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INTERLABORATORY CEC AND EXCHANGEABLE CATION STUDY OF BENTONITE BUFFER MATERIALS: II. ALTERNATIVE METHODS

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Abstract—Bentonites are candidate materials for encapsulation of radioactive waste. The cation exchange capacity (CEC) has proven to be one of the most sensitive parameters for detecting changes in mineral properties in bentonite-alteration experiments. An interlaboratory study of CECs and exchangeable cations for three reference bentonite buffer materials that were used in the Alternative Buffer Material test (ABM) project in Äspö, Sweden, was conducted to create a suitable database. The present study focused on CEC accuracy and compared CEC methods where care was taken to prevent dissolution of soluble minerals such as calcite and gypsum. The overall quality of the CEC and exchangeable cation values measured using non-Cu-trien CEC methods were good, with CECs of 74−91±0.5−3.3 meq/100 g and exchangeable cation values of 22−61±1.2−3.9 meq/100 g Na^+, 7−23±0.8−1.5 meq/100 g Mg^{2+}, and 19−39±0.8−1.6 meq/100 g Ca^{2+}. The precision was comparable to the standard Cu-trien method even for exchangeable Ca^{2+}, although the laboratories used different solution/solid ratios and reaction-time parameters for Cu-trien which affect carbonate dissolution. The MX80 and Dep.CAN bentonite exchangeable Ca^{2+} values were more accurate than standard-Cu-trien values. Using the optimized methods of this study, MX80 and Dep.CAN exchangeable Ca^{2+} values averaged 20.2±1.6 and 38.8±1.4 meq/100 g which amounts to ~70% of the inflated Cu-trien values. A more complex analysis of the CEC data using different methods, anion analyses, and mineralogical analysis is necessary to obtain plausible and accurate CEC values. Even with a more complicated analytical procedure, the CEC and exchangeable cation values were still not accurate enough because of excess anions. Chloride, sulfate, and dolomite might have increased the exchangeable Na^+, Mg^{2+}, and Ca^{2+} values.

Key Words—Ammonium Acetate, Ammonium Chloride, Bentonite Buffer, CEC, Cu-trien$_{5xcalcite}$, Exchangeable Cations, Interlaboratory Study.

INTRODUCTION

The cation exchange capacity (CEC) and exchangeable cations of soils and clays have been determined since 1852 and a long list of publications proves that cation-exchange data are of great importance but difficult to measure reliably. Cation exchange capacity results can be used in agricultural and geotechnical applications. Bentonites are candidate materials for encapsulation of radioactive waste. The CEC has proved to be one of the most sensitive parameters for detecting changes in mineral properties in alteration experiments. Important properties in theses systems are swelling capacity and illitization (Kaufhold and Dohrmann, 2010a, 2010b). The precision of the Cu-trien method, which was tested for suitability in the course of an interlaboratory study of CECs and exchangeable cations of bentonite buffer material, was evaluated by Dohrmann *et al.* (2012). Those authors reported values for typical interlaboratory precision for buffer materials and concluded that "Based on the measured precision, greater measured differences in Cu-trien CEC and exchangeable cation values of bentonite buffer samples, before and after an experiment, might be actual differences. Great care must be taken when interpreting measured CEC differences, and analytical characterization of any structural changes may be needed."

In understanding transport processes in a clay buffer, good CEC-method precision is important but does not guarantee accuracy. A CEC method that consistently produces similar values is precise, but the actual CEC may be higher or lower. This is of particular importance for exchangeable cations because soluble phases are typically present in such clays and are at least partly

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dissolved during CEC experiments. The resulting exchangeable cation values are inflated. For a discussion of this problem see Dohrmann and Kaufhold (2009, 2010). Here, the intention is to reach the lowest possible level of systematic error. Minimizing systematic errors increases the probability that the measured values are closer to the true (accurate) values. Definite, true values cannot be stated; the most plausible values are those which are more or less free of any known error. Such plausible values should also have low data scatter. The key parameters to evaluate the structural degradation of smectites, such as illitization, are of course the (index cation) CEC and the X-ray diffraction (XRD) pattern characteristics. Both measurements are necessary because, for example, measured deviations in CEC from the initial values in the samples do not necessarily mean that the mineral structures were degraded. Such differences may have been caused by pH changes as well.

Cation exchange capacity is also influenced by a variety of experimental factors. The known variable cation exchange properties and mineral-alteration processes in soils, such as pH which governs variable charge, also apply to bentonite buffer systems. Therefore, soil processes that are related to CEC and exchangeable cations were listed for an overview of pathways that can lead to inaccurate cation exchange results.

