WATER VAPOR SORPTION ON LITHIUM KAOLINITE

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ABSTRACT

A sorption apparatus consisting of (1) a high vacuum system ($<10^{-5}$ mm Hg), (2) an oil manometer to determine the equilibrium vapor pressure, (3) a quartz helix to determine weight of adsorbate, and (4) a constant temperature control for the adsorption chamber has been used to obtain water vapor sorption isotherms on kaolinite. Equilibrium between water vapor and the clay surface can be obtained in 2 hours with this equipment. The estimated error in relative pressure (P/P_0) and amount of water adsorbed (X) are $\pm$ 0.001 and $\pm$ 0.07 mg H_2O/g clay respectively. Reproducibility of sorption isotherms for clay samples similarly prepared are within these limits. When retested those clay samples that had stood in the laboratory for a few weeks gave sorption isotherms slightly different from the initial isotherm. This variation, while not excessive, seriously limited interpretation of the sorption data.

In order to study the variation of sorption characteristics with curing conditions, two samples were stored at an elevated temperature (70°C) under two different conditions of moisture content and pressure; one sample as a water slurry (1 g clay per 10 ml H_2O) and the other completely dry in an evacuated ($<10^{-5}$ mm Hg) container. The effect on the sorption isotherms was in both cases very marked but of a different character.

Compared with the sorption behavior of the initial Li kaolinite, the sample stored as a slurry showed greater water adsorption at all values of P/P_0 and a disappearance of the marked hysteresis which persists to very low P/P_0 on the initial sample; however, when stored in vacuo, Li kaolinite at all values of P/P_0 adsorbed less water than the initial Li kaolinite. Data are presented to show that the sample stored as a slurry has been converted to an Al kaolinite. The reduced water sorption upon storage in vacuo is shown to be a permanent change.

INTRODUCTION

Considerable research has been, and continues to be, devoted to the study of water vapor sorption on clay. Unfortunately, the experimental conditions are poorly defined for many of the data reported in the literature, so that these data have only limited usefulness. Clay-water interactions are of vital interest to all the various aspects of clay technology. Sorption from the vapor phase under controlled experimental conditions offers a fruitful approach to a more thorough understanding of clay-water interactions.

The long term objective of this research is to investigate the changes in water sorption following various chemical treatments to the clay surface. Early in the work it was noticed that the sorptive character of any particular kaolinite sample is a rather transient phenomenon; i.e., the sorptive character changes with time. This behavior is nothing new; however, the changes observed were sufficient to make a rational interpretation of the data difficult. It was therefore decided to investigate the changing character of the kaolinite water sorptive surface with the hope that some limits could be placed on the extent of the change and that an understanding of the nature of this change in sorptive

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character could be obtained. This paper describes the results observed on the changes in the sorptive character of kaolinite that occur with time under various experimental conditions.

MATERIALS

Natural kaolinite from Bath, South Carolina, was used.[1] The kaolinite is essentially free from impurities because x-ray diffraction of the $+10\mu$ fraction, about 10 percent of the sample, and of the -0.05μ fraction, about 10 percent of the sample, showed only kaolinite reflections. The cation exchange capacity of the kaolinite was 2.7 ± 0.1 meq/100 g as determined by the ammonium acetate method (Peech and others, 1947, p. 9–11).

Lithium kaolinite was prepared from the natural kaolinite as follows: 6 g of clay extracted five times with 100 ml portions of $1M$ LiCl solution at pH 5.5; time of contact for each extraction 10 minutes. The resultant clay was repeatedly extracted with distilled water until the supernatant was free of chloride ions. Experiments showed that the sorption characteristics of the Li kaolinite were not affected by changing the pH of the extracting solution from 5.5 to 3.0 or by removing the excess salt with ethanol or water. The clay paste was dried 1 to 3 hrs. in an air oven at 70°C and then crushed to pass a no. 60 sieve (0.25 mm openings). This homoionic kaolinite is the starting material for the various treatments described under the section on Procedure. Al and Cs kaolinite were prepared in a similar fashion except that the appropriate chloride salt was substituted for LiCl.

APPARATUS

Sorption isotherms were determined with a specially constructed sorption system. The essential features of the apparatus, shown schematically in Figure 1, are: (1) a high-vacuum system ($<10^{-5}$ mm Hg) to insure that only the partial pressure of the desired vapor is available to the sorption sites, (2) an oil manometer to determine the equilibrium vapor pressure, (3) a calibrated quartz helix to determine the adsorbent weight and weight of adsorbate without opening the system, (4) a constant temperature water bath ($24.66 \pm 0.05°C$) to insure constant temperature in the sorption chamber, and (5) an adsorbate reservoir sealed into the system so that only the desired adsorbate vapor enters the sorption chamber.

Silicone oil, Dow Corning no. 703, having a density of 1.075 ± 0.001 g/ml at 26.0°C is used as the manometer fluid. Different lots of the silicone oil showed

