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ABSTRACT

In the current KBS-3H disposal concept, titanium is foreseen as shell material surrounding canister-bentonite modules. The reactivity of Ti towards the bentonite clay has been the focus of an experimental programme. Here we report on three studies carried out between 2013–2015.

In the first study, the nature of Ti in natural clays was analysed by X-ray absorption spectroscopy. The results indicated that Ti in MX-80 bentonite is incorporated in the clay structure, whereas in the high Ti-containing Rokle bentonite, Ti occurs predominantly as separate TiO$_2$ phase (anatase).

In the second study, synthetic montmorillonite (“Ti-free”) was exposed to Ti foil and Ti powder at 80 °C for periods up to 20 months. Spectroscopic analysis (XANES, EXAFS) revealed that Ti released by corrosion had reacted with the clay mineral and was incorporated in a newly formed phyllosilicate structure. No indications of the formation of a separate TiO$_2$ phase were found. From micro-XRF analyses the amount of Ti transferred to the clay could be estimated. The derived average corrosion rates were found to be in the range of about 1–10 nm/a.

In the third study, hydrothermal tests at 200 °C with synthetic montmorillonite and Ti foil and Ti powder were conducted. Microscopic and spectroscopic analysis indicated no changes of the clay mineral under neutral and acidic conditions, but some alteration under alkaline conditions. These alterations, however, occurred independently of the addition of Ti.

Based on the obtained results, the effect of Ti on the bentonite buffer is expected to be very limited.

Keywords: KBS-3H, supercontainer shell, titanium-clay interaction, bentonite, montmorillonite
Titaanimetalliseoksia on ehdotettu käytettäväksi KBS-3H loppusijoitusratkaisun asennuspakkausten bentoniittipuskuria ympäröivän kuoren materiaalina. Tässä raportissa esitetään tulokset vuosina 2013-2015 suoritetuista titaanin ja bentoniittisaven vuorovaikutuskokeista.

Tutkimuksen ensimmäisessä osassa titaanin esiintyminen luonnonsavissa analysoitiin XRay absorptiospektroskopian avulla. Tulosten perusteella MX-80 bentoniitissa Ti esiintyy savirakenteessa kun taas paljon Ti sisältävässä Rokle bentonitiissa Ti esiintyy pääosin erillisenä TiO₂ faasina (anatase).

Toisessa osassa synteettinen ”Ti-vapaa” montmorilloniitti annettiin olla vuorovaikutuksessa Ti-folion ja Ti-pulverin kanssa 80°C:n lämpötilassa 20 kuukauden ajan. Spektroskooppisten analyysien (XANES, EXAFS) perusteella, korroosiossa vapautunut Ti oli reagoinut savimineraalin kanssa liittyen muodostuneeseen phyllosilikaattirakenteeseen. Mikro-XRF analyysien perusteella saveen siirtyneen Ti määriä voitiin arvioida. Titaanin keskimääräinen korroosionopeus oli 1 – 10 nm/vuosi.

Kolmannessa osassa suoritettiin hydrotermisiä kokeita 200°C:ssa jossa seurattiin Ti folion ja pulverin vuorovaikutusta synteettisen montmorilloniitin kanssa. Mitään muutosta savimineraalissa ei havaittu mikroskooppisten ja spektroskooppisten analyysien perusteella neutraaleissa ja happamissa oloissa, mutta jotakin muutoksia oli havaitavissa alkalisissa olosuhteissa. Nämä muutokset havaittiin riippumatta Ti lisäyksestä.

Tulosten perusteella titaanilla on hyvin rajallinen vaikutus bentoniittipuskuriin.

Avainsanat: KBS-3H, asennuspakkauksen kuori, titaani, titaani-savivuorovaikutus, bentoniitti, montmorilloniitti.
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1 INTRODUCTION

The KBS-3 disposal method, based on multiple barriers, is the selected spent fuel disposal method in both Sweden and Finland. There are two design alternatives for the KBS-3 method: KBS-3V in which the canisters are emplaced in individual vertical deposition holes and KBS-3H in which several canisters are emplaced in horizontal deposition drifts. Posiva and SKB are conducting a joint research, demonstration and development (RD&D) programme with the overall aim of establishing whether KBS-3H represents a feasible alternative to the reference concept KBS-3V.

An important component in the KBS-3H disposal concept is the supercontainer shell (SC) surrounding the canister and the bentonite blocks (Figure 1-1). In the original design, carbon steel was selected as shell material (SKB/Posiva 2008). Anaerobic iron corrosion releases large amounts of hydrogen into the repository environment (King, 2008). Furthermore, corroded iron species strongly interact with the bentonite clay and may – at least locally – impair the safety functions of this barrier (Birgersson & Wersin; Wersin & Birgersson 2014). Because of these adverse effects, titanium rather than steel has been selected as supercontainer shell material in the new KBS-3H design (SKB 2012; Posiva 2012). This metal is known to display very low corrosion rates and low mobility over a wide range of environmentally relevant conditions (Schutz 2005; SKB, 2012; Posiva 2012).

![Figure 1-1. Supercontainer shell design in the KBS-3H concept (SKB 2012; Posiva 2012).](image-url)
Indications from literature

The corrosion of Ti in clayish environments and interactions between titanium and clay have received little attention so far. Azumi et al. (2000) and Azumi & Seo (2003) conducted electrochemical corrosion studies on Ti in bentonite suspensions. They found that an anodic Ti oxide film formed in all samples which was however unstable at higher temperature (80°C). In samples containing carbon steel and Ti-clad carbon steel, galvanic coupling between Ti and Fe was observed, resulting in a significantly higher anodic corrosion rate at the Fe side, whereas at the cathodic side the TiO₂ passive layer was affected. A pioneer long-term study on Ti corrosion in contact with compacted bentonite at 95°C was carried out by Olefjord and co-workers within the corrosion programme of the Swedish Nuclear Fuel and Waste Management (SKB) (Mattsson & Olefjord 1984; Mattsson et al. 1990; Mattsson & Olefjord 1990). The main findings from that work were (i) that the overall corrosion rates were very low (≤1nm/a) and similar in simulated groundwater solution and in compacted bentonite, (ii) the film growth was independent of ionic strength and composition of the Ti alloy and could be described by an empirical logarithmic rate law, and (iii) the only Ti species identified in the clay matrix was TiO₂, although this aspect was not studied in detail.

Nevertheless, the knowledge on the reactivity of Ti with clay materials is of fundamental importance in the context of assessing the overall performance of the barrier systems. In particular potentially adverse effects of titanium and its corrosion products need to be assessed in detail. It is important to constrain the chemical nature of the species formed after the Ti corrosion products have reacted with clay barrier materials. Possible molecular interaction mechanisms of Ti with clays include: i) sorption by cation exchange, ii) specific (inner-sphere) sorption to clay edge sites, iii) substitution of Al and Si by Ti in octahedral or tetrahedral clay sites and iv) precipitation of secondary phases such as TiO₂, Ti-Fe oxides or Ti silicate phases. Sorption processes and the formation of nano-crystalline or amorphous (‘gel-like’) Ti-oxide phases may influence the retention characteristics and the swelling properties of the clay barrier. Identifying the predominant molecular interaction processes is crucial in order to assess potential impacts on safety functions of the clay barrier. Consequently, there is need for analytical investigations capable in providing molecular level information. However, two main obstacles turn molecular-level investigations on the Ti-clay interaction into a real challenge. First, based on the extremely low corrosion rates and low solubility of Ti⁴⁺, only small amounts of reaction products can be expected to be formed during experimentally accessible timescales. Second, the considerable levels of geogenic Ti present even in ‘purified’ natural clay samples generally mask the molecular characteristics of the Ti reaction products. It should be noted that, to the best of our knowledge, no other study has so far looked at potential mineralogical or structural changes in the clay as a result of Ti-clay interactions.

Summary of preliminary titanium-clay interaction study (Wersin et al. 2010):

The main objective of this study conducted in the years 2007−2010 was to set up and to initiate an experimental programme on Ti-clay interaction which should yield relevant information with regard to the reaction of Ti with the clay and the possible impact on the buffer’s performance. It comprised two aspects: 1) a literature review and 2) a
preliminary experimental Ti-clay interaction study. The outcome from the literature review has been summarised above.

The preliminary study involved two series of experiments. In the 1st series, purified MX-80 bentonite was mixed with metallic Ti nanopowder and foil at different pH and temperature conditions. After several months, solid and solute samples from the first set of tests were analysed by wet chemistry and quantitative X-ray fluorescence spectrometry. The chemical speciation of Ti was analysed with X-ray absorption spectroscopy (XAS). In addition to reacted samples, a number of reference and starting materials (e.g. MX-80, Rokle bentonite, Opalinus Clay, Illite du Puy) were characterized by XRF and XAS. The preliminary results showed that:

- Natural clay materials contain significant but variable amounts of Ti. The standard purification procedure for bentonites to remove accessories does not or only barely removes Ti.
- The titanium in the natural clay materials Rokle bentonite and Opalinus Clay occurs as microcrystalline TiO₂ (presumably as anatase). On the other hand, the Ti spectra in MX-80 and Illite du Puy suggested the presence of structural Ti in the smectite, but the evidence was not conclusive.
- The exposure of purified MX-80 to titanium powder at room temperature within a period of five months did not lead to measurable additional Ti in the clay.