Systematic studies comparing the accuracy of bentonite CEC and exchangeable cation values from different laboratories are not available. Ongoing discussions are focused on whether CEC and exchangeable cation values obtained from different methods can be classified as operationally correct, *i.e.* they are correct regardless of any systematic errors that may have occurred in a given sample caused by exchange solution/mineral interactions. The long list of specialized CEC methods has already shown that this hypothesis is invalid. The key is to distinguish between erroneous and accurate or more plausible CEC and exchangeable cation values, which could include ranges of values. As in the previous study on precision, the results of an interlaboratory ring test were evaluated to understand if CEC and exchangeable cation values of more specialized methods were more accurate, keeping in mind that deviations can also be explained by systematic scattering (precision).

General problems

In soil science, a deep understanding of the processes that occur during cation exchange experiments is required to interpret the CEC values measured. Many studies have dealt with these problems since the second half of the 19th century (summarized by Thomas, 1977), though some are still not understood clearly. Mehlich (1948) reported on co-adsorption of triethanolamine on expandable clay minerals during CEC experiments using triethanolamine-buffered barium chloride solutions. The processes were clarified using standard clay minerals (Weiss, 1958a, figures 1, 2).

Variation in reaction time was shown (Mehlich, 1948) to be critical if minerals (or microorganisms) reacted with the exchange solution and affected the CEC values. Relevant rock-forming minerals and gels that typically occur in soils were tested by Mehlich (1948) and he also studied their dissolution in reactions with Ba^{2+} index cations. Most critical reactions occurred with carbonates and phosphates. The CEC is often used to describe any exchange of cations in clay-rich samples; however, whether all cation-exchange processes should be characterized by the term CEC is unclear. Traditionally, CEC methods were used to understand nutrient availability for agricultural problems. Some important cations such as K^+ and NH_4^+ are (at least partly) specifically adsorbed or fixed, but the other typical cations of non-acidic soils (Na^+, Mg^{2+}, and Ca^{2+}) are usually fully reversibly adsorbed. The latter process includes differences in adsorption affinity which are described as selective adsorption (*e.g.* McBride, 1979). In the present study, CEC was used for 'normal' fast and reversible cation-exchange processes in the sense of Bache's (1976) definition: "Cation exchange capacity is, therefore, a measure of the ability of a soil to adsorb cations in such a form that they can be readily desorbed by competing ions." This definition derives from the early works of van Bemmelen (*e.g.* 1888) which were summarized by Beneke and Lagaly (2005).

Of course the most important CEC property is reversibility, which was reported first by Johnson (1859). Reversibility of cation exchange is a criterion which is not easily fulfilled for natural zeolites, illites (frayed edge sites), and vermiculites. Sawhney (1972) reviewed selective sorption and fixation of cations and concluded that K^+ fixation is different between di- and trioctahedral 2:1 clay minerals. Two main factors are responsible. "First, the vertically oriented OH-dipole of the hydroxyls in trioctahedral layer silicates results in a weaker bonding of the K^+ than the inclined OH-dipole in the dioctahedral layer silicates. Second, the smaller size of the octahedral sheet in dioctahedral minerals produces shorter K–O bonds, hence K^+ is held more tightly in dioctahedral minerals." The resulting selectivity of edge interlayer sites of illite for K^+ is ~500 times greater than for Ca^{2+}. Selectivity of different index cations used for different CEC methods will produce CEC results that differ with respect to K^+ exchange if samples contain substantial amounts of illite with frayed edges (Jackson, 1963). If vermiculites are studied, cation exchange will depend on size and charge of the index cation. Monovalent index cations such as NH_4^+ will allow less exchange of interlayer cations because these monovalent cations will be fixed and followed immediately by contraction of the interlayer space (Graf von Reichenbach, 1966). Those cations that are still in the center of the crystals will be desorbed much more slowly. If divalent cations are used, contraction is avoided and the resulting extraction of interlayer cations

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will exceed that of monovalent cations (*e.g.* Schwertmann, 1966). In such minerals, cation selectivity is large, which means that zeolites, in particular, contradict the definition of CEC given by Bache (1976). Some examples are listed to clarify what is not included in 'normal' CEC processes.

(a) Using step-wise intercalation of alkylammonium cations into the interlayer space, micas can be transformed into a Na^+-exchanged form using $C_2H_5ONa^+$ (Weiss *et al.*, 1956). After air-drying, these Na^+-intercalated micas can be cation exchanged but, after drying at 50ºC, the Na^+-micas become collapsed (Weiss, 1958b). Na^+-micas could be exchanged into a Ca^{2+}-exchanged form using aqueous $CaCl_2$ solutions. The Weiss study proved the existence of expandable Ca^{2+}-micas, though also demonstrated that these exotic cation-exchanged minerals are not comparable with those found in typical clays and soils.

