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To Josefin
1. Introduction

1.1 Background - the deep geological repository in Sweden

For almost 40 years commercial nuclear power has been a keystone in the energy power production in Sweden and in many other countries. Approximately half the current Swedish electricity production comes from nuclear power, which presently generates 200-300 metric tons of radioactive spent nuclear fuel on an annual basis. In order for the radioactivity of certain long-lived radioactive fission products in the spent fuel to decay to natural levels of the bedrock, it must be stored for 100,000 years. For this purpose the Swedish Nuclear Fuel and Waste Management Company (SKB) has recently proposed a multi-barrier concept called KBS-3 for long term storage of the spent fuel. According to this proposal, the repository would be placed 500 m down in crystalline basement bedrock according to Figure 1, in the municipality of Forsmark. The KBS-3 concept consists of four different independent barriers (SKB Technical report, TR-10-12). The first barrier (to the left in Figure 1), is the spent fuel matrix itself mainly consisting of UO$_2$(s) (~95%) which due to its very low water solubility will prevent release of radionuclides from the fuel matrix under reducing conditions. The second barrier consists of a cast iron insert, surrounded by a copper canister. The former will mainly provide mechanical support and serve as a chemical buffer against corrosive species in the event of canister failure. The copper canister will primarily act as a corrosion barrier but also give some mechanical support.

Figure 1. The Swedish KBS-3 concept for long term storage of spent nuclear fuel.
The third barrier consists of the compacted bentonite clay, which is the focus of this thesis. The compacted bentonite will primarily function (i) as a mechanical barrier due to its plastic properties and (ii) as a transport barrier owing to its compact microstructure. Bentonite consists of particles made up of several ~1 nm thick layers of montmorillonite, which is the actual clay mineral and main component of bentonite. The particles have the ability to expand through the intrusion of water between the negatively charged montmorillonite layers. The latter property gives rise to excellent sorption capacity, especially for multivalent cations such as many of the actinides present in the spent nuclear fuel. The capacity for swelling ensures low free porosity and hydraulic conductivity, high swelling pressure and plasticity. The high swelling pressure leads to sealing of small fractures in the fourth barrier, which consists of approximately 500 m of granitic bedrock. Under favorable conditions (low groundwater flow, high ionic strength), transport of most radioactive species would be prevented by sorption/precipitation on the fracture surfaces. In a natural fracture, the fracture-filling material and the microscopic fractures of granite present an enormous surface area available for radionuclide sorption. Because of this, many hazardous radionuclides with short or intermediate half-lives, such as $^{137}$Cs ($t_{1/2}$ 30.1 y), $^{90}$Sr ($t_{1/2}$ 28.8 y) and $^{241}$Am ($t_{1/2}$ 432.2 y), will decay substantially before reaching the biosphere by groundwater flow. The principle behind having these four independent barriers is that if one barrier fails, the other barriers will still be able to prevent transport and spread of radionuclides. Hence, the overall functionality of the final repository would not have to rely on its weakest link. For the bentonite barrier, the worst case scenario involves the release of radionuclides due to copper canister failure, and such overall conditions that the functionality of the bentonite barrier might be in jeopardy. In general, chemical and physical changes in the bentonite buffer and the overall repository are believed to depend mainly on groundwater composition, redox conditions, groundwater flow paths and flow rate, and possible movements in the bedrock.
2. Objectives of this thesis
The main objectives of this work were to investigate three different topics relevant for the bentonite barrier, namely:

- The microstructural properties of compacted bentonite, by \textit{i}) testing the possibility of colloid transport and \textit{ii}) by determining the interparticle and interlayer porosity, i.e. the free porosity in the saturated compacted bentonite by a basal spacing analysis (Paper I and II, respectively).

- Potential $\gamma$-radiation-induced effects on \textit{i}) montmorillonite colloid stability and changes in sol/gel properties, \textit{ii}) the structural Fe(II)/Fe(III) ratio in montmorillonite and its effect on the montmorillonites reactivity towards one of the major oxidants formed upon water radiolysis, $\text{H}_2\text{O}_2$, and \textit{iii}) radionuclide retention in compacted bentonite (Paper III-V, respectively).

- Potential interactions of bentonite particles with Silica sol, i.e. the $\text{SiO}_2$-colloids that are planned to be used as an injection grout during construction of the repository (Paper VI).
3. The third barrier in KBS-3

3.1 The physical bentonite barrier

In the KBS-3 model the bentonite will be placed in the deposition holes as 35 cm thick compacted rings around the copper canister. After deposition the bentonite, which will be compacted to a dry density of approximately 1.57 g/cm$^3$, will be saturated by the surrounding groundwater to a final saturated density of 2.0±0.05 g/cm$^3$ (TR-10-15). Upon saturation by the surrounding groundwater the bentonite barrier will create a high swelling pressure, the magnitude of which will depend on the bentonite type and to some extent on the ionic strength of the groundwater. In general, the swelling pressure of bentonite displays an almost exponential increase with increasing dry density, from approximately 1-100 bars for dry density 0.65-1.65 g/cm$^3$ (TR-06-30). Due to the compact microstructure in saturated compacted bentonite resulting in very low hydraulic conductivity (~10$^{-12}$-10$^{-14}$ m/s), diffusion will be the only possible transport mechanism. Due to the impermeability of saturated compacted bentonite the barrier will substantially retard both inward transport of possible external corrosive species and outward leaching of radioactive species. Since most radioactive species are positively charged (with the exception of $^{99}$TcO$_4^-$, $^{129}$I, $^{79}$SeO$_4^{2-}$), transport of these radioactive species will be especially retarded due to sorption to the negatively charged surface of montmorillonite. Due to the plasticity and high swelling pressure of the bentonite barrier, small intersecting fractures formed by bedrock movements will be sealed, at least as long as changes in groundwater composition and flow rate do not endanger the stability of the bentonite barrier, i.e. induce generation and transport of bentonite colloids, away from the barrier.

3.2 Evolution of the bentonite barrier

Even with the low hydraulic conductivity of the intact bedrock and the bentonite barrier, the repository must be considered to be an open system due to the long time period of interest (≥ 100 000 years). Over time, the conditions in the repository will unavoidably change, which will introduce thermal and chemical gradients and thus the possibility of physical and chemical alterations in the bentonite barrier. Initially, during the construction phase of the repository, Silica sol, i.e. SiO$_2$-colloids, is planned to be pumped into drilling holes or fractures during the excavation of the host rock. After being mixed with 1.6 wt% NaCl, these colloids will aggregate and undergo gel formation in the boreholes/fractures, reducing the hydraulic conductivity and groundwater inflow to desired levels (< 1 L per minute and 60 m tunnel, R-08-123). Since all anticipated grouting operations will take place before deposition of the bentonite barriers, the probability of the SiO$_2$-colloids encountering the bentonite barrier is low. However, if the bentonite barrier were to encounter the hydrolyzed SiO$_2$-colloids under conditions favorable for aggregation during the construction phase or later, the expected properties of the bentonite
barrier at the bentonite/bedrock interface might be altered. After the first 100 years the initially altered state of the repository due to the deposition process can be assumed to have reached an anoxic 'equilibrium' state, only perturbed by reactions caused by relatively stable groundwater flow. Thus, from this point the groundwater composition will determine both the salinity and the precipitation/dissolution reactions, which will mainly be of calcite, silicate, iron-oxyhydroxides, sulphides, gypsum and fluorite. However, due to the slowly decaying fission processes in the spent fuel, the temperature of the bentonite buffer is after 100-300 years is anticipated to increase up to about 90°C (SKB criterion 100°C), followed by a gradual decrease. The effect of elevated temperatures will be increased reaction rates, which can affect various precipitation/dissolution reactions in the bentonite, for example increased silica release and subsequent precipitation at the canister/bentonite and bentonite/rock interface respectively (TR-93-03; TR-06-11). Furthermore, in this initial stage of the repository, the bentonite barrier will unavoidably be exposed to ionizing radiation, primarily γ-radiation from $^{137}$Cs (R-99-74; TR-06-09). In the first 300 years, i.e. ten times the half-life of $^{137}$Cs, the accumulated γ-dose outside the copper at the canister/bentonite interface will be ~40-200 kGy (1 Gy = 1 J/kg) depending on the type of fuel deposited, calculated from an initial average γ-dose rate outside the copper canister of 0.1-0.5 Gy/h, see Figure 2 (1077112, unpublished SKB report, TR-04-06, R-99-74).  

![Figure 2](image.png)

**Figure 2.** Accumulated γ-dose from $^{137}$Cs adsorbed by the bentonite barrier, calculated for different initial dose rates, 0.1-0.5 Gy/h (SKB criterion is 1 Gy/h).

The following period from a few hundred years to 10 000 years will be the most crucial period for the repository, since after 10 000 years the radioactivity will have decreased to 1% of the initial activity. In this period, possible climate change and movements of shorelines are the only main events believed capable of affecting the repository, but not to the extent of endangering its integrity. After 10 000 years the repository may be affected by permafrost and glacial cycles. The permafrost itself is not expected to reach repository depth but can still affect the composition
and flow paths of the groundwater. Due to downward displacement of salt upon freezing, the salinity of the repository may increase. Glaciation and deglaciation, i.e. build-up and melting of thick ice sheets above the repository, may lead to intrusion of glacial melt water and to upconing of underlying and more saline groundwater. Intrusion of low ionic strength glacial melt water, due to the high static pressure created by the overlying thick ice sheet (up to 2 km), may deplete Ca\textsuperscript{2+} from the bentonite buffer and eventually lead to bentonite erosion (R-06-103). With knowledge of the present groundwater conditions at various depths at different sites in Sweden (and in Finland), and since groundwater changes that have occurred in the past are still traceable, the magnitude of the future alterations in groundwater composition of a Swedish repository can be predicted. In general, the groundwater composition at repository depth has varied, and will continue to vary from extremely saline (brine and seawater) to low ionic strength (glacial melt water) (TR-01-28).
4. Bentonite clay

4.1 Composition of montmorillonite

The composition of bentonite differs depending on its origin. This is because bentonite contains montmorillonite, formed from the alteration of volcanic ash, as well as a range of accessory minerals. Different commercial bentonites usually consist of >60 wt% of a moderately charged smectite called montmorillonite which is a 2:1 phyllosilicate mineral, with one dioctahedral sheet sandwiched between two tetrahedral sheets (Bergaya et al., 2006). Figure 3 (bottom image) shows two neighboring montmorillonite layers (according to the widely accepted Hofmann-Endell-Wilm structure), truncated to approx. 9 and 22 Å along the $a$ and $b$ axis, respectively.

![Figure 3](image)

**Figure 3.** Top left image: the dioctahedral sheet from above, with Al$^{3+}$ being the central ion. Top right image: the tetrahedral sheet from above, with Si$^{4+}$ being the central ion. Bottom image: the generic crystal structure of montmorillonite, with exchangeable cations located between two montmorillonite layers separated with a basal spacing of 15 Å (water molecules not shown). Unit cell data from (Viani et al., 2002).
The structure of montmorillonite is usually described as having monoclinic symmetry, with the angles of the unit cell being 90°, 99.9° and 90° (α/β/γ), with cell parameters ~5.2; ~9.0; ~9.5 Å (a/b/c), respectively. Since the unit cell of montmorillonite contains the interlayer void, the precise unit cell dimensions depend not only on the specific structural formula of the montmorillonite (due to different geological and geographical origins) but also on the hydration state. The main implication of this is the increase in the c-dimension, and in the b-dimension to some extent (Ravina and Low, 1972), with increasing water content since the unit cell measured by for instance X-ray diffraction (XRD) also contains the interlayer water molecules. Note that since montmorillonite is monoclinic, the basal spacing (d_001), i.e. the shortest distance between two identical basal planes of neighboring layers, is different than the unit cell dimension c.

As for the chemical composition, Si⁴⁺ is exclusively found in tetrahedral coordination to 4 O in the basal tetrahedral sheets. Al³⁺ is mainly positioned in the central dioctahedral sheet in octahedral coordination to 4 O (shared with the silicate sheet) and 2 OH groups. Isomorphous substitution of Si⁴⁺, primarily by Al³⁺, in the tetrahedral sheets and of Al³⁺, primarily by Mg²⁺ (but also Fe²⁺), in the dioctahedral sheet (see structural formula below) results in a net negative charge of the montmorillonite layer. This excess charge is balanced by exchangeable cations, usually Na⁺, Ca²⁺, Mg²⁺ and K⁺, in the interlayer voids, see Figure 3 (Bergaya et al., 2006). A representative structural formula of Na-montmorillonite (originating from Wyoming MX-80) as determined in TR-06-30 is:

\[(\text{Al}_{3.11}\text{Fe}_{0.37}\text{Ti}_{0.01}\text{Mg}_{0.48})(\text{Si}_{7.92}\text{Al}_{0.08})\text{O}_{20}(\text{OH})_{4}\text{Na}_{0.65}\]

From the structural formula it follows that the molecular weight of this Na-montmorillonite is 744 g/mol. In the structural formula above, Fe²⁺ was neglected and Fe³⁺ was assumed to exclusively exist in the silicate sheets, even though to the best of the author’s knowledge this has not been proven. Due to isomorphic substitution, the surfaces or faces of the montmorillonite layers contain a permanent negative charge, whereas the charge at the edges, which is small compared with the total charge of a particle, is pH-dependent. In general, at alkaline pH, the edges are negatively charged whereas at acidic pH the edges are positively charged, due to protonation of the different silanol (≡Si-O/ OH), aluminol (≡Al-OH/OH²⁺) and bridged silanol/aluminol groups (Tournassat et al., 2004). The point of zero charge (pzc) of the layer edge is generally reported to be < pH 7. However, precise determination of the different intrinsic pKa values and of the charge and number of the specific surface active sites on the layer edges is not straightforward and significant discrepancies in these values can be found in the literature (Bourg et al., 2007b). In the interlayer voids two types of hydration complexes can be formed,
the so-called inner-sphere and outer-sphere complexes. For inner-sphere complexes the interlayer cation is directly bound to the basal surface of the montmorillonite layer, whereas for outer sphere complexes, the interlayer cation is fully hydrated, interacting with the clay surface through its water ligands.

From the unit cell dimensions and structural formula, many macroscopic properties can be estimated, such as specific surface area, grain density and charge density. For instance, from the molecular weight, $M_W$, i.e. 744 g/mol (including the Na$^+$) the mineral density of this Na-montmorillonite was estimated to be 2.78 g/cm$^3$, in good agreement with experimental results (TR-06-30). From the Na$^+$ content it follows that the surface charge density is $\sim$0.11 C/m$^2$ or one positive charge per 0.7 nm$^2$ (on each side). The total specific surface area, $S_{A,\text{Tot}}$, upon many of the desired properties of montmorillonite depend, can be approximated from the unit cell area $A_{UC}$ ($a \times b = 46.7 \pm 0.1$ Å$^2$), $M_W$, as well as the Avogadro number $N_A$ according to Equation 1. This is because the total specific surface area, $S_{A,\text{Tot}}$, is dominated by the specific surface area of the layer faces, $S_{A,\text{faces}}$ due to the leaf-like geometry of the montmorillonite layers.

$$S_{A,\text{faces}} = 2A_{UC} \frac{N_A}{M_W} \quad \text{Equation 1}$$

For a typical Wyoming Na-montmorillonite, $S_{A,\text{faces}}$ is approx. 755 m$^2$/g. The specific surface area of the montmorillonite edges, $S_{A,\text{edges}}$, is estimated to be approx. 1% of the $S_{A,\text{faces}}$ (Tournassat et al., 2003; Cadene et al., 2005). Thus, for a typical Wyoming Na-montmorillonite $S_{A,\text{Tot}}$ is approx. 763 m$^2$/g. Furthermore, for Wyoming Bentonite MX-80, taking not only the surface edge area but also the surface area of the accessory minerals into account, the total surface area $S_{A,\text{Tot}}$ can be expressed as:

$$S_{A,\text{Tot}} = 2A_{UC} \frac{N_A}{M_W} \beta \left( \frac{S_{A,\text{faces}} + S_{A,\text{edges}}}{S_{A,\text{faces}}} \right) + S_{A,\text{acc}}(1 - \beta) \quad \text{Equation 2}$$

where $\beta$ is the smectite fraction in the sample. The specific surface area of the accessory minerals can be assumed to be small compared with the surface area of the montmorillonite layers. Thus, it is obvious that the two terms within the brackets in Equation 2 have a minor effect on the total specific surface area. From Equation 2 it follows that the total specific surface area of Wyoming Bentonite MX-80 equals $751.5 \times \beta + C$ (m$^2$/g), where $C$ corresponds to the specific surface area of the accessory minerals, which is generally, not known (here assumed to be 10 m$^2$/g). Thus, assuming a montmorillonite content of 83% gives a total specific surface area of 634 m$^2$/g for Wyoming Bentonite MX-80 (TR-06-30).
4.2 Microstructural properties of bentonite

In clay science there is as yet no uniform nomenclature regarding the terminology for clays or clay minerals. In this thesis an individual montmorillonite layer is simply called a layer, which in turn is made up of sheets, two tetrahedral and one dioctahedral, see Figure 3. A stack of layers is denoted a particle (in the literature also called tactoid, crystallite or simply stack). Microstructure in this context means the structural configuration of montmorillonite particles in the submicron range to individual layers, either in the compacted state or when dispersed. In order to understand the microstructure of water saturated bentonite, it must be appreciated that the microstructure is primarily controlled by the amount of swelling. The main characteristics and factors influencing the swelling and the microstructure of bentonite are:

- Montmorillonite content in the bentonite
- Type and fraction of exchangeable cations, as well as other adsorbents such as organic material
- Degree of water saturation, i.e. the water to solid ratio
- Mechanical and preparative history
- Ionic strength
- pH
- Temperature

Starting with the particles themselves, the reported size and size distribution usually depends on the type of measurement technique used (Plaschke et al., 2001). In the dry state, ground bentonite consists of grains (size 10-1000 µm) in which the basic units consist of particles, which themselves consist of individual montmorillonite layers. These particles are usually 3-25 nm thick (when dry) with a diameter of 50-500 nm. Depending on the type of exchangeable cation, these particles consist on average of 3-5 montmorillonite layers for Na-montmorillonite and 10 montmorillonite layers for Ca-montmorillonite (TR-01-08, TR-06-30). Individual montmorillonite layers have irregularly edged contours and a thickness of approx. 9.5 Å, with length and width ranging from 50-500 nm. Due to the large aspect ratio (area1/2/thickness) of the montmorillonite particles, they are highly flexible (Sato et al., 2001). Data from direct observations or measurements of dispersed individual montmorillonite particles, i.e. montmorillonite colloids, are scarce in the literature but can be obtained by X-ray microscopy (Niemeyer et al., 1994; Schulze et al., 1999, p. 207; Degueldre et al., 2009). A handful of AFM and TEM studies characterizing montmorillonite particles on a firmer statistical basis in the dry state also exist (Vali and Bachmann, 1988; Plaschke et al., 2001; Cadene et al., 2005; Ploehn and Liu, 2006). Figure 4 shows an AFM image of a Na-montmorillonite particle consisting of five layers from this work in the dry state.
4.2.1 Swelling and microstructure of compacted bentonite

In order to achieve the desired properties of the bentonite barrier, the bentonite must be highly compacted so as to ensure low hydraulic conductivity and a high swelling pressure, as well as stiffness and strength to support the canister holding the nuclear waste (TR-10-15). In other words, the water content and total porosity of the bentonite barrier must be relatively low. In general, when swelling is constricted by constant volume in the deposition hole, a high swelling pressure builds up, itself a function of compaction and the type of counter-ion/ions. Because of the great swelling capacity of compacted bentonite, the size of the interparticle voids, which is debated in the literature, would intuitively be comparatively small. This is mainly because of the high swelling pressure and flexibility of the montmorillonite layers (Sato et al., 2001), and the shape and size heterogeneity of both the montmorillonite and accessory mineral particles, ensuring an efficiently packed microstructure.

