EFFECTS OF SOME WATER REPELLENTS ON THE STRUCTURE AND WATER SORPTION OF SMECTITE

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Abstract—Waterproofing treatment is important for the preservation of smectite-rich rocks because of their shrinking and swelling properties. The effects of water repellents on the smectite structure and the water sorption of untreated and treated smectites were studied using X-ray diffraction. The hydrophobic Wacker BS 290 (around 100% silane/siloxane) does not prevent water from sorbing on the interlayer surface of smectite because the hydrophobic silane/siloxane is not intercalated into the interlayer space, but adsorbed onto the external surface of smectite. However, the hydrophilic Wacker BS 1001 (water-soluble emulsified silane/siloxane) prevents water from sorbing onto the interlayer surface beyond 33.3 wt.% because the hydrophobic part of the intercalated surfactant has a poor affinity for water. These results imply that water repellent containing a surfactant is suitable for smectite-rich rocks, but the expansion of smectite by intercalation of the surfactant is likely to influence volume change in smectite-rich rocks. This study notes that smectite within a rock can be one of the most important factors influencing the effectiveness of waterproof treatment. This study proposes that an intensive preliminary examination should be performed before applying water repellents to rocks, and furthermore, encourages development of new chemical reagents suitable for protecting smectite-rich rocks from moisture.

Key Words—Moisture Controls, Smectite, Stone Conservation, Surfactant, Water Repellents, XRD.

INTRODUCTION

Water repellents have been used to preserve the original shapes and structures of stone against water, one of the most damaging agents. Silicon-based water repellents, which contain silanes, oligomeric and polymeric siloxanes or silicon resins are most commonly used because of their good affinity for stone (Horie, 1987; Weber and Zinsmeister, 1991; Delgado Rodrigues and Charola, 1996). Silicon-based water repellents are usually divided into two types: hydrophobic and hydrophilic; the latter contains a surfactant to make water-soluble dispersions or microemulsions. Studies of the chemical or physical characteristics of water repellents (*e.g.* Horie, 1987; Newey *et al.*, 1992) and their appropriate applications on various stones (*e.g.* Charola and Delgado Rodrigues, 1996; Delgado Rodrigues and Charola, 1996; González *et al.*, 2000) have been performed because unsuitable water repellent causes the failure of a particular treatment. Wendler *et al.* (1992) and Snethlage *et al.* (1995) reported that when a clay-rich sandstone was treated with hydrophobic monomer silanes, its hygric dilatation increased compared with an untreated one. On the other hand, the treatment of water-soluble bifunctional alkylammonium decreased the hygric dilatation of the clay-rich sandstone.

Since the 1950s, experimental and theoretical studies on the formation and properties of smectite intercalated with various chemical species have been performed in response to the growing importance of agricultural and industrial applications and environmental pollution (*e.g.* Theng, 1974; LeBaron *et al.*, 1999; Alexandre and Dubois, 2000). With respect to stone conservation, several researchers have reported that the stone containing smectite is susceptible to contour scaling damage and irreversible rock structure deterioration due to the swelling and shrinking of the smectite (Helmi, 2000; Kim *et al.*, 2000; Wüst and McLane, 2000), and that the smectite affects the efficacy of waterproof treatment (Snethlage, 1984; Wendler *et al.*, 1992; Snethlage *et al.*, 1995). Snethlage (1984) conducted the treatment of 85% Na-montmorillonite with hydrophobic water repellents (Wacker 290S, Wacker 190S and Wacker 090S) and reported that the difference in d_{001} value, between the wet (at 100% relative humidity, RH) and dry (at 0% RH) samples treated with water repellents, was larger than that of an untreated sample by 0.29–0.63 Å. He noted that the hydrophobic treatment did not prevent the swelling of smectite from moisture. However, there has been no study on the influence of hydrophilic water repellent containing surfactant on smectite. This paper reports the effect of hydrophobic and hydrophilic silicon-based water repellents on the smectite structure and their efficacy against moisture using X-ray diffraction (XRD).

