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CO_2 effect on the pH of compacted bentonite buffer on the laboratory scale

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ABSTRACT: Disposal of Finnish spent nuclear fuel is planned to be based on the KBS-3 repository concept. The role of the bentonite buffer in this concept is essential, and thus the behaviour of the bentonite has to be known. The experiments in this paper concentrated on providing information about the effects of carbon dioxide $CO_2(g)$ partial pressure on compacted sodium bentonite, giving an insight into the buffering capacity. The experimental setup consisted of a hermetic box which had a CO_2-adjusted atmosphere, and the bentonite was in contact with this atmosphere through water reservoirs. The results indicated that it is possible to measure online the changing pH in the porewater inside compacted bentonite using IrOx electrodes. It was found that the pH fell if the CO_2 partial pressure increased above atmospheric conditions. The experimental results indicated a greater fall in pH than in our model in the test cases where CO_2 was present. The pH in the experiment with 0 P_{CO_2} remained nearly constant throughout the 5 month period. On the other hand, the pH dropped to near 6 with 0.3 P_{CO_2} and to 5.5 with 1 P_{CO_2}.

KEYWORDS: bentonite, pH, carbon dioxide, buffer, alteration, compaction.

Many countries, including Finland, are planning to use bentonite as a buffer material around the waste canisters in their high-level radioactive waste disposal concept. The Finnish plan follows the KBS-3 (KärnBränsle Säkerhet) concept, which aims at long-term isolation and containment of the spent fuel assemblies in copper canisters with a nodular cast iron insert. The canisters are emplaced over 400 m deep into the crystalline bedrock. Each canister is separated from the bedrock by bentonite (the buffer) rings and placed in a drilled borehole. The purpose of the buffer material is to maintain the integrity of the canisters by protecting them from detrimental Thermal-Hydraulic-Mechanical-Chemical-Biological (THMCB) processes and to limit and retard the release of any radionuclides in the case of a damaged canister (Pastina & Hellä, 2006).

The knowledge of pH conditions is essential for performance assessment (PA) since pH strongly affects the mobility of most relevant radionuclides (see e.g. Kohlicková & Jedináková-Krizová 1998). The subject has been studied earlier by Wersin (2003). In these studies he used the approach of Bradbury & Baeyens (1997, 1998) to model the results of Muurinen & Lehikoinen (1999), who studied the changes in porewater chemistry in compacted bentonite in different ionic strengths and in different solid/liquid ratios. Wersin (2003) made a sensitivity analysis of different parameters affecting the bentonite porewater and found that the main reactions controlling major ion chemistry were calcite and gypsum equilibrium, Na-Ca exchange reactions and de-protonation of functional surface groups. The uncertainty in pH was found to be mainly affected by the P_{CO_2} of the surrounding host rock. In the paper by Wersin (2003) it was clearly suggested that diffusion experiments on compacted samples should be performed, focusing only on the identification and quantification of surface exchange and sorption reactions.

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The electrodes used in this paper were tested previously by Muurinen & Carlsson (2007, 2010) who measured the pH and Eh inside the compacted bentonite and in pore water that had been squeezed out during the compaction of the clay. The performance of electrodes was tested at different compaction densities and by saturating the bentonite with deionized water, with 1 M NaOH conditions remaining constant. The results indicated the usefulness of IrO_x electrodes for measuring the pH of the porewater inside the compacted bentonite (Muurinen & Carlsson, 2007).

In the paper of Muurinen & Carlsson (2010) the model of Bradbury & Baeyens (2002, 2003) was tested for the pH measurements with IrO_x electrodes with different bentonite/external water ratios (chloride porosity). The model assumes that the initial state of the edge site in the bentonite is in equilibrium with the atmospheric carbon dioxide. The results showed that the model of Bradbury & Baeyens (2002, 2003) is quite capable of modelling the results from the compacted samples and it is possible to use IrO_x electrodes for diffusion experiments also (Muurinen & Carlsson 2010).

The aim of the experiments reported here was to study how carbon dioxide CO_2(g) partial pressure affects both the pH in the compacted MX-80 bentonite and the buffering capacity of bentonite.

EXPERIMENTAL

Materials

The Wyoming MX-80 bentonite used in these experiments consists mainly of sodium montmorillonite and smaller amounts of other minerals (quartz, calcite, feldspar, etc.) (Kiviranta & Kumpulainen, 2011). The beneficial properties of bentonite are mainly determined by this montmorillonite mineral (see, e.g. Grauer, 1986). These properties include the sorption capability during canister failure, the ability to swell upon saturation with water, the mechanical and chemical protection around the canister, and good enough thermal conductivity to dissipate the heat emitted by the waste.