In this work the microstructure of compacted saturated bentonite is quantified in terms of the relative amounts of coexisting hydration states (see below for explanation) and the different porosities namely \( i \) the interlayer porosity, \( ii \) the interparticle porosity, hereafter denoted the free porosity and \( iii \) and the total porosity, which is the sum of the former two.

\[
\varepsilon_{\text{Tot}} = \varepsilon_{\text{II}} + \varepsilon_{\text{Free}} = 1 - \frac{\rho_{\text{Dry}}}{\rho_{\text{Clay}}}
\]

Equation 3
The total porosity is usually calculated from the dry density, since the interlayer porosity and the free porosity are usually not known. If the mineral composition of the bentonite is well characterized and the total porosity or the corresponding water content is known, both the interlayer and the interparticle porosity can be estimated by comparing the average interlayer distance, \( t_{\text{avg}} \), with the corresponding maximum theoretical interlayer distance possible, \( t_{\text{max}} \). This latter distance corresponds to an interlayer distance where all the water molecules can be found in the interlayer voids and at the layer edges (minor contribution), i.e. when there is no free porosity. Thus, from this it follows that the interlayer porosity, \( \varepsilon_{il} \), can be obtained from:

\[
\varepsilon_{il} = \varepsilon_{\text{Tot}} \frac{t_{\text{avg}}}{t_{\text{max}}}
\]

*Equation 4*

From this equation it follows that the free porosity can be described by:

\[
\varepsilon_{\text{free}} = \varepsilon_{\text{Tot}} \left(1 - \frac{t_{\text{avg}}}{t_{\text{max}}}\right)
\]

*Equation 5*

This theoretical maximum interlayer distance \( t_{\text{max}} \) can be obtained from the theoretical maximum basal spacing \( d_{\text{max}} \) minus the layer thickness \( t_{\text{Mont}} \), approx. 9.5 Å. The theoretical \( d_{\text{max}} \) can be obtained from the specific surface area \( S_A \) and the dry density \( \rho_{\text{dry}} \) for a pure montmorillonite by Equation 4. Theoretically, \( d_{\text{max}} \) can be understood as the maximum distance between uniform two-dimensional layers packed as close as possible to each other, see Figure 5.

\[
d_{\text{max}} = 1/\left(\rho_{\text{dry}} \frac{S_A}{2}\right)
\]

*Equation 6*

For bentonite however, which contains additional non-swelling mineral particles and thus a lower smectite content, \( \beta \), the corresponding maximum interlayer distance is larger and can be expressed as:

\[
t_{\text{max}} = \left(1 - \frac{\rho_{\text{dry}} \beta}{\rho_{\text{clay}}} - \frac{\rho_{\text{dry}} (1-\beta)}{\rho_{\text{acc}}}\right)/\left(\rho_{\text{dry}} \frac{S_A \varepsilon_{\text{Tot}}}{2}\right)
\]

*Equation 7*
The maximum possible basal spacing $d_{\text{max}}$ of bentonites as a function of montmorillonite content ($\beta$), ranging from 0.5 to 1.0 (increments of 0.1) increasing in the direction of the arrows. The solid lines display $d_{\text{max}}$ versus bentonite dry density, g/cm$^3$ (left axis) whereas the dashed lines display $d_{\text{max}}$ versus water content, m$_{\text{H}_2\text{O}}$/m$_{\text{clay}}$ (right axis).

Figure 6 displays the corresponding $d_{\text{max}}$ values as a function of $\beta$, versus dry density (g/cm$^3$) and water content (m$_{\text{H}_2\text{O}}$/m$_{\text{clay}}$). Thus, from these equations both the interlayer and interparticle porosity can be estimated with knowledge of the degree of average interlayer swelling, i.e. $t_{\text{avg}}$, or the corresponding average basal spacing, $d_{\text{avg}}$, which can be obtained from neutron or X-ray diffraction experiments. The interlayer swelling of bentonite and homo-ionic montmorillonites has been widely studied in the literature. However most previous diffraction studies have traditionally been based on interlayer swelling as a function of relative humidity, RH%, under free swelling conditions, whereas saturation of the bentonite barrier will proceed through the aqueous phase from the groundwater under confined conditions. Thus, most XRD data reported may not necessarily be representative of the engineered bentonite barrier. This is because in the latter case the degree of swelling is primarily governed by the compaction and the volume available, whereas in the former case the interlayer swelling is limited by the water activity, $a_{\text{H}_2\text{O}}$, i.e the RH% value/100, (usually < 0.8) and the type of counter-ion.

When there is no swelling, i.e. when dehydrated, the forces present acting on the negatively charged montmorillonite layers and the interlayer cations are the attractive electrostatic forces as well as the layer-layer van der Waals attraction. Upon initial saturation the montmorillonite layers in the bentonite undergo crystalline swelling due to discrete intercalation of 0-4 layers of water molecules between the individual layers. The main driving force for this process is the hydration of the interlayer counter-ions, as well as the hydration of the basal surfaces to some
extent. These different states of hydration, hereafter denoted 0W-4W, create interlayer distances which are essentially discrete in nature (Ferrage et al., 2005a). In the literature the corresponding basal spacings for the 0W-4W states are usually reported as: 9.5-10.1(0W); 12.0-12.7(1W); 15.0-15.7(2W); 18-19(3W) and 21.4-22(4W) Å, corresponding to an approximate water layer thickness of 3 Å (Norrish, 1954; Kozaki et al., 1998; Saiyouri et al., 2004; Ferrage et al., 2005a; 2005b; 2007; 2010). The 4W hydration state is uncommon and has to the author’s knowledge only been reported for Wyoming Bentonite MX-80, not for homo-ionic Na- or Ca-montmorillonites. However, because of interstratification of different hydration states, the average basal spacing usually deviate from these ideal basal spacings due to swelling heterogeneity in the clay (Tamura et al., 2000; Saiyouri et al., 2004; Ferrage et al., 2005a; 2005b; 2007).

Upon further increase in water content, if monovalent counter-ions such as Na\(^+\) and Li\(^+\) (mainly outer-sphere interactions) but not K\(^+\) or Cs\(^+\) (mainly inner-sphere interactions) are the dominant counter-ions, a transition from crystalline swelling to so-called osmotic interlayer swelling is possible. This gradual transition is explained by the formation of repulsive diffuse double layers when the interlayers expand from 3W/4W to >10W (Norrish, 1954). The main driving force for this type of swelling is electro-osmotic repulsion of the repulsive diffuse double layers formed. For a Na-montmorillonite, this transition leads to a jump in the basal spacing from a 3W state of ~19 Å to ~35-40 Å. Since the osmotic interlayer swelling is governed by the electro-osmotic forces, it also depends on the bulk ionic strength. For NaCl, with increasing concentration the basal spacing of Na-montmorillonite has been shown to be proportional to \([\text{NaCl}]^{-1/2}\), until \([\text{NaCl}] < 0.3\) M, where osmotic interlayer swelling is not possible (Amorim et al., 2007; Norrish, 1954; Suzuki et al., 2005). In a Ca\(^{2+}\)-dominated montmorillonite osmotic interlayer swelling is not possible at all due to the higher valence, resulting in so-called ion-ion correlation forces (Kjellander et al., 1988). In mixed Na\(^+\)/Ca\(^{2+}\) montmorillonite systems the actual limits and swelling behavior in the region of crystalline and osmotic swelling thus depend on the amount and type of counter-ions available, as well as montmorillonite layer charge and charge location. (Norrish, 1954; Amorim et al., 2007; Segad et al., 2010) and (TR-09-34). Regarding mixed Na\(^+\)/Ca\(^{2+}\) montmorillonite systems (similar to Wyoming Bentonite MX-80) it must be borne in mind that Ca\(^{2+}\) has much higher affinity to the negatively charged montmorillonite layers compared with the Na\(^+\) due to its higher charge. When mixed, the Na\(^+\)/Ca\(^{2+}\) ratio in the interlayers can be calculated from selectivity coefficients using the Gaines-Thomas equation. In experiments, this has been found to vary between approx. 2-8 M, increasing with increasing clay density (Gaines Jr and Thomas, 1953; Sposito et al., 1982; Sposito et al., 1983; Missana and García-Gutierrez, 2007) and (TR-09-34).
4.2.2 Montmorillonite settling and sediments
Effects on the sol/gel properties that depend on ionic strength, pH and temperature, can be studied in sedimentation experiments and colloid generation and free swelling experiments. Hence, these types of experiments can contribute to the understanding of montmorillonite colloid stability, aggregation mechanisms and settling behavior, without perturbation of the system by an external force as in rheological experiments. Regarding sedimentation experiments, a full description of the settling behavior on the microstructure scale for these anisotropic montmorillonites particles is lacking and results are not always easy to interpret (Lapides and Heller-Kallai, 2002). However, two distinct types of settling/sedimentation processes, free and structural settling, can usually be distinguished. In free settling, the rate of colloid aggregation is significantly lower than the rate of settling due to low ionic strength and individual particles settle independently. As the colloid concentration slowly decreases, a compact sediment (filter cake) forms at the bottom of the vessel used. In structural settling, induced by for instance addition of electrolyte, the rate of 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 processes of the aggregates, and a sharp interface (a mudline) between a clear supernatant and the montmorillonite phase is seen, as the latter is pulled down by gravitational forces. After some time (weeks) a constant sediment volume is eventually formed. In the region of this transition point, where the rates of colloid aggregation and settling are comparable, even larger final sediment volumes are usually seen. The actual transition point in ionic strength between the free and structural sedimentation process can be used as a measure of colloid stability.

4.2.3 The colloidal properties of montmorillonite
A colloid is a particle small enough that the random Brownian forces acting upon it exceed the gravitational forces, making the particle remain dispersed in a solution for a very long time. According to the most common definition, this means that the sizes of colloids range from ~1 nm to ~1 µm. If the bentonite barrier comes into contact with water-bearing fractures and low ionic strength groundwater (glacial melt water), generation and further transport of montmorillonite colloids, is possible. Thus, loss of bentonite from the barrier will greatly depend on the colloid stability. The charged surface of a colloidal particle attracts an equivalent amount of opposite charge. Some of the counter-ions are specifically adsorbed on the colloid surface, forming the Stern layer. The concentration of counter-ions gradually decreases with distance from the surface, until it reaches the concentration in the bulk solution. Together, these two layers of opposite charge form the electric double layer. The thickness of the electrical double layer depends on the type and concentration of ions in the suspension as well as the temperature and
surface potential. The stability of montmorillonite colloids can be predicted (at least qualitatively) using DLVO theory. This theory basically describes the interaction of two charged surfaces as the total energy, \( V_T \), that results from the sum of the interaction energy due to electro-osmotic repulsion, \( V_R \), between the electric double layers and the interaction energy due to Van der Waals attraction \( V_A \).

\[
V_T(h) = V_R(h) + V_A(h) \quad \textit{Equation 8}
\]

were \( h \) is the distance between the two surfaces. The theory and actual expressions of DLVO theory can be found elsewhere in textbooks (Israelachvili, 1992; Hunter, 1993). In this context it is enough to present two common expressions for the repulsive and the attractive contributions to the total interaction energy, for two spherical particles of radius \( r \) and interparticle distance \( h \).

\[
V_R(h) = 4\pi\varepsilon\varepsilon_r \left( \frac{k_B T}{z e} \right) \frac{r^2}{h+2r} \psi_s^2 e^{-\kappa h} \quad \textit{Equation 9}
\]

\[
V_A(h) = -\frac{A_r}{12h} \quad \textit{Equation 10}
\]

where the \( \varepsilon \) and \( \varepsilon_r \) are the dielectric constants for vacuum and water, \( k_B \) is the Boltzmann constant, \( z \) is the ion valency and \( e \) the elementary charge. \( \kappa^{-1} \) is the Debye length, also called the screening length which is a measure of the electric double layer thickness and depends primarily on the ionic strength. The constant \( A \) which can be obtained from the Lifshitz theory is the Hamaker constant and represents the interparticle interaction due to the Van der Waals forces. An example of DLVO interaction curves are shown in Figure 7 for two colloids with a Hamaker constant of \( 1 \times 10^{-20} \) J, surface potential, \( \psi_s \), -48 mV, ionic strength corresponding to 50 mM NaCl. When two particles do collide they can form an aggregate. Colloid aggregation can be represented by the bimolecular reaction:

\[
n + n = n_2 \quad \rightarrow \quad \frac{dn}{dt} = 2k[n]^2 \quad \textit{Equation 11}
\]

where \( k \) is the rate constant for the aggregation process and \([n]\) is the concentration of particles. From kinetic theory, the average translational kinetic energy of any type of particle in equilibrium with its surroundings is \( 3/2 k_B T \) (1/2 \( k_B T \) in each of the x, y and z directions). Hence to overcome an energy barrier of \( 20 k_B T \), like that shown in Figure 7, a sequence of Brownian collisions successfully promoting the translational kinetic energy must occur for two particles to aggregate. Thus, it is ultimately the maximum barrier height, \( V_{T,\text{max}} \) that will govern the rate of aggregation. In general, a barrier height of > 25 \( k_B T \) is assumed to keep a dispersion stable for months.
Figure 7. Example of DLVO interaction energy between two colloids plotted against the particle distance.

If the maximum total energy is positive, but lower than ~15 $k_B T$, aggregation will be slow but inevitable at long times. If the maximum of the total interaction energy is zero or negative for two approaching particles, attraction dictates and the system will be unstable, since every collision between particles will lead to aggregation. The colloid stability of montmorillonite dispersions as a function of ionic strength, pH and temperature has been reported elsewhere (Swartzen-Allen and Matijevic, 1976; Tombacz, 2004; Bergaya et al., 2006; Garcia-Garcia et al., 2006; 2007). In general, the colloid stability of montmorillonite has been found to decrease with increasing ionic strength, decreasing surface charge/potential of the colloids and the pH of the solution, qualitatively in line with DLVO theory. For instance, the relationship between concentrations of Na\(^+\), Ca\(^{2+}\) and Al\(^{3+}\) in terms of aggregation power (comparable to the Schulz-Hardy rule) has been determined experimentally for 0.025% Na-montmorillonite dispersions (Lagaly, 2003) as:

$$[Na^+] \approx \frac{1}{12} [Ca^{2+}] \approx \frac{1}{63} [Al^{3+}]$$

Equation 12

For a 0.025% Na-montmorillonite dispersion, a NaCl concentration of approx. 10 mM at a slightly alkaline pH is sufficient to induce severe aggregation within 24 hours. The decrease in colloid stability with decreasing pH is due to charge reversal of the layer edge charge, from negative at alkaline pH to positive at low pH.

It must be noted, however, that DLVO theory is only a general framework that not all colloids obey. Compared with montmorillonite colloids, the hydrolyzed SiO\(_2\)-colloids which may be used
as an injection grout in the repository, show very high stability under relatively high ionic strength (< 0.1 M NaCl) at slightly alkaline conditions and around its own point of zero charge, pH ~2 in discordance with DLVO. This phenomenon may partly be explained by the unusually low Hamaker constant of the SiO₂-colloids, ~0.65 ×10⁻²⁰ J, which has the unusual property of decreasing with increasing ionic strength (Bergna, 1994, Chp. 7). 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 do aggregate however and usually coalesce irreversibly into larger particles and aggregates. Upon aggregation, either due to high ionic strength or because of dehydration, the hydrolyzed SiO₂-colloids may form covalent siloxane bonds through the reactive siloxane surface groups. 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 present at these edges. Thus, if SiO₂-colloids show a large tendency for heterogeneous aggregation with the montmorillonite particles, the colloidal properties of the modified montmorillonite particles may change drastically from those of unmodified montmorillonite. However, 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.

4.3 Radiation chemistry in bentonite

Deposition of ionizing radiation in any adsorbent material leads to ionizations and excitations. Due to the high energy of ionizing radiation, compared with the energy of chemical bonds (5-15 eV), one single adsorbed α or β-particle, γ-photon or neutron, may result in > 100 000 ionizations and excitations in the adsorbent material. In a solid material such as bentonite, the direct effects of γ-irradiation (such as a 0.662 MeV γ-photon from ¹³⁷Cs) can be manifested as charge separations, formed mainly by the process of Compton scattering (Gournis et al., 2000). Both native and artificial radiation-induced defects of varying stability can exist in bentonite (Fukuchi, 1996; Gournis et al., 2000; Pushkareva et al., 2002; Sorieul et al., 2005; Allard and Calas, 2009). However, the concentrations of these defects are too small to have any significant effect on montmorillonite surface properties (~10¹⁶ spins/g natively, ~10¹⁸ spins/g after several MGy). However, in the event of failure of the copper canister, the release of α-particles from emitted recoiling nuclei could give significantly higher doses locally, resulting in lattice dislocations and possibly mineral amorphization, if subjected to several GGy (Allard and Calas, 2009; Fourdrin et al., 2010).

