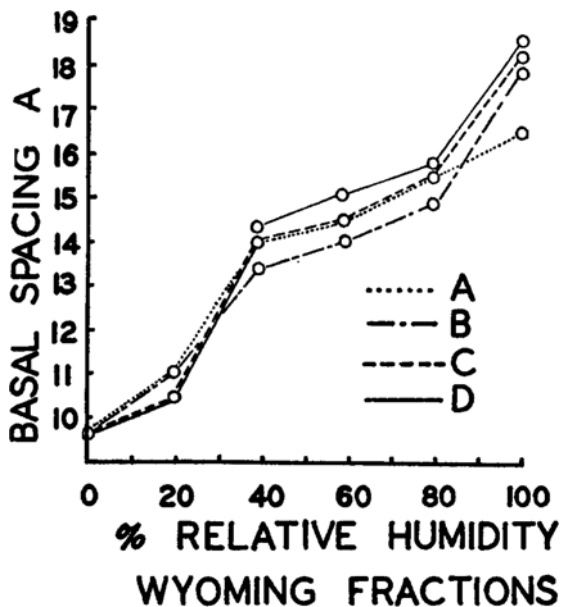

FIGURE 8.—Basal spacing (angstroms) versus per cent relative humidity for the Wyoming fractions. A, 2–1 micron; B, 0.4–0.3 micron; C, 0.15–0.05 micron; and D, less than 0.05 micron.

Extending the explanation given for the discussion of the API fine fractions, it is concluded that at low humidities the clays with the high charge density, the coarse fractions, will expand the greatest because of either cation or silicate layer hydration. At high humidities the coarse fractions or fractions that possess high charge densities expand the least because of strong binding force between the silicate layers. The fine fraction or fractions that possess low charge densities expand the most at high humidity because of the weak binding force between the silicate layers and because of the strong adsorption force of the liquid molecules.

Diffraction patterns taken of the API fine and coarse fractions, and the Wyoming fractions treated with different normalities of potassium chloride solutions, neither support nor refute the preceding conclusions. They do, however, show that the degree of hydration is reduced with the introduction of potassium into the interlayer positions and this reduction is steadily increased with an increase in the normality of the potassium chloride solution. Figure 9 shows this reduction for the API fine fractions.
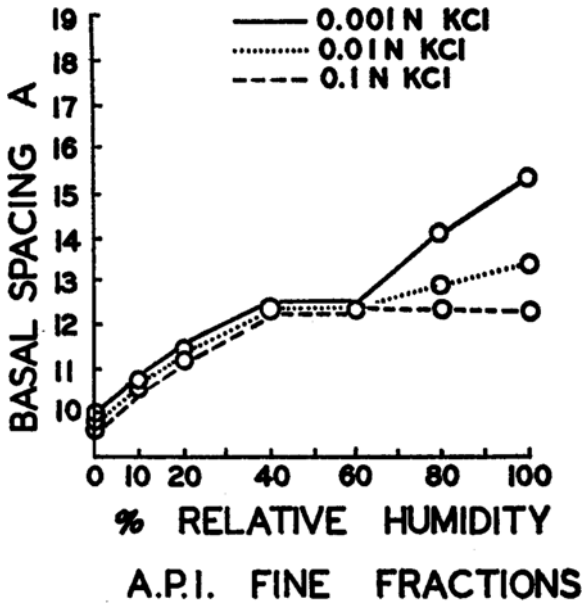
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FIGURE 9.—Basal spacing (angstroms) versus per cent relative humidity for API fine fractions treated with different normalities potassium chloride solutions.

Close examination of the X-ray diffractions suggests that some of the clay fractions studied exhibit what appears to be

(1)   physical mixtures of particles with different hydrations,
(2)   interlayer mixtures of hydrates, and
(3)   a combination of these two, interlayer mixtures within the physical mixtures.

The physical mixture (Fig. 10) is best exemplified by the coarse fraction of API sample No. 21 at 60 per cent RH. The diffraction curve exhibits maxima at 5.1 and 6.2 Å, indicating that the third order of the two-layer hydrate and the second order of the one-layer hydrate is present and well developed. This accounts for the presence of two distinct particles, one type hydrated to one layer of water, and the other hydrated to two layers of water.

An interlayer mixture (Fig. 10) is suggested by the diffraction curve of the API fine fraction of sample No. 21 at 80 per cent RH. The position of the maximum occurs around 5.5 Å, indicating a basal spacing of 11 Å. This suggest that each clay particle possesses a combination of a one-layer and two-layer hydrate in an interlayer fashion.

The last type of hydration, that of the interlayer mixtures within the

HYDRATES
2   1
LAYER   LAYER

PHYSICAL MIXTURE

INTERLAYER MIXTURE

COMBINATION, INTERLAYER
WITHIN PHYSICAL MIXTURES
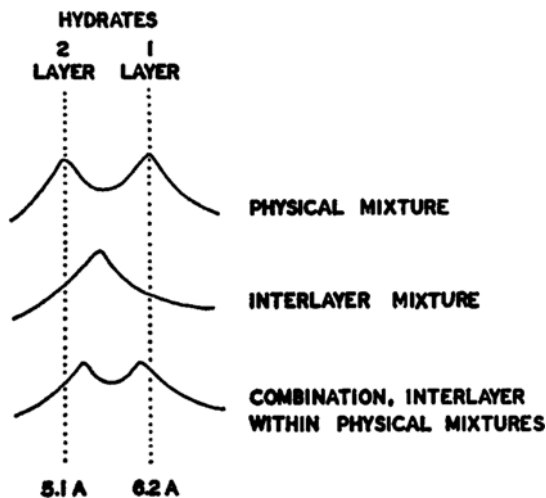
5.1 A   6.2 A

Figure 10.—Clay particle mixtures produced at particular relative
humidity levels.

physical mixtures (Fig. 10), is exemplified by the fine fraction of API
sample No. 20 at 40 per cent RH. Two maxima are present as in the pure
physical mixture type, although both maxima occur at a basal spacing
other than that of the pure one-layer and two-layer hydrates. This sug-
gests that there are some particles within the clay sample that have
predominately hydrated to one layer of water and that others have hydrated
to two layers of water. Both types of particles, however, contain small
percentages of the other hydrates, which produce a shift from the normal
basal spacing.

SUMMARY

It is necessary to point out that this paper is not intended to be a
presentation of a new method for montmorillonite identification. It does,
however, suggest a useful procedure for gaining information as to chemical
composition through the study of interlayer expansion.

Because of the effect of interlayer cation, adsorbed liquid, and particle
size on expansion, it becomes evident that these variables must be taken
into account if emphasis is to be placed on measurements such as base
exchange, rheological properties of the clay suspensions, bleaching and
adsorption capacities, differential thermal analysis and X-ray diffraction.

ACKNOWLEDGMENT

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