

MONITORING WATER-CHEMISTRY EVOLUTION IN THE BENTONITE BUFFER USING MAGNETS: EFFECTS OF CORROSION ON BUFFER STABILITY

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Bentonite has been chosen as a buffer material by several national nuclear-waste management companies because of its swelling capacity and low water permeability, and because it retards the transport of radionuclides and corrosion products toward the geosphere. The aim of the present study was to develop a magnetic material that has the ability to detect changes in groundwater compositions in an underground nuclear-deposit facility through variation in its magnetic properties with time.

The present study has investigated the effect of the corrosion of NdFeB magnets on the Na-bentonite buffer under different environmental conditions. Seven different aqueous solutions were used for long-time exposure tests (70°C, 5 months) with fragments of NdFeB magnets and powdered Na-bentonite. The corrosion of NdFeB alloy had no detectable effect on the mineralogy of the clay minerals, and any change on the bentonite matrix, measured through X-ray diffraction analysis, was related to the different initial chemistry of the solutions.

1. Introduction

With the development of the policy to implement geological disposal of nuclear waste in the UK, and the quest for a suitable location or locations for the Geological Disposal Facility (GDF), short- and long-term passive and remote monitoring of the bentonite-based Engineered Barrier System (EBS), typical of a number of disposal concepts, has emerged as a key issue. As part of a major Engineering and Physical Sciences Research Council-Nuclear Decommissioning Authority (EPSRC-NDA)-sponsored research consortium focused on the monitoring of EBS, the capability of selected permanent magnets to be employed to detect the evolution of groundwater chemistry within the EBS is being investigated. The commercial N42-grade NdFeB alloy magnet was chosen to investigate the variation in magnetic properties with time as a consequence of reactions and corrosion. The final aim was to develop a sensor that may be monitored remotely. From the perspective of the integrity of the EBS, the

question of whether the corrosion processes, which enable magnetic monitoring, affect negatively the performance of the bentonite buffer itself, must also be asked.

Bentonite has been chosen as a buffer material by several national nuclear-waste management companies because of its swelling capacity and low water permeability, and because it retards the transport of radionuclides and corrosion products toward the geosphere (Madsen, 1998).

The interaction between bentonite and iron (Fe) has been investigated to model montmorillonite stability and the evolution of the waste canister–bentonite buffer interface through time (Wilson *et al.*, 2006; Marty *et al.*, 2010) and its dependence on alkalinity (Charpentiera *et al.*, 2006) or salinity (Milodowski *et al.*, 2007).

Corrosion of Fe-bearing materials leads to precipitation of microcrystalline oxyhydroxides as common products in a first aerobic corrosion during which all oxygen available in the system is consumed. This is followed by anaerobic corrosion which is said to determine the long-term behavior of the canister/bentonite system (Kaufhold *et al.*, 2015). At temperatures of $<100^{\circ}\text{C}$, smectites are transformed into Fe-smectites or 7 Å phases (berthierine) (Kaufhold *et al.*, 2015). Above 150°C , they transform into 14 Å phases (chlorite, saponite) (Wersin and Mettler, 2006; Wersin *et al.*, 2008).

2. Materials and methods

The present study investigated the effects of corrosion of permanent NdFeB magnets on natural Na-bentonite MX80 from Wyoming (USA), previously characterized by Madsen (1998) and Pusch (2006). Compacted MX80 clay ‘doughnuts’ were supplied by RS minerals (Cleveland, UK) and ClayTechAB (Lund, Sweden). Phase quantification was given by Madsen (1998).

The corrosion of the NdFeB magnets (grade N42 NdFeB permanent alloy) within the bentonite buffer was investigated in a saturated and sealed environment, using deionized water, chloride (1 M NaCl, KCl, and CaCl_2), and hydroxide (0.1 M NaOH and KOH, and 0.05 M $\text{Ca}(\text{OH})_2$) solutions. The 5-month experiment (at a constant temperature of 70°C) was performed using 50 mL borosilicate glass serum bottles, filled with powdered MX80 Na-bentonite mixed with fragments (size ranging from 5 mm to 1 cm) of NdFeB magnets (clay:magnet volume ratio 19:1) and aqueous solution (solution accounted for 70% and solids for 30% of the volume). The bottles were left with 25% void space and were sealed using butyl rubber septa and high-temperature resistant silicon paste.