Several studies have investigated γ-radiation effects on bentonite at low water contents (as in the bentonite barrier) (Gournis et al., 2000; Negron et al., 2002; Pushkareva et al., 2002; Plötze, 2003; Huang and Chen, 2004) as well as (TR-93-03). Even at very high doses (several MGy) only small or
insignificant effects have generally been found on both physical and chemical properties of bentonite and montmorillonite, such as increased specific surface area, structural Fe(II) content and mineral dissolution as well as slightly increased basal spacing of montmorillonite. For $^{137}$Cs γ-radiation, bentonite and water have attenuation coefficients of similar magnitude (Groenevelt, 1974). Thus, the amount of energy of the γ-radiation deposited in the bentonite barrier relative to the amount of energy deposited in the interlayer and pore water is roughly proportional to the bentonite dry density versus the bulk density in the bentonite barrier, i.e. 75-80% in the bentonite and 20-25% in the interlayer and pore water. In radiolysis of pure water the short-lived the primary products are the solvated electron $e^{-}_{(aq)}$, the hydroxyl radical $\cdot OH$, the hydrogen atom $\cdot H$, while the molecular products are $H_2O^+$, $H_2O_2$ and $H_2$ (Spinks and Woods, 1990). Thus, both reducing agents, mainly $e^{-}_{(aq)}$ and $\cdot H$, and oxidizing agents, $\cdot OH$ and $H_2O_2$, can be formed from radiolysis of water. The effect of radiolysis in the interlayer and pore water strongly depends on the type of radiation, as well as available dissolved solutes (Eriksen et al., 1987) and (TR-83-27; TR-88-22). This is because the radiation chemical yields, i.e. the G-values (which describe the number of moles formed per unit energy deposited, μmoles/J) of the primary water radiolysis products are strongly dependent on the Linear Energy Transfer (LET) value of the specific type of radiation. The LET is defined as the energy absorbed per unit path length in the adsorbing material (keV/μm). In a system irradiated with β- or γ-radiation (low LET), the radical products $\cdot OH$, $e^{-}_{(aq)}$, and $\cdot H$ are formed in higher yields than the molecular products $H_2O_2$ and $H_2$. For α-radiation (high LET) the molecular yields are higher, due to recombination reactions of the radical species, resulting in net decomposition of water. Table 1 displays the G-values from γ-irradiation and high energy β-radiation.

<table>
<thead>
<tr>
<th>Species</th>
<th>$e^{-}_{(aq)}$</th>
<th>$\cdot OH$</th>
<th>$H_2O^+$</th>
<th>G($H_2O_2$)</th>
<th>$\cdot H$</th>
<th>$H_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>G μmol/J</td>
<td>0.28</td>
<td>0.28</td>
<td>0.28</td>
<td>0.0725</td>
<td>0.062</td>
<td>0.0466</td>
</tr>
</tbody>
</table>

Radiation effects on montmorillonite mineralogy or its sol/gel properties when the water content is high have not been studied in detail. For montmorillonite dispersions, it is possible that the colloidal montmorillonite particles can be subjected not only to direct effects of radiation (radiation directly absorbed by the solid) but also indirect effects (reactions with aqueous radiolysis products) due to the high water content and the high surface to volume ratio. For instance, if manifested as permanent effects, the γ-radiation from $^{137}$Cs during the first 300-years ($10\times t_{1/2}$) may induce changes in the montmorillonite surface properties, affecting the behavior of future bentonite colloids.
In a previous study, treatment with ozone, which in an impure system such as a Na-montmorillonite dispersion rapidly decomposes to short-lived radicals, was found to increase the colloidal stability of Na-montmorillonite colloids (Chheda et al., 1992). Intuitively, the effect of water radiolysis on the montmorillonite particles would mainly be governed by the total Fe content in the clay (≤ 3 wt%) and the corresponding structural Fe(II)/Fe(III) ratio, since none of the other main constituents of montmorillonite (Al, Si, Mg or O) displays any redox chemistry. Under ambient conditions (when in contact with air), the Fe(II)/Fe(III) ratio in the native bentonite is low, usually ≤ 5%. However, upon reduction to elevated Fe(II)/Fe(III) ratios, changes in several physical properties such as swelling pressure, total layer charge and cation exchange capacity (CEC), as well as other microstructural properties have been found in smectite gels (Stucki et al., 1984; Lear and Stucki, 1987; Lear and Stucki, 1989; Khaled and Stucki, 1991; Stucki and Tessier, 1991; Stucki et al., 2002).
5. Theory

5.1 Diffusion radionuclides in bentonite

Several diffusion and microstructural models for radionuclide transport in compacted saturated bentonite exist in the literature, addressing different types of porosities available for transport or different transport processes, i.e. surface diffusion (cations), ion exclusion (anion), etc. In these models compacted bentonite is generally considered to be either a multi-porosity material (Kozaki et al., 1998; 2001; Bourg et al., 2003; 2006; 2007a; Van Loon et al., 2007) or a single-porosity material (Birgersson and Karnland, 2009; Grambow et al., 2010). Interestingly, in the two latter studies radionuclide transport is not assumed to take place in the same type of porosity. In this work however, it was deemed sufficient to use the classical pore diffusion model (Crank, 1975) and (TR-84-05) in order to qualitatively examine potential γ-irradiation effects on cationic radionuclide diffusion.

In general, diffusion of molecules or particles is simply the process of leveling out gradients of the chemical potential through random molecular and particle collisions. In bulk water the flux (in the x-direction) of a component, $J_x$, is proportional to its concentration gradient $dC/dx$.

$$J_x = D_w \frac{dC}{dx}$$  \hspace{1cm} \textit{Equation 13}

This relation is called Ficks first law and is valid for steady state diffusion. $D_w$ ($m^2/s$) is a proportionality constant called the diffusion coefficient is equal to $RT/NAf$, where $R$ is the gas constant, $T$ the absolute temperature, $NA$ the Avogadro constant and $f$ a friction constant. However, for diffusion in a porous medium such as bentonite, this diffusion coefficient also depends on the tortuosity and the constructivity of the pores. The tortuosity, $\tau^2$, is a winding factor since the diffusive path in a porous medium is anything but straight. For bentonite this tortuosity factor increases with compaction and is to some extent dependent on the direction of compaction (Sato and Suzuki 2003). For bentonites with high smectite content the anisotropy of the smectite particles leads to a preferential orientation when compacted, which gives higher $\tau^2$ values in the direction of compaction. The constructivity factor, $\delta$, is a measure of the diffusion volume along the diffusion path. In saturated bentonite this diffusion volume is assumed to be constant throughout the sample, i.e. the porosity is the same everywhere (not decreasing, $\delta < 1$, or increasing, $\delta > 1$), and thus $\delta$ equals 1. From the tortuosity and constructivity the pore diffusion coefficient is then defined as:

$$D_p = D_w \frac{\delta}{\tau^2}$$  \hspace{1cm} \textit{Equation 14}
Then Fick’s first law in one dimension for diffusion in porous medium becomes:

\[ J_x = \varepsilon D_p \frac{dc}{dx} \]  

*Equation 15*

where \( \varepsilon \) is the total porosity and \( C_p \) the pore concentration. Note that in this equation it is assumed that the total porosity is available for transport which is highly debatable, especially for anions. If the diffusing component undergoes sorption to the porous medium, the apparent diffusion coefficient \( D_a \) is further reduced compared with the pore diffusion coefficient by:

\[ D_a = D_p \left( \frac{\varepsilon}{\varepsilon + \rho K_D} \right) \]  

*Equation 16*

where \( \rho \) is the dry density and \( K_D \) a sorption coefficient defined as:

\[ K_D = \frac{n_s/m}{n_{aq}/V} = \frac{n_s}{n_{aq} \times \nu/m} \]  

*Equation 17*

where \( n_s \) and \( n_{aq} \) are the number of moles of the component sorbed and amount of the component in the aqueous phase respectively, and \( V/m \) is the volume to mass ratio which determines the dimensions of \( K_D \), usually given as cm³/g.

From diffusion experiments the apparent diffusion coefficient, \( D_a \), and the effective diffusion coefficient, \( D_e \), can be determined. The apparent diffusion coefficient describes the overall macroscopic diffusion rate whereas the effective diffusion coefficient describes the actual diffusion within the porous medium. The effective diffusion coefficient and the apparent diffusion coefficient are related by the following equations:

\[ D_e = \alpha D_a; \quad \text{where} \quad \alpha = \varepsilon + \rho K_D \]  

*Equations 18a,b*

\( \alpha \) is a capacity factor describing the ability of the porous medium to accumulate and harbor the diffusants. For cations undergoing sorption, Equation 19 summarizes the relationship between the different diffusion coefficients. From this equation we see that for species not undergoing sorption, the apparent diffusivity equals the pore diffusivity.

\[ D_W > \frac{\varepsilon}{\varepsilon + \rho K_D} > D_e > D_a \]  

*Equation 19*

For the type of diffusion experiments performed in this work using a ‘semi-infinite source’ (constant inlet concentration), and if the diffusants are able to diffuse through the bentonite slab and the experiment is prolonged until steady-state conditions are achieved, the apparent and the effective diffusion coefficient can be calculated by means of parameters that are either controlled or monitored in the experiment, using equation 20 and 21, respectively (TR-84-05).
where:

\( J \) is the flux through the bentonite slab (N/s)
\( L \) is the thickness of the bentonite slab (m)
\( A \) is the surface area perpendicular to the diffusion direction (m²)
\( C_0 \) is the concentration in the inlet solution (N/m³)
\( C_L \) is the concentration in the outlet solution (N/m³)
\( t_e \) is the time lag, the point where the asymptote of the break-through curve intercepts the time axis (s).

However, in practice steady-state conditions are seldom achieved, at least not for strongly sorbing diffusants. Furthermore, in evaluation of the experimental results, the effects of the end filters must be considered since they will also influence the overall diffusion. Because of this, a finite difference-based model, ANADIFF, developed for the particular experimental setup (TR-96-16) was used in this work for data evaluation. In general, by setting up the equations describing the fluxes through the bentonite slab and the two end filters, accounting for the porosity of the filters \( \varepsilon_f \) and the corresponding diffusion coefficients, \( D_f \), as well as the boundary conditions, the ANADIFF code was used to evaluate the experimental results.

5.2 One-dimensional XRD profile modeling

The purpose of one-dimensional XRD profile modeling is to perform peak decomposition of the 00l reflections formed by constructive interference of X-rays scattered by layered clay particles in powder XRD diffraction experiments. From diffraction experiments the periodic distances in crystals or mineral particles are normally obtained using Bragg's law:

\[ n\lambda = 2d_{001} \sin \theta \]  

where \( n \) is an integer, \( \lambda \) the wavelength of the X-rays (here CuK\(_\alpha\), 1.54187 Å), \( d_{001} \) the basal spacing and \( \theta \) the incident diffraction angle. However, in terms of diffraction and especially when looking at the 00l reflections, clay minerals differ significantly from other minerals. This is due to chemical heterogeneity, layer and stacking defects as well as the small thickness of the layered clay particles. Because of this, clay particles are often regarded as pseudo-crystals, since they give relatively broad reflections of low intensity which sometimes depart significantly from the expected Bragg angles due to interstratification, small particle size, defects and so on. In order to deal with this issue one-dimensional XRD modeling and analysis (i.e. profile fitting) is
needed. With XRD profile fitting, it is not only possible to attain an average basal spacing, $d_{avg}$, but also the relative interlayer type abundance, i.e. the distribution of the different hydration states, the average particle orientation and a notion of the particle size, or more precisely the number of scattering montmorillonite layers. Furthermore the optimal $d_{00l}$ values for each discrete hydration state can be obtained. The underlying theories to different formalisms are described in detail elsewhere, see (Moore and Reynolds, 1989; Reynolds, 1989; Drits and Tchoubar, 1990; Ferrage, 2005). The following text only briefly covers the one-component formalism used in this work to fit experimental XRD profiles displaying osmotic interlayer swelling, as described in (Moore and Reynolds, 1989; Reynolds, 1989). This formalism is equivalent to, albeit mathematically different from, the matrix formalism described in great detail in (Drits and Tchoubar, 1990). In its general form, the diffracted X-ray intensity for a layered clay mineral form can be expressed as:

$$ I(\theta) = LPG^2 \Phi $$  \hspace{1cm} \text{	extit{Equation 23}}

where $LP$ is the combined Lorentz-Polarization factor, the value of which depends on the geometry of the instrument and the preferred orientation of the particles, as well to a lesser extent on polarization effects of the X-rays.

$$ LP = (1 + \cos^2 2\theta) \psi / \sin \theta $$ \hspace{1cm} \text{	extit{Equation 24}}

$\psi$ is the so-called powder ring distribution factor and represents the fraction of layers in the sample orientated so that they diffract into the receiving slit for a specific angle, which depends on the size of the Soller slits and the mean degree of particle orientation (MPO), $\sigma^*$, where the preferred particle orientation decreases from fully ordered to completely random with increasing $\sigma^*$ in the range of 0-45°. For randomly orientated particles $\psi$ is proportional to $1/\sin \theta$; and for perfectly orientated particles $\psi$ is constant. For this reason, well-orientated clay aggregates produce much stronger diffraction intensities than do poorly or randomly oriented particles. $G^2$ is the squared continuous one-dimensional layer structure factor, which governs the intensity of the X-rays scattered from each unit cell as a function of $\theta$. $G$ depends upon the phase angle of the scattered X-rays from all the atoms in the one dimensional unit cell and is given by:

$$ G(\theta) = \sum_j p_j f(\theta)_j \cos(4\pi z_j \sin \theta / \lambda) + i \sum_j p_j f(\theta)_j \sin(4\pi z_j \sin \theta / \lambda) $$ \hspace{1cm} \text{	extit{Equation 25}}

Since only the 00$l$ reflections are of interest, the summations is taken normal to the basal plane over all the $j$-type atoms, where $z_j$ is the atomic position along the $z$-axis and $p_j$ the occurrence of each atom. Note that for centro-symmetric structures such as montmorillonite, the sine term in Equation 25 cancels leaving only the first cosine term, if the center of the one-dimensional unit cell is defined from the center of the dioctahedral sheet. $f(\theta)_j$ represents the temperature-
corrected scattering factor, $f_0$, of each atom, which depends on the number of electrons in each atom and the Debye-Waller factor, which describes the attenuation of the scattering factor due to thermal motion. Figure 8 shows $G^2$ calculated for the 0W-4W hydration states.

Figure 8. The squared layer structure factor $G^2$ for the 0W-4W states.

The term $\phi(\theta)$ is the interference function, which is a continuous periodic trigonometric function describing the Bragg reflections of a periodic structure such as a stacked montmorillonite layers, with unit integrated peak intensity and peak width inversely proportional to the number of layers. In other words, whereas $G^2$ represents the scattering amplitude for each unit cell in the direction of $\theta$, $\phi(\theta)$ represents the scattering intensity from a layered particle where each layer scatters like a single electron. In its idealized form $\phi(\theta)$ for crystal particles is given by:

$$
\phi(\theta) = \frac{\sin^2(2\pi ND\sin \theta / \lambda)}{\sin^2(2\pi D\sin \theta / \lambda)}
$$

Equation 26

where $N$ is the number of periods and $D$ the period distance (or basal spacing). The product of $N$ and $D$ thus equals the particle size, which can also be obtained with the Scherrer equation from the FWHM of the 001 reflection (Moore and Reynolds, 1989). However, for clay particles which may display size polydispersity and have layer stacking defects, the interference function is better described by a Fourier series, enabling the interaction between any two adjacent layers to be accounted for. Expressed as an Fourier series, combining Equations 7b, 9b and 11 in (Reynolds, 1989) describes the one-component interference function used in this work.
\[
\phi(\theta) = \frac{1}{\langle N \rangle} \left[ \langle N \rangle + 2 \sum_{n=1}^{N=N_2} \left( \sum_{N=N_1}^{n=N-1} p(N)(N-n) \right) e^{-8\pi^2 n a^2 \sin^2 \theta / \lambda^2} \cos(4\pi n d_{001} \sin \theta / \lambda) \right]
\]

\text{Equation 27}

where \( \langle N \rangle \) is the average number of layers in the particles. The layer size distribution is described by the \( p(N) \) term and determines the peak shape of the XRD reflections. This term is usually described as being either uniform, i.e. having equal proportions of the smallest particles to the largest, or as lognormal which seems to be more in line with the physical size of natural clay particles (Drits et al., 1998; Mystkowski et al., 2000). However, since clay particles are far from crystalline, the size distribution may also be described using the concept of mean defect-free size. This concept which is used in this work to represent the case with a random distribution of defects, according to \( e^{-(N-1)/\delta} \), where \( \delta \) corresponds to the mean defect-free size (Ergun, 1970). Hence, when using this concept the apparent size distribution will always result in a smaller average particle size than the physical size distribution. This factor generally decreases with water content, from approx. 2-7. The \( \alpha \) parameter in Equation 27 is a size strain parameter, which is used to model another type of defect, namely deviation from a fully discrete basal spacing, \( d_{001} \), (similarly to the Guinier defects, i.e. first and second type of disorder, see (Drits and Tchoubar, 1990)). The effect of this parameter is increased broadening and reduced peak intensity with increasing reflection order. Figure 9 displays \( \phi(\theta) \) as a function of mean defect-free distances representative for the montmorillonite used in this study and the effect of size strain.

