

# Mineralogical investigations of the first package of the alternative buffer material test – II. Exchangeable cation population rearrangement

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**ABSTRACT:** Bentonites are candidate materials for the encapsulation of radioactive waste. In the ‘Alternative Buffer Material test’ (ABM), compacted ring-shaped blocks of eleven different buffer materials (mainly bentonites) were packed vertically on top of each other with an iron tube as heater in the centre. These buffer materials started with various exchangeable cation populations (EC<sub>population</sub>). The first ‘ABM package’ was terminated 28 months after installation and the bentonites had been exposed to the maximum temperature (130°C) for about one year. The aim of the present study is first: to describe modification of the cation exchange population, and second to understand the influence of the groundwater on cation exchange at different scales. No significant horizontal variation of any exchangeable cation (EC) was detected between 1 and 7 cm distance from contact with the iron tube. Large total differences of the EC<sub>populations</sub>, however, were observed for the individual blocks after the field experiment ( $n = 21$  blocks) with respect to the composition of the reference materials. The average cation exchange capacity (CEC) values of the analysed bentonites ( $n = 9$  blocks) decreased by 5.5 meq/100 (1.1–8.8 meq/100 g) after the experiment. Exchangeable Na<sup>+</sup> and Mg<sup>2+</sup> decreased on average, whereas Ca<sup>2+</sup> increased. This trend was pronounced in the top region of the parcel (upper seven blocks). Although most changes occurred on the large scale of the whole test parcel, small but important changes were also recorded in the vertical direction on the centimetre scale. The observed differences cannot be explained assuming simply that a bentonite reacts only with neighbouring blocks, which would mean that the system was more or less closed. The differences are much larger and the only conclusion from this observation is that the whole package seems to be influenced by the groundwater which was added from a water tank at the experiment site, enabling at least partial equilibration between the different blocks.

**KEYWORDS:** CEC; exchangeable cation population; bentonite buffer; Cu-trien<sub>5</sub> × calcite; ethanolic ammonium chloride solution, alteration. URL.

Bentonites are candidate materials for the encapsulation of radioactive waste. Concepts for deep

geological storage of such waste are based on bentonite buffers which are parts of engineered barrier systems. Under repository conditions, the long term stability of these engineered barrier systems in crystalline as well as in argillaceous rocks depends on the stability of the smectite

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minerals, particularly with respect to the swelling capacity and cation exchange capacity (CEC).

Experiments for the evaluation of the integrity of bentonite barrier systems have been performed on different scales: (1) lab scale with the possibility to vary different parameters; however, such experiments were often far from realistic. More realistic were (2) field experiments of intermediate size which were performed in hard rock laboratories or underground rock laboratories. Real scale experiments (3) in underground research laboratories have been rarely conducted, mainly because of the enormous amounts of material, preparation and construction work required. All scales are necessary to understand the processes related to cation exchange. The most important scale with respect to long-term safety analysis is the real scale. Exchangeable cation population ( $EC_{\text{population}}$ ) studies are necessary to understand processes such as bentonite erosion in engineered barrier systems. Bentonite erosion is affected by the amount of exchangeable sodium (e.g. Kaufhold & Dohrmann, 2008; Missana *et al.*, 2011), and chemical or physical processes that can affect the erosion such as redistribution of the  $EC_{\text{population}}$  have to be understood.

#### *Laboratory-scale studies – the small scale*

Madsen (1998) studied relevant properties of two bentonites which were well established in radwaste studies: MX80 ( $\text{Na}^+$ -smectite) and Montigel ( $\text{Ca}^{2+}$ - $\text{Mg}^{2+}$ -smectite). He compared their behaviour with altered K-bentonites and concluded that even if strong illitization would occur, “the fixed  $\text{K}^+$  in the illite-smectite mixed-layer is not hydrated” and that the remaining divalent exchangeable cations would preserve significant swelling capacity.

Other studies concentrated on performance of sodium bentonites in many different fields of application which were relevant for safety assessment. Of particular importance is the sealing capacity, which requires high smectite contents. Yong (1999) pointed out that, on the one hand, the sealing capacity of smectitic clays (bentonites) in the presence of water is “both a design consideration and a problem”. High sealing capacities are favourable because sealing elements will be homogenous and cracks/fissures can be closed via self-sealing. On the other hand, prediction of the extent and rates of swelling, wetting performance

when swelling pressures develop, and redistribution of densities and water contents are problematic. Although model developments were quite successful, these problems are still not solved and, as the authors pointed out, all these problems were linked to clay microstructures which were strongly influenced by the distribution of ECs.

The distribution of the ECs is also influenced by accessory minerals of bentonites, particularly when compacted bentonites were subjected to a heat source. Arcos *et al.* (2000) tried to quantify and to model reactions of typical accessory minerals. In their model they used calcite, siderite, quartz,  $\text{SiO}_2$  (amorphous) and anhydrite in combination with realistic pore water, cation exchange competition and pyrite as a redox buffer. The relevant output of their model was that cation exchange reactions were still influencing the ionic composition of pore water after 100,000 years. The authors concluded that “The main process affecting the trace mineral behaviour in bentonite is cation exchange”. Montes-H *et al.* (2005), for example, confirmed this.

#### *Field experiments – the intermediate scale*

Plötze *et al.* (2007) studied the stability of a bentonite buffer (Almeria, Spain) in a small-scale heater experiment which was carried out at the underground laboratory in Mont Terri, Switzerland. The heater element had a diameter of 10 cm and was held at a constant surface temperature of 100°C. The blocks were water saturated for 35 months before an 18 month long heating phase was started. The authors concluded that the bentonite showed only very weak modifications during the heater experiment, such as cementing or aggregation processes. No mineralogical alteration other than cation exchange and very minor changes in layer charge density of smectites could be observed. Samples from the heater region showed an increase in exchangeable magnesium. The total layer charge density of the smectites decreased slightly; however, IR fitting of the OH stretching region did not show significant changes of the octahedral composition.

Olsson & Karnland (2011) studied the mineralogical and chemical characteristics of bentonite blocks (MX80, Wyoming, USA) used in the ‘Long Term Test of Buffer Material’ (LOT) project at the Äspö hard rock laboratory (HRL), Sweden. This project was initiated by the Swedish Nuclear Fuel

and Waste Management Co. (SKB). In that project, samples were kept under repository-like conditions: The A2 test parcel was subjected to elevated temperatures (up to 130°C) and hydration by a Na-Ca-Cl type groundwater for almost six years before it was retrieved and analysed. The experimental design was such that nearly 40 bentonite blocks with a diameter of 28 cm and a height of 10 cm were packed on top of each other to give a 4 m high column. The blocks in the lower 2 m were heated to 130 °C by heater elements inside a central Cu tube, simulating the heat plume of the waste. The bulk density after hydration was reported as 2000 kg m<sup>-3</sup>. The main results were that (a) sulfate was redistributed horizontally in the heated part of the buffer – anhydrite accumulated in the warmer parts, whereas gypsum was dissolved in the peripheral parts of the buffer; (b) Cu was incorporated in the bentonite matrix at the surface of the Cu tube, indicating corrosion of the tube; (c) exchangeable sodium was replaced by exchangeable calcium and magnesium in the warmest zone; and (d) magnesium was also enriched by other processes which could not yet be clarified, possibly by incorporation of magnesium into the structure of montmorillonite.

Wersin *et al.* (2007) reviewed the knowledge on the performance of the bentonite barrier at temperatures above 100°C and concluded that for “more reliable information at temperatures beyond 130°C, a series of long-term experiments examining hydraulic, mechanical and mineralogical changes under realistic conditions would be useful”.

### Real-scale studies

In the Canadian Underground Research Laboratory, a bentonite-based tunnel sealing experiment (TSX) was conducted between 1998 and 2004 in an intact volume of rock within a granitic pluton. Dixon *et al.* (2007) reported on the evolution of two bulkheads, one of which consisted of high-performance concrete and the other of blocks of compacted sand-bentonite material. The TSX was installed in a 3.5 m high by 4.25 m wide tunnel located 420 m below the surface. Heating occurred for a period of approximately one year, and after five years of operation the TSX was dismantled and sampled. To date, no mineral or EC<sub>population</sub> analyses from this experiment have been published.

Dueck *et al.* (2011) reported on hydro-mechanical and chemical-mineralogical analyses of the

bentonite buffer from a full-scale field experiment called ‘Canister Retrieval Test’ (CRT), which was larger than the LOT test. The compacted bentonite surrounding a copper canister equipped with heaters had been subjected to heating at temperatures up to 95°C and hydration by natural Na-Ca-Cl type groundwater for almost five years at the time of retrieval. The bentonite blocks used were 1640 mm in outer diameter and 1050 mm in inner diameter. The same kind of bentonite (MX80, Wyoming, USA) was used but, even at these lower temperatures, sulfate in the bentonite was redistributed and accumulated as anhydrite close to the canister. The authors observed a loss in exchangeable Mg<sup>2+</sup> in the outer parts of the blocks.

