



Research Paper

Cation exchange capacity- An alternative method to investigate the geological barrier for landfills?

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ABSTRACT

Clays and clay minerals are ideal raw materials for geological barriers and landfill liners because of their low-hydraulic permeabilities, their swelling properties and adsorption capacities. The geological barrier is a supplementary barrier beneath the body of the landfill, intended to protect the environment from uncontrolled leachate from the waste material. An Austrian standard defines the process for site exploration and the required laboratory tests and parameters for the analysis of the geological barrier. The most important laboratory tests besides grain size analysis are the Atterberg limits and the determination of the clay mineralogy using X-ray diffraction. However, the analysis of the cation exchange capacity (CEC) is not included in the list of laboratory tests. CEC is a numerical value that describes the physical properties of clays, such as the diffusion of charged and uncharged molecules and the cation retention. Hence, the objective of this study is to clarify whether the determination of the CEC using the Cu-trien method represents a possible alternative to currently used laboratory tests.

For this purpose, three samples (loess, sand and clay) from two landfill sites owned and operated by Zöchling GmbH as well as six mixtures of these samples with varying compositions were examined for their mineralogical, chemical and geotechnical properties. The samples consisted of varying amounts of quartz, feldspar, calcite, dolomite and the clay minerals smectite, illite, kaolinite, vermiculite and chlorite. The results showed that the bulk clay mineralogy correlates well with the Atterberg liquid limit ($R^2 = 0.73$) and the CEC ($R^2 = 0.88$) and furthermore, the results of the two methods – Atterberg liquid limit and CEC- even correlated better ($R^2 = 0.95$).

This demonstrates that the CEC can be an alternative to the Atterberg liquid limit and/or the analysis of the mineralogical composition of the material. Advantages of the CEC are rapidness, its good reproducibility and cost-efficiency of the analyses compared to the other two methods. Based on the results of this study, a partial substitution of the currently used laboratory tests is considered feasible and CEC could at least be used for fast and efficient screening.

1. Introduction

Clay minerals are used in many areas of our modern society ranging from medicine to raw material in the construction industry. Due to their special properties, they can be used in a variety of ways. Clays have been an important raw material for the waste management industry for decades. In landfill construction, clays and clay-containing soil mixtures are used to seal the landfill (Oluwapelumi, 2015; Afolagboye et al., 2017). In addition to surface coverage and landfill base sealing, this also applies to the construction of artificial geological barriers.

An artificial geological barrier plays an essential role in modern landfill construction as it represents an additional layer that protects the

environment from uncontrolled emissions of the stored waste (Musso et al., 2010). The barrier must meet two requirements: It must have a low permeability coefficient and have the ability to adsorb pollutants (Czurda, 2006). Similar statements also result from point # 5 of ÖNORM S 2074-1 (2004), which defined the requirements for an investigation of a landfill site and thus the necessary laboratory tests and parameters for the artificial geological barrier. According to ÖNORM S 2074-1 (2004), the most important parameters for artificial geological barriers are the permeability coefficient and the deformation behavior. Compacted clays, which contain in particular the clay minerals smectite and vermiculite have a natural low permeability coefficient and, in addition, have the ability to swell and adsorb pollutants (Bahmani and Bayram,

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2018). The permeability coefficient gives an indication how quickly a liquid can flow through a rock or soil. It depends on a variety and combination of factors, such as sediment porosity, grain size, capillary radius and clay content. Experiments have shown that the permeability coefficient decreases with increasing clay content (Shevvin et al., 2006). Clays minimize the potential for leakage and the associated risk of transport of pollutants into the environment (Chen et al., 2014), and hence meet the requirements of an artificial geological barrier. It is therefore important to investigate and characterize the material of such a barrier for the presence and specific properties of the clay minerals. One of the most important laboratory tests according to ÖNORM S 2074-1 (2004) are the Atterberg limits. A positive correlation between the Atterberg liquid limit and the proportion of swellable clay minerals in the sample material has already been discussed in literature (Schmitz et al., 2004) and will also be examined in this work. The second important laboratory test for determining clay mineralogy is X-ray diffraction. Based on this analysis, a quantification of the most important clay minerals in the sediment can be carried out.

This study aims to answer the question of whether cation exchange capacity has the capability to replace the laboratory tests proposed and recognized in ÖNORM S 2074-1 (2004). This would apply to both the previously mentioned, time-consuming, analyses of the Atterberg liquid limit as well as the determination of clay mineralogy using X-ray diffraction.