The final XRD profile, as a function of mean degree of particle orientation \( \sigma^* \), is shown in Figure 10, as background subtracted and normalized to the 001 reflection. As can be seen (on the right hand axis), the reflection intensity increases dramatically with increasing particle orientation, especially for higher order reflections. For comparison, an experimental XRD profile from an oriented Muscovite sample is also shown, illustrating the broad peak width of clays compared to other more crystalline minerals.
Figure 9. The periodic interference function $\phi(\theta)$, calculated for a 3W state of 18.9 Å with mean defect-free distances ($\delta$) of 4.5; 3; 2; 1 and 0. The thick line shows the effect of size strain ($\alpha = 3$ and MDF = 3) on $\phi(\theta)$.

In order to deal with more than one component, i.e., more than one layer or interlayer type, every possible sequence of interstratified scattering layers or interlayers with different $d_{001}$ values and layer structure factors $G$ must be accounted for. This can be accomplished by using the concept of Reichweite together with the matrix formalism described in Drits and Tchoubar, 1990, or the recursive mathematical method used by Reynolds. Of the different types of software that currently exist for this type of one-dimensional XRD profile fitting, Newmod (by R.C. Reynolds) or similar software (Mulcalc, Winstruct) has received much attention so far and has recently been updated with a newer version, Newmod+ (Yuan and Bish, 2009). However, in order to accurately fit the experimental XRD profiles over a wide angular range, the distribution of water molecules in the different interlayers of the clay particles has to be explicitly adjusted (which mainly affects the $G^2$ functions) (Ferrage et al., 2005). Because of this the software MODXRSD (Plançon, 2002) based on the matrix formalism described in (Drits and Tchoubar, 1990) was used in this work to fit the experimental XRD profiles displaying crystalline swelling only, since this software lets the user modify the unit cell data. In addition to all aforementioned parameters, several instrumental and experimental parameters must be accounted for in order to fully describe a realistic XRD profile apart from Equation 23. The most important instrumental correction accounts for the size of the irradiated footprint of the incident X-ray beam, which either may be either angle dependent or constant, due to either fixed or programmable divergence slits (PDS), respectively. As for the experimental parameters the mean particle size, $\langle N \rangle$, basal spacing, $d_{001}$, and the unit cell volume
as well as the sample density, $\rho$, and mass absorption coefficient, $\mu^*$ must be correlated for in order to obtain the correct absolute XRD intensity (Reynolds, 1983). Furthermore, it is well known that modeled XRD profiles overestimate the scattered intensity at low angles, an effect that increases with increasing FWHM of the 001 peak (Plançon, 2002; Wilson et al., 2004; Ferrage et al., 2005b; Yuan and Bish, 2010). Therefore, in order to fit the experimental XRD profiles at low angles the combined modeled XRD profiles were background-subtracted as in (Wilson et al., 2004).

**5.2.1 XRD profile fitting - Crystalline swelling**

In order to determine the average basal spacings for samples subjected to crystalline swelling only, the experimental XRD profiles were fitted manually with a linear combination of two-component MODXRSD pre-generated XRD profiles. This was accomplished for the hydration states corresponding to 0W-4W, by i) varying the interstratification in each of the 0W-4W states and ii) varying and averaging the mean defect-free domain size and iii) the first type of size strain according to Guinier (see Drits and Tchoubar (1990) for details) after intensity normalization. Furthermore, in the fitting procedure the pre-generated XRD profiles were further adjusted in order to account for iv) particle orientation, $\sigma^*$, v) fixed footprint intensities (i.e. PDS mode) and vi) the ideal discrete basal spacings $d_{\text{inW}}$ (independently). Table 2 summarizes the parameters and their respective values used for the pre-generated MODXRSD profiles. The resulting 250 (25×5×2 for i, ii and iii above, respectively) pre-generated profiles (and averages thereof) were then used to fit the experimental XRD profiles in a spreadsheet.

![Figure 10. Background subtracted and normalized XRD profiles displaying a 3W state of 18.9 Å with mean degree of particle orientations, $\sigma^*$, of 1, 3, 6, 12 and 45°, with the relative intensities of the 001/reflections decreasing with increasing $\sigma^*$ and $l$. The dotted and dashed curves show the corresponding relative intensities of the 001 and 006 reflections as a function of orientation (right and top axes). Grey thin line shows an experimental XRD profile of the Muscovite for comparison.](image-url)
Table 2. Parameters varied in the two-component pre-generated XRD profiles.

<table>
<thead>
<tr>
<th>nW</th>
<th>d_{nW}</th>
<th>P_A</th>
<th>Size strain</th>
<th>MDF, δ</th>
<th>MPO, σ*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0:9.5</td>
<td>1</td>
<td>0</td>
<td>0.9</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>1:12.4</td>
<td>0.9</td>
<td>20</td>
<td>1.5</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>2:15.6</td>
<td>0.75</td>
<td>3.0</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3:18.9</td>
<td>0.5</td>
<td>4.5</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4:21.8</td>
<td>0.25</td>
<td>7.0</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0:1</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>12</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>22</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>45</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Basal spacings later adjusted independently ±0.5 Å.

b Interstratification fraction of component A, where P_A+P_B = 1.

The atomic positions in the unit cell were taken from (Moore and Reynolds, 1989) after modification to a base-centered unit cell. As for the interlayer species, Gaussian-like distributions were used to approximate the location of H_2O in the interlayers (Ferrage et al., 2005a). In reality, however, the H_2O distribution is not strictly Gaussian shaped, and varies with counter-ion type and number of water molecules in the interlayer, which has been shown in Molecular Dynamics and Monte Carlo simulations (Chang et al., 1995; Chávez-Páez et al., 2001a; Chávez-Páez et al., 2001b; Tambach et al., 2004; Tao et al., 2010). The H_2O distributions for the 1W-3W states used in this work were obtained by fitting a modeled XRD profile to an experimental XRD profile of a montmorillonite sample displaying a nearly homogeneous 1W-3W state, by varying the Gaussian-like H_2O distribution using a trial and error approach, see Figure 2 and Figure 3 in Paper II. Typical structural input data for the 3W state is shown in Appendix III. The 4W hydration state (which is less common) was taken as a doublet 2W hydration state. Figure 11 shows a set of background subtracted pre-generated XRD profiles converted to PDS intensities, corresponding to the 0W-3W hydration states, δ=3 and σ*=6°.

![Figure 11](image-url). Selection of the background subtracted XRD profiles corresponding to 0W-3W pre-generated with MODXRSD. Interstratification fractions of 1; 0.9; 0.75; 0.5 for the most abundant hydration state.
5.2.2 XRD profile fitting - Osmotic interlayer swelling
For samples displaying well-defined XRD reflections due to osmotic interlayer swelling at water contents where small basal spacings (< 20 Å) due to discrete crystalline swelling would not be expected, the one-component formalism described in (Moore and Reynolds, 1989; Reynolds, 1989) and in section 5.2 was used to evaluate the experimental XRD profiles. This was accomplished after intensity normalization by varying the optimal basal spacing ($d_{001} > 35$ Å), particle size and surface roughness and by using a cosine based layer structure function and considerable size strain ($\alpha > 4$) to remove reflections higher than 3.
6. Materials

6.1 Bentonite

The bentonite used in this study was Wyoming bentonite MX-80 from the American Colloid Co., hereafter denoted MX80. The exchangeable cations and mineralogical composition of MX80 bentonite as the calculated average of the five samples of MX80 described in TR-06-30 are given in Table 3 and Table 4 below. The cation exchange capacity, CEC for MX80 is ~0.75meq/g.

**Table 3.** Exchangeable cation composition of Wyoming bentonite MX-80.

<table>
<thead>
<tr>
<th>Exchangeable cation</th>
<th>% sat.</th>
<th>st. err % sat.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>74.8</td>
<td>4.7</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>16.7</td>
<td>4.5</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>6.7</td>
<td>0.8</td>
</tr>
<tr>
<td>K⁺</td>
<td>2.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Total</td>
<td>100.2</td>
<td></td>
</tr>
</tbody>
</table>

**Table 4.** Mineralogical composition of Wyoming Bentonite MX-80.

<table>
<thead>
<tr>
<th>Phase</th>
<th>% by mass</th>
<th>st.err % by mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montmorillonite</td>
<td>82.14</td>
<td>2.05</td>
</tr>
<tr>
<td>Illite</td>
<td>0.71</td>
<td>0.07</td>
</tr>
<tr>
<td>Albite</td>
<td>1.32</td>
<td>0.71</td>
</tr>
<tr>
<td>Anatase</td>
<td>0.19</td>
<td>0.16</td>
</tr>
<tr>
<td>Anorthite</td>
<td>1.93</td>
<td>0.69</td>
</tr>
<tr>
<td>Calcite</td>
<td>0.23</td>
<td>0.41</td>
</tr>
<tr>
<td>Cristobalite</td>
<td>0.70</td>
<td>0.77</td>
</tr>
<tr>
<td>Goethite</td>
<td>0.15</td>
<td>0.25</td>
</tr>
<tr>
<td>Gypsum</td>
<td>0.92</td>
<td>0.29</td>
</tr>
<tr>
<td>Haematite</td>
<td>0.22</td>
<td>0.30</td>
</tr>
<tr>
<td>Lepidocrocite</td>
<td>0.58</td>
<td>0.23</td>
</tr>
<tr>
<td>Magnetite</td>
<td>0.14</td>
<td>0.10</td>
</tr>
<tr>
<td>Muscovite</td>
<td>3.31</td>
<td>1.14</td>
</tr>
<tr>
<td>Orthoclase</td>
<td>0.30</td>
<td>0.59</td>
</tr>
<tr>
<td>Pyrite</td>
<td>0.60</td>
<td>0.16</td>
</tr>
<tr>
<td>Quartz</td>
<td>2.90</td>
<td>0.49</td>
</tr>
<tr>
<td>Tridymite</td>
<td>3.24</td>
<td>1.25</td>
</tr>
<tr>
<td>Organic C</td>
<td>0.22</td>
<td>0.05</td>
</tr>
<tr>
<td>Total</td>
<td>99.92</td>
<td></td>
</tr>
</tbody>
</table>

6.2 Homo-ionic montmorillonite

In order to obtain a pure homo-ionic montmorillonite, the native bentonite must be washed and cation-exchanged and sometimes undergo further treatments, preferably by procedures documented in the literature. In this work three types of homo-ionic montmorillonites were used.
In Paper I-IV, montmorillonite originating from MX80 was used, denoted as WyNa or WyCa. This montmorillonite was washed and either Na\(^+\) or Ca\(^{2+}\)-exchanged by the method described in (TR-06-30) or in Sposito et al. (1981).

In Papers V and VI, the Na\(^+\) dominated reference clay Wyoming Swy-2 montmorillonite, supplied by the Clay Mineral Society was used. This clay was either used as received (denoted SwyNa) or Na\(^+\) exchanged and subjected to a citrate-carbonate treatment in order to remove free Fe-oxides (denoted SwyNa\(_w\)). Organic residues were removed by an H\(_2\)O\(_2\) treatment and the remaining carbonate was removed by stirring at pH 1 for several hours, after which the remaining dispersion was neutralized with NaOH. For more details, see Paper V.

### 6.3 Gold colloids

The gold colloids (2, 5 and 15 nm stock solutions) used in Paper I were obtained from BBInternational, UK. The 5 and 15 nm gold colloid stock solutions were synthesized from 0.01 wt\% HAuCl\(_4\) and citrate, while the 2 nm gold colloid solution was synthesized from 0.001 wt\% HAuCl\(_4\) using sodium thiocyanate as a reductant. To increase gold colloid stability, low concentrations of the stabilizing agent mercaptosuccinic acid were used. Figure 12 shows a TEM image of the spherical 15 nm gold colloids.

![Figure 12](image)  
**Figure 12.** A transmission electron microscopy (TEM) image of the 15 nm gold colloids dried on a carbon coated copper grid.
6.4 Silica colloids
The type of silica colloid used in this study was the commercial Silica sol, Meyco MP 320 from EKA Chemicals, Sweden. The surface groups of these negatively charged SiO$_2$-colloids are hydrolyzed and the particle size ranges from 3-70 nm, with an average size of approximately 15 nm.

6.5 Humics
A commercial humic standard supplied by the International Humic Substances Society, IHSS Soil 1S102, was used in this work. The humic substance (HS) was dispersed in NaOH at pH 13 under stirring for several hours and neutralized by to pH 7.
7. Experimental
Hereafter follows a short description of the experimental techniques and methods used in this work. For more comprehensive details, please see Papers I-VI.

7.1 Experimental techniques

7.1.1 Experimental diffusion setup
Illustrations of the experimental diffusion setup used in Papers I, II and V are seen in Figure 13 and Figure 14. In order to prepare confined saturated bentonite or montmorillonite samples, cylindrical plugs of the respective clay material (length 5 mm, diameter 10 mm) were compacted and confined between filters in PEEK cells. To avoid leakage of the clay, the filters were sealed by O-rings. The clay plugs were water saturated and equilibrated for > 4 weeks prior to each experiment. In the diffusion experiments the resulting equilibration solutions were used both as outlet and inlet solutions after equilibration, where the latter also contained the different tracers. After termination of the diffusion experiments, all diffusion cells were disassembled and the clay plugs were extruded and sliced into thin sections. By controlling the water content and measuring the tracer concentration (or activity) of each section, concentration profiles of the tracers within the clay plug could be obtained.

![Diffusion cell illustration](image1)

**Figure 13.** Illustration of the type of PEEK diffusion cell used in Papers I, II and V.

![Diffusion cell experiment](image2)

**Figure 14.** Example of typical in-diffusion experiments. Left image shows 8 diffusion cells from the 5 nm gold colloid experiment (Paper I), with the PEEK cells containing bentonite of different compactions (lower left), outlet solutions (lower right) and the inlet solutions on top of the peristaltic pump. Right image shows a similar diffusion setup with 16 diffusion cells using radionuclides as tracers in a glove-box with an inert atmosphere (Paper V).
7.1.2 Basal spacing determination using XRD

In order to study the interlayer swelling of montmorillonite in Papers II and VI, the basal spacings were measured by powder X-ray diffraction, using a PANalytical X’Pert PRO instrument and CuKα radiation. All samples were rotated at 16 rpm and measured with a fixed footprint, i.e. with a programmable divergence slit (PDS). The size of the two Soller slits was 2.3° (Paper II) or 4.6° (Paper IV) and the scan speed 2°/min. To avoid changes in the samples water content all mounts were covered with a thin Kapton® film during the experiments.

7.1.3 γ-radiation experiments

The γ-irradiations in this work (Papers III-V) were performed using a Gammacell 1000 Elite 137Cs-source, with a dose rate of 0.15 Gy/s (as determined by Fricke dosimetry). By using various additives in the irradiated samples the redox conditions were directed towards more reducing or oxidizing conditions in some experiments. For instance, in N2O saturated solutions the e−(aq) is quantitatively converted into OH•, i.e. increasing the primary yield of OH• by a factor of 2, resulting in an overall oxidizing environment. Correspondingly, the OH• radical can be converted into a reducing radical by the addition of iso-propanol (2-PrOH), resulting in an overall reducing environment, due to the formation of a α-hydroxyl-alkyl radical. In the presence of O2, the solvated electron e−(aq) is rapidly converted into O2− and the hydrogen atom, •H, is converted into HO2+, resulting in increased concentrations of H2O2 (Spinks and Woods, 1990). In order to irradiate samples under anoxic conditions, samples were either degassed with N2 for a minimum of 30 min or prepared in a glove box (< 5 ppm O2).

7.1.4 Colloid size and aggregation experiments using PCS

In order to measure the colloid size of montmorillonite and montmorillonite aggregates Photon Correlation Spectroscopy (PCS) was used in Papers III and VI. The instrument used was a BI-90 Particle Sizer (Brookhaven Instruments Inc.) with a 488 nm 2 W Lexus Laser Model 95 Ion Laser at a fixed scattering angle of 90°. The PCS 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, depends on both colloid concentration, size and geometry. 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.

7.1.5 Structural Fe(II) and Fe(III) investigations

Out of the major constituents of montmorillonite, iron is the most important redox active element. In this work (Papers III-V), the structural Fe(II)/Fe(III) ratio (or the corresponding Fe(II)/FeTot ratio) in Na-montmorillonite was determined by spectrophotometry using the 1,10-phenantroline method described in (Amonette and Templeton, 1998). In this method,
montmorillonite, either dispersed or in powder form, is added to a heated acid mixture consisting of 1,10-phenantroline, HF and H₂SO₄. After complete digestion, the structural Fe(II) was determined by UV/VIS spectroscopy at 510 nm with a Jasco V-630 UV/VIS-Spectrophotometer. Since the Fe(III)-phen complex is colorless, the total structural Fe and structural Fe(III) concentrations were obtained after complete reduction by light or a chemical reductant such as hydroxylamine.

7.1.6 H₂O₂ determination
The H₂O₂ concentrations in montmorillonite dispersions were determined with an iodometric method, see reaction 1 and 2.

\[ \text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{I}^- \rightarrow 2\text{H}_2\text{O} + \text{I}_2 \]  \hspace{1cm} \text{Reaction 1}

\[ \text{I}_2 + \text{I}^- \rightarrow \text{I}_3^- \]  \hspace{1cm} \text{Reaction 2}

Thus, the H₂O₂ concentration could be analyzed with UV/VIS spectroscopy after filtration of the montmorillonite dispersions with a syringe filter by observing the I₃⁻ concentration at 360 nm.

In general, 0.100 mL of freshly prepared 1 M KI and 0.100 mL HAc/NaAc buffer containing a few drops of 3wt% (NH₄)₂Mo₇O₂₄ (ADM) were added to 0.5 mL of a sample filtrate in a total volume of 2 mL (Patrick and Wagner, 1949; Ovenston and Rees, 1950; Nimura et al., 1992).

7.1.7 Elemental analysis using ICP-OES
In order to measure the gold concentrations in Paper I and to perform a montmorillonite solubility measurements, elemental analysis was performed using inductively coupled plasma optical emission spectrometry (ICP-OES), with a Varian Vista AX instrument equipped with an axial torch for increased sensitivity, spray nebulizer and a micro-concentric spray chamber, at the Department of Geology and Geochemistry, Stockholm University.

