

EFFECT OF HEATING ON SWELLING AND DISPERSION OF DIFFERENT CATIONIC FORMS OF A SMECTITE

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Abstract—The effect of heat treatments on the swelling, dispersion, particle charge and particle aggregation of Li-, Na-, K-, Mg-, Ca- and Al-Wyoming bentonite was investigated. Before thermal treatment, unheated (25 °C) Li-, Na- and K-clays showed increased d_{001} spacing on glycerol solvation and dispersed spontaneously in water. Mg-, Ca- and Al-clays did not disperse spontaneously in water, but the d_{001} spacing increased upon glycerol solvation. After heating at 300 °C or above, none of these clays dispersed spontaneously. However, swelling varied with the type of cation and the temperature of heating.

The results generally suggested that swelling and dispersion of homoionic Wyoming bentonite after heating at various temperatures depended upon the nature of bonding between clay particles and the cations. Enhanced swelling and dispersion of clays indicated the more ionic character of the cationic bonding than cases where heating resulted only in swelling, with polar covalent bonding of cations to clay surfaces allowing limited hydration. It is also suggested that, when both swelling and dispersion as a result of thermal treatment are absent, a covalent bond is formed between cation and clay surface.

Thermal treatment apparently affects the bonding in different ways. It appears that the smaller cations (ionic radius <0.7 Å) Li, Mg and Al migrate to octahedral vacant sites and form covalent bonds after heating at 400 °C; this drastically reduces the negative charge. This process for Li-clays occurred even at 200 °C. The larger cations (ionic radius > 0.9 Å) Na, K and Ca apparently did not migrate into the lattice sites after heating to 400 °C; a high proportion of them were exchangeable. The data for exchangeable cation, particle charge and clay particle size were consistent with the postulated effect of the nature of cationic bonding upon swelling and dispersion properties.

Key Words—Cationic Clay Bonding, Dispersion, Particle Charge, Swelling, Thermal Treatment, X-ray Diffraction.

INTRODUCTION

The swelling and dispersion of clays in salt-free water are functions of exchangeable cations and layer silicate structure. These processes are governed by the balance between attractive and repulsive forces arising from intermolecular and electrostatic interactions between the solution and solid phases in the suspension. Many workers have studied the relationship between clay swelling and clay crystallographic factors. Suquet et al. (1975) and Horvath and Novak (1975) found that total layer charge plays a major role in the expansion properties of layer silicates. Chorom and Rengasamy (1995) showed that net particle charge is the most important factor controlling clay dispersion for a range of pH and ionic strength values. Glaeser and Mering (1968), Jenkins and Hartman (1982), Slade et al. (1991) and Sato et al. (1992) investigated the effect of interlayer cations, net layer charge and charge location (octahedral or tetrahedral) on the expansion properties of smectites. The general conclusion was that the basal spacings of tetrahedrally-charged smectites were smaller than those of octahedrally-charged smectites under the same hydration and solvation conditions. Conversely, Schultz (1969) suggested that the expansion properties did not depend on the charge location, but on the total net charge and the amounts of structural (OH).

The thermal treatment of smectites saturated with Li has been shown to reduce their layer charge as well as cause a decrease in exchangeable Li (Hoffman and Klemen 1950; Lim and Jackson 1986; Jaynes and Bigham 1987). A similar reduction in charge has also been found when Mg²⁺ or Al³⁺ saturated clays were heated to 300 °C (Greene-Kelly 1955; Glaeser and Mering 1968). The mechanism of charge reduction was argued to be the migration of these cations of small radius into vacant octahedral sites to reduce the octahedral charge. However, this hypothesis has been disputed by Tettenhorst (1962).

Some recent studies have suggested that hydration forces are more important in swelling than Derjaguin-Landau-Verwey-Overbeek (DLVO) forces (Low 1981; Pashley 1985; Israelachvili and McGuiggan 1988). Hydration reactions during clay swelling and dispersion are controlled by electron-acceptor and electron-donor (EAED) interactions between water molecules, clay surfaces and exchangeable cations (Christenson and Horn 1985; van Oss et al. 1990). These are also referred to as acid-base (AB) reactions, based upon the Hard-Soft Acid-Base (HSAB) concept of R.G. Pearson (Huheey et al. 1994). Rengasamy and Sumner (1996) proposed that HSAB reactions lead to different types of bonding between clay surfaces and cations—namely, covalent, polar covalent and ionic—which control

hydration (and, hence, swelling and dispersion properties) of soil clays.

