

WATER-VAPOR ADSORPTION ON CLAYS

by

ROBERT T. JOHANSEN AND H. N. DUNNING

Petroleum Experiment Station, Bureau of Mines, U.S. Department of the Interior,
Bartlesville, Oklahoma

ABSTRACT

The distinctive response of clay minerals to water indicated that it should be possible to determine the water sensitivities of sedimentary rock samples directly by water-vapor adsorption measurements. Therefore, the adsorption of water-vapor by standard clay samples and by core samples from oil-producing formations has been investigated.

Water-vapor adsorption isotherms of the montmorillonite and kaolinite samples are characteristic of the clay type and serve as an aid in their identification. The illite isotherm was intermediate between those of the other two types.

Water-vapor adsorption by core samples from oil-producing formations varied with the contents of swelling clays and with water-sensitivities as indicated by previous x-ray analyses and permeability studies. Core samples containing montmorillonite clay adsorbed water vapor strongly and exhibited typical adsorption-desorption hysteresis. Correlations of nitrogen and water-vapor adsorption studies with clay analyses and permeability measurements show that the water-vapor adsorption method is a promising means for the direct measurement of the water sensitivities of sedimentary formations.

INTRODUCTION

The adverse effects of clay minerals indigenous to petroleum-producing formations on waterflooding and well-completion methods recently has received considerable attention. A knowledge of the types and amounts of clay minerals present would allow estimates of the response of such formations to injected or infiltrated water.

A method for the direct evaluation of "water sensitivity" has been developed based on the measurement of water-vapor adsorption. The correlation of such data with the results of nitrogen-adsorption measurements provides valuable information on the content and properties of clay minerals in sedimentary rocks. The method is relatively simple and has the advantage that it may be used with small, irregularly shaped chips or shale-streaked samples as well as with typical core samples.

Recent studies by Keenan *et al.* (1951) showed that the adsorption of nitrogen and water vapor on a non-swelling clay apparently occurred on essentially the same surface. However, Mooney and associates (Keenan *et al.*, 1951; Mooney *et al.*, 1952a) observed that with montmorillonite, water vapor was adsorbed between the platelets, as well as on the surface available for nitrogen adsorption. The adsorption isotherms of water vapor on a swelling clay were not reproducible, apparently because adsorption is sensitive to the initial water content of the clay. Mooney *et al.* (1952a) reported

that the desorption isotherms were reproducible and generally capable of interpretation by the BET theory.

These results indicated that it should be possible to determine the water sensitivities of core samples directly by water-vapor adsorption measurements. Therefore, a fundamental study was made of water-vapor adsorption on API reference clay minerals. These clays have been investigated extensively by many laboratories, so that a large amount of information concerning their properties is available in an API report (1949). A homoionic montmorillonite also was prepared and studied by water-vapor and nitrogen adsorption. Finally, water-vapor and nitrogen adsorption measurements were made on several core samples from petroleum-producing formations. The results corroborated the previously established clay contents and water sensitivities of these samples.

ACKNOWLEDGMENT

The authors gratefully acknowledge the assistance of O. C. Baptist who supplied the core samples and data on their clay contents and water sensitivities and also are indebted to P. B. Lorenz for helpful comments and suggestions.

EXPERIMENTAL

The API reference clay samples used in this study were H-26, a montmorillonite from Clay Spur, Wyo.; H-35, an illite from Fithian, Ill.; and H-5, a kaolinite from Bath, S. C. Another montmorillonite sample (BC-Volclay) was obtained from the American Colloid Co. of Chicago, Ill.

The core samples used were from three petroleum-producing formations in the Wyoming area—the Tensleep, Second Frontier and Newcastle sands—and will be referred to by the name of the sand from which they were taken. These samples were prepared and studied extensively by Baptist and Sweeney (1955, 1957), who determined their compositions by x-ray analysis and their water sensitivities by permeability measurements.