7.1.8 Nanoparticle characterization using AFM
In order to characterize individual particles and aggregates of montmorillonite and other nanoparticles in Paper VI, Atomic Force Microscopy (AFM) was used. All AFM samples were prepared onto a freshly cleaved mica substrate under ambient conditions by drying an aliquot of a highly diluted dispersion. The measurements were performed in tapping mode (mainly) using a Veeco Multimode IIIA AFM with an E-scanner. DP14/SCD/AIBS cantilevers from MikroMasch were used with resonance frequency ~160 kHz, spring constant 5.7 N/m and tip radius < 7 nm.

7.1.9 Nanoparticle characterization and elemental analysis using SEM/EDS
In order to study and perform elemental analysis of individual montmorillonite and other nanoparticles used in Paper VI, a JEOL JSM9460LV Scanning Electron Microscope (SEM), fitted with Electron Dispersive Spectroscope (EDS), was used. The SEM samples were prepared by
spin-coating a diluted aliquot of the dispersions onto a carbon tape under ambient conditions. In order to verify the Al and Si contents of the studied particles, elemental analysis using EDS was performed on selected samples.

7.1.10 Nanoparticle characterization using TEM
In Paper I, Transmission Electron Microscopy (TEM) images were taken in order to study the 15 nm gold colloids in the inlet and outlet solutions. This was done by drying an aliquot of the solutions onto a carbon-coated copper grid and taking images with a Philips 100 kV Technai transmission electron microscopy instrument operating at 70 kV, at the Department of Fibre and Polymer Technology at KTH.

7.2 Experimental methods

7.2.1 Colloid diffusion experiments
Colloid diffusion experiments were carried out to investigate the microstructure of water saturated compacted bentonite and the microstructural constraints for colloid transport, i.e. to find possible ‘cut-off’ limits regarding colloid size. This was accomplished through three diffusion experiments with colloidal tracers (gold colloids) of different sizes (2, 5, 15 nm) and different compactions of bentonite. Gold colloids were chosen since they can be obtained with a well-defined geometry (spherical) and a sharp size distribution. Each of the three series of experiments ran for four months. The outlet solutions were monitored on a weekly or biweekly basis. Occasional sampling from the inlet solutions was also performed in order to monitor the gold colloid stability. The outlet solutions were analyzed with ICP-OES at 267.594 nm. The colloid stability in the inlet solutions of the 2 nm gold colloid experiment was also monitored by ICP-OES, since 2 nm gold colloids solutions are too small to give rise to the surface plasmon effects. The colloid stability in the inlet solutions of the diffusion experiments using 5 and 15 nm gold colloids was monitored with UV/VIS spectroscopy, since they are colored. In addition, in the 15 nm gold colloid diffusion experiment, TEM images of the inlet and outlet solutions were taken after about half the experimental time. The different compactions and the final pH values and conductivities used in each of the three diffusion series are shown in Table 5. The final concentrations of the gold colloids in the inlet solutions and of the mercaptosuccinic acid (which was used as a stabilizing agent), are shown in Table 6.
Table 5. Dry densities of MX80 used in each diffusion experiment. Gold colloid size in brackets is the size reported by the supplier.

<table>
<thead>
<tr>
<th>Gold colloid size, nm</th>
<th>Dry densities of MX-80 in PEEK cells, g/cm³</th>
<th>pH</th>
<th>Conductivity, μS/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.6</td>
<td>1.0</td>
<td>1.4</td>
</tr>
<tr>
<td>5 (5.5)</td>
<td>0.5</td>
<td>0.8</td>
<td>1.0</td>
</tr>
<tr>
<td>15 (14.3)</td>
<td>0.6</td>
<td>0.8</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table 6. Gold colloid and mercaptosuccinic acid concentrations in the diffusion inlet solutions.

<table>
<thead>
<tr>
<th>Gold colloid size, nm</th>
<th>Gold colloid conc., C₀/ppm</th>
<th>Mercaptosuccinic acid conc., μM</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>4.6</td>
<td>4.0</td>
</tr>
<tr>
<td>5 (5.5)</td>
<td>5.5</td>
<td>8.6</td>
</tr>
<tr>
<td>15 (14.3)</td>
<td>5.5</td>
<td>2.0</td>
</tr>
</tbody>
</table>

To ensure that the gold colloids used would not undergo substantial sorption onto bentonite, the sorption coefficient, $K_D$, was determined prior to the diffusion experiments for both the mercaptosuccinic acid-stabilized and the untreated gold colloids, according to Equation 28 (compare with Equation 17):

$$
K_D = \frac{[Au]_{Ref} - [Au]_{Aq}}{[Au]_{Aq}} \times \frac{V}{m} \text{ cm}^3/\text{g}
$$

Equation 28

where $[Au]_{Ref}$ and $[Au]_{Aq}$ are the reference gold concentration and the gold concentration in the equilibrated solution, respectively. The sorption experiments were performed by equilibrating the gold colloids with bentonite in centrifugation tubes with a solution volume to bentonite mass ratio of 200 and analyzing the gold concentrations with ICP-OES. Since the sorption experiments included separation of the bentonite using centrifugation, the sorption experiment was best performed using the 5 nm colloids, since they were lighter and hence less sensitive to centrifugal forces than the 15 nm gold colloids.

7.2.2 Microstructure and interlayer swelling investigation

In order to study the microstructure of bentonite and homo-ionic montmorillonites and to compare interlayer swelling induced by saturation under different conditions, the different clay materials were either equilibrated as a function of relative humidity, RH% (or more precisely water activity) under free swelling conditions for 2 months, or directly from the aqueous phase. In the former case, the samples were saturated in both adsorption and desorption experiments through the vapour phase using various saturated salt solutions yielding different well-documented RH% values, see Table 2 in Paper II. In the latter case, samples were both saturated under confined conditions as well as under unconfined conditions. For the confined samples, denoted with a subscript c, plugs of compacted MX80 and WyNa with varying dry density were saturated with 1 mM NaCl in the same cells as used in Paper I, see Figure 13. Samples saturated from the aqueous phase under unconfined conditions, denoted with a subscript s, were prepared
in sealed plastic syringes. All samples saturated from the aqueous phase were saturated for ≥ 4 weeks prior to measurements. Table 7 summarizes the different clay samples investigated. The water content of all samples was determined gravimetrically directly after the measurements and after drying at 393° K for at least 24 h.

Table 7. Summary of the different samples series investigated with XRD in this work.

<table>
<thead>
<tr>
<th>Clay Subscript</th>
<th>C&lt;sub&gt;a&lt;/sub&gt;</th>
<th>S&lt;sub&gt;b&lt;/sub&gt;</th>
<th>Ads/Des&lt;sub&gt;c&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry density, g/cm&lt;sup&gt;3&lt;/sup&gt;</td>
<td>Rel. hum, RH%</td>
<td></td>
</tr>
<tr>
<td>MX80&lt;sub&gt;x&lt;/sub&gt;</td>
<td>0.5-1.8</td>
<td>0.5-1.0</td>
<td>0-100</td>
</tr>
<tr>
<td>WyNa&lt;sub&gt;x&lt;/sub&gt;</td>
<td>0.5-1.8</td>
<td>-</td>
<td>0-100</td>
</tr>
<tr>
<td>WyCa&lt;sub&gt;x&lt;/sub&gt;</td>
<td>-</td>
<td>-</td>
<td>0-100</td>
</tr>
</tbody>
</table>

<sup>a</sup> Satuated from aq. phase under confined conditions.
<sup>b</sup> Satuated from aq. phase under non-confined conditions.
<sup>c</sup> Satuated from vap. phase under both adsorption or desorption conditions.

7.2.3 Effect of γ-radiation on bentonite and Na-montmorillonite

Since radiation effects on bentonite and Na-montmorillonite have not been studied in detail, colloid stability and sedimentation experiments were performed on γ-irradiated and unirradiated dispersions in order to investigate possible changes in the colloid and chemical/physical properties of bentonite and montmorillonite.

7.2.3.1 Aggregation kinetics experiments

The γ-irradiated and unirradiated Na-montmorillonite dispersions were characterized by measuring the average hydrodynamic diameter and concentration with PCS. Furthermore, the relative colloid stability and thus the rate of aggregation of γ-irradiated and unirradiated dispersions with concentrations of 0, 10, 15, 20, 25 mM NaCl was monitored for 5 days. By taking small aliquots from the top of the 0.08 % Na-montmorillonite dispersions, a constant size distribution was obtained since the sedimentation of larger aggregated colloids/particles proceeded faster than the rate of aggregation at the corresponding ionic strengths used (García-García et al., 2007). In this way the PCS count rate could be used as a measure of colloid concentration.

7.2.3.2 Sedimentation experiments

Two different sedimentation experiments were performed with irradiated and unirradiated bentonite and Na-montmorillonite dispersions. This type of experiment showed better reproducibility than other measurement techniques such as PCS (at high ionic strength) and appeared to be more sensitive than zeta-potential measurements. The sedimentation experiments were performed in standard test tubes as a function of ionic strength. In the first sedimentation experiment Na-montmorillonite (0.2 wt%) and bentonite (0.5 wt%) dispersions were γ-irradiated for 48 h (26 kGy) under different redox conditions, see Table 8. Unless
otherwise stated, the dispersion was γ-irradiated under anoxic conditions. After irradiation, NaCl was added to the γ-irradiated and unirradiated samples to give the final NaCl concentrations. The samples were left to stand for several weeks and photographed for documentation.

**Table 8.** Redox conditions used for the γ-irradiations performed in the first sedimentation experiment and in the spectrophotometric structural Fe investigation using WyNa.

<table>
<thead>
<tr>
<th>Redox conditions</th>
<th>WyNa wt%</th>
<th>MX80 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anoxic – N₂ degassed</td>
<td>0.4</td>
<td>1.0</td>
</tr>
<tr>
<td>Oxygenated (air sat.) – Not degassed</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>Oxidizing – N₂O degassed</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>Reducing – 2-PrOH, N₂ degassed</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>Reducing – 2-PrOH, N₂O degassed</td>
<td>0.4</td>
<td>-</td>
</tr>
</tbody>
</table>

*0-400 mM NaCl.

*0-250 mM NaCl. Ｏ₂ is primarily formed from ｅ⁻(aq) and ｅ⁻H.

*0-250 mM NaCl. Primary radical is ‘OH.

*0-250 mM NaCl. Primary radical is ｅ⁻(aq) and 2-PrOH.‘

In a second sedimentation experiment, the critical salt concentration (CSC) to induce severe aggregation and settling within 24 hours was investigated by visual observation, using 0.025 % Na-montmorillonite dispersions. This experiment was performed as a function of irradiation time (irradiation dose) and Na-montmorillonite concentration during the γ-irradiations (0.04, 0.4 and 4 % respectively). Above the CSC, a distinct mudline (interface between an aqueous and a sediment phase) could be seen after 24 hours. To study the effects of the molecular radiolysis products, the CSC of unirradiated Na-montmorillonite subjected to H₂O₂ (2 mM) and H₂[ε] (~0.78 mM by H₂ saturation at 1 atm) was also investigated.

### 7.2.3.3 Solubility analysis

In order to investigate changes in Na-montmorillonite solubility upon γ-irradiation, elemental analysis of the supernatants from γ-irradiated and unirradiated dispersions was performed using ICP-OES. In order to avoid possible effects of the accessory minerals in bentonite purified Na-montmorillonite was used in these experiments. This was achieved by γ-irradiating Na-montmorillonite dispersions (0.4 %) for 0, 12 and 48 hours (corresponding to doses of 0, 6.6 and 26.6 kGy) and filtering the dispersions twice with 10 kDa MWCO ultrafilters prior the ICP-OES measurements.

### 7.2.4 Characterization of the structural Fe(II)/Fe(III) content in montmorillonite and the reactivity towards H₂O₂

In order to study the effect of γ-radiation on the structural Fe(II)/Fe(III) content in montmorillonite and its influence on montmorillonites reactivity towards H₂O₂, three different experiments were performed in which both these two properties were measured. In the first experiment, the effect of γ-irradiation under the same redox conditions probed in the
sedimentation experiments was tested with the WyNa clay, see Table 8. In the second set of experiments, washed and purified Na-montmorillonite (SwyNa) dispersions of different concentrations were irradiated with different γ-doses under anoxic conditions, see Table 9. In the third type of experiment, 0.4 wt% Na-montmorillonite dispersions were irradiated under strictly reducing conditions (by the addition of 2-PrOH) in order to study the effects of very high structural Fe(II)/FeTOT ratios. After the irradiations both the structural Fe(II)/Fe(III) content and the decomposition rate of H₂O₂ in the montmorillonite dispersions were determined by UV/VIS spectroscopy, using the 1,10-phenantroline method (Amonette and Templeton, 1998) and by iodometry.

**Table 9.** Summary of the experiments performed with the of the SwyNa dispersions in the structural Fe(II)/Fe(III) determinations and H₂O₂ measurements (concentrations in wt%).

<table>
<thead>
<tr>
<th>Irr. time</th>
<th>Anoxic cond.</th>
<th>Reducing cond.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂O₂</td>
<td>Struct Fe(II)/FeTOT</td>
</tr>
<tr>
<td>0 h</td>
<td>0.4</td>
<td>0.1; 0.25; 0.5</td>
</tr>
<tr>
<td>1 h</td>
<td>0.4</td>
<td>0.1; 0.25; 0.5</td>
</tr>
<tr>
<td>3 h</td>
<td>0.4</td>
<td>0.1; 0.25; 0.5</td>
</tr>
<tr>
<td>6 h</td>
<td>0.4</td>
<td>0.1; 0.25; 0.5</td>
</tr>
<tr>
<td>12 h</td>
<td>0.4</td>
<td>0.1; 0.25; 0.5</td>
</tr>
<tr>
<td>24 h</td>
<td>0.4</td>
<td>0.1; 0.25; 0.5</td>
</tr>
</tbody>
</table>

**7.2.5 Radionuclide retention experiment**

In order to investigate the effects of γ-radiation on radionuclide retention in compacted saturated bentonite and Na-montmorillonite, sorption and in-diffusion experiments were performed with monovalent ¹³⁷Cs⁺ and divalent ⁶⁰Co²⁺ as tracers, in a batch sorption experiment and in a diffusion experiment using the diffusion setup described in 7.1.1, respectively. In order to relate the results of the two types of experiments, the same experimental matrix was used. In general, duplicate samples were either unirradiated or irradiated, after different pre-treatments. The irradiated samples were irradiated either under anoxic or oxic conditions, as fully dehydrated (dry) or saturated (wet), with or without the presence of HS (0.1g/L). See Table 10 for a summary of the different sample types. The irradiation time was 5 days, corresponding to approx. 65kGy.

In the diffusion experiment, native MX80 and purified Na-montmorillonite SwyNa₂w samples were prepared with a similar montmorillonite dry density, i.e. a clay dry density values of 1.6 and 1.5 g/cm³ (see Figure 6) and a volume to mass ratio of 170 and 140, respectively. The samples were saturated with 0.05 M Na₂SO₄ for 6 weeks prior to the addition of the radioactive tracers and 5 μM inactive carrier isotopes to the inlet solutions. To maintain an oxygen-free environment during the entire course of the diffusion experiment for the samples irradiated under anoxic conditions (N₂), the entire diffusion setup was kept in a glove box, with an oxygen...
concentration of ≤5 ppm, see Figure 14. Sampling of the outlet solutions for γ-activity was drawn on a weekly basis for 80 days, whereafter the experiment was terminated and the clay plugs extruded and sliced into thin sections in order to obtain the tracer concentration profiles. Finally, the activity of each section was measured quantitatively with γ-spectrometry after gravimetric control.

In the batch sorption experiments using both MX80 and the different homo-ionic montmorillonites: SwyNa, WyNa and WyCa, dispersed samples were prepared with a volume to mass ratio of 200, i.e. similar to the diffusion experiment samples. Since the sorption of radionuclides is pH dependent, the pH was adjusted to approx. 9 using a borate buffer. As with the diffusion samples, the experiment with samples pre-irradiated under anoxic conditions were performed in a glove box. After 5 days of equilibration, the clay suspensions were centrifuged for 30 min at 6000 rpm, where after the activity in the supernatants and in reference samples not containing clay, was analyzed quantitatively with γ-spectrometry. Finally the sorption coefficient, \( K_d \) was calculated from the activity in the supernatants and that in the reference samples using Equation 17.

### Table 10: Summary of diffusion and batch sorption experiments performed in Paper V.

<table>
<thead>
<tr>
<th>Clay</th>
<th>Atmosphere</th>
<th>γ-irradiated</th>
<th>unirradiated</th>
</tr>
</thead>
<tbody>
<tr>
<td>MX-80</td>
<td>( N_2 )</td>
<td>wet</td>
<td>wet + HS</td>
</tr>
<tr>
<td>Na/Ca-mont</td>
<td>( N_2 )</td>
<td>dry</td>
<td>wet + HS</td>
</tr>
<tr>
<td>Na/Ca-mont</td>
<td>( O_2 )</td>
<td>dry</td>
<td>wet + HS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
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</table>

#### 7.2.6 Effects of Silica sol on bentonite

Since Silica sol has been proposed to be used as an injection grout during the excavation of the repository, the affinity between SiO\(_2\)-colloids and bentonite and Na\(^+\) or Ca\(^{2+}\)-montmorillonite was investigated. This was achieved by mixing SiO\(_2\)-colloids and the respective clay material in different amounts and subjecting the mixed dispersions to different treatments in terms of elevated ionic strength, dehydration and Na\(^+\)/Ca\(^{2+}\) content. With these mixed dispersions a series of qualitative free swelling and settling experiments was undertaken and selected samples were characterized with AFM, SEM/EDS and PCS. In order to investigate whether the SiO\(_2\)-colloids could affect the interlayer swelling of bentonite at high water contents, the basal spacings \( (d_{001}) \) of MX80 were also measured as a function of SiO\(_2\) content by powder XRD. After mixing the dispersions were dried, ground and saturated at 85 RH% in order to form a ~2W hydration state, by equilibrating with a saturated KCl solution through adsorption.
8. Results and discussion

8.1 Microstructure investigation

8.1.1 Colloid diffusion experiments
From batch sorption experiments with the gold colloids the measured sorption coefficients, $K_D$, was 43 cm$^3$/g and 60 cm$^3$/g for the stabilized and untreated gold colloids, respectively. These values were slightly higher than expected considering the apparently unfavorable charge conditions but in line with sorption data for sorption of succinic acid on montmorillonite (mainly outer-sphere interactions) at the same volume to solid mass ratio as in the gold colloid sorption experiments (Kang and Xing, 2007). The gold colloid stability in the inlet solutions was monitored with UV/VIS for the red-colored 5 and 15 nm gold colloids and with ICP-OES for the 2 nm gold colloids. For the 2 nm gold colloids, no significant loss in gold concentration was found during the course of the experiment. However, in the 5 nm gold colloid experiment the absorbance maximum in the inlet solutions decreased by 10-20 % in the different samples, while in the 15 nm gold colloid experiment it decreased by 30-60 %. After half the experimental time in the 15 nm gold diffusion experiment, TEM images were taken from both inlet and outlet solutions. One representative TEM image is shown in Figure 15. The images of the inlet solutions revealed individual gold colloids as well as dimeric, trimeric and larger aggregates. Many of the gold colloids seen in the TEM images were associated to bentonite residues. However, some of the aggregation and sorption to the bentonite residues most probably occurred while drying the colloid solution sample on the carbon-coated copper grid in ambient atmosphere. Gold colloids were not observed in the TEM images of the outlet solutions.