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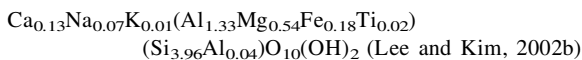
MATERIALS AND METHODS

Smectite

The smectite sample (Bentonil-GTC4) was obtained from Süd-Chemie Korea Co. It comprises mainly mont-

morillonite and has the chemical formula:

$$Ca_{0.13}Na_{0.07}K_{0.01}(Al_{1.33}Mg_{0.54}Fe_{0.18}Ti_{0.02})$$
$$(Si_{3.96}Al_{0.04})O_{10}(OH)_2 \text{ (Lee and Kim, 2002b)}$$

with minor quartz, illite and heavy minerals as impurities (<5%) (Lee and Kim, 2002a). The <2 µm fractions of smectite were obtained by wet sedimentation. Its cation exchange capacity (CEC), specific surface area and layer charge were measured as 1.04 mol/kg, 754.8 m^2/g and 0.345 equiv/(Si,Al)$_4$O$_{10}$, respectively (Lee and Kim, 2002a). No other pretreatments were carried out for the sample.

Water repellents

The two silicon-based water repellents (Wacker BS 290 and Wacker BS 1001) used in this study were manufactured by Wacker-Chemie GmbH. The Wacker BS 290 (hereafter W290) is a hydrophobic agent composed of ~100% silane/siloxane (Wacker-Chemie GmbH, 2001a). The Wacker BS 1001 (hereafter W1001) is a hydrophilic agent comprising ~50% water-soluble emulsified silane/siloxane, and it differs from W290 in that it contains surfactant for the emulsification of silane/siloxane (Wacker-Chemie GmbH, 2001b). The chemical and physical characteristics of these products are shown in Table 1.

Application of water repellents to smectite

Each of the smectite samples (0.1 g) was placed in a 25 mL centrifuge tube containing 6 mL of water repellent diluted to 0, 7.7, 11.1, 20.0, 33.3 and 100 wt.%. The W290 was diluted in ethanol, and the W1001 was diluted in distilled water. The suspensions were ultrasonically dispersed for 2 min. They were then treated by the following three different methods.

Method 1: simple reaction. The smectite was treated with water repellent without shaking, in order to achieve a condition similar to the actual stone surface application. The suspensions of water repellent-treated smectite were then centrifuged at 10,000 rpm at 25ºC for 5 min, and the supernatant liquids were decanted. The smectite was then dried as oriented aggregates on glass slides at 10–20ºC and relative humidity of 40–60% for 4 weeks.

Method 2: shaking reaction. The suspensions of smectite in water repellent were shaken on a reciprocating shaker at 250 rpm at 10–20ºC for 67 h. The oriented smectite samples were made in the same way as for method 1.

Method 3: washing after shaking reaction. The suspensions of smectite in water repellent were shaken on a reciprocating shaker at 250 rpm at 10–20ºC for 67 h. The smectite treated with W290 was washed with both ethanol and distilled water, while the one treated with W1001 was washed with both 50% ethanol solution and distilled water. Since W1001 is hydrophilic, 50% ethanol solution was used. The washing was performed by shaking the suspensions, centrifuging the suspensions at 10,000 rpm at 25ºC for 5 min, and then decanting the supernatant solutions. This process was repeated 3–5 times. Distilled water was used at the final stage of washing for both repellents because of the possibility of the highly volatile ethanol disorienting the oriented smectite. The smectite was dried as oriented aggregates on glass slides at 10–20ºC and 40–60% RH for 4 weeks.

Moisture controls

The oriented smectite samples treated with W290 and W1001 (0, 7.7, 33.3 and 100 wt.%), respectively, were left for 3 months at 10–20ºC and 40–60% RH allowing

Table 1. The chemical and physical characteristics of Wacker BS 290 and Wacker BS 1001 (Wacker-Chemie GmbH, 2001a, 2001b).