The BC-Volclay was converted to a homoionic sodium form by treatment in an ion-exchange column according to the method of Lewis (1953). A 1 percent suspension of the clay was sedimented in a tall cylinder for 20 hr and the sediment discarded. Then the suspension was allowed to flow through a 1 × 20 in. column containing an ion-exchange resin of the sulfonic acid type—Dowex 50. The resin previously had been treated with a 1 percent solution of sodium chloride and then flushed with distilled water until the effluent showed no traces of sodium, either by the zinc-uranyl acetate or flame test. The delivery rate was maintained between 5 and 8 ml/min., a slow enough rate to permit essentially complete cation exchange, according to Lewis (1953).

The surface areas of the samples were determined by the use of a standard BET nitrogen-adsorption apparatus, as described by Harkins (1952) and by Brunauer, Emmett and Teller (1938), at liquid-air temperatures. The

powder samples were loaded into sample holders in such a way as to minimize dead space. The core samples were mounted in specially designed holders consisting of a capillary tube sealed to a longer piece of glass tubing of a diameter just large enough to accommodate the sample. The open end of the tubing then was sealed as close as possible to the core sample without charring. The measurement of surface areas of sedimentary rock samples has been discussed in detail by Brooks and Purcell (1952).

The water-vapor adsorption study was performed with a gravimetric apparatus similar to that of Keenan *et al.* (1951), Mooney *et al.* (1952a, 1952b) and Wiig and Juhola (1949) and was designed to accommodate six samples simultaneously. A schematic drawing of the apparatus is shown in Fig. 1. The two large flasks serve as ballast flasks and reservoirs for water vapor. Triple-distilled water was charged to the reservoir by vacuum distillation. Mercury was used in the manometer to avoid the necessity for

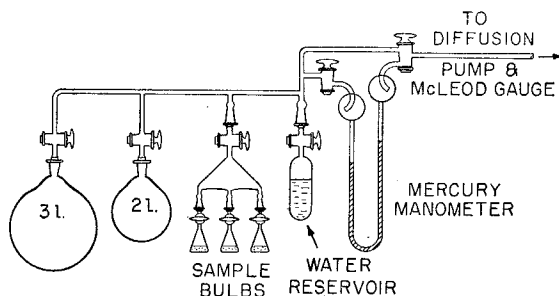


FIGURE 1.—Water-vapor adsorption apparatus.

corrections due to dissolution of water vapor in the manometric fluid. Mercury levels were measured with a cathetometer capable of being read to 0.0001 cm, and the experiments were conducted in an air-conditioned laboratory maintained at $25 \pm 1^\circ\text{C}$. For measurement of water-vapor adsorption, the sample bulbs were first cleaned, dried, and weighed and the stopcocks left ungreased. The clay samples were loaded into the bulbs through the barrel of the stopcock. The stopcocks then were carefully cleaned of clay and greased with a minimum amount of high-vacuum lubricant. The sample holders were attached to the apparatus by greased, standard taper joints and evacuated to constant weight. During this evacuation, care had to be taken to prevent overly rapid evolution of gas, which tends to entrain the sample.

The samples were degassed at 25°C . Extended evacuation was required for sensibly complete degassing of the consolidated samples. The nitrogen surface areas and water-vapor adsorption values of the clays were determined with duplicate samples, while with the cores the same samples were used for measuring both properties.

After the system had been evacuated, the reservoir flasks were filled with the desired amount of water vapor and the system was allowed to come to

equilibrium during a 20 hr period. The results of Mooney *et al.* (1952a) indicated that this period would be satisfactory; the present studies corroborated these results. Finally, the stopcocks of the individual sample holders were closed, and the samples removed from the apparatus; the lubricant was removed from the standard taper joints with a lintless paper moistened with chloroform. The amount of water vapor adsorbed then was determined directly by weight. Successive measurements were made at increasing values of relative pressure (P/P_0).

Desorption of water vapor was investigated with samples that previously had been saturated with water vapor. In these studies, the reservoir flasks were partly evacuated, the stopcocks to the sample holders were opened, and the system was allowed to come to equilibrium at successively lower relative pressures. The amount of water desorbed was measured directly by weight, using the procedures described above.

The adsorption-desorption isotherms of the core samples were determined in much the same way as were those of the clay samples. Because of the relatively small amount of clay minerals in these cores, the weight of water vapor adsorbed was quite small. Therefore, the dead space of the sample holder was reduced to a minimum. Vacuum corrections were negligible with properly designed apparatus.