(b) Diffusion-controlled cation-exchange processes in vermiculites were studied by Walker (1959). The reaction time always depends on the minerals present; it may be too short, such as for vermiculites or in general for aggregated particles, or too long for the replacement of fixed cations. Grim (1962) summarized as follows: "The rate of the cation exchange reaction varies with the clay mineral, the concentration of the cations, and the nature and the concentration of the anions. In general, the reaction for kaolinite is most rapid, being almost instantaneous. It is slower for montmorillonites and attapulgite and requires even longer, perhaps hours, to reach completion for the illites and chlorites."

(c) Echle (1978) conducted experiments to transform loughlinite and sepiolite. He treated sepiolite in a way that XRD patterns of dried reaction products were congruent with XRD patterns of loughlinite. He used NaOH solutions and varied pH, cation concentration, and reaction time. Transforming loughlinite to give XRD patterns congruent with those of sepiolite was much easier using deionized water only; such reaction products could then be retransformed using Na^+ ions.

(d) Different clays were studied, using Cu(II)-triethylenetetramine, by Meier and Kahr (1999) who compared CEC values with ammonium acetate CEC values. They found a good correlation for bentonites, K-bentonites, illite, and kaolinite; huge differences occurred, however, for Ca^{2+}-dominated clinoptilolite. They concluded that "structural holes in clinoptilolite are accessible to the small ammonium ion but not to the larger Cu complex, which exchanges with only surface-site cations."

Using CEC as a description of alkylammonium exchange, fixed-cation replacement in vermiculites, sepiolite-to-loughlinite transformation, and Cu(II)-triethylenetetramine exchange in smectitic interlayers is, however, questionable. The term CEC should be used with care. It should be used to describe reversible cation exchange processes. In many studies any replacements of cations were described with the term CEC, regardless if these exchanges were reversible.

The comparability of CEC data determined using different index cations was discussed by Okazaki *et al.* (1962), who concluded that several problems might occur: fixable index cations; concurrent changes in pH during the experiment; equimolar cation exchange (*e.g.* if $MgOH^+$ complexes are formed which is usually the case at high-pH values but was also reported for low-charge clay minerals, see Weiss, 1958c, 1959); hydrolysis of the index cation; incomplete replacement of initially adsorbed cations; and incomplete replacement of index cations, as well as unwanted mineral dissolution of some of the samples (see also Mehlich, 1948). Papanicolaou and Overstreet (1969) added salt retention and loss of organic matter (see also Riehm *et al.*, 1954), both during the steps for removal of excess salt, as well as geometry of soil particles to that list.

Soluble minerals and excess electrolyte

Gypsum, calcite, and dolomite are well known to dissolve during experiments conducted to exchange cations from soils and clays. Sources of errors were discussed comprehensively by Dohrmann (2006a, 2006b) and Dohrmann and Kaufhold (2009, 2010). Dissolution of these minerals causes an excess of exchangeable Ca^{2+} in the order of gypsum > calcite > dolomite. Dissolution of dolomite also caused an excess of Mg^{2+}. The CEC values were also inaccurate due to other more complicated mechanisms, particularly for the barium chloride method (precipitation followed by dissolution of Ba-carbonate in calcareous soils, and the possible precipitation of $BaSO_4$ during Ba^{2+} desorption if soils were gypsiferous) and the ammonium acetate method (desorption of ammonium after ammonium saturation during washing of excess salt if carbonate relicts were still present). The problem of inflated Ca^{2+} values caused by dissolution of calcite and dolomite can be minimized if calcite-saturated exchange solutions are used (Dohrmann, 2006c, Dohrmann and Kaufhold, 2009). This pre-treatment suppresses calcite dissolution using methods with single-step exchange of index cations, such as the monovalent $AgTU_{calcite}$ (silver(I) thiourea), the divalent Cu-trien$_{5xcalcite}$ (copper(II) triethylenetetramine), and the trivalent $CoHex_{calcite}$ (cobalt(III) hexamine). For gypsiferous bentonites, a combination of results was successful for exchangeable Ca^{2+} calculation, namely, gypsum concentrations based on XRD Rietveld quantification were used to correct Cu-trien$_{5xcalcite}$ Ca^{2+} values assuming that all gypsum was dissolved (Dohrmann and Kaufhold, 2010). Using this tool, detection of excess Na^+/Mg^{2+} was possible, which correlated well with high Cl^- concentrations in dilute suspensions indicating the presence of excess electrolyte. Typical electrolyte concentrations may arise from entrapped sea water.