Such real-scale experiments are helpful to scale up lab study and field study results to repository-like conditions. However, in all former real-scale and intermediate scale experiments, only one type of bentonite was used. SKB started an intermediate scale field experiment called ‘Alternative Buffer Material test’ (ABM) project (SKB, 2007) to overcome this problem.

### ABM design

The setup of the ABM experiment is similar to the Swedish KBS-3 concept with a metal canister surrounded by clay situated in crystalline bedrock at approximately 500 m depth (SKB, 2007; Eng *et al.*, 2007). This experiment was similar to the LOT experiment; the differences are mainly the scale, which is smaller for ABM, and that the canister is made of common carbon steel instead of copper. The reason for not using a copper pipe, as in most of the experiments at Äspö HRL, was to be able to study the effects of corroding steel in close contact with the buffer material.

The bore holes had a diameter of 30 cm and a depth of 3 m. The outer diameter of the blocks was 280 mm, the inner diameter was 110 mm, and the height was 100 mm. In each experimental package, three electrical heaters were installed to yield the target temperature in the bentonite blocks. A main heater ran along the entire package length (Fig. 1). Two additional heaters were installed, one at the bottom and another at the top to compensate for the temperature loss at the top and bottom and to give a more homogenous temperature distribution throughout the package length.

The experiment consisted of three packages in three separate boreholes; the duration was planned

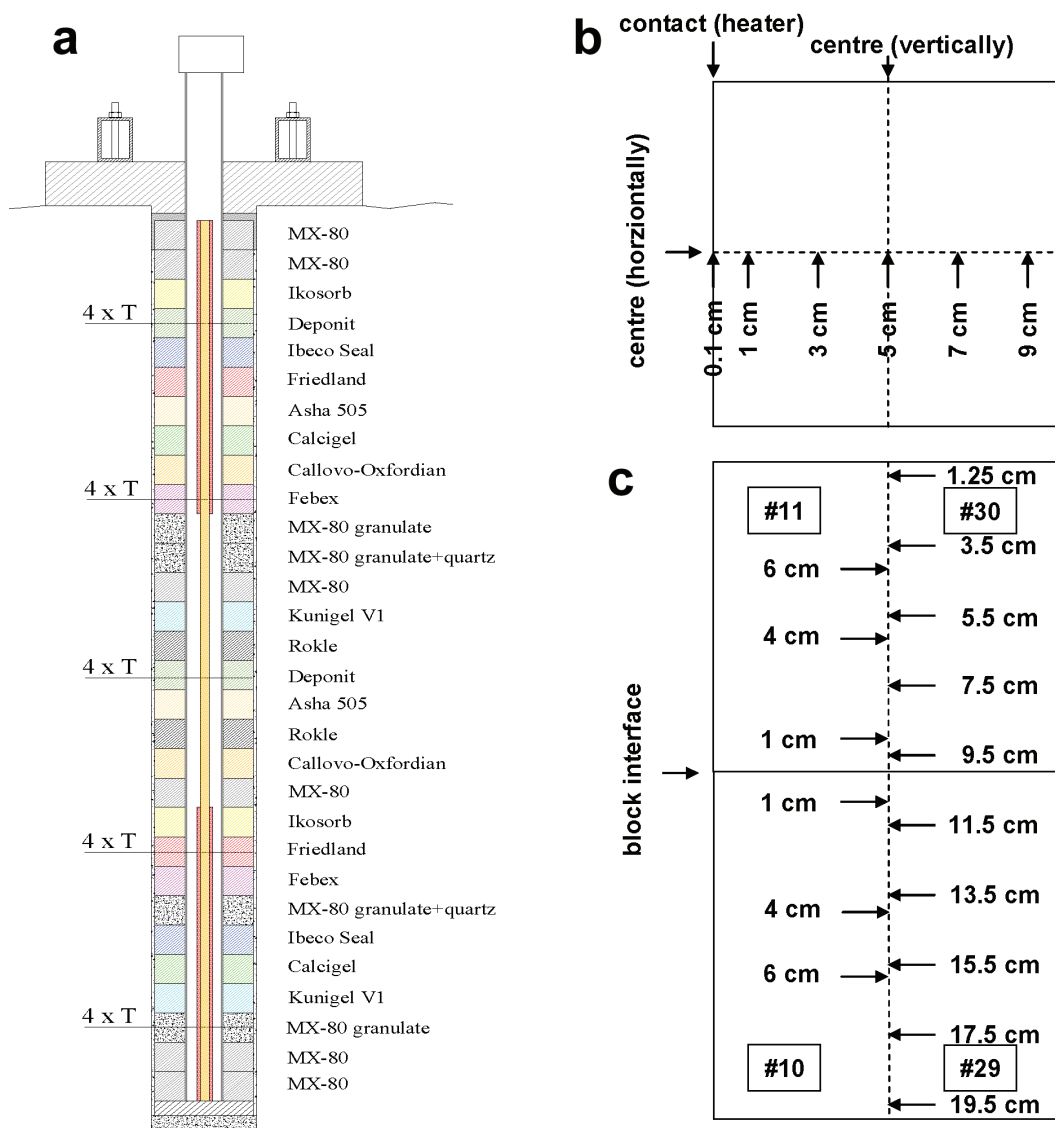


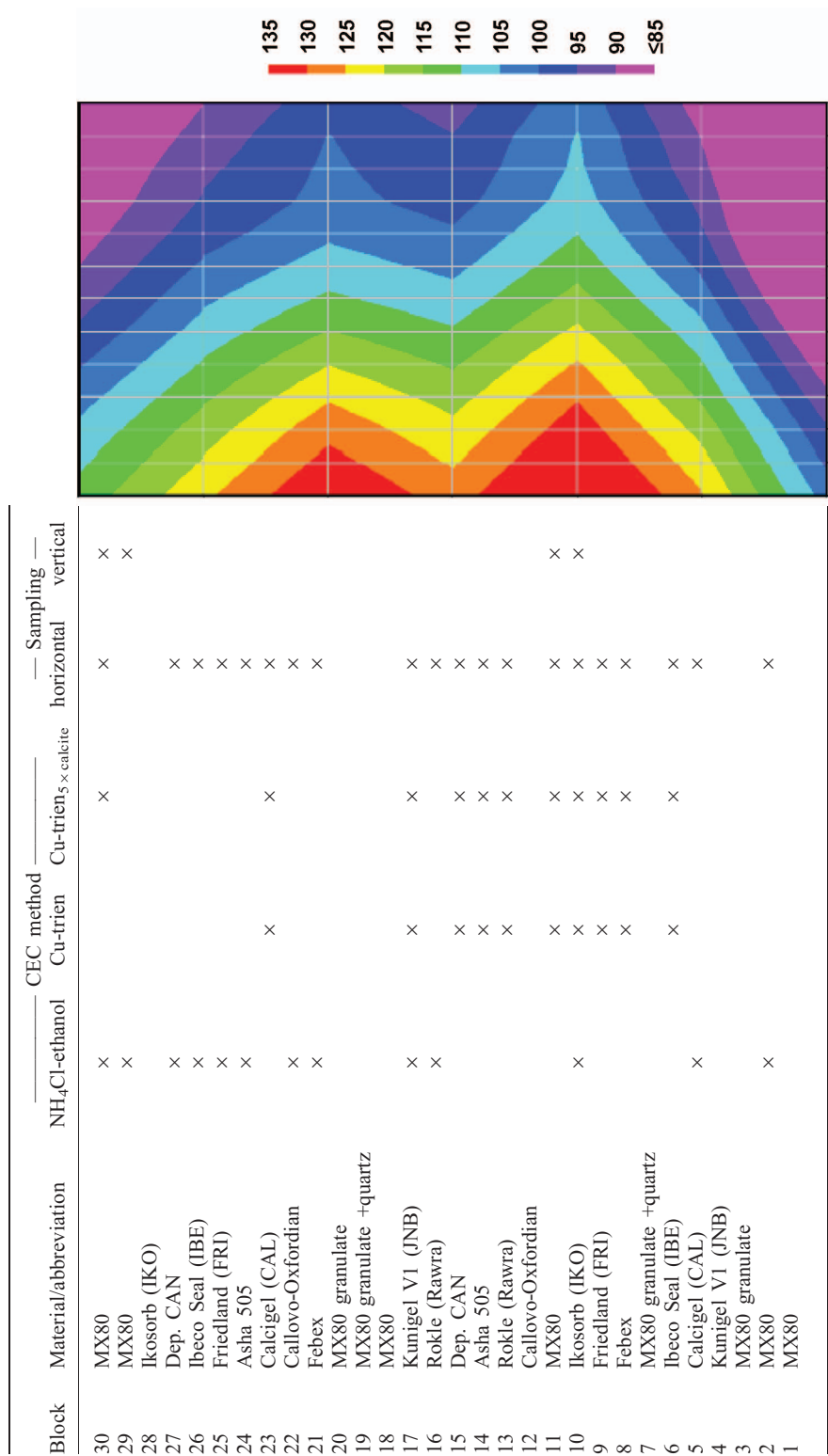
FIG. 1. (a) Experimental setup of the ABM 1 package. 4XT marks the position of thermocouples. Block numbering starts from the bottom to the top. (b) Horizontal sampling of the blocks. (c) Vertical sampling of the blocks #11 and #10 (left, bentonite/ bentonite interface) and of the blocks #30 and #29 (right, bentonite/cement interface).

for one, three and five years followed by excavation. ABM aimed at using greatly different buffer materials (mostly bentonites) packed on each other. Eleven different clays were compacted to rings (with the exception of four steel cages containing granulated material) positioned on top of each other, encapsulating the tube. All reference materials except MX80 were installed two times in

the test parcel, and all but MX80 were separated by other blocks (Table 1). MX80 was installed six times as pure MX80 block, two times as MX80 granulate, and two times as 'MX80 granulate + quartz'. The EC<sub>populations</sub> of the different reference materials were significantly different.

