Clays and Clay Minerals, Vol. 60, No. 2, 162–175, 2012.

INTERLABORATORY CEC AND EXCHANGEABLE CATION STUDY OF BENTONITE BUFFER MATERIALS: I. Cu(II)-TRIETHYLENETETRAMINE METHOD

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Abstract—Bentonites are candidate materials for encapsulation of radioactive waste. The cation exchange capacity (CEC) has proved to be one of the most sensitive parameters for detecting changes of mineral properties such as swelling capacity and illitization in alteration experiments. Whether measured differences in CEC values of bentonite buffer samples before and after an experiment are (1) actual differences caused by clay structural changes such as illitization or (2) simply data scatter due to the different methods used by international research teams is an open question. The aim of this study was to measure the CEC of clay samples in five different laboratories using the same method and to evaluate the precision of the values measured. The Cu-trien method and four reference materials of the Alternative Buffer Material (ABM) test project in Äspö, Sweden, were chosen for this interlaboratory study. The precision of the Cu-trien method, which uses visible spectroscopy, was very good with a standard deviation of ±0.7−2.1 meq/100 g for CECs that ranged from 11 to 87 meq/100 g. For the same CEC range, analysis of Cu-trien index cations using inductively coupled plasma (mass spectrometry) and atomic absorption spectroscopy were less precise with a standard deviation of ±2.8−3.9 meq/100 g. 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. Compared with results from the 'International Soil-Analytical Exchange' (iSE) program for soils, most absolute concentrations were much larger for the clays studied; however, for the two parameters exchangeable Ca^{2+} and CEC the range was similar to the iSE ring test and, most importantly, the precision was comparable. Future studies should discuss the accuracy of CEC and exchangeable cation values and compare them to alternative CEC methods in which care is taken to prevent dissolution of soluble minerals, such as calcite and gypsum.

Key Words—Bentonite Buffer, CEC, Cu-trien, Exchangeable Cations, Interlaboratory Study.

INTRODUCTION

Cation exchange capacity (CEC) is an important property of clay minerals which measures the degree to which a soil or clay can exchange cations with a solution. "Cation exchange is a consequence of negative electric charges on the colloidal clay and humus particles of the soil matrix" (Bache, 1976). For CEC measurements, so-called index cations are used. These are adsorbed on exchange sites replacing the originally adsorbed exchangeable cations. In bentonites, most of the CEC is based on the permanent negative charge of smectites which is mainly balanced by exchangeable cations in the interlayer region. The CEC and exchangeable cations of soils and clays have been determined since the early work of Way (1852). Numerous publications about various methods have discussed the validity of results of CEC procedures for a wide variety of natural materials. This long list of publications shows that, on one hand, cation exchange data are very important but, on the other hand, difficult to measure reliably.

Bentonites are candidate materials for encapsulation of radioactive waste. The CEC has been shown to be a sensitive parameter in alteration experiments to detect mineral-property changes such as swelling capacity and illitization (*e.g.* Kaufhold and Dohrmann, 2010a, 2010b). Whether measured differences in CEC values of bentonite buffer samples before and after an experiment are (1) actual differences caused by clay structural changes such as illitization or (2) simply data scatter due

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DOI: 10.1346/CCMN.2012.0600206

https://doi.org/10.1346/CCMN.2012.0600206 Published online by Cambridge University Press

to the different methods used by international research teams is an open question.

The degree of complexity is larger for soils than for sedimentary clays and bentonites. In contrast to most clay raw materials, soils contain large amounts of variable charges (organic matter, oxyhydroxides) which make CEC and exchangeable cations more difficult to determine in soils: "Thus it is obvious that CEC is not a soil property that is independent of the conditions under which it is measured. Different results will be obtained with different methods" (Rhodes, 1982). However, CEC measurements of bentonites and clays from geological studies also suffer from systematic methodological problems.

General problems (precision)

Dohrmann and Kaufhold (2010) compared CECs measured by two methods for a set of 14 calcareous bentonites. The results of repeated series of measurements of whole sample sets were compared with each other. If the same method was repeated, typical data scattering was recorded. Differences in results (3 sigma) between the two different methods were significantly larger than the precision for single methods. This means that, apart from scattering, systematic deviations occurred: "... decrease of precision between both methods is observed for $Mg^{2+}/Ca^{2+}/Na^{+}/K^{+}$ cations (±3.8/±6.5/±2.8/±0.6 meq/100 g) where average values are 23.6/33.0/29.7/2.4 meq/100 g for $CoHex_{calcite}$ (E) and 22.1/30.9/30.6/2.2 meq/100 g for Cu-trien$_{5xcalcite}$ (C). The reason for the systematic differences of Mg and the CEC are not yet understood."

Ciesielski and Sterckeman (1997) reported systematic differences between three CEC methods (48 soils). Ammonium acetate (pH = 7) extracted more K^{+} than Co(III) hexamine ($y = 1.175\ x$, $R^2 = 0.917$); though after variation of the analytical procedure (percolation instead of batch), the slope of the regression turned out to be $y = 0.978\ x$. Differences for exchangeable Ca^{2+} were large for calcareous soils because dissolution of calcite is different depending on the type of index cation solution. Comparability was very good for Mg^{2+} if the barium chloride method (unbuffered) was compared with Co(III) hexamine: $R^2 = 0.995$. The CEC was also comparable (the CEC of barium chloride method was determined *via* "compulsive" (Bascomb, 1964) exchange with magnesium sulfate) between both methods, $R^2 = 0.977$, because both exchange solutions were unbuffered. pH buffering of ammonium acetate solution was very effective (figure 2 in Ciesielski and Sterckeman, 1997) whereas the final pH in experiments with Co(III) hexamine was similar to the pH in water. Probably because of the pH-dependent charge sites in the 48 soils, correlations between the buffered ammonium acetate method and the unbuffered Co(III) hexamine method were not good.

Tucker (1954) studied the influence of reduced solubility of Ca carbonates in 1M NH_4Cl solutions in 60% ethanol and 40% water. He used different approaches with/without additional ammonia and found very good agreement for exchangeable Ca^{2+} and Mg^{2+} in 18 calcareous soils. Precision was usually very good with average Ca^{2+} values of 16.5 and 16.4 meq/100 g and Mg^{2+} values of 11.7 meq/100 g for both methods. At the lowest measured Ca and Mg concentrations, the scatter was 12% and 14%, respectively.

Matsue and Wada (1985) reported exchangeable Na^{+}, K^{+}, Mg^{2+}, and Ca^{2+} values of four variable-charge soils using Sr^{2+} and NH_4^{+}. The low absolute exchangeable Na^{+} and K^{+} values (0.1−1.0 meq/100 g) explain the large 50% relative differences and average 10−13% differences between the methods. For the larger 0.5−19 meq/100 g exchangeable Mg^{2+} and Ca^{2+} values, the maximum differences were 6−7% with average differences of 1−2%.

Seven low-CEC kaolins (2−8 meq/100 g) containing traces of impurities (mainly mica, smectite, and vermiculite) were studied by Lim *et al.* (1980) who found average differences of 15% for methods based on Ca^{2+} and K^{+}; these results are of limited use, however, because K^{+} may have been (partly) specifically adsorbed (= fixed).