Based on the outcome of 1st series, a 2nd series of experiments was designed which included synthetic “Ti-free” montmorillonite (rather than natural clay), higher temperatures (80 °C) and a reaction time of 4.5 months. The objective of this setup was to increase the Ti transfer rates from the metal surfaces to the clay. The main outcome from these experiments was:

- As revealed from spectroscopic analysis (micro-XRF and XANES) on the reacted materials, the use of synthetic montmorillonite combined with the increase of temperature allowed to partly overcome the experimental problems noted in the 1st series. Thus, Ti background concentrations were effectively very low and Ti transfer to the clay mineral could be identified with spectroscopic analysis.
- On the other hand, the spectroscopic data highlighted further weaknesses in the setup. Thus the use of Ti nanopowder was shown to be not recommendable because of difficult separation from the clay.
- It was recommended to carry out a 3rd experimental series of "accelerated tests" with an optimised experimental setup. This setup was applied in the subsequent study presented below.

Scope of this experimental study:
With aid of an optimised experimental setup the main objective is the identification of the nature of the Ti species transferred to the clay from the corroding metal source. A second objective is the estimation of the transfer rate of Ti from the metal to the clay.

The following approach was adopted: A 3rd series of batch experiments with Ti foil/Ti coarse powder and synthetic Na-montmorillonite at 80 °C was conducted for periods of
7 and 20 months. The solids were subsequently analysed by X-ray absorption spectroscopy (XANES and EXAFS). Furthermore, hydrothermal tests at 200 °C with the same materials were carried out for 1 and 4 months. The solids from those tests were subsequently analysed by XRD, SEM and NMR spectroscopy. Finally, the spectroscopic analysis (XANES, EXAFS) of natural clays, studied in the 1st series, was refined.

The report is organised as follows: In Chapter 2, the refined spectroscopic analysis of titanium in natural clays is presented. Chapter 3 documents the hydrothermal tests conducted at 200 °C. Chapter 4 reports on the batch experiments performed at 80 °C. The conclusions of the studies and their implications for the bentonite buffer within the KBS-3H concept are presented in Chapter 5.
2 THE NATURE OF TITANIUM IN NATURAL CLAYS

2.1 Experimental

Wyoming bentonite (‘MX-80’, American Colloid Co.) was obtained within the framework of the Alternative Buffer Material (ABM) project (Svensson et al. 2011). Both, the raw material and the separated clay fraction were used for subsequent spectroscopic analysis. The clay fraction in homoionised Na-form was prepared according to the purification procedure described in Karnland et al. (2006). Despite of rigorous purification procedure, purified MX-80 contained in addition to smectite, also trace amounts of mineral impurities as well as organic matter. Titanium was not enriched nor decreased in the clay fraction (Table 2-1) indicating that it was either structurally bound within montmorillonite crystal framework or present as clay-sized accessory minerals.

Besides MX-80 bentonite, different well characterised reference clay materials were analysed with regard to the coordinative environment of Ti. The selected materials were a high Ti bentonite from the Czech Republic (Rokle), Illite du Puy from France and Opalinus Clay from Switzerland.

The Rokle material originates from argillised volcanoclastic accumulations of Tertiary age (Konta 1986) located in the north Bohemian volcanic area in the northwest of Prague (Czech Republic). The Rokle material was obtained within the framework of the Alternative Buffer Material (ABM) project (Svensson et al. 2011) and used in this study as received.

Illite ‘du Puy’ clay material originating from a geological clay deposit located in the region of Le-Puyen-Velay (Haute-Loire) in France was provided by the Waste Management Laboratory of Paul Scherrer Institute (Villigen Switzerland). The illite material was conditioned by repeated re-suspension in 1M NaCl solutions to remove soluble salts and less soluble minerals such as calcite, and to transfer the clay into its homo-ionic Na-form. For storage, the conditioned clay was freeze dried after washing with Milli-Q water to remove excess electrolytes. Further details regarding location of the clay rock deposit, pretreatment and chemical as well as mineralogical characterization can be found elsewhere (Gabis 1958; Bradbury & Baeyens 2009; Glaus et al. 2010). As documented by Glaus et al. (2010), titanium concentration was not affected by the extensive preconditioning procedures, again pointing towards structurally bound Ti in the illite or to the existence of highly insoluble mineral phases in association with the clay particles.

Opalinus Clay rock material was obtained from the Mont-Terri underground rock laboratory (URL) located in the NW of Switzerland (Thury and Bossart 1999). Research galleries have been excavated into the Early Dogger Opalinus Clay Rock formation (Thury & Bossart 1999). The clay content of the rock formation varies from 40% to 80%, being complemented mainly by quartz, calcite, siderite, pyrite, or feldspar. Details concerning mineralogy and chemical characteristics can be found elsewhere (Thury 2002).
The total geogenic Ti content of these four natural analogue materials was measured by energy-dispersive X-ray fluorescence analysis using a Spectro X-LAB 2000 spectrometer (SPECTRO Analytical Instruments). To minimize matrix effects, the clay materials were diluted with wax (Licowax C, HOECHST) prior to pellet production. Ti content was calculated using the fundamental parameter method in order to minimize effects of the variations in the different matrix compositions. Obtained total Ti concentrations and comparisons to literature values are given in Table 2-1. The obtained concentrations show good agreement with literature values except for the MX-80 material where a somewhat lower Ti concentration was obtained.

### 2.2 Spectroscopic results

The XANES spectra of the four natural analogue materials and the corresponding zoom-in of the pre-edge region are shown in Figure 2-1. The features of the main edge are predominately caused by multiple scattering phenomena and therefore closely linked to the molecular geometry of the Ti atoms (e.g., Ti-O bond length and bond angles). Complementary, the pre-edge features indicate electronic excitations probing the characteristics of the molecular bonds formed by Ti. Normalized intensities in combination with the resonance energies of these pre-edge features are closely related to coordinative distortions and oxidation state (Waychunas 1987; Farges 1996; Farges et al. 1997).

For all samples, the main edge energy is similar and indicative of Ti being present as Ti$^{4+}$. Further, mean positions and intensities point towards a common six-fold, octahedral coordination. However, despite identical Ti$^{4+}$ oxidation state and octahedral coordination, based on their pre-edge characteristics, the recorded four spectra of the natural Ti containing clay materials can be readily divided into two groups. Within each group, high spectral similarities are observed. The Ti K-edge XANES obtained for the Rokle and the OPA clay rock samples are in close agreement with anatase (TiO$_2$ with tetragonal crystal symmetry), as shown in Figure 2-1. The pre-edge features and the

### Table 2-1: Total geogenic Ti content of natural clay materials.

<table>
<thead>
<tr>
<th>Clay Material</th>
<th>Ti content (as wt% TiO$_2$)</th>
<th>Method and reference</th>
<th>Samples used in present study (wt% TiO$_2$ by XRF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial MX-80</td>
<td>0.15</td>
<td>ICP-AES (Wersin et al. 2010)</td>
<td>0.09</td>
</tr>
<tr>
<td>Purified MX-80</td>
<td>0.14</td>
<td>ICP-AES (Wersin et al. 2010)</td>
<td>n.d.</td>
</tr>
<tr>
<td>Illite du Puy raw product</td>
<td>0.73</td>
<td>ICP-AES (Glaus et al. 2010)</td>
<td>n.d.</td>
</tr>
<tr>
<td>Illite du Puy cond. to Na$^+$-form</td>
<td>0.72</td>
<td>ICP-AES (Glaus et al. 2010)</td>
<td>0.71</td>
</tr>
<tr>
<td>Rokle</td>
<td>3.87</td>
<td>ICP-AES (Svensson et al. 2011)</td>
<td>3.88</td>
</tr>
<tr>
<td>Opalinus Clay</td>
<td>0.95+/-0.1</td>
<td>ICP-AES (Techer et al. 2009)</td>
<td>0.76</td>
</tr>
</tbody>
</table>
envelope of the main edge are indicative of crystalline particles. A significant fraction of amorphous or nano-sized TiO$_2$ in the natural materials can be excluded due to the absence of an additional characteristic resonance at 4972 eV typical for non-crystalline or nano-crystalline TiO$_2$ (Fernandez-Garcia et al. 2007; Flank et al. 2009). Note that the spectroscopic signature of the tetragonal TiO$_2$ polymorph rutile is not compatible with those of Rokle and OPA, as already shown in Wersin et al. (2010). The second group including MX-80 and Illite du Puy exhibits a strong enhancement of the second pre-edge resonance (at 4971.5 eV), while the intensities of the first and third peak nearly vanish. Such an increase in intensity of the central pre-edge feature without a significant shift of its resonance energy can be attributed to an increased distortion of the octahedral coordination of Ti (Waychunas 1987; Behrens et al. 1991; Farges 1996; Jiang et al. 2007). Ti species in MX-80 and Illite du Puy have a similar electronic structure (and similar degree of reduced symmetry) as Ti in titanite, but bond distances deviate as indicated by the difference in the multiple scattering features.