In the present study, we investigated the effects of heating to 400 °C on charge reduction, swelling and dispersion of a smectite saturated with Li, K, Na, Mg, Ca and Al. We present these properties and relate them to the type of bonding resulting from EAED interactions during heating.

MATERIALS AND EXPERIMENTAL METHODS

Clay Preparation

Wyoming bentonite was dispersed, fractionated and deferrated by conventional procedures (Jackson 1969). X-ray diffraction (XRD) revealed no crystalline impurities in the Wyoming bentonite sample. Clays that were homoionic in Li, Na, K, Mg, Ca and Al were prepared by treating the clay fractions with 1 M chloride solutions, 3 times at 24-h intervals. Afterward, the clays were dialysed against distilled water until chloride-free. Then the salt-free clay samples were freeze-dried and stored at room temperature (25 °C). Samples of the homoionic clays were heated for 6 h at 100, 200, 300 and 400 °C in a muffle furnace. The clays were cooled in a desiccator and placed in a sealed glass container kept at 25 °C. Electrical conductivity (EC) and pH were determined using a 1:10 water extract.

Exchangeable Cations and Cation Exchange Capacity

The extraction of the exchangeable cations was carried out by shaking 20 mg of the homoionic clays with 10 mL of 1 M NH₄Cl solution in a centrifuge tube overnight, followed by centrifugation and collection of the supernatant solution. In the 2 subsequent extractions, the samples were centrifuged after 2 h shaking. These extractions were combined and the cations (Na, Li, K, Mg, Ca and Al) displaced by NH₄Cl were measured by inductively coupled plasma atomic emission spectrometry (ICPAES). The total negative charge (or CEC) of the clays was taken to be the sum of the charges on cations displaced by 1 M NH₄Cl.

X-ray Diffraction Studies

One mL of 1% suspension of the clays was pipetted onto zero background silica wafers and step scanned at 40 kV and 30 mA over 3–33° (0.02°/s) in a Philips 1729 X-ray diffractometer with Co radiation fitted with a graphite monochromator. Interlayer swelling was monitored by XRD patterns of the samples after glycerol solvation (Sato et al. 1992).

Measurements of Dispersible Clay

The amount of spontaneously dispersible clay was determined by the following method. Ten mL of distilled water was added to 20 mg of the clays and kept overnight without any disturbance. After 24 h, the supernatant solution of this suspension was siphoned to

measure the proportion of clay remaining in suspension.

The amount of mechanically dispersed clay was measured by the following method. A mixture of 20 mg of clay and 10 mL distilled water was shaken for 24 h. After shaking, the sedimentation time was set for 16 h for all measurements. Then the supernatant liquid was siphoned to estimate the mechanically dispersed clay. The proportions of total clay in both suspensions were determined turbidimetrically using an HACH turbidimeter (Chorom et al. 1994). A calibration curve was used to convert turbidity to amounts of dispersed clay.

Zeta Potential Measurements

The ζ -potential is related to the electrophoretic mobility of the particles by the Smoluchowski equation (Pashley 1985):

$$\zeta = 4\pi \eta \mu_e / \epsilon \quad [1]$$

where ζ is zeta potential in mV, μ_e is electrophoretic mobility ($\mu\text{m s}^{-1} \text{V}^{-1} \text{cm}^{-1}$), η is the viscosity of the medium, and ϵ is the dielectric constant. For aqueous media at 25 °C, the relationship between electrophoretic mobility (generally expressed in $\mu\text{m/s/V/cm}$) and ζ -potential in mV, is 12.85 mV per mobility unit. The ζ -potential was measured by using a Malvern Zetasizer model Zetamaster particle electrophoresis analyser. All ζ -potentials were measured at a constant 20 °C and at a constant field strength of 80 V cm⁻¹. Measurements were conducted with a run time of 30 s and final values were averaged over 10 runs. Suspensions 0.1 g L⁻¹ of the clays were prepared in deionized water, sonifying for 30 s and shaking for 2 h in a Spex mixer mill. The ζ -potentials measured in this study were negative in sign, because the clay particles moved towards the cathode. The pH values were monitored and are presented in Table 1.

