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Cation exchange capacity of bentonite in a saline environment

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ABSTRACT

Cation exchange capacity (CEC) is one of the basic characteristics of clays and clay minerals. Accessory minerals, such as carbonates, can influence the measured value of the CEC because of their dissolution.

In the present study, the CEC of Ca-/Mg-bentonite Calcigel® was studied by the Cu-trien method in the presence of NaCl at various concentrations (0–20 wt%). These conditions simulate the states of bentonite in geotechnical barriers during their hydration with saline solutions, e.g., in underground radioactive waste deposits.

First, changes in the pH value, which were induced by Cu-trien and NaCl, were investigated, and the CECs of Calcigel/NaCl mixtures were measured and analyzed. Second, the influence of NaCl on the UV/Vis spectra of Cu-trien was tested. Third, the impacts of Cu-trien (3.33×10^{-3} mol l^{-1}) and NaCl on the solubilities of carbonate and dolomite were analyzed.

The change in carbonate solubility, based on variations in the NaCl concentrations as well as the Cu-trien additions, has been identified as the main factor influencing the determination of the CEC of Ca-/Mg-bentonite Calcigel®. With this knowledge of the solubilities of carbonates under controlled conditions and with the knowledge of bentonite mineral compositions, it is possible to correct the determined values of the cation exchange capacity.

1. Introduction

Due to their unique properties, clays and clay minerals are widely used as geotechnical barriers in the environmental engineering field, among others, at radioactive waste disposal sites. The geotechnical barrier consists of three components: buffer, backfill, and hydraulic sealing system (Breidung et al., 2000). Within the sealing systems, clays come into contact with rock-pore fluids, i.e., saline solutions (Emmerich et al., 2009; Königer et al., 2008). Therefore, used clays can contain approximately 0.4–9 wt% of the electrolytes (Emmerich et al., 2009). The concentration of the electrolytes can affect the properties and reactivities of clays.

The stabilities of 36 different bentonites in concentrated NaCl solutions (6 mol l^{-1}) were studied by Kaufhold and Dohrmann (2009). At moderate pH and up to at least 60 °C, these clays were stable. Only in the cases of high temperatures and high concentrations of K^+ was the process of illitization on the montmorillonite likely to occur (Honty et al., 2004). However, measurements of the cation exchange capacities (CECs) of clay minerals can be affected by the surrounding conditions.

CEC is one of the basic characteristics of clays and clay minerals. It determines the physical and chemical properties of clays and clay minerals, e.g., cation exchange and transport, hydration and swelling, in geotechnical barriers and many other applications.

Determination of the CECs of clays can be challenging due to the presence of soluble accessory minerals, e.g., carbonates, and/or due to the enrichment of soluble salts from their application. The solubility of calcite and dolomite is usually low but can increase in solutions with high electrolytic concentrations (Coto et al., 2012; Harvie et al., 1984; Millero et al., 1984; Wolf et al., 1989). The dissolution of calcite and dolomite results in concentrations of Ca^{2+} and Mg^{2+} in the supernatant that are not equivalent to those of the clay mineral charge (Dohrmann and Kaufhold, 2009). The presence of additional cations in the dispersion can change the balance of the exchange of exchangeable cations with index cations. The kinetics of the ion exchange process and the dissolution process can also be affected by the particle size, which may be affected by the presence of inorganic salts (Cho and Komarneni, 2009; Penner and Lagaly, 2000; Tournassat et al., 2011).

There are several studies that have investigated the CEC determination of calcareous clays using different approaches. One of the approaches was to find appropriate index cation and to prevent the solubility of the carbonates by solvent. The idea was to use ethanolic mixtures of LiCl–CsCl (Neal, 1977). Hissink and Tucker suggested

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reducing soluble calcite through a double leaching procedure (Hissink, 1923; Tucker, 1954). Another approach was to use solutions of metal organic cations, such as silver–thiourea (AgTU) (Dohrmann, 2006), cobalt(III) hexamine (CoHex) and copper triethylenetetramine (Cu-trien) (Dohrmann and Kaufhold, 2009), which were presaturated with calcite, which may avoid additional dissolution of calcite from the bentonite samples. These methods provide satisfactory results at moderate pH and when no other soluble minerals are present. However, these methods are inappropriate for bentonites without calcite and for clays with different soluble minerals, e.g., dolomite, gypsum or even NaCl.

The copper triethylenetetramine (Cu-trien) method is based on a one-step exchange process where all exchangeable cations in the interlayers of smectites and at the edges of clay minerals are replaced by the Cu-trien complex ($[Cu(trien)]^{2+}$) over the pH range of 5–10 (Meier and Kahr, 1999). This method has been explored and improved by many authors (Ammann et al., 2005; Bergaya and Vayer, 1997; Czímerová et al., 2006; Delavernhe et al., 2018; Dohrmann and Kaufhold, 2009; Stanjek and Künkel, 2016). The main advantages of this method are its speed, simplicity and the high affinity of the Cu-trien complex for cation exchange with clay minerals (Ammann et al., 2005; Bergaya and Vayer, 1997; Fletcher and Sposito, 1989). Also important is the stability of the spectral behavior of Cu-trien at moderate pH (5.2–10.7) and temperatures (Ammann et al., 2005; Delavernhe et al., 2018; Stanjek and Künkel, 2016). However, no information is available about the spectral properties of the Cu-trien complex in the presence of a high concentration of electrolytes.

