

WATER-UPTAKE CAPACITY OF BENTONITES

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Abstract—The present study compares the water-vapor adsorption capacity of bentonites (natural cation population) with the Enslin-Neff method. Water-vapor adsorption at 50% r.h. (relative humidity) or 70% r.h. is known to depend heavily on the amount of permanent charge and on the type of exchangeable cation. At ~80% r.h. Na⁺- and Ca²⁺/Mg²⁺-dominated bentonites take up equal amounts of water. Comparing the water-uptake capacity at 80% r.h. with the cation exchange capacity (CEC) revealed a close correlation between these two variables. Appreciable scatter apparent from this plot, however, suggests that additional factors influence the water-uptake capacity. Water adsorption at external surfaces was considered to be one of these factors and was, in fact, implicated by N₂-adsorption data. The ratio of external/internal water ranged from 0 to 1, which suggests that water-adsorption values cannot be applied in the calculation of the internal surface area without correction for external water.

The Enslin-Neff water-uptake capacity, on the other hand, is unaffected by microstructural features (*e.g.* specific surface area and porosity). The amount of exchangeable Na⁺ is the most important factor. However, the relationship between the Na⁺ content and the Enslin value is not linear but may be explained by percolation theory.

Key Words—Bentonite, Enslin-Neff, Swelling Capacity, Water-vapor Adsorption.

INTRODUCTION

The most characteristic feature of bentonite is its swelling capacity in small polar solvents. In most industrial and geotechnical applications the swelling capacity of bentonites with water is important and several different methods exist for determining the water-uptake capacity or the properties which depend on it (*e.g.* Klute, 1986). Most of the water is adsorbed as hydration water surrounding exchangeable cations in the interlayer region of smectites. A simplified assumption is that hydration water occurs as individual layers in the interlayers, which sometimes is a valuable model. From the physicochemical point of view, however, the uncharged interlayer surface (space between the focus of the permanent charges) is considered to be less hydrophilic than the areas in which the hydratable exchangeable cations are located (*e.g.* Prost, 1975; Sposito and Prost, 1982; Yariv, 1992; Yariv and Michaelian, 2002). Hence, the water-uptake capacity is heavily dependent on the composition of the exchange population (type of exchangeable cations), the type of smectite, the layer-charge density (LCD), and charge location (*e.g.* Laird, 1999). The distribution of water in the interlayer, therefore, is said to be heterogeneous. Some additional water can be adsorbed by micro- or even mesopores. This additional water has been termed ‘external water’ (*e.g.* Prost, 1975).

To understand smectite swelling processes, the structure of the water adsorbed must be understood. Several studies exist which differentiate between the different hydration states (*e.g.* Sposito and Prost, 1982). Classically one-, two-, and three-layer smectite hydrates are distinguished, which are simple models that are applicable in a wide range of instances. The actual structure of water adsorbed to smectites is known to be more complicated and has been investigated extensively (*e.g.* Sposito and Prost, 1982; Cases *et al.*, 1997; van der Gaast *et al.*, 1997; Ferrage *et al.*, 2005).

The goal of the present study was to discuss and assess the (mineralogical) significance of parameters describing the water-uptake capacity. Thirty-six bentonites with their natural cation occupation as well as two mixed-layer illite-smectite-dominated clays were investigated with respect to their water-uptake capacity from the gaseous phase and in contact with liquid water. The results are discussed with respect to the parameters determining the water-uptake capacity. Additional focus is placed on the identification of the influence of subordinate parameters which do not determine the water-uptake capacity but which may be responsible for the scattering of the data obtained.

MATERIALS AND METHODS

Thirty-six different bentonites as well as two illite-smectite-dominated clays were used in this study. The precursor materials were characterized by Kaufhold and Dohrmann (2008a), Kaufhold *et al.* (2008), and

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Dohrmann and Kaufhold (2009). Ufer *et al.* (2008) determined the quantitative mineralogical composition of the bentonites but did not consider the mixed-layer illite-smectite samples (numbers 30 and 35). The sample assignments were changed accordingly: Ufer *et al.* (2008) sample 31 was referred to as sample 30 and sample 36 was referred to as sample 34.