Water repellents	Wacker BS 290	Wacker BS 1001
Silicone active agent	Silane/siloxane (Alkylsilicone resin with alkoxy groups)	Silane/siloxane (Alkylalkoxysilane and -siloxane, emulsion in water)
Supplied as	Around 100% concentrate (liquid)	Around 50% emulsion (liquid)
Solubility in water	Virtually insoluble	Completely miscible
Color	Opaque	White
Odor	Mild	Mild
Flash point	~38ºC	–
Ignition temperature	>280ºC	395ºC
Vapor pressure	<50 hPa (at 20ºC)	23 hPa (at 20ºC)
Density	1.05 g/cm^3 (at 25ºC)	0.95 g/cm^3 (at 20ºC)
pH	–	~8
Viscosity	15–19 mPas	~12 mPas (at 25ºC)
Complements [1]	Methanol (>0.3%)	Alpha-i-tridecyl-omega-hydroxypolyglycolether (<5.0%) 3-(2-Aminoethylamino) propyltrimethoxysilane (<1.0%)

[1] Not all of the complements added to the water repellents are indicated in this table to protect commercial patent rights.

an appropriate polymerization. The samples were then conditioned under two different moisture environments as shown below.

Dry treatment. The oriented smectite samples were dried at 30°C and 0% RH for 95 h.

Wet treatment. Following the dry treatment, several droplets of distilled water were dripped onto the samples which were then left at 10–20°C and 40–60% RH for 2 h.

X-ray diffraction

The d_{001} values of the oriented smectites treated with water repellents, including dry and wet treatment, were recorded using CuKα radiation from a powder X-ray diffractometer (Rigaku RAD 3-C) with a graphite monochromater. The operating conditions were 40 kV and 30 mA in a continuous scan mode at a scanning speed of 2°2θ min⁻¹ with the slit set at 1°–0.15 mm–0.3°. Oriented mounts were analyzed under ambient room conditions (10–20°C and 40–60% RH). The d values of samples treated with water repellents were measured in the range from 2 to 35°2θ, and from 2–10°2θ for samples treated by drying and wetting within a short time (4 min) to reduce the influence of surrounding relative humidity.

RESULTS AND DISCUSSION

Effect of water repellents

The smectite treated with W290 (hereafter W290-smectite) by either method 1 or 2 showed no appreciable changes in d_{001} values regardless of the concentration (Figure 1a,b). This suggests that the silane/siloxane is not intercalated into the interlayer spaces of smectite, but adsorbed onto the external surface of the smectite. As the concentration increases from 0 to 33.3 wt.%, the d_{001} value of smectite treated with W1001 (hereafter W1001-smectite) gradually increases from 12.7 to 17.9 Å in method 1, and from 12.7 to 17.0 Å in method 2 (Figure 2a,b). It is well known that the cations located in the interlayer space of smectite are exchangeable with cationic surfactants because the surfactant is hydrophilic as well as hydrophobic in nature (Alexandre and Dubois, 2000). Unlike W290, W1001 contains a surfactant to emulsify the silane/siloxane. This means that the expansion of the d_{001} value of the smectite is caused by the intercalation of surfactant into the interlayer space. Our experiments show that the intercalation depends strongly upon the amount of W1001 in solution. Over a given temperature range, the two parameters defining the layer spacing of a smectite are the properties of the intercalated chemical species (*e.g.* the chain length of the organic part of surfactants and the charge and radius of chemical species) and the properties of the
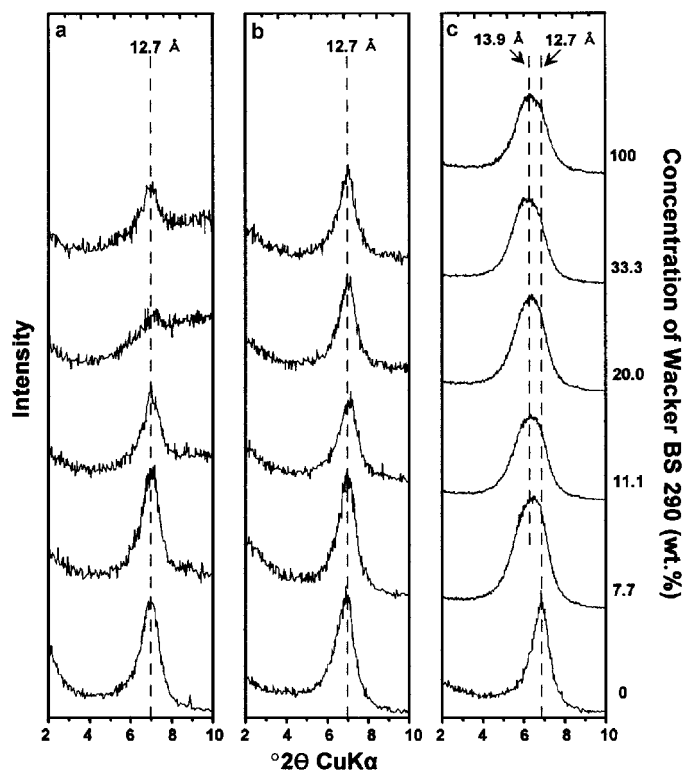

