

X-RAY DIFFRACTION STUDIES OF ORGANIC CATION-STABILIZED BENTONITE¹

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ABSTRACT

Studies of quaternary ammonium chlorides containing long unsaturated hydrocarbon chains have shown their effectiveness in stabilizing soils primarily by waterproofing the clay fraction. The nature of the interaction between organic salts and Wyoming bentonite was studied by means of X-ray diffraction.

Treatment of bentonite with a dialkyl dimethyl ammonium salt in an amount less than the exchange capacity results in the appearance of water-stable spacings of 10, 13 and 19 Å, but only if the sample has been dry cured. Moist curing a bentonite paste results in a marked expansion of the lattice despite treatment. The necessity of dry curing may relate to orientation of organic cations around bentonite aggregates; grinding prior to rewetting destroys the waterproofing action, and the clay lattice again expands.

Additions of the quaternary ammonium cations close to or in excess of the exchange capacity of the bentonite waterproofs regardless of dry curing or grinding, or both. Clays treated in this manner show spacings of the pure crystalline chemicals and other spacings which relate to interlayer penetration by water. There is no direct evidence for interlayer penetration by the organic cation, perhaps because of the unwieldy tetrahedral arrangement of the organic molecule. The degree to which organic cations are held depends on the nature of the surface as the cations are readily leached from quartz powder but are held more strongly on kaolinite and bentonite.

INTRODUCTION

Investigation of organic cationic materials for use as soil stabilizers began at Iowa State University about 1947 (Davidson, 1949; Davidson and Glab, 1949). Since then, laboratory evaluations of many different cationic chemicals have shown quaternary ammonium salts to be the most effective of any, and use of one of these preparations is now in the test road stage.

Addition of a quaternary ammonium salt to a montmorillonitic soil causes marked changes in its physical properties, such as reducing its plasticity index. Most important is that the wettability of the soil is decreased; it has been waterproofed. The degree of waterproofness is influenced by the amount

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and type of clay mineral present, the amount of cation added, the amount of moisture present and conditions of curing or ageing (Davidson, Demirel and Rosauer, 1962; Kardoush, Hoover and Davidson, 1957).

Since the most abundant clay mineral in Iowa soils is montmorillonite (Hanway, Handy and Scott, 1960), research was undertaken to study the nature of the interaction between a quaternary ammonium salt and Wyoming bentonite.

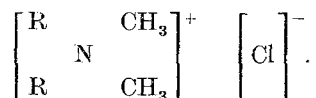
Acknowledgment is expressed to Armour Industrial Chemical Company for samples of Arquad 2-18 and 2HT and to American Colloid Company for the Wyoming bentonite.

MATERIALS

Quaternary Ammonium Chlorides

A quaternary ammonium salt results from complete substitution of organic groups for hydrogens on the nitrogen atom of an ammonium salt. The possible number of such salts is very large owing to the wide variety of groups which may be linked to the amino nitrogen without destroying its basicity.

One group example of these salts is dialkyl dimethylammonium chloride, in which two carbon chains and two methyl groups are attached to the nitrogen. The general formula is



Salts with carbon chains from 8 to 18 carbons long are readily available. A dioctadecyl dimethylammonium chloride, for example, may be thought of as similar to NH_4^+Cl^- in which the hydrogens have been replaced by two methyl groups and two carbon chains, each chain being 18 carbons long.

In the present study two quaternary ammonium salts were used: Arquad 2-18 and Arquad 2HT, trade names for industrial chemicals manufactured by the Armour Industrial Chemical Company. In this paper these will be referred to as 2-18 and 2-18/16, respectively. The Arquad 2-18 is believed to have two alkyl groups each 18 carbons long. According to the manufacturer's data Arquad 2HT contains about 24 percent hexadecyl, 75 percent octadecyl and 1 percent octadecenyl groups.

Both chemicals were obtained in the powdered form, and are slightly soluble or dispersible in water. At concentrations above about 35 percent in water, gels are obtained.

Wyoming Bentonite

This material was obtained from the American Colloid Company, and is known as Volclay, Wyoming type. Wet analysis indicates that 87-89 percent of the particles are smaller than 0.5μ . The exchange capacity was determined to be 98 meq/100 g.

EXPERIMENTAL PROCEDURES

Pure Chemicals

The two organic powders were analyzed by X-ray diffraction using a G. E. XRD-5 diffractometer with filtered chromium radiation. The organic chemicals were X-rayed both as randomly oriented powders and as oriented specimens, i.e. suspensions dried on a glass slide.