The water-uptake capacity was determined both by applying defined relative humidity (water-uptake from the gaseous phase) and by using the Enslin-Neff method (Enslin, 1933; Neff, 1959) which was recently modified by Dieng (2005, 2006) and assessed by Kaufhold and Dohrmann (2008b). The Enslin-Neff method is used to determine the water-uptake capacity of a solid (clay) in direct contact with liquid water and is commonly used to assess the geomechanical stability, *e.g.* in civil engineering, or for quality control in the bentonite industry.

The defined relative humidity for measuring water-uptake capacity from the gaseous phase was provided by a climate oven (Binder APT.line KBF). The actual relative humidity in the oven was checked by separate measurements using a high-quality humidity sensor (Dostmann electronic GmbH, Thermohygrometer P670). In addition, an internal laboratory standard (Georgia attapulgit) was used in each measurement series in order to ensure comparability of the values obtained. For the water-uptake capacity measurement, 500 mg of each powdered sample was weighed in an aluminum cup (4 cm diameter) and the adsorption capacity was recorded gravimetrically at 50, 70, and 90% relative humidity (r.h.) at 30°C. The samples were maintained at the designated relative humidity for 1 week and weighed outside the oven afterward. Transfer from the oven was performed with minimum

contact to the atmosphere. Finally, the samples were dried at 105°C in order to determine the initial dry mass.

The Enslin-Neff water-uptake capacity (resulting in the so called Enslin-Neff values) was determined by the Dieng apparatus (Dieng, 2005, 2006; Kaufhold and Dohrmann, 2008b).

For investigation by scanning electron microscopy, an FEI Quanta 600 F, operated in low-vacuum mode (0.6 mbar), was used. Coating of the samples with gold or carbon was unnecessary. The microscope is equipped with the EDAX EDX-system Genesis 4000.

The specific surface area (SSA) was determined by N₂ adsorption from adsorption and desorption isotherms measured by a Micromeritics Gemini III 2375 surface area analyzer with approximately 100 mg weight. Samples were predried at 105°C for 12 h and 25 adsorption points were collected.

RESULTS AND DISCUSSION

Water-uptake capacity from the gaseous phase

The water uptake-capacity is known to depend heavily on the amount of exchangeable cations as shown, for example, by Kaufhold (2005, 2006) who studied ~50 different homoionic Ca²⁺ bentonites at 53% r.h. However, Kaufhold (2005, 2006) did not study the effect of different cations and almost all samples were derived from one mining district only.

The water-uptake capacity, as expected, depends heavily on the total amount of charge represented by the CEC (Figure 1). Nevertheless, appreciable scatter was observed, which was not observed by Kaufhold (2005, 2006) probably because the bentonites were derived from a limited regional distribution (almost all

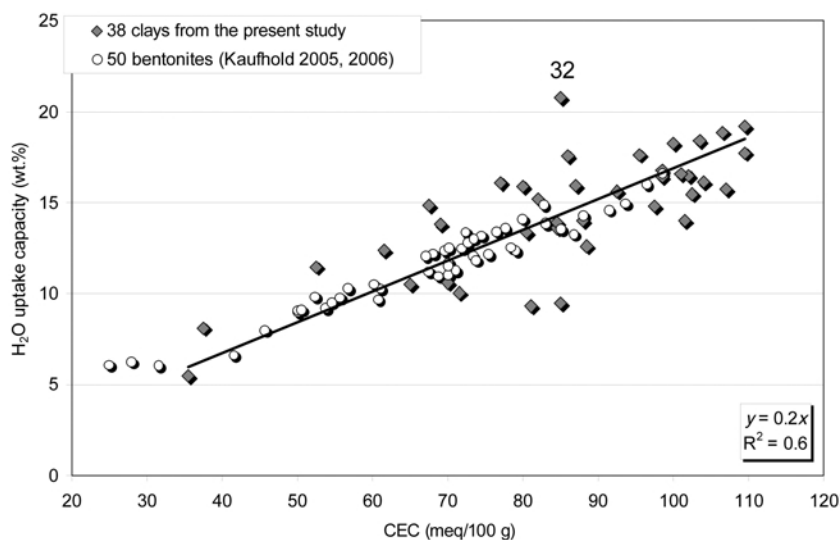


Figure 1. Water-uptake capacity of the 38 samples from the present study with their natural cation population (\blacklozenge), and of 50 bentonites (\circ), mainly from Bavaria (Kaufhold 2005, 2006), compared with the CEC (70% r.h.); errors: CEC ± 1 meq/100 g, H₂O uptake capacity ± 1 wt.%.

