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Geochemical Evolution of Mg-Bentonite Affected by the Contact of Carbon Steel and a Hydrothermal Gradient

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Abstract: Carbon steel and bentonite are materials selected as engineered barriers for high-level radioactive waste confinement. Their long-term interaction must be evaluated to confirm the barrier's stability. Three laboratory experiments of the carbon steel—Mg-bentonite interaction were conducted for 1, 6, and 22 months under a hydrothermal gradient. Changes in bentonite's water content, specific surface area, and cation exchange capacity were measured. Mineralogy was studied by X-ray diffraction and scanning electron microscopy. The redistribution of aqueous species and the redox state of iron were determined across the bentonite columns. Results indicated water saturation after 22 months. The specific surface area of bentonite was reduced near contact with the steel, while the cation exchange capacity mostly decreased at 3–6 mm from the steel interface. The corrosion rate decreased with time and bentonite enriched in Fe in the first 1.5 mm from the steel contact. The formation of new Fe-bearing minerals, such as di-tri ferri-sudoite, magnetite, hematite, maghemite, lepidocrocite, siderite and ankerite was observed. Aqueous species redistributed in the porewater of bentonite with decreasing concentrations of Fe and Cl as a function of time and increasing concentrations of Na, Ca and SO₄ after 22 months. This occurs under conditions where the bentonite is saturated with Mg, which conditioned the formation and nature of iron clay minerals with time.



Citation: Mota-Heredia, C.; Cuevas, J.; Fernández, R. Geochemical Evolution of Mg-Bentonite Affected by the Contact of Carbon Steel and a Hydrothermal Gradient. *Appl. Sci.* **2024**, *14*, 1259. <https://doi.org/10.3390/app14031259>

Academic Editor: Syed Minhaj Saleem Kazmi

Received: 23 January 2024

Revised: 30 January 2024

Accepted: 1 February 2024

Published: 2 February 2024



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Keywords: Mg-montmorillonite; carbon steel; bentonite; hydrothermal gradient

1. Introduction

Bentonite is a clay material proposed for use as an engineered barrier in deep geological repositories (DGRs). Deep geological disposal consists of isolating high-level radioactive waste (HLRW) from the biosphere by keeping it in underground galleries, normally at a depth of 300 to 1000 m depending on the specific location, within stable host geological formations. The low solubility and solid form of the waste is considered a barrier itself. The waste is encapsulated in a metallic container, a second barrier, that depending on each DGR concept can be made of copper–copper alloys (e.g., Swedish and Finnish concept) or carbon steel (e.g., as considered in Switzerland, the United Kingdom, France or Germany) [1]. The canisters are placed within the galleries and surrounded by barriers of compacted clay, typically composed of bentonite, until all of the galleries are completely sealed. In clayey formations, it is essential to insert a concrete barrier between the bentonite layer and the geological formation to provide structural support for the galleries' construction. The combination of mechanical and physicochemical protection is referred to as the engineering barrier (third barrier), while the natural geological formation or bedrock is considered a natural barrier (fourth barrier). Ensuring safety requires ongoing and proper long-term maintenance, along with vigilant monitoring of the installation [2–6].

Carbon steel is the metal chosen by countries, such as Spain, Switzerland, Japan or Belgium to manufacture the canister that insulates the HLRW [2,7–9]. This material has been studied, showing good properties for use in DGRs, such as a low corrosion rate or a long lifetime [10,11].

Bentonite is a clay rock frequently produced by the hydrothermal alteration or diagenesis of acidic-to-intermediate chemistry volcanic glass [12]. Under these conditions, montmorillonite is the main clay mineral, a phyllosilicate belonging to the smectite group [13]. Due to the properties of smectite, such as high swelling capacity, high cation exchange capacity and high chemical stability, bentonite is a competitive material used as an engineered barrier in HLRW management in DGRs [7,14,15].

HLRW will generate heat due to the decay of radionuclides. This heat will be transferred to the container for decades. The temperature is expected to rise to 100 °C at the surface of the canisters, although higher temperatures have recently been considered to reduce galleries spacing [16,17]. Due to the elevated temperature, geochemical interactions between the metal vessel and the bentonite will occur [10,18].

The canister should keep its structural integrity without cracks for at least 1000 years. The corrosion of the canister will depend on the environmental conditions. Temperature, groundwater, bentonite's porewater chemistry, especially the pH and the concentrations of chlorides, sulfur species and carbonates, the redox conditions, including the effect of gamma radiation, microbial activity and the degree of bentonite saturation are factors that will influence the formation of corrosion products as well as the corrosion rate [1,14].

The bentonite barrier will be subjected to hydration conditions in contact with the bedrock. Therefore, the location of the DRG is also a variable to consider, since the hydrogeochemical conditions of the host rock will affect the bentonite barrier, providing hydration with variable salt content. Low saline host rocks (e.g., Grimsel granite formations in Switzerland), high saline rocks (e.g., clay formations in Switzerland, France or Spain) or even marine-type porewater formations (e.g., granite formations in the Forsmark area, Sweden) have been studied [19–22].

It is predictable that full saturation of the bentonite barrier will be reached before dissipation of the thermal gradient, which will take place between 100 and 1000 years after deposition, depending on the particular characteristics of the repository [7,23–27]. In addition, the water vapor produced in the hot part of the bentonite, close to the canister, could recondense in cooler areas, influencing the redistribution of aqueous species in bentonite's porewater [28]. The saturation of the bentonite barrier involves a swelling process that redistributes the mass, changing the dry density, and as a consequence, the porewater chemistry, that is in equilibrium with the mineralogy [29,30]. Also, changes in the water content and chemistry mainly modify the exchangeable cation distribution and, in general, aqueous ion concentrations like Cl^- , SO_4^{2-} , Na^+ , K^+ , Ca^{2+} , Mg^{2+} or $\text{Fe}^{2+/3+}$ [31,32].

Due to the interaction between the steel and bentonite, redox reactions will occur on the surface of the steel and resulting soluble species and Eh/pH conditions will be transferred to the bentonite, generating potential mineral changes. Due to the variability of the existing candidate bentonites, with different mineralogies and exchangeable cation distributions [6,32–35], and the particular geochemical conditions that may occur depending on the design of the DGR, steel–bentonite interactions may produce different effects [36].

The interaction between steel and bentonite can lead to alteration processes like dissolution or re-precipitation of accessory minerals, i.e., short-term dissolution of CaCO_3 followed by precipitation of magnesium or iron carbonates due to cation exchange, where Mg or Fe ions replace Ca cations [37]. In addition, accessory silica minerals such as cristobalite and quartz, as well as montmorillonite, can undergo dissolution processes, contributing to the formation of iron silicates, such as nontronite or ferric chlorite [38]. Pignatelli et al. [39] reported the formation of iron-rich T–O phyllosilicates like greenalite and cronstedtite, in addition to magnetite, illite and chlorite, in an experiment in which Callovo-Oxfordian clay was mixed with metallic iron and iron powder, kept at 90 °C for 6 months, and then the temperature gradually reduced by 10 °C monthly until reaching 40 °C. The variety of Fe-bearing minerals that could be formed depends on Fe/Si and Al/Si ratios and pH but also could be mediated by silica dissolution and carbonates [39–41].

Experimental investigations have shown the accumulation of Mg in the hotter zone of bentonite, near the canister surface, regarding FEBEX in situ experiments [18]. The same trend was also found in several bentonite analyses in the ABM-II experiment explained by the increase in exchangeable Mg near the hot steel–bentonite interface [41,42] and by the precipitation of MgSO_4 in evaporation surfaces near this interface [36]. This accumulation, displacing cations such as Ca^{2+} , promotes the formation of 2:1 magnesium silicate mineral. Fernandez et al. [43] reported the formation of trioctahedral saponite and chlorite phases or brucite-like sheet phases from montmorillonite modification mediated by high Mg and Fe content in porewater. Svensson [44] also observed saponite formation at the iron–bentonite interface in in situ experiments performed at the hard rock laboratory in Äspö, Sweden. A modeling simulation of the iron–bentonite interaction provided by Savage et al. [45] suggested a sequence of predominancy of Fe-bearing minerals over time, with magnetite prevailing at the first stage. The magnetite led to cronstedtite (kaolinite-serpentine group) with a general formula $(\text{Fe}^{2+}, \text{Fe}^{3+})_3(\text{Si}, \text{Fe}^{3+})_2\text{O}_5(\text{OH})_4$ that dominated the corrosion products for the first 500 years. The next Fe-bearing minerals transformation was reported to form berthierine and, in some cases, chlorite. Wilson et al. [46] reported the formation of iron-rich saponite or 1:1 minerals at $<150^\circ\text{C}$ through geochemical modeling. Other studies reported the formation of chlorite or non-swelling minerals in hydrothermal systems and consequently, the reduction of the swelling capacity of smectite [47,48]. The formation of magnetite and siderite as corrosion products was also predicted by a carbon steel–bentonite interaction model [48].

It is accepted that reservoir conditions will evolve with time, with temperatures at the canister–bentonite interface expected to increase to $\sim 100^\circ\text{C}$ for the first 10–100 years after DGR post-closure [1]. This temperature is estimated to be maintained for up to 1000 years [49], after which the temperature is estimated to gradually decrease to $80\text{--}50^\circ\text{C}$, over a period of 1000 to 10,000 years [37]. Numerous studies, performed either at laboratory scale or long-term in situ experiments and geochemical modeling, reported the migration of Mg in the bentonite to the hottest zones near the canister surface [18]. That caused the enrichment in Mg at the canister–bentonite interface, allowing interaction with ions in solution like Fe^{2+} , Fe^{3+} , Na^+ , K^+ or Ca^{2+} , and forming minerals like saponite, chlorite group or ankerite $(\text{Ca}(\text{Fe}^{2+}, \text{Mg})(\text{CO}_3)_2)$ [37,44,50]. Mg enrichment in bentonite has also been observed by diffusion towards the alkaline interface of cement-based materials used as engineered barriers in some DGR concepts [6,51,52]. Despite all these studies, the interaction between magnesium bentonite and carbon steel under conditions of saturated and depleted Mg DGR is not well known.