The resultant clays were sampled at the magnet–matrix (bentonite) interface washing the magnet with acetone. Clays were prepared as oriented mounts on glass slides, and then analyzed, after air drying and glycol solvation as described by Moore and Reynolds (1997), using a Bruker (Coventry, UK) D8 Advance Diffractometer with a sol-x energy dispersive detector and $\text{CuK}\alpha$ radiation (measurement range = $2\text{--}70^{\circ}2\theta$, step size = $0.02^{\circ}2\theta$, step time = 1.5 s). Background removal was performed by means of an automatic function and calibration using the quartz 001 peak at $26.6^{\circ}2\theta$. The bentonite samples reacted with saline waters (1 M NaCl, KCl, and CaCl_2) contained precipitated Fe-(oxyhydr)oxides which were digested using a dithionite-citrate system buffered

with Na bicarbonate (after Mehra and Jackson, 1958). The same specimens were also sampled in areas outside the visible reaction haloes to evaluate any changes in the areas unaffected by Fe-(oxyhydr)oxide precipitation.

3. Results and discussion

Samples reacting in saline environments showed corrosion effects (Figure 1) resulting in disaggregated magnet fragments. A red halo at the bentonite–water interface became a distinguishing feature, fading to a yellow to greenish gray color toward the bentonite matrix. This was due to precipitation of Fe (oxyhydr)oxides during aerobic corrosion.

The sample reacting with deionized water showed disaggregation of the magnets, but featured no reddish halo in the matrix. Interestingly, samples reacting in alkaline environments showed only partial oxidation of the magnets, with the formation of a layer of oxyhydroxides ($\text{Nd}(\text{OH})_3$ and FeOOH) on the magnet's surface, as measured using semi-quantitative X-ray diffraction (XRD). The study of oxides and oxyhydroxides is not immediately relevant to the present study; these are addressed by Rigonat *et al.* (2015). The XRD patterns of air-dried and ethylene-glycolated clays collected from the deionized water-treated sample showed the series of basal reflections characteristic of Na-montmorillonite and, thus, shifted toward lower diffraction angles after glycol solvation (Figure 2).

The XRD pattern of the air-dried samples after reaction with alkaline solutions (Figure 3) revealed slightly asymmetric 001 reflections centered at 12.6 Å for the bentonites reacted in NaOH solution. KOH solution-treated samples showed peaks centered

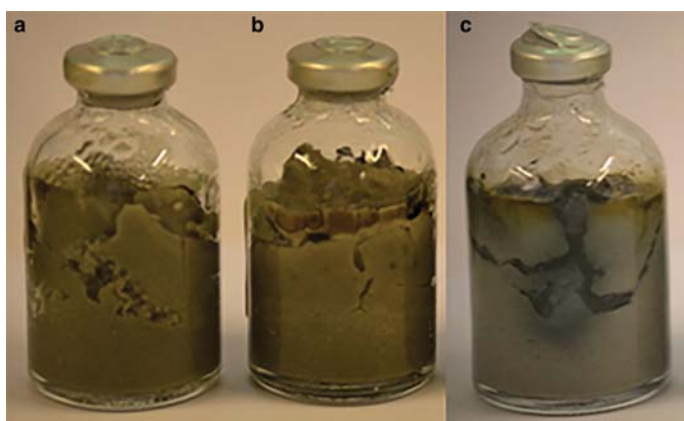


Figure 1. Post-extraction pictures of NdFeB/bentonite mixtures reacted with (a) distilled water, (b) 0.1 M Na(OH) solution, (c) and 1 M NaCl solution. The red patina visible in the samples in the middle and on the right is caused by precipitation of Fe (oxyhydr)oxides.