RESULTS AND DISCUSSION

The surface areas of the clay samples as measured by nitrogen adsorption are listed in Table 1. These values agree with those of other workers using similar samples. Keenan *et al.* (1951) and Mooney *et al.* (1952a) report that the surface area of a natural montmorillonite and kaolinite were 27 and 18.6 m²/g, respectively. The surface area of the illite sample was relatively

TABLE 1.—SURFACE AREAS OF CLAY SAMPLES BY NITROGEN AND WATER-VAPOR ADSORPTION

Sample	Geographical Location	Surface Area, m ² /g		Ratio W/N
		Nitrogen:	Water Vapor	
Bentonite H-26	Clay Spur, Wyo.	30 ± 1.0	164 ¹	5.5
			206 ²	6.9
BC-Volclay	Wyoming	38 ± 3.0	138 ¹	3.6
			195 ²	5.1
Sodium Volclay	Wyoming	38 ± 1.0	203 ¹	5.3
			250 ²	6.6
Illite H-35	Fathian, Ill.	56 ± 1.0	52 ¹	0.9
			82 ²	1.5
Kaolinite H-5	Bath, S.C.	16 ± 1.0	12 ^{1,2}	0.8

¹ Values from adsorption measurements.

² Values from desorption measurements.

high. However, the sample is mainly of the potassium type, and earlier work by the Cornell group (1951) showed that a homoionic potassium illite had a surface area of 88.4 m²/g. A natural illite (grundite) was reported to have a surface area of 39.2 m²/g.

The surface area of the BC-Volclay sample was not changed by the ion-exchange method used in making it homoionic. With the exception of this one clay, samples were treated as nearly alike as possible. The small difference between the BC-Volclay samples and the reference bentonite sample is attributed to differences in the formation of those clays. The well defined crystalline kaolinite sample has the smallest area of the samples studied since its structure leaves no room for gaseous molecules to penetrate beyond the outer surface. For this reason, gases adsorb and desorb from its surface more easily and reversibly than from the other types of clay.

TABLE 2.—SURFACE AREAS OF CORE SAMPLES AS MEASURED BY NITROGEN ADSORPTION

Core Designation	Number	Surface Area (m ² /g)
Tensleep	3066 MI	0.54 ± 0.02
„	3055	0.49 ± 0.01
„	3049 MI	0.54 ± 0.01
„ (pyridine extracted)	3049 MI	0.71 ± 0.01
Second Frontier	4357	1.97 ± 0.02
„	4355	3.20 ± 0.05
„	4351	2.54 ± 0.01
„ (crushed)	4351	2.55 ± 0.02
Newcastle	4373	0.46 ± 0.03
„	4375	0.68 ± 0.01
„	4369	3.18 ± 0.01
„ (crushed)	4369	3.15 ± 0.05

The surface areas of the core samples are listed in Table 2. Two of the core samples were crushed to grain size and their surface areas remeasured to determine if the nitrogen penetrated the entire sample. The data indicate that consolidation does not interfere with surface-area measurements, in agreement with the observations of Brooks and Purcell (1952). The Tensleep core sample seemed to have some organic material remaining in the core despite its extraction with toluene. Therefore, the surface area of one sample from this sand was measured, the core extracted with pyridine, and the surface area redetermined. The extracting liquid became colored, indicating removal of some organic residue. Subsequent measurement showed that the surface area increased slightly. Values of surface area less than about 1 m²/g may involve considerable errors. However, the precision of the measurements was acceptable, as shown in Table 2.