This research aims to improve the understanding of the interaction between carbon steel and Mg-bentonite under hydrothermal conditions at an evolved scenario in a DGR, where Mg-montmorillonite is assumed to be the dominant mineral. The research employed compacted bentonites that were hydrated with a saline solution and heated at 100°C from a steel plate, creating a hydrothermal gradient in opposite directions (heat and hydration). Laboratory-scale experiments were conducted for periods of 1, 6 and 22 months using FEBEX Mg-bentonite, pretreated with MgCl_2 , with the objective to examine the behavior of this bentonite and the development of corrosion products at the steel plate surface.

2. Materials and Methods

2.1. Experimental Setup

Cylindrical bentonite blocks were created using homogeneous bentonite powder with its natural moisture content. The blocks were 21 mm in height and 50 mm in diameter and were compressed uniaxially within a steel mold to a dry density of $1.65\text{ g}\cdot\text{cm}^{-3}$. Each block of 77.5 g was weighed before placing it in the cell. This mass was determined considering a 14 wt.% of bentonite's natural moisture content stored in the laboratory.

The experiments were performed using hydrothermal cells of in-house design (Figure 1), as described in Mota-Heredia et al. [53]. The cells were maintained in a glove box under N_2 atmosphere during the whole experimental time to prevent oxidation in case of a potential

leakage in the system and to favor dismantling under anoxic conditions. A thermal gradient was established by setting constant temperatures of 100 °C at the heater (lower bentonite column end) and 40 °C at the hydration zone (upper bentonite column end). Three cells were studied after reaction for 1, 6 and 22 months.

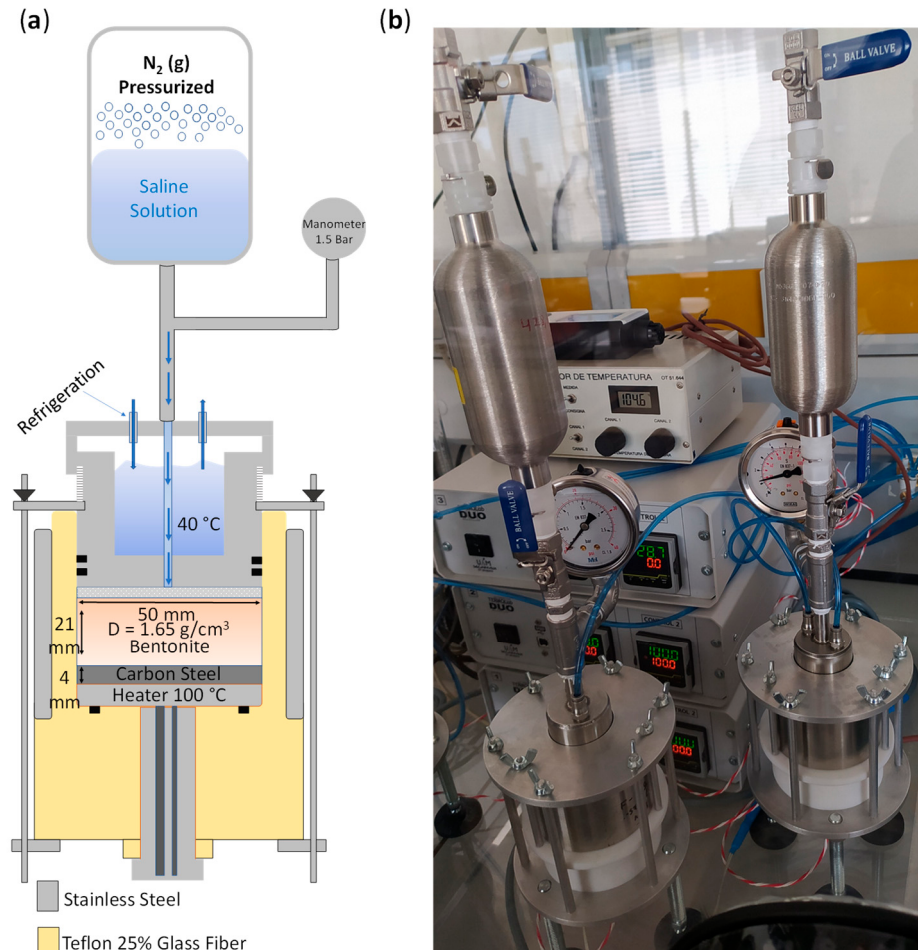


Figure 1. (a) Scheme of a hydrothermal cell, and (b) photograph of the experimental setup showing two cells and the electronic temperature controls at the back.

2.2. Materials

To simulate hydration from the clayey host rock, a synthetic saline solution of dominant Na-Cl-SO₄-type water, described in Mota-Heredia et al. [53] was used.

In this study, FEBEX bentonite from Cortijo de Archidona, Serrata de Níjar, Almería, Spain [54,55], considered the standard buffer material for radioactive waste storage in Spain [56], was pre-treated to produce Mg-bentonite. Natural bentonite contains 85 ± 10 wt.% montmorillonite [57], and accessory minerals, such as quartz, cristobalite, calcite and feldspars. It also contains traces of Fe minerals such as magnetite and goethite. The exchangeable complex of montmorillonite is composed of approximately 1/3 Ca²⁺-, 1/3 Na⁺- and 1/3 Mg²⁺-mol fractions. In this study, FEBEX bentonite was pre-treated with MgCl₂ with the objective to replace exchangeable Ca²⁺, Na⁺ and K⁺ with Mg²⁺. The pre-treatment process was described in detail in Fernandez et al. [52].

TStE 355 carbon steel discs were used to simulate the canister surface. The dimensions were 50 mm in diameter and 4 mm thick. Before settling in the cells, the c-steel discs were cleaned with ethanol and sonicated. Fe is present at more than 97 wt.% but small amounts of C, Cr, Mo and Mn are present in the steel composition.

2.3. Sample Segmentation

The three cells were dismantled after 1, 6 and 22 months. The steel–bentonite columns were embedded with a low-viscosity epoxy resin Araldite 2020™ to avoid the deformation and dehydration of bentonite and to keep the samples away from atmospheric oxygen. The embedded samples were cured at room temperature in the glove box until resin hardening was achieved. Samples were then suitable for cutting and segmentation.

A Struers™ (Champigny sur Marne, France) Secotom-6 saw machine was used to cut the cells using a cooling oil that covered the external bentonite surface while cutting. This oil did not chemically interact with bentonite but prevented exposure to atmospheric oxygen. Longitudinal cuts, parallel to the steel–bentonite interface, were performed in cylindrical bentonite samples with the Secotom-6 saw, while a cutter was used for cross-sections, perpendicular to the interface. To analyze reactivity along the hydrothermal gradient, samples were cut to ensure that sufficient material was available for each characterization technique, in agreement with the sampling method previously used by Mota-Heredia et al. [53].

2.4. Analytical Methods

The water content was calculated by mass difference of samples before and after heating to a constant weight at 105 °C. The specific surface area (SSA) was determined by nitrogen adsorption using a Gemini V analyzer from Micrometrics Corporate (Norcross, GA, USA) and calculated by the BET method. The samples were ground and dried at 90 °C for 24 h. Subsequently, the samples were degassed at 90 °C for at least two hours using a nitrogen gas stream and analyzed using the 5-point isotherm method as in Cuevas et al. [51].

The cation exchange capacity (CEC) was determined using the Cu-trien method [58], with modifications made for clays as in Ammann et al. [59]. The absorbance was measured at 577 nm using the UV–Visible Spectrophotometer Genesys 150 from ThermoScientific (Thermo Fisher Scientific, Waltham, MA, USA).

Analysis of major ions including Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- and SO_4^{2-} was performed using a Metrohm 802™ compact IC plus (from Metrohm, Herisau, Switzerland) through ion chromatography. A 0.15 solid/liquid ratio was used to mix the samples with deionized water in order to obtain the aqueous extracts. The samples were then subjected to 24 h of interaction with water on a shaker, followed by centrifugation for 30 min at 10,000 rpm. Finally, the aqueous extracts were filtered using syringe filters with a pore size < 0.45 µm.

Longitudinal thin section samples were prepared for scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) analyses. Each sample was dried by immersion in liquid nitrogen inside a vacuum chamber. After that, the samples were embedded and polished. The procedure is detailed in Mota-Heredia et al. [53]. A Q150T-S Quorum sputter coater system from Quorum Technologies (Lewes, UK) was used to coat the samples with Au.

Surface and morphology images were captured using a Hitachi S–3000N SEM (Hitachi, Japan) that was coupled with an EDX XFlash® 6130 Bruker detector (Bruker Corporation, Billerica, MA, USA) for semi-quantification analyses of chemical composition. Internal standard quantitative analyses were used for EDX quantification. The equipment operated under high vacuum conditions with an accelerating voltage of 20 keV, a lifetime of 40 s, a working distance of 15.0 to 18.5 mm and a beam current of 300 mA.