Weiss (1958) carried out extensive cation exchange studies using carefully purified and homoionic clay minerals (kaolinite, illite, beidellite, montmorillonite). He varied index cations (and sometimes used identical cations with different anions) and washing techniques (water, alcohol) as well as pH (table 7 in Weiss, 1958). Use of Mn^{2+} at a moderate pH of 7.5 was critical because it was obviously adsorbed as $Mn(OH)^{+}$ (equimolar). The author concluded that all methods gave results which can be used for rough characterization of CEC. When homoionic Na^{+} clays were exchanged with NH_4^{+}, the effects of six different monovalent anions on exchangeable cation amounts were small. CECs of 8.2±0.2 meq/100 g for kaolinite and 87±2 meq/100 g for montmorillonite were determined (table 9 in Weiss, 1958). Note that data scatter relative to the magnitude of the CEC value for kaolinite was very similar to montmorillonite.

Apart from the scientific studies, interlaboratory test programs (ring tests) are very useful in clarifying whether the different values measured for a property of the same material are identical and within the data scatter range (*i.e.* standard deviation) or not. Here, values measured using different methods can also be compared.

Numerous CEC and exchangeable cation ring-test results are available from soil science laboratories that participate in the 'International Soil-Analytical Exchange' (iSE) program organized by the Wageningen Evaluating Programs for Analytical Laboratories (Wepal) (Houba *et al.*, 1996). Six different CEC methods were tested (four times per year), three of which represented effective CEC (pH = 7) and the other

https://doi.org/10.1346/CCMN.2012.0600206 Published online by Cambridge University Press

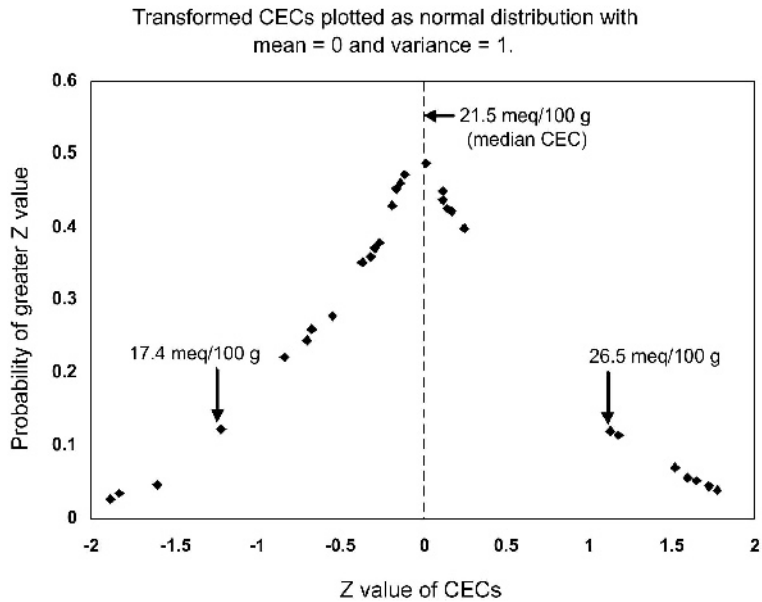


Figure 1. CEC values reported by iSE (2006) were standardized to normal distribution using the instructions and the Z value *vs*. probability table of Steel and Torrie (1980). (Z value = standard score which indicates by how many standard deviations the value is above or below the mean.) The CEC values with Z >1 or <1 can be deemed questionable.

three potential CEC (pH = 8.1) results. Typical results returned from 30 laboratories (iSE, 2006) ranged from 15 to 29 meq/100 g (one outlier with 34.3 meq/100 g was removed) with a median value of 21.5 meq/100 g and the so-called MAD (median of absolute deviations) of 1.3 meq/100 g (n = 72). MAD is a statistical parameter which is used in the iSE program. Outliers do not change the value of the MAD. Each data point in Figure 1 represents the median value (n = 1–4) of one laboratory. These CECs were standardized to normal distribution using the instructions and the Z value *vs*. probability table of Steel and Torrie (1980). The distribution clearly shows that a large group of CEC values with Z >1 or <−1 can be judged questionable.

All the CEC data points in Figure 1 are represented by two single numbers in Table 1 (here, 21.5 meq/100 g = median and 1.3 meq/100 g = MAD, n = 72). The results of the other five methods were significantly larger (median = 27.6 meq/100 g) for this standard soil (Riverclay, iSE 2006) although three of the methods were 'effective CEC' methods using unbuffered solutions. The absolute number of results (n = 70) for all these methods was slightly smaller than that of the first-mentioned method ($NH_{4\text{-acetate, (pH = 7)}}$), however. This means that comparability may be limited. If the $CEC_{NH_4\text{-acetate, (pH = 7)}}$ values were smaller than the results for all other CEC methods used, the trend could be pronounced as being method-dependent and should have been noticed for other soils also. Based on the analysis of the standard material clay (ISE, 2008, Table 1), however, another CEC method, $CEC_{pot.\ BaCl_2\text{-TETA (pH = 8.1)}}$, deviated systematically whereas $CEC_{NH_4\text{-acetate (pH = 7)}}$ was close to the median value. Obviously no simple trend and no simple reason for such systematic differences can be identified. The results of individual exchangeable cations were very similar for both samples (Table 1, 'Riverclay' upper part, 'clay' lower part) and all six methods used. The number of results (up to 100) did not have a significant influence. The MAD values for Ca^{2+} were very large for Riverclay. This can be explained by the fact that the Riverclay sample contains calcite, which was dissolved during the CEC analysis (for a discussion of this problem see Dohrmann, 2006a, 2006b). Among the 132 different Ca^{2+} analyses, variation was extremely large, indicating that the wrong CEC method was chosen (Dohrmann and Kaufhold, 2009).

The aim of the present study was to measure the CECs and the exchangeable cations of clay samples in five different laboratories using the same method and evaluate the precision of the measured values. The Cu-trien method was chosen because this method is fast and applied in many bentonite-research laboratories, particularly in the bentonite industry for quality control (*e.g.* Kaufhold and Dohrmann, 2003). The Cu-trien method was first published in German (Kahr and Meier, 1996) and then in English (Meier and Kahr, 1999); see also Bergaya and Vayer (1997) who worked with an alternative Cu complex. Ammann *et al.* (2005) reported on Cu-trien problems with pH variations using bentonites and recommended using a tris buffer (tris-(hydroxy-methyl)aminomethane, pH = 8) to stabilize pH for more reliable visible spectroscopy analysis (VIS). Using inductively coupled plasma/atomic absorption spectroscopy (ICP/AAS) analysis for measuring the residual Cu content of the Cu-trien solution is an

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https://doi.org/10.1346/CCMN.2012.0600206 Published online by Cambridge University Press

Table 1. CEC and exchangeable cation results of six different soil-CEC methods determined for two standard soils (#989 Riverclay and #961 Clay) reported by iSE (2006, 2008), with data summarized from that report. Median values which were questionable and MAD values which indicate problematic results are marked in italics. Median and MAD values are given in meq/100 g.

