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The Influence of Heat Pre-Treatment on the Sorption of Water Vapour on Bentonite

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Abstract. Sorption isotherms of water vapour on bentonite from the Rokle locality of northwest Bohemia in the Czech Republic were measured and analysed after being treated with heat. Protracted sorption measurements were performed at 30°C in the range of water vapour relative pressures between 0.12 and 0.94. Prior to sorption measurements, the bentonite samples were exposed to flowing dry nitrogen for 18 hours at 115, 220 and 300°C. Compared to the sample heated at 115°C, the bentonite samples that were treated at 220 and 300°C exhibited a decrease in water vapour sorption capacity. This decrease in sorption capacity was accompanied by structural changes that were confirmed by X-ray diffraction analysis.

Keywords: adsorption, bentonite, montmorillonite, water vapour

1. Introduction

Bentonite from the Rokle area is considered to be a potential backfilling material for highly radioactive waste repositories. Of primary importance is the interaction of backfilling materials with water vapour. There is a large body of literature dealing with the interaction of pure smectites with water. Some of these studies report findings related, in particular, to well-defined homoionic montmorillonites and their adsorption-desorption isotherms involving water vapour (Xu et al., 2000; Cases et al., 1997), as well as related heats of adsorption (Cancela et al., 1997; Iwata et al., 1989; Keren and Shainberg, 1975). Another important feature of smectites is their dilatation upon contact with water vapour. For the montmorillonites, there are a number of studies that deal with the dependence of its basal spacing relative to its water content (Bérend et al., 1995; Chiou and Rutherford, 1997; Keren and Shainberg, 1975), presence of exchangeable cations (Mooney et al., 1952), etc. Thus, it was revealed that water is sorbed mainly in the interlayer space of smectites and that adsorption-desorption isotherms exhibit hysteresis. It was also observed, in the above mentioned studies, that the heat of water immersion exhibits a step change upon change in the amount of water adsorbed. There is also literature available that relates the dependency of the sorption capacity relative to the size, charge and hydration energy of the exchangeable cations in homoionic montmorillonites. However, there are many fewer papers available regarding heteroionic montmorillonites and clays containing smectites.

The scope of the present study is to examine the properties of Rokle bentonite. Heating of the backfilling material due to residual radioactivity may considerably change the regime in the repository, in particular, due to the changes of the sorption capacity of the bentonite. The main objective of the study is to investigate the influence of heat treatment of the bentonite prior to sorption relative to the amount of sorbed water, and to relate the contingent changes to changes in smectite structure and/or the content.

2. Materials and Methods

2.1. Material Characterization

In this study, raw bentonite from the Rokle locality was investigated. Samples were dried under room conditions, crushed and sieved to grain size 0.2 to 0.25 mm. The chemical and phase compositions of the sample are given in the Results section.

2.2. Drying and Heat Pre-Treatment of Samples

Prior to sorption measurements, samples were heated for 18 hours at 115, 220 and 300°C in a flow of dry nitrogen (at a linear flow rate of 27 $\text{cm}\cdot\text{min}^{-1}$). Heat-treated samples were used for sorption measurements immediately after drying. The amount of water that was adsorbed during handling of the sample after the drying step (weighing and placing into desiccators) was found to be negligible. Water losses of samples heated at 115, 220 and 300°C were 9.95, 11.35 and 12.13% of initial weight respectively.

2.3. Protracted Isotherm Measurement

Adsorption isotherms were measured by exposing about one gram of bentonite, which was kept in a desiccator, to water vapour at a defined partial pressure p/p_o until equilibrium was reached. Appropriate partial pressures of water vapour used in the isotherm measurements correspond to equilibrium vapour pressures above saturated solutions of selected salts, see Table 1.

Desiccators with samples were placed in a Binder GmBH model KB 115 Air Thermostat Cooling Incubator, which has a constant temperature accuracy of ±0.1°C. The amount of adsorbed water was estimated gravimetrically as m_w/m_s (m_w = mass of adsorbed water [g], m_s = mass of dry sample after drying at given temperature [g]). The time necessary to reach adsorption equilibrium was about five to six weeks. Measurements were carried out at 30°C. The values of m_w/m_s were plotted against the corresponding values of p/p_o.