**Figure 2-1.** XANES spectra showing pre-edge structure of Ti of four natural clays; left: complete spectra; right: close-up of pre-edge spectra.

Figure 2-2 depicts the full EXAFS spectra measured for Ti in both, the Rokle and the OPA material. For comparison, the spectrum of micro-crystalline anatase (TiO$_2$) is included in Figure 2-2 as well. The close agreement is readily apparent. Accordingly, the predominant molecular-level coordination of Ti in these two natural clay rock
materials is in the form of anatase. Compared to the synthetic reference material, only a slight reduction in the EXAFS amplitude can be noticed. This observation is consistent with a moderately increased structural disorder of the anatase in the natural samples as compared to the synthetic material. Consistent with the pre-edge and XANES analysis discussed before, the presence of a significant fraction of amorphous Ti-oxide can be excluded. The existence of anatase is further confirmed by synchrotron-based powder X-ray diffraction measurements of the Rokle and OPA material. The corresponding XRD pattern of the Rokle sample is illustrated in Figure 2-3. A clear trace of the expected anatase pattern can be recognized in the diffractogram despite the pronounced mineralogical complexity. While not as evident due to the reduced total Ti concentration, there is ample evidence for the presence of anatase in the OPA sample as well (data not shown).

![EXAFS spectra of Rokle bentonite and Opalinus Clay in comparison with that of micro-crystalline anatase.](Image)

**Figure 2-2.** EXAFS spectra of Rokle bentonite and Opalinus Clay in comparison with that of micro-crystalline anatase.
Figure 2-3. XRD pattern of Rokle bentonite in comparison with that of anatase. Monochromatic synchrotron radiation of 16keV (0.7749 Å) delivered by a Si111 double crystal monochromator was used.
3 HYDROTHERMAL TESTS AT 200 °C

3.1 Scope

The purpose of these high temperature tests was to accelerate corrosion and Ti-clay interactions and thus to complement the batch experiments, which were performed at lower temperatures (Wersin et al. 2010 and chapter 4). In addition, the suitability of NMR as analytical method should be tested. The same types of materials (Ti as foil or coarse powder, synthetic montmorillonite) and same solutions (0.01 M NaCl at different pH conditions) were used, but exposed to a temperature of 200 °C. After reaction the samples were analysed by SEM, XRD and NMR. The analysis by X-ray absorption spectroscopy (XANES) was also attempted, but because of insufficient separation of the clay from the Ti particles, no meaningful data could be obtained so far (section 5.2).

3.2 Experimental

3.2.1 Synthesis of synthetic montmorillonite

The large scale synthesis of Na-Montmorillonite was performed in acid and fluoride medium according to Reinholdt et al. (2001). To obtain a Na-montmorillonite having the following theoretical formula: Na0.4(Al1.6Mg0.4)Si4O10(OH,F)2, 2760 g of distilled water, 43.40 g of a 5wt% aqueous solution of hydrofluoric acid (HF, 40%; BDH), 8.95 g of sodium acetate (NaCOOCH3, 99%; Fluka), 46.61 g of tetrahydrated magnesium acetate (Mg(COOCH3)2 4H2O, 99%, Fluka), 56.65 g of boehmite (Al2O3, 77wt% Pural SB1; Condea), 130 g of silicon oxide (SiO2, 99.5%, Aerosil 130; Degussa) were mixed. The formed hydrogel was matured under stirring during 2h before being hydrothermally treated at 200 °C for 72h in a PTFE-lined steel autoclave under autogeneous pressure. After cooling to room temperature the solid was recovered by filtration, thoroughly washed with distilled water and dried at 60 °C during 12h. The obtained solid was then ground to a fine powder form. The chemical composition determined by X-ray fluorescence spectrometry and 27Al solid state Nuclear Magnetic Resonance spectroscopy is Na0.34(Al1.49 Mg0.37)(Si3.83Al1.28)O10(OH1.95F0.05).

The BET surface area of the unreacted Na-montmorillonite determined N2 adsorption is 110 m²/g.

3.2.2 Procedure for hydrothermal tests

A set of three sub-series with a total of 9 samples was prepared. Common to all samples, 1 g of Na-montmorillonite was dispersed in 50 mL of a 0.01 M aqueous solution of sodium chloride (NaCl, 99 wt%, Fluka). In order to study the influence of the pH, the pH was adjusted to 2 by using an aqueous solution of hydrochloric acid (HCl, 37 wt%, Fluka), 7 (no addition), and 12 with an aqueous solution of sodium hydroxide (NaOH, 99 wt%, Aldrich).

A first sub-series of three samples were transferred to a PTFE-lined stainless steel autoclave without the addition of Ti and put in an oven at 200 °C for a period of 1 month. To the remaining two sub-series, a titanium source was added. One sub-series of
experiments received coarse titanium powder (325 mesh, 99.5% purity, American Elements), while to a final sub-series titanium foils (0.1 mm thickness, 99.5% purity, American Elements) were added. Prior to the addition of titanium powder (2 g per sample) and titanium foils (2 g) the solutions were flushed under argon for 30 minutes (to eliminate all oxygen present).

A second flush step was performed after adding the titanium powder or foils to the montmorillonite suspensions for a duration of 30 minutes. Finally, the suspensions were transferred into autoclaves at 200 °C for 1 month and 4 months, respectively. All samples prepared for hydrothermal treatment at 200ºC are presented in Table 3-1.

At the end of the hydrothermal treatments, autoclaves were opened and the solutions were centrifuged to recover the solid. Solids were then dried at 60 ºC for 12h before being analysed.

After treatment, all samples were characterized by X-Ray diffraction with an X’Pert Pro diffractometer from Panalytical company employing the Cu Kα (1.5418 Å) radiation produced by an excited copper anticathode. The diffractograms were continuously recorded as the sample and detector rotated at 2θ in the angular range from 3° to 70°. Data obtained were analysed and processed with the software X’Pert HighScore.

The SEM images were collected using a PHILIPS XL30 microscope. Prior analysis, a small amount of the sample was placed on a tablet with carbon adhesive tape. The tablet was then put on an aluminium holder and metallized under vacuum by cathodic pulverization forming a gold nanolayer (10 to 20 nm) on the entire tablet surface.

$^{29}$Si MAS-NMR spectra were obtained on a Bruker MSL-300 spectrometer at 59.63 MHz, 4 kHz spinning speed, 2 $\mu$s excitation pulses ($\pi/2$ pulse width of 4 $\mu$s) and 80 s recycle time. Chemical shifts of silicon were referenced to tetramethylsilane (TMS) using a secondary standard of trimethylsilyl ester of cubic octameric silicate (Q8M8) at -109.7 ppm (the more shielded signal). $^{27}$Al MAS-NMR spectra were obtained on a

**Table 3-1.** Batch samples with synthetic Na-montmorillonite: labelling, titanium source form, temperature, initial pH and reaction time.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Type of Ti (2 g)</th>
<th>T (°C)</th>
<th>pH</th>
<th>Reaction time (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B4</td>
<td>-</td>
<td>200</td>
<td>7</td>
<td>30</td>
</tr>
<tr>
<td>B5</td>
<td>-</td>
<td>200</td>
<td>12</td>
<td>30</td>
</tr>
<tr>
<td>B6</td>
<td>-</td>
<td>200</td>
<td>2</td>
<td>30</td>
</tr>
<tr>
<td>E10</td>
<td>Coarse powder</td>
<td>200</td>
<td>7</td>
<td>30</td>
</tr>
<tr>
<td>E11</td>
<td>Coarse powder</td>
<td>200</td>
<td>12</td>
<td>30</td>
</tr>
<tr>
<td>E12</td>
<td>Coarse powder</td>
<td>200</td>
<td>2</td>
<td>30</td>
</tr>
<tr>
<td>E19</td>
<td>Foil</td>
<td>200</td>
<td>7</td>
<td>120</td>
</tr>
<tr>
<td>E20</td>
<td>Foil</td>
<td>200</td>
<td>12</td>
<td>120</td>
</tr>
<tr>
<td>E21</td>
<td>Foil</td>
<td>200</td>
<td>2</td>
<td>120</td>
</tr>
</tbody>
</table>
Bruker MSL-300 spectrometer at 78.21 MHz, 10 - 12 kHz spinning speed, 0.7 µs excitation pulses (π/2 pulse width of 9 µs for an aqueous solution) and 1 s recycle time.