A study was conducted to determine the chemical composition in a longitudinal profile of bentonite, in the direction from the heater to the hydration zone. The images were largely magnified at the hottest zone where chemical variations were expected to be more significant. About 20 analyses were conducted over a thickness of 2 mm at the steel–bentonite interface, 15 analyses over a thickness of 3 mm at the hydration zone and 60 analyses at the intermedium zone over a thickness of 16 mm, although the number of analyses and thicknesses may vary slightly from sample to sample. EDX analyses were used to observe the diffusion of Fe along the bentonite and concentration changes of elements such as Mg, Ca, Na, K, Cl, S and Fe. The data were processed by removing

C and O from the concentrations and recalculating the rest of the elements to achieve 100 wt.%. The mineralogy of bentonite was also analyzed on fresh fractured samples to observe the morphologies of the reaction products. Small samples that either fell apart or were manually separated were used for this study.

To compare the redox state of Fe along the bentonite block in the longest experiment (after 22 months), the 1,10-phenanthroline photochemical method was used [60,61]. This method allowed for discrimination between ferrous and total iron in mineral samples. The Fe^{3+} was calculated by the difference between total Fe and Fe^{2+} .

To study the mineralogical changes in the bentonite block and at the steel interface, X-ray diffraction (XRD) was conducted using a Bruker D8 Discover diffractometer with a Ge monochromator and a lynxeye XE-T fast detector (Bruker Corporation, Billerica, MA, USA). The patterns were measured within a $3\text{--}70^\circ$ 2θ range, with 0.02° angular increments and 1 s times. The device was set at 40 kV and 40 mA. Bentonite mineralogy was studied over five sections, sampled with respect to the distance to the carbon steel. The samples were ground and XRD powder was measured.

To study the corrosion product crusts at the carbon steel–bentonite interfaces, the crusts were studied without grinding and additional extra samples of the bentonites in contact with the corrosion crusts were ground and analyzed. To prevent the oxidation of possible reduced compounds during the sampling and XRD analyses, the low background airtight Bruker holder A100B138-B141 was used for the sections closest to the crust to analyze the powder and non-ground crust.

3. Results

Physical–Chemical Characterization

The bentonite's water content after 1 and 6 months of reaction remained similar to the initial 15 wt.% (Figure 2a) but after 22 months increased to 31–33 wt.% along the whole column. A strong decrease in the bentonite's SSA (Figure 2b) was observed in the sections close to the heater, decreasing from $79\text{ m}^2/\text{g}$ to $4.6\text{--}11.1\text{ m}^2/\text{g}$ at the contact with the steel (a SSA reduction of 75–88%). The SSA trend in the three experiments was similar, decreasing towards both ends of the bentonite column but more intensely near the heater. The SSA values after 1 month were lower than those after 6 and 22 months, respectively, but considering the standard deviation of the measurements, this might not be relevant.

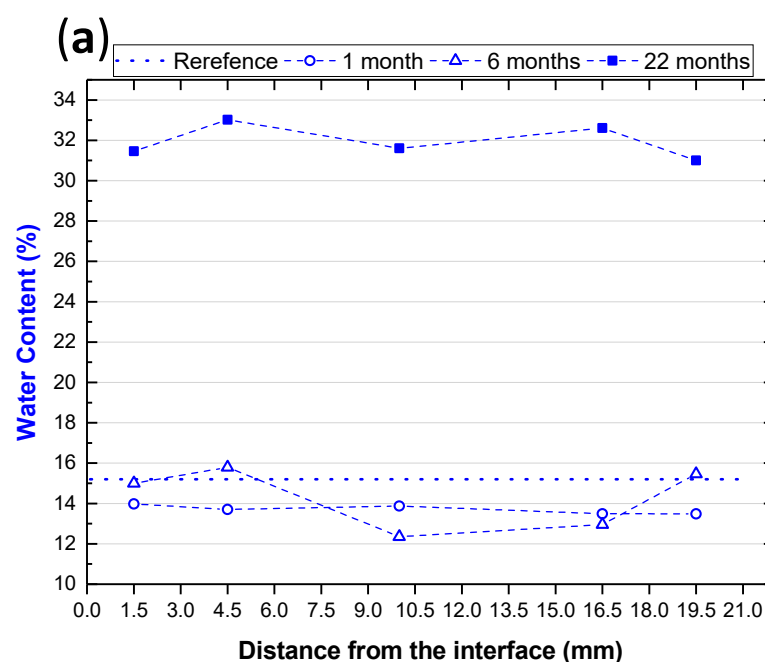


Figure 2. Cont.

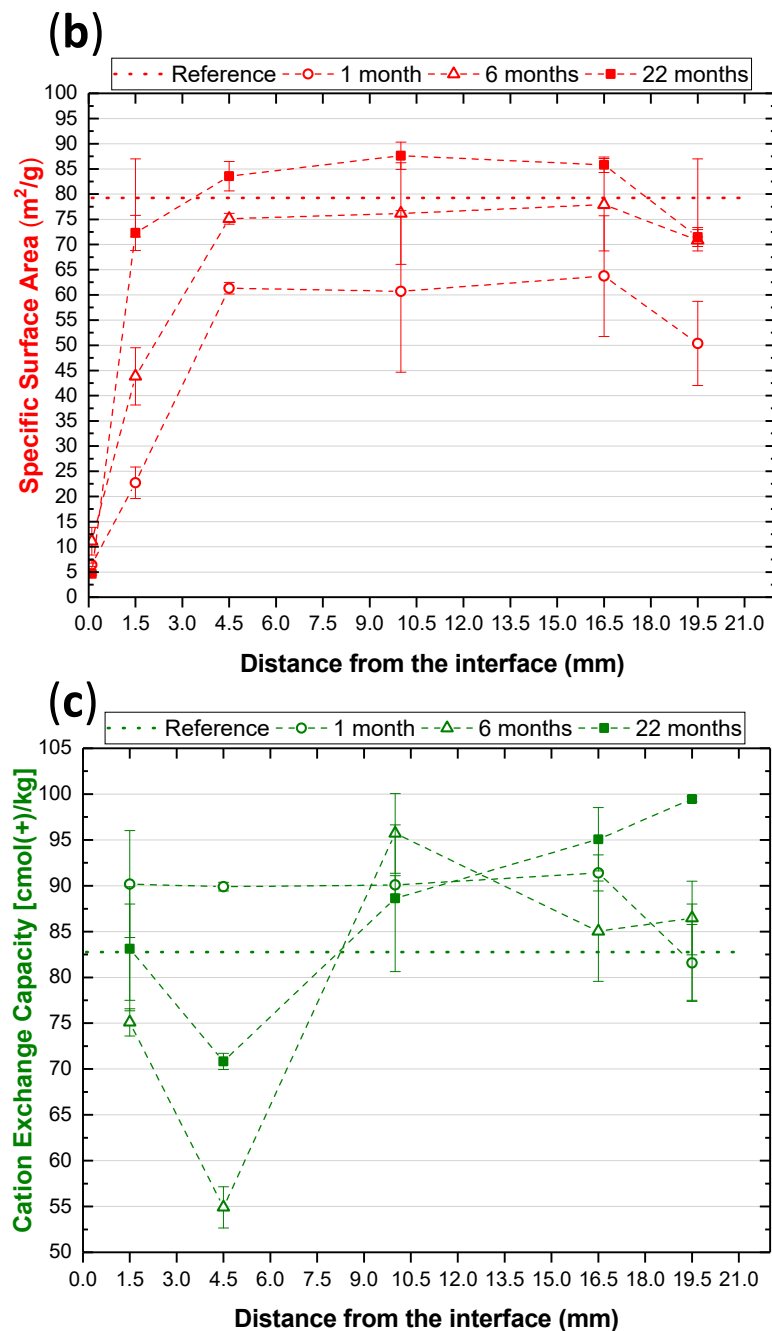
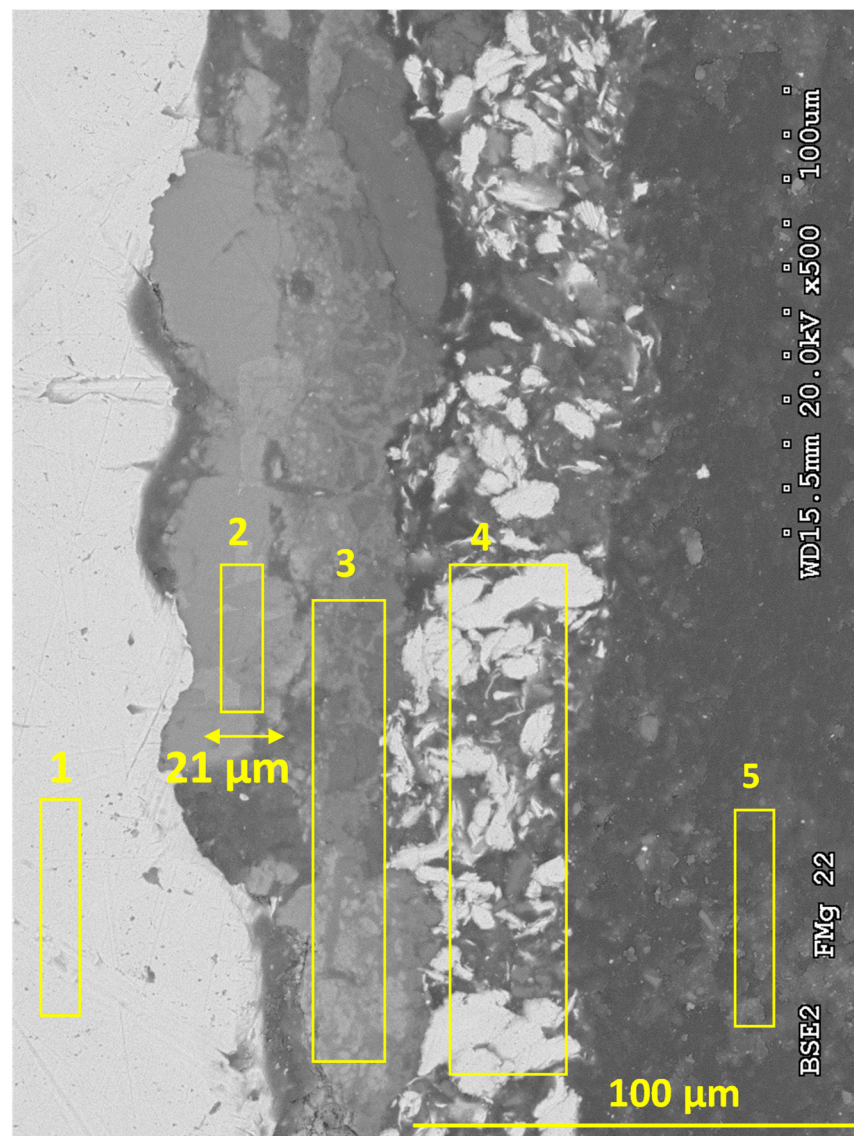


