

Effects of the injection grout Silica sol on bentonite

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Abstract

Silica sol, i.e., colloidal SiO₂, may be used as a low-pH injection grout for very fine fractures in the construction of deep geological repositories for radioactive waste in Sweden and in Finland. If the bentonite barrier encounters SiO₂-colloid particles under conditions favorable for aggregation, there is concern that it will modify the bentonite barrier at the bentonite/bedrock interface. In this study qualitative experiments were performed with mixed dispersions of SiO₂-colloids and bentonite or homo-ionic Na/Ca-montmorillonite. Samples were prepared at different colloid concentrations and treated under various conditions such as low and high ionic strength (0.3 M NaCl), as well as dehydration and redispersing. Free swelling and settling experiments were performed in order to qualitatively compare the conditions in which SiO₂-colloids affect the bulk/macro properties of bentonite. In order to study specific SiO₂-colloid/montmorillonite interactions and preferred type of initial aggregation, dilute dispersions of homo-ionic montmorillonite dispersions mixed with varying concentrations of SiO₂-colloids were prepared and selected samples were characterized by PCS, SEM/EDS, AFM and PXRD. The results from this study show that bentonite and montmorillonite particles can be modified by SiO₂-colloids when mixed in comparable amounts, due to dehydration or high ionic strength. Some indications for increased colloidal stability for the SiO₂-colloid modified clay particles were also found. From the AFM investigation it was found that initial attachment of the SiO₂-colloids in Na⁺ dominated samples seemed to occur on the edges of the montmorillonite layers. In Ca²⁺ dominated samples not subjected to excess NaCl, SiO₂-colloid sorption onto the faces of the montmorillonite layers was also found. In all, contact between the bentonite barrier and ungelled Silica sol should preferably be avoided.

1. Introduction

During the construction phase of the deep geological repositories for nuclear waste in Sweden and Finland, the hydraulic conductivity of the bedrock must be controlled and kept at a low level which is to be accomplished by the use of suitable injection grouts. A potential candidate for very fine fractures is the gel formed from injected Silica sol (hydrolyzed SiO₂-colloids), using NaCl as an accelerator. Compared with other conventional cement-based injection grouts, silica sol has the ability to seal finer fractures with apertures of 10-170 μm, and gives rise to leachate water with pH < 11 (Bodén and Sievänen, 2005, Funehag, 2008, Hölttä, 2008). As many other countries, Sweden and Finland also plan to use compacted bentonite as a barrier in their multi-barrier concepts for storage of nuclear waste. So far the effects and possible interactions of the hydrolyzed silica sol particles with bentonite under repository conditions have not been well studied. Regardless of how or when the bentonite barrier may be subjected to SiO₂-colloids, the effect of deposition of large quantities of hydrolyzed SiO₂ into the immediate vicinity of the bentonite barrier should be investigated. In this study the general effects of SiO₂-colloids on bulk/macro properties of bentonite is investigated as well as the initial and preferred form of montmorillonite/SiO₂-colloid aggregation in mixed montmorillonite/ SiO₂-colloid systems.

1.1 Background

During excavation of the host rock silica sol is planned to be pumped into drilling holes or fractures, directly after mixing with an accelerator composed of 10 weight % NaCl in a 5:1 ratio of SiO₂-colloids to NaCl. This procedure induces rapid colloid aggregation and gel formation in the boreholes/fractures usually within 1 hour and reduces the hydraulic conductivity and groundwater inflow to desired levels (< 1 L per minute and 60 m tunnel, Funehag, 2008). Since a full deterministic description of the fracture zones often is very difficult, grouting is always subjected to uncertainties. If the injected SiO₂-colloids would encounter large water-bearing fractures, dilution with decreasing aggregation rate and increasing gel time is probable. The final extent

and methodology of grouting is never determined *a priori*, but worked out along the way during the construction of the repository (Emmelin et al. 2007).

The probability however of the hydrolyzed SiO₂-colloids encountering the bentonite barrier is considered to be low since most expected grouting operations will take place before deposition of the bentonite barriers. If the bentonite barrier would encounter the hydrolyzed SiO₂-colloids under conditions favorable for aggregation during the construction phase or later, the expected properties of the bentonite barrier at the bentonite/bedrock interface may be altered. This may affect future colloid generation and bentonite erosion in the event of intrusion of glacial melt water, which is one of the most critical scenarios for the bentonite barrier since mass loss can be substantial under certain conditions (Le Bell, 1978, Laaksoharju and Wold, 2005, Neretnieks et al. 2009). On the other hand, if the gel from Silica sol deposited in the fracture zones proves to be stable towards time and changing groundwater conditions, erosion of bentonite may be inhibited. The long-time behavior and stability of the silica sol gel itself is not well known, but it is generally assumed that it will be in operation and remain stable for 100 years. Release of the primary hydrolyzed SiO₂-colloids from the gel is expected to be small (Hölttä et al. 2009), especially at elevated ionic strength. The solubility the amorphous SiO₂-particles are expected to be approximately one magnitude higher than quartz (Gunnarsson and Arnórsson, 2000, Karnland et al. 2007). Thus with changing groundwater conditions, the SiO₂ gel would be more likely to undergo solubility-precipitation reactions compared to similar crystalline minerals present in the bedrock.

In general, under low ionic strength groundwater conditions direct aggregation between hydrolyzed SiO₂-colloids and bentonite particles would not be expected due to the unfavorable charge conditions between the negatively charged particles. However, when subjected to dehydration or elevated ionic strength, especially in the presence of Ca²⁺ (Iler, 1979, Lee and Moon, 2004, Kinsela et al. 2010), the SiO₂-colloids will unavoidably aggregate and

coalesce into larger particles and aggregates, either with bentonite or with other SiO₂-colloids.

Compared with montmorillonite colloids, hydrolyzed SiO₂-colloids show much higher colloid stability at slightly alkaline conditions, even under relatively high ionic strength (Iler, 1979). Thus, if the hydrolyzed SiO₂-colloids prove to be reactive towards montmorillonite, an increase in colloid stability of the modified montmorillonite/SiO₂-colloid particles compared to montmorillonite particles is probable. When aggregating homogeneously, either under high ionic strength or because of dehydration, the hydrolyzed SiO₂-colloids can form covalent siloxane bonds through the reactive siloxane surface groups (Iler, 1979). In the presence of bentonite, the same type of irreversible reaction may occur along the edges of the montmorillonite layers due to the silanol bonds at the montmorillonite edges. If the hydrolyzed SiO₂-colloids show a large tendency for heterogeneous aggregation, i.e., react and aggregate irreversibly with the edges of the montmorillonite particles, both the physical/macro properties (swelling pressure, rheology) and the colloidal properties of the silica-modified montmorillonite particles may be drastically different from those of unmodified montmorillonite. With regards to this, there is concern that SiO₂-colloids may considerably change the bulk properties and colloidal behavior of bentonite.