Chemical shifts of aluminium were referenced to a 1M Al(NO₃)₃ aqueous solution with a chemical shift of 0 ppm.

¹⁹F MAS-NMR spectra were obtained on a Bruker DSX-400 spectrometer at 379.23 MHz with a Hahn echo pulse sequence (π/2 pulse - τ - π pulse - τ - acquisition), 10 kHz spinning speed, π/2 pulse width of 7 µs and 20 s recycle time. The value of τ is synchronized to a rotation period of the spinner (τ = 100 µs). Chemical shifts of fluorine were referenced to liquid CFCl₃ with a chemical shift of 0 ppm. Free Induction Decay (FID) signals were treated after collection following a standard procedure using the software WIN-NMR (Bruker software). The FID signals were smoothed in order to reduce the background noise. Base-line was also corrected if it was necessary.

3.3 Results

3.3.1 Microscopic observations (SEM)

SEM micrographs of Na-montmorillonite after synthesis are shown with increasing magnification in Figures 3-1 a-c. The particles exhibit the characteristic gypsum like morphology of 2:1 phyllosilicates. Corresponding images after one month of aging are depicted in Figure 3-1 for treatment under (d) acid, (e) neutral, and (f) alkaline conditions.
Figure 3-1. SEM micrographs of synthetic Na-montmorillonite. Unreacted material shown with increasing magnification in (a) to (c). Aged material after one month in acidic conditions (d), neutral conditions (e) and alkaline conditions (f).

It is worth noting that for the clay material aged under alkaline conditions, the surface of the clay particles appears to be scratched, indicating that the alkaline medium may have affected the particle structure. For the case of aging in the presence of titanium powder for a period of 1 month, no significant morphological change is observed, whatever the pH (Figure 3-2). However, by using coarse powder of metallic titanium as Ti source, corresponding Ti particles are detected frequently (arrow in Figure 3-2). EDX analysis allowed recording distribution maps of titanium within the montmorillonite sample (images not shown). It is evidenced, that titanium and montmorillonite particles are completely separated. No diffuse distribution of Ti in the clay particles could be detected. However, with a Ti detection limit of 10000 ppm, the SEM-EDX technique has to be considered of limited sensitivity. Due to the low corrosion rates of metallic Ti,
only trace concentration of reacted Ti can be expected to be found in the clay material. The presence of titanium particles means that the used separation method was not successful, preventing XAS analysis of these samples. In samples for which titanium foils were introduced as Ti source, down to the detection limit of SEM-EDX, no titanium was measured.

3.3.2 Crystallographic observations (XRD)

The laboratory based X-ray diffraction results of pristine Na-montmorillonite and after different treatments are shown in Figure 3-3. The pristine Na-montmorillonite after synthesis exhibits the expected reflections of the (001), (110; 020), (005), (130, 200) (210 and (060) planes (Reinholdt et al. 2001). The \(d_{001}\) value is equal to 15.3 Å whereas the \(d_{060}\) value is equal to 1.49 Å, as expected for a di-octahedral phyllosilicate. After aging for 1 month at 200 °C under neutral conditions, a decrease in intensity and a widening of the (001) reflection is exhibited. This observation can be attributed to a disorganisation of the layers. Aging under acid conditions for 1 months results in a slight shift of the (001) reflection toward higher angle, which is attributed to a partial substitution of protons for sodium cations. In the case of alkaline treatment, several modifications can be recognized. First, the reflection of the (001) plane is slightly shifted towards higher angles. This is due to a less important hydration sphere around the interlayer cations (in the present case sodium). In addition, a reduction of the di-octahedral character (20 = 61°, \(d_{060} = 1.49\) Å) and an increase of the tri-octahedral one (20 = 60°, \(d_{060} = 1.52\) Å) is observed. The tri-octahedral appearance in alkaline condition has already been observed (Finney et al. 2006; Becerro et al. 2009). Some sharp peaks are also observed, which are related to the presence of NaCl which was not fully removed by washing. It can be concluded that the hydrothermal treatment does not induce detectable structural modifications at acid or neutral pH. In contrast, aging under alkaline conditions leads to structural changes.

The XRD patterns of the samples after one month of treatment in the presence of titanium powder are similar to the blank samples (Figure 3-3a, c). In line with the
detection of Ti particles by SEM, reflections of metallic Ti are observed in the XRD pattern.

After an extended hydrothermal treatment of 4 months in the presence of titanium foils, differences develop. Indeed, the X-ray diffraction pattern (Figure 3-3d) display significant changes compared to pristine montmorillonite. A shift of the (001) reflection toward higher angles is observed on the diffractogram of sample E19, corresponding to a decrease of the $d_{001}$ spacing (from 15.3Å to 13.6Å). Moreover, one additional reflection appears at 4.1 degrees two theta (with an associated periodicity of 21.6Å). This reflection may be attributed to either the intercalation of one species or to an increasing disorder in the layer stacking. The first hypothesis can be rejected as under the present experimental conditions no large polycations based on titanium (such as $\{[(TiO)_{8}(OH)_{12}]^{4+}\}$) can be formed. Besides the (hkl) reflections attributed to Na-montmorillonite, the diffractogram of the sample treated under high pH conditions shows a series of narrow peaks corresponding to a well crystallized phase, this latter being also present in the XRD pattern of the blank sample prepared in the same conditions (not shown). This new pattern is consistent with the main reflections of analcime (NaAlSi$_2$O$_6$:H$_2$O), a zeolite mineral. The transformation of components of bentonite into zeolite upon alkaline treatment has previously been reported in the literature (Ruiz et al., 1997).
Figure 3-3. Comparison between the XRD patterns of pristine montmorillonite sample (a), aged sample without Ti after 1 month at 200 °C (b), aged sample in the presence of Ti grains after 1 month at 200 °C (c), and aged sample in the presence of Ti foil after 4 month at 200 °C (d).
3.3.3 Molecular level observations (NMR)

The $^{29}$Si MAS NMR spectrum of the reference-montmorillonite (Figure 3-4) displays resonances corresponding to Si($n$Al) ($n$ ranges from 0 to 3) environments where $n$ represents the number of tetrahedral Al atoms that are next-nearest neighbours of Si. The main resonance with a chemical shift of $\delta = -93.9$ ppm is attributed to a Si(0Al) type environment where a given Si is surrounded by three Si in the tetrahedral sheet as expected for a montmorillonite. The shoulder with a chemical shift at $\delta = -88.6$ ppm corresponds to a Si(1Al) type environment, representing a single Si-Al substitution in one of the edge shared next-nearest tetrahedral sites. The large resonance centered around $\delta = -110.5$ ppm is characteristic of disordered (SiO$_4$)$_n$ entities and indicates the presence of small amounts of amorphous SiO$_4$ clusters in the system (Reinholdt et al. 2001).

$^{29}$Si NMR

![Graph showing decomposition of the $^{29}$Si MAS NMR spectrum of the pristine Na-montmorillonite (upper) and the reacted montmorillonite after one month at different conditions.]

Figure 3-4. Decomposition of the $^{29}$Si MAS NMR spectrum of the pristine Na-montmorillonite (upper) and the reacted montmorillonite after one month at different conditions.
In the case of the clay material aged during one month without the addition of Ti under neutral and acid conditions, the same resonances are observed. Accordingly, under these conditions, no structural changes are detected within the sensitivity of the employed NMR technique. In contrast, the situation changes by aging the clay in alkaline solutions. The intensity of the resonance around -110 ppm is significantly enhanced compared to the pristine Na-montmorillonite. Similar, the resonance around δ = -88.6 ppm is also enhanced. Both observations underline that the alkaline treatment leads to structural modifications. This finding is in line with the observations made by X-Ray diffraction as discussed above. Based on analysis of $^{29}$Si MAS NMR spectra, the addition of Ti powder or Ti foils does not induce changes in the clay structure measurable by $^{29}$Si MAS NMR.