The Tetrahedral-Octahedral-Tetrahedral (TOT) layer structure of montmorillonite has a permanent negative charge, which is compensated by the exchangeable cations within the area of the interlayer space. In aqueous solutions, these cations can undergo a stoichiometric exchange with cations in a solution. The total amount of exchangeable cations is called the cation-exchange capacity (CEC) (see, e.g. Kaufhold & Dohrmann, 2013). According to Kaufhold *et al.* (2008) the form of these cations can affect the pH at small solid/liquid ratios which is not the case in highly compacted bentonites (Muurinen & Carlsson, 2010). There is also a second category of reactive sites related to montmorillonite. These are called surface hydroxyl groups and they are located along the edges of the TOT layers. These sites can protonate/deprotonate according to the pH in the surrounding solution, which means that the hydroxyl groups can function as a powerful pH buffer (Bradbury & Baeyens, 2002).

Concept

The experimental setup consisted of a hermetic box with a CO_2-adjusted atmosphere, diffusion cell, pH electrodes, compacted bentonite sample, and water reservoirs (Fig. 1). The gas in the hermetic box was in contact with the external solution of the diffusion cell. The geometry of the bentonite was cylindrical, the diameter of the sample was 20 mm, and the length 20 mm. The samples were compacted to a dry density of 1.57 g/cm^3. The volume of each external water reservoir was 50 ml, and these were filled with 0.1 M NaCl at the beginning of the test. The bentonite samples were fully saturated by the deionized water mixed into the bentonite before compaction. The CO_2 partial pressures were kept constant through the experiment by changing the gas in the hermetic box twice a month. The temperature was 25°C in all four experiments. All of the experiments were carried out with unpurified MX-80 bentonite.

Test cases

The experiment was conducted under three different conditions with the same apparatus. The only parameter that was varied in these experiments was the partial pressure of CO_2. All the three experiments, which are listed in Table 1, were sustained at atmospheric pressure, and in two cases the other gas besides CO_2 was argon. The reservoir water pH was evaluated through modelling before the experiment with the Geochemist's Workbench (GWB). The water reservoir pH under test case atmosphere means that there is no buffer present.

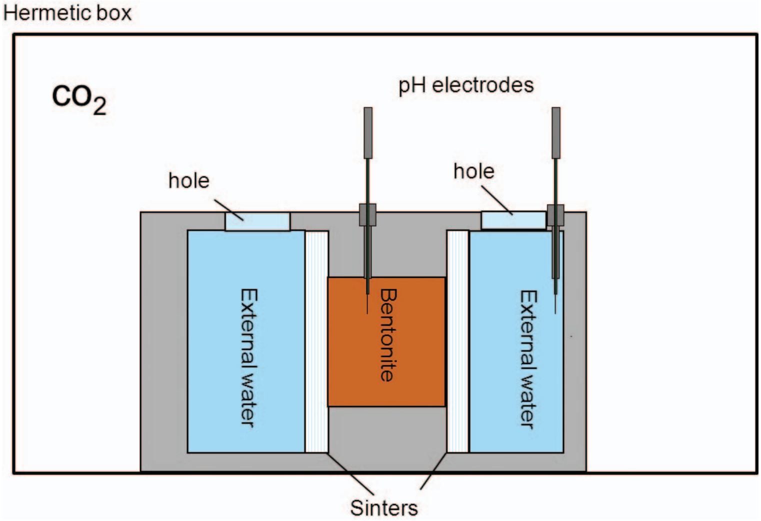

FIG. 1. Schematic picture from the experimental setup.

Analyses

The pH was measured online from the porewater of the bentonite and water reservoir with calibrated pH-electrodes (Muurinen & Carlsson, 2009). However, during the experiment, leakage-free single-junction reference electrodes were observed to shift during the experiments under acidic conditions. Therefore, the external water pH values were measured by a commercial Ross electrode about once a month. These values were used to calculate theoretical values for the reference electrodes to match the online measurements and the Ross electrode measurements from the external water. The same calculated reference electrode values were used for the IrOx electrodes which were employed to measure the pH inside the bentonite. Some uncertainties lie in this method and therefore more research will be undertaken to verify these results.