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[1] The clay trade name "Peerless Kaolin" was purchased from R. T. Vanderbilt Co., N.Y.C.
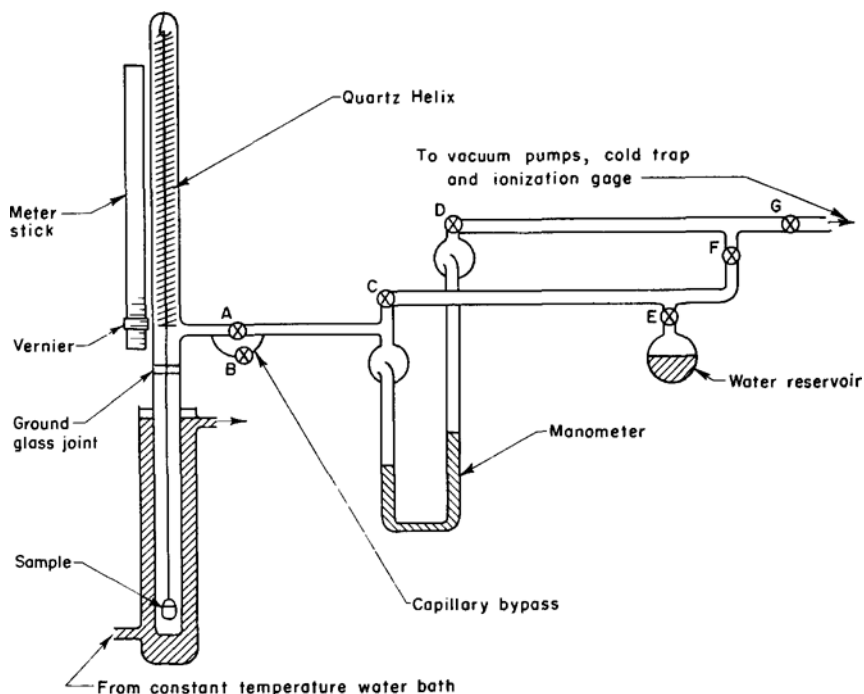
FIGURE 1. — Water sorption apparatus; schematic; not to scale.

as much as 1 percent difference in density. The manometer is read with a cathetometer to ± 0.2 mm. All pressure readings are corrected to mm Hg at 0°C. The experimental error in the relative pressure, P/P_0, is then ± 0.001. The small temperature coefficient for the silicone oil density is negligible within room temperature fluctuations. Water adsorption by the manometer fluid gave a vapor pressure reduction within the sorption system of 0.01 P/P_0 units per 24 hours. While this change is ten times the experimental error in determining P/P_0 it does not influence the results because equilibrium is obtained in a few hours. Even where a long time is allowed for equilibration of a given point, an easily measured change in weight of water adsorbed by the clay accompanies the change in vapor pressure due to water adsorption or desorption by the manometer fluid.

The extension of the quartz helix, obtained from Microchemical Specialties Co., Berkeley, California, is measured with a vernier-equipped meter stick. Employing a 10x reading glass to facilitate reading, the helix extension can be reproducibly determined to ± 0.03 mm. For both helices in use, the extension is 2.4 mg/mm and is linear in the weight range 900 to 1200 mg. The error in reading the helix gives an error in determining the weight of water adsorbed per gram of clay of ± 0.07 mg/g.

Room temperature was maintained at $26 \pm 1°C$; fluctuations within this limit had no effect on the pressure readings.

Ernsberger's (1953) equation for temperature correction of the quartz helix was found to be completely satisfactory.

TABLE 1.—AGING CONDITIONS FOR LI KAOLINITE USED IN SORPTION STUDIES[1]

Code	Name	Water Content (percent)	Time (days)	Temp. (°C)	Pressure
A	Initial	0.7	0	25	1 atm
B	Slurry aged at 25°C	1000.	111	25	1 atm
E	Slurry aged at 70°C	1000.	111	70	1 atm
C	Vacuo aged 195 days	00	195	70	10^{-5} mm Hg
J	Vacuo aged 90 days	00	90	70	10^{-5} mm Hg
Q	Vacuo aged 60 days	00	60	70	10^{-5} mm Hg

[1] All samples prepared from natural kaolinite as follows: 6 g clay extracted five times with 100 ml portions of $1M$ LiCl at pH 5.5; time of contact for each extraction, 10 minutes.

PROCEDURE

Li kaolinite samples were aged under different conditions as given in Table 1. Aging as used herein is a general term to denote storage of samples under various conditions of time, moisture, temperature, and pressure. At the completion of the prescribed aging period, samples were taken for readily extractable alumina and pH determination, exhaustive extraction of alumina, and water sorption.

Readily extractable alumina is defined as the alumina in the supernatant after extraction of a 5 g clay sample with 25 ml of $1N$ ammonium acetate solution at pH 4.8 and employing a 2-hour extraction period. The alumina in the supernatant is determined by the use of aluminon reagent (Peech and English, 1944, p. 173). Exhaustive extraction of alumina is obtained by extraction of a 1-g sample 22 times with 100-ml portions of $1M$ LiCl solution at pH 3.0 and a time of contact of 24 hours for each extraction. Each supernatant is analyzed for alumina in order to determine the total alumina removed during the protracted extraction. The pH is measured at 1 g clay per 10 ml H_2O with a Beckman Model H-2 pH meter.

Prior to the taking of sorption data, the 1.1-g clay sample is outgassed 48 hours under a vacuum of 10^{-5} mm Hg and at a temperature of 70°C. This procedure has been shown to be equivalent to the weight loss obtained by drying to constant weight in air at 115°C (Mooney, Keenan, and Wood, 1952). The determination of the weight of water adsorbed depends upon the difference in weight between the dry clay reading and the reading at any given vapor pressure; therefore, if the dry weight readings taken at the beginning and completion of each run did not agree within ± 0.03 mm, the data were not used.