	CEC			Na			K			Mg			Ca		
Method	Median	MAD*	*n*	median	MAD*	*n*	median	MAD*	*n*	median	MAD*	*n*	median	MAD*	*n*
ISE 2006 (Riverclay)															
Potential CEC NH_4-acetate (pH=7)	*21.5*	1.3	72	0.27	0.03	*100*	0.48	0.04	134	2.62	0.22	118	*31.3*	7.1	132
Potential CEC $BaCl_2$-TETA (pH=8.1)	28.6	1.0	16	0.22	0.01	*8*	0.54	0.02	11	2.51	0.05	10	26.7	1.8	11
Potential CEC NH_4-Cl (BZE)	26.5	*3.9*	5	0.29	0.02	*5*	0.63	0.01	4	2.23	0.80	14	24.2	0.8	10
Effective CEC 0.01M $BaCl_2$ (ISO 11260)	29.7	1.9	10	0.23	0.04	*9*	0.35	0.15	11	2.27	0.32	11	27.6	*3.6*	11
Effective CEC 0.01M BaCl2 (UNEP/UN...)	29.7	*2.8*	21	0.21	0.01	*18*	0.34	0.02	22	2.48	0.03	16	26.9	1.6	24
Effective CEC Co-Hexamine	24.6	1.0	18	0.23	0.01	*16*	0.40	0.03	21	2.30	0.12	21	23.1	0.4	17
Median value of all methods	27.6	1.6		0.23	0.02		0.44	0.03		2.39	0.17		26.8	1.7	
ISE 2008 (clay)															
Potential CEC NH_4-acetate (pH=7)	9.69	0.88	92	0.08	0.01	86	0.21	0.01	123	0.65	0.04	114	8.10	0.42	120
Potential CEC $BaCl_2$-TETA (pH=8.1)	*13.9*	*1.7*	30	0.11	0.04	12	0.23	0.03	12	0.64	0.08	13	8.24	0.58	13
Potential CEC NH_4-Cl (BZE)	10.2	0.4	14	0.08	0.01	15	0.20	0.00	15	0.69	0.03	19	8.64	0.58	20
Effective CEC 0.01M BaCl2 (ISO 11260)	8.07	0.84	5	0.08	0.03	3	0.25	0.01	4	0.68	0.04	5	8.63	1.10	5
Effective CEC 0.01M BaCl2 (UNEP/UN...)	8.90	0.02	16	0.07	0.00	11	0.17	0.01	21	0.63	0.01	19	7.81	0.33	25
Effective CEC Co-Hexamine	8.87	0.29	14	0.08	0.01	15	0.18	0.01	17	0.67	0.01	12	7.87	0.24	16
Median value of all methods	9.30	0.61		0.08	0.01		0.21	0.01		0.66	0.04		8.17	0.50	

* MAD = median of absolute deviations

Table 2. Amounts of exchange solution, water, and sample mass used in the different laboratories and their influence on the maximum possible CEC.

Lab	Cu-trien (M)	Cu-trien (mL)	Water (mL)	Buffer (mL)	Sample mass (mg) Bentonite	Sample mass (mg) COX	%/Cu-trien adsorbed (max.)	Max possible CEC (meq/100 g)	Elemental analysis
Lab 1	0.015	10	25	–	200		~60%	~145	ICP
Lab 2	0.015	20	50	–	400±50		~60%	~45	ICP
Lab 3-1 (setup1)	0.01	10	50	–	200		83%	107	AAS
Lab 3-2 (setup2)	0.01	20	40	–	200		42%	213	AAS
Lab 4	0.02	5	44	1	130–140	500	58%	152	AAS
Lab 5	0.01	10	50	–	80+120	200+300	50%+34%	177 (120 mg)	ICP

alternative to avoid such pH influences on CEC results caused by systematic errors in VIS spectroscopy analysis.

The clays studied are reference materials of the Alternative Buffer Material (ABM) test project (SKB, 2007). The ABM is an SKB (Swedish Nuclear Fuel and Waste Management Co) project with international partners collaborating on laboratory experiments and analyses (Eng *et al.*, 2007). Differences in CEC results may be used to understand whether minerals in the bentonites were degraded structurally during a large-scale laboratory experiment. The question of which CEC and exchangeable cation differences are acceptable as unsystematic statistical errors is very important, particularly if results from different laboratories are compared.

MATERIALS AND METHODS

Four reference materials of the ABM project were chosen for this interlaboratory study of CEC analyses: MX80 (bentonite, Wyoming, USA), COX (clay stone, Callovo-Oxfordian clay formation, France), Dep.CAN (Deponit CAN bentonite, Milos, Greece), and ASHA (#505, bentonite, Ashapura, India).

Most of the ABM samples were relatively coarse grained. In several CEC procedures, the sample mass used was low (down to <100 mg). For this purpose, the samples had to be powdered, achieved using a hammer mill (250 μm mesh). These powders were split using a riffle splitter to give 20 g each. Three sample splits were chosen at random to check homogeneity. X-ray fluorescence (XRF) and X-ray diffraction (XRD) analyses were performed to ensure that the samples were homogeneous enough for an interlaboratory study.

The XRD patterns were recorded using a PANalytical X'Pert PRO MPD theta–theta diffractometer (Netherlands) (CoKα radiation generated at 40 kV and 40 mA), equipped with primary and secondary soller slits, scientific X'Celerator detector, and a sample changer (sample diameter = 16 mm). The samples were investigated from 2 to 90º2θ with a step size of 0.0167º2θ and a measuring time of 10 s per step. For specimen preparation the back-loading technique was used.

The chemical composition (XRF) of powdered samples was determined using a PANalytical Axios and a PW2400 spectrometer (Netherlands). Samples were prepared by mixing with a flux material and melting into glass beads. The beads were analyzed by wavelength dispersive XRF. To determine loss on ignition (LOI), 1000 mg of sample material was heated to 1030ºC for 10 min. The calibrations were validated regularly by analysis of reference materials and 130 certified reference materials (CRM) were used for the correction procedures.

The Cu-trien method was used in every laboratory involved in the assessment; several variations of the method exist, however (Tables 2, 3), compared to the initial publication of Meier and Kahr (1999). In brief, the Cu-trien complex was added to clay; the resulting slurry

Table 3. Homogenization steps of Cu-trien solution and clay used in the different laboratories.

Lab	Before addition of Cu-trien: Technique 1	Time (min)	Technique 2	Time (min)	After addition of Cu-trien: Technique 3	Time (min)
Lab 1	Hand shaking	15	Sonication	10	Rocking platform	30
Lab 2	Vibrating table	120			Vibrating table	30
Lab 3-1					Shaker	120
Lab 3-2					Shaker	120
Lab 4			Sonication	3	30 times end over end, manually	
Lab 5					End-over-end shaking	120

https://doi.org/10.1346/CCMN.2012.0600206 Published online by Cambridge University Press

was homogenized, allowed to react for 55–150 min, and then centrifuged. After centrifugation, the clear supernatant was analyzed for the remaining Cu-trien index cation concentration and for the concentration of the exchangeable cations. These measured concentrations were used to calculate CECs and exchangeable cation values. The CEC was calculated by the difference between the initial and the remaining Cu-trien index cation concentration.