In contrast to Part I of this study (Dohrmann *et al.*, 2012), which focused on precision using a single method

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(Cu-trien), the present study (Part II) focused on CEC accuracy and compared CEC methods in which care was taken to prevent dissolution of soluble minerals such as calcite and gypsum. The clays studied are the same bentonite reference materials from the Alternative Buffer Material (ABM) test project (SKB, 2007) which were used in an experiment at the hard rock laboratory in Äspö, Sweden. The ABM is an SKB (Swedish Nuclear Fuel and Waste Management Co) project with international partners who have collaborated in the laboratory experiments and analyses (Eng *et al*., 2007).

The question to be answered is whether measured differences of CEC values can be evaluated as: (1) actual CEC differences caused by, for example, the structural degradation of clay minerals (*e.g*. illitization); or (2) simply as scattering. The same problem appears if differences in exchangeable cation values were measured. These could have been caused, for example, by redistribution of cations on exchange sites during a hard rock laboratory experiment (Olsson and Karnland, 2011). During the Long Term Test of Buffer Material (LOT) experiment, exchangeable Mg^{2+} was enriched in the warmest zone of the bentonite buffer and exchangeable Na^{+} was partly replaced by Ca^{2+}. Such experimental exchangeable cation values measured in a laboratory could be evaluated as actual changes or simply as data scatter.

Scatter of measured CEC or exchangeable cation values is typically larger if research teams from different countries are involved in the same project. Differences in barrier material exchangeable cations, in particular, can be useful in understanding transport processes in these materials. To determine which CEC or exchangeable cation values are accurate (true values) and to determine how precisely these values can be measured by comparing results from different laboratories is very important. Conclusions drawn from such experiments could be used in concepts for long-term safety assessment of barrier systems.

MATERIALS AND METHODS

Three reference materials that were used in the ABM project were chosen for this inter-laboratory CEC study: MX80 (bentonite, Wyoming, USA), Dep.CAN (Deponit CAN bentonite, Milos, Greece), and ASHA (#505, bentonite, Ashapura, India). The bentonites were homogenized and characterized as described by Dohrmann *et al*. (2012). Instead of using the standard Cu-trien method, other methods were used to measure CECs and exchangeable cations to minimize errors caused by carbonate and gypsum dissolution. All participating laboratories submitted values measured by so-called 'alternative methods' though both approaches used in Laboratory 3 were combined in the Cu-trien standard methods list because they were relatively similar. Laboratory 4 measured CEC only and Laboratories 1 and 2 measured exchangeable cations only. Laboratory 5 submitted both exchangeable cation and CEC values. Laboratory 5 calculated the CEC values after adsorption of the Cu-trien index cation using both visible spectroscopy (VIS) and elemental analysis (ICP). The CEC (VIS) and CEC (ICP) values were treated separately in order to check if Cu-trien index cation determination by one or both analytical methods is problematic. Both Cu-trien index cation concentrations were used to calculate the CEC. The introduction of two separate CEC methods was not intended. The key parameters of the methods used by the different laboratories are summarized in Table 1.

The index cations used were ammonium and Cu-trien (modified from the standard Cu-trien method). After addition to the clay, ammonium must be submitted to repeated exchange steps because a single step does not guarantee complete cation exchange. Centrifugation and collection of the reacted solutions were performed after each addition of NH_4Cl. Two laboratories exchanged three times with NH_4Cl, one laboratory exchanged six times with NH_4Ac (ammonium acetate), and all of these laboratories added ethanol. After the experiments, ethanol was evaporated from the filtrate or supernatant and the volume was adjusted by addition of deionized water. Laboratories 1 and 2 used ~80% ethanol in the NH_4Cl solution, which was added to minimize carbonate dissolution. In contrast, Laboratory 4 only used ethanol in the last two washing steps to remove excess NH_4Ac before adsorbed ammonium was measured by Kjeldahl distillation and the CEC was calculated. Ammonium solution concentrations of 0.15 M in Laboratory 2, 0.5 M in Laboratory 1, and 1.0 M in Laboratory 4 were used. Elemental analysis (ICP) was used to quantify the Na^{+}, K^{+}, Mg^{2+}, and Ca^{2+} exchanged cations in the sample solutions. The Cu-trien solution was prepared in Laboratory 5 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 as described by Dohrmann and Kaufhold (2009) in order to suppress calcite dissolution. This Cu-trien$_{5xcalcite}$ approach, however, does not prevent dissolution of gypsum (Dohrmann and Kaufhold, 2010). The calcite-saturated complex solution was added to the clay; the slurry was homogenized, allowed to react for 2 h, and centrifuged. After centrifugation the clear supernatant was analyzed for the concentrations of the exchangeable cations (ICP) and for the remaining Cu-trien index cation concentrations (ICP and VIS). These measured concentrations were used to calculate CEC values and exchangeable cations values. The CEC was calculated by the difference between the initial and the remaining Cu-trien index cation concentration.