The first out of three 'ABM packages' was heated from the start and the buffer materials were exposed

TABLE 1. Positions of the different clay materials in the test parcel, and sampling and analysis scheme. The figure on the right shows the maximum temperature (°C) of the test package up to 6 cm from the contact to the iron tube as measured with thermocouples.



NH<sub>4</sub>Cl-ethanol-0.18 M NH<sub>4</sub>Cl in 83% ethanol.

for the maximum temperature (around 130°C) for about one year. The packages were moistened by groundwater from fractures ('Äspö water') and optionally also artificially from an installed wetting system using the same groundwater. Water saturation using titanium pipes is described by Eng *et al.* (2007) as follows: "The saturation system aims at simulating water bearing fractures in the rock wall. This is done by installing four pipes along the outer edge of each package. The pipes are connected to a water tank at the experiment site. At the location of the simulated fractures ... 'every 10 cm'...small holes are drilled in the pipes, allowing water to leak onto the buffer blocks." The near-neutral Äspö water used for saturation is a sodium-calcium-chloride dominated groundwater (each ~2500 mg l<sup>-1</sup> Na<sup>+</sup> and Ca<sup>2+</sup>, ~8500 mg l<sup>-1</sup> Cl<sup>-</sup> and ~500 mg l<sup>-1</sup> SO<sub>4</sub><sup>2-</sup>) with minor contents of Mg<sup>2+</sup>, Br<sup>-</sup> and K<sup>+</sup> (all <100 mg l<sup>-1</sup>).

ABM 1 was terminated 28 months after installation. Almost all geochemical and mineralogical alterations of the different bentonites (apart from ECs) were restricted to the contact between iron and bentonite (Kaufhold *et al.*, 2013); however, cation exchange processes were not included in the first part of the study. The aim of this second part is first to describe modification of the cation exchange population, and second to understand the influence of the groundwater on cation exchange at different scales.

## MATERIALS AND METHODS

### Sampling

After excavation, the blocks were sampled at different distances from the contact to the iron tube (Fig. 1b) and from bentonite/bentonite and bentonite/cement interfaces (Fig. 1c). To study the horizontal direction, samples were taken from the central part of the blocks (see also Kaufhold *et al.*, 2013). For buffer materials sampled by the German laboratory, the sample labelled '0.1 cm' was collected by scraping off the surface layer of bentonite blocks at the contact to the iron tube with a sharp knife. The other samples were taken at 1, 3, 5 and 7 cm from the contact with the iron tube (German laboratory) and at 1, 5 and 9 cm (Swedish laboratory). In two selected small-scale studies (blocks 29 and 30 and blocks 10 and 11), the vertical direction was also sampled by taking samples in the direction parallel to the heater at approximately the centre of the

blocks. For the two upper blocks 29 and 30, a narrow profile was sampled starting at 1.25 cm from the upper level of block 30 (bentonite/cement interface at the top of the ABM parcel). The other samples were taken in increments of 2 cm from 3.5 down to 19.5 cm from this bentonite/cement interface. For blocks 10 and 11, samples were taken on both sides of the bentonite/bentonite interface at distances of 1, 4 and 6 cm. Excavation of the ABM experiment could not be performed in an O<sub>2</sub>-free atmosphere. Accordingly no glove box was used in the laboratory, and possible exchangeable Fe(II) could not be determined.

### CEC and EC methods

Two different CEC-index cations were used, providing accurate CEC and EC<sub>population</sub> values even in calcareous bentonites (Dohrmann *et al.*, 2012a, b): ammonium (method 1) and Cu(II)-triethylenetetramin (methods 2 and 3). In this joint project, the ammonium chloride method was used in the Swedish laboratory, whereas the other methods were used in the German laboratory. The standard Cu(II)-triethylenetetramin (Cu-trien) method has the advantage that it requires only 200 mg of sample, but the EC values suffer from partial carbonate dissolution, leading to overestimated exchangeable calcium values. Therefore, the Cu-trien<sub>5 × calcite</sub> method, which uses calcite saturation of the exchange solution, is preferable (Dohrmann & Kaufhold, 2009), although typically 1000 mg of sample are consumed. This is a large amount of material for some samples, such as the contact zone between the iron tube and the buffer material. In some experiments, only small sample quantities were available and the advanced Cu-trien<sub>5 × calcite</sub> method could not be applied. In such cases, only a few selected samples of the horizontal profile were analysed by Cu-trien<sub>5 × calcite</sub>, (a whole set includes samples from the contact to the iron tube and four samples from the central parts; see Fig. 1b). All measurements were performed in duplicate.

*Method 1.* EC values were determined using NH<sub>4</sub>Cl (ammonium chloride, 0.15 M) in ~83% ethanol following Belyayeva (1967). Ethanol was used instead of water to minimize the dissolution of carbonates and gypsum. NH<sub>4</sub><sup>+</sup> exchange was repeated three times because the selectivity of NH<sub>4</sub><sup>+</sup> is low, and in contrast to index cations such as the di-valent Cu-trien (Meier & Kahr 1999) and the mono-valent silver-thiourea (Dohrmann, 2006),

a single exchange step does not guarantee complete cation exchange. After  $\text{NH}_4^+$ -saturation and washing, ethanol was evaporated from the filtrate/supernatant and the volume adjusted by deionized water addition followed by ICP analysis of the ECs. No ammonium analysis was performed; accordingly no index cation CEC values were calculated. This method uses 800 mg sample for a single measurement.

*Method 2.* The CEC was determined according to Meier & Kahr (1999) using the standard Cu-trien method as discussed and modified by Kaufhold & Dohrmann (2003). After Cu-trien saturation, centrifuged solutions were diluted followed by ICP analysis of the ECs as well as of Cu, which allowed calculation of CEC values. Cu-trien was also analysed by VIS spectroscopy to cross-check the ICP-Cu concentration. This method uses a total of 200 mg sample for two repetitions.

*Method 3.* The  $\text{Cu-trien}_{5 \times \text{calcite}}$  method was used to minimize carbonate dissolution. The  $\text{Cu-trien}_{5 \times \text{calcite}}$  solution was prepared by mixing 300 mL of 0.01 M Cu-trien solution with 1500 mL of deionized water in a 2 L beaker and 2 g of fine-grained calcite to pre-saturate the solution and suppress calcite dissolution as described by Dohrmann & Kaufhold (2009). After  $\text{Cu-trien}_{5 \times \text{calcite}}$  saturation, centrifuged solutions were diluted followed by ICP analysis of the ECs and Cu, allowing calculation of CEC values. The Cu-trien complex concentration was also analysed by VIS spectroscopy to cross-check the ICP-Cu concentration. This  $\text{Cu-trien}_{5 \times \text{calcite}}$  approach does not prevent dissolution of gypsum (Dohrmann & Kaufhold, 2010) and uses 1000 mg sample for two repetitions.

For ICP-OEC analysis the following techniques were used: argon radial plasma, nebulisers (cross-flow and modified Lichte), no auxiliary gas flow, gain value for plasma (1.400 W), calibration every 7th measurement.

## RESULTS AND DISCUSSION

### *Horizontal variation of the CEC and the ECs within individual blocks*

Horizontal variation of the  $\text{EC}_{\text{population}}$  was expected to be clearly visible (as for the MX80 bentonite in the LOT project) because the temperature was higher at the contact with the iron tube than at the outer parts of the bentonite blocks (Table 1). Exchangeable cation (EC) values of block No. 17 (#17), Kunigelt V1 (JNB), are given

in more detail in Table 2, because #17 is a typical example and this block was sampled by both laboratories.

*Reference material.* The JNB reference material is a  $\text{Na}^+$ -bentonite (86–100% exchangeable  $\text{Na}^+$ ) with minor amounts of exchangeable  $\text{Ca}^{2+}$  (6–9%, only methods 1 and 3), and trace amounts of exchangeable  $\text{Mg}^{2+}$  (1–3%) and  $\text{K}^+$  (0–2%) (Table 2). The CEC values varied between 59–64 meq/100 g.