With the high vacuum and small sample size, the time of equilibration of the water on the kaolinite is very short. Figure 2, where the amount adsorbed (X)
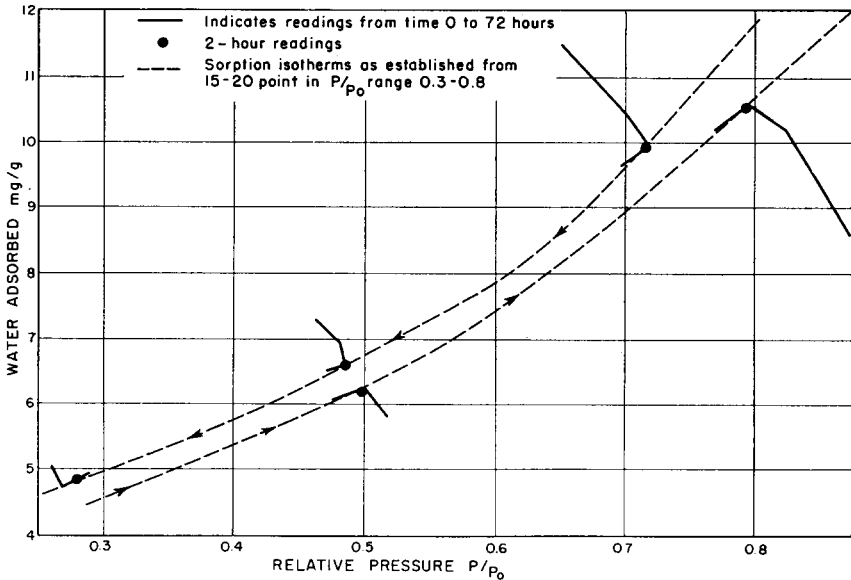
FIGURE 2. — Segment of sorption isotherm showing approach to equilibrium.

and the relative pressure (P/P_0) have been plotted on an expanded scale for a portion of the isotherm, illustrates the approach to equilibrium. Weight and pressure readings were made immediately after raising or lowering the vapor pressure and subsequent readings were made at 0.25, 0.5, 1.2, 4, 8, 24, 48, and 72 hours. The solid lines in Figure 2 indicate the changes observed throughout the time period and the black dots indicate the 2-hour readings. These data show that 2 hours is sufficient time to reach equilibrium. The continuing change with time is due to adsorption of water by the manometer fluid; however, this effect does not materially influence the results. Hence the procedure was adopted of allowing each point to equilibrate a minimum of 2 hours and generally not more than 4 hours, although occasionally a point would stand for 16 hours.

RESULTS

Reproducibilities of both the adsorption and desorption branches of the isotherm for separate runs on the same sample were found to be well within the estimated experimental error. Where various treatments are to be evaluated, knowledge regarding the reproducibility of samples prepared by the same method is desirable. Figure 3 clearly demonstrates that the reproducibility of the adsorption and desorption branches of the isotherm for separately prepared samples is excellent. These results provide a reproducible reference with which to compare the influence that different treatments have on the water sorption behavior of Li kaolinite.
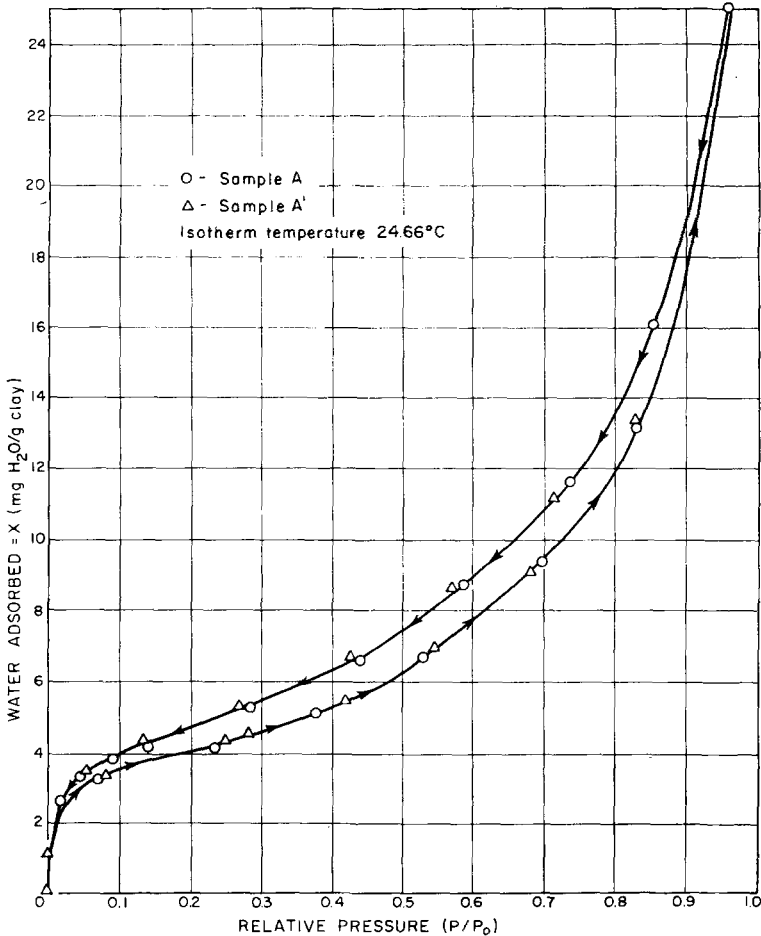
FIGURE 3. — Water vapor sorption isotherms for Li kaolinite as initially prepared.

While the reproducibility of the water sorption isotherms on Li kaolinite is excellent if the sorption data are taken very shortly after the sample has been prepared, samples that stood in the laboratory for a few weeks showed slight deviations in their sorption behavior. In order to understand what happens during this time lapse, termed herein "aging," and in the hope that the changes would be magnified, samples were aged at a higher temperature, 70°C. Aging conditions for the different samples are given in Table 1.