Clay Particle Size

Clay particle size in the suspension after mechanical dispersion was measured by submicron particle sizer Nicomp Model 370 using photon correlation spectroscopy as the mean of an assumed Gaussian distribution.

RESULTS AND DISCUSSION

Chemical Properties

The effects of heating on the chemical properties of Wyoming bentonite saturated with Li, Na, K, Mg, Ca and Al are shown in Table 1. In general, pH values of the 1:10 suspension in distilled water depended upon the nature of cation. Among monovalent cationic clays, Li- and Na-clays had higher pH values than K-clays. Furthermore, divalent cationic clays had higher pH values than Al-clays (Table 1). In the suspension of unheated clays (25 °C), the dissociation of cations and subsequent hydrolysis reactions led to the

Table 1. The effect of heating on pH, EC, the concentration of the saturating cation in 1:10 clay-water extract, exchangeable cation and total negative charge of homoionic Wyoming bentonite.

Cation (M-clay)	Temper- ature of heating °C	pH	EC μS cm ⁻¹	Dissociation cation mg L ⁻¹	Exchangeable cation						CEC
					Li	Na	K	Mg cmol _c kg ⁻¹	Ca	Al	
Li (0.68)†	25	6.11	34	2.8	85	4	0	1	4	0	94
	200	6.62	7	0.3	18	2	0	1	2	0	24
	400	6.94	4	0.2	6	0	0	1	1	0	8
Na (0.97)†	25	6.27	47	4.6	0	79	0	1	13	0	93
	200	6.35	15	3.9	0	72	0	2	11	0	88
	400	6.52	12	2.3	0	65	1	2	11	1	80
K (1.33)†	25	5.47	54	19	0	5	78	1	1	0	86
	200	5.61	10	4.3	0	5	68	1	0	0	76
	400	5.83	8	2.0	0	3	60	2	0	1	66
Mg (0.66)†	25	6.08	10	1.2	0	2	0	78	0	0	81
	200	6.54	6	0.6	0	2	1	69	0	1	73
	400	6.69	3	0.3	0	2	1	9	0	1	14
Ca (0.99)†	25	6.43	9	1.8	0	2	0	1	77	0	80
	200	6.54	6	0.8	0	2	0	0	69	0	71
	400	6.83	6	0.2	0	2	0	0	58	0	60
Al (0.51)†	25	4.87	8	0.2	0	2	0	3	1	71	77
	200	4.91	6	0.1	0	2	0	2	1	62	68
	400	5.12	4	0.1	0	2	0	2	1	13	18

† Crystal ionic radii (Å).

changes in H⁺ concentration. For Al³⁺, even though the dissociated ions were very low, strong hydrolysis reactions released more H⁺ ions and the pH was 4.87. Upon thermal treatment, the pH increased for all cationic clays, suggesting that the cations are more strongly bound to the clay surface. This is clearly shown in the decreased amounts of cations dissociated in water with increase in temperature of heating (Table 1). Electrical conductivity (EC) values also reflected the same trend.

Thermal treatment of cationic clays reduced the total negative charge (CEC) and the amount of exchangeable cations as the heating temperature increased (Table 1). As the cations become more strongly bound to surface -O or -OH, exchange by NH₄⁺ becomes more difficult. However, the extent of charge reduction depended on the nature of cation and the temperature of heating. As the valency of the cations increases, the bonding being stronger, the total charge estimated by NH₄⁺ exchange is reduced (Table 1). Thus, in Li-clays, the charge reduced drastically after heating at 200 °C from 94 to 24 cmol_c kg⁻¹. After heating at 400 °C, the charge reduced to 8 cmol_c kg⁻¹. However, in Na-clays the reduction was minimal compared to Li-clays. The reduction in K-clays was similar to Na-clays, even though the total charge was lower. Among divalent cations, the charge reduction in Mg-clays was similar to Li, with huge reduction only after heating at 400 °C. The Ca-clays were similar to K- and Na-clays, with minimal charge reduction. The trend in Al-clays was similar to Li- and Mg-clays.