Figure 1. XRD patterns of smectite treated with Wacker BS 290 as the concentration increases (0, 7.7, 11.1, 20.0, 33.3 and 100 wt.%). (a) method 1 (simple reaction), (b) method 2 (shaking reaction), (c) method 3 (washing after shaking reaction).
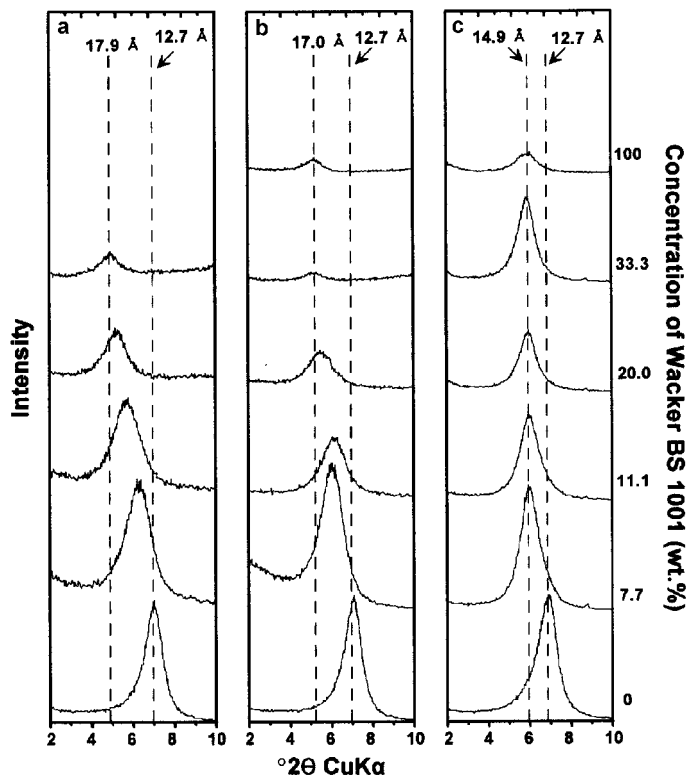
Figure 2. XRD patterns of smectite treated with Wacker BS 1001 as the concentration increases (0, 7.7, 11.1, 20.0, 33.3 and 100 wt.%). (a) method 1, (b) method 2, (c) method 3.

clay (*e.g.* the type of cations in the interlayer, layer charge and CEC) (Theng, 1974; Alexandre and Dubois, 2000). A quantitative description of the change in layer spacing cannot be given because W1001 is a mixture containing various kinds of chemical species, and all complements of W1001 are possibly under the protection of commercial patent rights. However, it is evident that the d_{001} value depends strongly on the amounts of W1001 adsorbed into the interlayer space of a smectite. As the concentrations of W290 and W1001 increase, the d_{001} peaks become slightly broader and weaker. This may be due to disordering by the presence of W290 on the external surface of the smectite and W1001 on the interlayer and external surfaces of the smectite.