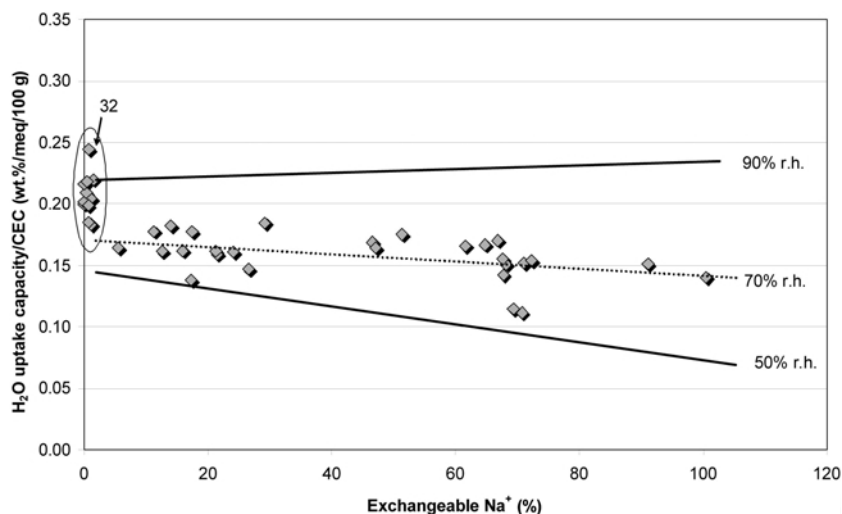


Figure 2. Water-uptake capacity vs. CEC depending on the percentage of interlayer Na^+ (\diamond = values determined at 70% r.h.; in the case of 50% r.h. and 90% r.h. only regression curves are shown, which were calculated from samples with $\text{Na}^+ > 3$ meq/100 g).

from Bavaria). The effect of the type of exchangeable cation was supposed to be subordinate at 70% r.h. according to Montes *et al.* (2003) and to Figure 2.

One goal of the present study was to identify parameters (other than the CEC) which affect the water-vapor uptake capacity. Unfortunately, the production of pure smectite fractions is (1) laborious and (2) often impossible. Therefore, in order to be able to study different bentonites, independent of the CEC, the water-uptake capacity determined at 50, 70, and 90% r.h., respectively, was divided by the total CEC resulting in the value 'water-uptake capacity per CEC.' Using this value makes possible the comparison of the water-uptake capacities of bentonites with different smectite contents and/or layer-charge densities (LCD).

The water-uptake capacity results were compared with the amount of exchangeable Na^+ , because the hydration behavior of Na^+ is known to differ significantly from that of Ca^{2+} and Mg^{2+} (Figure 2). Na^+ is given in % (meq Na^+ /CEC) in order to minimize the effect of the smectite content.

At 50% r.h., Na^+ -dominated smectites adsorb significantly less water than Ca/Mg -dominated clays. A comparable hydration state of Na^+ and $\text{Ca}^{2+}/\text{Mg}^{2+}$ is observed at ~80% r.h. which is in good agreement with the assertion by Montes *et al.* (2003). At 90% r.h. Na^+ is hydrated by more water molecules than Ca^{2+} and/or Mg^{2+} . Interestingly a significant scatter was observed in case of the Na^+ -free samples (marked by an ellipse in Figure 2). Sample 32 is highlighted because of the extraordinarily large water-uptake capacity compared to the other $\text{Ca}^{2+}/\text{Mg}^{2+}$ bentonites and, hence, was considered further. Using SEM, Klinkenberg (2008) investigated all bentonites with respect to their microstructure. She found that bentonite 32 contains a large amount of fine smectite fibres forming three-

dimensional networks which contain a large number of mesopores (Figure 3). All other parameters of this bentonite (CEC = 80 meq/100 g, LCD = 0.26 eq/FU, Fe_2O_3 content = 8 wt.%, pH = 7.4 as well as X-ray diffraction, infrared, and differential thermal analysis data) were unremarkable.