The aim of this study was to understand the influences of various NaCl concentrations on the CEC determination of calcareous bentonite by the Cu-trien method and find a means of correction for CEC determination with respect to this influence.

2. Experimental procedure

2.1. Materials

A blended Ca-/Mg-bentonite Calcigel® that was provided by Clariant (Bavaria, Germany) was used as supplied. This material has been extensively characterized as a potential reference buffer/backfill material in the context of geotechnical barriers and has been reported as either Calcigel or Montigel (Emmerich et al., 2009; Königer et al., 2008; Madsen, 1998; Schanz et al., 2018). Calcigel® is a Ca-/Mg-bentonite that contains not only calcite but also higher amounts of dolomite. In lab experiments on the hydraulic properties of this bentonite for application in geotechnical barriers, it has been exposed to artificial pore fluids with various NaCl concentrations. However, these experiments were dismantled and CEC should be determined in order to monitor and understand the exchange and transport processes of cations.

The mineralogical composition was determined by coupling the quantitative analysis performed by Rietveld analysis using AUTOQUAN software (V 2.8.0; GE Inspection Technologies GmbH, Ahrensburg, Germany) of the X-ray diffraction (XRD) (Bruker AXS GmbH, Karlsruhe, Germany) patterns with the chemical analysis of the solid done by X-ray fluorescence (XRF) analyses. Calcigel® contained mainly Ca-/Mg-montmorillonite (65%) with approximately 6–9% carbonates (Table 1).

Synthetic calcium carbonate ($CaCO_3$) (≥99%, Merck KgaA, Darmstadt, Germany) was used as received.

A natural dolomite (unknown origin) was gently ground in an agate mortar (Pulverisette, FRITSCH GmbH, Idar-Oberstein, Germany), sieved to a size of < 355 µm, and a representative sample was prepared by the quartation process. The composition of the dolomite, $Ca_{1.02}Mg_{0.98}(CO_3)_2$ with > 99% purity, was determined by a combination of leaching in HCl (36%) and the subsequent analysis of the solution by ICP-OES (Optima 8300 DV, Perkin Elmer Inc., Waltham, MA, USA) with XRD analysis. From the ICP-OES measurements, a trace amount of Fe (< 1% of total cations) was determined.

Table 1
Mineral phase contents of Calcigel®.

Mineral phase	[%]
Montmorillonite	65
Mica (dioctahedral)/Illite	12.5
Quartz	7
Kaolinite	3
Chlorite	2
Orthoclase	2
Plagioclase (Albite)	1
Calcite	2–3
Dolomite	4–6

For each material (Calcigel®, calcite and dolomite), eight stock samples were prepared by mixing with NaCl (≥99%, Merck KgaA, Darmstadt, Germany) in different ratios. The final sample mass was 1 g, and the samples contained 0, 1, 2.5, 5, 7.5, 10, 15, or 20 wt% NaCl. Samples were homogenized in an agate mortar, and the resulting mixtures were stored in polyethylene bottles.

2.2. Methods

Cation exchange capacity (CEC) was measured by the Cu-trien method according to Meier and Kahr (1999) with changes according to Steudel et al. (2009). Approximately 50 mg of sample was weighed into a 50 ml centrifugation tube. Then, 10 ml of Millipore water and 5 ml of a copper-triethylenetetramine (Cu-trien) solution, at a concentration of 0.01 mol l^{-1}, were added. The dispersions were shaken for 3 h and then centrifuged at 4500 rpm for 10 min (Multifuge 3_{S-R}, Heraeus Holding GmbH, Hanau, Germany). Subsequently, the absorbances of the supernatants at a wavelength (λ) of 580 nm were determined by a UV-Vis spectrophotometer (Genesys 10 UV, Thermo Electron Corporation, Waltham, MA, USA) using polystyrene microcuvettes (Lab logistics Groups GmbH, Meckenheim, Germany) with a path length of 1 cm.

The concentrations of Cu-trien in the supernatants were determined from a calibration curve. The values of CEC in cmol(+) kg^{-1} were calculated by equation (1).

$$CEC = \frac{\nu_{Cu-trien} * [c_{Cu-trien} * V_{Cu-trien} - c_{Cu-trien,\ supernatant} * (V_{Cu-trien} + V_{H_2O})]}{m_{anhydrous\ sample}} \quad (1)$$

where $\nu_{Cu\text{-}trien}$ was the valence of the Cu-trien complex (equal to 2 for measurements at a pH between 5.2 and 10.7), $c_{,Cu\text{-}trien}$ was the concentration of initial Cu-trien complex in [mol l^{-1}], $V_{,Cu\text{-}trien}$ was the volume of the initial Cu-trien solution in [ml], $c_{Cu\text{-}trien,supernatant}$ was the concentration of the Cu-trien complex in the supernatant in [mol l^{-1}], V_{H2O} was the volume of deionized water in [ml], and $m_{anhydrous\ sample}$ was the mass of the anhydrous sample in [g]. The CEC values are given with respect to total anhydrous solid, which was based on the water content that was determined after heating to 200 °C. Therefore, m of anhydrous samples was calculated by equation (2).

$$m_{anhydrous\ sample} = m_w * (1 - w) \quad (2)$$

where m_w is weight of used sample [g] and w is water content related to the initial (wet) mass of the sample, that was determined after heating to 200 °C for 24 h.

pH was measured using a FiveEasy FE20 pH meter equipped with an Inlab® Expert Pt1000 electrode (Mettler Toledo, Greifensee, Switzerland).