Adsorption isotherms obtained after various aging conditions are shown in Figure 4. Sample E, Li kaolinite aged in a water slurry at 70°C, adsorbed more water at all values of P/P_0 than did the initial Li kaolinite, Sample A. Sample C, Li kaolinite vacuo aged 195 days, adsorbed about 25 percent less water at all values of P/P_0 than did the initial Li kaolinite, Sample A.
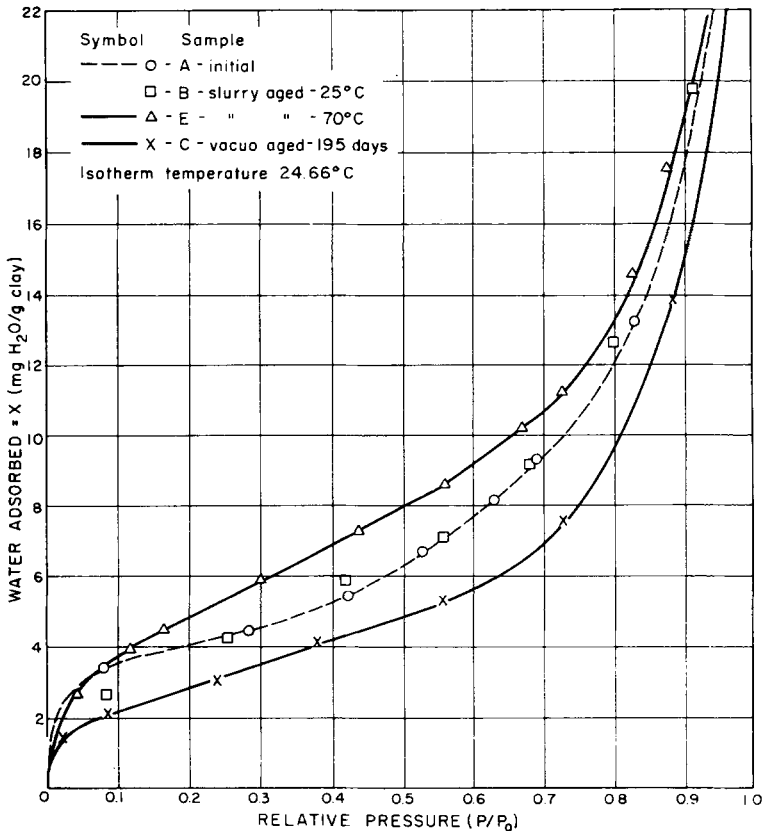
FIGURE 4. — Water vapor adsorption isotherms for Li kaolinite after various aging conditions.

The desorption isotherms for Samples A and B lie above the adsorption isotherm, giving rise to the phenomenon called hysteresis, which persists to very low values of P/P_0 for Samples A and B. In Sample E hysteresis is confined to the P/P_0 value range where capillary condensation would account adequately for the observed hysteresis.

Protracted extraction of the samples that had been aged in water slurry, and of the initial Li kaolinite, gave sorption isotherms that fall on a single curve (Fig. 5). This adsorption curve is not coincident with adsorption for Sample A because Sample A contains considerable readily extractable alumina. The hysteresis loop shown for the exhaustively extracted clays in Figure 5 is similar in size to that shown for Sample A in Figure 3. Protracted extraction of the Li kaolinite that had been vacuo aged changed the adsorption isotherm slightly, indicating that the reduced adsorption on the vacuo aged Li kaolinite is fairly permanent. Soaking the vacuo aged clay in liquid water 48 hours prior to making the sorption measurements results in an adsorption isotherm identical to
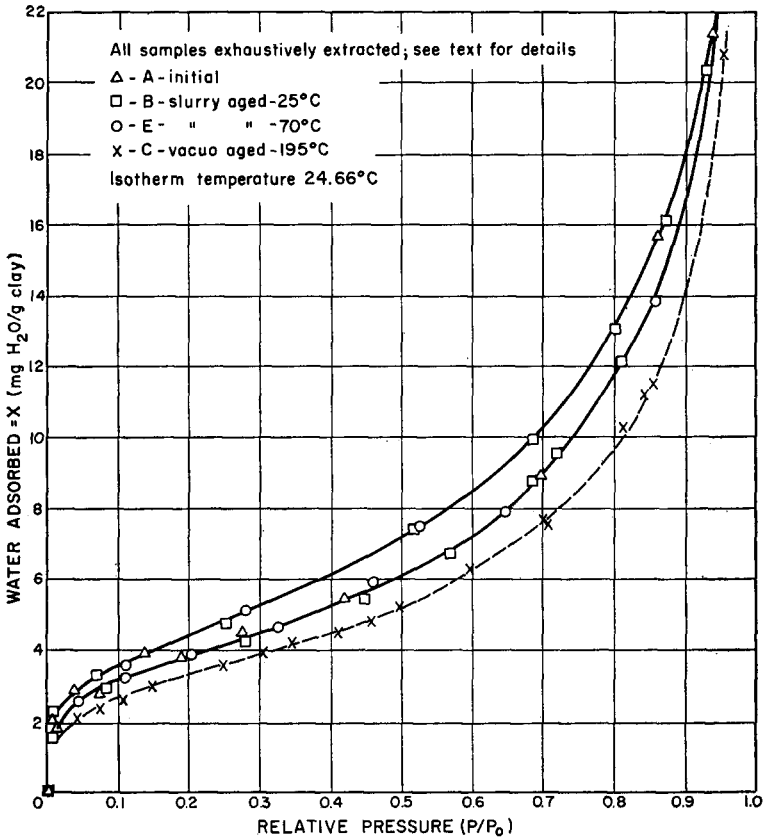
FIGURE 5. — Water vapor sorption isotherms for extracted Li kaolinites.

that obtained after protracted extraction of the vacuo aged clay.