Figure 2. Evolution of physical–chemical properties along the bentonite blocks after 1, 6 and 22 months: (a) water content (wt.%); (b) specific surface area (m^2/g); (c) cation exchange capacity (cmol(+)/kg).

Independently of the reaction time, the bentonite's CEC remained close to the initial reference value (83 ± 5 cmol(+)/kg) except in the section at 3–6 mm from the heater, where a relevant decrease was observed after 6 and 22 months, achieving values of 55 and 71 cmol(+)/kg, respectively (Figure 2c).

The corrosion rate calculated by measurements of corrosion thickness at the steel discs by SEM-EDX (Figure 3) indicated certain passivation with time. The measurements of the corrosion thickness considered the gray compact rim formed at the bright steel surface (Figure 3). A corrosion rate of $39.6 \mu\text{m}/\text{year}$ was calculated after 1 month of reaction, $20.0 \mu\text{m}/\text{year}$ after 6 months and $4.8 \mu\text{m}/\text{year}$ after 22 months (Figure 3).



Zone 1: C-Steel (98 Fe, 1 Si, 1 Mn, 0.3 Cr)

Zone 2: Steel corrosion (88 Fe, 9 Si, 2 Mg, 1 Cr, 0.6 Mn)

Zone 3: Steel corrosion-bentonite (41 Fe, 25 Si, 16 Mg, 10 Al, 4 Ca, 4 Mn)

Zone 4: Steel fragments (74 Fe, 17 Si, 6 Al, 2 Mg, 0.6 Mn, 0.5 Ca)

Zone 5: Resin-bentonite (19 Fe, 60 Si, 12 Al, 6 Mg, 3 Cl)

Figure 3. Backscattered electron image of FEBEX-Mg after 22 months, distinguishing four altered zones from the steel left part) and confirmed by the EDX composition shown below the image. The atomic % of each zone is given to differentiate the observed materials.

The concentration of the major elements in bentonite (Fe, Al and Si), determined by EDX analyses, remained stable over time, but a remarkable decrease in Al and Si, in agreement with an increase in Fe, was observed at 1–2 mm from the interface with the steel. Specifically, the increase in iron reached 1 mm from the interface after 1 month, 1.25 mm after 6 months and 1.5 mm after 22 months (Figure 4a,b). Quantitatively, Fe increased from an averaged 7.2 ± 0.7 wt.% to values > in a range 10–30 wt.% in a thickness of 0–5–1.5 mm from the interface, and values >80 wt.% at a very short distance from the interface (<0.2 mm).

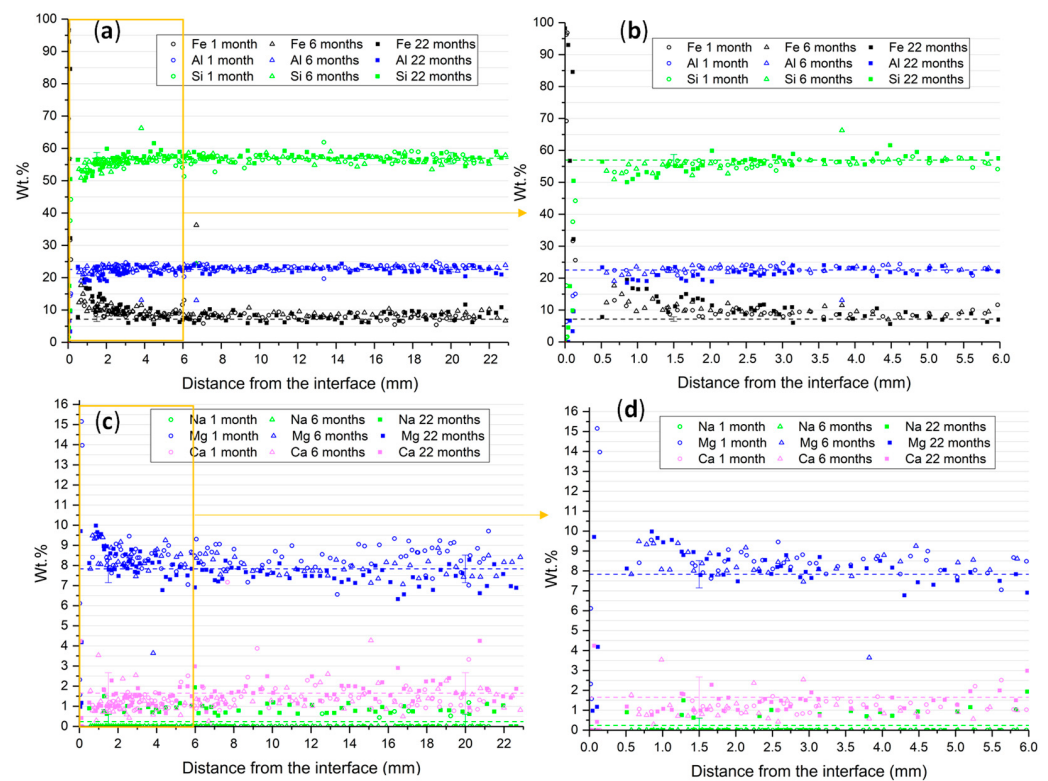


Figure 4. EDX chemical profiles in bentonite, expressed in wt.%: (a) Fe, Al and Si after 1, 6 and 22 months; (b) detail of (a) showing the first 6 mm from the steel interface; (c) Na, Mg and Ca after 1, 6 and 22 months; (d) detail of (c) showing the first 6 mm from the steel interface. Reference values represented by dash lines.

The evolution of Ca and Na, on the contrary, decreased over the first 1.5 mm from the interface, averaged values of 1.7 and 0.2%, respectively, from the original reference bentonite value. Inversely, Mg concentrated at this region and remained at relatively stable values beyond 1.5 mm from the interface (Figure 4c,d).

SEM images and EDX analyses performed on fresh fractured bentonite samples close to the steel interface showed incorporation of Fe into the smectite. Figure 5 shows the aspect of clay aggregates presumably produced during bentonite alteration and oxides found attached to the steel plate after 1, 6 and 22 months, which had evidence of formation of new Fe-rich silicates. Secondary mineral phases, with different morphologies, formed on the smectite surface (Figure 5a). EDX analyses expressed in atomic percentage showed that laminar morphologies (analysis 1) contained approximately 79% Fe and 21% Cl, while small micrometric spheres contained 95% Fe and 5% Cl. Both phases were attributed to the precipitation of iron oxides with variable amounts of chloride. After 6 months, iron oxide with additional chloride was observed (analysis 3), nucleating on aggregates with multidirectional micrometer fibers (Figure 5b). The altered clay shown by the morphologies observed in analyses 4, 5 and 6 presented high Fe content (>40%) and a Si/Fe ratio close to 1. Considering the atomic concentrations obtained by EDX, structural formulas were calculated using the model of a di-trioctahedral chlorite (i.e., [62]) structure, assuming the possibility of hydroxide precipitation in a previous dioctahedral smectite interlayer. They were calculated based on the anionic base ($-O_{10}(OH)_8$), distributing Al in the tetrahedral layer (T2 sites) [62,63] and in the octahedral layer (M1, M2 sites). Likewise, Fe was assigned as Fe^{2+} in the trioctahedral brucitic layer (M3, M4); assuming that the charge compensating the sum of the charges generated in T2 and M1, M2 must be produced due to the existence of a certain proportion of Fe^{3+} in the brucitic layer. Mg and part of the Fe and Al, not assignable to T2, M3 and M4, were assigned to the octahedral layer (M1, M2).