Cation exchange capacity (CEC) is the parameter that describes the extent to which clay minerals have the ability to bind cations and thus a variety of pollutants (Czurda and Wagner, 1991). There is no generally accepted or preferred method for its determination. A popular method was described by Chhabra et al. (1975), where silver thiourea is used. Alternatively, the methylene blue method can be carried out quickly, but is not as reliable as the other methods (Kahr and Madsen, 1995). The method proposed by Meier and Kahr (1999) which uses a Cu(II)-triethylenetetramine complex for exchange has been used for this study. A higher value of cation exchange capacity means that a higher amount of pollutants can be removed from the leachate by the clay (Kabir and Taha, 2004). One can thus hypothesize, that the cation exchange capacity is related, like the Atterberg liquid limit, to the proportion of swellable clay minerals in the sample material.

To test this hypothesis, three sediment samples and mixtures of these samples from two landfills owned and operated by Zöchling GmbH were tested in the laboratory for their mineralogical, chemical and geotechnical properties. The results of these analyses are compared to each other and the correlation between the Atterberg limits and the cation exchange capacity of the clay minerals is evaluated.

2. Geography and geology

The two landfill sites in Mistelbach and Kettlasbrunn are located approximately 50 km NE of Vienna in the Vienna Basin, Austria. The geology of the area around the two sites is characterized by sandy and clayey Pannonian (Neogene) sediments of the Vienna Basin with Quaternary loess sediments as top layer at the surface. At “Kettlasbrunn”, the Pannonian sediments are represented as well-developed alternating layers of clay and sand on top of thicker sandy and clayey layers (Fig. 1).

The “Mistelbach” landfill site (48°34'39.3"N, 16°36'15.2"E) is located to the east of the town of Mistelbach, and is a waste disposal site with an on-site waste treatment plant. The “Kettlasbrunn” landfill site (48°32'04.4"N, 16°39'10.4"E) is located to the south of the village Kettlasbrunn, approximately 5 km to the East of the “Mistelbach” site. This is also a waste disposal site and was partly still under construction at the time of sampling (Fig. 1). Both landfill sites were originally covered by loess sediments.

3. Materials and methods

The samples originate from two landfills owned and operated by

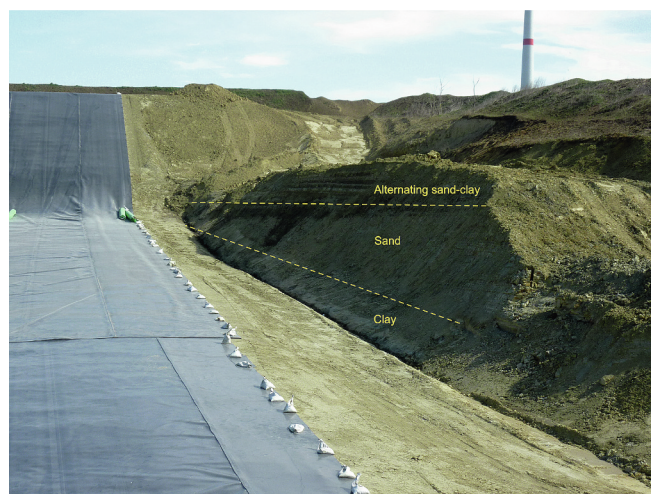


Fig. 1. Landfill Kettlasbrunn (under construction) in the Vienna Basin. Sampling points of the “clay” and “sand” samples are located next to the labels.

Zöchling GmbH. The loess sample was taken at the near surface from the northernmost part of the “Mistelbach” landfill site; the clay and sand samples were taken in the Kettlasbrunn landfill (for sampling co-ordinates see above; in Fig. 1 the “clay” and “sand” sampling points are indicated).

The mineralogical, chemical and geotechnical properties were determined on the three sediment samples (samples “loess”, “clay”, “sand”) taken from the landfill sites and three mixtures each of samples sand (S)-clay (C) and loess (L) -clay (C). 500 g of the mixtures S-C and L-C in the weight proportions 1:2, 1:1, 2:1 were produced using a mixing device. Additionally, one random mixture of clay and sand (C-S) from a local excavation of the “Kettlasbrunn” landfill was analyzed.

3.1. X-ray diffraction

The mineralogical composition of the samples was determined using X-ray diffraction (XRD). The powdered samples were pressed into sample holders and analyzed using a Panalytical X'Pert PRO X-ray diffractometer (CuK α radiation, 40 kV, 40 mA, step size 0.0167, 5 s per step). For quantification the samples were prepared randomly oriented. The interpretation was carried out with the programs X'Pert Data Viewer and X'Pert HighScore Plus. The bulk samples and also the clay fractions were quantified using the Schultz method (1964) which gives error limits of $\pm 10\%$. While this method is not as precise and accurate as the Rietveld method (Ufer and Raven, 2017), it allows a fast and practical semi-quantification for comparing a set of samples.