RESULTS AND DISCUSSION

CEC and exchangeable cations

Eighteen values were always used to determine the precision. Only one value was determined to be an outlier (CEC, $n = 17$).

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Table 1. Characteristics of the so-called 'alternative methods' used in the different laboratories.

Lab	NH_4Ac (M)	NH_4Cl (M)	Cu-trien$_{5xcalcite}$ (mL)	Repetitions *n*	Sample mass (mg)	Elemental analysis
Lab 1		0.50	*⅓ of 25	3	500	ICP
Lab 2		0.15	*⅓ of 50	3	800±50	ICP
Lab 4	1.0		25	6	100	Kjeldahl
Lab 5			0.01 50	1	400+600	ICP

* The total volume used was 25 mL or 50 mL, which was added in three portions of approximately equal volume.

	Dispersion after addition of the index cation					
Lab	Technique 1	Time (min)	Technique 2	Time (min)	Technique 3	Time (min)
Lab 1	Hand shaking	10	Sonication (homogenizer probe)	1.5	Rocking platform	30
Lab 2	Sonication (ultrasonic bath)	15	Vibrating table	120		
Lab 4	End-over-end shaking	(1) 1000; (2−5) short				
Lab 5	End-over-end shaking	120				

CEC

Average CEC values were 84±0.5 meq/100 g for Dep.CAN, 85±2.1 meq/100 g for MX80, and 91±3.3 meq/100 g for ASHA (Table 2). The precision of ±1σ for these data was not representative because too few (n = 5 to 6) values were available for each bentonite. Different index cations were used by the different laboratories and were determined using different techniques (Kjeldahl distillation, ICP analysis, and VIS spectroscopy), which typically increases the data scatter. Only the 91.1 meq/100 g value for Dep.CAN is questionable. Different methods always produce different CEC values. Identical CEC values might be found for one bentonite, whereas the differences may be relatively large for another. The Laboratory 4 Dep.CAN bentonite CEC values were quite large, the lower CEC value was in the upper range of all the other Cu-trien CEC values from the other labs, and the larger CEC value was 7 meq/100 g larger and qualified as an outlier. The classification as an outlier is supported by the observation of Meier and Kahr (1999) who compared four bentonites (SAz-1, Volclay, MX80, and Montigel) and found that Cu-trien CEC was on average 3% larger, which is the opposite of what was found by Laboratory 4. The CECs of the ASHA bentonite determined by NH_4Ac were 6 and 10 meq/100 g greater than the Cu-trien$_{5xcalcite}$ CEC values. This again differs from the trend proven by Meier and Kahr (1999). The pH value of the initial exchange solution differed (~pH 9 for the Cu-trien$_{5xcalcite}$ method, and pH 7 for the NH_4Ac method) but two of the three bentonites were calcareous. Calcite dissolution buffers the pH and influences the pH value during the cation exchange experiment. Parameters influencing this reaction are reaction time and carbonate content. As the pH of the Cu-trien$_{5xcalcite}$ solutions was generally greater than the pH of NH_4Ac solutions, the CEC values of Laboratory 5 should also have been larger (caused by variable charges); the opposite was found in the present study. Whether both CEC values were equally accurate is unclear; further repetitions or an extended ring test are needed for a reliable answer. Also unclear is whether the NH_4Ac method CEC value deviations were due to methodological differences alone or due to the large scattering because of individual errors. Using only results that were not questionable and ignoring outliers, the three bentonite CEC values were nearly identical to that reported by Muurinen (2010) and Dohrmann *et al.* (2012) for Cu-trien standard-method CECs.

Exchangeable cations

Exchangeable cation values and the calculated fraction of the CEC (%) (Table 4), based on the total average CECs and outlier-free CECs (Table 3), were compared with the Cu-trien standard method (Dohrmann *et al.*, 2012).

Exchangeable Na^+ and K^+. For two of the three bentonites, exchangeable Na^+ values were similar to values determined using the Cu-trien standard method and data scatter (±1.2 to ±3.9 meq/100 g) was low to intermediate. Average exchangeable Na^+ values were 2 meq/100 g lower (~3% relative) for the ASHA bentonite only, which contains chloride-rich pore water (Muurinen, 2010). The exchangeable Na^+ values measured by the two laboratories that used 80% ethanol solutions averaged 4 meq/100 g lower. Reduced solubility of Na^+-minerals in ethanol is not a likely explanation

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Table 2. CEC and exchangeable Na^+, K^+, Mg^{2+}, and Ca^{2+} values of the alternative methods used in the different laboratories. All values meq/100 g.