Analysis 4: $(\text{Fe}^{3+}_{0.33}\text{Fe}^{2+}_{0.67})(\text{OH})_2)_3(\text{Al}_{0.22}\text{Mg}_{0.40}\text{Fe}_{1.51})_2(\text{Si}_3\text{Al})_4\text{O}_{10}(\text{OH})_2$

Analysis 5: $(\text{Fe}^{3+}_{0.34}\text{Fe}^{2+}_{0.66})(\text{OH})_2)_3(\text{Al}_{0.25}\text{Mg}_{0.92}\text{Fe}_{1.09})_2(\text{Si}_{3.12}\text{Al}_{0.88})_4\text{O}_{10}(\text{OH})_2$

Analysis 6: $(\text{Fe}^{3+}_{0.37}\text{Fe}^{2+}_{0.63})(\text{OH})_2)_3(\text{Al}_{0.8}\text{Mg}_{0.6}\text{Fe}_{0.6})_2(\text{Si}_{3.5}\text{Al}_{0.5})_4\text{O}_{10}(\text{OH})_2$

The calculation reasonably corresponds to the intercalation of iron hydroxide into a smectite structure, although the iron proportions slightly exceed those present in the original octahedral sheet of FEBEX montmorillonite (Ca^{+2} homoionised: $(\text{K}_{0.04}\text{Ca}_{0.24}\text{Fe}_{0.06})(\text{Fe}_{0.09}\text{Al}_{1.41}\text{Mg}_{0.50})\text{Si}_{13.94}\text{Al}_{0.05}(\text{O}_{10}(\text{OH})_2)$ [64]. The substitution of aluminum in the tetrahedral sheet significantly increased compared to the average montmorillonite, while octahedral Mg remained in similar proportions as in the reference FEBEX.

Analyses on fresh fractured bentonite samples close to the interface after 22 months revealed a larger coating of smectite aggregates (Figure 5c), with a high content of Fe and Mg. The Si/Fe ratio calculated for analyses shown in Figure 5c exceeded 4, except for analysis 7, and differentiated by a single aggregate of brighter color that was 0.75. The structural formula calculated for analysis 7 was $(\text{Fe}^{3+}_{0.425}\text{Fe}^{2+}_{0.575})(\text{OH})_2)_3(\text{Al}_{0.48}\text{Mg}_{0.61}\text{Fe}_{1.02})_2(\text{Si}_3\text{Al})_4\text{O}_{10}(\text{OH})_2$, compatible again with the di-trioctahedral chlorite structure used to simulate an iron (II, III) hydroxide interlayer simulation. The iron proportion increased over the expected for intercalation. Some mixing of iron oxides and formation of new iron silicates could not be discarded.

Analyses 8–11 showed phyllosilicates rich in Mg and Fe and Si/Fe ratios higher than 4, revealing the necessary presence of iron oxides in the mixture.

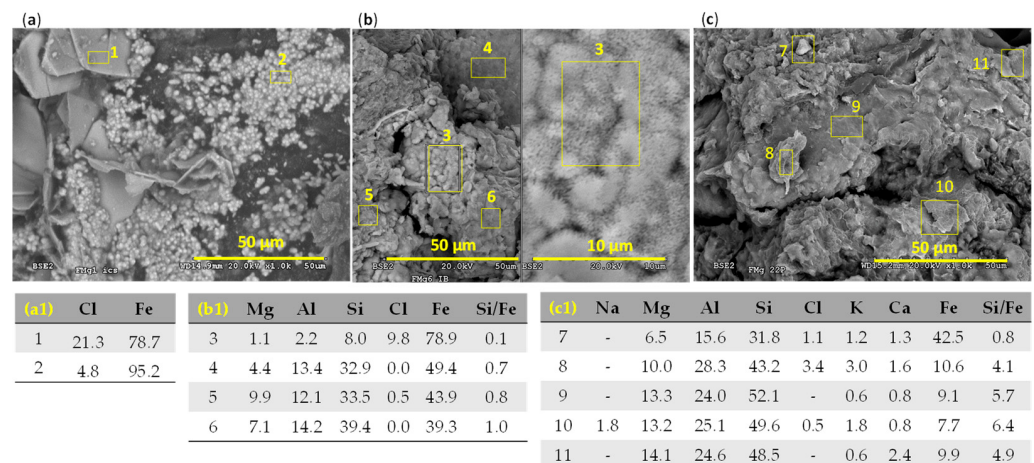


Figure 5. SEM images of details taken in fresh fractures close to the steel plate interface: (a) 1 month; (b) 6 months; (c) 22 months. (a1,b1,c1) include the composition of the zones marked in the respective subfigures. Data presented in atomic %. -: data below detection limits.

Figure 6 shows the concentrations of Fe^{2+} , Fe^{3+} and Fe_{total} along the bentonite column after 22 months. An increase in Fe^{2+} , Fe^{3+} and Fe_{total} was observed in a thickness of 2 mm from the interface with steel, compared to the reference concentrations in FEBEX-Mg-bentonite. A similar trend was observed for Fe^{2+} and Fe^{3+} over the whole bentonite column. At the hydration zone, 12–21 mm from the interface with steel, the concentrations decreased slightly below the reference values. Most of the increase in iron was presumably related to the presence of iron (III) oxides as there was an increase in Fe^{2+} from 0.13 ± 0.05 wt.% to 0.26 ± 0.08 wt.% in the section closest to the heater (0–1 mm). Fe^{3+} also increased in contact with the steel, from 3.0 ± 0.4 wt.% determined in the reference Mg-bentonite to 4.03 ± 0.04 wt.%. In the following section (1–2 mm), Fe^{2+} and Fe^{3+} concentrations decreased by 0.17 ± 0.01 wt.% and 3.85 ± 0.6 wt.%, respectively. At the 2–3 mm section from the heater, the Fe^{2+} and Fe^{3+} values remained in the order of the reference Mg-bentonite.

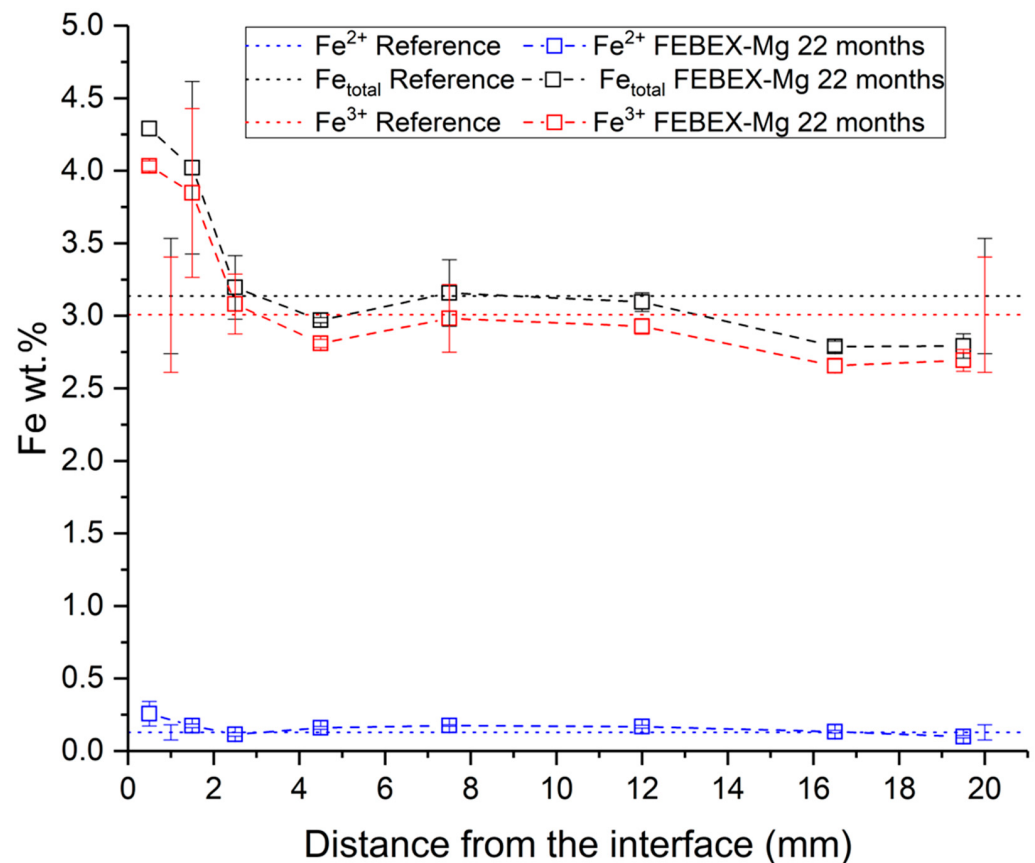


Figure 6. Concentrations of Fe^{2+} , Fe^{3+} and Fe_{total} along the bentonite column after 22 months. Units expressed in wt.%, referred to dry mass of solid sample.

The mineralogy of FEBEX-Mg-bentonite experienced minor changes over time (Figure S1, Supplementary Materials) considering the whole thickness of the bentonite disc. The main FEBEX-Mg-smectite XRD reflections were detected at 14.8 Å (001), 4.45 Å (020), 2.58 Å (110), 1.70 Å (210) and 1.50 Å (060). The reference material also presented quartz (4.25, 3.34 Å), cristobalite (4.04 Å), calcite (3.0 Å), and traces of magnetite (2.53 Å) and maghemite (2.52 Å), (Figure 7). The main mineralogical changes were observed near the steel interface (<3 mm). After 1 month, no minerals other than those present in the reference bentonite were detected, except ankerite, a $\text{Ca,Fe}^{\text{II}},\text{Mg}$ -carbonate (2.90 Å) in the section <3 mm from the steel interface. After 6 months, also in the section <3 mm from the steel interface, low-intensity reflections of ankerite and maghemite were also detected. After 22 months, the presence of a 7.05 Å reflection and the enhancement of a 4.8–4.7 Å band supported some evidence of di-tri ferric chlorite presence, presumably ferri-sudoite-like (in agreement with the SEM-EDX data). It is known that the 14 Å reflection of ferric (hydroxide layer) aluminous (octahedral layer) chlorite displayed a very small intensity compared to 7 and 4.74 Å reflections (i.e., [65]). The 14.8–14.6 Å basal spacing reflection predominant in most DRX patterns could contain smectite and the minor chlorite reflection. Ankerite (2.90 Å) was detected close to the steel interface (<3 mm). In the section at 3–6 mm, lepidocrocite ($\gamma\text{-Fe}^{3+}\text{O(OH)}$) (6.25 Å) and hematite (Fe_2O_3) (2.70 Å) were detected. Lepidocrocite was also detected in the section at 6–15 mm (Figure 7). Accessory minerals like muscovite (illite) and albite (plagioclases), present in the reference Mg-bentonite raw material, were randomly detected due to their heterogeneous distribution in bentonite.