Treatments of Bentonite, Kaolinite and Quartz

Initial investigations of the effects of organic cations on bentonite utilized the method whereby a suspension of bentonite was deposited on a porous porcelain sample holder by suction. Treatment then was accomplished by sucking a solution of the organic cation through the clay layer. However, uncertainties arose as to completeness of ion exchange. This method also did not allow for some of the test procedures regarding rewetting described later, and therefore it was abandoned.

A solution of 2-18 (0.008M) was added to a sample of air-dry bentonite and thoroughly mixed with a spatula until a smooth creamy consistency was obtained. Half of the sample thus prepared was stored in a closed container in which the relative humidity was close to 100 percent. The other half was stored in a desiccator over calcium chloride. To serve as a control another sample of bentonite was similarly prepared with distilled water, halved, and stored in the same containers. At intervals of time all samples were X-rayed.

In order to determine what effect the 2-18 treatment might have on the potential expansion of the bentonite basal spacing, water was added to all samples after initial X-ray analysis as follows: The water content of the samples stored under moist conditions was approximately doubled, and the samples were thoroughly mixed with a spatula. The samples stored under drying conditions were either (1) ground in an agate mortar before rewetting and mixing—designated mechanical rewetting—or (2) placed in contact with free water overnight in a covered petri dish and then smoothed into an X-ray sample holder for analysis—designated physical adsorption. After being rewetted, all samples were again X-rayed.

The effects of adding very large amounts of an Arquad to bentonite were next studied. For this purpose the 2-18/16 was chosen, and a solution with a concentration of 15 g/l. was prepared. The bentonite was first dispersed in distilled water, and by alternate sedimentation and redispersion all particles larger than one micron were removed. The concentration of this clay suspension was 20 g/l.

To three different aliquots of clay suspension sufficient 2-18/16 solution was added (1) to satisfy about 75 percent of the exchange capacity, (2) to exceed the exchange capacity by 52 meq/100 g and (3) to exceed the exchange capacity by 117 meq/100 g.

These samples were washed repeatedly with distilled water and filtered until the filtrate showed no chloride ion as determined with silver nitrate.

For comparison purposes, a fairly pure Florida kaolinite was treated several

times in excess of the exchange capacity with the same 2-18/16 solution. This sample was also washed, and the filtrate was tested for chloride ion. Also, pure quartz powder was ball milled in 2-18/16 solution.

RESULTS AND DISCUSSION

d-Spacings of Pure Chemicals

The solid 2-18 quaternary ammonium salt is a waxy, microcrystalline powder. The specific gravity is 0.96 (27.2°C/4°C), measured by displacement of a sodium chloride solution by use of a pycnometer.

Drying of a 2-18 suspension on a glass slide increases intensity of basal spacings, which occur at 32.8 Å with higher orders appearing to the 00·10

TABLE 1.—X-RAY DIFFRACTION DATA FOR TWO QUATERNARY AMMONIUM CHLORIDES

<i>hkl</i>	Arquad 2-18		Arquad 2HT	
	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
			200*	
			109* to 130*	40 to 70
			48.6*	10
			36.5* to 37.5*	50 to 170
001	38.6	0 to 25	32.0* or 32.8	100
002	32.8	100	16.0*	2
	16.4	6		
	15.6	4		
			12.3*	3
003	11.0	36	10.7*	7
004	8.28	8	8.00*	2
			7.32	7
005			6.40	2
006	5.51	7	5.35	4
			5.25	9
	5.19	5	5.17	3
			4.70	47
	4.67	37		
007	4.73	1.5	4.59	4
	4.20	12	4.22	14
008	4.13	2	4.03	4
	3.87	21	3.90	24
	3.82	3		
	3.72	3	3.70	9
	3.67	10		
	3.59	4		
	3.47	2		
00·10	3.32	0.3		
	3.17	1.5		

* Dried from a suspension on a glass slide.

(Table 1). Other spacings are more readily obtained from the randomly oriented powder, which also was used as a basis for estimation of diffractometer intensities.

The calculated length of each hydrocarbon chain of the 2-18 molecule is about 47 Å, indicating appreciable tilt or spreading of the chains to give the shorter basal spacing at 32.8 Å. Attempts to index the compound in the triclinic system by the third graphical method of Vand (1948) were not successful, owing perhaps to the bilateral nature of the molecule. Investigations of different portions of the dried 2-18 slide revealed another peak at 38.6 Å, believed to be a substitute basal spacing, perhaps indicating less tilt from the vertical.