The JNB reference material contains approximately 3 wt.% calcite. Calcite dissolution inflates exchangeable calcium values of method 2. This can be checked by the parameter ‘sum/CEC’, which was calculated by adding up all ECs (in meq/100 g) and dividing this sum by the CEC (in meq/100 g). Ideally this control value should give 1.00, which is more or less achieved using method 3,  $\text{Cu-trien}_{5 \times \text{calcite}}$ . For calculation of the exchangeable  $\text{Ca}^{2+}$  population (%/CEC), therefore only methods 1 and 3 were used. No CEC results were available for method 1, ethanolic  $\text{NH}_4\text{Cl}$ . Accordingly  $\text{EC}_{\text{population}}$  was calculated by dividing individual EC values by the parameter ‘sum of exchangeable cations’. For method 2 (standard Cu-trien) individual EC values were divided by the CEC because the ‘sum’ was inflated by calcite dissolution. For method 3,  $\text{Cu-trien}_{5 \times \text{calcite}}$ , the quotient ‘sum/CEC’ was close to the ideal value, which was expected to be similar for method 1 (ethanolic  $\text{NH}_4\text{Cl}$ ) as well (Dohrmann *et al.*, 2012b).

*Samples retrieved after the field experiment.* In contrast to what was assumed, no significant horizontal variation of ECs was detected for block No. 17 between distances of 1 and 7 cm from the contact to the iron tube (Table 2, Figure 2). Initially dominating exchangeable  $\text{Na}^+$  was reduced by half (44%, down from 94). The lack of horizontal variation of the ECs was not expected but it enabled a calculation of average values of the whole block. A second advantage was that the statistical basis of the averaged values of the reacted samples was improved ( $n = 15$  for  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$ ;  $n = 7$  for  $\text{Ca}^{2+}$  and  $n = 12$  for the CEC). The sample at the direct contact to the iron tube was not included in these average values, because the total mass of this layer was very small and it does not represent the bulk composition of the block. This contact region is important for understanding initial processes; however, it represents only part of the 0.1 cm thin surface layer of

TABLE 2. EC<sub>population</sub> of a representative buffer material (JNB). JNB-Ref = reference material; JNB-17 = block no. 17 retrieved after the field experiment. Percentages of individual cations were calculated in two ways, (i) with respect to the sum of ECs (methods 1 and 3) and (ii) in method 2 with respect to the CEC because for this method (Cu-trien), ECs were overestimated. Sample positions are indicated as distances from the contact with the iron tube in cm. Values affected by dissolution of soluble Ca phases are marked in italics. The quotient 'sum/CEC' should be close to 1, and values >1 indicate overestimated Ca<sup>2+</sup> values due to soluble minerals.

Method	Bentonite	Position (cm) from contact	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Sum/ CEC	CEC (meq/100 g)
			— (%/sum of cations) —					
NH <sub>4</sub> Cl-ethanol	JNB-Ref	reference	86	2	1	9		
NH <sub>4</sub> Cl-ethanol	JNB-17	1	41	2	9	47		
NH <sub>4</sub> Cl-ethanol	JNB-17	5	42	2	9	48		
NH <sub>4</sub> Cl-ethanol	JNB-17	9	43	2	8	47		
Cu-trien <sub>5</sub> × calcite	JNB-Ref	reference	91	0	1	6	1.06	62
Cu-trien <sub>5</sub> × calcite	JNB-Ref	reference	92	0	1	6	1.00	64
Cu-trien <sub>5</sub> × calcite	JNB-17	3	43	3	9	44	1.00	63
Cu-trien <sub>5</sub> × calcite	JNB-17	3	44	2	9	44	1.02	61
Cu-trien <sub>5</sub> × calcite	JNB-17	5	44	2	10	43	1.00	61
Cu-trien <sub>5</sub> × calcite	JNB-17	5	45	3	10	42	1.02	61
			———— (%/CEC) ————					
Cu-trien	JNB-Ref	reference	102	1	3	36	1.41	59
Cu-trien	JNB-Ref	reference	100	1	2	28	1.30	60
Cu-trien	JNB-17	0.1	41	0	9	86	1.37	49
Cu-trien	JNB-17	0.1	40	1	9	83	1.31	48
Cu-trien	JNB-17	1	45	1	9	74	1.29	58
Cu-trien	JNB-17	1	47	2	9	65	1.23	57
Cu-trien	JNB-17	3	43	1	10	74	1.29	58
Cu-trien	JNB-17	3	45	1	10	70	1.27	56
Cu-trien	JNB-17	5	43	1	10	74	1.29	58
Cu-trien	JNB-17	5	45	1	10	70	1.25	56
Cu-trien	JNB-17	7	46	2	10	68	1.25	59
Cu-trien	JNB-17	7	46	1	10	68	1.25	57
			———— Average ————					
methods 1–3	JNB-Ref		94	1	2	17	1.19	61
methods 1–3	JNB-17	1–9	44	2	9	58	1.18	59
methods 1 and 3	JNB-Ref					7	1.03	
methods 1 and 3	JNB-17	1–9				45	1.01	

~8% of the total surface of the blocks, and much less of the total volume.

The average exchangeable Ca<sup>2+</sup> proportion increased from 7 to 45% and was at the same level as the average exchangeable Na<sup>+</sup> proportion. The average exchangeable Mg<sup>2+</sup> proportion increased by the same factor of ~5–6 as the average exchangeable Ca<sup>2+</sup> proportion, from 2 to 10% exchangeable Mg<sup>2+</sup>. A small increase in exchangeable K<sup>+</sup> was observed; however the exchangeable K<sup>+</sup> values were too close to the detection limit to draw conclusions from this increase. CEC values were close to the reference CECs. The average CECs were 2 meq/100 g lower

than the average CEC of the reference bentonite. Such a small deviation cannot be interpreted as a real difference.

Only the sample which was collected close to the bentonite/heater contact differed significantly. This sample had 10% (relative) less exchangeable Na<sup>+</sup> than the other samples of the same block. The CEC of the contact sample decreased from 61 to 49 meq/100 g, which was probably caused by clinoptilolite dissolution (Kaufhold *et al.*, 2013).

Average EC values of each retrieved and analysed block were calculated in the same way as described for block No. 17, representing the



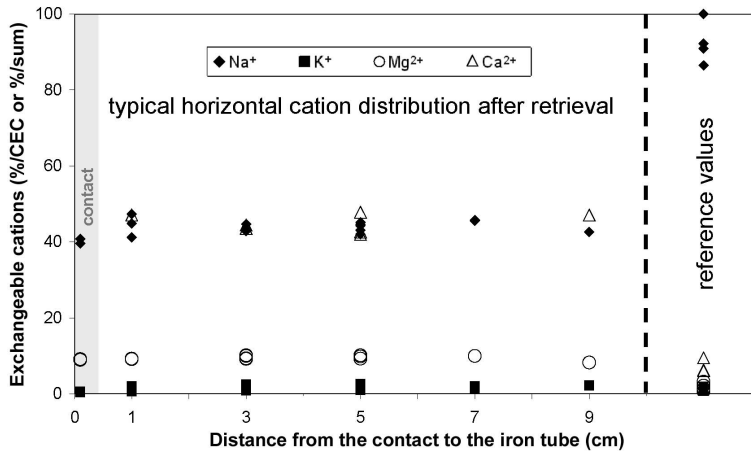


FIG. 2. Typical horizontal cation distribution after retrieval, values of block No. 17, Kunigel V1 (JNB). Reference values are reported on the right side.  $\text{Na}^+$  values decreased by half, and  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  values increased by a factor of  $\sim 5\text{--}6$ .

cation exchange population of the block. The average values are listed for the reference clays as well as for the samples from the field experiment (Table 3). As only two blocks were analysed by all three methods, the statistical basis is smaller for the other blocks:  $n=12$  for  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Mg}^{2+}$ , and for the CEC;  $n = 4$  for  $\text{Ca}^{2+}$  for the Cu-trien and Cu-trien<sub>5</sub> × calcite methods;  $n = 3$  for  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  for the  $\text{NH}_4\text{Cl}$  method).

#### *Average CEC and EC values of the whole parcel and the influence of the groundwater*

This section describes the vertical distribution of the ECs of the whole parcel in order to evaluate the influence of the groundwater at this larger scale. Prior to the field experiment, the  $\text{EC}_{\text{population}}$  differed from one block interface to the next. Compared to the reference materials, significant  $\text{EC}_{\text{population}}$  changes were observed after the field experiment (Table 3).

Large-scale variations of the whole test parcel (all 30 blocks) can be identified by a mass balance.  $\text{EC}_{\text{populations}}$  of the blocks were widely different. To identify trends with respect to large scale variations, average values of the ECs and CECs were calculated (Table 3, lower three rows). Such average values only have a meaning for mass-balance estimations. The data set is not complete because not all blocks were analysed after retrieval (ECs:  $n = 21$ ; CECs:  $n = 12$ ). Average values were calculated only for samples with complete sets of

data in both groups; i.e. reference materials and samples of the field test.