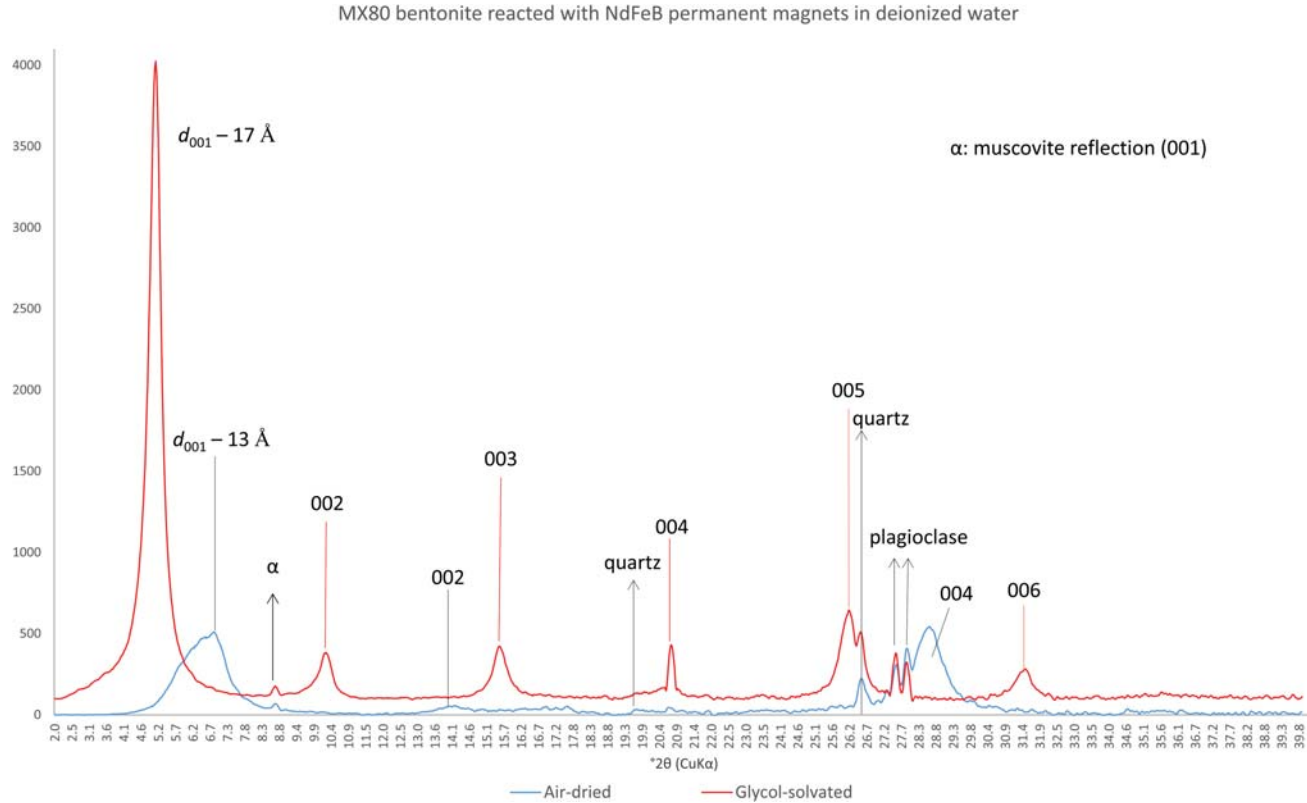


Figure 2. XRD traces of air-dried (blue) and glycol-solvated (red) clay from a Na-montmorillonite/NdFeB mixture reacted with deionized water. Red lines relate to reflections of ethylene-glycolated samples, black lines to air-dried samples, and black arrows to accessory minerals.