The data presented above, particularly of sample 32, indicated that microstructural features such as (small) mesopores can affect the water-uptake capacity of bentonites. Additional effects were likely but could not be identified by optical investigations. The specific surface area values as determined by N_2 adsorption are known to be affected by micropores (and small

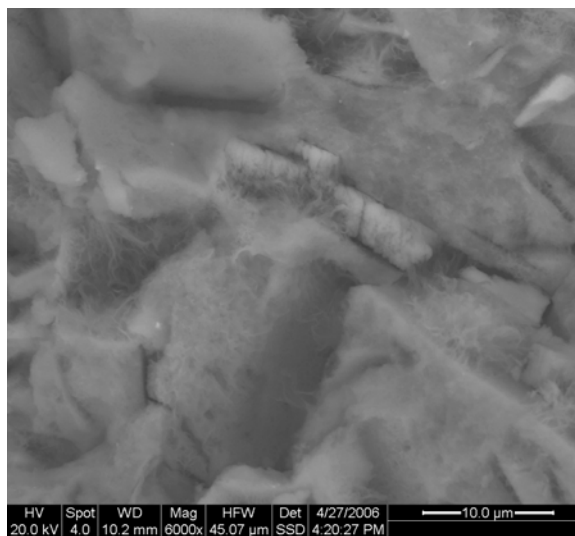


Figure 3. SEM image of the fibrous smectites forming a mesoporous network (sample 32).

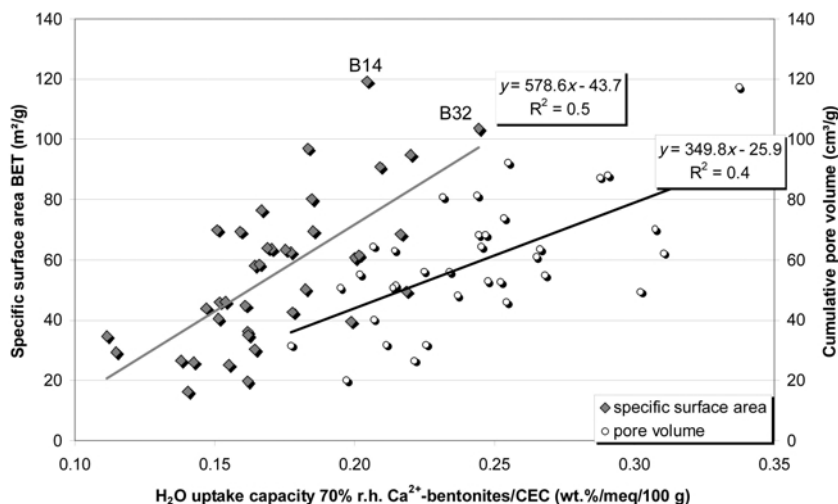


Figure 4. Dependence of water-uptake capacity (divided by the CEC) of homoionic Ca^{2+} bentonites at 70% r.h. on microstructural features derived from N_2 adsorption (specific surface area and cumulative porosity).

mesopores). Therefore, this method was considered to provide an applicable value describing at least some features of the microstructure. In order to further investigate the effect of microstructure on the water-uptake capacity all samples were saturated with Ca^{2+} and investigated with respect to the water-uptake capacity, specific surface area, and total porosity (Figure 4).

The trends prove the influence of microstructure on the water-uptake capacity (Figure 4). Of note is that the trend presented in Figure 4 depends on neither the CEC (because the water-uptake capacity is normalized to the CEC) nor the type of exchangeable cation (because of homoionic Ca^{2+} occupation of the interlayer). Moreover, the correlation with the specific surface area (N_2 -BET)

was independent of the relative humidity (between 50% and 90%, Figure 5).