Exchangeable  $\text{Na}^+$  made up nearly half (48%) of the  $\text{EC}_{\text{population}}$  of the reference blocks, but only 39% of the samples after the field experiment. Exchangeable  $\text{Mg}^{2+}$  decreased as well, from 18% to 15%. Exchangeable  $\text{Ca}^{2+}$ , on the other hand, increased from 32% to 45%, whereas exchangeable  $\text{K}^+$  remained stable. Initial average values of all 30 blocks were relatively close to those of the selected 21 blocks:  $\text{Na}^+$  (53%),  $\text{Mg}^{2+}$  (16%),  $\text{Ca}^{2+}$  (29%) and  $\text{K}^+$  (3%),

It may be argued whether the quantity “percentage EC/CEC” would be suitable for mass balance estimations, because absolute differences of ECs are not considered. Low-CEC materials with high  $\text{Ca}^{2+}$  percentages of the  $\text{EC}_{\text{population}}$  would overprint the high-CEC samples. To identify such influences, average EC values of the 21 blocks were calculated, confirming the %EC/CEC values listed above: Exchangeable  $\text{Na}^+$  averaged 36 meq/100 g in the reference blocks, but only 26 meq/100 g in the samples after the field experiment. Exchangeable  $\text{Mg}^{2+}$  decreased as well, from 13 meq/100 g to 10 meq/100 g). Exchangeable  $\text{Ca}^{2+}$  on the other hand increased from 24 meq/100 g to 34 meq/100 g, and exchangeable  $\text{K}^+$  remained stable (from initially 1.7 to 1.5 meq/100 g). Initial average exchangeable cation values of all 30 blocks were relatively close to the selected 21 blocks:  $\text{Na}^+$  (39 meq/100 g),  $\text{K}^+$  (1.6 meq/100 g),  $\text{Mg}^{2+}$  (11 meq/100 g) and  $\text{Ca}^{2+}$  (21 meq/100 g).

TABLE 3.  $E_C$ -population (%) and CEC (meq/100 g) values of the reference samples and of the samples retrieved after the field experiment (averages of 1–9 cm).

Block	Material/abbreviation	Reference material			Retrieved samples 1–9 cm (averages)								
		Na <sup>+</sup> (%)	K <sup>+</sup> (%)	Sum (meq/100 g)	Na <sup>+</sup> (%)	K <sup>+</sup> (%)	Mg <sup>2+</sup> Ca <sup>2+</sup> sum (meq/100 g)	CEC (meq/100 g)					
30	MX80	69	2	8	24	103	85	49	3	7	41	100	
29	MX80	69	2	8	24	103	85	41	2	13	44	100	
28	Ikosorb (IKO)	56	2	24	19	100	90	41	2				
27	Dep. CAN	27	2	27	46	102	84	25	2	10	63	100	
26	lbeco Seal (IBE)	87	3	4	7	100	88	24	1	11	63	100	
25	Friedland (FRU)	69	8	22	2	101	23	37	6	11	46	100	21
24	Asha 505	67	1	15	20	103	91	23	1	13	63	100	
23	Calcigel (CAL)	3	2	22	72	100	65	23	2	13	65	102	64
22	Callovo-Oxfordian	24	11	29	35	100	12	44	8	26	22	100	12
21	Febex	25	1	39	34	100	98	23	1	16	60	100	
20	MX80 granulate	69	2	8	24	103	85						
19	MX80 granulate +quartz	69	2	8	24	103	59						
18	MX80	69	2	8	24	103	85						
17	Kunigel V1 (JNB)	94	1	2	7	100	61	42	2	9	47	100	57
16	Rokle (Rawra)	1	2	21	76	100	74	34	1	14	51	100	
15	Dep. CAN	27	2	27	46	102	84	36	2	17	50	104	76
14	Asha 505	67	1	15	20	103	91	33	1	21	49	103	83
13	Rokle (Rawra)	1	3	24	71	99	74	41	3	21	44	109	71
12	Callovo-Oxfordian	24	11	29	35	100	12						
11	MX80	69	2	8	24	103	85	54	1	17	37	109	76
10	Ikosorb (IKO)	56	2	24	19	100	90	45	2	18	36	100	87
9	Friedland (FRU)	69	8	22	2	101	23	59	9	19	13	100	21
8	Febex	27	3	37	33	100	101	42	3	23	34	102	95
7	MX80 granulate +quartz	69	2	8	24	103	59						
6	lbeco Seal (IBE)	90	4	6	8	109	88	40	4	12	50	106	80
5	Calcigel (CAL)	4	2	19	76	100	65	44	2	8	47	100	
4	Kunigel V1 (JNB)	94	1	2	7	100	61						
3	MX80 granulate	69	2	8	24	103	85	60	2	10	28	100	
2	MX80	69	2	8	24	103	85						
1	MX80	69	2	8	24	103	85						
1–30	Average (only of those blocks which were analysed after retrieval; exchangeable cations: $n = 21$ ; CEC: $n = 12$ )	48	3	18	32		66		39	3	15	45	62
1–30	MIN	1	1	1	2		12	23	1	7	13		12
1–30	MAX	90	11	39	76		101	60	9	26	65		95

sum = 'sum of exchangeable cations'. Reference material: CEC values for 'MX80 granulate + quartz' were calculated by multiplying pure MX80 values by a factor of 0.7, based on a quartz content of 30 wt.%. Exchangeable  $\text{Na}^+$  values of blocks 9 and 25 were corrected to give  $\text{Na}^+ = 100 - \text{K}^+ - \text{Mg}^{2+} - \text{Ca}^{2+}$ . Exchangeable  $\text{Ca}^{2+}$  values of block 22 were corrected to give  $\text{Ca}^{2+} = 100 - \text{Na}^+ - \text{K}^+ - \text{Mg}^{2+}$ . Samples retrieved after the field experiment: Exchangeable  $\text{Ca}^{2+}$  values of blocks 9, 22, and 25 were corrected to give  $\text{Ca}^{2+} = 100 - \text{Na}^+ - \text{K}^+ - \text{Mg}^{2+}$ . Ethanolic  $\text{NH}_4\text{Cl}$  values of such samples were recalculated using the measured reference CEC to avoid largely overestimated  $\text{Ca}^{2+}$  percentages and accordingly diminished percentages for  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$ . Some reference blocks are listed with deviating  $\text{EC}_{\text{populations}}$  (e.g. IBE), although the same reference material was used. This was done because small variations of reference block EC values could be better compared with EC values of reacted blocks using the same method, which sometimes deviated by a few meq/100 g for individual ECs (compare blocks 6 and 26).

Average CEC values of all analysed blocks decreased slightly from initially 66 meq/100 g down to 62 meq/100 g after the experiment. Among the group of "true" bentonites, initial CECs vary from approximately 60–100 meq/100 g with an average of 82 meq/100 g. The drop in average bentonite CEC after retrieval was 5.5 meq/100 g (1.1–8.8 meq/100 g). The precision of the methods (1 sigma) was  $\pm 1$ –2 meq/100 g (Dohrmann & Kaufhold, 2009; Dohrmann *et al.*, 2012), which means that the measured CEC differences indicate genuine decreases for at least some of the bentonites. Such CEC decreases can be interpreted in several ways: (1) a 10% decrease of CEC values was typical for bentonites in laboratory experiments of 38 different bentonites with NaCl, KCl, and  $\text{Ca}(\text{OH})_2$  solutions (Kaufhold & Dohrmann, 2009, 2010a,b, 2011); (2) with decreasing exchangeable sodium content the pH decreased as well (Kaufhold *et al.*, 2008), which reduced the amounts of variable charge and lowered the measurable CEC. The same mechanism could have also lowered the CECs in the ABM samples. On the other hand, only 12 blocks were analysed with respect to the CEC, which was therefore possibly less representative than the EC values. Within these 12 blocks, the correlation between the difference in sodium concentration (in %) of the  $\text{EC}_{\text{population}}$  and the CEC decrease (in %) was very poor ( $R^2 = 0.36$ ). This does not support the hypothesis of pH influence.

Along with the overall exchange reactions, minimum and maximum values of individual ECs in individual blocks converged after the field experiment (Table 3, lower two rows). The lowest concentrations of the reference materials were close to zero (1–2%) for any EC, whereas maximum values varied significantly: the highest concentrations measured for exchangeable  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Na}^+$  were 11%, 39%, 76% and 90% were. After retrieval of the field samples, all minimum EC values apart from  $\text{K}^+$  increased as follows:  $\text{Mg}^{2+}$  from 1 to 7%,  $\text{Ca}^{2+}$  from 2 to 13%, and  $\text{Na}^+$  from 1 to 23%. All maximum EC concentrations decreased thus:  $\text{K}^+$  from 11 to 9%,  $\text{Mg}^{2+}$  from 39 to 26%,  $\text{Ca}^{2+}$  from 76 to 65%, and  $\text{Na}^+$  from 90 to 60%.