Swelling

The swelling of smectites depends upon their structures, their chemical compositions and the type of exchangeable cation. The variation of XRD patterns of Li-, Na-, K-, Mg-, Ca- and Al-Wyoming bentonite (Figures 1 and 2) before and after heating and re-expansion after glycerol solvation was studied. Table 2 shows the swelling obtained for dry and glycerol solvated samples. The *d*₀₀₁ spacings of Li-, K- and Na-Wyoming bentonite prior to heating correspond to a hydrated structure where the cations are located in the interlayer space and solvated by water molecules adsorbed from the atmosphere.

Lithium saturation and heating caused the Wyoming bentonite to become dark and also to develop hydrophobic character (that is, floating in water). Li-clays collapsed and remained unexpandable after being heated at 200–400 °C (Table 2). The XRD patterns of Li-clay after heating at 200–400 °C exhibit a *d*₀₀₁ reflection corresponding to 9.6 Å, even after treatment by glycerol.

The high charge reduction for Li-clay from 94 to 8 cmol_c kg⁻¹ after heat treatments is in good agreement with previous work. Calvet and Prost (1971) showed that the clay did not swell with water when the amount of exchangeable cation was lower than 50% of the original exchange capacity.

No differences were detected between XRD patterns of Na-clays heated at 100–400 °C and 25 °C (unheated). Even after thermal treatment (up to 400 °C), the hydrated sodium ions remained in the interlayer as reflected by *d*₀₀₁ spacings (Figure 1, Table 2). As a result