The presence of Al in the octahedral or tetrahedral sheet can be determined by $^{27}$Al MAS NMR spectroscopy (Figure 3-5). For the pristine montmorillonite, two resonances are observed. The main resonance with a chemical shift of around 5 ppm is attributed to octahedral Al (Al_{VI}), while the second feature of around 70 ppm is attributed to tetrahedral Al (Al_{IV}). This result supports the data obtained by $^{29}$Si MAS NMR and confirms Al-for-Si substitutions in the tetrahedral sheet. It is worth noting that the amount of Al in the tetrahedral sheet is considerably lower than the one in octahedral sheet, as expected. A comparison between the spectra of the blank samples aged in a NaCl or HCl solution and the pristine montmorillonite shows no detectable differences. During aging in a high pH NaOH solution, however, the detected amount of tetrahedral aluminium is enhanced. The alkaline treatment seems to affect the Al_{IV} and Al_{VI} proportions. This observation is in line with the evolution of the di- and tri-octahedral character by X-Ray diffraction. A third resonance with a chemical shift at δ = 57.8 ppm is attributed to Al_{IV}, but with a different local environment than the one observed at δ = 69.5 ppm. Summarizing the $^{27}$Al MAS NMR spectroscopy results, the structural changes of the montmorillonite on the molecular level could be established. For all chemical conditions and reaction times employed, the reaction with corrosion products of added titanium sources does not lead to detectable modifications in the aluminium environment.
By substituting fluoride ions for hydroxyl groups, $^{19}$F MAS NMR spectroscopy is a powerful tool to obtain information on the octahedral sheet occupancy. The $^{19}$F MAS NMR spectrum of Na-Montmorillonite displays several peaks with characteristic chemical shifts, each corresponding to a particular fluorine environment (Figure 3-6). The main observed resonance with a chemical shift of $\delta = -151.8$ ppm is attributed to a Mg-Al-$\square$ environment whereas the two additional resonances at $\delta = -175.5$ ppm and at $\delta = -130.1$ ppm are typical of a Mg-Mg-Mg environment and an Al-Al-$\square$ environment, respectively (the symbol $\square$ denotes a vacancy). In the case of samples aged without Ti addition in NaCl and/or HCl solution the basic resonances of the pristine material are observed. However the intensity ratios of the resonances are different. Compared to pristine Na-montmorillonite, the $\delta = -175.5$ ppm resonance is less pronounced for aged samples, while the resonance at $\delta = -130.1$ ppm gains in intensity due to hydrothermal treatment. In addition, in all treated samples, a new resonance appears at $\delta = -121.6$ ppm. This signature possibly represents an aqueous species due to a release of anionic fluorine into the solution. In the case of blank samples in NaOH solution, the resonance at $\delta = -130.6$ ppm is less intense than in the neutral and acidic blank samples, the $\delta = \dots$
-175.5 ppm resonance intensity is similar to the one at δ = -151.8 ppm showing that there is a modification of the fluorine environment.

After contact with titanium powder or titanium foils no differences can be observed for samples in NaCl or HCl solution when comparing with the corresponding spectra of Ti-free systems. The same observations are made for the alkaline treatment, however, one difference is the absence of the resonance at δ = -121.6 ppm.

Concerning the $^{19}$F solid-state NMR, we can conclude that the three treatments have an impact on the fluorine environment. The alkaline treatment influences the intensity of the different resonances of the spectrum (Figure 3-6). We can notice the δ = -121.6 ppm resonance in each blank samples and this with no relation with the kind of treatment it undergoes. However, this peak was observed to disappear after adding titanium in the solution. This may be attributed to the formation of a complex based on titanium and fluoride, but in order to support this hypothesis, further experiments would have to be carried out.

*Figure 3-6.* $^{19}$F NMR spectra of the pristine Na-montmorillonite (upper) and the reacted montmorillonite after one month at different conditions.
4 BATCH EXPERIMENTS AT 80 °C

4.1 Scope

The batch experiments on Ti-clay interaction constitute the main part of the experimental programme that was initiated in 2007. The list of all experiments (termed “samples”) since that time is given in Table 4-1. Here we report on the samples analysed during 2013-2015.

4.2 Experimental procedures

4.2.1 Experimental conditions

Sample preparation (3rd series)

Two grams of synthetic, Ti-free montmorillonite clay were weighed and dispersed into 80 mL of 0.01 M NaCl (99.9%, BDH Prolabo) solution. The suspension was transferred to a glovebox, and bubbled with N₂ for 30 minutes. For the investigations of the Ti reaction with synthetic clay, sample preparations were done inside an acrylic glovebox flushed with N₂. As a first of two alternative procedures, approximately 2 g of coarse Ti powder (325 mesh, 99.9% purity, American Elements) was added to the suspension. For the second alternative 2 g of Ti foil with specific surface area of 0.004 m²/g (0.1 mm thickness, 99.5% purity, American Elements) were added to the suspension. The Ti foil was etched in 1 M HCl overnight and flushed with ethanol and de-aired de-ionized water before adding it to the suspension. In addition, blank samples without addition of titanium were prepared. Then the vessels were closed, the stoppers were tightened with Teflon tape, the sample vessels were wrapped in aluminium foil to exclude the effect of light, and placed in a heater at 80 °C. The experimental settings for the samples reported here, and also all prepared samples from 1st, 2nd and 3rd series of Ti-clay interaction tests are summarised in Table 4-1.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Label</th>
<th>Type of montmorillonite (2 g)</th>
<th>Type of Ti present (2 g)</th>
<th>Dialysis bag</th>
<th>T (°C)</th>
<th>pH adjustment</th>
<th>Reaction time (months)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>TiNP-C-D-bulk</td>
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<td>nanopowder</td>
<td>yes</td>
<td>room</td>
<td>none</td>
<td>4*</td>
</tr>
<tr>
<td>2.</td>
<td>TiNP-C-D-bulk2</td>
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<td>yes</td>
<td>room</td>
<td>none</td>
<td>17.5*</td>
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<tr>
<td>3.</td>
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<td>yes</td>
<td>room</td>
<td>2.0</td>
<td>4*</td>
</tr>
<tr>
<td>4.</td>
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<td>yes</td>
<td>room</td>
<td>12.4</td>
<td>4*</td>
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<tr>
<td>5.</td>
<td>C-D-bulk</td>
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<td>-</td>
<td>yes</td>
<td>room</td>
<td>none</td>
<td>ongoing</td>
</tr>
<tr>
<td>6.</td>
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<td>nanopowder</td>
<td>no</td>
<td>room</td>
<td>none</td>
<td>4*</td>
</tr>
<tr>
<td>7.</td>
<td>C-D-pH2</td>
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<td>-</td>
<td>yes</td>
<td>room</td>
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</tr>
<tr>
<td>8.</td>
<td>C-D-pH12</td>
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<td>-</td>
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<td>room</td>
<td>12.4</td>
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</tr>
<tr>
<td>9.</td>
<td>C-D-bulk2</td>
<td>natural</td>
<td>-</td>
<td>yes</td>
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<td>none</td>
<td>ongoing</td>
</tr>
<tr>
<td>10.</td>
<td>TiFO-C-bulk</td>
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<td>no</td>
<td>room</td>
<td>none</td>
<td>4*</td>
</tr>
<tr>
<td>11.</td>
<td>TiFO-C-bulk2</td>
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<td>foil</td>
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<td>56</td>
</tr>
<tr>
<td>12.</td>
<td>TiFO-C-pH2</td>
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<td>foil</td>
<td>no</td>
<td>room</td>
<td>2.1</td>
<td>69</td>
</tr>
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<td>13.</td>
<td>TiFO-C-pH12</td>
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<td>69</td>
</tr>
<tr>
<td>14.</td>
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<td>yes</td>
<td>room</td>
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</tr>
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<td>15.</td>
<td>TiNP-C-D-pH2/2</td>
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<td>ongoing</td>
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<td>room</td>
<td>12.4</td>
<td>56</td>
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</table>

Table 4-1. Experimental settings for Ti-bentonite batch tests (1st series, samples 1-16; 2nd series, samples 17-30; and 3rd series, samples 31-36.)
<table>
<thead>
<tr>
<th>Sample number</th>
<th>Label</th>
<th>Type of montmorillonite (2 g)</th>
<th>Type of Ti present (2 g)</th>
<th>Dialysis bag</th>
<th>T (°C)</th>
<th>pH adjustment</th>
<th>Reaction time (months)</th>
</tr>
</thead>
<tbody>
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<td>17</td>
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<td>nanopowder</td>
<td>yes</td>
<td>80</td>
<td>none</td>
<td>4.5*</td>
</tr>
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<td>nanopowder</td>
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<td>80</td>
<td>none</td>
<td>ongoing</td>
</tr>
<tr>
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<td>nanopowder</td>
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<td>2.00</td>
<td>4.5*</td>
</tr>
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<td>nanopowder</td>
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</tr>
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<td>80</td>
<td>none</td>
<td>4.5*</td>
</tr>
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<td>none</td>
<td>56</td>
</tr>
<tr>
<td>23</td>
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<td>ongoing</td>
</tr>
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<td>SC-D-80-pH12</td>
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<td>80</td>
<td>12.00</td>
<td>ongoing</td>
</tr>
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<td>nanopowder</td>
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</tr>
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<td>25</td>
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<td>ongoing</td>
</tr>
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<td>nanopowder</td>
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<td>25</td>
<td>none</td>
<td>ongoing</td>
</tr>
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<td>-</td>
<td>no</td>
<td>80</td>
<td>none</td>
<td>7</td>
</tr>
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<td>no</td>
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</tr>
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<td>TiFO-SC-80-bulk</td>
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<td>foil</td>
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<td>20</td>
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<tr>
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<td>coarse powder</td>
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<td>20</td>
</tr>
</tbody>
</table>

*Results reported in Wersin et al. (2010).