The adsorption isotherms of water vapor on the three clay types are shown in Fig. 2. The large hysteresis effect with bentonite, a characteristic of this clay type, is evident. As observed by Keenan *et al.* (1951), the isotherm for kaolinite is readily reproducible and reversible. The isotherm for illite is intermediate between those of the two other types, as might be expected from its composition. The extent of hysteresis with the illite samples also is intermediate. The isotherm for montmorillonite is similar to those determined by Mooney *et al.* (1952a), indicating that, although the isotherm is not capable of description as one of the classical types, its general properties can be predicted. The steep section in the middle of the isotherm is characteristic of montmorillonite and is believed to be associated with the degree of hydration of the clay platelets; however, a rigid

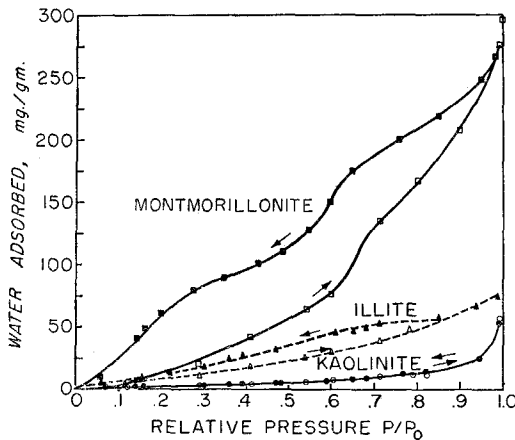


FIGURE 2.—Water-vapor adsorption of clay types.

interpretation has not been advanced. The desorption isotherm shows an even more pronounced change at about the same relative pressure (0.5–0.6). As observed by Mooney *et al.* (1952a), the desorption isotherms were reproducible while the adsorption isotherms were reproducible only after the first adsorption and then with difficulty. This indicates an apparent change in the clay structure, which does not return to the original condition upon desorption. Similar samples having their isotherms measured for the first time respond in a nearly identical manner under the same treatment. Some of the difficulties concerned with reproducibility of the adsorption isotherms probably can be explained by consideration of the hysteresis phenomenon. The beginning of the hysteresis loop is very near to zero relative pressure, and inability to dry a sample to this point may account for the lack of reproducibility of adsorption. The hysteresis phenomenon has been observed in nitrogen-adsorption measurements for several years and has been discussed by Brunauer (1945) and others, and recently by Carman (1953).

However, under usual conditions, the hysteresis loop is considered to be caused by capillary condensation and occurs at high relative pressures. Barrer and McLeod (1954) found hysteresis for all substances adsorbed on montmorillonite. The hysteresis loops closed at high relative pressures ($P/P_0 = 0.5$) with nonpolar molecules and extended to very low relative pressures with polar molecules. The hysteresis with nonpolar molecules was attributed to capillary condensation. The unusual hysteresis with polar molecules was attributed to a barrier caused by the surface energy required for penetration of the unswollen lattice by the adsorbate or for nucleation of the adsorbate-rich phase. According to this theory, metastable phases exist until a threshold value of relative pressure is reached. These concepts account rather successfully for the peculiarly shaped adsorption-desorption isotherms of montmorillonite.

The effect of making a clay sample homoionic, by exchanging the natural cations with sodium, was determined by measuring the nitrogen surface area and water-vapor adsorption of a natural and a homoionic clay (BC-Volclay). The specific surface area, as mentioned earlier, did not change appreciably owing to the ion-exchange treatment. The water-vapor adsorption was increased somewhat as a result of this treatment. However, the results still are comparable with those of the natural bentonite samples. These results corroborate measurements by the Cornell group (1951) and indicate that the natural Wyoming bentonitic clays were mainly of the sodium type. Mooney *et al.* (1952b) and Barshad (1955) report that the introduction of other cations, particularly divalent ones and hydrogen, is reflected by a marked change in the shape of the adsorption isotherm.

The difference between adsorption of water-vapor and nitrogen are made readily apparent by calculating the water-vapor surface areas (Table 1). The much larger areas available for water vapor than for nitrogen are a result of the swelling lattice; the larger areas of montmorillonite observed during desorption are a reflection of the hysteresis effect.

The ratios of water vapor to nitrogen surface areas for montmorillonite indicate the marked change in properties of such clays. Although the application of the BET theory for calculation of surface area from water-vapor data involves some assumptions as to the state of the adsorbed water molecules, these data indicate that such correlations allow ready differentiation of montmorillonites from other clay types.