In summary, several hypothetical scenarios of the hydrolyzed SiO₂-colloids encountering the bentonite (or vice versa) exist: *i*) Unforeseen SiO₂-colloid transport due to underestimation of the hydraulic capacity of the fracture zones and inadequate gel formation during grouting. *ii*) Transport of bentonite into fractures grouted with SiO₂-colloids, in the event of bentonite erosion. *iii*) Solubility-precipitation reactions of secondary SiO₂-particles with bentonite.

In this study the general effects of SiO₂-colloids on the bulk/macro properties of bentonite and more specifically the initial and preferred form of montmorillonite/SiO₂-colloid attachment in mixed montmorillonite/ SiO₂-colloid systems are investigated. Qualitative bulk/macro experiments and colloid/aggregate characterization of mixed bentonite/SiO₂-colloid systems has been performed

using Photon correlation spectroscopy (PCS), Atomic force microscopy (AFM), Scanning electron microscopy (SEM) and Powder X-ray diffraction (PXRD). In order to determine the possible conditions under which aggregation between montmorillonite and SiO₂-colloids would be possible, different screening aggregation experiments were performed under four conditions: *i*) Low ionic strength, *ii*) High ionic strength, *iii*) Dehydration (drying), and *iv*) High ionic strength and dehydration. Condition *i*) was taken as the reference case, since montmorillonite/SiO₂-colloid aggregation under ambient conditions is not expected. The high ionic strength conditions were set according to the corresponding NaCl concentration (0.3 M) used in injection experiments in Äspö Hard Rock Laboratory, Sweden. Would the bentonite barrier not be fully water-saturated when coming into contact with the SiO₂-colloids, either due to heat evolving from the nuclear fuel or due to slow water-saturation of the bentonite barrier, aggregation due to dehydration may also be a plausible scenario. This is because the SiO₂-colloids aggregate irreversibly if subjected to a water content below 35 weight %, according to the manufacturer.

2. Material and Methods

2.1 Materials

Silica sol is a commercially available product with several different applications. As an injection grout, silica sol has successfully been applied to several tunnel constructions in Sweden. The specific silica sol used in this study, Meyco MP 320 (EKA Chemicals, Sweden) has been tested as an injection grout *in situ* at Äspö Hard Rock Laboratory, Sweden and in Olkiluoto, Finland. This product consists of hydrolyzed and negatively charged SiO₂-colloids and has a particle size ranging from 3-70 nm, with an average size of approximately 15 nm. The bentonite used in this study was MX-80 Wyoming bentonite with a montmorillonite content of approximately 83%. The exchangeable cations for this bentonite are approximately: 75% Na⁺; 17% Ca²⁺; 7% Mg²⁺; 2% K⁺. The homo-ionic sodium and calcium montmorillonites used were purified MX-80 Wyoming bentonite according to Karnland et al., 2006. The CEC for MX-80 and the purified Na-montmorillonite measured by a modified Cu(II)-trien method is ~0.75 and ~0.85 meq/g, respectively (Karnland et al., 2006).

2.2 Method

2.2.1 Free swelling and settling experiments with bentonite

Free swelling and settling experiments were performed in order to qualitatively compare the conditions in which SiO₂-colloids affect the bulk/macro properties of bentonite. The experiments were performed with mixed bentonite and SiO₂-colloid dispersions under different conditions representing the four postulated scenarios, *i*) low ionic strength, *ii*) high ionic strength, *iii*) dehydration, and *iv*) high ionic strength and dehydration. In the free swelling experiments, 1 g of bentonite was allowed to expand in the presence of varying amounts of SiO₂-colloids, with or without NaCl addition to a total volume of 100 mL for 2 months. The final volume and appearance of the swelling bentonite-SiO₂-colloid mixtures were inspected visually and photographed. The samples were first prepared in 10 mL of water with 0; 0.1; 0.5 g SiO₂-colloids (with or without addition of NaCl(aq)). Water and SiO₂-colloids were added slowly in order to minimize dispersal of bentonite colloids. The dehydrated bentonite samples were mixed with 10 mL SiO₂-colloids (with or without addition of NaCl) and then dried at 60°C. Samples subjected to NaCl addition were kept for two days in 10 mL 300 mM NaCl. Thereafter the samples were finally diluted with Milli-Q water to a final volume of 100 mL giving a final NaCl concentration of 30 mM. This procedure was necessary because any changes in the colloidal stability and settling of bentonite would not be observed at high ionic strengths corresponding to 300 mM NaCl. The settling experiment was performed by dispersing the same samples and monitoring the settling behavior visually. In these types of experiments, two distinct types of settling processes, called free and structural settling, can usually be distinguished. In free settling, the rate of particle aggregation is significantly lower than the rate of settling due to large particle size or repulsion between particles/colloids. This settling behavior results in independent settling of the dispersed particles and a diffuse mud-line. With time, a relatively dense sediment forms at the bottom of the vessel. In structural settling, induced by addition of electrolyte or a change in pH, the rate of particle/colloid

aggregation is faster than the settling rate. At first the dispersion becomes more opaque, due to aggregation and formation of a volume-filling aggregate network. After some time, the network of aggregated particles breaks down, probably due to compaction and rearrangement of the aggregates, and a sharp interface (mud-line) between a clear supernatant and the montmorillonite phase is seen, as the latter is pulled down by gravitational forces. Within a subsequent period (usually weeks), a constant sediment volume is eventually formed. In the region of this transition point, where the rate of colloid aggregation and settling are comparable, even larger final sediment volumes are usually seen. Table 1 summarizes the conditions for the free swelling and settling experiments.

Table 1. Experimental conditions and treatments used in the free swelling and settling experiments. Note the different orders.

Sample treatment	$m_{\text{Bentonite}}:m_{\text{SiO}_2}$ (g)		
Untreated	1:0	1:0.1	1:0.5
NaCl addition (SiO ₂ +NaCl)	1:0	1:0.1	1:0.5
NaCl addition (NaCl+SiO ₂)	1:0	1:0.1	1:0.5
Dehydrated	1:0	1:0.1	1:0.5
NaCl addition + dehydrated	1:0	1:0.1	1:0.5
dehydrated + NaCl addition	1:0	1:0.1	1:0.5

2.2.2 Montmorillonite/SiO₂-colloid interactions

In order to study specific SiO₂-colloid/montmorillonite interactions and possible aggregation, dilute dispersions of homo-ionic Na-montmorillonite dispersions mixed with varying concentrations of SiO₂-colloids were prepared, photographed and selected samples were characterized by PCS, SEM/EDS, AFM and PXRD. Table 2 summarizes these mixed dispersions. In the AFM investigation, samples of homo-ionic Ca-montmorillonite were also studied. The water-dehydrated samples were first dried and then redispersed with water to the initial volume.