Finally, the most interesting factor which can be deduced from the data presented above (Figures 4, 5), irrespective of an estimated 10% effect of variable charge, was the number of water molecules per cation and the extent to which this value can be influenced by micro-/mesopores. The amount of water per charge in the case of Ca bentonites at 70% r.h. ranged from 0.11 to 0.24 wt.%*100 g/mmol (= g water/mmol). Hence, dividing 0.11 by 0.018 g/mmol (mmolar mass of water molecule) led to ~6.1. Considering 10% variable charge of the CEC increases the amount of water molecules per charge (= per cation) to almost 7. A value of 0.24

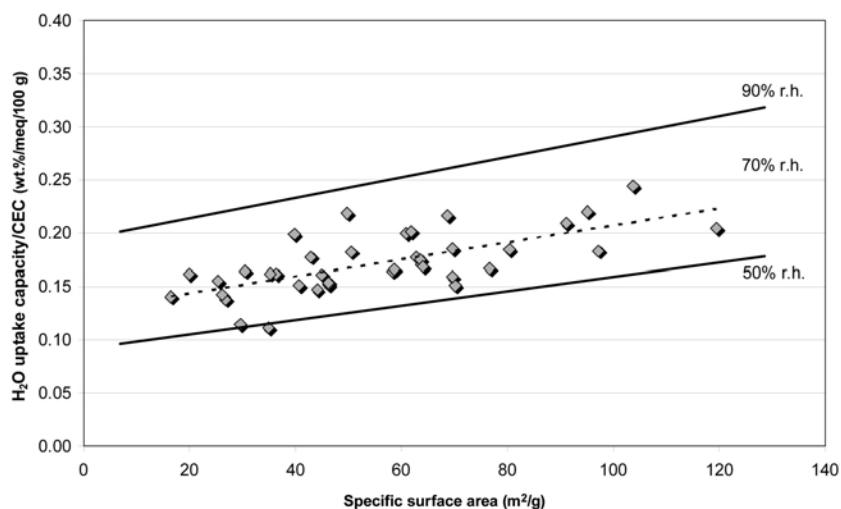


Figure 5. Water-uptake capacity of the Ca-saturated samples divided by the CEC compared with the specific surface area as determined by N_2 adsorption (BET method) at different relative humidities (\blacklozenge = values determined at 70% r.h.; in the case of 50% r.h. and 90% r.h., only regression curves are shown).

corresponds theoretically to 13 molecules of water per cation, which is probably incorrect because at 70% r.h. Ca-montmorillonites are known to be coordinated by six water molecules (octahedral coordination) corresponding to a basal spacing of 15–15.5 Å. Considering the extraordinary water-uptake capacity of bentonites with large specific surface area suggests that the water-uptake capacities determined experimentally were strongly affected by the microstructure. Excess water was probably not attached to the uncharged SiO₂ surface, but this is still the subject of debate. Finally, samples with small specific surface areas contained the expected six (or slightly more) water molecules per cation. These samples were believed to simply contain fewer micropores and/or small mesopores than the others. Most studies of water uptake by smectites focus on interlayer swelling and the effect of exchangeable cations (*e.g.* Cases *et al.*, 1997; Ferrage *et al.*, 2005). Some adsorption of water to the external surface is also known to exist. The present study indicates that the ratio of external/interlayer water at 70% r.h. can be significant, ranging from 0 to almost 1.

Water-uptake capacity as determined by Enslin-Neff

In a number of European countries the Enslin-Neff method is frequently used for quality control of different materials (not restricted to clays) as well as for scientific purposes. For the Enslin-Neff method, water is in direct contact with the sample powder, unlike in other cases where water adsorption is from the gaseous phase. The results obtained demonstrated that water-uptake capacity from the gaseous phase and the Enslin-Neff values were unrelated (Figure 6).

Enslin-Neff values are known to depend to a significant extent on the type of exchangeable cation, particularly on the amount of Na⁺ (Neff, 1959). All

Enslin-Neff values, therefore, were compared with the amount of exchangeable Na⁺ of the clays (Figure 7). Enslin-Neff values are commonly defined as ‘g of water uptake compared to the initial weight.’ In order to be able to compare the water-uptake capacity of both experimental setups, Enslin-Neff values were given in ‘wt.% water uptake compared to the dry mass of clay.’