Alternative methods	MX80		Dep.CAN		ASHA	
	dupl. 1	dupl. 2	dupl. 1	dupl. 2	dupl. 1	dupl. 2
Exchangeable Na^+						
Lab 1	56.4	57.8	21.4	20.3	56.8	54.9
Lab 2	60.4	58.7	22.4	23.2	62.6	60.5
Lab 5	59.9	59.5	23.6	23.5	65.1	65.0
Exchangeable K^+						
Lab 1	1.6	1.6	1.6	1.5	0.4	0.5
Lab 2	1.8	1.7	1.5	1.6	0.5	0.4
Lab 5	1.9	1.7	1.8	1.9	0.5	0.7
Exchangeable Mg^{2+}						
Lab 1	7.9	7.8	23.4	22.3	14.4	14.1
Lab 2	5.8	6.2	21.4	20.7	13.9	12.0
Lab 5	6.1	6.3	24.4	24.6	13.1	13.0
Exchangeable Ca^{2+}						
Lab 1	24.4	25.4	47.6	46.1	19.9	19.2
Lab 2	18.9	18.4	37.1	38.2	18.4	17.6
Lab 5	21.9	21.6	37.3	40.6	18.2	18.2
CEC						
Lab 4	84.8	80.3	84.2	*91.1*	93.6	96.8
Lab 5 (VIS)	83.8	85.7	83.7	83.1	88.6	87.8
Lab 5 (ICP)	86.3	86.6	84.7	83.7	89.8	88.3
Sum−CEC						
Lab 1			not determined			
Lab 2			not determined			
Lab 4			not determined			
Lab 5 (VIS)	5.9	3.6	3.3	7.5	8.2	9.1
Lab 5 (ICP)	3.4	2.6	2.3	6.9	7.0	8.5

for the lower values, which would make the results more accurate than Cu-trien$_{5xcalcite}$ Na^+ values. Greater scatter is a more reasonable explanation because laboratories that used 80% ethanol solutions produced values which ranged from 54.9 to 62.6 meq/100 g Na^+ (a relatively large 10−15% difference).

The exchangeable K^+ values were as low as the Cu-trien standard method, but the precision was improved from ±0.2−0.4% to ±0.1−0.2%. The larger (two to five times) sample mass used when exchangeable K^+ was investigated may explain the greater precision for K^+ values because K^+ concentrations were usually very low and relatively close to the ICP analysis detection limit.

Exchangeable Mg^{2+}. For most samples, exchangeable Mg^{2+} values were similar to the Cu-trien standard method values. The Dep.CAN bentonite contained dolomite which is partially soluble in CEC solutions. The ethanol solutions clearly suppressed dolomite solubility because the exchangeable Mg^{2+} values averaged 2.3 meq/100 g lower than in the Cu-trien standard method (22.0 *vs.*

Table 3. CEC values (meq/100 g) (present study, outliers were ignored) compared with published data using the Cu-trien method. Note that CEC (VIS) and CEC (ICP/AAS) represent CEC values using the same Cu-trien index cation but the CEC was calculated based on visible spectroscopy analysis (VIS) or elemental analysis (ICP/AAS).

CEC	MX80	Dep.CAN	ASHA
CEC, present study (average of different methods)	85	84	91
CEC (Cu-trien, VIS, n = 8), Dohrmann *et al.* (2012)	84	82	86
CEC (Cu-trien, ICP/AAS, n = 10), Dohrmann *et al.* (2012)	85	83	86
Muurinen (2010)	87	83	89

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Table 4. Calculated exchangeable cation population in % with respect to CEC (Table 2). The upper part contains all results (without outliers), whereas, the lower part contains only exchangeable Ca^{2+} values that were judged to be most plausible as discussed in the text.

Exchangeable cation population	MX80	Dep.CAN	ASHA
Results from all labs			
Na^{+}/CEC (%)	69	27	67
K^{+}/CEC (%)	2	2	1
Mg^{2+}/CEC (%)	8	27	15
Ca^{2+}/CEC (%) (all labs)	26	49	20
Control sum (%)	105	105	103
Most plausible Ca^{2+} results only			
Na^{+}/CEC (%)	69	27	67
K^{+}/CEC (%)	2	2	1
Mg^{2+}/CEC (%)	8	27	15
Ca^{2+}/CEC (%) (all)			20
Ca^{2+}/CEC (%) (labs 2 and 5 only)	24	46	
Control sum (%)	103	102	103

24.3 meq/100 g). Laboratory 5 used a calcite-saturated exchange solution and measured 24.5 instead of 23.7 meq/100 g by the Cu-trien standard method. This difference was unlikely to have been caused by greater dolomite solubility because Mg^{2+} values were ~50% lower in experiments using pure dolomite and the Cu-trien$_{5xcalcite}$ method. Based on the available data, it is unclear whether these differences are within the typical scattering range for different laboratories/different methods or whether ammonium/ethanol methods suppressed dolomite solubility more effectively.