2.2.2.1 Size and concentration measurements using PCS

The mixed dispersions of Na/Ca-montmorillonite and SiO₂-colloids were measured with dynamic light scattering using photon correlation spectroscopy (PCS) approximately one month after preparation. Prior to each measurement, the sample vials were

shaken manually in order to disperse all particles. The samples were then left to stand for 1 hour to ensure settling of larger particles. Except for a few of the most concentrated and water-dehydrated samples, the samples were measured undiluted. The PCS instrument used was a BI-90 Particle Sizer, (Brookhaven Instruments Inc.) with a 488 nm laser and fixed scattering angle of 90°. This technique enables the hydrodynamic diameter of monodisperse colloids and particles of size 10-2000 nm to be measured. The output signal, given in counts/s, is dependent on colloid concentration as well as size. Hence for polydisperse colloids or dispersions with bimodal size distributions as in this study, this technique can only be used qualitatively in order to compare similar dispersions, since larger particles will dominate both the PCS count rate and the size estimation.

Table 2. Summary of the mixed SiO₂-colloid/montmorillonite dispersions.

		$m_{\text{Na/Ca-mont}}:m_{\text{SiO}_2}$ (wt%)	NaCl (M)	Dehydrated
A	1	0.1:0.0	-	x
	2	0.1:0.0	0.3	-
	3	0.1:0.0	0.3	x
B	1	0.1:0.01	-	x
	2	0.1:0.01	0.3	-
	3	0.1:0.01	0.3	x
C	1	0.1:0.1	-	x
	2	0.1:0.1	0.3	-
	3	0.1:0.1	0.3	x
D	1	0.1:0.4	-	x
	2	0.1:0.4	0.3	-
	3	0.1:0.4	0.3	x
E	1	0.0:0.4	-	x
	2	0.0:0.4	0.3	-
	3	0.0:0.4	0.3	x

2.2.2.2 Particle size and elemental analysis with SEM/EDS

A JEOL JSM9460LV scanning electron microscope (SEM), fitted with electron dispersive spectroscopy (EDS), was used to study larger aggregates from the water-dehydrated and redispersed mixed montmorillonite/SiO₂-colloid dispersions shown in Table 2. The SEM samples were prepared by spin-coating a diluted aliquot of the dispersions onto a carbon tape. Since dehydration (drying) was one of the hypothetical scenarios for montmorillonite/SiO₂-colloid interactions, drying effects during the AFM

sample preparation was not seen as a problem. Elemental analysis by EDS was performed on aggregates and particles in order to verify the Al and Si contents. By comparing the Al/Si ratios it was possible to calculate the relative abundance of montmorillonite to SiO₂-colloids by comparing the Al/Si ratio obtained by EDS with the theoretical Al/Si ratio, which was calculated from the mass of montmorillonite and the mass of added SiO₂ for the specific dispersion.

2.2.2.3 Montmorillonite/SiO₂-colloid characterization using AFM

An AFM investigation was performed on selected samples from Table 2 in order to study individual small montmorillonite/SiO₂-colloid particles and their preferred way of aggregation under dehydration. The AFM measurements were performed in dry state in tapping mode (unless otherwise stated) with a Veeco Multimode IIIA AFM with an E-scanner. DP14/SCD/AIBS cantilevers were used (MikroMasch) with resonance frequency 160 kHz, spring constant 5.7 N/m and tip radius < 7 nm. The AFM samples were prepared by drying an aliquot of a diluted dispersion (1:100) onto a freshly cleaved mica substrate at ambient temperature.

2.2.2.4 Basal spacing measurements using PXRD

The intensities and widths of the *00l* XRD peaks are known to depend on the average crystallite (particle) size (Moore and Reynolds, 1997). In order to investigate whether the size and basal spacings (*d*₀₀₁) of the montmorillonite layers in bentonite were affected by aggregation with SiO₂-colloids, PXRD measurements were performed of dehydrated bentonite/SiO₂-colloid samples as a function of varying SiO₂ content. The samples were prepared by mixing 1 weight % bentonite with SiO₂-colloids in ratios of 100:0, 80:20, 50:50, 20:80, 0:100 (bentonite:SiO₂-colloids). The samples were dried, ground and saturated at 85 RH% by adsorption for 2 months by equilibrating with a saturated KCl solution. The measurements were performed in reflection mode (Bragg-Brentano geometry) using a PANalytical X'Pert PRO instrument with CuK_α radiation and with a programmable divergence slit. The samples were covered by a Kapton film to avoid drying effects and scanned from 3-25° (2θ) with a scan speed of 2°/min.

3. Results and discussion

3.1 Free swelling and settling experiments with bentonite

3.1.1 Free swelling experiments

The results from the free swelling experiments after approximately four weeks, when no further free swelling was observed, are schematically depicted in Fig. 1. The different colors of the diagram bars represent the different bentonite/SiO₂-colloid phases that could be distinguished visually. Small differences can be seen between the different samples but the general trends were (starting from the bottom): A dark bentonite phase consisting of montmorillonite and the accessory minerals was seen in all samples. Above this phase, a more diffuse lighter phase dominated by montmorillonite with or without SiO₂-colloids was usually seen. A clear and well-separated white phase, presumably dominated by the white SiO₂-colloids could only be seen in two samples (B and C, the highest SiO₂-concentrations). The untreated samples (A) showed slightly larger sediment volumes with increasing SiO₂ content, which may simply be due to the increase in total mass and volume of the samples. In contrast, the samples subjected to NaCl addition (sample B and C, final concentration 30 mM) showed decreasing sediment volumes with increasing SiO₂ content, meaning that the SiO₂-colloids in combination with high ionic strength slightly decreased the free swelling capacity of the bentonite. The B and C samples also had smaller sediment volumes compared with the corresponding A samples. This suggests that larger or fewer aggregates are formed when SiO₂-colloids are added to bentonite at high ionic strength. For samples subjected to dehydration with or without NaCl addition, complete aggregation of the SiO₂-colloids would be anticipated. For these samples no consistent trend in swelling capacity was found, which may reflect the complexity of mixed and aggregating dispersions. All samples subjected to NaCl addition displayed clear supernatants and well defined mudlines. For samples not subjected to NaCl addition, the dehydrated samples which were modified by SiO₂-colloids (D) displayed more diffuse mudlines compared to the untreated samples, indicating an increase in colloid generation upon SiO₂ modification.

3.1.2 Sedimentation experiments

Photographs of the mixed bentonite/SiO₂-colloid dispersions after 1 hour of settling are shown in Fig. 2. In terms of free and structural settling, all the samples prepared at low ionic strength, i.e., the untreated (not shown) and dehydrated dispersions, displayed similar free settling behavior with diffuse mud lines for several weeks. However, dispersions subjected to high ionic strength showed large differences. An increase in SiO₂-colloid content drastically increased the contribution of free settling, indicating higher colloidal stability towards ionic strength (diffuse mudlines) or formation of larger aggregates (rapid settling).