The sorption data may be summarized as follows:

1. Li kaolinite aged in a water slurry at 70°C adsorbs more water at all values of P/P_0 than does the initial Li kaolinite. Hysteresis in this slurry-aged clay disappears for values of $P/P_0 < 0.3$. Protracted extraction of clay slurry aged at 70°C shows sorption behavior identical to the unaged Li kaolinite similarly extracted; i.e., the water adsorption is reduced and the hysteresis loop, which persists to very low values of P/P_0, is restored.

2. Li kaolinite vacuo aged at 70°C for 195 days adsorbs 25 percent less water at all values of P/P_0 than does the initial Li kaolinite. Protracted extraction of the Li kaolinite changes the adsorption isotherm only slightly. The reduced water adsorption which results from vacuo aging is quite permanent.

Data for readily extractable alumina, pH, and total alumina removed during protracted extraction are given in Table 2. The rate of alumina extraction is shown in Figure 6. Variation in the extraction time has an insignificant effect

Table 2.—Chemical Data for Kaolinites Used in Sorption Studies

Sample		Readily Extractable Alumina[1] (mg Al/g)	pH[2]	Total Alumina Removed During Protracted Extraction[3] (mg Al/g)
Code	Name			
A	Initial Li Kaolinite	0.10	6.4	------
	Extracted Sample A	------	6.5	1.85
B	Slurry Aged, 25°C	0.18	6.8	------
	Extracted Sample B	-----	....	1.48
E	Slurry Aged, 70°C	0.04	4.8	------
	Extracted Sample E	------	....	1.08
C	Vacuo Aged, 70°C	0.10	4.8	------
	Extracted Sample C	------	....	1.20

[1] 5 g clay shaken 2 hours with 25 ml $1N$ ammonium acetate solution at pH 4.8, centrifuged and supernatant analyzed for Al.
[2] 1 g clay/10 ml H_2O.
[3] Details given in text.

upon the shape of the curves in Figure 6. For the initial Li kaolinite and the vacuo aged Li kaolinite, the rate of alumina extraction starts high and then rapidly drops to a fairly low and constant value. For slurry-aged Li kaolinite, however, the rate of alumina extraction starts low, rises to a maximum, and then drops to about the same constant value as for the other two samples. After protracted extraction, the constant amount of alumina extracted each time, 0.6 mg Al/g clay, is believed to represent crystal solubility.
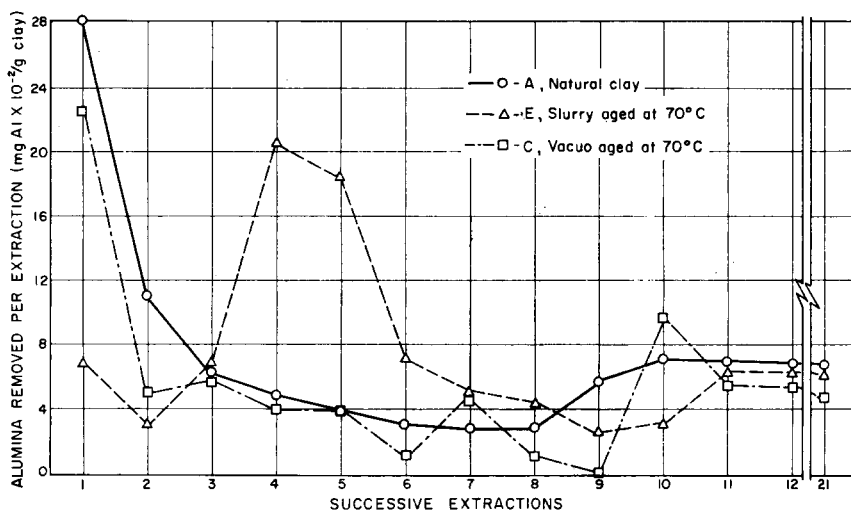

Figure 6. — Alumina removed in successive extractions.

DISCUSSION

Both the sorption and chemical data indicate that aging of the clay stored at high water content (slurry) is quite different from that of clay stored at zero

water content (vacuo). Slurry-aged Li kaolinite can be quite easily reconverted to a lithium kaolinite having sorption characteristics identical to a lithium kaolinite sample that has not been aged. For vacuo-aged Li kaolinite the reduced water adsorption appears to be a permanent charge. The two cases, therefore, are treated separately.

Slurry Aging

The difference in readily extractable alumina between Samples A and E suggests that the difference in the adsorption isotherms for Samples A and E may be related to some variation in the chemical nature of the alumina associated with the Li kaolinite. Two likely variations in the alumina associated with clay when slurry aged (Sample E) are either a change in the nature of amorphous alumina or a change from amorphous alumina to exchangeable alumina. Conversion of Li kaolinite to Al kaolinite is favored because montmorillonoid is known to convert spontaneously to an Al clay with time (Mathers, Weed, and Coleman, 1955). The sorption behavior of Al kaolinite relative to Li kaolinite largely hinges on the hydration of the exchangeable ions associated with the clay.

Before hydration of exchangeable ions is discussed, a consideration of the nature and abundance of exchange sites on kaolinite is necessary. Schofield and Samson (1953) present a convincing argument that the exchange sites on kaolinite, in acid media, must arise from isomorphous substitution. In fact, as they point out, if exchange sites on kaolinite are due to so-called "broken bonds" at crystal edges, then below pH 3.0 kaolinite would have no cation-exchange capacity. Table 3 shows that kaolinite does maintain a very significant proportion of its exchange capacity to quite low pH values. From Table 3, it is estimated that at least two-thirds of the exchange capacity is due to isomorphous substitution. Since the most likely place for isomorphous substitution is in the tetrahedral layer, any ion that is sufficiently small to enter the hexagonal holes in the oxygen network of the tetrahedral layer will produce a stronger bond because of the small distance between exchangeable ion and origin of charge deficiency.

