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# X-Ray Diffraction Studies of Quaternary Ammonium Treated Montmorillonite<sup>1</sup>

M. KESAREE, T. DEMIREL and E. ROSAUER<sup>2</sup>

*Abstract.* This study was undertaken to investigate the water-proofing effect of quaternary ammonium ions on montmorillonite.

The interaction between a quaternary ammonium ion and montmorillonite was investigated on the basis of basal spacings and electrokinetic behavior of the compound formed.

## INTRODUCTION

Addition of a quaternary ammonium salt to a soil markedly decreases its wettability and by waterproofing the clay fraction imparts some structural strength (1, 2, 3).

The appearance of water-stable spacings in X-ray diffraction studies further confirms the waterproofing effect of quaternary ammonium salts on montmorillonite. These characteristic water-stable spacings suggest a suitable method for the investigation of the mechanism of interaction between a quaternary ammonium salt and a clay mineral (4, 5).

In an earlier investigation conducted in this laboratory the effect of the method of preparation, curing and aging on the distribution of the quaternary ammonium ion on the surface of montmorillonite was emphasized. It was found that addition of a quaternary ammonium salt to montmorillonite in quantities equal to or in excess of its exchange capacity waterproofs the clay regardless of curing or grinding. However, when the amount of salt added is below the exchange capacity, the degree of waterproofness is dependent on the method of treatment and curing (5). The present work was undertaken to investigate the nature of the interaction between a quaternary ammonium ion and montmorillonite on the basis of basal spacings and the electrokinetic behavior of the compound formed.

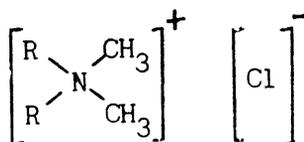
## MATERIALS

### *Quaternary Ammonium Salt*

The quaternary ammonium salt used in this study is available in the powder form as Arquad 2HT from the Armour Industrial Chemical Company. Its general formula is

<sup>1</sup>The subject matter of this report was obtained as a part of Projects 450-S and 340-S of the Iowa Engineering Experiment Station, under the sponsorship of the Iowa Highway Research Board, Iowa State Highway Commission.

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According to the manufacturer's data the carbon chains of this compound are 24 percent hexadecyl, 75 percent octadecyl and 1 percent octadecenyl.

*Montmorillonite*

This material is known as Volclay, Wyoming bentonite, and was supplied by the American Colloid Company. It has an exchange capacity of 98 m.e./100 gm and 87 to 89 percent particles smaller than 0.5 micron.

*Chemicals*

Analytical reagent grade sodium sulfate and potassium ferrocyanide were used. The calcium acrylate was technical grade.

PREPARATION OF SAMPLES

A stock solution of Arquad 2HT was prepared by dispersing 15 gm of the powder in sufficient distilled water to make a total volume of 1000 cc.

550 gm of bentonite were dispersed in 16.5 liters of distilled water. The dispersion was allowed to stand for 4 days after which the supernatant suspension was syphoned into another carboy. The syphoned suspension was shaken well, allowed to stand for another 4 days, and again syphoned. This process was repeated 12 times after which the final suspension contained 20 gm of solids per liter. X-ray diffraction showed the suspended material to be pure montmorillonite.

*Arquad-Bentonite I*

1750 cc bentonite suspension as prepared above were mixed with 350 cc of Arquad 2HT stock solution, and the mixture was stirred for several days. It was then filtered and the residue was redispersed in distilled water and again filtered. Successive redispersions and filtrations were made until the filtrate was found to be free of chloride ion. The residue was dried in air and ground with a mortar and pestle to pass through a 140 mesh U. S. standard sieve. By weighing the sample it was found that all the added Arquad had been adsorbed by the bentonite. Calculations based on amounts of materials used in the preparation showed that Arquad-bentonite I had a composition corresponding to 22 milli-equivalents of Arquad 2HT/100 gm of Arquad-bentonite I (or 87 milli-equivalents of bentonite/100 gm of Arquad-bentonite I or 26 milli-equivalents of Arquad 2HT/100 gm of bentonite). The sample was then aged under ambient laboratory conditions for several months.

### *Arquad-Bentonite II*

The composition of Arquad-bentonite II was calculated to be as follows: 79 milli-equivalents of Arquad 2HT/100 gm of Arquad-bentonite II (or 54 milli-equivalents of bentonite/100 gm of Arquad bentonite II or 25 milli-equivalents of excess Arquad/100 gm of Arquad-bentonite II). This sample was also aged for several months under ambient laboratory conditions.

### *Arquad-Bentonite-Acrylate*

This was prepared by successive extractions of Arquad-bentonite II with  $\frac{1}{2}$  N calcium acrylate. The equivalent amount of acrylate solution used in the extraction was more than the equivalent amount of Arquad 2HT held by the bentonite. Extractions were continued until the filtrate was free of chloride ion. Then the sample was washed with distilled water until the filtrate was free of calcium ion. The sample was dried and ground to pass through a 140 mesh U. S. standard sieve.

### *Arquad-Bentonite-Sulfate*

This was prepared by successive extractions of Arquad-bentonite samples I and II with 1 N sodium sulfate until the filtrates were free of chloride ions. The equivalent amount of sulfate used in the extractions was more than the equivalent amount of Arquad 2HT held by the bentonite. Then the samples were washed with distilled water until the filtrates were free of sulfate ions. After drying the samples were ground.