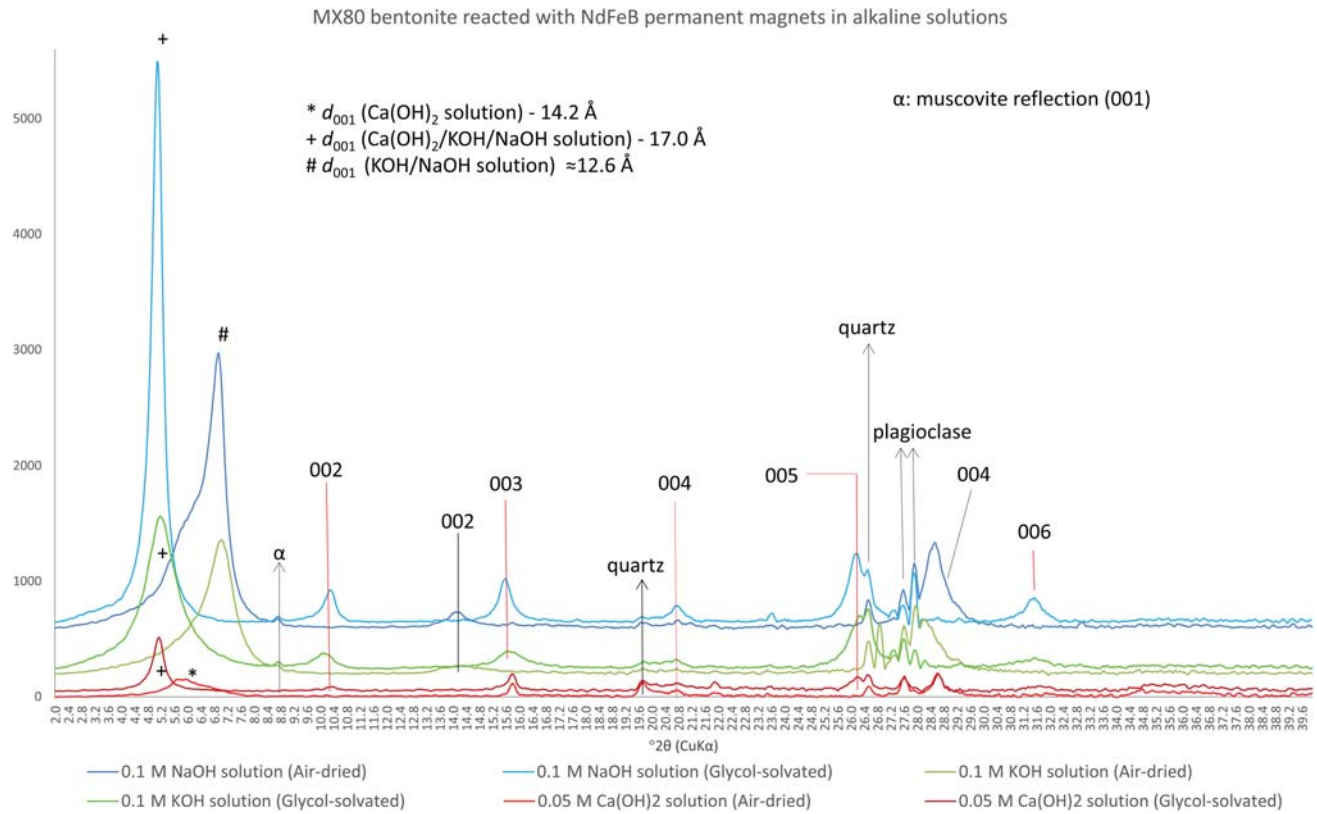


Figure 3. XRD traces of air-dried and glycol-solvated clays from Na-montmorillonite/NdFeB mixture reacted with alkaline solutions. Red lines relate to reflections of ethylene-glycolated samples, black lines to air-dried samples, and black arrows to accessory minerals.