The upper part (blocks 24–30) of the ABM 1 parcel has lost (desorbed) more sodium and incorporated (adsorbed) more calcium than the middle and the lower parts. Exchangeable sodium was initially (63%) more concentrated in the upper part than in the whole parcel (53%). Exchangeable

calcium concentration of blocks 24–30 was initially (20%) lower than in the whole parcel (29%). The lower twenty-three blocks averaged 50% exchangeable  $\text{Na}^+$  and 32% exchangeable  $\text{Ca}^{2+}$ . After the field experiment these blocks (blocks 1–23) had an average of 41% exchangeable  $\text{Na}^+$  and 42% exchangeable  $\text{Ca}^{2+}$ . The upper seven blocks (blocks 24–30) started with even more exchangeable  $\text{Na}^+$  (63%) but ended with less exchangeable  $\text{Na}^+$  (33%) than the lower twenty-three blocks. Exchangeable  $\text{Ca}^{2+}$ , on the other hand, was initially lower in this upper part (20%) and subsequently higher (53%). The average exchangeable  $\text{Mg}^{2+}$  loss in the upper part of the parcel was small (–3%) and the exchangeable  $\text{K}^+$  loss was close to detection limit (–1%). In the lower part (blocks 1–23), no loss of exchangeable  $\text{Mg}^{2+}$  and  $\text{K}^+$  was detected. These pronounced differences can only be explained by taking into account interaction with the groundwater, which was added from a water tank at the experiment site using perforated titanium pipes allowing water to leak onto the buffer blocks.

*Redistribution of exchangeable cations of the same materials in different parts of the parcel*

During the ABM experiment, a significant redistribution of *exchangeable cations* of the individual blocks occurred (Table 3, Fig. 3). The general trend for most blocks (all bentonites) was:

(i) The higher the initial exchangeable sodium (calcium, magnesium), the more sodium (calcium, magnesium) was lost during the experiment.

(ii) The target cation exchange population has a typical range for each EC: ~8–15% exchangeable  $\text{Mg}^{2+}$ , ~25–30% exchangeable  $\text{Na}^+$  and ~45% exchangeable  $\text{Ca}^{2+}$ . Below this target concentration, a block typically gained the respective cation by ion exchange (net adsorption), whereas above this target concentration, a block lost significant amounts by ion exchange (net desorption).

(iii) In total fourteen blocks lost exchangeable  $\text{Na}^+$  and  $\text{Mg}^{2+}$  and seven blocks gained exchangeable  $\text{Na}^+$  and  $\text{Mg}^{2+}$ . Exchangeable  $\text{Ca}^{2+}$  was desorbed only from five blocks; all other sixteen sampled blocks were enriched in exchangeable  $\text{Ca}^{2+}$ . All of the seven upper blocks gained exchangeable  $\text{Ca}^{2+}$ , but most of these blocks were initially very rich in  $\text{Na}^+$ .

*Influence of initial composition, neighbouring blocks, and relative position within the test parcel on cation redistribution.* Seven blocks (apart from

MX80, which was used more than two times) were sampled twice after retrieval of the ABM parcel. These blocks were always ‘sandwiched’ by other blocks. The question arises whether the initial composition of the neighbouring blocks of the ‘doubly analysed blocks’ had an influence on the cation redistribution of the differently sandwiched blocks. If the differently sandwiched blocks would not have been influenced by their neighbouring blocks, gains or losses of the three major ECs  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  should have the same trend and occur to approximately the same degree in both sampled blocks. This is the case for Calcigel (CAL), FRI, IBE and Rokle, but Asha 505 (Asha), Dep.CAN, and Febex behaved differently, having net gains or losses of these major cations in both sampled blocks with opposite signs (Fig. 4).

Example 1 (Fig. 4): The  $\text{Ca}^{2+}$ ( $\text{Mg}^{2+}$ )-rich buffer material Calcigel (CAL) gained large amounts of exchangeable  $\text{Na}^+$  (+40%) but lost exchangeable  $\text{Mg}^{2+}$  (–11%) and large amounts of exchangeable  $\text{Ca}^{2+}$  (–29%) at block position 5. The same material gained less exchangeable  $\text{Na}^+$  (+19%) at block position 23, exchangeable  $\text{Mg}^{2+}$  loss was similar (–9%) and loss of exchangeable  $\text{Ca}^{2+}$  (–7%) was less pronounced than at position 5. However, gains and losses showed the same trends at both block positions. This trend was confirmed for FRI, IBE, and Rokle. The most important reason for this trend could be that all of these bentonites were initially dominated by a single exchangeable cation,  $\text{Ca}^{2+}$  (Febex and Rokle) or  $\text{Na}^+$  (FRI and IBE).

Example 2 (Fig. 4): The buffer material Febex with an initial composition of  $\text{Mg}^{2+} \geq \text{Ca}^{2+} > \text{Na}^+$  gained large amounts of exchangeable  $\text{Ca}^{2+}$  (+26%) but lost exchangeable  $\text{Mg}^{2+}$  (–23%) with a minor loss of exchangeable  $\text{Na}^+$  (–3%) at block position 21. The same material gained large amounts of exchangeable  $\text{Na}^+$  (+15%) at block position 8 whereas exchangeable  $\text{Ca}^{2+}$  was at the same level (–1%) as the initial material. Apart from the low concentration of exchangeable  $\text{K}^+$ , the only cation which showed a similar loss at both positions 8 and 21 was exchangeable  $\text{Mg}^{2+}$  (–14%).

Asha and Dep.CAN also showed a non-uniform behaviour similar to Febex (Fig. 4). Dep.CAN had no single dominating EC, which is similar to Febex. Asha, on the other hand, was dominated by  $\text{Na}^+$ . Both Asha blocks were embedded between two  $\text{Mg}^{2+}$ -rich blocks; however at position 14, Asha gained exchangeable  $\text{Mg}^{2+}$  whereas at position 24 exchangeable  $\text{Mg}^{2+}$  was lost. Block 24 belongs to

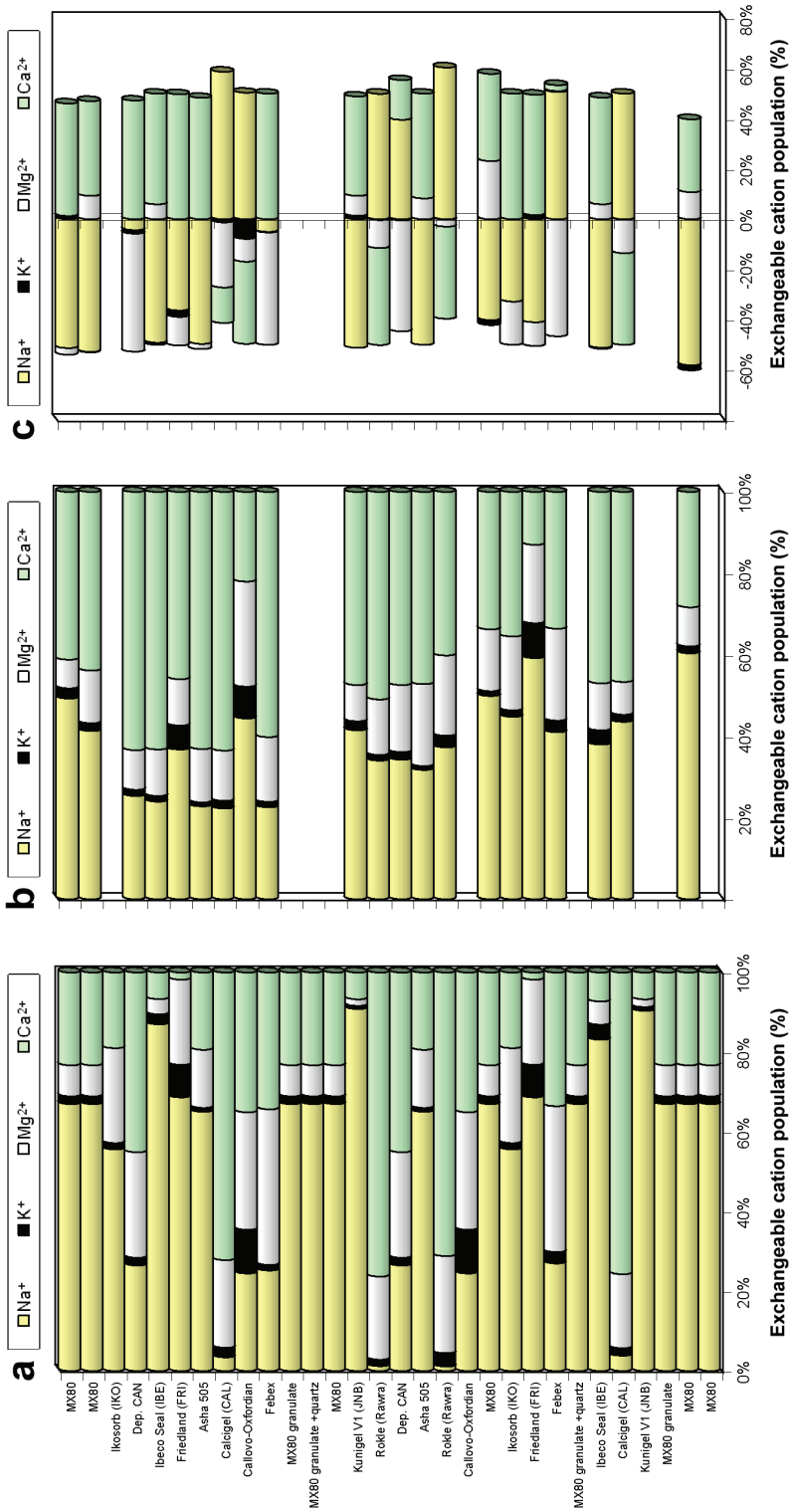


FIG. 3. Distribution of the EC<sub>population</sub> (%) of (a) the reference clays, (b) the samples after the field experiment and (c) decreases and increases of the EC<sub>population</sub> of the samples after the field experiment.