Sample dismantling

1st series (samples 11, 12, 13 and 16)

Ti-clay interaction sample dismantling of the 1st batch test series was done in the laboratory air.

After a reaction period of 56 months (samples 11 and 16) or 69 months (samples 12 and 13) samples were dismantled by removing the titanium foil or dialysis bag with Ti nanopowder inside. After removal of titanium, the clay suspensions were centrifuged for 2.5 h (samples 12 and 13) or ~5 h (samples 11 and 16) in 11 000 rpm, and the solution was separated from the sedimented clay.

2nd series (samples 22 and 27)

Ti-clay interaction sample dismantling of the 2nd batch test series was done inside an acrylic glovebox flushed with N2 (except centrifugations).

After a reaction period of 56 months (sample 22) or 55 months (sample 27), samples were dismantled by removing the dialysis bag containing Ti nanopowder (sample 27) or by removing part of the Ti nanopowder manually with assistance of centrifugation (1460 rpm, 5 minutes) (sample 22). However, in case of sample 22, a lot of the Ti nanopowder was left to the sample. After removal of part of the titanium nanopowder in sample 22, the clay suspension was centrifuged for 15 min in 11 000 rpm, and the solution was separated from the sedimented clay.
3rd series (samples 31-36)

Ti-clay interaction sample dismantling of the 3rd batch test series was done inside acrylic glovebox flushed with N2 (except centrifugations).

After a reaction period of 7 months (samples 31, 32 and 35) or 20 months (samples 33, 34 and 36), samples were dismantled by removing the titanium foil or separating the coarse Ti powder from the clay by means of centrifugation (1460 rpm, 5 minutes; sedimenting particles larger than 1µm).

After removal of titanium (foils or coarse powder), the supernatant clay suspensions were centrifuged for 15 min in 11 000 rpm, and the solution was separated from the sedimented clay. After centrifugation, metallic Ti was still visible in the bottom of the centrifugation tubes of samples 35 and 36. Apparently the coarse Ti powder (325 mesh) used in two samples of the 3rd sample series (without dialysis bags) contained also a fraction of smaller Ti metal particles, which could not be separated completely from the synthetic montmorillonite by a single centrifugation step. Hence, the top portions of the sediment in samples 35 and 36 were scooped off by a laboratory spoon for re-suspension and repeated centrifugation.

All samples

All sedimented fractions were washed with pure ethanol and sent in the moist state to PSI. Subsequent spectroscopic analyses at PSI were performed on the moist sediment samples (section 4.1.2).

Solution pH was measured after the separation of sedimented clay inside glovebox (except samples from 1st batch test series were measured in the laboratory air) and electric conductivity (EC) of the solution in the laboratory air (see Table 4-2). Solutions were filtered through a 0.2 µm pore size membrane filter, and analysed for Ti, Ca, Mg, K, Na, Al, Si and Fe at Labtium Oy with ICP-AES.

Visual observations

After dismantling, it was noticed that Ti-foils in samples 32 and 33 had dark spots unlike the Ti-foils in samples 11, 12 and 13 (Figure 4-1). In addition, Ti-foils in sample 13 appeared overall slightly darker than in samples 11 and 12 (Figure 4-1).

The appearance of Ti-foils in samples 13, 32 and 33 could indicate that Ti-foil had reacted in some extent during the experiment (see Figure 4-1). From the Ti-foil containing samples which were dismantled, samples 11, 12 and 13 were kept in room temperature and laboratory air during the experiment whereas samples 32 and 33 were kept at 80°C in a N2-glovebox. The pH of samples 11, 32 and 33 was not adjusted, but samples 12 and 13 were adjusted to pH’s 2.1 and 12.5, respectively, at the beginning of the experiment. Hence, the elevated temperature (80 °C) and alkaline conditions may induce reactions in Ti-foils.
4.2.2 Spectroscopy of natural clay samples and batch samples

Synchrotron-based X-ray absorption near edge structure spectroscopy (XANES) and extended X-ray absorption fine structure spectroscopy (EXAFS) were conducted at the microXAS beamline (X05LA) of the Swiss Light Source. Insertion device radiation was monochromatized using Si(111) crystals in fixed exit geometry. The energy calibration was carried out repeatedly using a metallic Ti(0) reference foil. Additional titanium reference materials included the two polymorphs of TiO₂, rutile and anatase, as well as the calcium titanium nesosilicate titanite (CaTiSiO₅). The additional reference materials were measured in transmission after appropriate dilution in boron nitride.

According to their low Ti concentration, the natural analogue materials as well as the synthetic montmorillonite samples had to be measured in fluorescence mode. Fluorescence radiation was detected by a single element Si drift diode (SDD) detector (Ketek®). To minimize the absorption of the emitted Ti-Kα fluorescence radiation (4.5108, 4.5049 keV) by the ambient air, the sample to detector path was purged with He (purging collimator nose attached to the Ketek detector).
All samples were investigated as received without any further treatment. The dry natural analogue clay materials and the humid synthetic clay mineral samples (residual moisture after centrifugation) were loaded in dedicated sample holders and closed up with Kapton films.

Of the 11 samples sent by B+Tech, only samples 31, 32, 33, 35 and 36 were analysed by EXAFS spectroscopy. The other samples displayed too high background Ti in the clay (samples 11, 12, 13, 16 with natural clay) or too low transferred Ti amounts (sample 22). Samples 31 and 34, where no Ti had been added, showed very low but detectable Ti in the synthetic montmorillonite (data not shown) confirming that the synthesis procedure was appropriate. Note that after the 2nd series (samples 17-30) a new detector with better resolution was installed, enabling Ti measurements at lower contents.

For the measurements of the reference materials and the natural analogue samples, a slit beam size of 500 x 500 mm$^2$ was employed. Due to the sporadic occurrence of metallic Ti abrasion particles within the autoclaved synthetic clay samples, these samples had to be analyzed using a microfocused beam (approximately 5 μm [hor] x 3 μm [ver]). Most appropriate sample volumes free of abrasion particles were identified based on micro-XRF mapping prior to the collection of micro-XAS data from appropriate locations. Processing of the raw EXAFS data and subsequent analysis were carried out using the DEMETER package (Ravel & Newville 2005). Measured EXAFS spectra were compared to simulated spectra using the FEFF8 ab initio EXAFS software package (Rehr et al. 1992; Rehr & Albers 2000; Rehr et al. 2009). For the EXAFS simulations related to the experimental Ti-synthetic clay system, the amplitude reduction factor and Debye–Waller factors were estimated based on the analysis of the Ti reference compounds.

For the four natural analogue materials, synchrotron-based powder X-ray diffraction analysis was performed at the Materials Science beamline of the Swiss Light Source following their standard protocol.

### 4.3 Results

#### 4.3.1 Wet chemistry

The pH, electric conductivity (EC) and ICP-AES analysis results of separated solution phases of dismantled samples are presented in Table 4-2. Therein, also the initial pH and EC of samples right after preparation (measured before addition of Ti) are presented.

In general, the pH- and EC-values of clay-containing samples had changed only slightly during reaction period of the experiments. The samples, which had adjusted pH (2 or 12) showed higher EC-values and Na contents in the separated solution phases than the samples without pH-adjusting, which is considered to be caused by the NaOH or HCl added during the pH adjusting. The Si, Al and Mg contents were elevated in the pH-adjusted alkaline samples, which may indicate dissolution of clay mineral. Of the
dismantled samples, only sample 13 showed a slightly elevated Ti level in chemical composition of the separated solution phase (with the techniques used). The method detection limits vary between samples, which were analysed on different occasions (samples 11, 16, 31, 32 and 35 were dismantled and analyzed on a different occasion than the rest of the samples) (Table 4-2).

### 4.3.2 Spectroscopy

Figure 4-1 and 4-2 depict the X-ray absorption spectroscopic results detailing the molecular-level environment of Ti after corrosion and subsequent reaction with the synthetic montmorillonite. Figure 4-1 focuses on the XANES results while the EXAFS data are shown in Figure 4-2. The two samples which differ only in reaction times exhibit distinct and nearly identical pre-edge signatures (Figure 4-1, bottom). Comparing with reference compounds and natural analogue materials (Figure 4-1, top), the pre-edge signature of the Ti reacted with clay are indicating an octahedral coordinated, moderately distorted Ti site. Based on this observation, the formation of nano-crystalline or amorphous (‘gel-like’), high symmetry Ti-oxide phases like anatase or rutile or Ti-Fe oxides phases can be ruled out. Further, the Ti substitution in tetrahedral clay sites is not compatible with the pre-edge feature either.