Most laboratories varied the ratios of complex, water, and sample mass (Table 2); two laboratories used 0.01 M, two used 0.015 M, and one used 0.02 M Cu-trien. Only one of the laboratories used the tris pH buffer. For elemental analysis, ICP (laboratories 1, 2, and 5) and AAS (laboratories 3 and 4) were applied. Elemental analysis was used to quantify the exchangeable cations Na^+, K^+, Mg^{2+}, and Ca^{2+}. The Cu-trien index cation concentration was always measured by VIS spectroscopy (578 nm) and labeled CEC (VIS); however, most laboratories also used elemental analysis to quantify the Cu-trien index cation concentration. These values were labeled CEC (ICP/AAS). The CEC (VIS) and CEC (ICP/AAS) were treated separately to check for problems with the determination of the Cu-trien using one or the other of the analytical tools. Both concentrations were used, however, to calculate the CEC only. All of the laboratories also varied homogenization steps to ensure well dispersed suspensions and complete cation exchange (Table 3). One of the participating laboratories applied two relatively similar approaches for CEC determination using 10/20 mL of Cu-trien and 50/40 mL of water (laboratory 3, setup 1/setup 2). Both approaches were within the typical Cu-trien/water ratio of all laboratories and were, therefore, both included in the comparison. No laboratory used sonication during interaction of the exchange solution with the samples. Three of the five laboratories performed an homogenization step of clay with water before they added the complex solution. Two of these three laboratories also treated the suspension with ultrasound (3−10 min), one of them after an initial 15 min period of manual shaking. All laboratories dispersed the slurry of 'clay + water + Cu-trien' and the time taken for this varied from 30 to 120 min in automatic machines, or, as in one case, slurries were turned manually end-over-end. These steps are very similar and, therefore, were not listed in Table 3. Finally, all laboratories centrifuged the slurries.

Variation of sample mass (or Cu-trien addition) is important because, on one hand, precision can be improved. On the other hand, using too much clay (too little Cu-trien) would mean that insufficient Cu(II)-trien cations would be present in solution to saturate all exchange sites (exchange competition) or even not enough to allow theoretically for a 100% saturation. Dohrmann and Kaufhold (2009) discussed this problem as follows: "The exchange competition limit usually ranges from 50 to 75% of the initial complex concentration. If more than a critical amount of index cation is adsorbed then the CEC value is systematically reduced. On the other hand, a minimum of index cation adsorption in the range of 5% or more is necessary. If less is adsorbed, the uncertainty of elemental or complex analysis (ICP or VIS spectroscopy, both ~±1%) increases the scattering."

Based on these considerations, two parameters were calculated for each laboratory. (1) The maximum percentage of Cu-trien adsorbed during the experiment for the sample with the largest CEC (% Cu-trien adsorbed (max.), Table 2). This parameter gives an idea of possible exchange competition problems. If '% Cu-trien adsorbed (max.)' was close to 100% this would represent an experiment in which complete removal of Cu-trien from solution may have occurred. The CEC value calculated from such an experiment would be systematically too small.

Using 200 mg of bentonite (along with 10.0 mL of Cu-trien) resulted in an adsorption of 83% (max.) of the initial Cu-trien concentration (laboratory 3-1). Laboratory 2 used 400 mg of bentonite (with 20 mL of 0.15 M Cu-trien) and the maximum adsorption was ~60%. Approximately the same amount was adsorbed by the combinations used in laboratory 4 (5 mL of 0.02 M Cu-trien, 130−140 mg sample mass) and laboratory 1 (10 mL of 0.015 M Cu-trien, 200 mg sample mass). Laboratory 5 used less sample (120 mg with 10 mL 0.01 M Cu-trien) and recovered 50% of the initial Cu-trien concentration whereas laboratory 3-2 used 20 mL 0.01 M Cu-trien but only 200 mg bentonite, which gave the lowest Cu-trien adsorption of ~42%.

(2) The second parameter gives the maximum possible CEC of a theoretical bentonite sample at 100% removal of the complex during the experiment. Of course 100% would not be a good choice to exclude exchange competition problems; nevertheless, a rough idea is given of the upper CEC level to which the bentonites could be studied.

Laboratory 3-1 used a combination of sample mass (200 mg) and Cu-trien (10 mL 0.01 M) addition which resulted in at most 83% of the initial Cu-trien concentration for the samples studied. If such a combination is used then only bentonites with a CEC of <107 meq/100 g can be studied (ignoring exchange competition). Smaller sample mass or larger Cu-trien index cation concentrations are recommended to ensure that bentonites with larger CECs can also be analyzed. Laboratory 3-2 used 20 mL of Cu-trien (0.01 M) and 200 mg of bentonite allowing for very large CEC values above the theoretical limit for bentonites (smectites) of >200 meq/100 g. Here, only 42% of the Cu-trien index cations were adsorbed in the experiment with the bentonite which had the largest CEC value. Laboratories 1, 2, and 4 were well above the upper limit for smectites (max. possible CEC $\approx$ 150 meq/100 g).

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Laboratory 5 used two different sample masses (80 mg and 120 mg). For the larger sample mass, the maximum CEC would be 177 meq/100 g (again ignoring exchange competition), though such a value (similar to laboratories 1, 2, 4, and 3-2) is larger than the largest CEC possible for smectites.

Variation in sample mass as applied by laboratory 5 allows detection of systematic problems that would occur if Cu-trien adsorption (of a large sample mass experiment) would be affected by exchange competition (closer to 100% Cu-trien adsorption). In this case the result of a 'smaller sample-mass experiment' would theoretically still be within the unaffected range whereas the CEC value of a 'larger sample mass experiment' would already be too small.

Homogeneity of ABM bentonite splits

The homogeneity of ABM bentonite splits was evaluated based on XRF and XRD results. X-ray fluorescence chemical analysis of major oxides (Table 4) and trace elements (data not shown) revealed that the randomly chosen sample splits were very homogenous. The absolute differences for elemental concentrations <1 wt.% were very small. The largest relative differences for concentrations >1 wt.% occurred in (1) MX80 for the parameter Ca (CaO 5% relative), and (2) COX for the parameter K (K_2O 3% relative).

X-ray diffraction analysis of randomly chosen sample splits (Figure 2) also confirmed homogeneity as observed for major oxides and trace elements. The mineralogical composition of the bentonites was dominated by smectite (montmorillonite, $d_{060} \approx 1.50$ Å). The accompanying minerals were (1) MX 80: quartz, feldspar, muscovite/illite, cristobalite, gypsum, and pyrite; (2) Dep.CAN: feldspar, quartz, cristobalite, calcite, gypsum, anatase, and traces of dolomite/ankerite and pyrite; and (3) ASHA: kaolinite, goethite, anatase, and quartz. The mineralogy of the COX was dominated by phyllosilicates (containing also different mixed layer minerals), quartz, and calcite plus minor accessory minerals. In principle, the mineralogical composition of COX, as described by Vieillard *et al.* (2004), was confirmed.

According to XRF and XRD, the randomly chosen sample splits were homogeneous with respect to the requirements of a 'laboratory exchange of CEC measurements.'