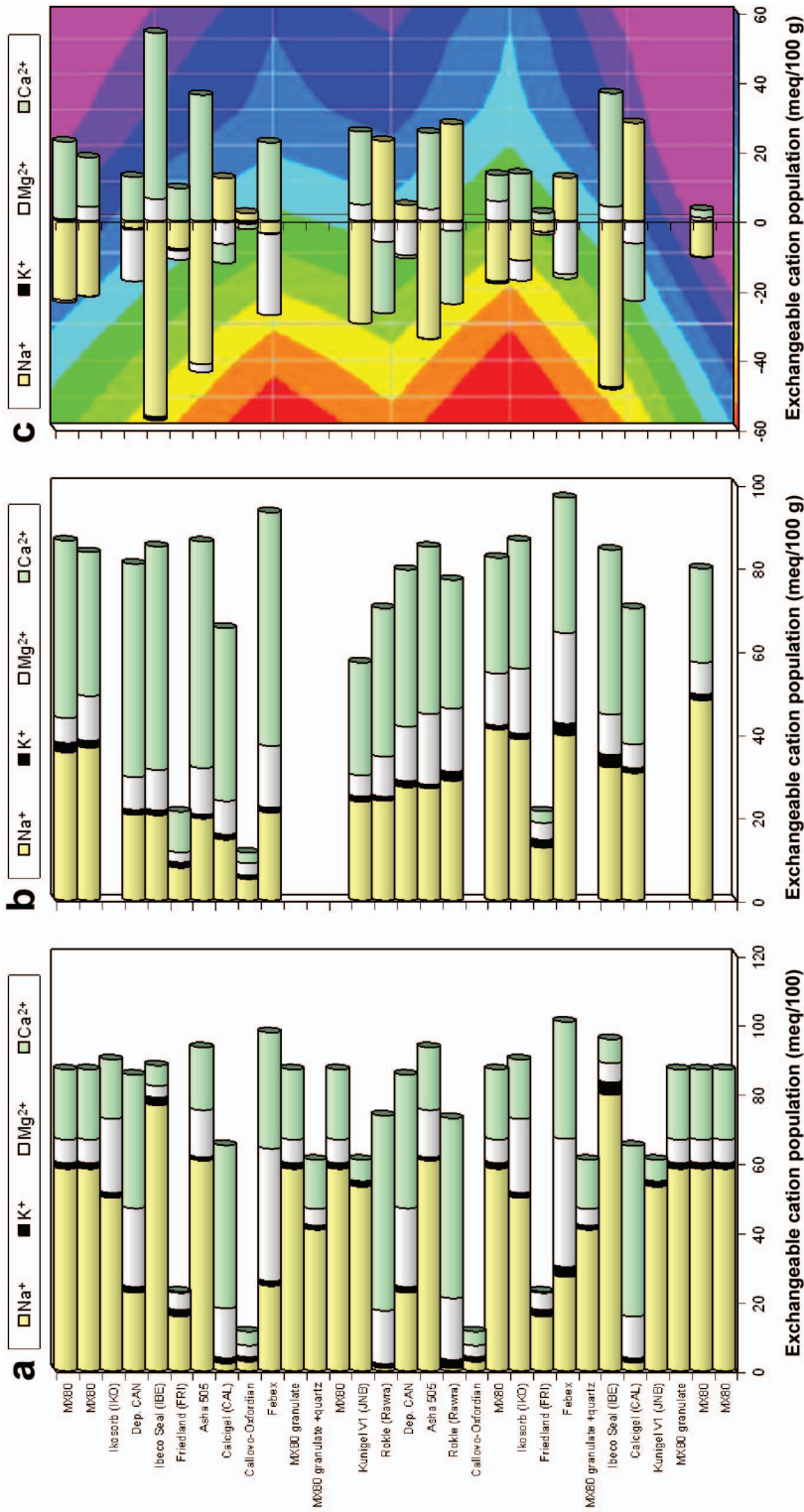


FIG. 5. Distribution of the  $EC_{\text{population}}$  (meq/100 g) of (a) the reference clays, (b) the samples after the field experiment and (c) decreases and increases of the  $EC_{\text{population}}$  of the samples after the field experiment with additional information on the temperature distribution of package 1 (hottest part  $>135^{\circ}\text{C}$ , coldest part  $<85^{\circ}\text{C}$ ).

79 meq/100 g which equals 87% of the  $EC_{\text{population}}$ ) and smaller changes at position 14 (in total 59 meq/100 g which equals 65% of the  $EC_{\text{population}}$ ). At both positions the temperature at the contact to the heater was approximately the same. No correlation of the extent of the redistribution of the  $EC_{\text{population}}$  with the peak temperatures at the contact with the iron tube could be observed for the other blocks of the studied ABM 1 parcel.

The total amounts of redistributed cations (all absolute cation differences were summed up) do not correlate at all with the CEC ( $R^2 = 0.01$ ). The smallest absolute redistribution of all bentonites was found in MX80 at position 2 (14 meq/100 g), however for the same material up to 46 meq/100 g were recorded at the other end of the test parcel.

These examples underline the hypothesis that material properties were not responsible for the observed EC redistribution, but changes can be explained by interaction with groundwater.

#### *Vertical distribution of ECs between different blocks and at the cement/bentonite interface on the centimetre scale*

Although most changes occurred on the large scale of the whole test parcel, small but important changes were also recorded in the vertical direction on the centimetre scale. Two hypotheses were studied. (i) Did all ECs equilibrate to the same degree at the direct contact between two blocks? (ii) Did the cement plug on top of the ABM test parcel influence the pronounced gain of exchangeable  $Ca^{2+}$  in the upper part?

*Equilibrium of ECs at the direct contact between two blocks.* Two adjacent blocks (MX80, No. 11, and IKO, No. 10) were used for a selected small scale study aiming at identifying vertical equilibrium conditions between neighbouring blocks. The CEC of IKO is approximately 15–20% larger than that of MX80. In the reference material, exchangeable  $Na^+$  (57 meq/100 g) was at the same absolute level in both blocks but differed with respect to the percentage of the  $EC_{\text{population}}$ . Exchangeable  $Ca^{2+}$  was larger in MX80 (24 meq/100 g; 29%) than in IKO (18 meq/100 g; 20%), but exchangeable  $Mg^{2+}/K^+$  was lower in MX80 (7/1.6 meq/100 g; 8/2%) than in IKO (24/2.2 meq/100 g; 29/2%). After the experiment, exchangeable  $Na^+$  had decreased significantly and exchangeable  $Ca^{2+}$  increased significantly. Both were at the same absolute level in both blocks (Fig. 6, right), but

differed with respect to the percentage of the cation exchange population (Fig. 6, left). Exchangeable  $K^+$  and  $Mg^{2+}$  were at different levels in both blocks after the experiment. Exchangeable  $K^+$  remained unchanged compared to the starting material, whereas exchangeable  $Mg^{2+}$  increased in MX80 (from 7 to 14 meq/100 g or from 8 to 18%) and decreased in IKO (from 24 to 19 meq/100 g or from 26 to 20%). Both blocks were sandwiched between FRI and COX with very low amounts of exchangeable  $Mg^{2+}$  (max. 5 meq/100 g). These blocks could not act as an exchangeable  $Mg^{2+}$  source, and the FRI block adjacent to the  $Mg^{2+}$ -rich block IKO had approximately the same amount of exchangeable  $Mg^{2+}$  after retrieval as before. Exchangeable  $Mg^{2+}$  did not migrate into the FRI block but it was transported from the IKO block into the MX80 block.

All ECs show bimodal concentration distributions with gaps of 2%, 5% and 7% for  $Mg^{2+}$ ,  $Ca^{2+}$  and  $Na^+$ , respectively. Assuming that equilibrium would have been established and assuming that selectivities would have been equal for both materials, the resulting distributions should have been equal for all ECs if expressed as %/CEC (Fig. 6 left). This is obviously not the case and it remains unclear if either the reaction time was too short or the selectivities are different.