After adsorption equilibrium was reached, each sample was transferred from its primary desiccator to the desiccator with the highest value of p/p_o (0.94). After equilibration at $p/p_o = 0.94$, samples were placed back into the primary desiccator with a corresponding lower partial pressure of water. The desorption isotherm was then measured.

Table 1. Salts used in desiccators.

Salt	p/p_o at 30°C
$LiCl\cdot H_2O$	0.12
$CaCl_2\cdot 6H_2O$	0.29
$Ca(NO_3)_2\cdot 4H_2O$	0.47
$NaNO_2$	0.63
NH_4Cl	0.77
$ZnSO_4\cdot 7H_2O$	0.87
$MgSO_4\cdot 6H_2O$	0.94

Table 2. Silicate analysis of bentonite (weight % are related to the weight of bentonite dried at 200°C).

Compound	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	H_2O	CO_2	SO_3
Weight %	47.28	4.61	1232	12.66	0.11	0.30	3.11	7.48	0.17	1.09	0.99	10.97	3.26	0.09

2.4. X-ray Analysis

Powder X-ray diffraction measurements were carried out for untreated bentonite and bentonite treated at 115, 220 and 300°C to determine structural changes due to heat pretreatment. The analysis was performed using a diffractometer from Siemens: D-5005, Cu K_α radiation, graphite monochromator, range 2θ 2–80°, one step 0.02°/10 s with a total time of 11 hours.

3. Results and Discussion

3.1. Chemical and Phase Analysis of the Material

The silicate analysis of bentonite and the chemical composition of samples are given in Table 2.

On the basis of previous X-ray measurements, as well as results obtained from chemical analysis, an estimate was made regarding mineralogical composition of the untreated sample of bentonite. This estimate was based on an average crystallochemical formula of clay phases given by Velde (1992), see Table 3.

Using the results of chemical analysis and crystallochemical formulae by Velde, we estimated that our sample of bentonite contained approximately 44 wt.% of an expandable smectite group mineral, e.g., montmorillonite, 18 wt.% of quartz, 13 wt.% of dioctahedral mica, e.g., illite, 13 wt.% of free ferric oxides, e.g., goethite, 8 wt.% of calcite, 5 wt.% of free titanium oxides, e.g., anatase and less than 1 wt.% of kaolinite.

3.2. Water Vapour Sorption

Sorption and desorption isotherms are summarized in Figs. 1 and 2. Figure 1 indicates there is a decrease of the adsorbed amount of water vapour as the pretreatment temperature increases. After activation at 115, 220 and 30°C, the samples did not keep their original properties. This indicates that the process was irreversible. Furthermore, some irreversible changes

Table 3. Typical crystallochemical formulae of selected clay minerals (Velde, 1992).

Kaolinite	$Al_2Si_2O_5(OH)_8$
Illite	$(K_{0.77}, Na_{0.01}, Ca_{0.02})\,(Al_{1.63}, Fe^{3+}_{0.03}, Fe^{2+}_{0.05}, Mg_{0.30}, Ti_{0.04})\,(Si_{3.40}, Al_{0.60})$
Montmorillonite	$(Ca,Mg)_{0.27}(Al_{1.56}, Fe^{3+}_{0.15}, Mg_{0.32}, Fe^{2+}_{0.01})\,(Si_{3.93}, Al_{0.07})$

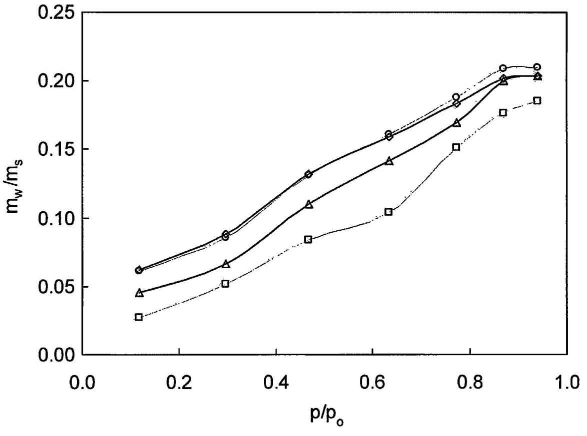

Figure 1. Adsorption of water vapour on bentonite at 30°C. Triangles and diamonds denote adsorption and desorption, respectively, for the sample pre-treated at 115°C. Squares denote adsorption for the sample pre-treated at 220°C and circles desorption for the temperature untreated sample; m_w/m_s is expressed in grams of H_2O per gram of dry sample after drying at a given temperature. For the untreated sample refer to the text.