To determine the impact of electrolytes on the spectral properties of Cu-trien, mixtures of Cu-trien ($c = 3.33 \times 10^{-3}$ mol l^{-1}) with NaCl concentrations of 0.0015, 0.01, 0.15, 2.50, and 5.00 mol l^{-1} and $MgCl_2$ and $CaCl_2$ in concentrations of 0.15 and 2.50 mol l^{-1}, respectively, were investigated by absorption spectroscopy using a CARY 5000 UV-Vis-NIR spectrophotometer (Agilent Technologies, Santa Clara, CA,

USA) using 1 cm quartz cuvettes (Hellma Analytics, Mullheim, Germany).

Pure calcite and dolomite were used as "blank correction samples". This method was outlined by Dohrmann and Kaufhold (2009) as a suitable subsidiary to CEC measurements of the calcareous clays by using calcite saturated Cu-trien solutions.

The solubilities of pure calcite and dolomite, as well as those of the carbonates in Calcigel®, were studied in Millipore water, NaCl solutions and Cu-trien solution (3.33×10^{-3} mol l^{-1}) under ambient conditions (temperature ≈ 23 °C and CO_2 partial pressure ≈ 4×10^{-4} atm). Measurements were performed in a manner comparable to CEC analysis conditions. Approximately 50 mg of sample was mixed with either 15 ml of deionized water or 15 ml of a Cu-trien (3.33×10^{-3} mol l^{-1}) solution and shaken for 24 h (different from CEC measurements). After, all of the samples were centrifuged at 4500 rpm for 10 min and filtered through a 0.45 µm filter (Syringe filter, cellulose acetate, d = 25 mm, LLG-Labware GmbH, Meckenheim, Germany).

The cation concentrations in the supernatants were subsequently analyzed by ICP-OES. When assessing the solubility of minerals, the concentrations of cations (Ca^{2+} and/or Mg^{2+}) in the supernatants were taken to be the solubility rates (except for in Calcigel®). The pH of the supernatant solutions was measured as well.

Each sample and parameter was measured in duplicate.

3. Results and discussion

3.1. CEC and exchangeable cations

The interlayer cations in the montmorillonite that was found in Calcigel® consist mainly of Ca^{2+} and Mg^{2+} with some Na^+ and K^+ (Table 2).

As Calcigel® was mixed with increasing amounts of NaCl, the relative Calcigel® content decreased, which was expected to cause the overall CEC to decrease as well (Fig. 1).

This trend was confirmed by measuring the CECs of Calcigel® with various amounts of NaCl. However, slightly increased CEC values, compared to those of the theoretical values, over the whole set of samples were observed. The CEC value of pure Calcigel® was determined to be ≈ 63 cmol(+) kg^{-1}. The addition of 1 wt% NaCl caused an increase in the CEC of ≈1.5 cmol(+) kg^{-1} instead of the predicted decrease of ≈0.8 cmol(+) kg^{-1} (Fig. 1, arrow 1). Almost the same CEC value is retained by the sample with 2.5 wt% NaCl (Fig. 1, arrow 2) as was obtained for the 1 wt% sample. Then, a decrease in the CEC values, which follows the theoretical decline, is observed.

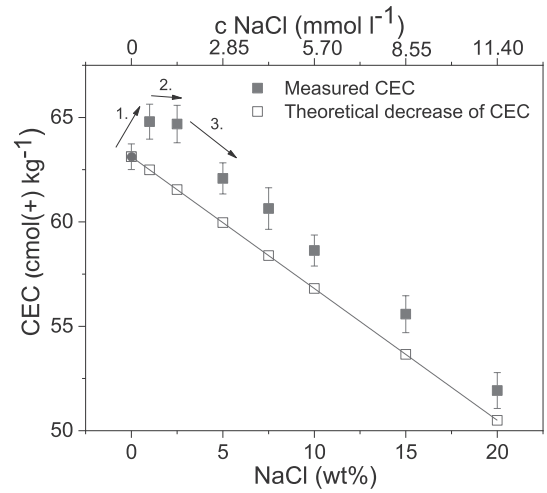

Fig. 1. CEC of Calcigel® as measured by the Cu-trien method. NaCl (wt%) is the solid content of NaCl in the Calcigel®/NaCl mixture. The theoretical decrease in CEC represents a decrease in the CEC based on the diluted weight of bentonite.