X-ray studies of the mixed chain length 2-18/16 chemical dried on a slide showed reduction in the basal spacing to 32.0 Å. The reduction is consistent in higher orders to 008, suggesting intimate intermingling of the two chain lengths in the material dried from suspension. The basal spacing is 32.8 Å in the 2-18/16 powder. There are some longer spacings which are perhaps the result of long-periodicity interlayering or scattering by individual crystallites.

Quaternary Ammonium Salt 21-8/16 with Quartz and with Kaolinite

The pure chemical basal spacing modification of 38.6 Å shows strongly in a quartz powder that was ball milled in the 2-18/16 solution and dried. Treated kaolinite gave spacings of about 19 and 13 Å. The 38.6 Å spacing thus appears to be a result of the ionic nature of silicate surfaces upon which the 2-18/16 crystallizes, and perhaps of the rate of drying.

Both samples were washed with water and again X-rayed. The spacings from the treated kaolinite were retained; however, the 38.6 Å spacing from the treated quartz disappeared.

Bentonite and Trace Amount of 2-18 Solution

X-ray diffraction of bentonite samples that had been treated with a trace amount of 2-18 solution showed that at the time of preparation both treated and untreated specimens have a basal spacing of 66 Å, and curing of these samples under moist conditions causes an increase in the basal spacing to more than 200 Å. As might be anticipated, prolonged dry curing causes a decrease in basal spacing, to 13 Å for the untreated specimen and 13 and 10 Å for the treated specimen (Table 2).

Upon physical absorption of water, more water is absorbed by the untreated dry-cured bentonite (82 and 19 Å) than by the comparable treated specimen (19 Å). In contrast all treated and untreated samples either moist cured or ground prior to rewetting show large water absorption and basal spacings too large to be measured, i.e. exceeding 200 Å.

For the present the following observations may be made: The initial 66 Å spacing appears due to interlayer penetration by water, as no difference was observed between untreated and treated specimens. Since the 2-18 solution

TABLE 2.—EFFECT OF 0.008 MOLAR DIOCTADECYL DIMETHYLAMMONIUM CHLORIDE (ARQUAD 2-18) SOLUTION ON THE BASAL SPACINGS OF SODIUM BENTONITE

Storage condition	Basal spacings in Ångströms			
	Untreated		Treated	
	Moist	Dry	Moist	Dry
As prepared	66	66	66	66
Three weeks	> 200	13	> 200	13 10
Physically adsorbed	—	82 19	—	19
Mechanically rewetted	—	94	—	94

was quite dilute, it is reasonable to assume that the exchange capacity of the bentonite is not completely satisfied with organic cations; yet some water-proofing action was obtained with the treatment, provided the sample was dry-cured. This finding agrees with Kardoush, Hoover and Davidson (1957), who found that dry curing resulted in higher strengths than moist curing. Organic coatings seemingly orient around bentonite aggregates as the sample dries, individual molecules lying close enough together to keep out water. X-ray tests on dry-cured specimens after mechanical rewetting show that grinding breaks or destroys the coatings and allows partial re-entry of water.

Bentonite and Large Amounts of 2-18/16 Solution

X-ray data presented in Table 3 show the 38.6 and 32.8 Å spacings that are characteristic of pure 2-18 chemical. The presence of one or the other or both appears to be influenced by the amount of water and concentration of chemical. These chemical basal spacings suggest that organic coatings must be at least several molecules thick on the clay to give a reflection. The organic coatings are held strongly enough that they are not readily washed off, as they were from quartz, suggesting ionic rather than van der Waals' attractions.

Typical treated-bentonite spacings are 19, 16 and 13 Å. Of particular interest is the 10 Å spacing, indicative of a dehydrated montmorillonite. The air-dry control gives 14.6 and 13 Å spacings; yet the treated bentonites retain a 19 Å spacing after air drying. Rewetting causes expansion of untreated bentonite, whereas the treated specimens still have a 19 and a 13 Å, and sometimes even a 10 Å, spacing.

TABLE 3.—EFFECT OF ADDITIONS OF LARGE AMOUNTS OF 2-18/16 (ARQUAD 2HT) SOLUTION ON THE BASAL SPACINGS OF SODIUM BENTONITE*

	Control < 1.0 μ Bentonite + H ₂ O	Amount of 2-18/16 solution added†											
		~ 75 meq/100 g				150 meq/100 g				215 meq/100 g			
Moist as prepared	109	<u>32.8</u>	<u>19</u>	10		<u>32.8</u>	<u>19</u>	13	10	94	<u>38.6</u>	<u>19</u>	13
Air dry overnight	<u>14.6</u> 13	38.6	<u>19</u>	13		32.8	19	13		94	<u>38.6</u>	<u>19</u>	13
Physically adsorbed	<u>19</u> 16										<u>38.6</u>	<u>19</u>	16 13
Mechanically rewetted	66	38.6	<u>19</u>	13		38.6	32.8	19	13		<u>38.6</u>	<u>19</u>	13

* Strongest peaks are underlined.