RESULTS AND DISCUSSION

CEC and exchangeable cations

The CEC and exchangeable cations results are reported in Tables 5–9 and Figures 3–4. Questionable results and outliers which are discussed in the text are marked in italics. For analysis of precision, 48 values were used throughout; only one parameter had fewer values (n = 40, CEC (ICP/AAS)). After the outliers were detected (Na/Mg/CEC (VIS): 2/6/4 values), they were excluded and not used to calculate precision values. Precision (standard deviation; outlier-free) was averaged for all remaining exchangeable cation and CEC values; CEC values were differentiated as CEC (VIS) (upper part of Table 5) and CEC (ICP/AAS) (lower part of Table 5). The single exchangeable cations (Table 6) were totalled, giving the parameter 'sum of exchangeable cations' which was used for calculation of the difference between the sum of exchangeable cations and the CEC ('sum–CEC') (Table 7). As bentonites have larger values than COX for most parameters, the values of standard deviations were averaged for the bentonites (Figure 3).

CEC (VIS)

Average CEC values for the three bentonites were in the range 82.2–86.5 meq/100 g and precision (±1σ) was reasonable: ±1.5 to ±2.1 meq/100 g (Table 5) with an average value for bentonites as a group of ±1.8 meq/100 g (Figure 3). The smallest (MIN) and the largest (MAX)

Table 4. XRF data (wt.%) of major oxides of random sample splits of the four ABM samples; the results were recalculated with respect to the loss on ignition (LOI) (LOI-free, *i.e.* ignoring values for loss on ignition, including those for adsorbed water). The numbers following the sample names indicate which of the 20 sample splits were chosen randomly.

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	MnO	TiO_2	P_2O_5	(SO_3)	Sum
MX80-06	67.3	21.0	4.1	1.4	2.5	0.6	2.3	0.0	0.2	0.1	0.4	99.8
MX80-11	67.3	21.0	4.1	1.4	2.5	0.6	2.3	0.0	0.2	0.1	0.4	99.8
MX80-18	67.1	21.0	4.1	1.4	2.5	0.6	2.3	0.0	0.2	0.1	0.4	99.7
COX-09	49.2	15.1	5.8	20.8	2.9	3.2	0.2	0.1	0.8	0.1	1.3	99.6
COX-14	49.2	15.1	5.9	20.8	2.9	3.2	0.2	0.1	0.8	0.1	1.3	99.6
COX-19	49.3	15.1	5.8	20.8	2.9	3.1	0.3	0.1	0.8	0.1	1.2	99.6
Dep.CAN-05	60.8	19.6	5.3	5.7	3.6	1.0	0.9	0.1	0.8	0.2	1.6	99.7
Dep.CAN-12	60.8	19.7	5.3	5.7	3.6	1.0	0.9	0.1	0.8	0.2	1.6	99.7
Dep.CAN-17	60.7	19.7	5.3	5.7	3.6	1.0	0.9	0.1	0.8	0.2	1.6	99.6
ASHA-05	54.2	24.3	14.6	0.8	2.2	0.1	2.2	0.1	1.3	0.1	0.1	99.8
ASHA-13	54.1	24.2	14.6	0.8	2.2	0.1	2.2	0.1	1.3	0.1	0.1	99.7
ASHA-18	54.1	24.4	14.6	0.8	2.2	0.1	2.2	0.1	1.3	0.1	0.1	99.8

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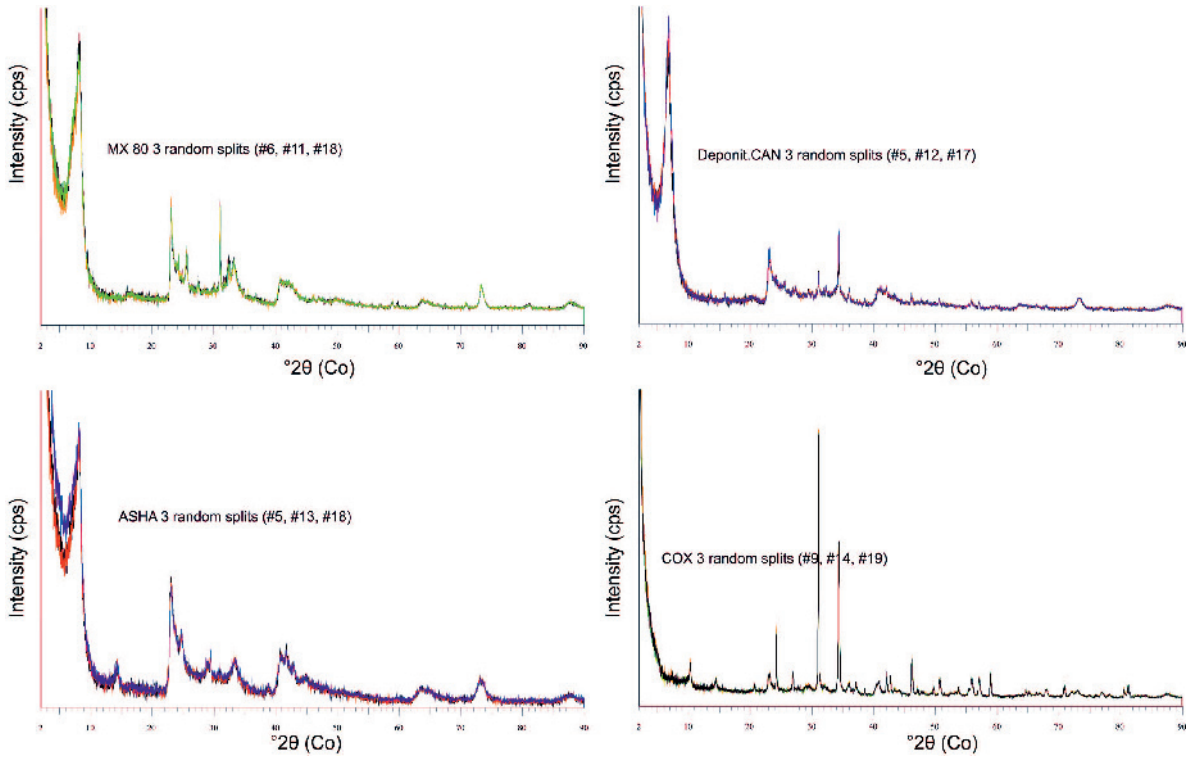


Figure 2. XRD patterns of three random splits of MX 80 (upper left), Dep.CAN (upper right), ASHA (lower left), and COX (lower right). The patterns were superimposed to identify intensity differences.

CEC values varied within the range 5–8 meq/100 g which is ~5–10% of the CEC. A set of parameters was calculated to evaluate how large relative differences of MIN and MAX values would affect the CEC. For the three bentonites, at most +3.8% (−4.6%) overestimated (underestimated) values with respect to an assumed correct average value would be obtained. This is relatively small, indicating good precision. The CEC (VIS) values were in good agreement with those reported by Muurinen (2010).

Table 5. CEC (VIS) and CEC (ICP/AAS) values (meq/100 g) from the different laboratories.