Exchangeable Ca^{2+}. The largest differences between the parameters measured with the Cu-trien standard method and this study were due to exchangeable Ca^{2+}. The ASHA bentonite contained no soluble Ca minerals and the exchangeable Ca^{2+} values should have been identical in this study; however, the values were 2 meq/100 g smaller using the alternative methods. No mechanism was identified to explain the smaller exchangeable Ca^{2+} values measured for the ASHA bentonite. The MX80 and Dep.CAN bentonites were calcareous with 1 and ~6 wt.% calcite, respectively. Total measured differences in the Ca^{2+} values followed the calcite contents. The total Ca^{2+} difference was 4.5 meq/100 g for MX80 and 8.5 meq/100 g for Dep.CAN. Soluble Ca minerals typically inflate Ca^{2+} values, which means the lower Ca^{2+} values of calcareous bentonites are probably more accurate (Dohrmann, 2006a).

Ammonium salts are known to dissolve carbonates and sulfates. The use of ethanol solutions alone to limit carbonate dissolution, discussed for MX 80, was clearly not fully successful. The more concentrated 0.5 M NH_4Cl solution (~25 meq/100 g, Laboratory 1) extracted more Ca^{2+} than the less concentrated 0.15 M solution (~19 meq/100 g, Laboratory 2). Both laboratories used a similar solution/solid ratio on three occasions (16–17 mL solution/800 mg clay, Laboratory 2; ~8 mL solution/500 mg clay, Laboratory 1). The largest difference may have been caused by the use of an ultrasonic homogenizer probe (Laboratory 1) for dispersion after addition of NH_4^+ index cations. All these factors explain the differences in measured exchangeable Ca^{2+}. The exchangeable Ca^{2+} values for Laboratory 2 were relatively close to those for Laboratory 5, which used calcite-saturated Cu-trien solutions. The ammonium-ethanol method of Laboratory 2 measured slightly lower Ca^{2+} values for Dep.CAN than the Cu-trien$_{5xcalcite}$ method and the MX80 Ca^{2+} values were significantly lower (18.7 *vs*. 21.8 meq/100 g). The MX80 bentonite contains gypsum and the question remains whether more gypsum than calcite dissolved.

The accuracy can only be checked with the whole data set using differences between the sum of exchangeable cations and the CEC. Therefore, only the averages of both CEC methods for the calcareous and gypsiferous bentonite, MX80, and for the calcareous bentonite, Dep.CAN, from Laboratories 2 and 5 were used. The exchangeable Ca^{2+} values were 21 instead of 30 meq/100 g for MX80 and 38 instead of 54 meq/100 g for Dep.CAN compared with the Cu-trien standard method.

Sum of exchangeable cations in relation to the CEC

Ideally, the sum of exchangeable cations should be as large as the CEC. The difference between the sum of exchangeable cations and the CEC ('sum–CEC,' Dohrmann *et al*., 2012) was used for quality control of the whole data set. Only one laboratory reported both exchangeable cations and CECs using alternative methods (Table 2). The Cu-trien$_{5xcalcite}$ method was used to minimize carbonate dissolution. Accordingly, exchangeable Ca^{2+} values were improved in comparison to conventional Cu-trien protocols applied to identical samples. This was a great success because without any

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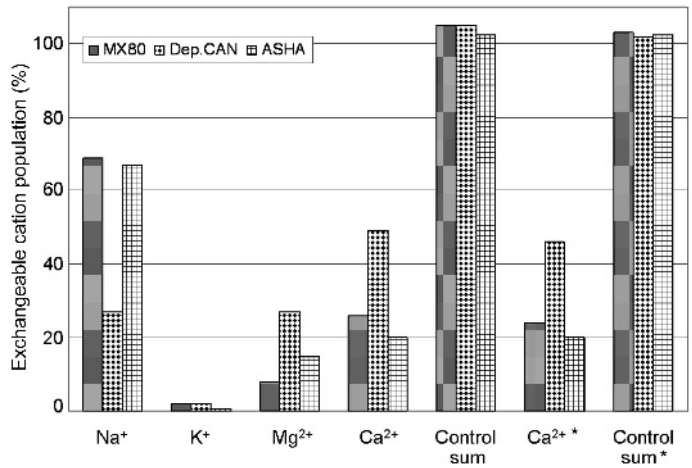


Figure 1. Calculated exchangeable cation population (%) with respect to CEC (Table 4). * Most plausible data.