On the assumption of uniform distribution, the charge density can be computed. For this particular kaolinite, the specific surface is about 12 m^2/g and the exchange capacity, 2.7 meq/100 g, which gives a reciprocal charge density of approximately 75A^2/exchangeable ion site. In other words, the distance between exchangeable ion sites is at least 8A. This means that for a single Al ion to neutralize two exchangeable ion sites on a single crystal face[1] the bond length will be at least 4A. In view of the fact that exchangeable ion bond strengths are fairly low to begin with, this long bonding would greatly weaken the exchangeable Al-to-clay bond. A more likely possibility is that the ex-

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[1] One Al ion could neutralize two exchange sites on opposing crystal faces of two different kaolinite particles; however, the chances are slight that the majority of exchangeable Al ions could be so satisfied, particularly in view of the fact that the favored stacking of kaolinite units is silica sheet to gibbsite sheet and not silica sheet to silica sheet.

Table 3.—Kaolinite Cation-Exchange Capacity as a Function of pH of
the Extracting Solution

pH	Cation-Exchange Capacity (meq/100 g)
3.0	1.75 ± 0.05[1]
4.2	1.90 ± 0.10
5.0	2.40 ± 0.05
7.0	2.70 ± 0.20
9.2	3.70 ± 0.3

[1] Average deviation from mean of 4 determinations except at pH 7.0, where 8 determinations were made.

changeable Al ion is present as a complex ion such as $Al(OH)_2^+$. Whatever the exact nature of the exchangeable Al, it would appear that a dry Al clay would not be nearly as stable a structure as a dry Li clay, whereas in water the reverse would be true.

When dry clay is exposed to H_2O vapor, water is taken up by the clay surface and by the exchangeable ions. The ease of ion hydration depends upon whether the tenacity of the clay for the ion or the tenacity of the water for the ion predominates.

Exchangeable Li ions which probably are situated in the hexagonal holes in the tetrahedral oxygen layer have their hydration retarded because the ion hydration tendency cannot overcome the combined effect of stearic hindrance and the relatively stable exchangeable ion bond in the dry clay. At higher P/P_0 the exchangeable Li ions do hydrate, and on desorption the hydrated Li ions resist dehydration, thus giving rise to a marked hysteresis to very low P/P_0.

On the other hand, exchangeable Al ions which are probably present even in a dry clay as a complex ion, $Al(OH)_2^+$, would not fit into the hexagonal hole in the oxygen layer; therefore, the bond between exchangeable Al ions and the clay is much weaker than the bond between exchangeable Li ions and the clay. The result is that exchangeable Al ions hydrate readily at very low P/P_0 and desorption is essentially the reverse of adsorption; i.e., there is no hysteresis at low P/P_0.

Because of the differences in chemical behavior of Al versus Li, there are other changes that one would expect to result from the conversion of Li kaolinite to Al kaolinite. Al kaolinite should differ from the initial Li kaolinite in the following respects: (1) have a lower pH; (2) adsorb more H_2O at any value of P/P_0 less than near saturation; (3) have less readily extractable alumina; (4) have a different rate of alumina extraction during the protracted extraction procedure; and (5) have about the same total extractable alumina because appreciable readily extractable alumina is present in the particular initial Li kaolinite used. A comparison of the data for Li kaolinite, Sample *A*, with the data for Sample *E*, a supposed Al kaolinite, shows that the above predictions are completely satisfied. The difficulty with which the exchangeable Al is replaced would seem to contradict the premise that exchangeable Al is

more loosely bound to the clay than exchangeable Li; however, in the extraction data presented in Figure 6, the exchangeable ions are fully hydrated because there is just one gram of clay per 100 ml of solution, while during adsorption there is from zero to 0.01 ml water per gram of clay. In fact, the resistance of Al to displacement by Li is what one would expect from the normal lyotropic series.

In view of the fact that exchange reactions are reversible, two further predictions can be made if Sample E is an Al kaolinite. By ion exchange, it should be possible to restore Sample E to Li clay, and it also should be possible to prepare an Al clay without aging the sample. The adsorption isotherm, and the hysteresis loop which persists to very low values of P/P_0 shown in Figure 5, clearly indicate that Sample E, the Al kaolinite, has been restored to a Li kaolinite. Al kaolinite, Sample K, has adsorption and desorption isotherms identical to those of Sample E as shown in Figure 7. Thus, all aspects of the sorption and chemical data on Sample E, Li kaolinite stored in a water slurry 111 days at
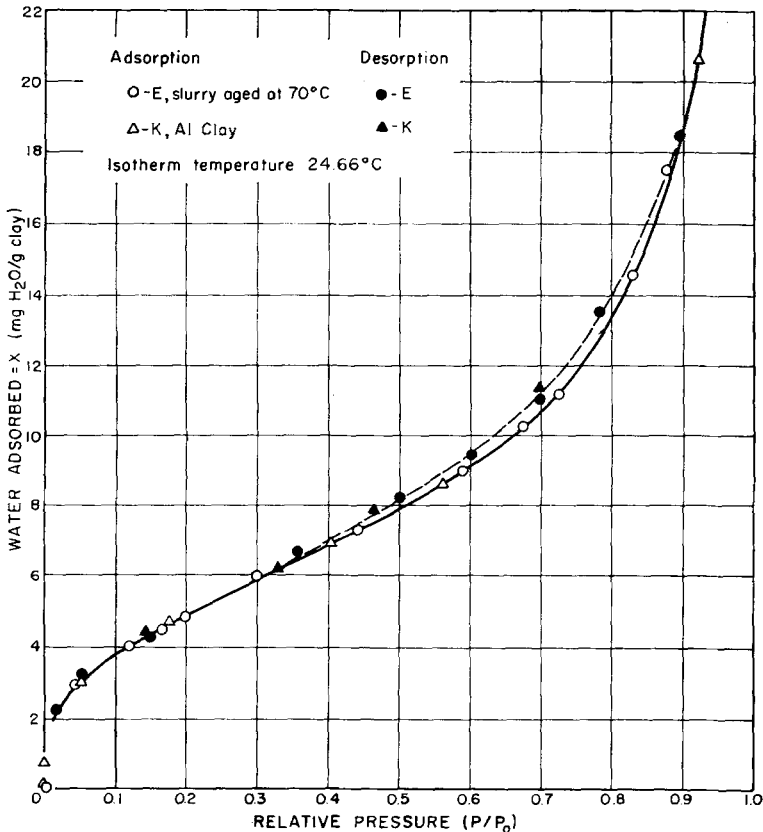