Cu-trien	Cu-trien mL	Water mL	Buffer mL	– MX80 – dupl. 1	dupl. 2	– COX – dupl. 1	dupl. 2	– Dep.CAN – dupl. 1	dupl. 2	– ASHA – dupl. 1	dupl. 2
CEC (VIS)											
Lab 1	10	25	–	85.9	85.6	11.6	11.5	83.6	83.8	86.5	86.9
Lab 2	20	50	–	84.2	83.2	11.1	10.7	81.1	80.2	86.2	86.6
Lab 3-1	10	50	–	83.7	81.0	*4.3*	*4.3*	79.3	80.0	*82.5*	83.2
Lab 3-2	20	40	–	82.8	82.2	*4.6*	*5.2*	80.4	81.8	86.0	85.1
Lab 4	5	44	1	86.0	84.8	11.2	11.2	84.3	83.7	89.5	89.8
Lab 5	10	50	–	84.5	83.4	9.6	10.1	84.8	83.1	88.3	86.9
Muurinen (2010) (reference samples, page 32)				87				83		89	
CEC (ICP/AAS)											
Lab 1	10	25	–	92.4	90.9	10.3	14.4	88.8	87.3	90.8	90.2
Lab 2	20	50	–	85.5	82.7	13.2	13.0	79.9	80.7	84.6	86.3
Lab 3-1	10	50	–	80.6	79.4	11.3	9.6	76.8	78.1	80.2	79.9
Lab 3-2	20	40	–	83.7	83.1	16.4	16.1	81.3	82.4	85.7	86.7
Lab 4	5	44	1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Lab 5	10	50	–	85.0	84.5	7.8	9.4	86.3	84.3	90.5	88.3

n.a. – not applicable
Questionable results and outliers shown in italics.

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Table 6. Exchangeable Na^+, K^+, Mg^{2+}, and Ca^{2+} (ICP/AAS) values (meq/100 g) from the different laboratories.

Cu-trien	– MX80 –		– COX –		– Dep.CAN –		– ASHA –	
	dupl. 1	dupl. 2	dupl. 1	dupl. 2	dupl. 1	dupl. 2	dupl. 1	dupl. 2
Exchangeable Na^+								
Lab 1	56.3	56.4	2.6	2.6	22.1	22.3	62.5	61.4
Lab 2	60.6	62.8	3.6	3.2	25.0	24.6	67.6	65.8
Lab 3-1	58.0	56.6	2.5	2.5	22.3	22.2	60.8	61.2
Lab 3-2	57.0	57.2	2.4	2.3	22.3	22.2	61.9	61.8
Lab 4	*40.8*	*37.8*	2.1	2.1	20.2	18.8	*53.7*	67.4
Lab 5	60.1	59.3	2.5	2.6	23.0	23.1	63.1	63.3
Exchangeable K^+								
Lab 1	1.5	1.5	1.7	1.9	1.4	1.1	0.6	<0.2
Lab 2	2.0	2.1	2.0	2.0	2.0	1.9	0.7	0.6
Lab 3-1	1.5	1.5	1.7	1.7	1.6	1.6	0.4	0.4
Lab 3-2	1.5	1.5	1.6	1.6	1.6	1.6	0.5	0.5
Lab 4	2.8	1.2	1.3	1.5	2.2	1.3	0.6	0.1
Lab 5	1.9	2.3	1.9	2.0	1.4	1.9	0.4	1.0
Exchangeable Mg^{2+}								
Lab 1	7.5	7.5	3.6	3.5	25.1	25.4	14.9	14.7
Lab 2	7.3	7.4	3.7	3.7	25.1	24.3	13.6	13.6
Lab 3-1	6.6	6.4	3.3	3.2	23.6	23.3	13.2	13.3
Lab 3-2	6.6	6.6	3.3	3.2	24.6	24.2	14.0	14.2
Lab 4	*10.2*	*10.1*	4.1	4.1	*31.7*	*31.7*	*18.4*	*18.6*
Lab 5	6.3	6.3	2.9	2.8	23.7	23.6	13.2	13.0
Exchangeable Ca^{2+}								
Lab 1	*29.8*	*30.5*	*24.5*	*24.3*	*54.2*	*54.3*	20.9	20.7
Lab 2	*29.7*	*30.0*	*16.1*	*16.2*	*52.3*	*50.8*	20.4	20.5
Lab 3-1	*29.9*	*30.8*	*21.0*	*19.9*	*54.9*	*54.3*	21.0	20.9
Lab 3-2	*29.3*	*28.9*	*23.0*	*23.7*	*54.3*	*54.9*	20.5	21.0
Lab 4	*31.8*	*31.2*	*12.4*	*12.8*	*56.1*	*56.4*	20.7	20.8
Lab 5	*28.2*	*28.1*	*15.6*	*12.1*	*57.8*	*50.3*	20.0	19.8

No systematic differences were detected upon variation of parameters such as amounts of exchange solution, water, and sample mass or any of the homogenization steps used in the different laboratories (as discussed above) which were used to disperse the slurries of clay material and the exchange solution added.

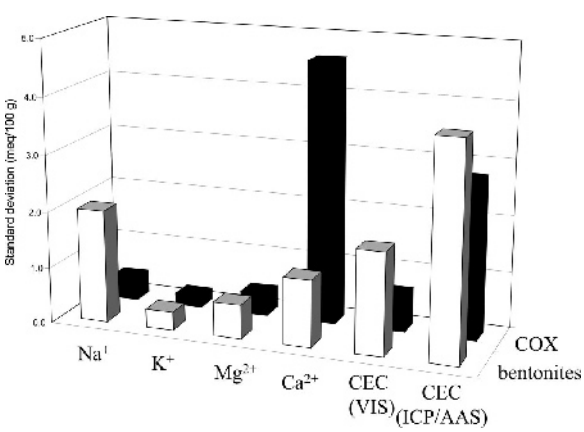


Figure 3. Precision (standard deviation) of exchangeable cations and CEC values.

One set of CECs was significantly smaller than the rest of the CEC values (laboratory 3-1, ASHA); these values were not classified as outliers, however, because they overlapped with the average CEC within analytical error.

Two data sets were clearly detected as outliers: COX CECs were on average 8.8±3.0 meq/100 g but with MIN/MAX values which spread over a large CEC range for this low-CEC material. Accordingly, average values were recalculated ignoring the outliers of laboratories 3-1 and 3-2, giving averages of 10.9±0.7 meq/100 g. As expected, precision was poorer for low-CEC materials, an absolute difference of 1 meq/100g already represents a relative difference of nearly 10%. Treatment of outliers (Table 6) was the same as described for all other parameters in the following sections.

CEC (ICP/AAS)

The CEC (ICP/AAS) results of bentonites varied within a similar absolute range of 82.6−86.3 meq/100 g (VIS: 82.2−86.5 meq/100 g) but had a poorer precision (±1s) of ±3.8 meq/100 g (Figure 3, Table 5). The smallest (MIN) and the largest (MAX) CEC values varied per sample within a range of 11 to 14 meq/100 g which was ~8−16% of the CEC. This larger scattering was also

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Table 7. Sum of exchangeable cations minus CEC, calculated for CEC after chemical analysis 'CEC (ICP/AAS)' and after VIS spectroscopy 'CEC (VIS)'. All values meq/100 g.