**Table 4-2.** pH, electric conductivity and chemical composition of separated solution phase from dismantled 80 °C Ti-clay interaction samples.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Initial pH</th>
<th>Final pH</th>
<th>Initial EC (µS/cm)</th>
<th>Final EC (µS/cm)</th>
<th>Ti (mg/l)</th>
<th>Ca (mg/l)</th>
<th>Mg (mg/l)</th>
<th>K (mg/l)</th>
<th>Na (mg/l)</th>
<th>Al (mg/l)</th>
<th>Si (mg/l)</th>
<th>Fe (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.</td>
<td>Nd</td>
<td>7.39</td>
<td>nd</td>
<td>1199</td>
<td>&lt;20</td>
<td>0.45</td>
<td>3.85</td>
<td>1.13</td>
<td>283</td>
<td>22.90</td>
<td>68</td>
<td>5.36</td>
</tr>
<tr>
<td>12.</td>
<td>2.1</td>
<td>3.15</td>
<td>nd</td>
<td>3060</td>
<td>&lt;0.01</td>
<td>0.56</td>
<td>4.26</td>
<td>4.66</td>
<td>539</td>
<td>1.17</td>
<td>101</td>
<td>2.77</td>
</tr>
<tr>
<td>13.</td>
<td>12.5</td>
<td>12.17</td>
<td>nd</td>
<td>8020</td>
<td>0.52</td>
<td>&lt;0.1</td>
<td>6.52</td>
<td>2.77</td>
<td>1404</td>
<td>48.2</td>
<td>823</td>
<td>10.9</td>
</tr>
<tr>
<td>16.</td>
<td>12.4</td>
<td>12.19</td>
<td>nd</td>
<td>6420</td>
<td>&lt;20</td>
<td>0.10</td>
<td>1.31</td>
<td>2.30</td>
<td>1306</td>
<td>9.13</td>
<td>649</td>
<td>2.11</td>
</tr>
<tr>
<td>22.</td>
<td>5.44</td>
<td>6.94</td>
<td>nd</td>
<td>1574</td>
<td>0.02</td>
<td>0.16</td>
<td>19.9</td>
<td>3.39</td>
<td>303</td>
<td>0.24</td>
<td>70.1</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>27.</td>
<td>8.15</td>
<td>4.37</td>
<td>nd</td>
<td>1483</td>
<td>&lt;0.01</td>
<td>0.63</td>
<td>0.22</td>
<td>10.9</td>
<td>283</td>
<td>&lt;0.05</td>
<td>0.43</td>
<td>0.16</td>
</tr>
<tr>
<td>31.</td>
<td>7.10</td>
<td>7.19</td>
<td>1246</td>
<td>1339</td>
<td>&lt;20</td>
<td>0.17</td>
<td>5.70</td>
<td>0.74</td>
<td>262</td>
<td>0.37</td>
<td>71</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>32.</td>
<td>7.14</td>
<td>7.36</td>
<td>1259</td>
<td>1352</td>
<td>&lt;20</td>
<td>0.16</td>
<td>5.68</td>
<td>0.87</td>
<td>264</td>
<td>0.34</td>
<td>68</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>33.</td>
<td>7.12</td>
<td>7.11</td>
<td>1268</td>
<td>1328</td>
<td>&lt;0.01</td>
<td>0.14</td>
<td>5.57</td>
<td>0.68</td>
<td>263</td>
<td>0.28</td>
<td>73.2</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>34.</td>
<td>7.08</td>
<td>7.22</td>
<td>1272</td>
<td>1334</td>
<td>&lt;0.01</td>
<td>0.14</td>
<td>5.73</td>
<td>&lt;0.5</td>
<td>265</td>
<td>0.25</td>
<td>70.3</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>35.</td>
<td>7.09</td>
<td>7.32</td>
<td>1268</td>
<td>1324</td>
<td>&lt;20</td>
<td>0.18</td>
<td>6.09</td>
<td>0.83</td>
<td>255</td>
<td>0.23</td>
<td>60</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>36.</td>
<td>7.07</td>
<td>7.30</td>
<td>1256</td>
<td>1338</td>
<td>&lt;0.01</td>
<td>0.20</td>
<td>5.98</td>
<td>&lt;0.5</td>
<td>266</td>
<td>0.16</td>
<td>64.2</td>
<td>&lt;0.05</td>
</tr>
</tbody>
</table>

*Abbreviations: nd = not determined*
Figure 4-1. XANES spectra (Ti pre-edge structure) of samples 32 and 33 as well as of reference materials; upper: full spectrum; lower: close-up of pre-edge spectra.
The EXAFS data depicted in Figure 4-2 provide an additional piece of critical information. Despite the trace amount of Ti associated with the clay, EXAFS data of reasonable quality could be obtained for two samples. The two spectra show a good agreement. Most relevant, the observed beat pattern is indicative of more than one dominant scattering pair. This observation is further emphasized by the radial distribution function depicted in the inset. In addition to a first coordination sphere, two prominent scattering contributors are located at increased distances. The existence of second/third shell contributions at the observed distances typical for molecular bond distances which preclude outer sphere sorption of being the dominant mode of Ti interaction with the clay. Moreover, the observed magnitude of these higher shell scattering contributions even makes specific (inner-sphere) sorption to clay edge sites or planar sites rather unlikely. This leaves the structural incorporation of Ti into octahedral sites of the clay as a final plausible reaction mechanism. The corresponding reaction mechanism involving Co(II) and Ni(II) was introduced by Charlet and Manceau as ‘neoformation of clays’ (Charlet & Manceau 1994). In addition to a first oxygen shell, two additional scattering contributions are diagnostic for the formation of a phyllosilicate-like local structure: First, a second shell of nearest metal atoms at approximately 3.1Å representing the metal centers of edge-sharing polyhedral in the octahedral sheet. Second, the simultaneous detection of Si (or substituting cations like Al) backscatters at approximately 3.25 Å (Charlet & Manceau 1994). Preliminary EXAFS fitting based on these three characteristic scattering pairs yield already a satisfactory agreement with the experimental data. The mechanism of neoformation of clay-like structures in the present systems is consistent with the finding of structural rearrangements occurring during hydrothermal treatment (at 200°C) as elaborated by XRD and NMR analysis (discussed above). As further indication, the aqueous solutions of the experiments conducted at 80°C contain considerable amounts of Si, Al, and Mg documenting the dissolution of initial clay and being available for the neoformation of clay minerals.
Figure 4-2. EXAFS spectra of samples 32 and 33 in comparison with spectrum obtained from blind prediction (see text).

In order to further test the hypothesis of neoformation of clay minerals, EXAFS simulations have been conducted contrasting the calculated spectrum of several hypothetical reaction products with the experimental data. The closest match between simulation and experimental data was obtained for Ti incorporated in the octahedral sheet surrounded by (Al, Mg)-centered octahedra and vacancies. For illustration, the corresponding hypothetical molecular structure is depicted in Figure 4-3. Obviously, due to the large variability of possible combinations of neighbouring polyhedral (Al$^{3+}$-centered, Mg$^{2+}$-centered or vacancies), no ‘unique’ molecular geometry can be anticipated. The EXAFS spectra obtained for varying occupancies in the edge-shared polyhedral of the octahedral layer (but still maintaining the geometrical conformation of a phyllosilicate-like local structure) yield only subtle changes which cannot be further refined based on the quality and range of the present experimental EXAFS data. However, consistent with the previous conclusions, alternative reaction products such as Ti-oxide formation, Ti substituting in the tetrahedral layer or Ti sorption result all in considerably worse agreement with the experimental spectra.
4.3.3 Amount of Ti in the clay

With aid of $\mu$-XRF spectra, the content of Ti was quantified. The values for samples 32, 33 and 36 are listed in Table 4-3.

**Table 4-3. Ti concentrations of synthetic montmorillonite exposed to Ti foils or grains. Based on $\mu$-XRF spectra; values likely represent upper limits.**

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Ti material</th>
<th>Reaction time (days)</th>
<th>TiO$_2$ content (ppm)</th>
<th>Ti content (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>foil</td>
<td>218</td>
<td>~200</td>
<td>~120</td>
</tr>
<tr>
<td>33</td>
<td>foil</td>
<td>601</td>
<td>~300</td>
<td>~180</td>
</tr>
<tr>
<td>36</td>
<td>coarse powder</td>
<td>612</td>
<td>~250</td>
<td>~150</td>
</tr>
</tbody>
</table>

Because of the low amounts which are rather close to the detection limit the analytical uncertainties are rather large (about a factor of 2). The data likely represent upper limits.
5 DISCUSSION AND CONCLUSIONS

5.1 Nature of titanium in natural bentonites

The titanium in MX-80 bentonite was determined to be 0.09 wt% and 0.08 wt% Ti for the raw and purified clay, respectively (Table 2-1). This suggests that Ti is contained predominantly in the montmorillonite structure, which is confirmed by spectroscopic analysis (Chapter 2). Thus, Ti is likely contained as Ti$^{4+}$ in the octahedral structure. From the chemical data of the purified MX-80, it is estimated that Ti makes up 0.013 atoms per O$_{24}$ cell, which is in line with estimations of Karnland et al. (2006) for MX-80 bentonite.