FIGURE 7. — Water vapor sorption isotherms for Li kaolinite slurry aged at 70°C and for Al kaolinite.

70°C, verify the hypothesis that aging of Li kaolinite at high water content pro-
duces an Al kaolinite.

As the only difference in aging conditions between Samples B and E is the
higher temperature employed for Sample E, Sample B is considered to be an
intermediate stage in the aging process between the initial Li kaolinite, Sam-
ple A, and Al kaolinite, Sample E. The sorption and chemical data for Sample
B suggest that this intermediate stage consists of a sloughing off of alumina,
probably at the edges of kaolinite crystals. Given sufficient time this alumina
would take up exchangeable ion sites but by elevating the temperature, as was
done for Sample E, the reaction is accelerated.

Vacuo Aging

The data for Sample C, vacuo aged 195 days, show that vacuo aging results
in a permanently reduced water sorption. Since the reduced sorption is fairly
uniform over a large segment of the isotherm, the decreased water sorption on
vacuo-aged clay, Sample C, may be adequately explained by a decrease in the
surface area available for adsorption. The fact that protracted extraction of
the vacuo-aged clay gave the same isotherm as the vacuo-aged clay soaked in
liquid water shows that ion exchange is not responsible for the reduced water
sorption. Therefore, the nature of the changes that take place in lithium kaoli-
nite upon vacuo aging is quite different from the changes discussed for slurry-
aged lithium kaolinite.

One hundred ninety-five days is a sufficiently long time that any further
change is probably slight. In an attempt to ascertain how rapidly the reduced
water adsorption takes place, samples of lithium kaolinite were prepared and
aged under exactly the same conditions as Sample C except that the time of ag-
ing was changed from 195 days to 60 and 90 days. Adsorption isotherms for
different times of vacuo aging are given in Figure 8 along with the adsorption
isotherms for the initial lithium kaolinite. The ordinate scale in Figure 8 was
expanded to magnify the differences between the various aging times. The dif-
ference in water adsorption between 90 and 195 days of vacuo aging is slight.
In order to obtain a first approximation as to the ultimate sorption reduction,
that is, the amount of reduction that would occur in an infinite time, the aver-
age percent reduction in water adsorption between $P/P_0 = 0.1$ and $P/P_0 = 0.7$
for the unaged clay and for 90 and 195 days vacuo aged was plotted against the
reciprocal of time $(1/t)$ and extrapolated to $1/t = 0$. This extrapolation gives
25 ± 2 percent reduction in water adsorption. Figure 8 shows that the change
effected in 60 days is as permanent as the change after 195 days, the only differ-
ence being that the amount of reduction in 60 days is about one-half that ob-
tained after 195 days.

The fairly uniform reduction in water adsorption over a large segment of
the isotherm shown by all the vacuo-aged samples indicates that the reduction
could be adequately accounted for by lowering the surface area. This hypo-
thesis was tested in the following manner. The general B.E.T. equation (Bru-
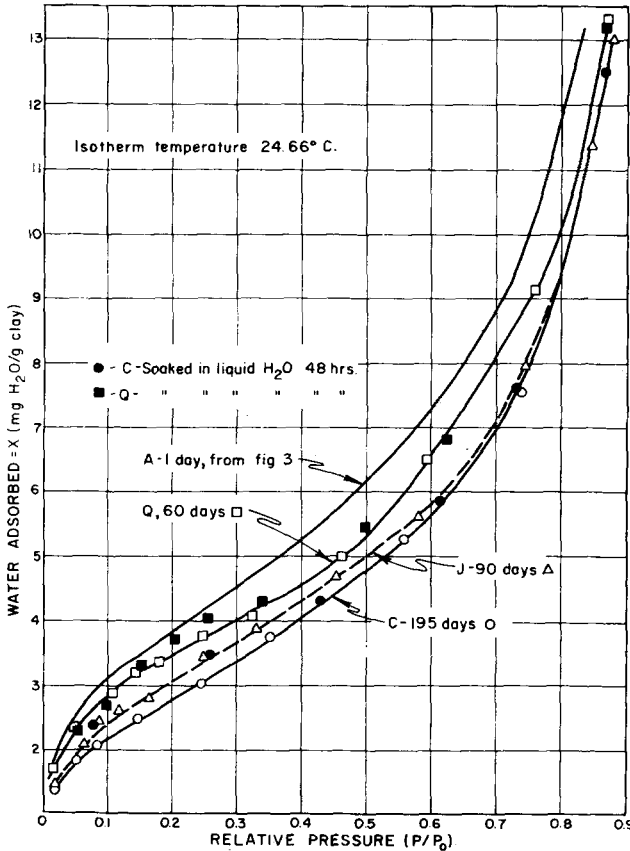nauer, 1945, p. 154) for the best fit is calculated for the initial unaged lithium

FIGURE 8. — Water vapor adsorption after storage at 70°C in vacuo.

kaolinite. Then the surface area constant in this equation is reduced by 22 percent, which is the average reduction observed after 195 days of vacuo aging. Employing the general B.E.T. equation with the lower surface area constant, the computed isotherm agrees quite well with the observed 195-day isotherm.