![Figure 15](image.jpg) TEM image of an inlet solution sample showing the 15 nm gold colloids (as dark round spots) and bentonite residues.
During the entire course of the diffusion experiments no gold was found within the detection limits of the ICP-OES in the outlet solutions. Thus, no break-through of gold colloids was observed at any dry density in any of the three diffusions experiments, see Figure 2 in Paper I. The occasional negative concentrations recorded resulted from sample dilutions and measurement uncertainties at these low concentrations. The total gold concentration profiles from the three series of diffusion experiments are given in Figure 3 in Paper I. Only for the smallest gold colloid and the lowest dry density used could a clear exponential gold concentration gradient be detected, i.e. for the 2 nm gold colloids at a bentonite dry density of 0.6 g/cm³. Figure 16 shows the concentration profile for these 2 nm gold colloids with the distance on the x-axis in mm from the inlet filter. The corresponding apparent diffusivity ($D_a$) was calculated to be 3.5±1×10⁻¹³ m²/s, assuming diffusion from an ‘semi-infinite source’ (Crank, 1975) (see also method I in TR-84-05) and the ANADIFF code, taking the filters into account (TR-96-16).

In addition to physical filtration by the microstructure of bentonite, the effect of ‘anionic exclusion’, i.e. electrostatic repulsion, probably also impeded diffusion of the negatively charged gold colloids in the compacted bentonite (TR-96-16; Van Loon et al., 2007). The extent of this effect was not investigated, but since the sorption experiments revealed small but significant sorption of the gold colloids onto bentonite ($K_d = 43$ cm³/g), any ‘anionic exclusion’ effect could not totally exclude gold colloid-bentonite interactions. However, the results from the diffusion experiments showed that saturated compacted bentonite successfully filtered inorganic colloids, except for very small colloids at almost 5 times the anticipated water content of the bentonite barrier.

![Figure 16](image.png)

**Figure 16.** The 2 nm gold colloid concentration profile in the bentonite pellet with dry density 0.6 g/cm³.
These findings are in agreement with those of earlier diffusion investigations using gold colloids (Nowak, 1983; Kurosawa and Ueta, 2001). The apparent diffusivity obtained in the present study for the 2 nm gold colloids (~3.5±1×10^{-13} \text{ m}^2/\text{s} at 0.6 \text{ g/cm}^3) is about one order of magnitude lower than the apparent diffusivity values found for small organic colloids at various compactions (Wold and Eriksen, 2007; Ijimia et al., 2009). Since the organic colloids are expected to be less charged than the gold colloids, they would be less subjected to ‘anionic exclusion’ effects, leading to higher apparent diffusivity values compared with the gold colloids. The higher apparent diffusivities of the humic and lignosulphonate colloids may also reflect the ability of the organic colloids to adapt their conformation to their surroundings.

8.1.2 Basal spacing analysis

In order to investigate the microstructure of bentonite and homo-ionic Na\(^\pm\) and Ca\(^{2+}\)-montmorillonite, the basal spacings were determined by powder XRD and one-dimensional XRD profile fitting. Due to the large number of parameters used in this type of modeling, an absolute perfect fit over a wide angular range is difficult to achieve. However, in order to only obtain an average basal spacing this is not crucial since many parameters, such as the precise chemical composition and atomic location in the interlayers mainly govern the relative intensities of the different 00l reflections and not their position. Thus, the use of the two-component pre-generated XRD profiles is legitimized. Furthermore, with the pre-generated profiles a good fit can usually be acquired within < 5 min, compared with hours or days trying to fit every possible parameter using a trial and error approach (Plançon and Roux, 2010). In Figure 2, Paper II, the nearly-homogeneous experimental profiles which were used to acquire the H\(_2\)O distributions (Figure 3, Paper II) for the pre-generated profiles are shown. In order to acquire a good fit, the usual fitting procedure involved (first step) peak shape fitting of the 001 reflection (<10° 2θ) together with particle orientation optimization and background subtraction, followed by adjustment of the ideal d\(_{nw}\) values (second step) was performed (mainly at 28-30° 2θ). These two steps were usually repeated 2-3 times in order to obtain a good fit, using 3-5 pre-generated profiles. The accuracy of this method is illustrated in Figure 17, which shows an example of one experimental profile of MX80c (dry density 1.55 g/cm\(^3\)), fitted with three different modeled composite profiles with the same distribution of hydration states, namely 30.7 % 2W; 60.3 3W and 5% 4W but with d\(_{nw}\) values varied in steps of 0.1 Å. Hence, in this example the different ideal basal spacings of the different hydration states (0W-4W) are varied, resulting in a change in the average basal spacing d\(_{avg}\) with 0.1 Å. As can be seen from the intensity separation between the experimental and modeled profiles (shown beneath each respective pair of profiles) a difference of 0.1 Å (corresponding to ~1/30 of the diameter of a H\(_2\)O molecule) is small but not
insignificant (see the encircled areas). Figure 4, Paper II, shows the corresponding effect of keeping the ideal $d_{nw}$ values fixed and instead changing $d_{avg}$ with 0.1 Å by varying the distribution of the respective hydration states.

![Figure 17](image)

**Figure 17.** An experimental XRD profile (small circles) compared with three different modeled XRD profiles (grey lines) with different ideal $d_{nw}$ values. Starting from the top, the $[d_{nw} d_{nw} d_{nw}]$ values are (in Å) [15.55; 18.90; 21.70], middle [15.65; 18.90; 21.80], and bottom [15.75; 19.00; 21.90]. The thin solid line shows the difference between the experimental and modeled intensities.

Figure 18 shows a selection of composite 001 reflections from the experimental clay samples saturated from the aqueous phase and the corresponding modeled profiles, as a function of dry density. For these MX80c, MX80s and the WyNaC samples (see Table 7), quite broad and often asymmetric 001 reflections were observed revealing the heterogeneous character of crystalline swelling in these Wyoming clay materials, in agreement with (Ferrage et al., 2007) but in contrast to Na-montmorillonite XRD data for Kunipia-F (Kozaki et al., 1998) displaying very homogeneous interlayer swelling. For the MX80c samples, the minimum FWHM values observed for the interstratified 001 reflections displaying 2W and 3W states were approximately 0.85° 2θ. Interestingly, for MX80 samples saturated to the 2W state, no trend in the FWHM values with grain size could be observed (except for the smallest size fraction) by measuring different size of < 20, 45-70, 70-140 and 140-160 μm as well as native MX80. At higher water contents (< 1.3 g/cm³), where the introduction of osmotic interlayer swelling would be anticipated, significant differences were found between the MX80c and the MX80s samples. For the former set of samples, no clear transition
to osmotic interlayer swelling could be observed, despite the apparent decrease in the amount of crystalline swelling. This was also observed in (Kozaki et al., 1998; Muurinen et al., 2004), who also saturated their samples under confined conditions. For the MX80_s samples, however, relatively well defined reflections could be observed at angles corresponding to both crystalline (3W and 4W) and osmotic interlayer swelling. This shows that osmotic interlayer swelling of MX80 at these water contents is possible, as previously shown in SAXS investigations (Muurinen, 2009; Segad et al., 2010), despite the anticipated elevated ionic strength in the so-called pore water (Bradbury and Baeyens, 2003). For the WyNa_c samples at high water contents however, a well-defined osmotic interlayer was observed, in line with previous results by (Norrish, 1954). For dry densities where well-defined 001, 002 and occasionally 003 reflections were observed, i.e. 0.6-0.8 g/cm³, the one-component formalism described in 5.2.2 was used to obtain an average basal spacing. However, due to the high dependence on accurate sample alignment at these low angles as well as uncertainties in other both experimental and instrumental parameters, these reported basal spacings are only approximate. The WyNa_c samples with dry densities 0.4 and 0.5 g/cm³ did not display any clear diffraction peaks due to osmotic interlayer swelling. This is most likely due to the sensitive and disordered microstructure that exists for randomly orientated samples at such high water contents.

Figure 18. The experimental and fitted XRD profiles. Left image shows MX80_c (black crosses), fitted (solid line) and MX80_s (grey crosses). Right image shows WyNa_c (black crosses) and fitted (solid line).
Figure 19. Relative abundance of the 0W-4W interlayer types for a) MX80C as a function of bentonite dry density; and b) WyNaC and MX80C as a function of montmorillonite dry density.

From the XRD profile fitting of crystalline swelling, the relative abundance of the different interlayer types (0W-4W) was obtained. With this information and together with the ideal \( d_{nw} \) values, the average basal spacing could be calculated for the different samples. Figure 19a,b shows the fitting results from the MX80C and the WyNaC samples. The vertical error bars correspond to ± 0.1 Å. For the MX80C samples, starting at the highest dry density investigated, 1.8 g/cm\(^3\), the 2W state is the dominant interlayer type, with only small amounts of 1W and 3W states. With decreasing dry density, a gradual increase in the 3W state proceeds to almost 100% at approx. 1.4-1.5 g/cm\(^3\) at the expense of the 1W and 2W states. Below 1.4 g/cm\(^3\) the amount of the 4W state increases rapidly, but not to the same extent as the 2W and 3W states at higher dry density. This suggests that the 4W state alone is not energetically stable but merely acts as a bridge between crystalline and osmotic interlayer swelling. Below 1.3 g/cm\(^3\) the fitting
A procedure using pre-generated XRD profiles was not successful, indicating transition to osmotic interlayer swelling. Figure 19b shows the corresponding interlayer type abundance for WyNaC together with the data for MX80C, here recalculated to the equivalent montmorillonite dry density, using the equations described in section 4.2.1. The WyNaC samples evidently displayed a more homogeneous overall hydration state between 1.5-1.8 g/cm³ compared with the MX80C samples, although the mean defect-free distances and the corresponding FWHM values of both the MX80C and WyNaC samples generally were very similar, see Appendix II. Between 1.3-1.5 g/cm³ in dry density, no significant differences in the relative interlayer type abundance were observed between the WyNaC and the MX80C samples. For instance, at the calculated montmorillonite dry density of 1.47 g/cm³ to be used in the KBS-3 concept (assuming a bentonite with similar montmorillonite content as in MX80), the overall hydration state of WyNaC was estimated to be 60-65% 3W and 35-40% 2W, i.e. very similar to the MX80C samples. This indicates that the presence of the accessory minerals does not affect crystalline swelling at these dry density values.

Figure 20. Average basal spacings as a function of water content, $m_{\text{H}_2\text{O}}/m_{\text{clay}}$ for the a) WyNa samples b) WyCa samples; and c) MX80 samples.
In order to compare the average basal spacings obtained from the XRD profile fitting for the different samples saturated under free swelling conditions (as a function of %RH) with the samples saturated under confined conditions (from the aqueous phase), it is useful to present the data as a function of water content ($m_{\text{H}_2\text{O}}/m_{\text{clay}}$), instead of the traditional way of reporting the average basal spacings as a function of %RH, see Appendix I. Figure 20 shows a summary of the average basal spacings for the different clay materials at low and moderate water contents, see Table 7. The dashed lines in the figures represent the maximum possible basal spacing as a function of water content, assuming montmorillonite fractions of 0.98 for the WyNa and WyCa and 0.83 for MX80. Focusing on water contents relevant for the bentonite barrier $> 0.2 \, g_{\text{H}_2\text{O}}/g_{\text{clay}}$, one can see that the samples saturated under free swelling conditions at constant RH% usually displayed reduced swelling compared with samples saturated under confined conditions. Furthermore, large discrepancies between samples saturated under adsorption conditions compared with samples saturated under desorption conditions were usually found, indicating the presence of swelling hysteresis. Thus, from Figure 20 it is evident that samples saturated under free swelling conditions at constant %RH may not be as representative of the bentonite barrier as those saturated under confined conditions.

Several studies (Kozaki et al., 2001; Bourg et al., 2003; Muurinen et al., 2004; Suzuki et al., 2004; Wersin et al., 2004; 2006; Van Loon et al., 2007; Muurinen, 2009) as well as (TR-90-43) have suggested that local low density regions or even coherent channels between the montmorillonite particles can constitute a significant fraction of the total porosity, for dry density values $< 1.8 \, g/cm^3$. However, in this work the measured basal spacings of MX80 and WyNa were found to be in close agreement with the theoretical maximum basal spacing indicating that the free porosity is small, see Figure 20 and Figure 11 in Paper II. Figure 21 shows the resulting free porosities using equation 5 for the samples saturated under confined conditions in this study, as well as free porosities reported in the literature. At dry density $> 1.4 \, g/cm^3$, the average free porosity for the MX80 and the WyNa samples used in this study was found to be 1.5±1.5%, i.e. ≤ 3% and thus significantly lower than previously reported in the literature. At dry density ≤ 0.8 g/cm³, both the Norrish (1954) samples and the WyNa samples demonstrated that the free porosity at these low compactions would also constitute quite low volume fractions as at dry density $> 1.4 \, g/cm^3$. This indicates that the free porosity may also be small in the transition region between crystalline and osmotic interlayer swelling, meaning that the apparent increase in free porosity at dry density $< 1.4 \, g/cm^3$ may be explained by the transition from crystalline to osmotic interlayer swelling with decreasing dry density.
Figure 21. Estimates of the free porosity from this study (using Equation 5) and different studies in the literature. MX80C (white circles); WyNaC/S (grey circles); Norrish (1954) Na-montmorillonite (white squares); Kozaki et al. (1998; 2001) Na-montmorillonite (light grey triangles); and Muurinen et al. (2004) washed bentonite MX-80 (black diamonds). Theoretical estimates for the free porosity of Na-montmorillonite by Bourg et al. (2003) (dashed line); Suzuki et al. (2004) (white triangles); and for Bentonite MX-80 by Van Loon et al. (2007) (black crosses).

To summarize, even for dry density \( < 1.4 \text{ g/cm}^3 \), the free porosity may be quite small. In fact, the main microstructural voids for dry density \( < 1.4 \text{ g/cm}^3 \) seem to be the interlayer voids formed by osmotic interlayer swelling. With decreasing dry density, these voids will increase in number, but not in size, until the corresponding dry density becomes \( \approx 0.7 \text{ g/cm}^3 \) for bentonite and \( \approx 0.8 \text{ g/cm}^3 \) for Na-montmorillonite. For higher dry density values in the region of only crystalline swelling (\( > 1.4 \text{ g/cm}^3 \)), the free porosity is below 3\% and may decrease with increasing dry density. Thus the dominant impact of the free porosity on transport processes should apparently be questioned.

In general, the free porosity hypothetically be considered to i) be distributed approximately equally between the particles or ii) be more locally concentrated in between fewer particles, forming channels as described in (Pusch et al., 1990). For interparticle transport of the gold colloids used in this study to be possible, the interparticle voids would have to constitute a connected network of voids (i.e. case ii) themselves larger than the interlayer distances. This latter criterion is difficult to fulfill with a small free porosity. At dry density 0.6 g/cm\(^3\) the osmotic interlayer swelling is anticipated to dominate the microstructure and the average interlayer distance is expected to be approximately 4 nm, as calculated from Equation 7 and seen in SAXS investigations (Muurinen, 2009; Segad et al., 2010). If a connected network of interparticle voids were to exist, assuming a planar and wedge-like geometry and 10-20
montmorillonite layers/particle, these interparticle voids would be of a similar size to the interlayer distances themselves, i.e. making in the concept of interparticle voids and free porosity becoming a bit futile. The mere fact that neither transport of the 2 nm gold colloids could not be found at dry densities higher than 0.6 g/cm³, nor the fact that transport of any larger colloids could be found at any dry density, suggests that for the 2 nm gold colloids the interlayers comprises the bottle necks for transport and that interparticle voids of sizes of a few tens of nm do not exist in highly compacted saturated bentonite.

8.2 Investigation on the effects of γ-radiation on bentonite

In the first study concerning γ-irradiation effects on bentonite and Na-montmorillonite, the effects on colloid stability and settling behavior was investigated (Paper III). In the second study the effects of γ-radiation on the structural Fe(II)/FeTot ratio were investigated, as well as the resulting changes in montmorillonites reactivity towards H₂O₂ (Paper IV). In the third and last study on this topic, the effects of γ-radiation on compacted bentonite and purified Na-montmorillonite was investigated in terms of radionuclide retention in diffusion experiments using both a weakly and a strongly sorbing tracer, Cs⁺ and Co²⁺, respectively (Paper V).