The settling experiment was terminated after approx. 1 year. The final sediment volumes are schematically depicted in Fig. 3. For the untreated samples no significant trend in final appearance could be seen. For the dehydrated samples at low ionic strength (D), the increase in sediment volume can be explained by formation of larger aggregates upon desaturation. The B, C and E samples which were all subjected to NaCl addition displayed clear supernatants and denser final sediment volumes with increasing SiO₂-colloid content. This indicates that free settling behavior increases with increasing SiO₂-colloid content. For the F samples, no general trend in sediment volume could be seen. The smaller impact of the SiO₂-colloids on the B and F samples may have resulted from a less homogeneous mixture of bentonite and SiO₂-colloids due to the preceding addition of NaCl, which induces the formation of large bentonite aggregates.

3.2 Montmorillonite/SiO₂-colloid interactions

In order to verify that mixed particles and aggregates of montmorillonite and SiO₂-colloids are formed under high ionic strength treatment or by dehydration, dilute dispersions of homo-ionic Na-montmorillonite and SiO₂-colloids were prepared, see Table 2. Fig. 4 shows a photograph of the dehydrated and redispersed Na-montmorillonite/SiO₂-colloid samples, A₁-E₁ from table 2, after 1 hour. Note the increasing opacity with increasing amount of SiO₂-colloids for the

dispersions containing both Na-montmorillonite and SiO₂-colloids, indicating larger particle sizes with increasing SiO₂ content. Without Na-montmorillonite, large needle-shaped SiO₂-particles in the mm range were formed (sample to the right).

3.2.1 Size and concentration measurements using PCS

The results from the PCS investigation generally revealed large differences between reference samples of both Na-montmorillonite and SiO₂-colloids and the mixed dispersions. Interestingly, the measured PCS count rate for a mixed dispersion consisting of 0.1:0.4 weight-% Na-montmorillonite and SiO₂-colloids (6.9 Mcps) was found to be approximately the sum of the corresponding pure dispersions, see the reference samples in Fig. 5. The measured particle size (85 nm) was approximately the average (by weight) of each corresponding dispersion. Fig. 5a shows the PCS results from the water-dehydrated and redispersed mixed Na-montmorillonite/SiO₂-colloid dispersions from Fig. 4, along with untreated reference samples of both Na-montmorillonite and SiO₂-colloids. The most notable effect was an increase in PCS count rate with increasing SiO₂-colloid content in the mixed dispersions and a decrease in count rate for the water-dehydrated and pure SiO₂-colloid sample compared with its reference. Note the dilution factor for the sample with the montmorillonite:SiO₂ ratio of 0.1:0.4 weight-%. The particle size for samples with a montmorillonite:SiO₂ ratio of 0.1:0 and 0.1:0.01 and subjected to 0.3 M NaCl addition was not stable and exceeded 2 μm (Fig. 5b and c). Interestingly, the particle size found at higher concentrations of SiO₂-colloids was consistently around 800 nm. As with the water-dehydrated samples, the PCS count rate for the samples subjected to high ionic strength increased dramatically with increasing SiO₂-colloid content for the mixed dispersions and decreased for pure SiO₂-colloid dispersions. Hence, these results indicate that both dehydration and high ionic strength treatment modify montmorillonite.

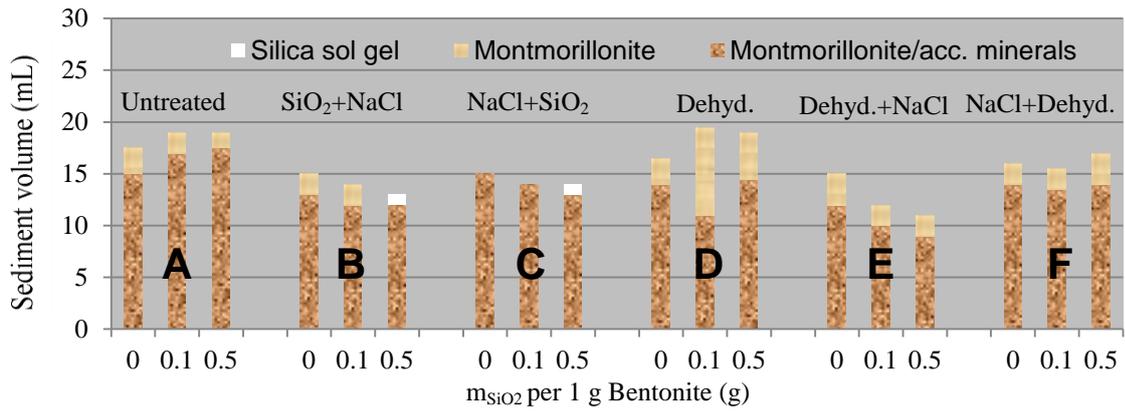


Figure 1. Schematic representation of the final sediment volumes in the free swelling experiment.

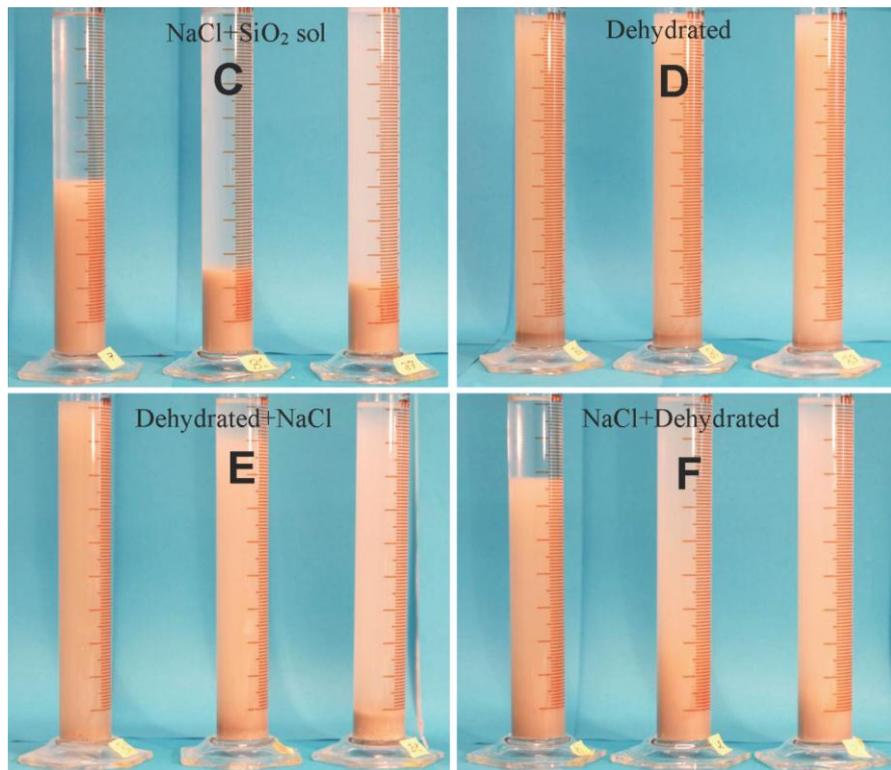


Figure 2. Settling of the mixed Bentonite/SiO₂ colloid dispersions, t=1 hour. SiO₂ and bentonite concentrations as in Figure 1 and 3.