### *Arquad-Bentonite-Ferrocyanide*

Arquad-bentonite ferrocyanide samples were prepared by successive extractions of Arquad-bentonite I and II with 0.1 N potassium ferrocyanide solution. The procedure was the same as described above.

## EXPERIMENTAL PROCEDURE

### *Electrophoretic Movement*

Electrophoretic movement of bentonites treated with varying amounts of Arquad 2HT was studied using a U-tube equipped with two platinum electrodes and a direct current source. The DC source was a regulated power supply, Heathkit Model PS-4. 200 volts were applied between the two electrodes and the movement of the bentonite suspension was observed.

For this particular analysis only additional Arquad-bentonite samples were prepared to give a wider range of bentonites with increasing amounts of adsorbed Arquad. Results are reported in Table 1.

### *Anion Exchange Capacity*

5 gm of Arquad-bentonite I and II were leached with 1N  $\text{Na}_2\text{SO}_4$  solution 3 times. Titration of the filtrate with silver

nitrate showed the chloride content to be 30 milli-equivalents/100 gm of Arquad-bentonite II. The method used was the "adsorption indicator method for chlorides" (6). Results are given in Table 1.

*X-Ray Diffraction Analysis*

The samples were analyzed by X-ray diffraction using a G.E. XRD-5 diffractometer with filtered chromium radiation. The diffraction maxima for Arquad-bentonite II were also checked using filtered copper and molybdenum radiations. All samples were X-rayed dry, immediately after wetting and after storage for one day at 100 percent humidity. The data are presented in Table 2.

RESULTS AND DISCUSSION

Observations of the electrophoretic movement are given in Table 1. Bentonite treated with Arquad 2HT in excess of its exchange capacity shows a movement toward the cathode. This suggests that the quaternary ammonium ion is a potential determining ion for bentonite. The quaternary ammonium ion, if used in sufficient amounts, combines with the clay mineral to form a new compound having a positive surface charge. It was therefore expected that this compound would have an anion exchange capacity. Measurements reveal that Arquad-bentonite II has an anion exchange capacity of about 30 milli-equivalents per 100 gm. This value is in fair agreement with the value of 25 milli-equivalents per 100 gm which was the calculated composition of Arquad-bentonite II.

Table 1. Electrophoretic movement and anion exchange capacity of bentonite treated with various amounts of Arquad 2HT

Amount of Arquad 2HT in milli-equivalents per gm of bentonite	Charge on particles	Anion exchange capacity milli-equivalents per 100 gm of Arquad-bentonite
0.26 (Arquad-bentonite I)	negative	Could not be determined
0.64	negative	
1.28	positive	
1.44 (Arquad-bentonite II)	positive	30
2.05	positive	
3.84	positive	

X-ray diffraction data for Arquad-bentonite II having various kinds of adsorbed anions are included in Table 2. The spacings which appear in the dry treated specimens are characteristic for the anionic treatment. These spacings are water-stable, and appear to be first-, second- and third-order reflections.

Table 2 shows that the basal spacing decreases as the negative charge on the ion increases. This may be attributed to the dis-

Table 2. X-ray diffraction data for Arquad-bentonite I and II<sup>1</sup>

Sample	Treatment								
	Dry			Wet (immediately)			Wet (after 1 day)		
Arquad-bentonite I Cl <sup>-</sup>	~27	~14		~19					
Arquad-bentonite I SO <sub>4</sub> <sup>-2</sup>	~27	~14		~19		~16	~41	~20	~18
Arquad-bentonite I [Fe(CN) <sub>6</sub> ] <sup>-4</sup>	~33	~13		~28	~14				
Arquad-bentonite II [Acrylate]	41.0	19.9	13.3						
Arquad-bentonite II Cl <sup>-</sup>	39.8	19.3	13.0	39.8	19.3	13.0			
Arquad-bentonite II SO <sub>4</sub> <sup>-2</sup>	38.6	18.5	12.6	38.6	18.5	12.6	38.6	18.5	12.6
Arquad-bentonite II [Fe(CN) <sub>6</sub> ] <sup>-4</sup>	32.4	15.4		34.5	17.0		34.5	17.0	

<sup>1</sup> Diffractometer data

tortion of the hydrocarbon chains of the quaternary ammonium cation due to the large size and charge of the anion adsorbed.

A resume of the X-ray diffraction data for Arquad-bentonite I is also given in Table 2. Typical X-ray diffraction charts show a very broad peak representing a combination of the basal spacings of Arquad-montmorillonite and sodium montmorillonite. The spacings reported in Table 2 are therefore average values and represent the spacings of both sodium and Arquad montmorillonite which merge in the broad peak.

As Table 2 shows all three Arquad-bentonite I samples were not water-stable. All Arquad-bentonite II samples were water-stable with the exception of Arquad-bentonite II ferrocyanide. Here the slight expansion upon wetting can be attributed to the effect of the anion.

#### CONCLUSIONS

The large quaternary ammonium ion of Arquad 2HT is a potential determining ion for montmorillonite and when mixed with a montmorillonitic clay in amounts exceeding its cation exchange capacity reverses its surface charge.

The arrangement of the quaternary ammonium ion of Arquad 2HT on the monmorillonite surface is such that its c-axis is perpendicular to the clay surface.

When bentonite is first treated with Arquad 2HT in excess of its exchange capacity and is then treated with various anions, the resultant basal spacings reflect influence of the size and charge of the anion. These spacings are stable in water.

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