Effect of moisture controls

Although the d_{001} value of untreated smectite (12.73 Å) shrinks to 11.59 Å through dry treatment, the d_{001} values show an average 0.46 Å decrease in W290-smectite and no decrease (except for the smectite treated by method 1 and 2 in 7.7 wt.%) in W1001-smectite (Table 2). This suggests that the water repellent-treated smectites contain a small number of water molecules in their interlayer spaces under dry conditions.

The d_{001} value of dried untreated smectite expands to 15.38 Å (two-layer hydration) through wet treatment (Table 2). It is well known that both Ca- and Na-

smectites can exhibit crystalline swelling (up to 20 Å) at 100% RH and Na-smectite, in particular, can also exhibit osmotic swelling (>40 Å) (van Olphen, 1991; McBride, 1994). This limited expansion might be due to the short time (2 h after applying water drops) allowed for swelling. The d_{001} values of W290- and W1001-smectites also expand by wet treatment. However, the degree of change in the d_{001} value varies with the type and concentration of water repellents as well as the methods applied. We can describe the difference in d_{001} value (Δd_{001}) between the wet and dry samples as follows:

$$\Delta d_{001} = d_{001w} - d_{001d} \qquad (1)$$

where d_{001w} and d_{001d} are the d_{001} values measured after wet and dry treatments.

The Δd_{001} value of the untreated smectite is 3.79 Å (Figure 3). However, the Δd_{001} values of W290-smectites are consistently ~7 Å under both methods 1 and 2, but ~5 Å under method 3. The concentration of W290 has little or no influence on the Δd_{001} value of smectite beyond 7.7 wt.%. This phenomenon suggests that W290 does not prevent water from sorbing onto the interlayer surface of smectite, because the hydrophobic silane/siloxane is not intercalated into the interlayer space, resulting in no interlayer expansion, as shown in Figure 1a,b. However, the Δd_{001} value of W1001-smectite depends largely on the concentration of

Table 2. Variation of d_{001} values (Å) of water repellent-treated smectites under different moisture environments.

Water repellents	Reaction methods [1]	Concentration (wt.%)	After treatment (Å)	Moisture controls (Å)	
				d_{001d}	d_{001w}
Untreated		0	12.73	11.59	15.38
Wacker BS 290					
	1	7.7	12.55	11.97	18.95
		33.3	12.55	11.94	19.28
	2	7.7	12.73	12.23	19.28
		33.3	12.62	11.94	19.11
	3	7.7	13.76	13.71	18.95
		33.3	14.11	13.63	18.63
		100	13.97	13.63	19.11
Wacker BS 1001					
	1	7.7	14.11	13.50	19.11
		33.3	17.95	17.95	19.11
	2	7.7	14.72	13.30	18.95
		33.3	17.05	17.05	19.11
		100	17.05	17.05	18.32
	3	7.7	14.72	14.72	19.11
		33.3	14.97	14.97	17.95
		100	14.72	14.72	18.09

[1] Method 1 (simple reaction), method 2 (shaking reaction), method 3 (washing after shaking reaction)