The surface areas of the Tensleep and Newcastle samples, calculated from water-vapor adsorption, were about twice those calculated from nitrogen adsorption. The average values of surface areas of the Second Frontier samples calculated from water-vapor adsorption and desorption were 3.5 and 4.6 times those calculated from nitrogen adsorption. Reference to Table 1 shows that the ratio of "water-vapor" surface area to nitrogen surface area is highest for montmorillonite and least for kaolinite. Therefore, the high value of this ratio for the Second Frontier samples is indicative of the presence of montmorillonite clays, as is the pronounced adsorption-desorption hysteresis loop.

Because of the heterogeneous nature of sedimentary rock, a knowledge of the effect of various "impurities" on the type and extent of water-vapor adsorption by clays is of interest. The Cornell group (1951) reported that the introduction of impurities into clay samples either reduced the adsorption or had no effect. For petroleum-production applications, one of the more interesting "impurities" in clays would be silica or quartz. Therefore, several mixtures of the H-26 montmorillonite and quartz powder were prepared. The quartz powder had been carefully cleaned, ranged in diameter from 0.5 to 4 μ , and had a surface area of 3.9 m²/g. Because of its small particle size and consequent high surface area, this quartz would be expected to contribute as much or more to surface effects than would the quartz content of sedimentary rocks. The samples ranged from 20 to 100 percent montmorillonite, at approximately 20 percent intervals. The results showed that the

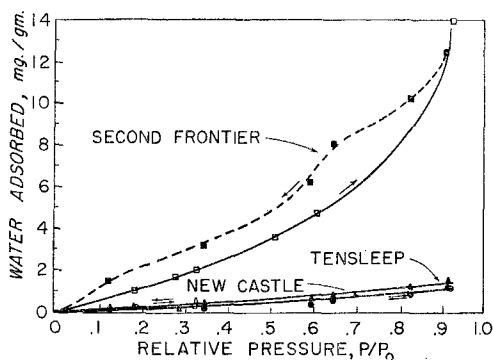


FIGURE 3.—Water-vapor adsorption on core samples.

type of adsorption was unaltered by the presence of the quartz. The decrease in adsorption was directly proportional to the amount of quartz, which apparently served as a diluent. Recalculation of the isotherms on a basis of clay content resulted in essentially identical isotherms.

The average values of water-vapor adsorption by the core samples from the three oil-producing sands are shown in Fig. 3. These results indicate a considerable response of the Second Frontier samples to water vapor and a very small response of the Tensleep and Newcastle samples. The difference between the Tensleep and Newcastle results is within experimental error.

Results of the water-vapor adsorption measurements may be correlated with the results of Baptist and Sweeney (1955), who reported that the Second Frontier samples were highly water sensitive. Samples of this sand having air permeabilities of less than 70 md. were almost completely plugged by fresh water. The results of Baptist and Sweeney (1955) also show that this sand contains a considerable amount (about 4 percent) of mixed-layer (montmorillonite-illite) clays. The other two sands were reported to contain no detectable amounts of such clays. The Newcastle and Tensleep sands

contain about 1–2 percent and 0.2 percent of illite, respectively. These workers observed that the Newcastle sand had a slightly greater water sensitivity than the Tensleep sand, corroborating their clay analyses. However, the difference was small, and both sands were relatively insensitive to water damage. These results agree with those from the water-vapor adsorption.

The Second Frontier samples, which contain montmorillonite–illite clays, respond to water vapor in a manner similar to that of standard montmorillonite types. Apparently, the ratio of “water-vapor” areas to nitrogen surface areas is indicative of the type of clay present while the extent of adsorption is indicative of the amount.

The results of the above water-vapor adsorption studies indicate that this method is applicable for determining the probable response of petroleum-producing formations to water injection. Highly water-sensitive sands are readily detected. This would appear to be a practical application of considerable merit. In addition, the water-vapor adsorption method is applicable for determining the water sensitivity of small, irregularly shaped chips or shale-streaked core samples. The apparatus and methods were designed to eliminate the effects of nonswelling clays and other unreactive solids. However, the method and apparatus may be readily modified to obtain more delicate delineation of similar, relatively nonreactive materials.

This method, in common with other core measurements, has the practical disadvantage that core samples may not be representative of the formation from which they are taken. However, Baptist and Sweeney (1955), after studying a large number of cores from each of these formations, concluded the clay contents of the formations involved had a general vertical distribution and that abrupt changes of properties were uncommon. Many oil-producing formations do not have these desirable characteristics. Therefore, results of tests such as these should be generalized only after a considerable number of samples have been studied. Statistical sampling and methods of evaluation are to be highly recommended.