The amount of titanium in the untreated Rokle bentonite was determined to be 3.9 wt% TiO$_2$ (Table 2-1). This is similar to the amount obtained by Karnland et al. (2006) (4.1 wt%), who reported a value of 4.8% for the purified clay$^1$. These analyses suggested that Ti is contained in the clay structure. Spectroscopic evidence shows however that Ti occurs predominately as separate TiO$_2$ phase (anatase). Evidently, this phase is not separated during purification procedure. There are no indications from XANES and EXAFS of structural Ti in the clay, thus this amount is at maximum $\sim$5% of the total Ti.

According to the data of Karnland et al. (2006) Rokle bentonite has favourable bulk properties, thus high swelling capacity and low hydraulic conductivity, in a similar range as MX-80. This suggests that the content and chemical environment of titanium in the bentonite has no significant effect on these properties.

5.2 Alteration at high temperature

The hydrothermal tests performed at 200°C on blank samples mainly underlined the structural changes occurring in montmorillonite, the alkaline treatments leading to the more pronounced changes. $^{19}$F solid-state NMR was expected to bring insight in the Ti-clay interactions/transfer, but since after contact with titanium powder or titanium foils no clear differences were noticed, no conclusion can be given. Indeed, $^{19}$F is a very sensitive probe to obtain information on the structure of clays (and in particular on the octahedral sheet), but if elements are present as traces (which is probably the case of Ti here) the detection limit is achieved, preventing any conclusion.

The determination of the local environment of Ti by XANES and EXAFS was not possible, because of the presence of Ti particles in the clay which could not be removed during the separation phase. These particles very likely did not originate from the equipment (autoclave, becher) which was free of Ti. Abrasion of the Ti foil might be an explanation although the suspensions were not actively agitated during the hydrothermal treatment.

---

$^1$ Note that in this study we did not purify Rokle bentonite.
5.3 Interaction of Ti with smectite

From visual observations and analyses of the separated solution phase, indications of Ti-reactions were observed only in samples with Ti-foils at elevated temperature (80 °C) or alkaline conditions. It appears that Ti foils were more reactive toward the clay compared to Ti grains (both materials are otherwise the same) because the former indicate slightly higher Ti-transfer rates to the clay. A reason for this may be the etching of the foils with HCl prior to the tests thus removing part of the TiO₂ coating. Note that in the hydrothermal tests the Ti-foils were not acid-treated contrary to the batch tests at 80 °C.

Ti-transfer and corrosion rate

The results from the Ti-clay interaction experiments at 80 °C showed measurable Ti in the clay. Thus, clay samples 32 (after 218 days) and 33 (after 601 days) exposed to Ti foil displayed ∼120 ppm and ∼180 ppm Ti, respectively. Clay sample 36 (612 days) exposed to coarse Ti powder displayed ∼150 ppm Ti.

Note that these estimates are derived from µ-XRF measurements and are rather imprecise (uncertainty about a factor 2), but represent rather upper limits (section 4.2.3). Nevertheless, they may serve to obtain rough upper estimates on Ti-clay transfer rates and corrosion rates.

The mass of Ti accumulated in the clay stemming from the corrosion of the Ti metal is converted to a transfer rate \( R_{tr} \) (g/a) by:

\[
R_{tr} = \frac{f_{Ti} M_{clay}}{t}
\]

where \( f_{Ti} \) is the mass fraction of Ti in the clay (g/g), \( M_{clay} \) is the total mass of the clay (2g) and \( t \) is the reaction time (a). The average corrosion rate \( R_{corr} \) (m/a) is then:

\[
R_{corr} = \frac{R_{tr}}{A_f \rho_{Ti}}
\]

where \( A_f \) (m²) is the surface area of the Ti metal and \( \rho_{Ti} \) the density of Ti (4.504·10⁶ g/m³).

The surface area \( A_f \) of the Ti foils with a thickness of 0.1 mm and a mass of 2 g is calculated to be 0.0089 m². Using the data from sample 32 with \( f_{Ti} = 120 \) ppm, \( t = 218 \) days (0.597 a) one obtains from eq. 5-1 a transfer rate of 4.02·10⁻⁴ g/a. Applying eq. 5-2 this yields and average corrosion rate of 1.00·10⁻⁸ m/a. The same calculation with sample 33 yields a transfer rate of 2.19·10⁻⁴ g/a and a corresponding average corrosion rate of 5.45·10⁻⁹ m/a. This is about a factor of 2 lower than that for shorter-term sample 32.

The corrosion rates can be also estimated for clay sample 36 exposed to coarse Ti powder for 612 days. For this sample, first the surface area of coarse Ti powder with 325 mesh size (∼ 0.044 mm grain size) needs to be estimated. Using the geometrical relationship for spherical particles (e.g. Nicholson 1994) the surface area \( s \) (m²/g) is:
where \( d \) is the Ti particle diameter \((4.4 \cdot 10^{-4} \text{ m})\). This yields a surface area \( (s) \) of \( 3.03 \cdot 10^{-2} \text{ m}^2/\text{g} \) and a total surface area \( (A_t) \) of \( 6.06 \cdot 10^{-2} \text{ m}^2 \). Note that this estimate corresponds to a lower limit because of abrasion and particle size reduction during the experiment. Using eqs. 5-1 and 5-2, one obtains an average corrosion rate of \( 6.56 \cdot 10^{-10} \text{ m/a} \). This is lower than obtained for the samples exposed to foils. One reason for this difference may be that the foils were etched with acid prior to use, but the Ti powder was not.

**Mechanism of Ti uptake in the clay**

Spectroscopic data point to the incorporation of Ti in an octahedral layer structure. Hence, the Ti uptake is explained by the neo-formation of a Ti-enriched phyllosilicate phase. Other pathways, such as formation of \( \text{TiO}_2 \), surface adsorption (by outer or inner sphere complexation) or incorporation in tetrahedral layers can be excluded based on combined XANES and EXAFS data. It should be pointed out that the detailed structure (number of neighbouring Mg, Al and vacancies) could not be unravelled due the limited spectral range and quality as well as the expected variability of the local coordination environments. During the formation of the Ti-enriched phyllosilicate phase, on the atomic level, different combinations of linked Mg\(^{2+}\), Al\(^{3+}\) octahedra and vacancies are chemically feasible and will likely be formed.

Similar uptake mechanisms have been reported for Co(II) and Ni(II) on phyllosilicates (Charlet & Manceau 1994). These authors proposed the formation of local clay mineral like metal clusters based on EXAFS spectroscopy. For Zn(II), the same type of precipitation mechanism on dioctahedral and trioctahedral smectites was postulated (Manceau et al. 2000, Schlegel et al. 2001), which was also based on EXAFS data.

**Uncertainties**

The extent and identification of Ti-clay interaction process are based on three samples exposed to Ti corrosion for a limited timeframe (max. 20 months). It should be noted that the synthetic montmorillonite has small particles with a high BET surface area of 115 \( \text{m}^2/\text{g} \), thus a factor of about 3-4 higher than montmorillonites display in MX-80 bentonite (e.g. Bradbury & Baeyens 2002). This may induce a higher reactivity of the synthetic clay mineral towards Ti. The mechanisms of Ti-transfer, however, are expected to be similar, because it is basically the same mineral (e.g. crystal structure, layer charge).

**Implications for the KBS-3H concept**

In spite of the simplicity of the experimental conditions (batch, synthetic montmorillonite, NaCl solutions), important conclusions with regard to the interaction of a Ti shell with the bentonite buffer can be drawn:

- The Ti released by corrosion reacts with the clay, leading to the incorporation of the metal in a clay-like structure. Thus, the Ti is effectively immobilised by this interaction process, which also strongly suggests that diffusion of Ti through the clay will be effectively restricted, and thus the impact on the buffer performance
will be limited. The used synthetic montmorillonite has small particles with a factor of 3-4 higher surface area than MX-80 montmorillonite. This suggests that the reactivity is higher than in natural montmorillonites.

- The ‘averaged’ coordination environment of Ti could be identified by means of X-ray absorption spectroscopy (XANES and EXAFS). Thereof, it can be inferred that Ti is incorporated in the octahedral layer of a neo-formed, Ti-enriched phyllosilicate phase. A unique molecular structure of the Ti coordination environment in the neo-formed clay could not yet be identified due to limited spectral range and quality as well as chemical and structural disorder inherent to phyllosilicates formed in environmental conditions.

- The Ti-clay interaction process is constrained by the slow corrosion rate of the metal surface which is supported by rough estimates from our data. It is tentatively suggested that corrosion rates will further decrease with increasing interaction times.
REFERENCES