#### *Influence of the cement plug on top of the ABM test parcel*

The bentonites of the top region of the ABM experiment were subjected to cement for a relatively short period of time. During concrete degradation, the early pore water leached may release sodium and potassium hydroxides (Sanchez *et al.*, 2006). The question was if the cement plug on top of the ABM test parcel had influenced the pronounced gain of exchangeable  $Ca^{2+}$  in the upper part. The distribution of ECs along a profile from the contact between the cement and the 'top blocks' (MX80, No. 30 and 29) was as expected. The hypothesis was that the cement acted as a  $Na^+$  and  $K^+$  source, which should have caused a pronounced effect on the uppermost parts of the bentonites. In the direct contact layer exchangeable  $Na^+$  and  $K^+$  concentrations should have been larger than below that layer, with decreasing concentrations downwards. After a few centimetres to decimetres, the general trend of exchangeable  $Ca^{2+}$  increase in the upper part of the whole test parcel should have



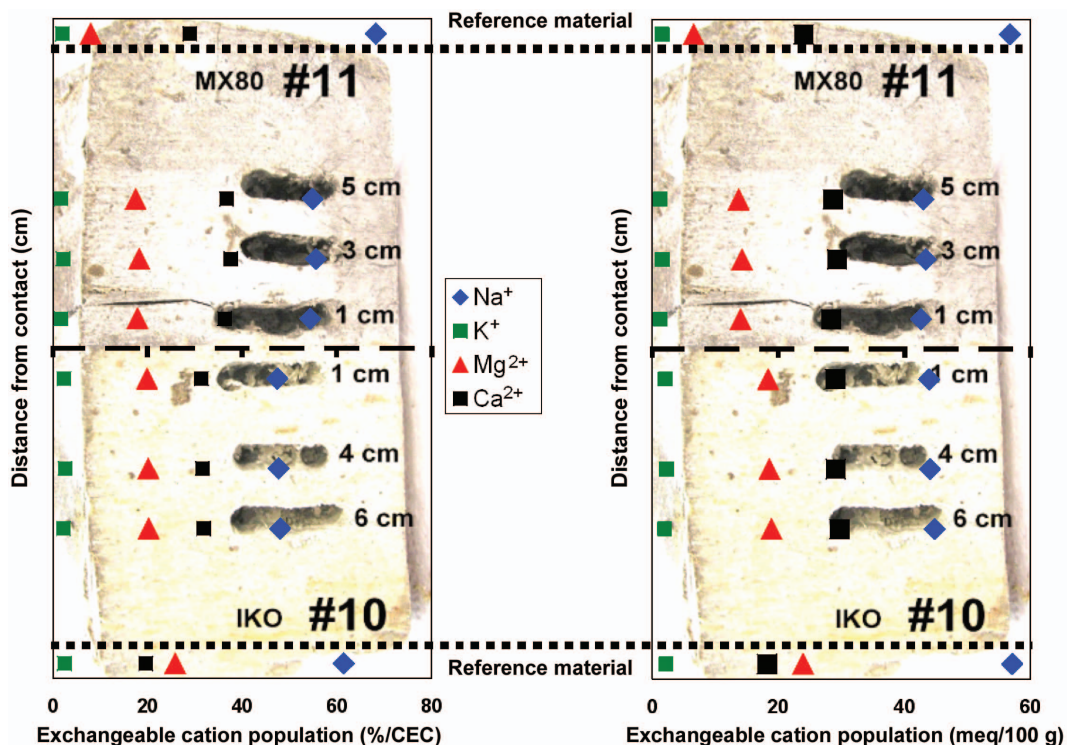


FIG. 6. Selected small-scale study aiming at identifying vertical equilibrium conditions (left in %/CEC, right in meq/100 g) between the two adjacent blocks MX80 (No. 11) and IKO (No. 10). The broken line marks the contact zone of the two blocks; the dotted line separates the EC values of the reference clays from the reacted clays. Results were measured using method 3 (Cu-trien<sub>5xcalcite</sub>).

caused an increase of exchangeable  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  with distance from the cement/bentonite interface. This was confirmed in the ABM experiment (Fig. 7).

Exchangeable  $\text{Ca}^{2+}$  increased from 40% at the top to 44% at the bottom of the lower block. The most significant increase was observed for exchangeable  $\text{Mg}^{2+}$ , starting from 6% at the top to 14% in the lowest sample. Exchangeable  $\text{Na}^+$ , on the other hand, decreased from 51% to 40%, and a minor decrease from 3% to 2% was observed for exchangeable  $\text{K}^+$ . Visual inspection indicated that iron corrosion has influenced the upper 3–4 cm. This was confirmed by XRF analysis. The iron content ( $\text{Fe}_2\text{O}_3$ ) was  $\sim 5$  wt.% in the cement/bentonite contact zone, and decreased to  $\sim 4$  wt.% in the lower parts of the two top blocks (Kaufhold *et al.*, 2013). The sodium ( $\text{Na}_2\text{O}$ ) content decreased continuously from 1.9 wt.% down to 1.4 wt.%. This continuous sodium decrease confirms the observed decrease in exchangeable  $\text{Na}^+$ . XRF analyses also

confirmed the continuously increasing portions of exchangeable  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ( $\text{MgO}$ : 2.3 to 2.6 wt.%;  $\text{CaO}$ : 1.6 to 2.3 wt.%). The structural elements of the smectites,  $\text{SiO}_2$  (67.1 wt.%) and  $\text{Al}_2\text{O}_3$  (21.1 wt.%), remained unchanged within  $\pm 0.1$  wt.%. Obviously the cement plug above the ABM test parcel directly influenced the top blocks, but the influence was limited to a range of only a few centimetres to decimetres.

## SUMMARY AND CONCLUSIONS

The results of previous field studies such as the LOT project led us to expect that horizontal variation of the  $\text{EC}_{\text{population}}$  would also be clearly visible in this field experiment. As in other heater tests, the temperature in the buffer materials was higher at the contact with the iron tube than with the outer parts. The horizontal variation of the ECs, however, was so small that no horizontal variation of any EC was detected for the retrieved blocks

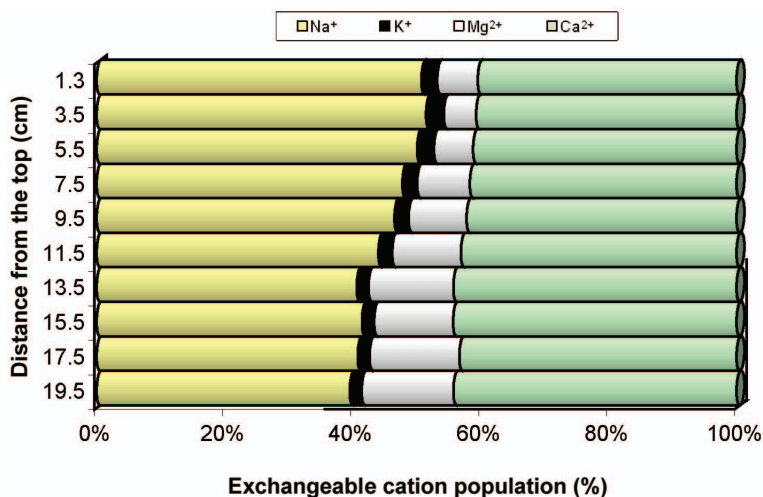


FIG. 7. Influence of the cement plug on top of the ABM test parcel on the  $EC_{\text{population}}$  in the two 'top blocks' (MX80, No. 30 and 29). The diagram shows the distribution of the  $EC_{\text{population}}$  (%/sum of cations) along a profile from the contact between the cement to the bottom of block No. 29. Results were measured using method 1.

between 1 and 7 cm from contact. Instead it was decided to calculate average values for the whole blocks of the field experiment and to use these average values for mass balance estimations.

Large total differences of the  $EC_{\text{population}}$ , however, were measured for the individual blocks after the field experiment ( $n = 21$  blocks) with respect to the composition of the reference materials. During the field experiment the bentonites had lost sodium and magnesium, and losses and gains were observed in all parts of the parcel, but the upper part had lost (desorbed) more sodium and incorporated (adsorbed) more calcium than the middle and lower parts. Two possible  $Ca^{2+}$  sources can be excluded, Ca-carbonates and Ca-sulfates, because Kaufhold *et al.* (2013) showed that both inorganic carbon and sulfur concentrations varied only insignificantly in the bulk blocks. The source of the observed gain in exchangeable  $Ca^{2+}$  was obviously groundwater. In general, the observed differences are too large to be explained assuming a closed system. The differences are much larger, and the only conclusion from this observation is that the whole package seems to have been influenced by groundwater which was added from a water tank at the experiment site, enabling at least partial equilibration between the different blocks.

Although most changes occurred on the large scale of the whole test parcel, small but significant changes were also recorded in the vertical direction

on the centimetre scale. The bentonites of the top region of the ABM experiment were subjected to cement for a relatively short period of time, which influenced the ECs over a distance of two blocks against the overall trend of exchangeable  $Ca^{2+}$  enrichment. In the vertical EC profiles of two adjacent blocks (block 10 and 11), all ECs show bimodal concentration distributions with gaps of a few percent for exchangeable  $Mg^{2+}$ ,  $Ca^{2+}$  and  $Na^{+}$ . It remains unclear if the reaction time was too short or if the selectivities are different.

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