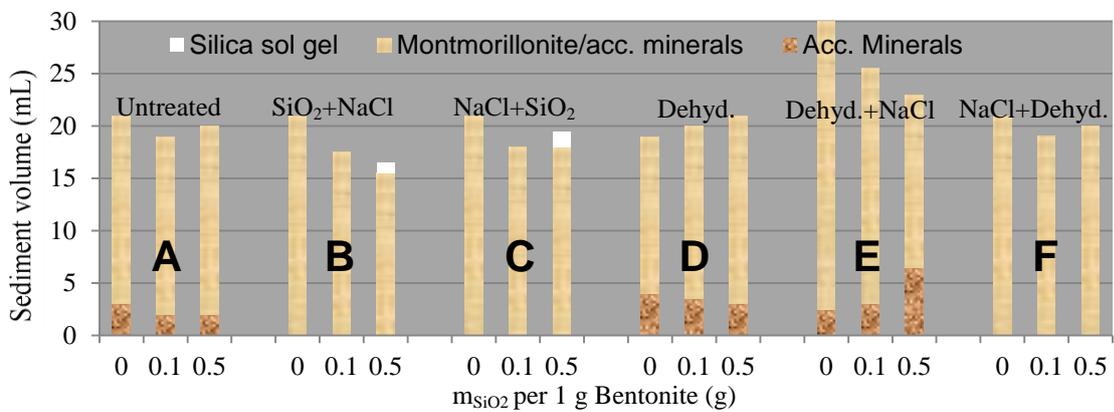


Figure 3. Schematic representation of the final sediment volumes in the settling experiment.

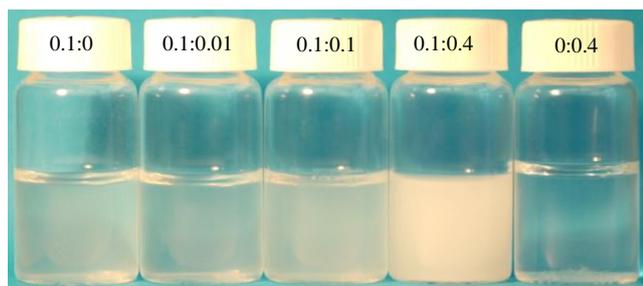


Figure 4. Dehydrated and redispersed Na-montmorillonite/SiO₂-colloid samples, A₁-E₁ from Table 2. The legends denote the weight % of montmorillonite:SiO₂.

3.2.2 Particle size and elemental analysis with SEM/EDS

In general, various types of particle shapes and sizes were observed in the SEM investigation, reflecting the polydisperse and heterogeneous character of the samples. Fig. 6 shows a representative SEM image (top image) from the sample with a montmorillonite/SiO₂ ratio of 0.1:0.4, displaying particles of various sizes. The insert image shows an individual particle in the μm size range displaying a flake-like appearance, while the lower image shows rectangular-shaped needles formed by a pure SiO₂-colloid dispersion subjected to dehydration. To ensure that the particles formed consisted of both montmorillonite and SiO₂-colloids, the Al/Si ratio of selected particles and aggregates (2-3 mappings per sample) was determined by elemental analysis using EDS. From the elemental composition of montmorillonite (Karnland et al., 2006), the theoretical Al/Si ratio for pure montmorillonite was found to be approximately 0.4. As can be seen, the EDS results (Fig. 7) are in good agreement with the theoretical Al/Si ratios. Even though these EDS results may not be representative for the whole particle population due to the heterogeneous character of the samples, they prove that mixed montmorillonite/SiO₂-colloids was formed.

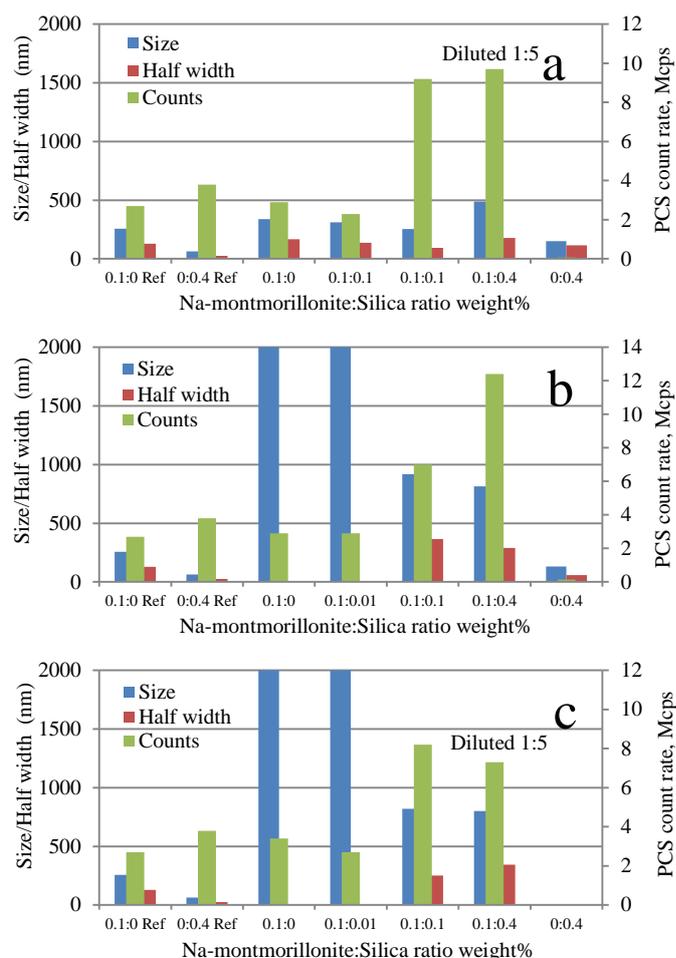


Figure 5. Results from the PCS measurements of mixed Na-montmorillonite/SiO₂-colloid dispersions. a) Water dehydrated and redispersed samples. b) Samples prepared in 300 mM NaCl. c) Samples prepared in 300 mM NaCl and then water dehydrated and redispersed.

3.2.3 Montmorillonite/SiO₂-colloid characterization using AFM

The main purpose of the AFM investigation was to study initial aggregation of SiO₂-colloids with both homo-ionic Na and Ca-montmorillonite. As with the samples studied with SEM, the AFM investigation revealed a multitude of particles and aggregates of different sizes. Representative images of individual mixed montmorillonite/SiO₂-colloid particles are shown in Fig 8-11. However, in all samples probed both unaggregated montmorillonite and SiO₂-colloids were formed to some extent, as well as larger aggregates of mixed particles. A general trend found was that Na-montmorillonite particles, unaggregated as well as aggregated, normally consisted of 1-3 montmorillonite layers, whereas Ca-montmorillonite particles with no

excess NaCl addition were less exfoliated. For the mixed Na-montmorillonite/SiO₂-colloid dispersions, initial SiO₂-colloid attachment occurred preferentially along the edges of the montmorillonite layers.