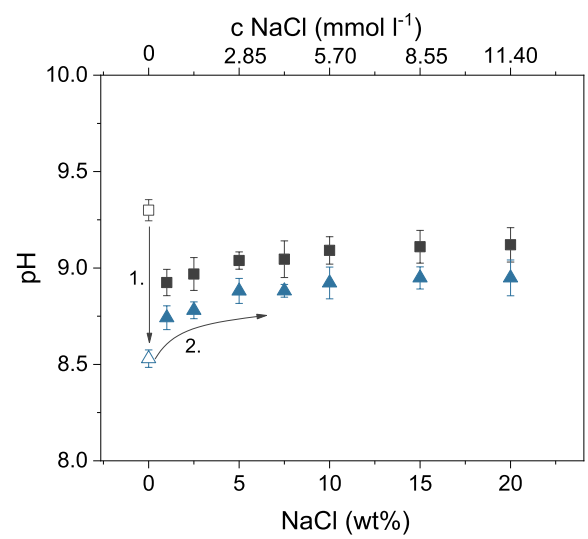

Fig. 2. The pH of Calcigel® dispersions. Squares mark the pH of mixtures of Calcigel® with NaCl in water, and triangles mark mixtures of Calcigel® with NaCl in a 3.33×10^{-3} mol l^{-1} Cu-trien solution. Empty marks indicate the pH of samples without the addition of NaCl.

3.2. Influence of pH

The pH of a pure Calcigel® (Fig. 2) dispersion (in H_2O) was determined to be ≈ 9.3. A small addition of NaCl (1 wt%) decreased the pH to ≈ 8.9. With increasing NaCl concentration, the pH value increased slightly to ≈9.1 for the sample with 5 wt% NaCl. However, with the addition of Cu-trien (the pH of a pure Cu-trien solution was ≈8.15), the pH of Calcigel® decreased to ≈ 8.53, and with the addition of NaCl, the pH slightly increased, thus and is copying the trends of mixtures in deionized water. The theoretical pH of NaCl at any concentration should be neutral (pH ≈ 7). However, this assumption is valid only for dilute solutions. According to Debye-Hückel theory, with increasing NaCl concentration, the ionic strength of the solution increases, which leads to a decrease in the activity of the H_3O^+ ions (Debye and Hückel, 1923; Wright, 2007). Therefore, the pH of the NaCl solution slightly increases (not shown) with increasing NaCl concentration. This can explain the increasing pH of the Calcigel®/NaCl mixtures with increasing concentrations of NaCl.

The lower pH of the Calcigel® dispersion with 3.33×10^{-3} mol l^{-1} Cu-trien followed by a rise in the pH after the addition of NaCl, partially explains the elevated CECs of the Calcigel®/NaCl mixtures. A slightly basic pH of 8.6–9 causes the edge charges of montmorillonite to become more negative, thus increasing the variable pH-dependent CEC by increasing the amount of cations that can be bound to the edges (Tournassat et al., 2011). An increase in the CEC of approximately 2.5 cmol(+) kg^{-1} has been measured for a pH increase from 8 to 9 for montmorillonites (Delavernhe et al., 2015).

Table 2
CEC and the exchangeable cations in Calcigel®.

	Na^+	Ca^{2+}	Mg^{2+}	K^+	Σ	CEC
cmol(+) kg^{-1}	9.7 ± 0.1	45.1 ± 1.5	21.2 ± 2.1	3.8 ± 0.1	79.6 ± 3.8	63 ± 2

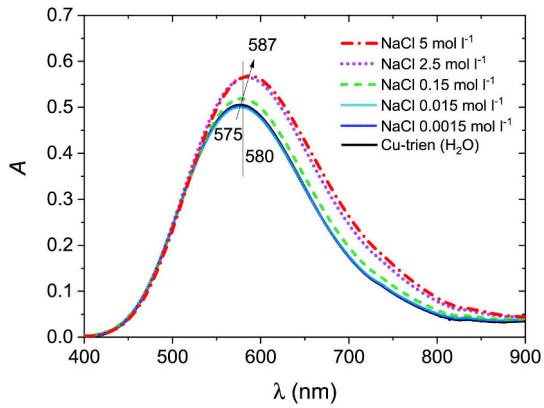

Fig. 3. Absorption spectra of 3.33×10^{-3} mol l^{-1} Cu-trien and Cu-trien/NaCl mixtures with concentrations of NaCl ranging from 0.0015 to 5 mol l^{-1}.

3.3. Spectroscopic properties of the Cu-trien solutions influenced by Ca^{2+}/Mg^{2+}/Na^{+} chloride salts

The pH values of mixtures of Calcigel® with NaCl in a 3.33×10^{-3} mol l^{-1} solution of Cu-trien vary between 8.6 and 8.95 (Fig. 2). In this pH range, Cu-trien exists as $[Cu(trien)]^{2+}$ with an absorption maximum at λ = 575 nm (Delavernhe et al., 2018).