The simplest method by which the surface area of a given kaolinite could be reduced would be to stick kaolinite particles together. Since the major contribution to surface area comes from the crystal faces (the ab plane), a face-to-face sticking of 2 particles reduces the surface area of these two particles approximately 25 percent. Two possible mechanisms that could cause kaolinite particles to stick together are: (1) cementation of kaolinite by amorphous alumina; or (2) twinning of kaolinite particles.

Alumina might act as a cement to glue kaolinite particles together; however, readily extractable alumina is the same for Sample C as for the initial lithium kaolinite, Sample A. If alumina were acting as a cement the amount of readily
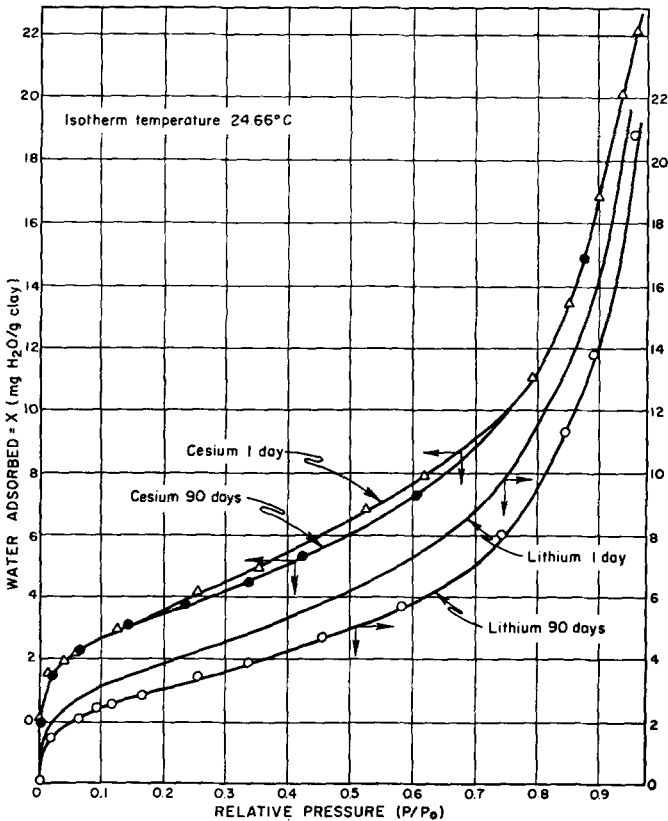
FIGURE 9. — Water vapor adsorption isotherms before and after vacuo aging of Cs and Li kaolinite. Read left-hand scale for cesium curves, right-hand scale for lithium curves.

extractable alumina should decrease; therefore, alumina does not seem to be a factor contributing to the reduced water adsorption of vacuo-aged clay. The similarity of the rate of alumina extraction during protracted extraction between A and C likewise indicates that there has been no significant change in alumina as a result of vacuo aging. It is concluded that cementation by alumina is probably not the mechanism whereby kaolinite particles are stuck together.

In the complete absence of adsorbed gases and with the small lithium ion present at the exchange sites, the crystal surfaces could essentially touch one another. In a kaolinite crystal the individual units stack oxygen surface to hydroxyl surface. Undoubtedly the most stable arrangement for the sticking together of kaolinite crystals is likewise the favored position of oxygen to hydroxyl. Statistically there is about a 50-50 chance that two kaolinite crystals will be in the favored position to form a twin. The probability of aggregates larger than twins is very small. If all particles in position to twin do stick to-

gether the surface area would be reduced approximately 25 percent. If this mechanism whereby larger kaolinite particles are formed is correct, it should be possible, by the use of a large exchangeable ion, to prevent the oxygen and hydroxyl surfaces of separate particles from approaching each other sufficiently close to coalesce. To test this hypothesis, Cs kaolinite was prepared. The diameter of the Cs ion is 3.30A, which means that the surface exchangeable Cs ions will rest on the oxygen surface and thus prevent the close approach of the hydroxyl surface of another kaolinite particle.

Figure 9 shows that the change in cesium kaolinite after 90 days vacuo aging is very slight compared with the change in lithium kaolinite after 90 days vacuo aging. The fact that isotherms for aged and unaged Cs kaolinite are the same below $P/P_0 = 0.15$ and above $P/P_0 = 0.70$ indicates that the slightly different water adsorption produced by aging of Cs kaolinite can not be due to a reduction in surface area. Further evidence that vacuo aging has produced larger particles and thus a lower surface area was obtained from particle size analysis of a kaolinite before and after vacuo aging. A kaolinite sample having a particle size distribution greater than 1 micron and less than 2 microns was prepared, made homoionic to lithium, and tested in the same manner as Sample J, vacuo aged 90 days. The water adsorption was reduced. Experimental difficulties prevented the completion of the sorption experiments. After vacuo aging a particle size analysis showed that about 20 percent of the particles were larger than two microns.

CONCLUSIONS

The water vapor sorption character of lithium kaolinite changes with time. The magnitude and nature of the changes are strongly influenced by the storage conditions. Lithium kaolinite allowed to stand in water will spontaneously convert to an Al kaolinite, and the water sorption of the clay is increased. Storage of lithium kaolinite in vacuo produces a permanent coalescence of kaolinite particles, which decreases the water sorption of the kaolinite.

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