8.2.1 Aggregation kinetics experiments

Immediately after irradiation of the different clay dispersions, no significant change in colloid concentration or colloid size could be observed by PCS. Upon addition of NaCl, however, a significant change in colloid stability was found, Figure 22, which shows the aggregation dynamics of γ-irradiated and unirradiated Na-montmorillonite (WyNa) dispersions with concentrations of 0, 10 and 15 mM NaCl. In Figure 22a, where no NaCl was added, the γ-irradiated and unirradiated dispersions show similar behavior. The colloid concentration is seen to decrease significantly in the two first days of monitoring, to reach a stable plateau. This is due to settling of the larger Na-montmorillonite particles, whereas smaller and more stable colloids remained dispersed. For the unirradiated dispersions, the colloid stability is seen to decrease steadily with increasing concentration of NaCl. For the γ-irradiated dispersions, even a NaCl concentration of 15 mM did not significantly change the PCS count rate. At 20 mM NaCl (not shown in Figure 22), the γ-irradiated dispersion displayed similar behavior of a continually decreasing count rate with time, but not as drastic as the corresponding unirradiated dispersion. The count rate curve of the γ-irradiated dispersion in 20 mM NaCl more resembled the count rate curve of the unirradiated dispersion at 10 mM NaCl.
Figure 22a-c. PCS count rates plotted as a function of aggregation time and NaCl concentrations for γ-irradiated (circles) and unirradiated (diamonds) Na-montmorillonite dispersions. a) 0 mM NaCl, b) 10 mM NaCl; and c) 15 mM NaCl.

Table 11 shows typical pH and conductivity changes in MX80 and WyNa dispersions after irradiation. As can be seen a slight decrease in pH and a small increase in conductivity were usually observed in the irradiated dispersions.

Table 11. Typical pH and conductivity of γ-irradiated and unirradiated 0.4 % dispersions

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>Conductivity, μS/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>γ-irradiated</td>
<td>unirradiated</td>
</tr>
<tr>
<td>MX80</td>
<td>9.1</td>
<td>9.3</td>
</tr>
<tr>
<td>WyNa</td>
<td>8.7</td>
<td>9.2</td>
</tr>
<tr>
<td></td>
<td>γ-irradiated</td>
<td>unirradiated</td>
</tr>
<tr>
<td></td>
<td>580</td>
<td>570</td>
</tr>
<tr>
<td></td>
<td>280</td>
<td>260</td>
</tr>
</tbody>
</table>

Since a decrease in pH and an increase in conductivity (increase in ionic strength) upon γ-irradiation would normally decrease the colloid stability of Na-montmorillonite, the effect of increased colloid stability upon irradiation is indeed surprising. Using DLVO theory, the corresponding increase in surface potential due to this radiation-induced effect was calculated in relative terms. At 15 mM, the aggregation rate was approximately 10 times higher for the unirradiated sample compared with the γ-irradiated, assuming second order aggregation kinetics. Thus, using the colloid stability ratio concept $W$ (Hunter, 1993) the difference in stability ratio between the γ-irradiated sample and the unirradiated sample ($W_{irr}/W_{unirr}$) is 10. The resulting difference in maximum potential energy $V_{t,max}$ (or activation energy, $E_A$, in the Arrhenius equation) from the relationship above is about 2.3 $k_B T$, which is a substantial difference in the repulsive barrier height in the context of slow aggregation. Using DLVO theory, it is possible to show that this difference in surface potential would only correspond to 0.57-0.67 mV (using planar-planar or sphere-sphere interactions). Such a small potential difference is hard to distinguish in zeta potential measurements.
8.2.2 Sedimentation experiments

In the first sedimentation experiment Na-montmorillonite (WyNa) and bentonite (MX80) were fully dispersed and left to settle upon addition of NaCl. In the case of Na-montmorillonite, the sedimentation experiment revealed two major differences between unirradiated and γ-irradiated dispersions. The NaCl transition concentration, i.e. the transition from free to structural settling, was higher for γ-irradiated than for unirradiated dispersions (10 compared with 5 mM, see Figure 23), indicating higher stability towards ionic strength for the γ-irradiated Na-montmorillonite dispersions, in line with the results from the aggregation kinetics investigation. For a given ionic strength, a clear aqueous phase above the mudline always appeared first for the unirradiated samples. At higher ionic strengths, >25 mM, the sediment volume was seemingly independent of NaCl concentration between 25-400 mM, but a comparison of γ-irradiated and unirradiated suspensions showed that the γ-irradiated samples had significantly larger sediment volumes. Irradiations under different redox conditions (see Table 8) gave similar results, with increasing sedimentation volumes for γ-irradiated dispersions (usually around 20-30%). Thus, an alteration of the structural Fe(II)/Fe$_{Tot}$ ratio could not by itself explain the this observed radiation-induced effect.

![Figure 23. Sedimentation profiles for pairs of γ-irradiated and unirradiated 0.2 % Na-montmorillonite dispersions (above) and 0.5 % bentonite dispersions (bottom) at different NaCl concentrations, 0-400 mM NaCl.](image)

For the bentonite dispersions too, the NaCl transition concentration between free and structural settling was higher for γ-irradiated samples than for unirradiated (17.5 and 10 mM
respectively). For higher ionic strengths, >25 mM, the time of formation of the final sediment was shorter for unirradiated bentonite dispersions compared with γ-irradiated. Contrary to the Na-montmorillonite experiment, the γ-irradiated bentonite dispersions at high ionic strength, >25 mM NaCl, displayed slightly smaller final sediment volumes compared with the respective unirradiated samples, possibly due to a higher Ca\(^{2+}\) content in the γ-irradiated samples. The effect of different free and structural settling behavior for the irradiated and unirradiated bentonite dispersions, respectively, is displayed in Figure 24. When colloid aggregation is rapid (resulting in structural settling) the larger accessory mineral particles get caught while settling their way down the test tubes, while when the colloid aggregation is slow (resulting in free settling), the accessory mineral particles settles freely and eventually forms a dense sediment on the bottom in the test tubes. For the irradiated bentonite dispersions this latter settling behavior occurred at higher NaCl concentrations compared to unirradiated bentonite dispersions.

![Figure 24](image.png)

**Figure 24.** Pair of test tubes containing irradiated (left) and unirradiated (right) bentonite dispersions viewed from below, showing the effect of free settling vs. structural settling.

Both the Na-montmorillonite and bentonite sedimentation experiments clearly show that the difference in sedimentation volumes is not a simple ionic strength effect, coming from the increase in conductance as measured in the γ-irradiated samples, since sedimentation volumes, at least above 25 mM, do not seem to be dependent on the ionic concentration. The difference in sedimentation volumes does not seem to come from the general decrease in pH either, since increasing the pH with small aliquots of boric acid to the same pH as the unirradiated samples did not make any significant difference. Washing the Na-montmorillonite repeatedly by centrifugation at 6000 rpm for 30 min and replacing the supernatant solution also had no effect on the difference in sedimentation volumes, which proves that the effect is inherent to the colloids themselves and not due to changes in the solution chemistry after irradiation. The second sedimentation experiment investigating the CSC for Na-montmorillonite dispersions showed that the addition of the molecular radiolysis products, H\(_2\)O\(_2\) and H\(_2\)(g), did not affect the CSC of unirradiated Na-montmorillonite. The CSC increased with irradiation time until a certain plateau was reached, see Figure 25. The CSC also increased with Na-montmorillonite concentration, at least within the concentration range investigated.
Thus, both the sedimentation experiments and the aggregation kinetics investigation revealed increased Na-montmorillonite colloid stability upon γ-irradiation. The possible reason for this is an increase in the surface potential of the Na-montmorillonite colloids. This would also explain the apparent loss of Na$^+$ from the filtrate solutions of γ-irradiated Na-montmorillonite dispersions. The apparent increase in this radiation-induced effect with Na-montmorillonite concentration as seen in Figure 25 cannot be explained by any direct γ-photon/Na-montmorillonite effect (direct hit). This is because the dispersions γ-irradiated at different concentrations in the CSC experiment were diluted to the same concentrations (0.025 %) before addition of NaCl. Thus, only an alteration of the overall system could remain after the dilution to the same Na-montmorillonite concentrations in the CSC experiment. This leads to the conclusion that the observed radiation-induced effect ought to be explained by indirect effects, i.e. by reactions with radiolysis products.

### 8.2.3 Solubility analysis

From the elemental analysis of supernatants from WyNa dispersions, it is evident that Na-montmorillonite is affected by γ-irradiation. Figure 26 shows the filtrate concentrations of Al, Si, Na and Ti from WyNa dispersions analyzed by ICP-OES as a function of γ-dose. Al$^{3+}$ and Si$^{4+}$ concentrations in the solution increased due to irradiation. The loss of Na$^+$ suggests an increase in surface charge of the Na-montmorillonite. Although an apparent increase of one of the minor constituents in montmorillonite was found (Ti) in the supernatants, no difference in Fe$^{2+}$/Fe$^{3+}$ or Mg$^{2+}$ could be found. In all, these changes in solubility can explain the small increase in conductivity for both Na-montmorillonite and bentonite dispersions. After γ-irradiation the Na-montmorillonite and bentonite dispersions also displayed a decrease in pH, see Table 11.
8.2.4 Structural Fe(II)/Fe(III) and H$_2$O$_2$ reactivity study

The main redox-sensitive element in montmorillonite is Fe. Because of this the structural Fe(II)/Fe(III) content in different Na-montmorillonite clays as well as the effect of an increased structural Fe(II) content on the decomposition rates of H$_2$O$_2$ were investigated. This latter effect is especially interesting since H$_2$O$_2$ is one of the major oxidants in many anticipated heterogeneous reactions in the repository environment. It is well known that in the presence of Fe(II) H$_2$O$_2$ is rapidly decomposed via the Fenton mechanism, reaction 3. Thus, it is probable that any increase in the structural Fe(II) content in montmorillonite upon irradiation, may also accelerate decomposition of H$_2$O$_2$ in a repository environment.

$$\text{Fe(II)}_{\text{Struct}} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(III)}_{\text{Struct}} + \cdot\text{OH} + \text{OH}^- \quad \text{Reaction 3}$$

In general, the structural Fe(II)/Fe$_{\text{Tot}}$ ratio in WyNa and SwyNa dispersions was investigated for both unirradiated and γ-irradiated dispersions under different redox conditions (see Table 8), with the spectrophotometric 1,10-phenanthroline method (Amonette and Templeton, 1998) Prior the irradiation experiments, the total Fe content of both these two clay materials was found to be very similar, nearly 3wt%. Figure 27 shows the structural Fe(II)/Fe$_{\text{Tot}}$ ratio for the WyNa clay under ambient conditions as well as after irradiation under oxidizing, oxic, anoxic and strictly
reducing conditions. For the unirradiated WyNa reference dispersion the structural Fe(II)/FeTot ratio was 5.5 %. Irradiation under air-saturated conditions did not affect the structural Fe(II)/FeTot ratio but irradiation under strictly oxidizing conditions (degassing with N₂O) significantly decreased it to 3.0 %.

Figure 27. Structural Fe(II)/FeTot ratios in duplicates of unirradiated and γ-irradiated WyNa dispersions, irradiated under different redox conditions, see also Table 8.

However, irradiation under anoxic conditions due to N₂ degassing significantly increased the structural Fe(II)/FeTot ratio to 9.8 %, which was in line with results from Mössbauer spectroscopy (not shown). The same occurred after irradiation under strictly reducing conditions (after addition of 2-PrOH), which significantly increased the structural Fe(II)/FeTot ratio to ~70 % under the given experimental conditions. Altogether, this shows that the native state of montmorillonite is rather oxidized and that the structural Fe(II) and the corresponding Fe(III) content in the clay may be affected by γ-radiation. With the purpose of investigating the dose dependence of this effect and the implications of elevated Fe(II) content on the reactivity towards H₂O₂, a second type of experiment was employed under deaerated conditions as a function of irradiation time. In this experiment both the structural Fe(II) and Fe(III) content and the decomposition rate of H₂O₂ in the dispersions were determined in parallel experiments. Due to reproducibility issues with the WyNa material and also native MX80, the purified SwyNa w clay from which free Fe-oxides and organic traces had been removed, was used in this experiment.

The dispersions were irradiated for 0, 1, 3, 6, 12 and 24 hours, corresponding to 0; 0.54; 1.62; 3.2; 6.5; 13.0 kGy. The resulting Fe(II)/Fe(III) contents in the γ-irradiated SWyNa w dispersions (0.4 wt%) is displayed in Figure 28. In general with increasing irradiation time an increasing Fe(II) content was found, except for the small decrease between the 12 h and the 24 h sample. As for the decomposition rates of H₂O₂, shown in Figure 29 for the 1h and the 24 h sample, a clear
trend in decomposition rates of H$_2$O$_2$ with irradiation time was found, in line with the increasing Fe(II) content upon γ-irradiation and reaction 3.

![Figure 28](image)

**Figure 28.** Structural Fe(II)/Fe$_{Tot}$ ratios in unirradiated WyNa dispersions (Ref) and WyNa dispersions γ-irradiated dispersions (n=2) under different redox conditions.

For the unirradiated reference dispersion (not shown), the decomposition rate of H$_2$O$_2$ was very slow, see Figure 1c, Paper IV. Not until 3 h of irradiation was a significant change in H$_2$O$_2$ decomposition rate observed. For the 6 h, 12 h and 24 h dispersions, the increase in H$_2$O$_2$ decomposition rate with increasing irradiation time was small.

![Figure 29](image)

**Figure 29.** H$_2$O$_2$ decomposition rates in SwyNa$_w$ dispersions irradiated a) 1 h b) 24 h.

In order to investigate the effect of extremely elevated structural Fe(II)$_{Strct}$/Fe$_{Tot}$ ratios and to relate the Fe(II) content to the H$_2$O$_2$ reactivity, γ-irradiations under strictly reducing conditions was also performed by the addition of 5 v% 2-PrOH. The resulting Fe(II)$_{Strct}$/Fe$_{Tot}$ ratios at different γ-radiation doses are displayed in the first six columns in Figure 30a. As can be seen, a significant increase in the structural Fe(II)/Fe$_{Tot}$ ratio with irradiation time was observed,
reaching 0.85 after 24 hours of irradiation, significantly exceeding the maximum structural Fe(II)/FeTot ratio obtained from the γ-irradiations under deaerated conditions. In order to prove the relation between the H₂O₂ decomposition rate and the structural Fe(II)/FeTot ratio, a series of consecutive H₂O₂ additions (at 0.2-0.4 mM) was made, see the outermost right columns in Figure 30a. As expected, with successive H₂O₂ additions, the structural Fe(II)/FeTot ratio decreased accordingly. As with the structural Fe(II)/FeTot ratio in this experiment compared to the structural Fe(II)/FeTot ratio in the previous experiment, the corresponding decomposition rates were significantly higher, shown in Figure 30b (arrows indicating the sampling times for Fe(II)/Fe(III) determination). Not until a structural Fe(II)/FeTot ratio of 0.2 was reached could a reduced decomposition rate be observed.

Altogether, the decomposition of H₂O₂ clearly was found to be dependent on the Fe(II)/FeTot ratio, presumably through the Fenton reaction (reaction 3). However reaction 3 could not solely explain H₂O₂ decomposition in the irradiated clay dispersions. This is because the effective/accumulated Fe(II) concentration (taking the repeated dilutions from the H₂O₂ additions into account) in the SwyNaₜ dispersions was significantly lower than the total accumulated addition of H₂O₂ (1.3 mmoles/L and 2.0 mmoles/L, respectively). One possible explanation for this extra loss of H₂O₂, which was not observed in unirradiated dispersions, could be through reaction with the OH⁻ radical formed in reaction 3.

![Figure 30. a) The relative Fe(II)/Fe(III) contents in the SwyNaₜ dispersions after γ-irradiation under strictly reducing conditions as a function of irradiation time. The six outermost columns (to the right) display the Fe(II)/Fe(III) contents after consecutive H₂O₂ additions to the 24 h sample. c) Decomposition of H₂O₂ after consecutive additions of 0.2 mM to WyNaₜ, irradiated for 24 h under strictly reducing conditions. Arrows indicate sampling for the Fe(II)/Fe(III) determinations in the left diagram.](image)

In the context of a future deep geological repository it is noteworthy that under anoxic conditions the structural Fe(II) content was seen to increase one power of magnitude to 25-
30%. If the oxidizing and reducing radicals formed upon water radiolysis would react with the structural Fe with similar rate constants, this increase can be explained by the fact that the initial reduction rate of structural Fe(III) would be higher than the corresponding oxidation rate of the structural Fe(II), since the initial structural Fe(II)/Fe(III) ratio is very low, ≤ 5 %. Altogether, this study clearly shows that the structural Fe(II)/Fe_{Tot} in Na-montmorillonite is altered by radiolysis products. This implies that γ-radiation may alter the overall redox properties of the bentonite barrier in a deep geological repository, and may accelerate the decomposition of one of the major oxidants formed upon water radiolysis, H_2O_2. In order to relate these results to those regarding increased colloid stability upon γ-irradiation, a final settling experiment with γ-irradiated and unirradiated 0.2 wt% WyNa_w dispersions was performed (not shown). After irradiation for 24 h, 15 mM NaCl was added to induce colloid aggregation and rapid settling. Compared to the unirradiated reference, irradiated WyNa_w dispersions displayed significantly slower settling rates, regardless of the samples were irradiated under anoxic or oxic conditions, or if 2 mM H_2O_2 was added to the dispersion (prior NaCl). Since both H_2O_2 and irradiation under oxic conditions suppresses the structural Fe(II) content in montmorillonite, these results indicate that the structural Fe(II)/Fe(III) ratio do not influence the colloid stability significantly. On the other hand, it is known that back and forth reduction and oxidation of structural Fe might induce irreversible structural changes in the montmorillonite structure (Stucki et al., 2002), which hence would not be well reflected by a net change in the structural Fe oxidation state upon γ-irradiation.