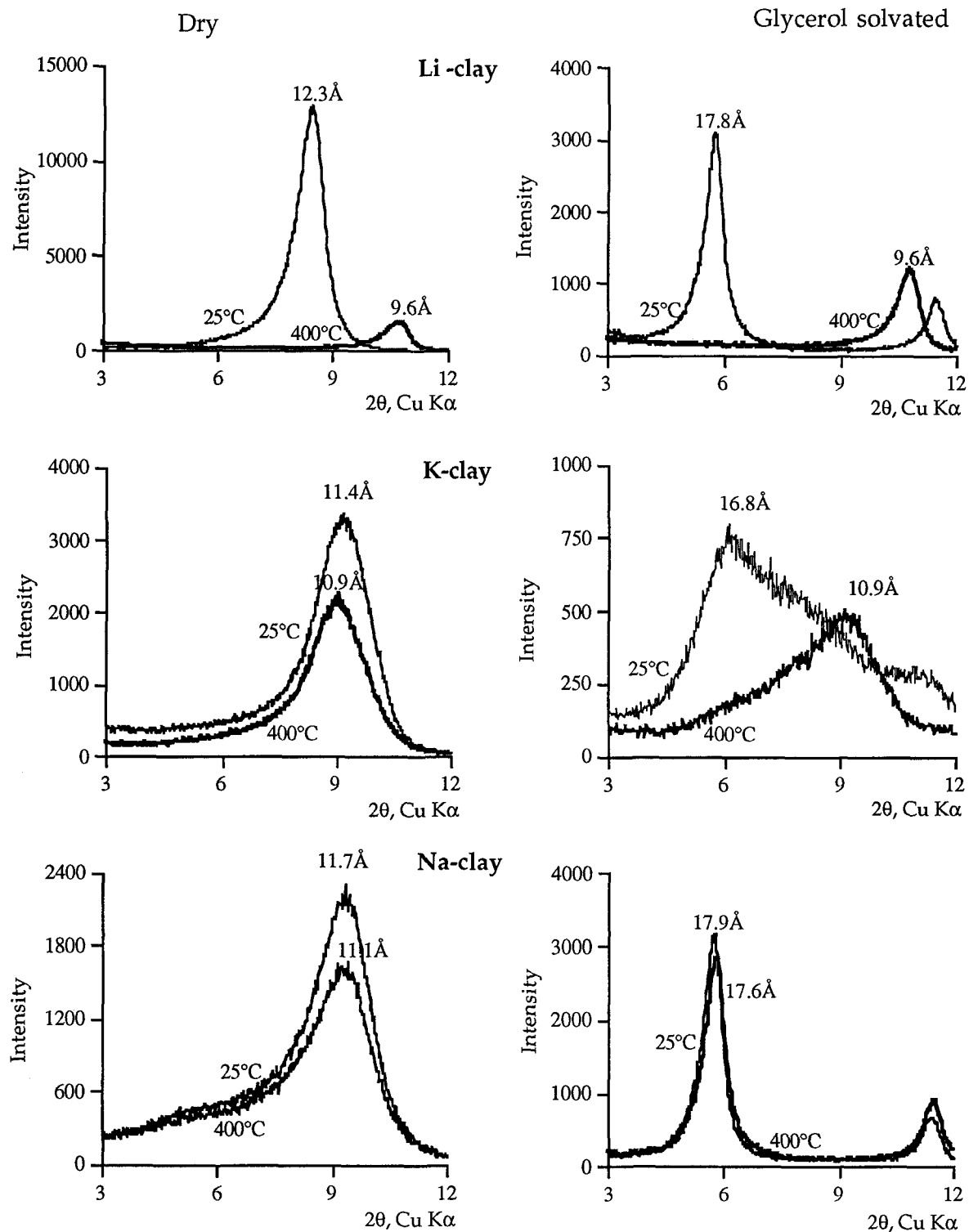


Figure 1. XRD patterns of the Wyoming bentonite saturated with Li, K and Na at different temperatures. The dry samples (left) and those glycerol solvated (right).