SUMMARY

The adsorption of water vapor by standard clay samples and by core samples from oil-producing formations has been investigated. The adsorption isotherms of montmorillonite and kaolinite are characteristic of the clay type and serve as an aid in their identification. The montmorillonite samples adsorbed water vapor strongly and exhibited a pronounced hysteresis loop in their adsorption-desorption isotherms. The desorption isotherm was reproducible but adsorption was sensitive to the original condition of the clay. Kaolinite samples adsorbed water vapor weakly and gave no evidence of adsorption-desorption hysteresis; the isotherms were readily reproducible. The isotherm of the illite samples studied was intermediate between those of kaolinite and montmorillonite.

Water-vapor adsorption by core samples from oil-producing formations varied with the contents of swelling clays and with water sensitivities as indicated by previous x-ray analyses and permeability studies. Correlations of nitrogen and water-vapor adsorption studies with clay analyses and permeability measurements show that the water-vapor adsorption method is a promising means for the direct measurement of the water sensitivity of sedimentary formations.

REFERENCES

- American Petroleum Institute (1949) Reference clay minerals: Research Project 49, New York.
- Baptist, O. C. and Sweeney, S. A. (1955) Effect of clays on the permeability of reservoir sands to various saline waters: Bureau of Mines Rep. of Investigations 5180, 23 p.
- Baptist, O. C. and Sweeney, S. A. (1957) Physical properties and behavior of the Newcastle oil-reservoir sand, Weston County, Wyo.: Bureau of Mines Rep. of Investigations 5331, 43 p.
- Barrer, R. M. and McLeod, D. M. (1954) Intercalation and sorption by montmorillonite: *Trans. Faraday Soc.*, v. 50, pp. 980-989.
- Barshad, Isaac (1955), Adsorptive and swelling properties of clay-water system: in Clays and clay technology, *California Div. of Mines Bull.* 169, pp. 70-77.
- Brooks, C. S. and Purcell, W. R. (1952) Surface area measurements on sedimentary rocks: *AIIME, Petroleum Trans.*, T.P. 3458, v. 195, pp. 289-296.
- Brunauer, Stephen (1945) The adsorption of gases and vapors. v. I. *Physical Adsorption*: Princeton University Press, Princeton, 511 pp.
- Brunauer, S., Emmett, P. H. and Teller, E. (1938) Adsorption of gases in multimolecular layers: *J. Amer. Chem. Soc.*, v. 60, pp. 309-319.
- Carman, P. C. (1953) Properties of capillary-held liquids. *J. Phys. Chem.*, v. 57, pp. 56-64.
- Cornell University (1951) Soil solidification research. Final report, 1946-51, v. II. Fundamental properties, clay-water system, 405 pp.
- Harkins, W. D. (1952) *The Physical Chemistry of Surface Films*: Reinhold Publishing Corporation, New York, 411 pp.
- Keenan, A. G., Mooney, R. W. and Wood, L. A. (1951) The relation between exchangeable ions and water adsorption on kaolinite. *J. Phys. & Coll. Chem.*, v. 55, pp. 1462-1473.
- Lewis, D. R. (1953) Replacement of cations of clay by ion exchange resins: *Ind. & Eng. Chem.*, v. 45, pp. 1782-1783.
- Mooney, R. W., Keenan, A. G. and Wood, L. A. (1952a) Adsorption of water vapor by montmorillonite, I. Heat of desorption and application of BET theory: *J. Amer. Chem. Soc.*, v. 74, pp. 1367-1371.
- Mooney, R. W., Keenan, A. G. and Wood, L. A. (1952b) Adsorption of water vapor by montmorillonite, II. Effect of exchangeable ions and lattice swelling as measured by x-ray diffraction: *J. Amer. Chem. Soc.*, v. 74, pp. 1371-1374.
- Wiig, E. O. and Juhola, A. J. (1949) The adsorption of water vapor on activated charcoal: *J. Amer. Chem. Soc.*, v. 71, pp. 561-568.