As expected, the Enslin-Neff values clearly correlated with the amount of exchangeable Na⁺. The data obtained, however, indicated that the water uptake does not depend linearly on the amount of exchangeable Na⁺ (although more data in the 30–60% range would have been interesting; Figure 7). An exponential approach to fitting the data was considered to be imperfect. In contrast, the observed data may be explained by percolation theory (*e.g.* Kesten, 2006), which means that bivalent cations (Ca²⁺ and Mg²⁺) determine the water-uptake capacity as long as they dominate the interlayer. Na⁺ hydration, in turn, must be strong enough to pull the layers apart in order to reach the characteristically large Enslin-Neff values. This expansion, apparently, is inhibited by bivalent cations in the interlayer up to a critical concentration. In contrast to the water uptake from the gaseous phase, Enslin-Neff values obviously depend to a much lesser extent on the specific surface area. Sample 32, which has a particularly large porosity (and SSA), showed an Enslin-Neff water-uptake capacity which corresponds to most of the Na⁺-poor clays. Obviously the expansion of the interlayer to the distance known for Na⁺ smectites at excess water (>19 Å) determines the Enslin-Neff values. The layer-charge density (LCD) determining the affinity of the TOT layers to each other might also play an important role. Surprisingly no significant effect of the LCD on the swelling capacity could be identified. High-charged domains, however, are still supposed to be

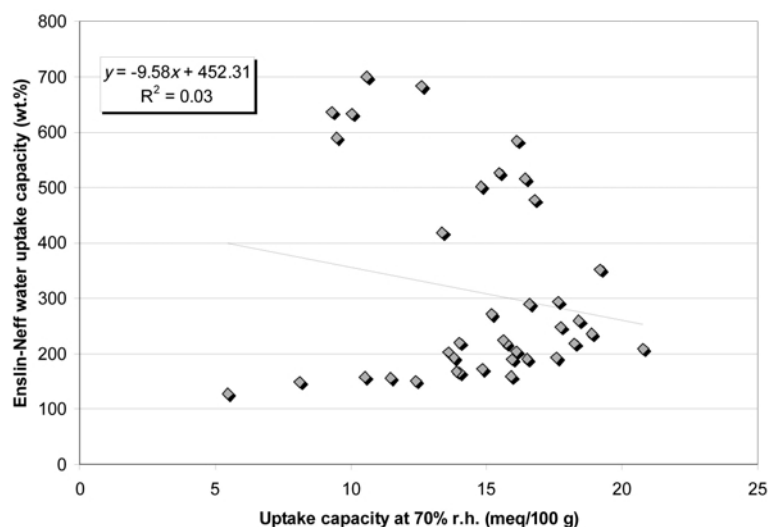


Figure 6. Comparison of the water-uptake capacity from the gaseous phase at 70% r.h. with Enslin-Neff values.

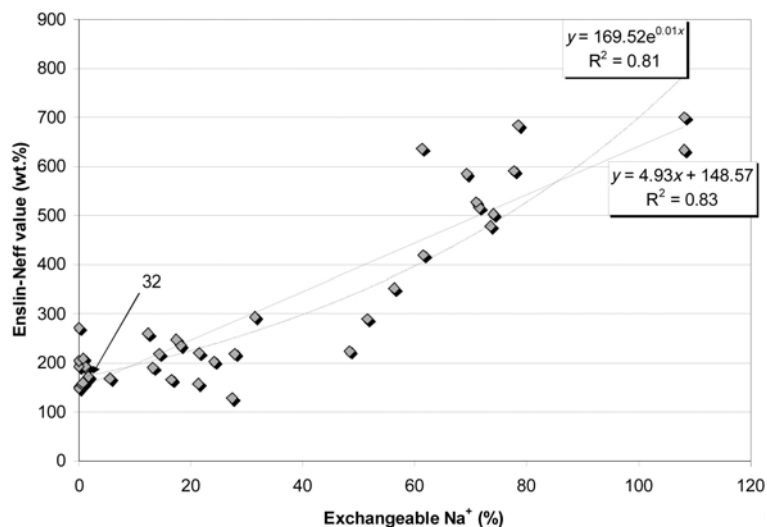


Figure 7. Enslin-Neff values compared with the amount of exchangeable Na^+ (the size of the diamonds corresponds to the accuracy as determined by Kaufhold and Dohrmann, 2008b).

relevant. Based on the data available in the present study this problem could not be solved because only two samples with $<30 \text{ meq}/100 \text{ g Na}^+$ were investigated with comparable LCD (but marked difference of the LCD distribution). Hence, a more detailed study based on suitable samples is required.