W1001. At a concentration of 7.7 wt.%, the Δd_{001} values (4.39–5.65 Å) are larger than that of the untreated smectite (3.79 Å). However, the Δd_{001} values (1.16–3.37 Å) at concentrations of 33.3 and 100 wt.% are smaller than that of the untreated smectite. This suggests that W1001 prevents water from further intercalation beyond 33.3 wt.%, because the surfactant, having a hydrophobic nature, has already intercalated into the interlayer space, resulting in the interlayer expansion as shown in Figure 2. The interlayer surface of the washed smectites (except for the W1001-smectite beyond 33.3 wt.%) sorbs less water than the unwashed ones (Figure 3). This might occur because of pre-existing ethanol and water in the interlayer space, as indicated by the d_{001} values of all washed W290-smectites expanding to 13.9 Å (Figure 1c). However, the increase of the Δd_{001} value of washed W1001-smectite beyond 33.3 wt.% might occur because the intercalated surfactant existing at low concentrations does not prevent water sorption. The intercalated surfactant seems to have been removed from the interlayer space of smectite during washing, as indicated by the d_{001} values of all washed W1001-smectites decreasing to 14.9 Å (Figure 2c).

IMPLICATIONS WITH RESPECT TO STONE CONSERVATION

The efficacy, harmfulness and durability of water-proofing treatment is influenced by the following factors: the sizes and shapes of testing specimens, the petrological characteristics, the porosity, the specific surface area, and the degree of deterioration of the stone, the salt content within stone, the type and concentration of water repellent, the type of solvent, the application procedure, and the environmental conditions during application, etc. (e.g. Weber and Zinsmeister, 1991; Snethlage et al., 1995; Charola and Delgado Rodrigues, 1996). Wendler et al. (1992) and Snethlage et al. (1995) proposed that the presence of smectite within a stone was also an important factor.
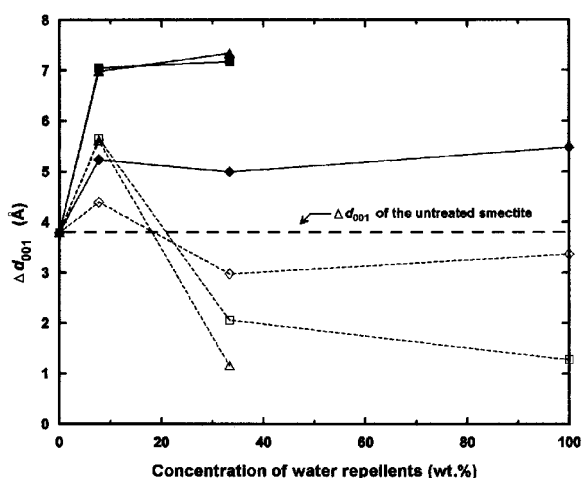

Figure 3. The difference (Δd_{001}) in d_{001} values between wet and dry smectites treated with water repellents vs. the concentration of water repellents. For Wacker BS 290, –▲– (method 1), –■– (method 2), and –◆– (method 3). For Wacker BS 1001, –△– (method 1), –□– (method 2), and –◇– (method 3). For clarity, the data points have been connected by lines.

In this study, it was observed that the hydrophobic W290 does not prevent water from sorbing onto the interlayer surface of smectite, as was also observed by Snethlage (1984). However, the hydrophilic W1001 prevents water from sorbing onto the interlayer surface beyond 33.3 wt.% and the efficacy of W1001 on smectite depends strongly on the amount of intercalated surfactant. The results of this study support the contention that the use of hydrophobic water repellents is not appropriate for the conservation of smectite-rich rocks, but the use of water repellents containing surfactant is appropriate, as proposed by Snethlage *et al.* (1995). However, the expansion of smectite, depending on the concentration of W1001, is likely to bring about a volume change in smectite-rich rocks. It is difficult to clarify the quantitative relevance of these results for protecting all types of rocks because there are many other factors influencing the effectiveness of the treatment. Also, the type and properties of smectite in individual stones could be different from those of the studied smectite. However, it is evident that the smectite within a rock can be one of the most important factors influencing the effectiveness of waterproofing treatments.

We propose that an intensive preliminary examination should be performed before the application of water repellents on rocks, and furthermore, encourage development of new chemical reagents suitable for protecting smectite-rich rocks from moisture.

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