Modelling

The pre-modelling of the experiment was performed using GWB to approximate the pH changes and the time needed to reach constant conditions. After the experiment, the model and the experimental results were compared. The model was arranged as a column model, where there was 2 cm of bentonite in the middle, and 50 ml water cells at both ends with inlets at the ends of the water cells. These inlets kept the outer CO_2 (g) partial pressure constant. The model included cation exchange, surface complexation and mineral equilibrium of calcite and gypsum. The relevant reactions in this experiment should be the surface complexation reactions, which can work as a pH buffer. According to Bradbury & Baeyens (2002) there are two different kinds of weak sites SOH (in MX-80) which can both protonate and deprotonate, according to the equations below:

TABLE 1. Test cases and evaluated water reservoir pH before the experiment.

Test	Bentonite type	Solution type	Partial pressure of CO_2 (atm)	Water reservoir pH under test case atmosphere	Evaluated water reservoir pH	Experimental time (months)
1	MX-80	NaCl (0.1 M)	0 (Argon)	7	~7	6
2	MX-80	NaCl (0.1 M)	0.3 (Argon)	5.7	6.2	6
3	MX-80	NaCl (0.1 M)	1	3.92	5.9	6

TABLE 2. Water and mineral composition in the model.

Ion/mineral	Bentonite water molality (mol/kg)	Water cell molality (mol/kg)	Mineral volume fraction in bentonite (%)
Na^+	0.127	0.1	
K^+	0.0031	traces	
Mg^{2+}	0.0041	traces	
Ca^{2+}	0.0103	traces	
SO_4^{2-}	charge balanced	traces	
$H_4SiO_4(aq)$	traces	traces	
Cl^-	traces	0.1	
Gypsum			0.36
Calcite			0.72
Na-montmorillonite			55.62

$$SOH + H^+ = SOH_2^+ \quad (1)$$
$$SOH = SO^- + H^+ \quad (2)$$

Parameters

The diffusion coefficient used for all ions was 10^{-10} m^2/s (the porosity 0.43 and tortuosity 0.12 of bentonite were included in the diffusion coefficient). GWB calculates porosity according to given volume fractions of the minerals and the fluids, and takes this into account when calculating the permeability of the material. The water composition and mineral volume fractions used in the modelling are listed in Table 2. The bentonite porewater was calculated such that the ion exchange and sorption sites were filled according to the experimental results of Kiviranta & Kumpulainen (2011). Mineral volume fraction and cation exchange composition were also taken from Kiviranta & Kumpulainen (2011) such that the gypsum and calcite amounts were from this report and the rest of the mineral volume fraction was supposed to be montmorillonite. The material in the report is called Wy–VT0002-BT1-3-Sa-R (Kiviranta & Kumpulainen, 2011).

TABLE 3. Selectivity coefficients and reaction for cation exchange on MX-80 (Bradbury & Baeyens, 2002).

Exchange reaction	Selectivity coefficient
$NaX + K^+ <=> KX + Na^+$	4
$2NaX + Mg^{2+} <=> MgX_2 + 2Na^+$	2.2
$2NaX + Ca^{2+} <=> CaX_2 + 2Na^+$	2.6

The cation-exchange capacity used was 93 meq/100 g (Kiviranta & Kumpulainen, 2011) The selectivity coefficients and cation exchange reactions can be found in Table 3.

The protolysis constants as well as surface areas of bentonite can be found in Table 4. The Thermoddem database was used in the calculations for the water chemistry part (Blanc *et al.*, 2007).

RESULTS AND DISCUSSION

At the beginning of the test the bentonite was in equilibrium with 390 ppm $CO_2(g)$ volume fraction of ambient air (partial pressure was about 39 Pa). The first test case shows that the pH rises slightly when the CO_2 (g) partial pressure decreases (Fig. 2). The pH results shown in the figures are

TABLE 4. Site types, capacities and protolysis constants (Bradbury & Baeyens, 2002).

Site types:	Site capacity (mol/kg)
Sw1OH	0.04
Sw2OH	0.04
Surface complexation reaction	log K_{int}
$Sw1OH + H^+ <=> Sw1OH^{2+}$	4.5
$Sw1OH <=> Sw1O- + H^+$	−7.9
$Sw2OH + H^+ <=> Sw2OH^{2+}$	6
$Sw2OH <=> Sw2O- + H^+$	−10.5