Interestingly five bentonites contain significant amounts of organic matter and those samples all have very low Enslin-Neff values. Organic matter may render the bulk surface hydrophobic and in turn repel some water, which then leads to a decrease in Enslin-Neff values. That mechanism could only be valid (if at all) in the case of $\text{Ca}^{2+}/\text{Mg}^{2+}$ bentonites because the sample with the largest organic-matter content (0.8 wt.% total organic carbon) is dominated by Na^+ and adsorbed as

much water as the other Na^+ -dominated bentonites (data from Kaufhold *et al.*, 2008).

Some of the data scatter of the low- Na^+ Enslin-Neff values may be explained by the amount of exchangeable Mg^{2+} (Figure 8) but the weak trend suggests that further parameters are involved, which could not be identified in the present study. These parameters may include: N_2 -adsorption data, grain-size distribution, CEC, LCD, elemental carbon analysis, pH, and chemical composition (X-ray fluorescence).

SUMMARY AND CONCLUSIONS

Thirty-six bentonites and two illite-smectite-containing clays were investigated with respect to water

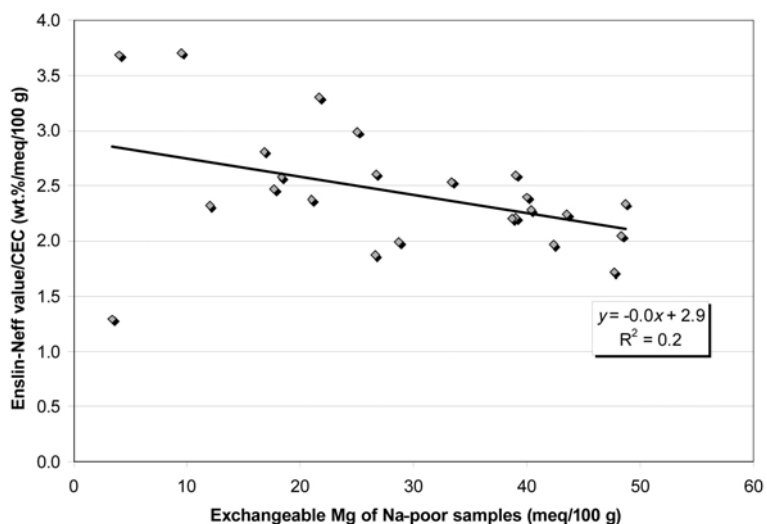


Figure 8. Enslin-Neff values of Na^+ -poor samples compared with the amount of exchangeable Mg^{2+} .

adsorption both from the gaseous phase as well as from contact with excess liquid water. The water-vapor uptake capacity of bentonites depended mainly on the CEC and to a lesser extent on the type of exchangeable cation. A negligible effect of the exchangeable cations was observed around 80% r.h. In contrast, microstructural features such as specific surface area and/or porosity affect the water-uptake capacity independent of the relative humidity but to a lesser extent than the CEC. This influence, however, can be significant in the case of special bentonites (with large N_2 specific surface area, SSA_{N_2}).

At 50–70% r.h., common Ca^{2+} -montmorillonites are believed to be hydrated by up to 6 water molecules per cation (octahedral coordination), a value which could be proved in the case of samples with a small SSA_{N_2} value. In the case of samples with greater SSA_{N_2} values, which are strongly affected by micropores and small mesopores, up to 12 water molecules per cation were calculated. At least some of these excess water molecules are believed to be located at the external surfaces, rather than in the interlayer because (1) >6 water molecules per cation would probably result in greater d values than observed (15–15.5 Å), and (2) the uncharged interlayer surface (between the charges) is believed to be relatively hydrophobic. In conclusion, the ratio of external/internal water ranges from 0 to 1 depending on the microstructure (porosity) of the bentonite. For the calculation of the SSA based on water-vapor adsorption data, a correction for the external water is required.

In contrast to water-vapor adsorption, Enslin-Neff values depend more on the amount of exchangeable Na^+ than on the CEC. No effect of microstructural features was observed. In contrast to the water-vapor adsorption, which depends linearly on the CEC (Kaufhold, 2005, 2006), the dependency of Enslin-Neff values and Na^+ may follow percolation theory (e.g. Kesten, 2006).

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