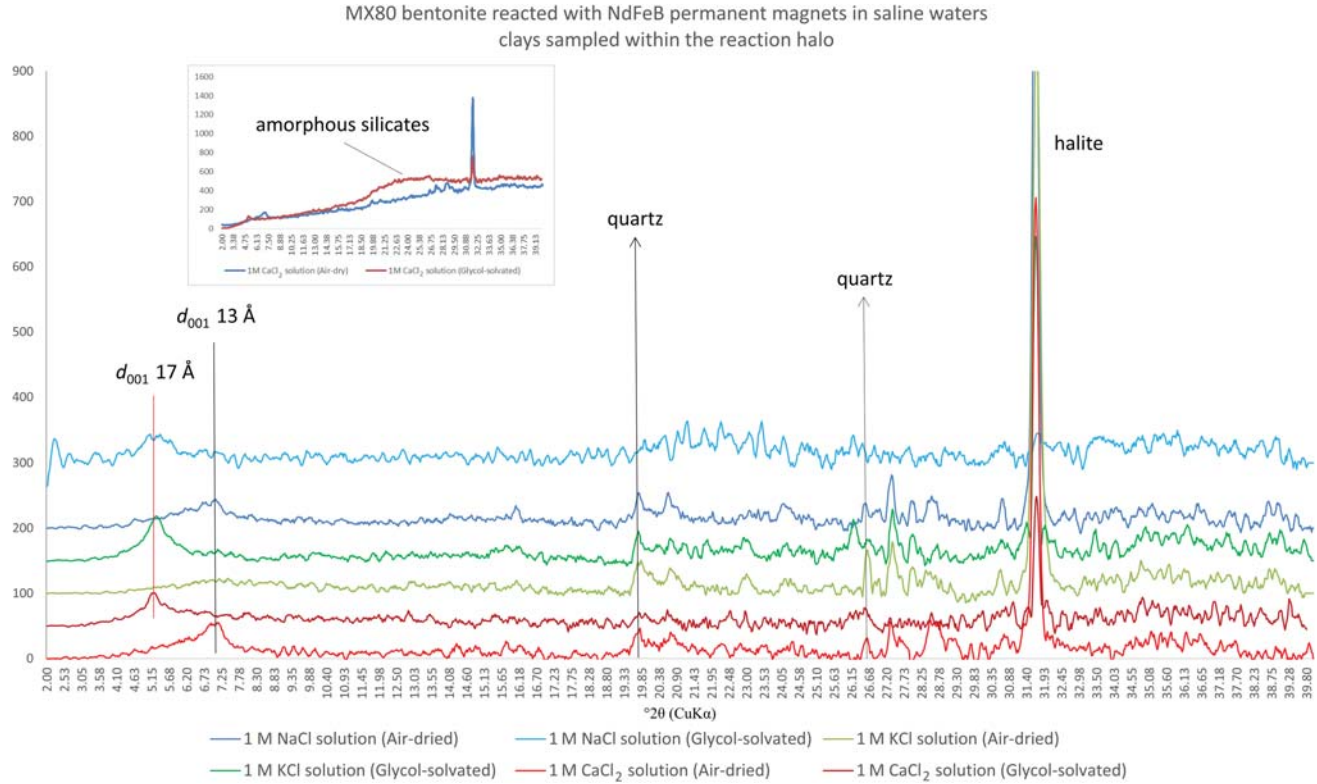


Figure 4. XRD traces of air-dried and glycol-solvated clays from Na-montmorillonite/NdFeB mixture reacted with saline solutions and sampled at the magnet/matrix interface. The traces were all smoothed and the background removed. An example of trace without background removal is displayed in the inset figure. All the 001 reflections are very small and broad (the air-dried KCl-solution trace is flat) but increase slightly in intensity and shift toward lower diffraction angles after glycol solvation. Red lines relate to reflections of ethylene-glycolated samples, black lines to air-dried samples, and black arrows to accessory minerals.