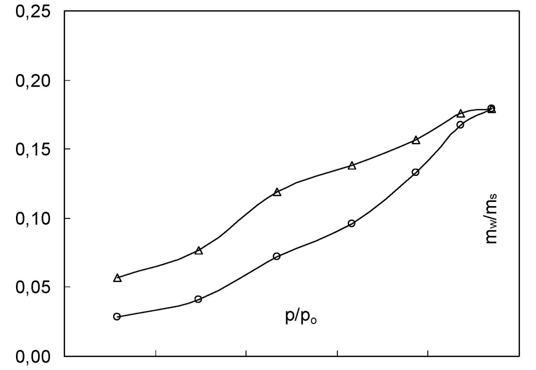

Figure 2. Adsorption and desorption of water vapour on bentonite at 30°C; circles and triangles denote adsorption and desorption for the sample treated at 300°C respectively; m_w/m_s is expressed in grams of H_2O per gram of dry sample after drying at a given temperature.

were also noticed in the X-ray diffraction patterns (see Section 3.3). The highest sorption capacity was found after heating at 115°C; the lowest was after heating at 300°C. There was a greater difference in sorption capacity between samples heated at 115 and 220°C than between those that were heated at 220 and 300°C. That is, a smaller decrease of water sorption capacity was observed for the sample treated at 300°C, compared to the sample treated at 200°C. That observation is consistent with the changes found from the X-ray spectra of the heat-treated samples. Additionally, there was a very small change of the peak intensity at $2\theta \cong 6.1^\circ$ between the samples treated at 220 and 300°C (cf. Fig. 3). This finding shows that after the activation at 220°C, the sample contained only a very small portion of smectite, which was transformed into illite during activation. It is plausible that cations with larger radii such as Ca^{2+} form a covalent bond with the clay surface after heating. For samples heated at 115 and 300°C, desorption isotherms were also measured, and a hysteresis loop was noticeable down to the region of $p/p_o = 0.1$ (see Figs. 1 and 2). Hysteresis of this type on smectites was reported by other authors (cf., e.g., Keren and Shainberg, 1975; Xu et al., 2000; Cases et al., 1997; Chiou and Rutherford, 1997). The difference between the corresponding equilibrium capacities of adsorption and desorption runs is more than an order of magnitude higher than the experimental error, which was set to ± 1 mg/g at $p/p_o = 0.1$. The amount of water vapour adsorbed on the untreated sample is given as $(m_f - m_i + m_{w115}) / (m_i - m_{w115})$, where m_f is a final mass of the samples after sorption $[g]$, m_i is an initial mass of the sample prior to sorption $[g]$ and m_{w115} is the mass of water removed after heating at 115°C $[g]$. At this stage, we have no information regarding multiple adsorption cycles because the experiments take a long time to complete. For example, only one cycle of activation-adsorption-desorption takes about 13 weeks.

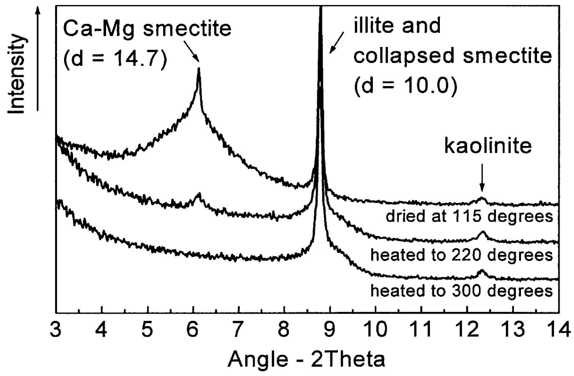

Figure 3. Powder X-ray diffraction patterns of bentonite pre-treated at given temperatures.