With increasing NaCl concentration, there is a slight shift of the absorption maxima to higher wavelengths (Fig. 3). With an increase of the NaCl concentration up to 2.5 mol l^{-1}, the absorption maximum shifts to 587 nm and the absorbance increases as well. Next, increasing the concentration of NaCl up to 5 mol l^{-1} causes only minor changes in the absorption spectra. The absorbance of Cu-trien at 580 nm, which is used for CEC determination, increases from 0.50 to 0.57. This represents a 14% increase in the absorbance, which can result in an underestimation of the measured CEC by almost −19 cmol(+) kg^{-1}. However, in the samples with concentrations of NaCl at 0.015 mol l^{-1} and below, the effects of a slight change in absorbance can cause an overestimation of the CEC by +1–2 cmol(+) kg^{-1}. This, combined with the increasing pH, can partially explain the overestimation of the CEC by the Cu-trien method.

Changes in the spectral behavior of the Cu-trien solutions were also observed in the presence of Mg^{2+} and Ca^{2+}chloride salts. At concentrations of 0.15 mol l^{-1}, all of the salts caused a similar increase in absorbance, but the shifts of the absorption maxima were different (Fig. 4). While Na^{+} caused a slight shift in the absorbance maximum to 578 nm, Mg^{2+} caused a shift to 580 nm and Ca^{2+} even further to 582 nm. Therefore, the absorbance of Cu-trien at 580 nm, which is used for CEC determination, increased in the presence of $CaCl_2$ (0.15 mol l^{-1}) from 0.50 to 0.53. With increasing concentrations of salts up to 2.5 mol l^{-1}, there are also significant changes in the absorbencies. The largest change was recorded in the presence of Ca^{2+} where the absorbance increased from 0.50 to 0.63 with a shift of the absorption maximum to 587 nm, which represents a 9 nm change in the peak wavelength with respect to that of the pure Cu-trien solution spectra. Therefore, the absorbance of Cu-trien at 580 nm, which is used for CEC determination, increased in the presence of $CaCl_2$ (2.5 mol l^{-1}) from 0.50 to 0.62.

Cu^{2+} cations in aqueous medium are hexa-coordinated. As a result of their octahedral symmetry, the four equatorial ligands are closer to the central atom than are the axial two (Salmon et al., 1988). The four equatorial positions are occupied by trien ligands while water molecules occupy the other two. By increasing the concentration of Cl^{-} ions, the two axial positions are gradually occupied by chloride ions. Because their effects as distal ligands are not great, a small but systemic change in the absorption wavelength is observed. The molar absorption coefficient should be affected by the increasing presence of cations.

3.4. Solubility of calcite and dolomite

The solubilization of carbonates is a complex process and is strongly affected by the process conditions, especially the temperature and atmospheric CO_2 pressure, as well as the ionic strength and pH of the solution. The dissolution of calcite can be described by the reaction equation (Brecevic and Nielsen, 1989):

$$CaCO_{3(s)} \leftrightarrow Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)}$$

Increased calcite solubility with increasing NaCl concentration was observed (Fig. 5). The solubility of a salt in the presence of other electrolytes is influenced by a phenomenon known as the ionic strength effect (Benezeth et al., 2018). Increasing the concentrations of Na^{+} and Cl^{-} ions results in a higher ionic strength of the solution (the ionic strength of a NaCl solution is equal to its concentration). Therefore, the ionic atmospheres of the ions increases, which leads to a reduction of the attractive forces between ions relative to their attraction in water. This leads to a shift in the equilibrium towards the products of dissolution and thus increases their solubility (Coto et al., 2012; Debye and Hückel, 1923; Pitzer, 1973). The solubility of the calcite increased from $1.33 \pm 0.21 \times 10^{-4}$ mol l^{-1} in deionized water to $2.08 \pm 0.03 \times 10^{-4}$ mol l^{-1} in a NaCl solution with a concentration of 1.14×10^{-2} mol l^{-1} (20% of sample mass), representing a solubility increase of almost 60%.

Furthermore, a significant increase in the solubility of calcite in Cu-trien solutions at a concentration of 3.33×10^{-3} mol l^{-1} was observed. This change can be explained by the same phenomenon of ionic strength increase. With an increase in NaCl concentration, the effects of Cu-trien are reduced (Fig. 5). The solubility of the calcite increased, on average, by approximately 8.2×10^{-5} mol l^{-1}, which represents a solubility increase of approximately 52%.