† Concentration of solution was 15 g salt per liter distilled H₂O.

Interaction of Quaternary Ammonium Salts and Wyoming Bentonite

The influence of organic compounds on the basal spacing of montmorillonite has been studied by various workers (Bradley, 1945; MacEwan, 1948; and Jordan, 1949), who related basal spacing to the interlayer position of the organic molecule.

It has also been shown that discrete hydrates of montmorillonite may occur (Bradley, Clark and Grim, 1937). Hydration is stepwise, i.e. in increments of 3 Å, or monomolecular layers of water. The basal spacings of 19, 16 and 13 Å for the control bentonite (Tables 2 and 3) are examples of such hydrates for a sodium bentonite.

The 13, 16 and 19 Å spacings also occurred in air-dried treated bentonites. To check whether these might be due to interlayer water or to organic cation a bentonite sample treated with 215 meq/100 g of 2-18/16 solution was heated to 190°C for 1 hr. The only noticeable effect was a change in the shape of the 13 Å peak. This therefore suggests that the 19, 16 and 13 Å spacings are not due to hydrated states of the bentonite, but to the organic chemical itself. If the 19, 16 and 13 Å spacings are due to interlayer water penetration of the bentonite, then the organic molecule must affect the energy with which water is associated with the clay crystal to such an extent that water is retained up to temperatures of 190°C. The 10 Å spacing occurs only with the treated specimens, suggesting that treatment weakens rather than strengthens the attractions of clay for water.

Two possibilities remain—that the 13, 16 and 19 Å spacings are from the clay-organic complex, or that they represent the pure chemical. We may note that the 19 and 13 Å spacings would coincide with second and third orders of the 38.6 Å spacing, but two questions arise: if the 19 and 13 Å peaks indeed represent second and third order spacings, why are they absent in the pure chemical (Table 1) and why do they appear in some treated bentonite specimens where the 38.6 Å spacing is absent?

Particularly significant is the great reduction in the amount of hydration of bentonite treated with organic chemical well below the exchange capacity. The organic molecule inhibits water penetration, indicating a coating of organic molecules surrounding aggregates of bentonite. The waterproofing action must be ascribed to the carbon chain since the amino nitrogen presumably would be sorbed on the clay. Coatings are broken by grinding. The fact that trace amounts are effective also suggests relatively little interlayer penetration by the organic chemical or the chemical would be lost in the clay.

In the bentonite treated near the exchange capacity, pure chemical basal spacings indicate that the chemical occurs as coatings several molecules thick around the outside of the clay, rather than as layers disseminated within the expansive structure of the clay.

The unusual effectiveness of the long-chain dialkyl dimethyl ammonium compounds compared to other organic cations as waterproofers for montmorillonitic soils therefore may relate to this apparent lack of penetration of the double-chain cations between the clay layers.

CONCLUSIONS

1. Expansion of dry-cured bentonite clay stabilized with trace amounts of organic cations is limited to give a maximum spacing of 19 Å, which corresponds to three layers of water. The dry-cured clay gives spacings of 10 and 13 Å, which also relate to interlayer water.

2. It is not necessary to satisfy the exchange capacity of a Wyoming bentonite to inhibit ingress of moisture. However, waterproofness of bentonite treated with trace amounts of chemical is dependent upon dry curing, perhaps to allow orientation of organic cations on the clay surface, and is destroyed by grinding.

3. Addition of organic cation to a bentonite suspension equal to or in excess of its exchange capacity waterproofs regardless of curing or grinding.

4. Clays treated with chemical equal to or in excess of the exchange capacity show spacings of 32.8 and 38.6 Å, or both, which coincide with basal spacings of the pure organic chemicals and indicate a multilayer organic coating on the clay. Other spacings appear to be higher orders of these or may relate to interlayer penetration by water. There is no direct X-ray evidence that the large organic cations penetrate between the clay layers. The lack of interlayer penetration may explain the unusual effectiveness of the dialkyl dimethyl ammonium compounds as waterproofers for montmorillonitic soils.

5. Sorption forces holding the organic cations to ground quartz are weak enough that the cation may be removed by washing. Sorption forces are stronger on bentonite or kaolinite surfaces, probably owing to increased ionic attractions, and the multilayer chemical coatings are retained.

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