8.2.5 Radionuclide retention study

After deposition of the nuclear fuel in the deposition holes, the bentonite barrier will be exposed to elevated levels of γ-radiation (mainly from ^{137}Cs) under different chemical conditions. Initially, oxic conditions will be prevalent in the deposition holes and the temperature will be high, due to ongoing fission processes in the nuclear fuel. With time, the oxygen in the repository will be consumed and the bentonite barrier will eventually become saturated from the surrounding groundwater. Because of this, the effects of γ-radiation on radionuclide sorption (K_a) and the apparent diffusivity (D_a) in bentonite were studied under different experimental conditions representing the chemical conditions in the deposition holes just described, i.e. oxic/anoxic and dry/wet conditions. Since native bentonite contains small amount of organic residues, which can enhance radionuclide transport (Wold and Eriksen, 2007) as well as accessory minerals, see Table 4, both MX80 and homo-ionic montmorillonite clays (SwyNa_w, WyNa and WyCa) was used, with or without the presence of organics (HS). A summary of the experimental conditions used in the sorption and diffusion experiments are shown in Table 10.
In the batch sorption experiments, the sorption of $\text{Co}^{2+}$ to irradiated MX80 dispersions was found to be significantly lower than to the unirradiated clay samples, regardless of the experimental conditions, see Figure 31a. This effect was also seen in the experiments with WyCa and $\text{Co}^{2+}$ as well as with the irradiated WyNa samples under certain conditions, see Figure 2, Paper V. Interestingly, for the $\text{H}_2\text{O}_2$ pretreated SwyNa$_w$ clay, relatively low $K_d$ values was found compared to the corresponding $K_d$ values obtained with WyNa or MX80 for both $\text{Co}^{2+}$ and $\text{Cs}^+$, and no significant change due to the different treatments could be found. Compared to the unirradiated reference sample not containing HS, for both the MX80 and WyCa samples the sorption of $\text{Co}^{2+}$ was further significantly reduced by the presence of HS. This effect can be explained by complexation of $\text{Co}^{2+}$ to the humic particles, which will increase the $\text{Co}^{2+}$ concentration out in solution significantly, since the HS cannot be separated by centrifugation. Except for the sample irradiated under anoxic conditions, the same effect was also found for the WyNa dispersions upon HS addition.

In the case of $\text{Cs}^+$, no significant radiation-induced effects was generally found since the clay affinity for $\text{Cs}^+$, which mainly undergoes sorption through ion-exchange, is relatively low, making the uncertainties larger. Also, since $\text{Cs}^+$ competes with the large excess of $\text{Na}^+$, a small radiation-induced effect may be hard to detect. As can be seen in Figure 31b with MX80, no apparent difference in sorption of $\text{Cs}^+$ was found upon irradiation. The difference in sorption capacity between the SwyNa$_w$ clay and the other clays is interesting since irradiation of WyNa under oxic conditions, which is known the lead to production of highly reactive oxygen species such as $\text{H}_2\text{O}_2$, also seems to reduce the overall sorption capacity. This suggests that $\text{H}_2\text{O}_2$ have a negative effect on the sorption capacity of montmorillonite.

![Figure 31. The $K_d$ values obtained from the batch sorption experiment with the native MX80 clay for a) $\text{Co}^{2+}$ and b) $\text{Cs}^+$.](image)
As for the diffusion results, in order to evaluate the diffusion data and obtain the $D_a$ and the $K_d$ values from both the concentration profiles and the breakthrough curves (Cs$^+$ only), while at the same time taking the diffusive resistance of the end filters into account, a finite-difference code called ANADIFF was used (Eriksen et al., 1999). Figure 32 shows typical experimental and simulated concentration profile and breakthrough data from one of the MX80 samples for both $^{137}$Cs$^+$ and $^{60}$Co$^{2+}$, sorbing through ion-exchange (mainly) or surface complexation and having $D_a$ values of $3 \times 10^{-12}$ m$^2$/s and $3 \times 10^{-14}$ m$^2$/s, respectively. Due to the high sorption affinity of Co$^{2+}$ through strong surface complexation to montmorillonite, which results in an overall low diffusivity, breakthrough of Co$^{2+}$ was not observed under any experimental conditions tested since the experiment only lasted 80 days. For Cs$^+$ which sorbs mainly through a weaker ion-exchange interaction, the situation was quite different, resulting in breakthrough after only a few weeks.

![Image](image.png)

**Figure 32.** Typical diffusion data of $^{137}$Cs$^+$ (black squares) and $^{60}$Co$^{2+}$ (white squares), showing the a) concentration profiles in the clay plug and b) breakthrough curve. The dashed lines shows the corresponding simulated data obtained with the ANADIFF code.

The $D_a$ values obtained from the ANADIFF simulations for Co$^{2+}$ are displayed in Figure 33. In general, the $D_a$ values of both Co$^{2+}$ and Cs$^+$ (not shown) were (for the same type of clay) in the same order of magnitude for irradiated and unirradiated samples (within a factor of 2) and in line with previously reported data (Molera and Eriksen, 2002). Thus, despite the lower $K_d$ values obtained for Co$^{2+}$ in the batch sorption experiments, no apparent radiation-induced effects on the overall diffusivities could be found under these experimental conditions.
Figure 33. The $D_a$ values for Co$^{2+}$ obtained in the diffusion experiments shown for each duplicate as obtained through radionuclide transport simulation with ANADIFF. See Table 10 for the different sample descriptions.

In order to investigate the actual impact of an altered $K_d$ value on the radionuclide retention, realistic radionuclide release was calculated for the bentonite barrier with ANADIFF. The calculations were performed for a bentonite barrier thickness of 0.35 m and three hypothetic radionuclides with different $D_a$ values, $5 \times 10^{-12}$, $5 \times 10^{-13}$ and $5 \times 10^{-14}$ $\text{m}^2/\text{s}$ respectively, and ignoring the radioactive decay. The resulting radionuclide release is plotted in Figure 34, both in relative terms after breakthrough (left axis) and as the retention time, here defined as the time in years to release 1/1000 of the inlet activity (right axis). In terms of retention time, the impact of $K_d$ is fairly small. For the different radionuclides, the retention time only increases with approx. 1/3 by a change in $K_d$ by a factor of 10 (for relevant $K_d$ values, i.e. 100-10000 $\text{cm}^3/\text{g}$).

Figure 34. A comparison of impact of different $K_d$ values on the radionuclide release through the bentonite barrier. The grey squares display the relative radionuclide release vs. $K_d$ after breakthrough (left hand axis) whereas the circled lines display the retention time before release 1/1000 of the diffusing inlet activity in years (ignoring radioactive decay) for $D_a$ values of $5 \times 10^{-12}$; $5 \times 10^{-13}$; $5 \times 10^{-14}$ $\text{m}^2/\text{s}$, respectively.
This means that with decreasing $D_a$ and increasing $K_d$ the relative impact of $K_d$ on the retention before radionuclide breakthrough increases. Taking the radioactive decay into account, this effect would be even larger. In terms of relative release after breakthrough however, shown on the left hand axis in Figure 34 as normalized to a $K_d$ value of 50 cm$^3$/g, the amount of radionuclides released, is as expected proportional to the $K_d$ value, and decreases approximately by a factor of 2 if the $K_d$ value is doubled. Thus, a radiation-induced effect such as the one found for MX80 in Figure 31 would then double the radionuclide release after breakthrough and decrease the time for breakthrough by approx. 10%, (obtained from data presented in Figure 34).

8.3 Investigation of SiO$_2$-colloid interaction with Bentonite

Since the SiO$_2$-colloids are well-known to aggregate and coalesce irreversibly under high ionic strength (> 0.1 M) or due to dehydration, SiO$_2$-colloids may influence future bentonite colloid generation and erosion in the event of contact between SiO$_2$-colloids and bentonite. Because of this, a series of experiments with mixed SiO$_2$/bentonite systems were performed (Paper VI). From free swelling experiments (not shown, see Table 1 in Paper VI), qualitative evidence of SiO$_2$-colloids reacting with and forming larger modified bentonite colloids at elevated ionic strength (0.3 M NaCl) were found, as well as indications of increased colloid stability. In the following settling experiments an increase in the SiO$_2$-colloid content was found to drastically increase the contribution of free settling (see definition in section 4.2.2), indicating either higher colloidal stability towards ionic strength (diffuse mudlines) or formation of larger aggregates (rapid settling). Together, the free swelling and settling experiments revealed that bentonite colloids are influenced by SiO$_2$-colloids under both high ionic strength and from dehydration. In order to study and characterize the assumed modified particles on an individual scale, Na-montmorillonite (WyNa) dispersions were mixed and treated with SiO$_2$-colloids in different ways, see Table 2 in Paper IV, and the resulting mixed dispersions were characterized visually and with PCS, AFM and SEM. The results from the PCS measurements also indicated that montmorillonite colloids are influenced by SiO$_2$-colloids under both high ionic strength and especially by dehydration, however only if mixed in comparable amounts (by weight). Figure 35 shows the mixed Na-montmorillonite:SiO$_2$-colloid samples subjected to dehydration. As can be seen, with increasing SiO$_2$-colloid concentration, the opaqueness increases indicating formation of larger particles, except when there is no Na-montmorillonite present (sample to the right). In this latter sample no colloids were formed since dehydrated pure SiO$_2$-colloids cannot be redispersed.
Figure 35. Dehydrated and redispersed Na-montmorillonite/SiO$_2$-colloid samples, A$_1$-E$_1$ from Table 2, Paper VI. The legends denote the wt % of montmorillonite:SiO$_2$.

Figure 36 displays a SEM image of the 0.1:0.4 wt% Na-montmorillonite/SiO$_2$-colloid sample from Figure 35. In general a variety of particles and particle sizes was found. However, when in large excess of SiO$_2$-colloids, µm sized particles were formed upon dehydration, i.e. several times the size of the original Na-montmorillonite particles (compare with Figure 4).

Figure 36. Top image: SEM image of dehydrated Na-montmorillonite/SiO$_2$-colloid sample (0.1:0.4 weight % when dispersed). Insert shows an individual mixed montmorillonite/SiO$_2$-colloid particle with a flaky structure.

In order to control the element composition in this mixed particles, the Al/Si ratio of selected particles and aggregates (2-3 mappings per sample/aggregate) were determined by elemental analysis using EDS. As can be seen in Figure 37, the elemental analysis results did prove that mixed montmorillonite/SiO$_2$-colloids were formed since the EDS results are in good agreement with the theoretical Al/Si ratios, calculated from the Al/Si ratio in montmorillonite (approx. 40%) and SiO$_2$ (0.0%).
With the purpose studying the initial aggregation between the montmorillonite and SiO₂-colloids, AFM was employed since this technique offers higher resolution than SEM. However, as with the samples studied with SEM, the AFM images revealed a multitude of particles and aggregates of different sizes. However, in all samples examined aggregates of mixed particles were formed to some extent. For Na-montmorillonite samples the SiO₂-colloids were found to be preferentially attached to the montmorillonite layer edges rather than the permanently negatively charged montmorillonite faces. Hence, upon attachment of SiO₂-colloids with Na-montmorillonite, the edges, where similar silanol and aluminol groups are situated and which do not hold a permanent negative charge, seems to be favored. Figure 38a shows a representative AFM image of a highly diluted Na-montmorillonite/SiO₂-colloid sample. Upon further attachment of SiO₂-colloids to/with the montmorillonite particles however, larger SiO₂-colloid aggregates was often seen to be formed with already attached SiO₂-colloids. Interestingly, for mixed Na-montmorillonite/SiO₂-colloid dispersions prepared at a similar high ionic strength (0.3 M NaCl) as that planned for use during grouting, a similar type of preferential SiO₂-colloid attachment onto the montmorillonite particles was generally observed. In addition, for those samples not subjected to pre-dehydration, numerous unaggregated SiO₂-colloids were also found, see Figure 9a in Paper VI. This was quite unexpected considering the high ionic strength in these samples and the fact that at the time of the AFM measurements, the samples were approximately 6 months old.
In the AFM investigation, mixed montmorillonite/SiO₂-colloid dispersions with Ca-montmorillonite were also prepared. Compared with the Na-montmorillonite samples, quite the opposite form of attachment of the SiO₂-colloids was found in Ca-montmorillonite (WyCa) samples since these particles were often found to be entirely covered by SiO₂-colloids, resulting in relatively large mixed particles, see Figure 10 and 11 in Paper VI. This indicated that Ca²⁺ induces montmorillonite face aggregation of the SiO₂-particles. Thus, in a repository environment, it is possible that the Na⁺/Ca²⁺ ratio will govern the preferred mode of attachment.

It is well known that when dispersed, the montmorillonite particles, i.e. the layer stacks, may undergo delamination to an extent which usually varies with the type and concentration of the counter-ions present, see section 4.2. Thus, in order to further test whether the SiO₂-colloids could influence the montmorillonite particle size in terms of thickness, i.e. have any effect on the interlayer distances or amount of delamination, XRD measurements on dehydrated bentonite/SiO₂-colloid samples were performed and are shown in Figure 39. From the 001 reflections, no significant change in either basal spacing (i.e. interlayer distance) or in peak FWHM was found with increasing SiO₂-content.
This shows that the SiO₂-colloids could not influence the actual delamination process nor act as a pillaring agent under the experimental conditions employed. Hence, although some indications of increased colloid stability were found in the free swelling and settling experiments, as well as in the PCS experiments, no indication of the SiO₂-colloids actually influencing montmorillonite particle delamination was found. Thus, the SiO₂-colloids would not be expected to contribute to the actual generation of montmorillonite colloids in the event of bentonite erosion.
9. Conclusions

This thesis investigated three different areas of interest concerning the bentonite barrier in a future deep geological repository for nuclear waste.

- From the microstructure investigation it can be concluded that highly compacted and saturated bentonite effectively filters even very small inorganic colloids due to its impenetrable microstructure. Colloid transport was not detected in any of the three diffusion experiments, except at the lowest compaction of bentonite tested, where the corresponding montmorillonite interlayer distance exceeded the colloid size (2 nm). However, since colloid transport was observed in one exceptional case, the conclusion was that electrostatic repulsion or ‘anionic exclusion’ effects could not entirely prevent interactions between the negatively charged gold colloids and bentonite. Overall, unless the bentonite barrier undergoes severe mass loss, colloid diffusion would not be expected through the bentonite barrier at significant rates. In the interlayer swelling investigation of compacted saturated bentonite and montmorillonite, the measured interlayer distances was found to agree well with the maximum interlayer distances, assuming no free porosity. This suggests that the importance of interparticle voids in saturated compacted bentonite is small (even at very low compactions), since the total free porosity of highly compacted bentonite (crystalline swelling only) was only ≤ 3 %, hence significantly lower than previously reported in the literature. Thus, the relevance of the free porosity for diffusive transport may also be small. Furthermore, the method of saturation was shown to substantially influence the interlayer swelling. At the water contents relevant for the bentonite barrier, saturation under free swelling conditions resulted in lesser interlayer swelling and swelling hysteresis recurrently compared with saturation from the aqueous phase under confined conditions.

- As for the radiation-induced effects on bentonite and montmorillonite dispersions, an increase in the colloid stability and altered settling behavior of montmorillonite was found, as well as an increase in the structural Fe(II)/FeTot ratio of montmorillonite, from approx. 3 % to 25-30 %. The observed radiation-induced effect on colloid stability was seen to increase with increasing montmorillonite concentration during the irradiation, implying indirect irradiation effects, i.e. reactions with short-lived radicals formed by radiolysis. The increase in the structural Fe(II)/FeTot ratio was also explained by reactions with short-lived radicals formed by radiolysis, yielding a higher production rate of structural Fe(II) over Fe(III), due to the low initial Fe(II)/FeTot ratio. This increase in the structural Fe(II)/FeTot ratio of montmorillonite was found to accelerate the
decomposition rate of H$_2$O$_2$, presumably by the Fenton reaction. However, although the increase in the structural Fe(II)/Fe$_{Tot}$ ratio intuitively would increase the montmorillonite surface charge, it could not explain the increase in colloid stability and altered settling behavior, since this effect also occurred during irradiations where the structural Fe(II)/Fe$_{Tot}$ ratio did not increase. In the radionuclide retention study, a radiation-induced decrease in the $K_d$ value was found for Co$^{2+}$ but not for Cs$^+$, suggesting that $\gamma$-radiation may alter the surface characteristics of montmorillonite governing surface complexation of Co$^{2+}$. The same trend was generally also found for homo-ionic Na- and Ca-montmorillonite clays, except when pretreated with H$_2$O$_2$, which was seen the decrease the sorption capacity ($K_d$) of montmorillonite, both for ionic-exchange and surface complexation interactions. As expected no difference for Cs$^+$ in the apparent diffusivity between unirradiated and irradiated samples was found. Neither was any effect found for Co$^{2+}$, likely due to the short experimental time and conditions used.

- In the investigation regarding the potential effects of SiO$_2$-colloids on the properties of bentonite particles, it was shown that bentonite and montmorillonite particles can be modified by SiO$_2$-colloids when mixed in comparable amounts (by weight), either at high ionic strength (0.3 M NaCl) or by dehydration. The heterogeneous aggregation between montmorillonite and SiO$_2$-colloids was in Na$^+$-dominated systems initiated by montmorillonite layer edge sorption, whereas with Ca$^{2+}$-dominated montmorillonite the sorption of SiO$_2$-colloids was less selective. Furthermore, the heterogeneous aggregation was not observed to alter the interlayer swelling, meaning that all sorption occurred on the external particle surfaces.
10. Acknowledgements
I would first of all like to thank my advisors Mats Jonsson and Susanna Wold, for their support, guidance and ideas during the course of this work and in the preparation of this thesis. Without your patience this work would not have been possible.

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At last (but not the least) I would like to thank my love Josefin, and the rest of my family, for all the patience and support they have shown and given me during this time.
11. References

11.1 SKB reports

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11.2 Articles and books


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12. Appendices

12.1 Appendix I

Figure A.1. The average basal spacing ($d_{001}$) and water content (wc) versus %RH for the clay materials examined in Paper II, compared to literature data. a) WyNa$_{Ads/Des}$ compared to (Berend, 1995); b) WyCa$_{Ads/Des}$ compared to (Cases et al., 1997) and c) MX80$_{Ads/Des}$ compared to (Devineau et al., 2006).
12.2 Appendix II

**Figure A.2.** The mean defect-free distance (MDF) plotted versus the water content \((m_{H2O}/m_{clay})\) for the different clay materials examined in Paper II. In a) MX80, WyNa, MX80Ads and MX80Des and in b) WyNa, WyNaAds, WyNaDes, WyCaAds and WyCaDes.
### 12.3 Appendix III

**Table A.1.** Structural data for the 3W state as used in MODXRSD.

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