3.3. Powder X-ray Diffraction Analysis of Heat Treated Samples

When comparing diffraction patterns of samples treated at 115, 220 and 300°C, one can see that the increase in temperature due to pre-treatment caused a significant decrease in basal spacing of smectite, from 14.7 Å when dried at 115°C to 10 Å when dried at 300°C cf. Fig. 3. After heating to 220°C, part of the original structure with basal spacing of 14.7 and 10 Å was still intact, but there was no intermediate stage. After heating to 300°C, the whole structure collapsed to 10 Å giving the (001) peak the highest intensity, together with illite. Powder X-ray diffraction patterns for the sample treated at 115°C were almost identical with those previously obtained on the untreated sample (Hradil et al., unpublished result).

Smectite group minerals are "2:1" layered silicates formed by two tetrahedral and one octahedral sheet between them ("TOT structure"). These three sheets form a layer. Layers that are stacked together form an interlayer space. Substitution of lower valence ions with higher valence in tetrahedral sheets (in beidellite and nontronite) or in octahedral sheets (in montmorillonites) results in a permanent negative surface charge of the layer. This negative surface charge can be balanced by cations that are loosely held in the interlayer space, and are therefore exchangeable (Elzea et al., 1994). Both the interlayer space and presence of exchangeable cations are considered important factors for water vapour sorption.

Water is sorbed mainly in the interlayer space of smectites, where it is (i) bonded to exchangeable cations as a hydration shell and (ii) hydrogen-bonded to apical oxygen atoms of silica tetrahedrons (Cases et al., 1997, Ransom and Helgeson, 1994). The hydration shell of cations constitutes up to three spheres. The first sphere is bonded to the cation with higher hydration energy than the other two spheres (Ransom and Helgeson, 1994). At the same relative vapour pressure, the adsorbed amount of water increases with increasing hydration energy of the exchangeable cations and decreases with increasing size of those cations (Xu et al., 2000; Bérend et al., 1995; Mooney et al., 1952;

Table 4. Literature data on sorption capacity of pure clay compounds (adsorbed amount is expressed in grams of H_2O per gram of sample, mont. = montmorillonite).

	Cases et al., 1997 30°C Adsorbed amount		Saada et al., 1995 20°C Adsorbed amount	
p/p_o	Mg-mont.	Ca-mont.	Illite	Kaolinite
0.12	0.0948	0.0597	0.0016	0.0007
0.29	0.1400	0.1227	0.0038	0.0016
0.47	0.1785	0.1724	0.0061	0.0026
0.63	0.2072	0.2011	0.0090	0.0039
0.77	0.2336	0.2254	0.0123	0.0052

Cancela et al., 1997). The uptake of water vapour in the interlayer space results in an increase of basal spacing of smectite, and causes changes in the geometrical arrangement of the crystallites. Water molecules bonded to exchangeable cations are removed during dehydration. The first hydration shell remains intact due to its relatively high hydration energy within a wide range of p/p_o, and thus basal spacing remains almost constant for the same range of p/p_o (Xu et al., 2000, Cases et al., 1997). Changes in geometry during the adsorption-desorption process can cause differences in the filling and emptying of interlayers. This is one of the reasons adsorption hysteresis occurs. The same phenomenon was observed in our study (cf. Figs. 1 and 2).

Sorption properties of each sample depend on the sample's composition and structure. The major components of bentonite responsible for water vapour sorption are smectites, illite and kaolinite. The highest sorption capacity for water vapour is due to smectites. Table 4 shows the sorption capacity for water vapour (in g H_2O per g of sample) of some pure bentonite compounds as reported by Cases et al. (1997) and Saada et al. (1995). The tabulated values were extracted from graphs presented in these studies.

As one can see from Table 4, the sorption capacity of Mg- and Ca-montmorillonite at 30°C is considerably higher than that of illite and kaolinite, which are reported at lower temperatures than the montmorillonites. Thus, our focus was on smectite (montmorillonite) that was present in bentonite in Ca-Mg form. In our analysis, this is considered the most important bentonite phase with regard to water vapour sorption. For that reason, we have neglected the corresponding contribution of illite and kaolinite. From the adsorbed amount of water vapour on pure homoionic Mg- and Ca- montmorillonite at $p/p_o = 0.29$ (see Table 4), one can obtain an average value for the adsorbed amount on montmorillonite in mixed Ca-Mg form of 0.1314 g/g at the same value of relative pressure p/p_o. When the adsorbed amount from our 115°C sample at $p/p_o = 0.29$ (i.e. 0.0594 g/g) is compared to the average value for Ca-Mg montmorillonite, it can be seen that it represents 45% of the value obtained in Ca-Mg montmorillonite. This result is consistent with our estimate of the amount of smectite in our bentonite.