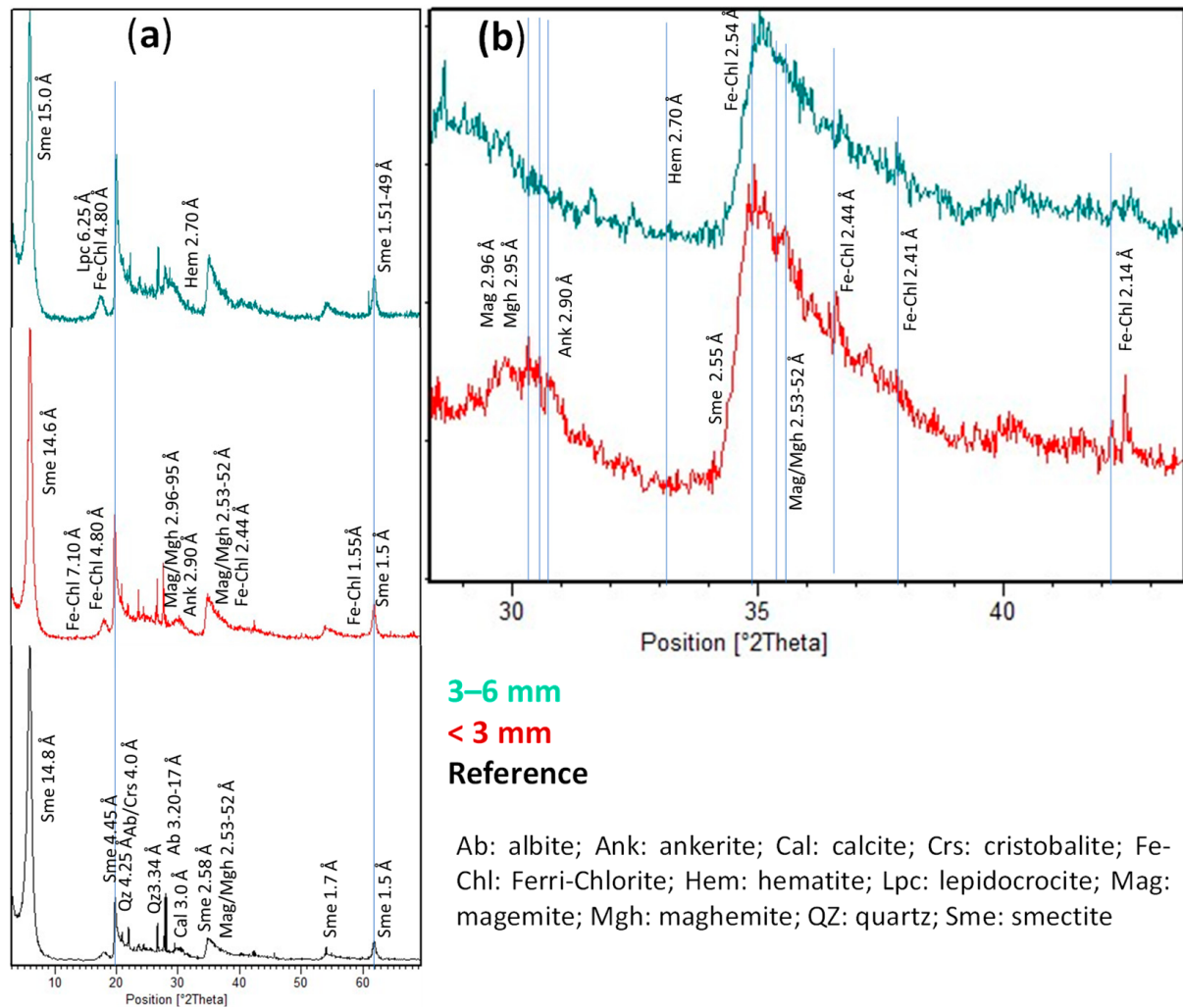


Figure 7. XRD on FEBEX-Mg sections from the steel interface after 22 months. (a) section at 3–6 mm (green upper diffractogram); section at 0–3 mm (red middle diffractogram); reference FEBEX-Mg (black bottom diffractogram); (b) zoom of the 29–44 2θ range.

The XRD patterns corresponding to the corrosion crusts that formed at the steel–bentonite interface were measured on both sides, the contact with steel (colored in fuchsia) and the contact with the bentonite (colored in orange) (Figure 8). Several intense reflections, observed at 6.40, 5.35, 4.84 and 3.52 Å, identified after 1 month, were not related to any mineral alteration but attributed to the adhesive used to fix the corrosion crust on the airtight holder. In addition, hematite (2.70 Å, 2.51 Å) and maghemite (2.94 Å, 2.52 Å) were detected, and siderite at a low intensity (2.79 Å). At the contact with the bentonite side, low-intensity reflections of ankerite (2.90 Å) and hematite (2.70 Å) were identified as corrosion products at the corrosion crust. The ferri chlorite phase (ferri-sudoite) (7 and 4.8 Å) was barely identified with other compatible reflections at 2.65 Å and 2.44 Å. Low-intensity reflections of magnetite/maghemite were observed.

After 6 months, reflections attributed to green rust (7.5 Å, 3.75 Å), maghemite and magnetite (2.96–95 Å and 2.53–2.51 Å) and siderite (low-intensity reflections at 2.79 Å) were observed in the corrosion crust at the contact with steel. Smectite, albite and quartz, already present in the original bentonite were detected. Ferri-sudoite was detected by the reflections at 7.05 Å, 4.80, 2.80 and 2.44. At the bentonite side, ferri-sudoite was detected too. Ankerite (2.90 Å), hematite (2.70 Å) and a maghemite/magnetite mix were identified as corrosion products. Siderite was not identified on this side.

After 22 months, more clear and intense reflections were observed regarding the altered products. The crust analyzed in contact with steel showed a main composition of siderite (2.79 Å). Smectite, ferri-sudoite and albite were detected as minor minerals. On the bentonite side, the main reflections were associated with ferri-sudoite (7.05 Å, 4.80 Å, 3.53 Å, 2.44 Å, 2.14 Å and 1.55 Å) and green rust (7.5 Å and 3.76 Å), but low-intensity reflections at 2.90 Å and 2.51 Å were attributed to ankerite and maghemite, respectively.

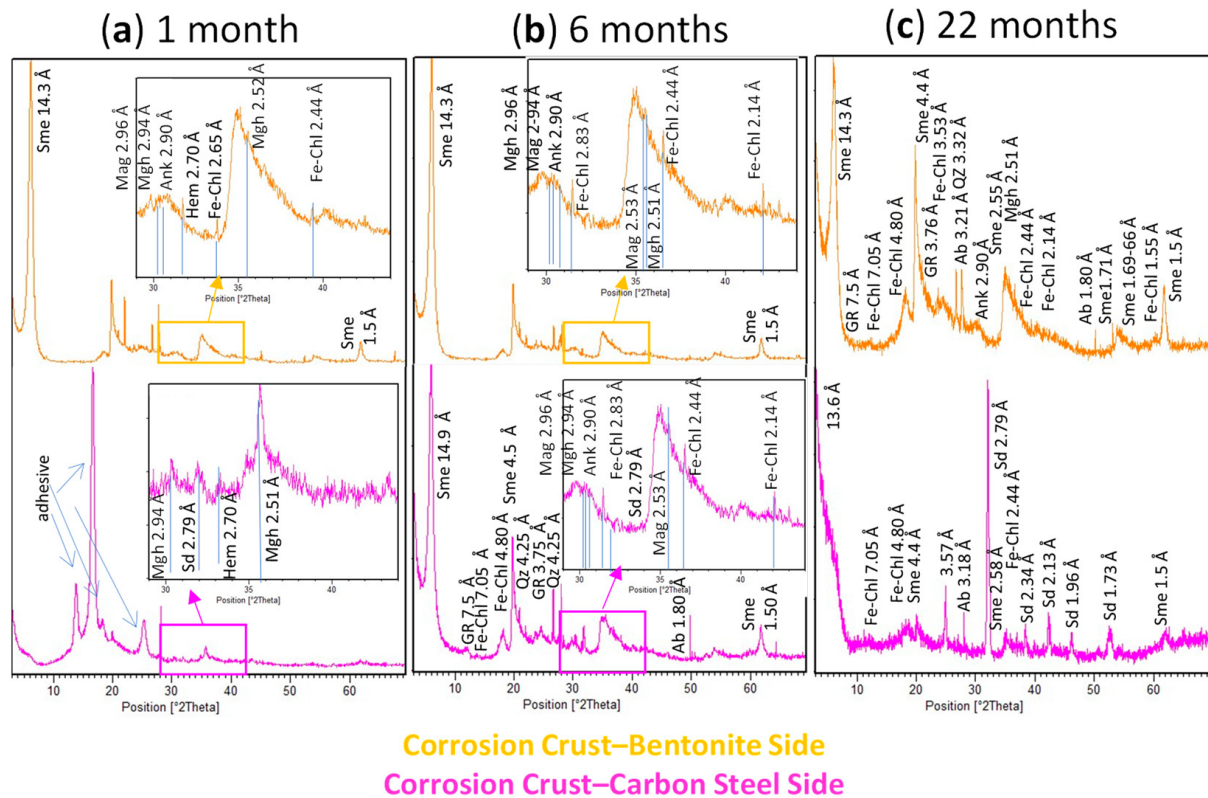


Figure 8. XRD of corrosion crusts examined from the contact with steel (fuchsia) and with bentonite (orange) after (a) 1 month; (b) 6 months; and (c) 22 months. Ab: albite; Ank: ankerite; Crs: cristobalite; GR: green rust; Hem: hematite; Mag: magnetite; Mgh: maghemite; Qz: quartz; Sd: siderite; Sme: smectite; Sud: sudoite.