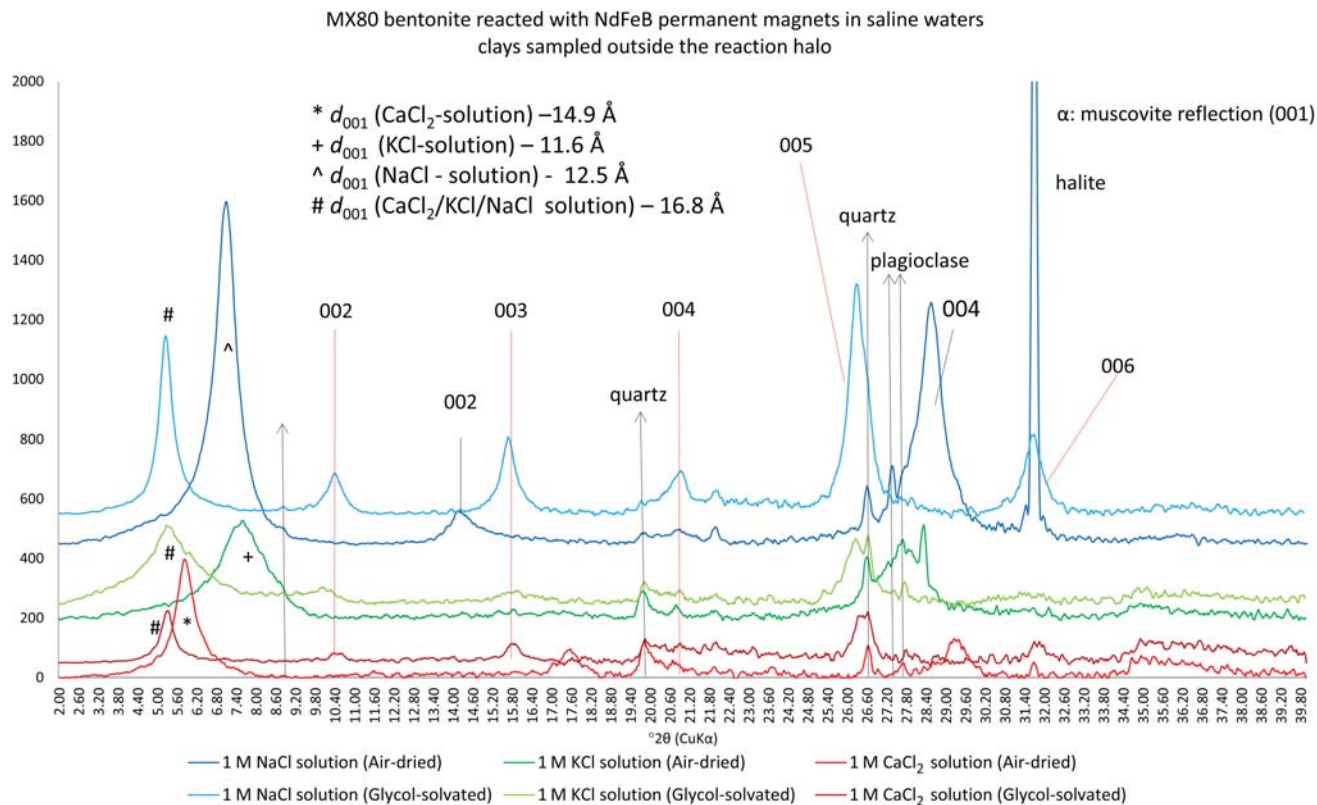


Figure 5. XRD traces of air-dried and glycol-solvated clays from Na-montmorillonite/NdFeB mixture reacted with saline solutions and sampled in the unaltered matrix. The positions of 001 reflections in the air-dried traces of KCl- and NaCl-solution treated samples ($\sim 1w$) show significant deviation from the CaCl₂ water-treated sample ($\sim 2w$) but they were all centered at 16.8 Å after glycol solvation. Red lines relate to reflections of ethylene-glycolated samples, black lines to air-dried samples, and black arrows to accessory minerals.

at slightly higher diffraction angles. The $\text{Ca}(\text{OH})_2$ solution-reacted bentonite contained a weaker and broader basal 001 reflection centered at $14.2^\circ 2\theta$. All of the traces collected after glycol solvation showed a shift of the first basal reflection toward lower diffraction angles (corresponding to a d value of 17.0 Å) and also a sharpening of the peaks. The different behavior of the air-dried $\text{Ca}(\text{OH})_2$ solution-treated sample with respect to the others is explained by the formation of interstratified Ca-Na-montmorillonite (McAtee, 1956)

The clays collected at the magnet–matrix interface in the samples reacted with chloride solutions showed very weak or flat reflections (Figure 4). The pattern for air-dried samples exhibited peak intensities which were 20 times lower than the samples in Figures 3 and 5. The 001 reflections from the glycol-solvated samples were sharper and slightly more intense, but still rather low. The traces without background removal showed a hump typical of amorphous silicates (Figure 4, inset).

The XRD patterns (Figure 5) of clays sampled in the matrix unaffected by corrosion or leaking of Fe revealed that the basal reflections for the air-dried KCl- and CaCl_2 -solution-treated samples were decreased significantly compared with the NaCl-solution reacted sample. The d_{001} value increased to 16.8 Å upon glycol solvation (Figure 5) and the glycol-solvated, KCl-treated sample had a broad peak that is well known for K-exchanged smectites.

4. Summary and conclusions

Tests on the NdFeB-bentonite mixtures showed that, after an initial period of aerobic corrosion which led to the deposition of Fe (oxyhydr)oxides at the solution–clay interface, the process switched to anaerobic corrosion (*cf.* Kaufhold *et al.*, 2015) which was particularly evident in samples corroded within chloride solutions. Powder XRD analyses run on the clays sampled in the corrosion-affected area in saline-treated samples revealed no reflections typical of Fe-bearing smectites, although their presence, as weakly crystallized phases, cannot be excluded. The changes in the samples reacted with K-rich solutions can be related to different cation:water ratios in the interlayer space due to K/Na cation exchange.

The changes in the positions of the peaks were attributed exclusively to K-Na and Ca-Na cation exchange in the interlayer; hence, the observed transformations are only related to the initial composition of the solution.

The clays collected at the magnet–matrix interface in the samples showing the most intense effects of corrosion, displayed very weak and broad basal reflections even after glycol solvation. These weak and broad reflections are thought to be related to a low-temperature dissolution/precipitation process. Broad, weak maxima are produced by the combination of the fine particle size and poor crystallinity with complex random interstratification (as found in soil profiles by Brown and Jackson, 1956). These clays formed at the interface, in a silica gel matrix, might represent a step of pure Na-montmorillonite evolution toward an Fe-enriched member proceeding from an aerobic to an anaerobic environment.

Experimental results indicate that under the environmental conditions applied, the corrosion of the NdFeB magnets is different, going from alkaline to saline, circum-neutral environments. The corrosion process does not cause a loss of performance of the clay in terms of swelling, as no corrosion-related, neoformed, non-swelling clay minerals were detected and all the changes in the bentonite matrix were related exclusively to the initial water composition.

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