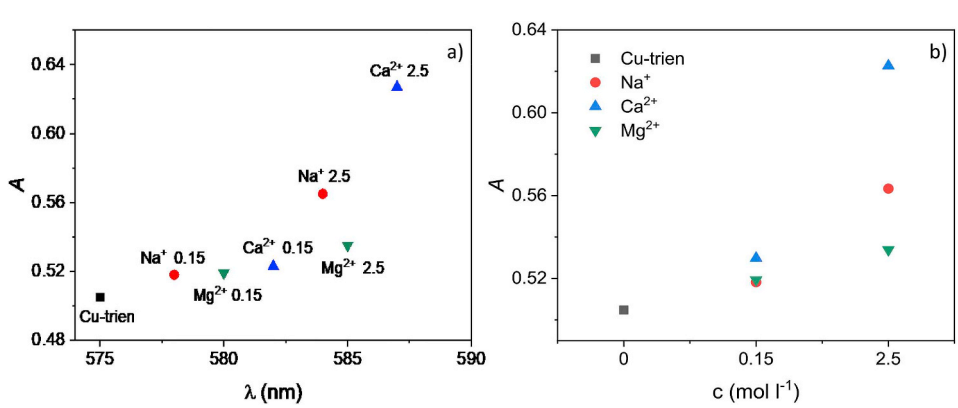

Fig. 4. a) Absorbances and wavelengths for the maximum absorbance of Cu-trien and mixtures of Cu-trien with NaCl, $MgCl_2$ and $CaCl_2$ at concentrations of 0.15 and 2.5 mol l^{-1}. b) Absorbances of Cu-trien and mixtures of Cu-trien with NaCl, $MgCl_2$ and $CaCl_2$ at concentrations of 0.15 and 2.5 mol l^{-1} at λ = 580 nm.

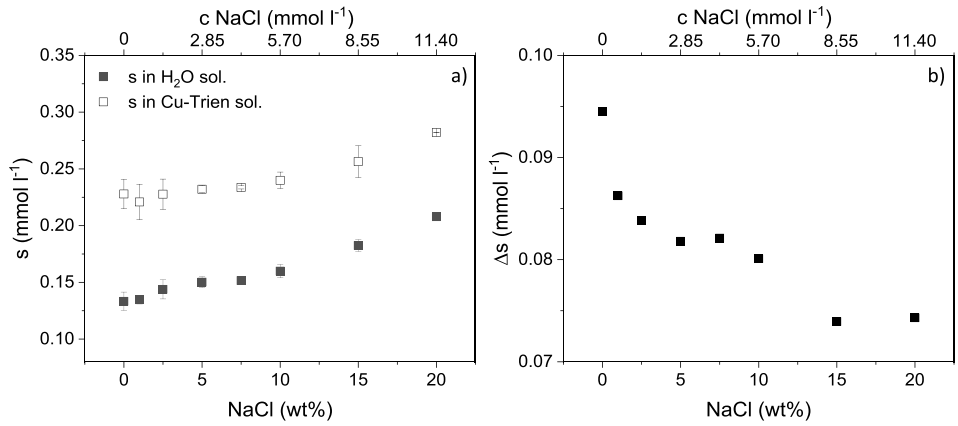

Fig. 5. a) Solubility (s) of calcite (Ca^{2+} mmol l^{-1}) in H_2O and Cu-trien solutions containing NaCl. b) Differences in solubility (Δs) of calcite (Ca^{2+} mmol l^{-1}) in H_2O and Cu-trien solutions containing NaCl.

The dissolution of dolomite is a more complex process that is more dependent on the presence of other cations in the solution. In aqueous systems, ideal dolomite can be considered to be an equimolar mixture of two carbonate components: calcite and magnesite. Observations on dolomite dissolution in water can be presented as two parallel simplistic reactions that are described as follows (Benezeth et al., 2018):

$$CaMg(CO_3)_{2(s)} \leftrightarrow MgCO_{3(s)} + Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)}$$

$$MgCO_{3(s)} \leftrightarrow Mg^{2+}_{(aq)} + CO^{2-}_{3(aq)}$$

where the second part is the rate-limiting reaction.

According to Michalowski and Asuero (2012), pure dolomite dissolves slower than does pure calcite. The effectiveness of dolomite dissolution is largely limited by the dissolution rate of the $MgCO_3$ component because the $CaCO_3$ component in dolomite dissolves rapidly.

The observed dolomite solubility is slightly different than that of calcite (Fig. 6). There is also a noticeable increase in the solubility with increasing NaCl concentration from $1.12 \pm 0.06 \times 10^{-4}$ mol l^{-1} to $1.52 \pm 0.15 \times 10^{-4}$ mol l^{-1}, a solubility increase of 36%. In comparison to the solubility increase of calcite, this increase is 20% less. Significantly different, compared to calcite, is the Cu-trien effect. The solubility of dolomite also increases, but an increase in the NaCl concentration caused an upsurge in dolomite solubility, which differs from the calcite solubility process.

The chemical properties of dolomite should be considered against those of the carbonate minerals calcite, $CaCO_3$, and magnesite, $MgCO_3$. The trigonal structure of calcite is composed of alternating layers of calcium and carbonate ions. The crystal structure of magnesite is the same as that of calcite, and the magnesite properties are similar to those of calcite (Michalowski and Asuero, 2012). This has also been demonstrated in dissolution experiments, where the trends in the solubility of magnesite were similar to those of calcite (not shown). Nevertheless, natural dolomite usually possesses a nonideal structure with structural defects, which can lead to completely different properties.

There are noticeably different release rates for Ca^{2+} and Mg^{2+} cations. Slightly more Mg^{2+} cations were released in the weaker NaCl solutions. With increasing NaCl concentration, the Ca^{2+} concentration dominates. The presence of Cu-trien has no significant effect on this ratio.