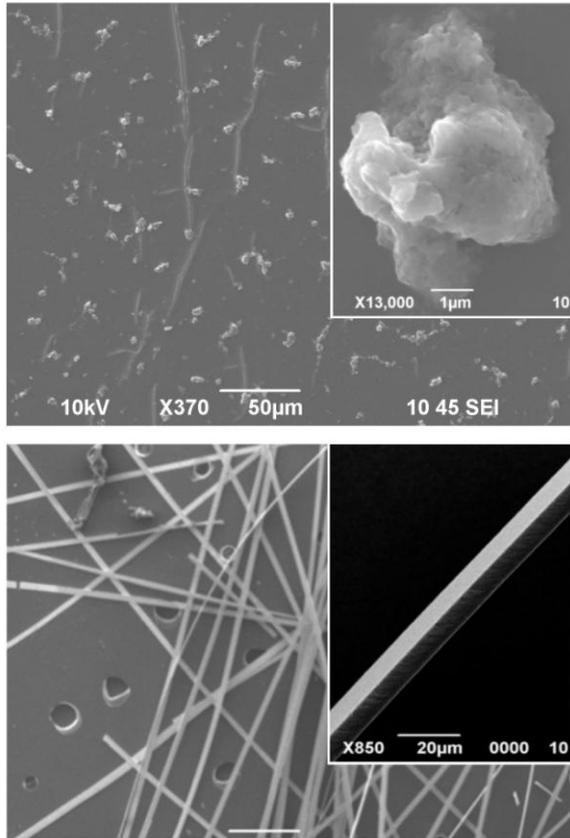


Figure 6. Top image: SEM image of dehydrated Na-montmorillonite/SiO₂-colloid sample (0.1:0.4 weight % when dispersed). Insert shows an individual particle. Lower image: Needles formed by dehydration of SiO₂-colloids in the absence of NaCl. The insert show a magnified Silica needle.

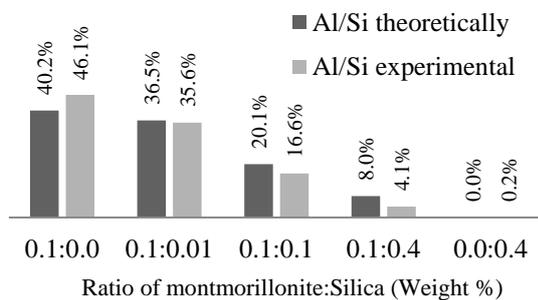


Figure 7. Theoretical and experimental Al/Si ratios obtained by EDS from the water dehydrated samples in Table 2. The concentrations of the Na-montmorillonite:SiO₂-colloid samples are those of the original dispersions in weight %.

The surfaces of the Na-montmorillonite layers are permanently negatively charged due to isomorphic substitution of Si⁴⁺ by Al³⁺ or Fe³⁺ in the tetrahedral sheet and of Al³⁺ by Fe²⁺ and Mg²⁺ in the octahedral sheet. Hence, upon attachment of SiO₂-colloids on a Na-montmorillonite layer, the edges, where similar silanol groups are situated and which do not hold a permanent negative charge, seems to be favored. Upon further attachment of SiO₂-colloids to/with the montmorillonite particles, larger SiO₂-colloid aggregates were often formed with already attached SiO₂-colloids. Shown in Fig. 8a is a representative AFM image from a pre-dehydrated sample displaying Na-montmorillonite particles in various states of aggregation with SiO₂-colloids.

For mixed Na-montmorillonite/SiO₂-colloid dispersions prepared at high ionic strength (0.3 M NaCl), a similar type of preferential SiO₂-colloid attachment onto the montmorillonite particles was generally observed. However for these samples not subjected to pre-dehydration, numerous unaggregated SiO₂-colloids were also found (Fig. 9a). This was quite unexpected considering the high NaCl concentration in these samples and the fact that at the time of the AFM measurements, the samples were approximately 6 months old. Fig. 9b and 9c show an individual Na-montmorillonite layer with SiO₂-colloids/aggregates attached along the edges and a height profile of the mixed Na-montmorillonite/SiO₂-colloid particle. For mixed Ca-montmorillonite/SiO₂-colloid dispersions subjected to 0.3 M NaCl addition, a similar preferred mode of attachment was commonly seen as with the mixed Na-montmorillonite dispersions (Fig. 10a). This can be explained by ion exchange since the corresponding charge fraction of Ca²⁺ in montmorillonite under these experimental conditions is estimated to be 1.1-2.3%, using the Gaines-Thomas equation (Gaines and Thomas, 1953) and different Ca²⁺/Na⁺ selectivity coefficients (2-5.3) found in the literature (Sposito, 1983a,b, Missana 2007, Birgersson et al. 2009).

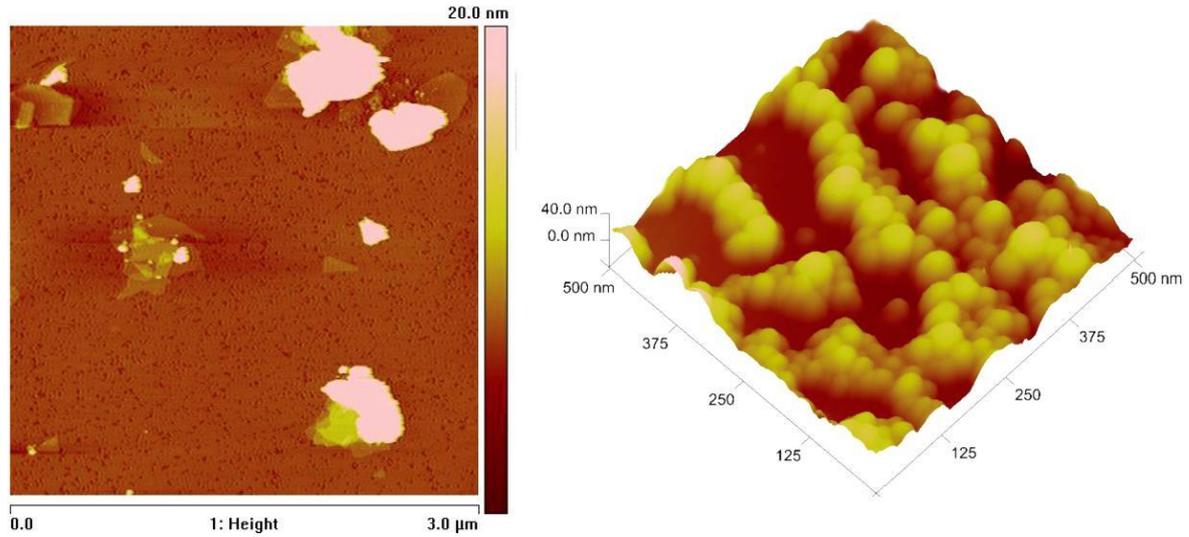


Figure 8. Left image: AFM image (contact mode) of free and mixed particles of Na-montmorillonite/SiO₂-colloids. Right image: 3D AFM image displaying high concentrations of SiO₂-colloids aggregated on a mica surface.