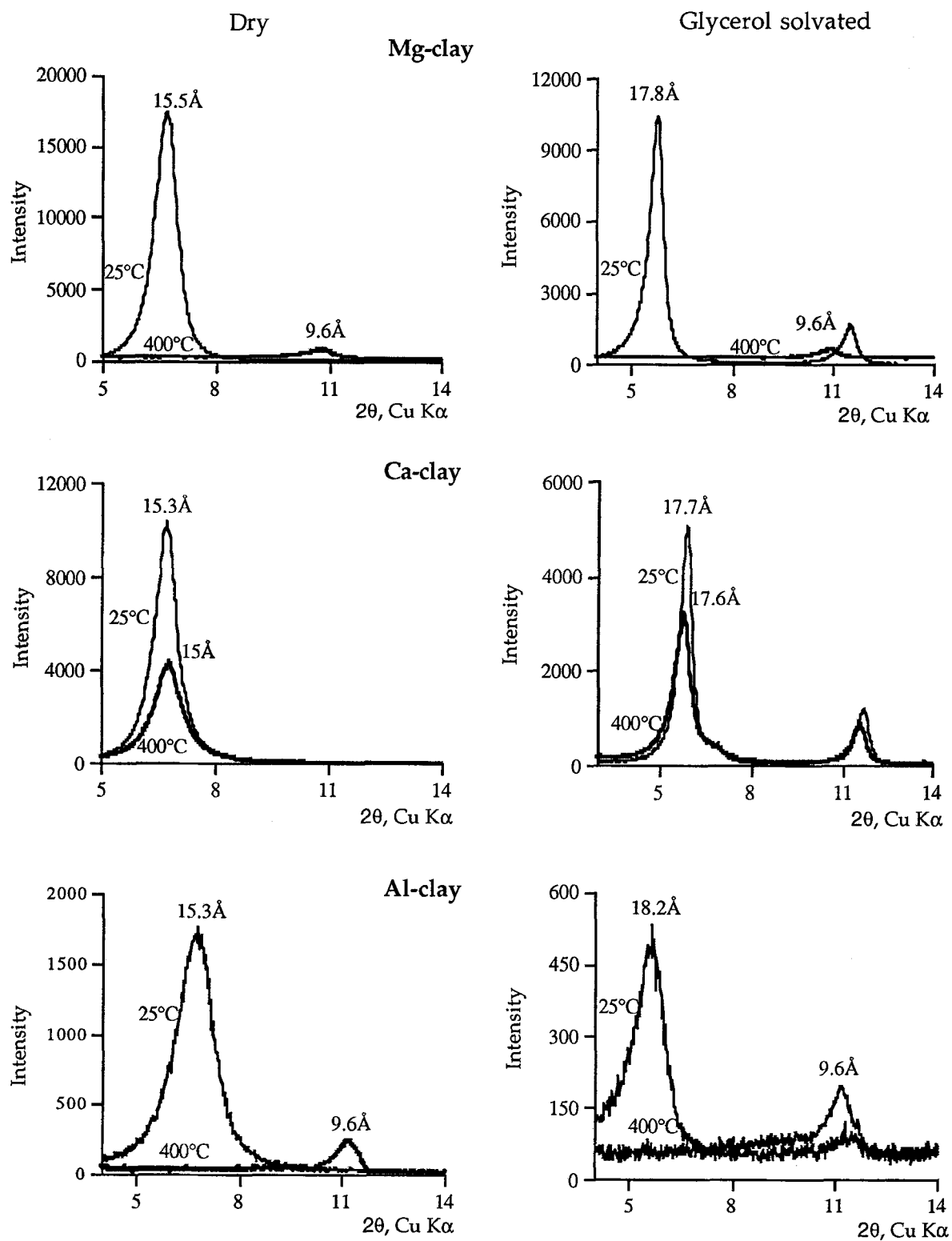


Figure 2. XRD patterns of the Wyoming bentonite saturated with Mg, Ca and Al at different temperatures. The dry samples (left) and those glycerol solvated (right).

Table 2. The effect of heating on swelling, dispersion, Zeta potential (ζ -potential) and mean particle diameter (MD) of homoionic Wyoming bentonite.

Cation M-clay	Temperature of heating °C	Swelling d_{001} Å dry glycerol	Dispersion (%)		pH	ζ -potential -mV	MD μ m
			Spontaneous	Mechanical			
Li	25	12.3 → 17.8	90	98	6.11	40.5	0.30
	100	12.2 → 17.8	70	72	6.34	36.1	0.75
	200	9.6 → 9.6	Nil	23	6.62	34.0	1.78
	300	9.6 → 9.6	Nil	6	6.73	33.6	2.42
	400	9.6 → 9.6	Nil	2	6.94	33.2	3.51
Na	25	11.7 → 17.9	80	98	6.27	39.1	0.33
	100	11.2 → 17.9	70	87	6.31	38.6	0.82
	200	11.1 → 17.6	22	82	6.35	38.4	1.04
	300	11.1 → 17.6	Nil	78	6.42	38.2	1.46
	400	11.1 → 17.6	Nil	67	6.52	37.7	1.75
K	25	11.4 → 16.8	55	86	5.47	37.3	0.75
	100	11.3 → 16.8	15	55	5.51	36.8	1.41
	200	11.3 → 16.8	2	41	5.61	36.7	1.61
	300	11.1 → 16.7	Nil	32	5.76	36.2	1.75
	400	10.9 → 10.9	Nil	18	5.83	35.2	2.21
Mg	25	15.5 → 17.8	Nil	25	6.08	28.8	0.82
	100	15.5 → 17.8	Nil	14	6.26	26.3	0.94
	200	15.1 → 17.8	Nil	11	6.54	25.3	1.34
	300	13.2 → 17.8	Nil	10	6.62	25.2	2.81
	400	9.6 → 9.6	Nil	2	6.69	24.9	3.32
Ca	25	15.3 → 17.7	Nil	18	6.43	24.7	1.06
	100	15.2 → 17.6	Nil	8	6.52	21.8	1.25
	200	15.2 → 17.6	Nil	6	6.54	19.9	1.92
	300	15.2 → 17.6	Nil	5	6.67	19.7	2.15
	400	15 → 17.6	Nil	3	6.83	19.4	2.79
Al	25	15.3 → 18.2	Nil	5	4.87	20.1	1.44
	100	15.3 → 18.2	Nil	4	4.89	19.4	1.86
	200	14.5 → 18.1	Nil	4	4.91	18.4	2.78
	300	14.1 → 18.1	Nil	3	4.99	17.9	4.65
	400	9.6 → 9.6	Nil	2	5.12	16.8	5.66

of glycerol solvation, d_{001} spacings of treated clays increased to 17.6 Å, indicating swelling even after heating to 400 °C. This behavior, as for the charge characteristics, is opposite to that of Li-clays.

The d_{001} spacings of K-clays heated to 300 °C and after glycerol solvation were similar to those of Na-clays. The charge reduction of K-clays after heat treatment is small compared to the drastic reduction in Li-clays (Table 1). Expansion in d_{001} spacing after glycerol solvation is observed even after heating at 300 or 400 °C (Table 2). Thus, it appears that K^+ does not migrate into the lattice sites, the interlamellar K^+ remaining exchangeable (Table 1). Heat treatments only reduce the amount of exchangeable K^+ . Apparently, K^+ in the interlayer space is progressively fixed or strongly bonded to the surface -O or -OH groups with increasing temperature.