Cu-trien	– MX80 –		– COX –		– Dep.CAN –		– ASHA –	
	dupl. 1	dupl. 2	dupl. 1	dupl. 2	dupl. 1	dupl. 2	dupl. 1	dupl. 2
Sum−CEC (VIS)								
Lab 1	*9.2*	10.3	20.8	20.8	19.2	19.3	12.4	9.9
Lab 2	15.4	19.1	14.3	14.4	23.3	21.4	16.1	13.9
Lab 3-1	12.4	14.4	24.1	23.1	23.1	21.4	12.9	12.7
Lab 3-2	11.5	12.0	25.7	25.6	22.5	21.1	10.8	12.4
Lab 4 (* result contains outliers)	*	*	8.7	9.4	*	*	*	*
Lab 5	12.1	12.5	13.4	9.3	21.0	15.8	8.3	10.1
Average	12.9	17.5	20.8	12.0				
Std. dev.	2.7	6.3	2.1	2.1				
Max	19.1	25.7	23.3	16.1				
Min	9.2	8.7	15.8	8.3				
Sum−CEC (ICP/AAS)								
Lab 1	2.7	5.0	22.1	17.9	14.0	15.8	8.1	6.6
Lab 2	14.1	19.6	12.2	12.1	24.5	20.9	17.7	14.2
Lab 3-1	15.5	16.0	17.1	17.7	25.6	23.4	15.2	16.0
Lab 3-2	10.6	11.1	14.0	14.7	21.5	20.5	11.1	10.7
Lab 4	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Lab 5	11.5	11.3	15.1	10.0	19.5	14.6	6.2	8.6
Average	11.7	15.3	20.0	11.4				
Std.dev.	4.8	3.3	3.9	3.9				
Max	19.6	22.1	25.6	17.7				
Min	2.7	10.0	14.0	6.2				

n.d. – not determined

visible in the percent values calculated from MIN and MAX values ranging from −7.4% to +9.0%. One set of CEC results (laboratory 3-1, ASHA) was significantly smaller than the rest of the results; these values were also not classified as outliers, however, because they overlapped with the average CEC within analytical error.

For the COX material, the clay differences were, again, much larger than for bentonites and the scattering was worse for CEC (ICP/AAS) than for CEC (VIS) (Figure 3); the resulting MIN/MAX under/overestimation was similar (~±35%). No clear outlier could be identified because the variation was very large.

Exchangeable Na^+, K^+, Mg^{2+}, and Ca^{2+}

Exchangeable Na^+. Two of the four clays were dominated by exchangeable Na^+ (Table 6). Three single results could be identified as outliers, all from Laboratory 4. Outlier-free results varied over a very large range from 2.6 to 63 meq/100 g. Relatively little scattering was noted for COX (±0.4 meq/100 g) and the bentonites (±1.6−2.3 meq/100 g, on average 2.0 meq/100 g, Figure 3). Exchangeable Na^+ (outlier-free results) reached values of 27% (Dep.CAN), 70% (MX80), and up to 73% (ASHA) of the total CEC (bentonites), and 24% of the total CEC (COX) (Figure 4).

Exchangeable K^+. Exchangeable K^+ values (Table 6) were small. They varied from 0.1 to 2.8 meq/100 g for all samples, from <1% to 2% of the total CEC for bentonites, and 16% of the total CEC for COX. Absolute scattering was relatively small (Figure 4) but the standard deviation in relation to the measured concentrations was large, as expected for such small concentrations (closer to detection limit of chemical analysis).

Table 8. Calculated exchangeable cation population (%) with respect to CEC (VIS).

Exchangeable cation population	MX80	COX	Dep.CAN	ASHA
Na^+/CEC (VIS) (%)	70	24	27	73
K^+/CEC (VIS) (%)	2	16	2	1
Mg^{2+}/CEC (VIS) (%)	8	32	30	16
Ca^{2+}/CEC (VIS) (%)	36	170	66	24
Control sum (%)	116	242	125	114

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Table 9. Exchangeable cation and CEC values including standard deviations (St. dev.) as determined by the different laboratories (without outliers). All values meq/100 g.

	MX80	COX	Dep. CAN	ASHA
Na^+	58.4	2.6	22.3	63.3
St. dev.	2.1	0.4	1.6	2.3
K^+	1.8	1.7	1.6	0.5
St. dev.	0.4	0.2	0.3	0.2
Mg^{2+}	6.9	3.4	24.3	13.8
St. dev.	0.5	0.4	0.7	0.6
Ca^{2+}	29.9	18.5	54.2	20.6
St. dev.	1.1	4.6	2.1	0.4
CEC (VIS)	83.9	10.9	82.2	86.5
St. dev.	1.5	0.7	1.9	2.1
CEC (ICP/AAS)	84.8	12.1	82.6	86.3
St. dev.	3.9	2.8	3.8	3.7

Exchangeable Mg^{2+}. Six single-exchangeable Mg^{2+} results (Table 6) could be identified as outliers, all from Laboratory 4, which used AAS instead of ICP analysis; the other AAS laboratory found results which were well within the range of all ICP laboratories. The conclusion is that the deviations may have been caused by individual errors. Exchangeable Mg^{2+} (outlier-free results) reached values of 8%/16%/30% (MX80/Dep.CAN/ASHA) and 32% (COX) of the total CEC; Mg^{2+} varied from 3.4 to 24.3 meq/100 g with scattering of ±0.4 to ±0.7 meq/100 g (Figure 4).

Exchangeable Ca^{2+}. The MX80, COX, and Dep.CAN contained soluble Ca minerals (calcite, gypsum), and all resulting Ca^{2+} values (Table 6) were erroneous and marked in italics. Dohrmann and Kaufhold (2010) described such values as $Ca^{2+}_{exc\text{-}inflated}$. The extent of Ca^{2+} overestimation was affected by the intensity and duration of experimental treatments, the solid/liquid ratio used, and the characteristics of the Ca minerals (type and grain size). No outliers could be identified for these three samples. Regardless of the poor starting conditions, the results returned were similar for the two bentonites MX80 and Dep.CAN: 29.9±1.1 meq/100 g and 54.2±2.1 meq/100 g. Using two different sample masses (while keeping all other parameters constant, Laboratory 5) allowed detection of partly soluble calcite in Dep.CAN: 50.3 meq/100 g (large sample mass) and 57.8 meq/100 g (small sample mass). Such dependency on sample mass is characteristic of calcite; both values were erroneous, therefore, but the larger value was even more erroneous than the smaller one (Dohrmann, 2006a). The same holds true for the $Ca^{2+}_{exc\text{-}inflated}$ values of COX clay. ASHA, on the other hand, contained no detectable concentrations of calcite or gypsum; scattering of this sample was very small (exchangeable Ca^{2+}: 20.6±0.4 meq/100 g) and exchangeable Ca^{2+} represented 24% of total CEC. For all other samples '% Ca/CEC' was too large (up to 170%, COX, Table 8, Figure 3) and the exchangeable cation population exceeded the CEC. The worst precision for all measured values in the whole ring test was 'exchangeable' Ca^{2+} of COX (Figure 4). Data scattering was approximately four times larger than the average precision of the three bentonites.