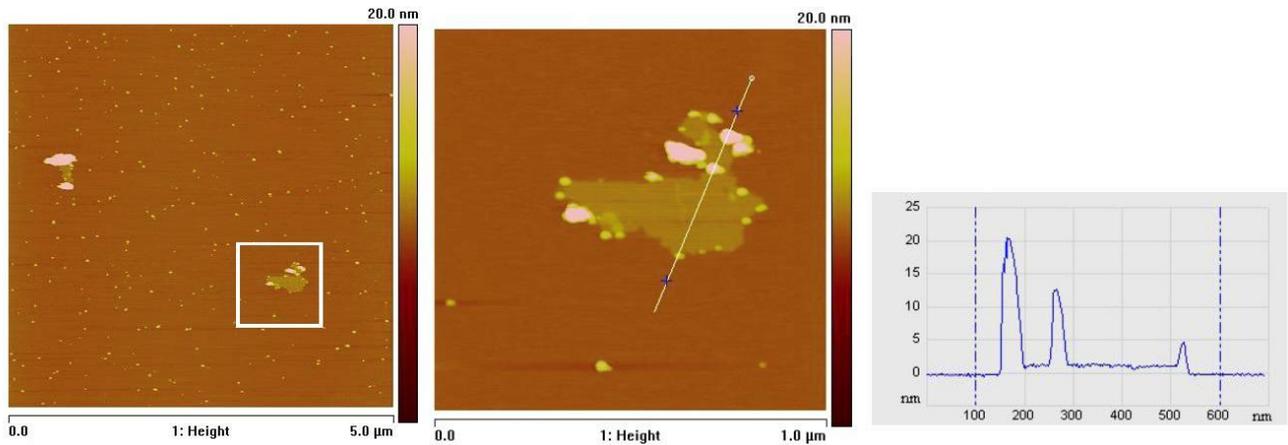


Figure 9. Left image: AFM image of two mixed Na-montmorillonite/SiO₂-colloid particles and unaggregated SiO₂-colloids. Middle image: Insert image shows SiO₂-colloids sorbed along the edges of a single Na-montmorillonite layer. To the right: Height profile from the insert image.

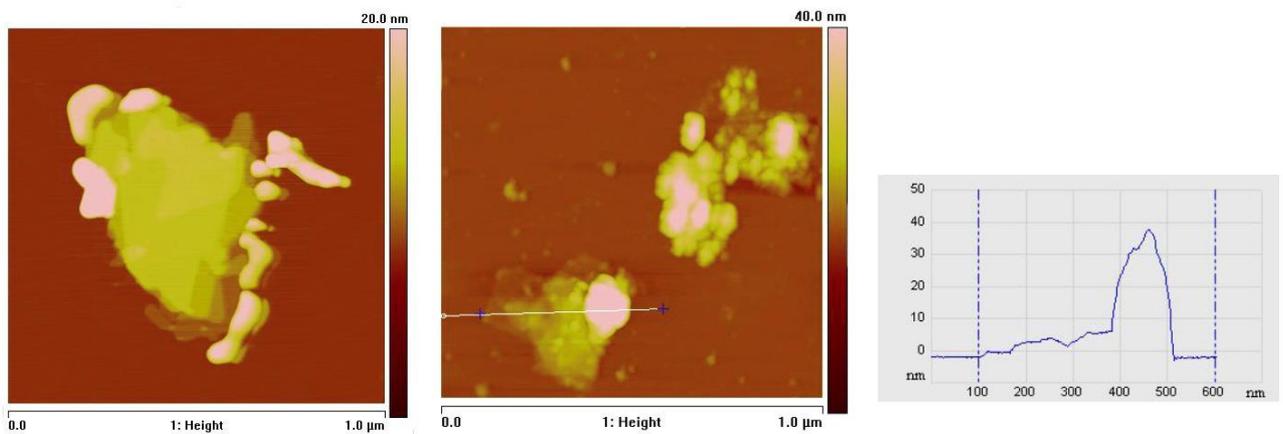


Figure 10. Left image: Sodium exchanged Ca-montmorillonite particle with edge-attached SiO₂-colloids from a water dehydrated dispersion containing excess NaCl. Middle image: Ca-montmorillonite particles with face-attached SiO₂-colloids from a dispersion with no excess NaCl. Right image: Height profile from the middle image.

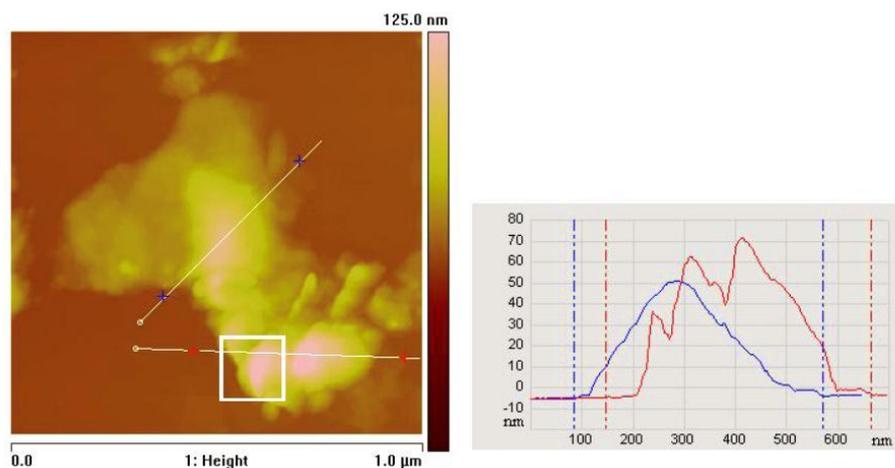


Figure 11. Left image: Large AFM image of Ca-montmorillonite particle covered by SiO₂-colloids. Right image: The corresponding height profile.

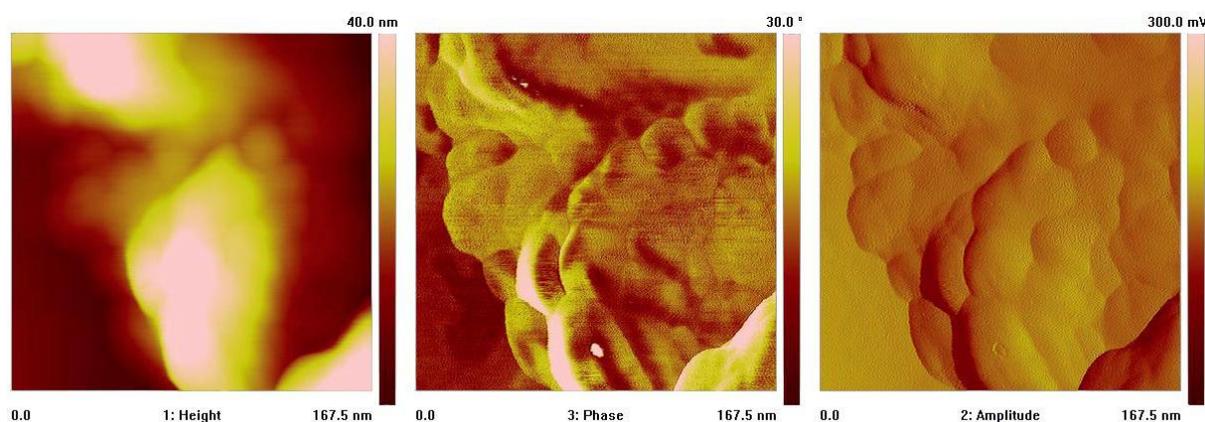


Figure 12. Magnified height, phase and amplitude AFM images (from left to right) from the white square in Fig. 11.