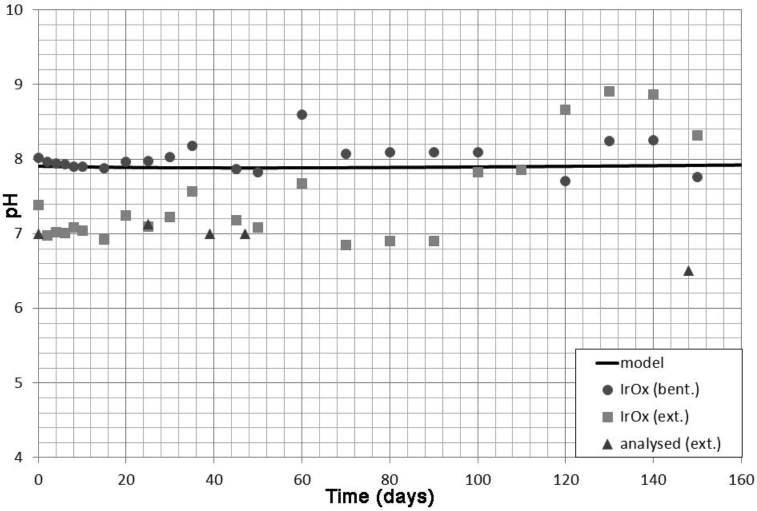

FIG. 2. Results of test case 1, CO_2 (g) partial pressure 0.

from the middle of the bentonite and from the external water solution. The results were analysed over 160 days. The pH of the external solution according to the modelling can be seen in Table 1. The meanings of the legends are ext.= external water measured with normal pH electrode and with our own handmade iridium-oxide (IrOx) electrode and the model legends refer to our calculated model. IrOx(bent.) means that the electrode was in the middle of the bentonite tablet. As can be seen from the figure, bentonite buffers the changes as the CO_2 (g) volume fraction decreases from 390 ppm towards zero. The differences in the external water results of the two different electrodes are related to the reference electrode calibration.

In the latter two tests, the pH falls as the CO_2 (g) partial pressure increases (Figs 3 and 4). Our model clearly gives a smaller decrease in pH than in the experiment. In test case two (Fig. 3), the pH in the experiment drops down from 9 to approximately 6,

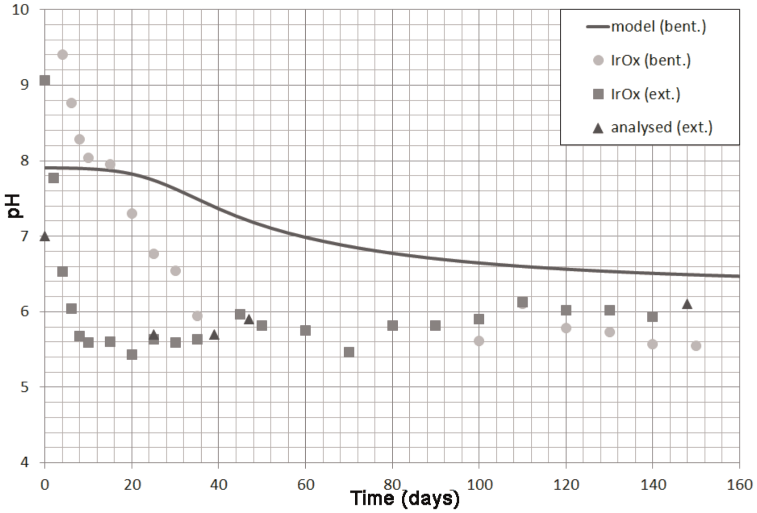

FIG. 3. Results of test case 2, CO_2 (g) partial pressure 0.3.

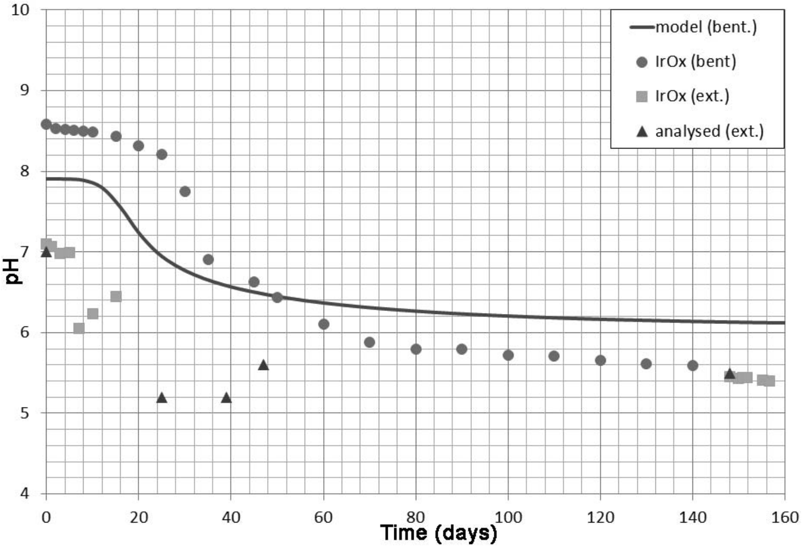

FIG. 4. Results of test case 3, partial pressure 1.

while the model shows only a drop to 6.5. The higher values for the IrOx(bent) electrode at the beginning could be related to the fact that it takes time for the electrode to find the equilibrium potential at the beginning of the test. The fact that test case 2 does not show a buffering trend at the beginning of the test is probably related to the fact that there were some problems with the reference electrode during the test.