The total amount of carbonates in the samples is known from the Calcitel® mineralogical composition (Table 1). Therefore, the theoretical amounts of Mg^{2+} and Ca^{2+} that can be dissolved from the calcite and dolomite of Calcitel® can be calculated. Fifty milligrams of pure Calcigel® can theoretically contain $\approx 1.65 \times 10^{-3}$ mol l^{-1} Ca^{2+} and $\approx 8.13 \times 10^{-4}$ mol l^{-1} Mg^{2+} (2.5 wt% of calcite and 4.5 wt% of dolomite), which originate from the admixtures of calcite and dolomite. All of the measured solubility values were lower than the theoretical contents of the cations. Thus, we can conclude that Calcigel® CEC measurements may result in the formation of a saturated solution after dissolution of the maximum amounts of calcite and dolomite. With this assumption, we divided the origins of the cations in the supernatants after CEC measurement into three effects (Fig. 7, Table S1). I: the dissolution of calcite and dolomite into water, II: the increase in solubility due to Cu-trien and III: cations originating from ionic exchange. In CEC

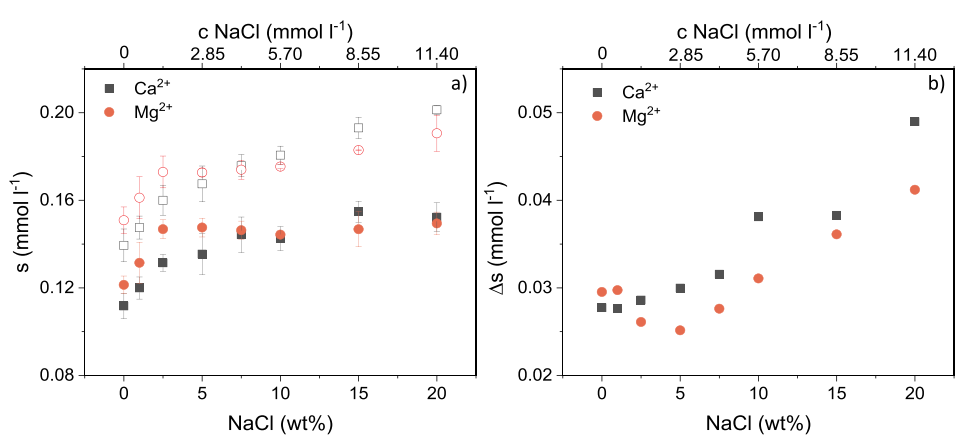

Fig. 6. a) Solubilities of dolomite (Ca^{2+} and Mg^{2+} mmol l^{-1}) in H_2O (solid symbols) and Cu-trien (empty symbols) solutions containing NaCl. b) Differences in the solubilities of dolomite (Ca^{2+} and Mg^{2+} mmol l^{-1}) in H_2O and Cu-trien solutions containing NaCl.

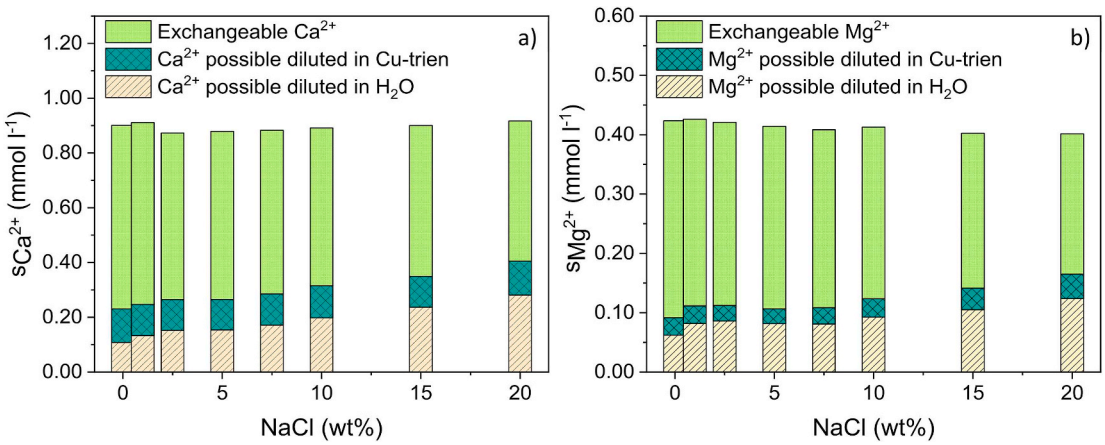

Fig. 7. The solubility contributions of calcite and dolomite to the analyzed concentrations of Ca^{2+} (a) and Mg^{2+} (b) ions in the supernatants of the Calcigel® samples.

Table 3
Concentrations of the cations in cmol(+) kg^{-1} and the sum of these concentrations in relation to the wt% of NaCl in Calcigel®/NaCl mixtures after correction.