As can be seen from Fig. 1, the loss of water adsorption capacity for the sample activated at 300°C, in comparison to the sample activated at 115°C, varies between approximately 16% at $p/p_o = 0.87$ and approximately 37% at $p/p_o = 0.12$. It is possible to distinguish the temperature intervals in which different types of water molecules are removed from bentonite upon heating. During heating in the temperature range of 20 to 100°C, free water molecules are removed from the interlayer space. Hydrogen-bonded water molecules and water molecules coordinated to exchangeable cations are removed in the range of 100 to 200°C. This can be extended up to 500°C (Cases et al., 1997). Even a relatively small loss of water between 115 and 300°C caused a considerable decrease in basal spacing of smectite present in the sample. This can be seen from powder X-ray diffraction patterns measured on samples for the same temperature interval. The respective basal spacing is reduced from 14.7 to 10.0 Å (cf. Fig. 3). This observation agrees with results reported in study by Helsen et al., 1975. These authors report (001) basal spacing for Ca- and Mg-montmorillonites of 14.2 Å. Cases et al. (1997) also reported the decrease in basal spacing from 15 to 10 Å for Mg-montmorillonite at 300°C, and for Ca-montmorillonite at 400°C. A step change in basal spacing of smectite was observed in our sample (an intermediate stage was omitted) due to removal of water from the sample by the above-mentioned heat treatment. This observation is in agreement with results obtained in studies by Mooney et al. (1952), Keren and Shainberg (1975), and Cancela et al. (1997), who reported step changes in basal spacing of montmorillonite relative to a continuous change of water content in the interlayer space. The change in basal spacing due to heat pretreatment reduced the interlayer space, which resulted in the reduction of sorption capacities of water vapour in samples heated to 220°C and 300°C, in comparison to the sample heated to 115°C. The amount of water adsorbed on the untreated sample was almost the same as that on the sample heated to 115°C (cf. Fig. 1). This finding is consistent with powder X-ray diffraction analysis. X-ray diffraction patterns of unheated samples (Hradil et al., unpublished results) and samples heated to 115°C were almost identical. Thus, we do not expect changes in structure due to heating to 115°C.

4. Conclusions

The properties of naturally occurring bentonite (Rokle deposit, Czech Republic) were analyzed in relation with properties of pure homoionic montmorillonites (Ca and Mg forms).

Sorption and desorption isotherm measurements of water vapour were carried out by protracted experiments on samples pretreated at temperatures between 115 and 300°C. The sorbed amount of water was considerably lower for samples pretreated at 220°C compared to those pretreated at 115°C. The sorption capacity for water was still lower for samples pre-treated at 300°C, but the decrease was not so noticeable. Adsorption of water vapour exhibited hysteresis for all the relative pressure ranges investigated in this study. There was only a slight difference in desorption isotherms of water on thermally untreated samples compared to those pretreated at 115°C. The amount of sorbed water was found to be dependant on the content of smectite present in the sample.

The effect of heat pretreatment of a sample on its structure was investigated by powder X-ray diffraction. It showed structural changes in smectite present in bentonite due to heat pretreatment at temperatures higher than 115°C. Powder X-ray diffraction patterns of unheated samples and those heated at 115°C were practically the same.

Nomenclature

m_f	Final mass of untreated sample at the end of sorption (g)
m_i	Initial mass of untreated sample at the beginning of sorption (g)
m_s	Mass of sample (g)
m_w	Mass of water sorbed on sample (g)
m_{w115}	Mass of water removed from untreated sample by heating at 115°C (g)
p/p_o	Relative water vapour pressure (−)

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References

Anderson, D.M. and G. Sposito, *Nature*, **199**, 1085 (1963).

Apelblat, A. and E. Korin, *Journal of Chemical Thermodynamics*, **30**, 59 (1998).

Bala, P., B.K. Samantaray, and S.K. Srivastava, *Bulletin of Material Science*, **23**, 61 (2000).