Among the divalent cations, d_{001} spacings of unheated (25 °C) clays (Table 2) indicated that interlayer divalent cations were more hydrated than K^+ . Spacings for Al-clays were also consistent with substantial cation hydration. Heating to 300 °C did not result in any substantial collapse of d_{001} spacing, which upon glycerol

solvation expanded with d_{001} spacings ranging from 16.7 to 18.2 Å. However, on heating at 400 °C, Mg- and Al-clays collapsed to a d_{001} spacing of 9.6 Å and did not expand with glycerol solvation (Figure 2). These results are consistent with migration of Mg and Al from the interlayer space to the vacant octahedral sites. Calvet and Prost (1971) showed that when Mg-montmorillonite and Ca-montmorillonite were heated at 400 °C, Mg^{2+} ions could migrate into the structure while Ca^{2+} ions could not. Alternatively, it can be suggested that these cations are strongly bonded to the clay surfaces while still remaining in the interlayers.

In general, peak intensity reduced with increasing temperature (Figure 1 and 2). The extent of peak intensity reduction was similar to the charge reduction. For Li-, Mg- and Al-clays, after heating at 400 °C, the charge reduction was drastic and the intensity of d_{001} peaks was also very low.

Dispersion

SPONTANEOUS DISPERSION. The results for spontaneous dispersion are presented in Table 2. All of the freeze-

dried monovalent cationic clays exhibited spontaneous dispersion when placed in distilled water. Li-clay had partial spontaneous dispersion after heating at 100 °C, while no dispersion was observed after heating at 200–400 °C (Table 2). K-clay had lower dispersible clay after heating at 100 and 200 °C and no spontaneous dispersion occurred after heating at 300 and 400 °C. Na-clay had spontaneous dispersion after heating to 200 °C, while no spontaneous dispersion occurred after heating at 300 and 400 °C. Di- and tri-valent cationic clays (before and after heating) did not exhibit spontaneous dispersion when placed in distilled water (Table 2).

MECHANICAL DISPERSION. The results for mechanical dispersion are given in Table 2. Compared with those treated at 25 °C, for clays heated at 400 °C, the dispersion of Li-clay particles decreased from 98 to 2%, Na-clay particles from 98 to 67% and K-clay particles from 86 to 18%. There was a greater reduction in mechanical dispersion for Li- and K-clays than for Na-clay after heating at >200 °C. The changes correspond to the charge reductions at higher heating temperatures.

Mechanical dispersion of unheated divalent and Al-clays was much lower than that of clays with monovalent ions (Table 2). When the temperature of heating increased from 25 to 400 °C, the percentage of dispersed clay in Mg-, Ca- and Al-clays all decreased to 2–3%.

Zeta Potential and Particle Aggregation

Table 2 shows the changes in the zeta potential (ζ -potential) as related to the temperature of heating. There is a decrease in the particle mobility (ζ -potential becomes less negative) when the temperature of heating increases from 25 to 400 °C. The decreases in ζ -potential suggest more aggregation of clay particles or the formation of large domains, and correspond to reduction in charge. In general, the ζ -potential did not change as much as expected on heating, possibly because charge reduction was due to a decrease in the CEC caused by irreversible collapse of the layers.

Mean diameters of the clay particles saturated with Li, Na, K, Mg, Ca and Al as measured by the sub-micron particle sizer are given in Table 2. The particle diameters are influenced by the nature of cations and temperature due to the aggregation of particles. Unheated clays (25 °C) showed increases in their diameters in the following order: Li < Na < K < Mg < Ca < Al. However, on heating at 200 °C, the particle size reflected the charge reduction. Thus Li-, Mg- and Al-clays, which showed greater charge reduction, had larger diameters compared to Na-, K- and Ca-clays. This indicates that stronger bonding and greater aggregation is responsible for the charge reduction.