Sum of exchangeable cations in relation to the CEC

Ideally, the sum of exchangeable cations should be as large as the CEC. This balance can be used for quality

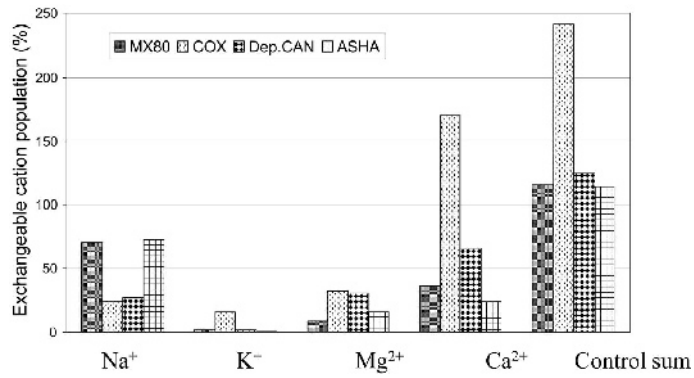


Figure 4. Calculated exchangeable cation population (%) with respect to CEC (VIS).

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control of the whole data set. If the CEC value is identical to the sum of exchangeable cations, systematic errors are unlikely. A simple parameter can be calculated from the measured data set: the difference between the sum of exchangeable cations minus the CEC ('sum−CEC'). This 'sum−CEC' quality parameter is often affected by the presence of (partially) soluble Ca minerals, however, as discussed for exchangeable Ca^{2+}. The difference 'sum−CEC' is then positive. The 'sum−CEC' may also be affected by electrolytes present in the pore water, *e.g.* if high Cl^- concentrations were detected which are indicative of such pore waters. Of course anion concentrations found in clay rocks, such as the COX clay used in the ABM project, may not represent *in situ* pore-water conditions because pyrite could have been oxidized during processing. This may have increased sulfate concentration; in the ABM project, however, these anion concentrations are present and must be considered. Anion concentrations (Cl^-, SO_4^{2-}) in reference bentonites MX80, ASHA, and Dep.CAN were reported by Muurinen (2010) and were similar to those of Svensson (2010) who also listed results for COX clay; no correction for anion composition was performed in this study because the aim was to compare the precision of CEC and exchangeable cation data. The 'sum−CEC' was calculated for CEC after chemical analysis 'CEC (ICP/AAS)' as well as for CEC after VIS spectroscopy 'CEC (VIS)'.

The parameters 'sum−CEC (VIS)' and 'sum−CEC (ICP/AAS)' of MX80, Dep.CAN, and COX (Table 7) were always positive because these clays contained soluble Ca minerals. Only the ASHA bentonite was free of calcite or gypsum, though soluble salts were present which may have caused excess exchangeable cations (probably Na^+ and/or Mg^{2+} if affected by chlorine-rich water). This led to positive 'sum−CEC (VIS)' values for ASHA ranging from 8.3 to 16.1 meq/100 g (Table 7). As expected, the results for the parameter 'sum− CEC(ICP/AAS)' for ASHA were similar and ranged from 6.2 to 17.7 meq/100 g (Table 7). The results from Laboratory 4 cannot be used here because exchangeable Na^+ and Mg^{2+} were probably incorrect, and the MX80 results were classified as 'occasionally close to zero.' For the other samples 'sum−CEC (VIS)' and 'sum−CEC (ICP/AAS)' values were also relatively far from zero: 12.9/11.7±2.7/4.8 meq/100 g (MX80), 17.5/15.3±6.3/3.3 meq/100 g (COX), and 20.8/20.0±2.1/3.9 meq/100 g (Dep.CAN). Scattering was relatively large and similar for both Cu-trien index cation quantification techniques (VIS and ICP/AAS). This was expected because scattering represented the sum of five independent analyses (exchangeable cations Na^+, K^+, Mg^{2+}, Ca^{2+}, and CEC) and, in the case of Ca^{2+}, the values were also affected by systematic errors.

Exchangeable cation population

Average values of exchangeable cations were used to calculate the exchangeable cation population in % with respect to CEC (VIS) (Table 8, Figure 4). Exchangeable cations exceeded the CEC as described previously.

Improvements after outlier detection

Laboratory 4 identified errors in their routine analysis and repeated CEC and exchangeable cation analysis. Repeated analyses were carried out exactly as described in Tables 2 and 3 except for the addition of solutions (45 mL of water plus 5 mL of Cu-trien and no buffer) with subsequent end-over-end dispersion (30 cycles) followed by 12 h waiting and centrifugation.

New results (average values ± scattering as reported in Table 9) were then well within the range of all other laboratories (Tables 5, 6). Only minor differences (compared to average values ± scattering, Table 9) were detected for exchangeable Na^+ (ASHA, −10%) and Ca^{2+} of the two calcareous/gypsiferous clays (MX80, −9%; COX, −47%), which means that these results were more plausible than the reported averages because dissolution of Ca phases was minimized (see also Dohrmann *et al.*, 2012). The present example illustrates that quality control, such as by the analysis of a CEC standard sample parallel to the samples studied, is recommended.

SUMMARY AND CONCLUSIONS

The precision of the Cu-trien CEC and exchangeable cation data was very good (Table 9). In future projects measured differences in CEC and exchangeable cation values can be evaluated as actual differences if these limits are overstepped.

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 in interpreting measured CEC differences, and analytical characterization of any structural changes might be needed.

Significant differences (large scattering) occurred for exchangeable Ca^{2+}, which was expected due to the presence of soluble Ca minerals (Tables 6, 8). Some minor problems were identified with outliers and these problems were improved by the participating laboratories.

The precision of the Cu-trien method, which uses visible spectroscopy, was very good with a standard deviation of ±0.7 to ±2.1 meq/100 g for CECs that ranged from 11 to 87 meq/100 g. For the same CEC range, analysis of Cu-trien index cations that used ICP and AAS were less precise with a standard deviation of ±2.8 to ±3.9 meq/100 g. Compared with the CEC and exchangeable cation results of the iSE program (Table 1), absolute values were much larger for the bentonites and the COX clay studied. For the two parameters exchangeable Ca^{2+} and CEC the range was similar to the iSE ring test. For such values only MAD data were available in the iSE statistics, though median

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values of these parameters were well within the range of scattering reported in the present study.

A further study will discuss the accuracy of CEC and exchangeable cation values (Dohrmann *et al.*, 2012) and will also compare alternative CEC methods where care was taken to prevent dissolution of soluble minerals such as calcite and gypsum.

ACKNOWLEDGMENTS

The authors are grateful to Natascha Schleuning, Wolfgang Glatte, and Frank Korte for their great analytical work. Comments and suggestions by an anonymous reviewer, by Javier Cuadros, and, in particular, by Associate Editor, William F. Jaynes, were valuable and helped to improve the manuscript.

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(*Received 27 June 2011; revised 6 April 2012; Ms. 584; A.E. W.F. Jaynes*)

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