Aqueous extracts were analyzed to study the redistribution of aqueous species in the bentonite porewater (Figure 9). After 1 month Cl^- varied within a range between 395 and 483 mM, similar to the reference FEBEX-Mg (455 ± 2 mM), concentrating at the middle of the bentonite column (6–15 mm). The same tendency was observed after 6 months but within a lower concentration range (220–280 mM). After 22 months, Cl^- decreased to lower concentrations, within a range of 54–58 mM. Mg^{2+} maintained concentrations close to the reference FEBEX-Mg (130 ± 6 mM), within a range between 100 and 166 mM after 1 and 6 months, but after 22 months Mg^{2+} concentrations decreased within a narrow range of 28–36 mM along the bentonite column. The rest of the ions analyzed (Na^+ , Ca^{2+} , SO_4^{2-} and K^+) were in a lower concentration range (3–58 mM). A general decrease of concentrations was observed with the increasing reaction time. After 22 months, Na^+ was determined to be within a range between 36 and 40 mM, while the reference Na^+ concentration was 15 ± 9 mM; Ca^{2+} increased up to 11–16 mM from the initial reference of 9 ± 2 mM; SO_4^{2-} increased to 9–12 mM from the reference of 5 ± 1 mM, and K^+ decreased from 10 ± 1 mM to 4 mM.

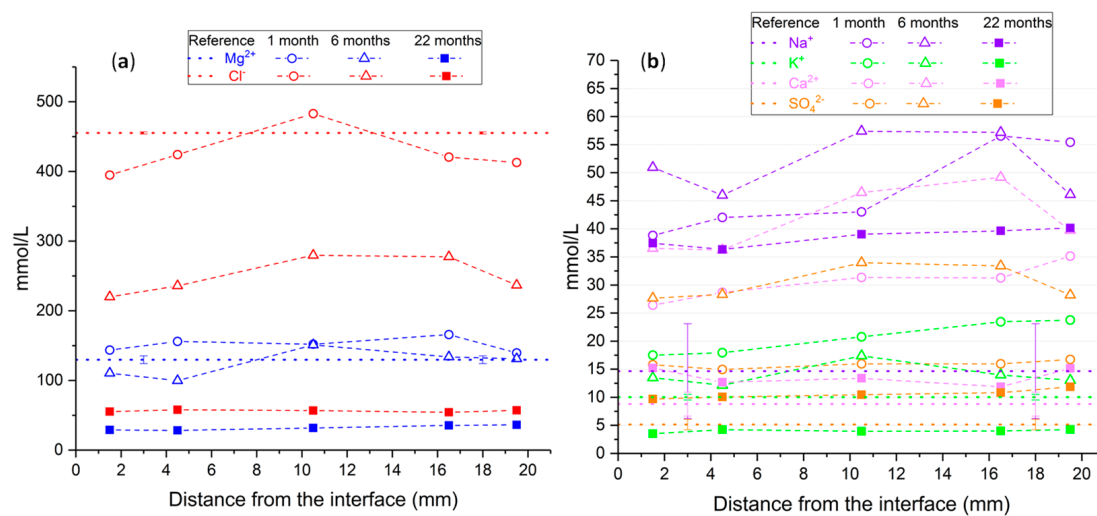


Figure 9. Ionic concentrations of aqueous extracts in bentonite sections parallel to the steel interface. (a) Mg^{2+} and Cl^{-} ; (b) Na^{+} , K^{+} , Ca^{2+} and SO_4^{2-} . References values represented by dotted lines.

4. Discussion

The experimental design provided data after 1, 6 and 22 months, allowing for the study of the temporal evolution of steel–bentonite interactions. The temporal evolution described how the progressive passivation of the steel surface occurred, visibly decreasing the corrosion rate with time. The longest experiment, performed for 22 months, unusually for this type of laboratory experiment, permitted the formation of a well-defined cemented crust at the steel–bentonite interface due to the precipitation of iron corrosion products that could be analyzed from both faces.

Due to the hydrothermal gradient, the bentonite's physical–chemical properties were modified. A rather homogeneous increase in water content was observed after 22 months (close to 30 wt.%) without apparent water content decrease as a function of distance to the heat contact. Similar experiments using natural FEBEX bentonite showed a slightly higher water content range (20–25 wt.%), achieved during a short time in the whole column (1 and 6 months) [53]. Since the pressure of water injection was relatively low (0.15 MPa) and the swelling properties of the Mg-saturated bentonite were homogeneous, hydration progressed very slow. The material was previously wetted and reprocessed to be Mg-saturated, so final mineral grains and grain size were artificially homogenized to <1 mm compared to natural FEBEX bentonite, which usually provided grains <5 mm with a visible heterogeneity of grain colors and different altered rock preserved grains (i.e., [66]). The great homogeneity, at small time lapses, could produce resistance to hydration at the swelling interface. There was no evidence of water loss associated with the thermal treatment or gradient in the short term that would have resulted in the dehydration of the bentonite near the heater, a phenomenon that was not detected, with values close to the initial moisture level being maintained. On the other hand, hydration was completed after 22 months, allowing for comparison of the short term (1 and 6 months) with the long-term (22 months), once the hydration front progressed. The bentonite's SSA remained in a range close to the initial reference values, except near the steel interface, due to the presence of corrosion products and modifications on the smectite, as observed by SEM-EDX and XRD, where minerals identified to be of the chlorite group and iron-rich were detected, mixed with the smectite matrix. Chlorite minerals were detected in a FEBEX in situ experiment by Wersin et al. [49] at a temperature of 50 °C and were synthesized at 300 °C in the presence of metallic Fe powder facing MX-80 bentonite [67], showing compositions and XRD powder patterns similar to those shown in this study.

The composition of materials corresponding to iron silicates, seeking locations free of chloride and analyzed by SEM-EDX, is compatible with ferric chlorites. Their elemental

proportions are consistent with the predominance of a di-octahedral character in the octahedral layer and tri-octahedral character with partially oxidized Fe^{2+} in the brucitic layer. Assuming the already described distribution model, the presence of typical reflections of ferric chlorites outlining a main reflection at 7 Å could be explained with a composition characteristic of ferri-sudoite (Figure 7).

The CEC remained within a range similar to the reference bentonite, except in the section at 3–6 mm from the steel interface that decreased after 6 and 22 months. This phenomenon is typically connected to the dissolution of montmorillonite and the neoformation of other non-swelling minerals such as chlorite or iron oxides. Fe^{3+} predominated over Fe^{2+} , which increased slightly by approximately 0.2 wt.% over the first 1.5 mm of bentonite from the steel interface. This was in agreement with the presence of tri- (Fe^{2+}) , di- (Al^{3+}) -chlorite mineral in minor amounts, coexisting with Fe(III) oxides, evidenced by the presence of hematite on the bentonite side and $\text{Fe}^{3+}/\text{Fe}^{2+}$ oxides, mainly magnetite, within the steel corrosion products. The decline in CEC observed in the present study was attributed to the formation of mixed iron oxides in the material rather than montmorillonite dissolution, as no peak broadening XRD evidence supported such dissolution (Figure S1).

After being exposed to a carbon–steel heater at 100 °C for 18 years in the in situ FEBEX experiment, a reduction in CEC was also observed in FEBEX bentonite [43]. That decrease was attributed to one of the following factors: an increase in the smectite layer charge, the reduction of Fe^{III} -bearing smectite, which induced the collapse of clay particles (not observed in the present research), or the shrinkage of lamellar particles induced by high salinity. In FEBEX bentonite, the salinity was nearly constant at each reaction time, except in the section closest to the hydration zone. Therefore, the decrease in CEC could not be ascribed to higher salinity resulting from direct contact with the saline solution. Dohrmann et al. [68] proposed that the potential decrease in CEC could be attributed to the increased experimental temperature and/or the development of corrosion products within the bentonite matrix. In the current set of experiments, it was noted that smectite aggregates at the steel–bentonite interface were coated with iron oxides, as illustrated in Figure 5, in agreement with the interpretation by Dohrman et al. [68].

The characterization of aqueous extracts from the bentonite porewater showed a decrease in K^+ concentrations after 22 months. It could have occurred due to a fixation of K^+ in the interlayer during the initial stages of illitization, as suggested by Kumar et al. [68,69], although the low general K^+ concentration provided no visible evidence for this, extracted from the XRD patterns. Another explanation for the general salinity reduction involving the remaining ions over the long term could be attributed to the formation of iron oxides, wherein ions subsequently associated to form complex minerals, such as green rust, producing an overall reduction of ions (chloride) in solution, as observed after 22 months of reaction.