DISCUSSION

The data on swelling, dispersion, particle charge and particle size show the influence of the nature of bonding of cations to clay surfaces and indicate how this bonding is affected by thermal treatment. Even though the cations studied (Li, Na, K, Mg, Ca and Al) are considered to form ionic bonds, any given hetero nuclear bond formed in natural systems has a mixture of covalent and ionic character. The degree of covalency in a bond involving metal cations is characterized by a softness parameter derived from ionization and ionic potentials (Misono et al. 1967). The Misono factor indicates the tendency of a metal cation to form a dative π -bond and the ability to enter into EAED or HSAB reactions. Based on these principles, Rengasamy and Sumner (1996) proposed the following factor:

$$\text{Flocculative power} = 100(I_z/I_{z+1})^2 Z^3 \quad [2]$$

where I_z and I_{z+1} are z^{th} and $z+1^{\text{th}}$ ionization potentials, respectively, of the cation and Z is its valency. This factor determines the degree of covalent bonding between cations and clay surfaces and hence their flocculative power. This factor increases in the order: Li(0.5) < Na(1.2) < K(1.9) < Mg(28.2) < Ca(43.5) < Al(155.8).

The cationic effects on unheated clays follow the above order in terms of swelling (during glycerol solvation) and dispersion. As the degree of covalency bonding increases between cation and clay surface, hydration of cations becomes increasingly difficult. Thus, Li-, Na- and K-clays swell and disperse spontaneously, whereas Mg-, Ca- and Al-clays swell but do not spontaneously disperse. However, polar covalent bonds can be disrupted by mechanical agitation. The mechanically dispersed clay decreases as the degree of particle aggregation increases, as indicated by the mean diameter of the particles (Table 2).

Thermal treatment affects these bonds in different ways. The smaller cations (ionic radius <0.7 Å) Li, Mg and Al apparently migrate to octahedral vacant sites (Calvet and Prost 1971) and form covalent bonds after heating at 400 °C, and reduce the negative charge drastically. This process starts at 200 °C for Li. Covalent bonding and charge reduction in the clays prevent hydration and hence produce no swelling and reduced dispersion. At lower temperatures of heating (100–300 °C), polar covalent bonding in Mg- and Al-clays is increased, due to polarization of atoms by thermal energy. Therefore, limited hydration results in swelling but not in spontaneous dispersion.

Larger cations (Na, K, Ca) apparently do not migrate into lattice sites on thermal treatment, but there is an increase in the degree of covalency of the bonding between cations and clay surfaces due to thermal effects. Therefore, heating of these clays results in swelling with only limited hydration. Ca-clays have

limited swelling even without heating; for K, stronger fixation occurs at 400 °C, without any swelling.

CONCLUSIONS

Swelling and dispersion of homoionic Wyoming bentonite after heating at various temperatures can be explained by the nature of bonding between clay particles and the cations. A degree of covalency exists in the ionic bonds between the clay surface -O or -OH and the cations, resulting in a polar covalent bond. The degree of covalency increases, as indicated by the flocculative power, in the following order: Li < Na < K < Mg < Ca < Al. In unheated clays, the more ionic nature of the bonding in Li-, Na- and K-clays leads to extensive hydration and hence to swelling and spontaneous dispersion. Increased covalency and polar covalent bonding in Mg-, Ca- and Al-clays result in limited hydration; therefore, these clays only swell and do not disperse spontaneously.

Upon thermal treatment, the bonding characteristics change according to the size of the cations. Smaller cations (ionic radius < 0.7 Å) Li, Mg and Al apparently migrate to the octahedral vacant sites and form covalent bonds after heating at 400 °C. This results in severe charge reductions and the cation becomes non-exchangeable. This process occurred even at 200 °C for Li-clays. After heating at 400 °C, these clays neither swell nor disperse spontaneously.

Larger cations Na, K and Ca apparently do not migrate to lattice sites on thermal treatment. However, upon heating to 400 °C, thermal energy leads to a higher degree of covalency in the polar covalent bond. The interlayer cations are still exchangeable at a reduced level, resulting in limited hydration. Therefore, these clays swell but do not disperse spontaneously. However, K-clays after heating at 400 °C do not swell, but interlayer K⁺ remains exchangeable. The data on d_{001} spacing, dispersible clay, particle charge, ζ -potential, exchangeable cations and particle size confirm these conclusions.

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