In samples prepared with Ca-montmorillonite that were pre-dehydrated and not subjected to NaCl addition, the Ca-montmorillonite particles were frequently either entirely or mainly covered by SiO₂-colloids, resulting in relatively large mixed particles, see height profiles in Fig. 10 and 11. This indicates that Ca²⁺ induces montmorillonite face aggregation of the SiO₂-particles. The SiO₂-colloid particles in the samples containing Ca-montmorillonite usually appeared less resolved than those in samples containing Na-montmorillonite, possibly due to larger height differences in the Ca-montmorillonite-containing samples. Fig. 12 shows a magnified height, phase and amplitude image from the AFM height image in Fig. 11, displaying a globular surface. The different preferred mode of attachment of the SiO₂-particles on Na-montmorillonite and Ca-montmorillonite respectively, may be explained by

the greater ability of Ca²⁺ to form bridging electrostatic bonds between the negatively charged surfaces compared to Na⁺. According to Iler (Chp. 4, 1979) this is because sorption of Ca²⁺ on a hydroxylated SiO₂-surface only replaces one proton per Ca²⁺ ion, leading to a localized positive surface charge. Another explanation could perhaps be the ion-ion correlation forces and fluctuations in the ionic clouds proposed for divalent ions in lamellar systems reported by Gulbrand et al. (1984) and Kjellander and Marčelja (1988).

3.2.4 Basal spacing measurements using PXRD

The PXRD tracings from bentonite samples dehydrated with varying amounts of SiO₂-colloids are shown in Fig. 13. In the low angle region, clear and broad *d*₀₀₁ peaks at 5.75° 2θ were seen for all bentonite samples. This diffraction peak corresponds

to an average basal spacing of 15.4 Å, resulting from a hydrated state of the montmorillonite interlayer consisting mainly of two water layers (Norrish, 1954, Ferrage et al. 2005). The higher order $00l$ peaks at higher angles were very weak. Thus no significant change in the 001 peaks upon increasing SiO_2 content could be found, except decreasing total intensity. This means that the SiO_2 -colloids do not alter the interlayer distances in the bentonite. Increasing SiO_2 content resulted in a broad amorphous peak situated around 22-23° 2θ . Furthermore, for the pure SiO_2 -colloid samples, no diffraction peak due to crystalline SiO_2 at 26.65° 2θ (not shown) could be found, proving that the SiO_2 -colloids are highly amorphous.

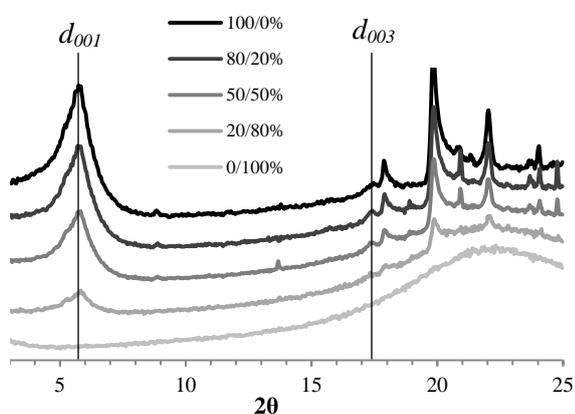


Figure 13. PXRD tracings of dehydrated Bentonite/ SiO_2 -colloid samples. The Bentonite: SiO_2 weight ratios are shown in %.

4.1 Summary and conclusions

In recent years many colloid-related issues have generated a lot of interest in the context of deep geological repositories for nuclear waste. Silica sol, i.e., colloidal SiO_2 , may be used as an injection grout in the excavation and construction of deep geological repositories for radioactive waste in Sweden as well as in Finland. If the SiO_2 -colloids would aggregate heterogeneously and irreversibly with bentonite and specifically the montmorillonite particles, there is concern that the properties of bentonite at the bentonite/bedrock interface might be affected. In this study several qualitative experiments were performed with mixed dispersions of SiO_2 -colloids and bentonite or homo-ionic Na/Ca-montmorillonite, prepared under various conditions such as high ionic strength (0.3 M NaCl), dehydration and varying SiO_2 -colloid

concentrations. The free swelling experiments with bentonite indicate that unaggregated silica sol, i.e., SiO_2 -colloids, under certain conditions can affect bentonites swelling capacity. In the settling experiment an increase in free settling behavior over structural settling was generally observed which indicates that the montmorillonite particles increase in size or gain increased colloidal stability towards ionic strength upon aggregation with SiO_2 -colloids. Probing with EDS in the SEM investigation confirmed that large mixed montmorillonite/ SiO_2 -colloid particles are formed. The PCS measurements also indicate that SiO_2 -colloids modify bentonite under both dehydration and high ionic strength conditions. For both dehydrated or high ionic strength treated samples no measurable difference was found when a small amount (10 % by weight) of SiO_2 -colloids relative the amount of montmorillonite were added, in either size or count rate. However further addition of SiO_2 -colloids resulted in drastically higher PCS count rates in all samples. This can only be explained by the formation of larger mixed particles, which also was seen in the SEM investigation. From the AFM investigation it was found that the preferred initial mode of attachment for Na-montmorillonite samples seems to be SiO_2 -colloid-montmorillonite-edge sorption. However for Ca-montmorillonite samples with no excess NaCl added, SiO_2 -colloid/montmorillonite-face attachment was found. From the PXRD investigation of mixed bentonite and SiO_2 -colloid samples, no difference in interlayer distances could be found. This indicates that attachment and SiO_2 -colloid sorption occurs on the extralamellar surfaces on the montmorillonite particles.

The results from this study show that bentonite and montmorillonite particles can be modified by SiO_2 -colloids when mixed in comparable amounts (by weight) under dehydration or high ionic strength (0.3 M NaCl). Some indications of increased colloidal stability for the SiO_2 -colloid modified clay particles were also found. Because of this it is suggested that contact between ungelled Silica sol and the bentonite barrier in the future deep geological repositories for radioactive waste in Sweden and in Finland is to be avoided.

In order to further assess the effects on SiO_2 -colloids on bentonite in future work, more quantitative colloid

stability experiments should be performed, preferably with better characterized and monodisperse montmorillonite and SiO₂-colloids, or perhaps other colloid analogues. Also, further tests on changes of the physical properties such as swelling pressure and rheology should be performed.

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