correction, 'sum−CEC (VIS)' values were much smaller: MX80 bentonite, 3.9 meq/100 g (Cu-trien$_{5xcalcite}$) *vs*. 11.4 meq/100 g; Dep.CAN bentonite, 5.0 meq/100 g (Cu-trien$_{5xcalcite}$) *vs*. 17.1 meq/100 g; ASHA bentonite, 8.2 meq/100 g (Cu-trien$_{5xcalcite}$) *vs*. 6.9 meq/100 g. The ASHA bentonite was non-calcareous and the calcite-saturated solutions used in alternative methods should not have affected ASHA exchangeable cation and CEC values. The sum of exchangeable cations should have agreed with Cu-trien CEC values, a point which was confirmed. The ASHA bentonite 'sum−CEC' values represent typical data scattering and the relatively large anion concentration (mainly Cl^-) explains the CEC overstep.

Actual exchangeable cation population

Exchangeable cation and CEC values (Table 2) were used to calculate the exchangeable cation population (%) with respect to the CEC (Figure 1). The ASHA and MX80 bentonites were dominated by exchangeable Na^+ (67/69% of the total CEC, Table 4), but the Dep.CAN bentonite had only 25% exchangeable Na^+. Exchangeable K^+ was a minor part of the exchangeable cation population of the bentonites. The exchangeable Mg^{2+} varied from 8 to 27% in the bentonites. As discussed above, evaluating exchangeable Ca^{2+} accuracy was more complicated. Table 4 was split into two parts to show the results of all laboratories on top (without outliers) and the results deemed most plausible on the bottom to improve accuracy. Without bothering with the small differences between the ammonium/ethanol method of Laboratories 1 and 2, the 'sum−CEC' data of the alternative methods (upper part of Table 4) were close to the optimum of 100% of the CEC (103−105%). Eliminating the four less plausible Ca^{2+} values (n = 14 instead of n = 18) brought the 'sum−CEC' values of the two calcareous bentonites closer to the optimum (102−103%/CEC, Figure 1).

Why, apart from typical scattering, was 100% not attained in any sample? All the bentonites had cations in excess of the CEC, which can be explained easily by excess electrolyte. The ASHA bentonite contained 3.2 mg/g chloride and 1.1 mg/g sulfate in aqueous extracts (Muurinen, 2010), whereas, the MX80 and Dep.CAN bentonites were dominated by sulfate (3.8 and 3.7 mg/g) with minor chloride (0.1 and 0.7 mg/g). These anions have corresponding cations (*i.e.* free salts) which were extracted during CEC measurements but did not compensate negative-charge sites on the clay minerals or organic matter.

SUMMARY AND CONCLUSIONS

The overall quality of CEC and exchangeable cation values submitted for this inter-laboratory study from alternative CEC methods was good. The precision (Table 5) was comparable to the Cu-trien method (Dohrmann *et al*., 2012). The scattering of some parameters was slightly larger or smaller, but all within the same range. The precision, even for exchangeable Ca^{2+}, was satisfactory, although none of the laboratories used identical solution/solid ratios or reaction-time parameters, which parameters are known to affect carbonate dissolution. Using methods in the present study to minimize calcite dissolution, MX80 and Dep.CAN bentonite exchangeable Ca^{2+} values were smaller and more plausible than standard Cu-trien values and the sum of exchangeable cations were closer to the CEC values. A complicated CEC analysis using different CEC methods, anion analyses, and mineralogical analyses is needed to obtain more accurate and plausible results. Excess sulfate probably results in inflated Ca^{2+} values (Bradbury and Baeyens, 1998) and excess chloride inflates Na^+ or Mg^{2+} values slightly.

In summary, only the CEC and exchangeable K^+ values could be classified as accurate with some doubt

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Table 5. Exchangeable cation and CEC data including precision (meq/100 g) as determined by the different laboratories (without outliers or values affected by carbonate dissolution).

	MX80	Dep.CAN	ASHA
Na^+	58.8	22.4*	60.8*
St. dev.	1.4	1.2	3.9
K^+	1.7	1.7	0.5
St. dev.	0.1	0.2	0.1
Mg^{2+}	6.7	22.8*/†	13.4*
St. dev.	0.8	1.5	0.8
Ca^{2+}	20.2#	38.8#/†	18.6#
St. dev.	1.6	1.4	0.8
CEC	84.6	83.9	90.8
St. dev.	2.1	0.5	3.3

* Inflated by chloride-rich pore water; # Inflated by sulfate-rich pore water; † questionable if inflated by dolomite dissolution.

about the CEC because ammonium acetate and Cu-trien$_{5xcalcite}$ differed by ~5–10 meq/100 g for the ASHA bentonite and explains the poor precision. Chloride, sulfate, and possibly dolomite might have inflated the exchangeable Na^+, Mg^{2+}, and Ca^{2+} values.

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