In test case 3 (Fig. 4), the model shows a drop from 8 to 6.1, but the experimental results clearly show a bigger drop in pH from 8.6 to approximately 5.5. In this figure, it is clearly visible that the bentonite buffers the pH change at the beginning of the test before the pH starts to fall. However, again the pH can be seen to exhibit a greater drop than in the model.

The differences between the modelling and experimental results is mainly related to the fact that GWB calculates some kind of equilibrium state (with model minerals) in water cells even if those cells do not include minerals. This leads to higher pH in water cells than in the experiment. The starting values in the outside water cells in the model was 6.2 for 0.3 P_{CO_2} (Fig. 3) and 5.9 for 1 P_{CO_2} (Fig. 4). In the experiment the starting points were respectively 5.6 and 5.2 at the beginning and the pH rose slightly during the test when the water cells were equilibrating with the bentonite pore water.

The Bradbury & Baeyens (2002) model does not take into account the electrostatic phenomena in the bentonite (see, e.g. Bourg *et al.*, 2007), which could also affect the modelling results. Bourg *et al.* (2007) also showed that none of the available surface complexation models work over the entire set of experimental conditions, which in our case are extended to high CO_2 fugacity. Additionally, in the experiment, some complexes can form, for example with CO_2 (g), which can interact with the surface complexation sites and could induce some effects on the results. The calibration, due to the fact that the reference electrodes did not work very well in acidic conditions, could affect the experimental results. Thus, additional experiments are needed to confirm these measurements and to understand the phenomena in bentonite better.

As can be seen, it is not possible to get the modelling results to match the experimental results perfectly. We tried to change the number of surface sites, but this just changed the point at which the pH starts to decrease from the original value. Changing the diffusion coefficient also affected this point, but the pH does not fall lower in the model owing to the external water in the model not having as low a value as in the experiment. The effect of calcite and gypsum minerals were also tested and it seems that in the compacted system the only feature buffering the pH changes is the surface protonation sites (as the water amount compared to the surface site

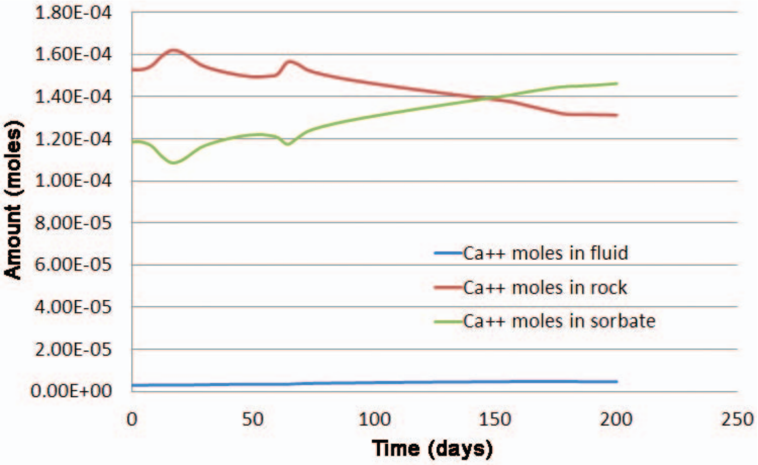

FIG. 5. Calcium amounts from the middle of the bentonite in the model (1 P_{CO_2} case).

amounts is very small). Gypsum dissolves after 50 days in the model and calcite is first precipitated but starts to dissolve after the gypsum is dissolved; however, the total amount is the same as the original amount at the end of the test time. The calcium fraction increases in the exchanger phase due to dissolving gypsum from 28% to 31%. The modelled calcium amounts in fluid, rock (minerals) and sorbate (cation exchanger) can be seen from Fig. 5.

CONCLUSIONS

We can see that the bentonite buffering capacity in the kind of conditions where the water/bentonite ratio is high does not prevent pH changes which happen rapidly after 20 days. The only feature buffering the pH changes inside compacted bentonite seems to be the surface protonation sites which can buffer the changes at about 0.3 pH units. However, reactions which have not been previously identified and contribute to the pH drop in addition to CO_2 equilibrium might also occur. Thus, we propose that more results are needed to conclude which kinds of phenomena occur inside the bentonite and whether the electrode calibration was the only reason for such low pH values.

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