Bérend, I., J.M. Cases, M. Francois, J.P. Uriot, L. Michot, A. Masion, and F. Thomas, *Clays & Clay Minerals*, **43**, 324 (1995).

Brooks, C.S., *Soil Science*, **99**, 182 (1964).

Brzek, Z., MS Thesis, Faculty of Science, Prague, Czech Republic, p. 96 (1997).

Cancela, G.D., F.J. Huertas, E.R. Taboada, F.S. Rasero, and A.H. Laguna, *Journal of Colloid and Interface Science*, **185**, 343 (1997).

Carr, D.D., A.F. Alsobrook, G.S. Austin, J.M. Barker, R.L. Bates, J.W. Baxter, H.L. Bourne, J.R. Dunn, B.H. Mason, H.N. McCarl, H.H. Murray, J.C. Norman, K.G. Papke, L.F. Rooney, and N. Severinghaus Jr., *Industrial Minerals and Rocks*, 6th edn., pp. 233–246, Society for Mining, Metallurgy, and Exploration, Inc., Littleton, 1994.

Cases, J.M., I. Bérend, M. Francois, J.P. Uriot, L.J. Michot, and F. Thomas, *Clays & Clay Minerals*, **45**, 8 (1997).

Chiou, C.T. and D.W. Rutherford, *Clays & Clay Minerals*, **45**, 867 (1997).

Chiou, C.T. and D.W. Rutherford, *Environmental Science & Technology*, **27**, 1587 (1993).

Fu, M.H., Z.Z. Zhang, and P.F. Low, *Clays & Clay Minerals*, **38**, 485 (1990).

Giacovazzo, C., H.L. Monaco, G. Artioli, D. Viterbo, G. Ferraris, G. Gilli, G. Zanotti, and M. Catti, *Fundamentals of Crystallography*, 2nd edn., pp. 553–559, Oxford Univesity Press, Oxford, 2002.

Grim, R.E., *Clay Mineralogy*, 2nd edn., McGraw-Hill Book Company, New York, 1968.

Helsen, J.A., R. Drieskens, and J. Chaussidon, *Clays and Clay Minerals*, **23**, 334 (1975).

Hensen, E.J.M. and B. Smit, *Journal of Physical Chemistry B*, **106**, 12664 (2002).

Hradil et al., *Unpublished results*.

Huang, W.L., W.A. Bassett, and T. Ch. Wu, *American Mineralogist*, **79**, 683 (1994).

International Critical Tables of Numerical Data, Physics, Chemistry and Technology, Vol. I, pp. 67, New York and London, 1926.

Iwata, S., F. Izumi, and A. Tsukamoto, *Clay Minerals*, **24**, 505 (1989).

Keren, R. and I. Shainberg,*Clays & Clay Minerals*, **23**, 193 (1975).

Levy, R. and C.W. Francis, *Clays and Clay Minerals*, **23**, 85 (1975).

Marere, V.M., H. Belarbi, P. Thomas, F. Morato, J.C. Giuntini, and J. M. Douillard, *Journal of Colloid and Interface Science*, **202**, 139 (1998).

Mooney, R.W., A.G. Keenan, and L.A. Wood, *Journal of the American Chemical Society*, **74**, 1371 (1952).

Ransom, R. and H.C. Helgeson, *American Journal of Science*, **294**, 449 (1994).

Ryndová, T., "Faculty of Science," MS Thesis, p. 51, Prague, 2000.

Saada, A., B. Siffert, and E. Papirer, *Journal of Colloid and Interface Science*, **174**, 185 (1995).

The Team of the Research Institutes of Ministry of Chemical Industry, *Physiochemical Tables*, Vol. I, p. 494, The National Publishing House of Technical Literature, Prague, 1953.

Velde, B., *Introduction to Clay Minerals*, p. 198, Chapmann & Hall, London, 1992.

Vlčková, L., *Bentonite—The Backfilling Material for the Permanent Radioactive Waste Repository*, Report, pp. 1–14, Czech Geological Institute, Prague, 1994.

Vokál, A., P. Chvátal and O. Záleská, in *Proceedings of the Bentonite and its Utilization Conference*, pp. 83–94, Keramost, Inc., Most, 1994.

Xu, W., C.T. Johnston, P. Parker, and S. F. Agnew, *Clays & Clay Minerals*, **48**, 120 (2000).