Fe-silicates and Fe-Cl corrosion products were detected, evidencing chloritization processes, as confirmed by XRD after 22 months of reaction. The formation of Fe-spicules or fibrous Fe-silicates was reported by Kaufhold et al. [70] in their SEM study on Fe–bentonite interactions. Previous experiments with MX-80 and FEBEX bentonite conducted for 1 and 6 months under the same experimental conditions showed similar precipitation of iron oxides in the corrosion layer at the steel–bentonite contact. The authors reported the formation of magnetite, maghemite and goethite after 1 and 6 months [53].

The increase in Fe content within the montmorillonite structure could be elucidated through various mechanisms, such as adsorption within the interlayer via cation exchange, adsorption at the edge sites of montmorillonite or association with corrosion products [36]. Additionally, redox reactions may have occurred, leading to the precipitation of Fe^{III} -oxides or mixed $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ -oxides and Fe^{II} -carbonates like ankerite and siderite. Soluble Fe^{2+} migrated into the bentonite as oxygen from the bentonite pores diffused to the steel surface. The interaction of iron with oxygen could have resulted in oxidation and subsequent precipitation on montmorillonite surfaces, forming iron (hydr)oxides like lepidocrocite. The calculated corrosion rate showed a reduction with increasing time, in agreement with

other studies [71–74]. Wersin et al. [75] reviewed the corrosion rates of four different in situ experiments, the FEBEX in situ experiment being one of them. A range of corrosion rates between 6 and 11 $\mu\text{m}/\text{year}$ were calculated for this experiment, conducted for 18 years at 70 °C, using carbon steel and FEBEX bentonite. In the present research at 100 °C and over the short term, compared to the FEBEX in situ experiment, the final corrosion rate was nearly in the same range or even lower but within the same order of magnitude as observed after 18 years. The Mg-saturated bentonite could enhance passivation, which will presumably be confirmed by ongoing longer-term experiments.

Taking into account the mineralogical observations, a scheme showing the reaction products at the steel–bentonite interface after at the three experimental times (1, 6 and 22 months) is presented in Figure 10. This scheme is based on those presented by Wersin et al. [75] and Hadi et al. [73]. Wersin et al. [75] studied corrosion in eight bentonites pre-saturated with Äspö groundwater heated to 130 °C in the ABM2 in situ experiment. Hadi et al. [73] studied the steel–bentonite interactions in the FEBEX in situ experiment, in which carbon steel, in contact with FEBEX bentonite, was heated at 100 °C for 18 years. The proposed scheme tries to visualize the different mineral phases detected after 1, 6 (presumably under unsaturated water vapor migration conditions) and 22 months (under water saturated conditions at the end of the experiment). The alteration thicknesses are not presented at scale but indicate the transformation of some phases into others. The increase of siderite with time as well as the presence of Fe^{2+} -silicates in a wider region after 22 months than after 1 and 6 months were observed by XRD. Although each zone is represented by solid colors, a mixture of minerals was observed at the interfaces of each zone.

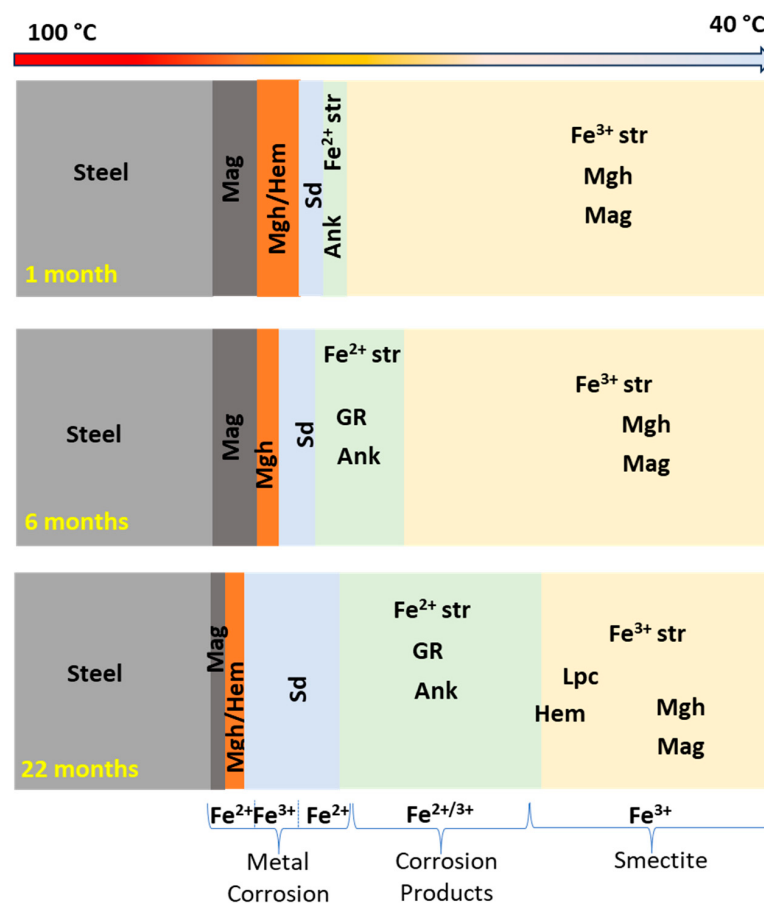


Figure 10. Proposed mineral phase evolution scheme for steel–FEBEX–Mg interface after 1, 6 and 22 months. Mag: magnetite; Mgh: maghemite; Hem: hematite; Sd: siderite; GR: green rust; Ank: ankerite; Lpc: lepidocrocite; using similar scheme and colors as in Hadi et al. [73].

Determinations on the iron redox state in bentonite, analyzed after 22 months of reaction, showed an increase of Fe^{2+} and Fe^{3+} near the steel interface (<2 mm), presumably affecting a larger thickness compared to less humid and earlier times (1 and 6 months under the same conditions). Magnetite formed as the main steel corrosion mineral, as observed in several water-saturated environments under reducing conditions (i.e., Schelegel et al. [76]). The determination of redox potential in the clay–metal-iron interface in a transient oxic to anoxic state is complex and ambiguous as many Fe^{3+} and Fe^{2+} minerals are involved and present in small quantities, making them difficult to identify.

Robinson et al. [77] established the presence of magnetite/maghemite-coupled minerals mainly controlling the Fe^{2+} redox solution equilibrium at pH 6.5–8.5, exhibiting more negative potential than the corresponding lepidocrocite and hematite at progressively less negative potentials. The expansion of the reducing front towards the bentonite may have led to the presence of these Fe^{3+} iron oxides in regions relatively far (up to 2 mm) from the interface where Fe^{3+} predominated. The potential intercalation of Fe^{2+} ions as hydroxide in a chloritic structure added complexity and probably further enhanced the transport of Fe^{2+} to the clay material. Wersin et al. [18] mostly identified the iron in the zone closest to the heater as Fe^{3+} , which was consistent with the detection of hematite, magnetite, maghemite and lepidocrocite in this zone. Fe^{2+} was oxidated partially to Fe^{3+} in the middle sections of the bentonite column, coexisting both species, although concentrations of Fe^{3+} were higher than Fe^{2+} .

5. Conclusions

Bentonite was slightly altered after 1 and 6 months, but the main alterations were observed after 22 months of reaction and well-defined mineralogical changes could be identified. The formation of secondary minerals coating the smectite were argued to explain the bentonite-specific surface area decreases at the steel interface. The enrichment in Fe in the bentonite was detected over the first 3 mm from the steel interface. However, the corrosion rate decreased to <5 $\mu\text{m}/\text{year}$ with the reaction time up to 22 months. Minor changes were noticed along the bentonite column beyond the first 3 mm from the steel interface, maintaining its original properties. The iron–bentonite interactions allowed the formation of corrosion products, several iron oxides like magnetite, maghemite or hematite, and iron carbonates like siderite, ankerite and green rust (containing chloride) to be identified. The geochemical evolution of bentonite promoted the formation of a chlorite phase of ferri-sudoite-like composition through the montmorillonite modification. The use of X-ray diffraction, the photochemical method with 1,10-phenanthroline and scanning electron microscopy analyses allowed the identification of these minerals.

The main mineralogical changes were found at the steel–bentonite interface, where the bentonite properties studied were modified by the precipitation of corrosion products, forming a low-porosity layer that could potentially clog bentonite pores and affect subsequent reactivity. Negligible smectite alteration was found in previous experiments of the Fe–bentonite interaction at low liquid/solid ratios, leading to uncertainties over the Fe-phyllsilicates that could form in such systems. However, the use of a bentonite containing Mg-smectite has favored the identification of bentonite mineral alteration, producing chlorite-type minerals that should be considered in future geochemical modeling of Fe–bentonite systems.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/app14031259/s1>: Figure S1: XRD of sections from the steel interface: (a) 1 month; (b) 6 months; (c) 22 months.

Author Contributions: Conceptualization, C.M.-H., R.F. and J.C.; methodology, C.M.-H., R.F. and J.C.; software, C.M.-H., R.F. and J.C.; validation, R.F. and J.C.; formal analysis, C.M.-H.; investigation, C.M.-H., R.F. and J.C.; resources, C.M.-H., R.F. and J.C.; data curation, C.M.-H., R.F. and J.C.; writing—original draft preparation, C.M.-H.; writing—review and editing, R.F., J.C. and C.M.-H.; visualization, C.M.-H., R.F. and J.C.; supervision, R.F. and J.C.; project administration, J.C.; funding acquisition, J.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research has been developed by the UAM AcMe research group to support the WP.2 EURAD-ACED project results, which has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No. 847593.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: The authors acknowledge the contribution of two anonymous reviewers for their suggestions to improve the quality of the manuscript.

Conflicts of Interest: The authors declare no conflicts of interest.

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