Sample (wt% NaCl)	c (cmol(+) kg^{-1})					
	Ca^{2+}	Mg^{2+}	K^+	Na^+	Σ	Theor
0	33.5 ± 0.2	16.6 ± 0.2	3.8 ± 0.1	9.7 ± 0.1	63.6 ± 0.4	63.1
1	33.2 ± 0.3	15.7 ± 0.1	4.4 ± 0.9	10.0 ± 0.1	63.3 ± 1.4	62.4
2.5	30.4 ± 0.1	15.4 ± 0.1	4.3 ± 0.1	9.9 ± 0.1	60.0 ± 0.2	61.5
5	30.7 ± 0.1	15.4 ± 0.1	3.7 ± 0.1	9.6 ± 0.1	59.3 ± 0.3	60.0
7.5	29.9 ± 0.1	15.0 ± 0.1	3.7 ± 0.1	9.5 ± 0.1	58.1 ± 0.6	58.4
10	28.8 ± 0.2	14.5 ± 0.1	3.7 ± 0.1	9.9 ± 0.1	56.9 ± 0.4	56.8
15	27.5 ± 0.1	13.1 ± 0.1	3.8 ± 0.8	9.6 ± 0.1	54.1 ± 1.0	53.7
20	25.6 ± 0.2	11.8 ± 0.2	3.6 ± 0.7	9.9 ± 0.1	50.9 ± 1.2	50.5

measurements, only a Cu-trien solution is used. However, the division of the H_2O and Cu-triene effects was used to demonstrate the effects of Cu-trien itself.

In samples with no NaCl content, 74.4% of Ca^{2+} and 78.4% of Mg^{2+} in the supernatants of CEC measurements were from cationic exchange. Almost 25.6% of Ca^{2+} and 21.6% of Mg^{2+} originated from the dissolution of calcite and dolomite. These dissolution amounts increased with increasing NaCl content in the Calcigel®/NaCl mixtures. The dissolution content of Ca^{2+} can be increased by up to ≈44% and that of Mg^{2+} by up to ≈41% in mixtures with 20% NaCl.

From the concentrations of cations in the supernatant of Calcigel® that were related to the exchange process, the CEC values were calculated in cmol(+) kg^{-1} (Tables 3 and S1). The values of the Na^+ concentrations were corrected with respect to the added amounts of NaCl.

For simplification, the solubilities and influences of the other mineral phases in Calcigel® were considered negligible because the corrected CEC values are in good agreement with the theoretical values (Fig. 1, Table 3).

4. Summary and conclusions

The CECs and exchange cations of Ca^{2+}/Mg^{2+} bentonite Calcigel® in various NaCl mixtures were studied to simulate the samples that are provided from various geotechnical applications in saline environments. Calcigel® is bentonite with moderate amounts of calcite and dolomite.

The CECs of the Calcigel®/NaCl mixtures did not decrease linearly with the dilution of the bentonite content in the mixtures. The measured CEC values of the Calcigel®/NaCl mixtures were 1–2 cmol(+) kg^{-1} higher than the predicted values. The addition of up to 2.5 wt% of NaCl caused an increase in the measured CECs. With a further increase in NaCl content, the measured CECs decreased, which was caused by a lower amount of bentonite and thus montmorillonite in the Calcigel®/NaCl mixtures.

The increase in the pH of the dispersions of Calcigel® in Cu-trien solutions from 8.53 ± 0.05 to 8.95 ± 0.09 from the addition of up to 2.5 wt% NaCl resulted in an increase of the variable charge on the edges of montmorillonite in bentonite and therefore to an initial increase in the CEC values. Afterward, dilution of the solid became more important as pH only slightly increased with further increases in NaCl content.

Both the increased NaCl concentration and the increased Ca^{2+} and Mg^{2+} concentrations in the Cu-trien solutions, resulting from the increased dissolution of calcite and dolomite, could shift the absorbance maximum of Cu-trien and increase its absorbance. This resulted in an underestimation of the CEC values as the absorbance measurements are performed at 580 nm. Regardless, the concentrations of NaCl during the CEC measurements are < 12 mmol l^{-1}, and the concentrations of Ca^{2+} and Mg^{2+} are lower than 1 mmol l^{-1}. Thus, the absorbance of Cu-trien at 580 nm is < 0.002, and its influence on CEC is +1 cmol(+) kg^{-1}.

Nevertheless, the presence of NaCl plays a significant role in the determination of exchangeable cations. Increasing the ionic strength by increasing the NaCl concentration significantly increased the solubilities of calcite and dolomite. Cu-trien amplified this phenomenon. Calcite has proven to be more prone to the effects of Cu-trien than is dolomite. However, with increasing NaCl concentrations, the effects of Cu-trien on dolomite solubility are more substantial. While studying the artificial Calcigel®/NaCl samples, the results from dissolution experiments following the proper conditions can be used as blanks for correction. In natural samples, where the dissolution of calcite and dolomite and the transport of Ca^{2+} and Mg^{2+} occurs due to the flux of NaCl, determination of the smectite content and the concentrations of exchangeable cations will be more complex. As quantitative analysis of hundreds of samples by Rietveld analysis of their XRD patterns is not feasible, NaCl content can be determined from the Cl^- concentration as

determined by ion chromatography, and dissolved carbonates can be estimated from the contact time. Thereafter, blank corrections could be applied.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apgeochem.2018.12.019.

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