To separate the clay minerals, the samples were first mixed with an H₂O₂ solution (15%) to remove the organic material. After completion of the reaction, the suspensions were dispersed with a 400 W ultrasonic rod for 3 min. The <2 μ m fraction was then separated using sedimentation in Atterberg cylinders. 50 mg of the clay fraction was mixed with 50 ml 1 N MgCl₂ or KCl and shaken overhead in a centrifuge tube for 24 h. The samples were then centrifuged in a Sigma 6-16 K centrifuge for 5 min at 1500 rpm, washed with deionized water and centrifuged again for 10 min at 4000 rpm. 1 ml of the suspension (10 mg/ml) was then pipetted onto a glass slide. The following samples were prepared for analysis: K-saturated, K + ethylene glycol saturated, K-550 °C tempered, Mg-saturated, Mg + glycerol saturated. The evaluation was carried out using the Data Viewer program based on the d-value positions according to Thorez (1976) and Moore and Reynolds (1997).

3.2. Total carbon (TC)

A LECO RC612 carbon-water analyzer was used to determine organic

(TOC) and inorganic carbon (TIC) by using the combustion method. For this purpose, 100 mg of the samples were progressively heated to 1000 °C. Organic carbon decomposed at around 550 °C, and inorganic carbon below 1000 °C. According to [ÖNORM EN 17505 \(2020\)](#) this procedure of determining TOC can be distorted by carbonates with a low thermal stability (eg. siderite). One method of overcoming this is to boil the sample before TOC analysis in hot HCl to remove the carbonates. The approach in this study was to determine the specific carbonate minerals with XRD before TOC analysis; only calcite and dolomite were detected. Each sample was analyzed twice. For calibration, the reference materials LECO LCRM 502–902 Carbon% 11.99 ± 0.05 , 502–905 Carbon% 4.99 ± 0.05 , and 502–696 Carbon% 1.02 ± 0.03 were used.

3.3. Grain size distribution (Sieving & SediGraph)

To determine the grain sizes, the samples were first mixed with an H₂O₂ solution (15%) to remove the organic material. After completion of the reaction, the suspensions were dispersed for 3 min with a 400 W ultrasonic rod. The grain size distribution was then determined using sieves with the following mesh sizes: 500 µm, 250 µm, 125 µm and 63 µm. The fraction <63 µm was analyzed until 0.2 µm using a Micro-meritics SediGraph III. The grain size distribution curve was generated using the program excel. Because of the poor sorting of the material and the resulting high uniformity coefficient, the determination of the permeability coefficient from the grain size distribution curve (eg [Beyer, 1964](#)) was not feasible.

3.4. Atterberg limits

Atterberg limits are a measure of the critical water contents of a fine-grained sediment. The liquid limit (LL) specifies the water content at which the clay can no longer maintain a molded shape and begins to flow. The plastic limit (PL) defines the minimum amount of water necessary to make the clay plastic. The determination of the Atterberg limits was carried out following Austrian standard [ÖNORM EN ISO 17892-12 \(2020\)](#).

3.5. Cation exchange capacity (CEC)

The CEC was determined following [Meier and Kahr \(1999\)](#). This method uses complexes of copper (II) ion with triethylenetetramine to determine CEC. A 0.01 M copper(II)-trien sulfate solution was prepared. 1.463 g of triethylenetetramine were dissolved in 100 ml of distilled water. Another solution was prepared by mixing 1.596 g of dry Cu(II) sulfate with distilled water to give 1 l of solution. These solutions were then mixed together.

50 ml distilled water were added to 500 mg of the bulk powdered sample, and dispersed by ultrasonic treatment (20 kHz, 1 min). While stirring the suspension, 10 ml of the solution of the Cu complex was added. After 3 min reaction time, the suspension was centrifuged with a Sigma 6-16 K centrifuge at 4000 rpm for 10 min. The clear, supernatant solution was carefully removed and the extinction was measured using a Merck spectrophotometer (Prove 300) at 585 nm in a 20 mm cuvette against water as a zero value. Each measurement was carried out five times and the mean value was calculated. The CEC was then calculated with reference to the dry clay weight using the following formula:

$$\text{CEC (mmol/100 g)} = (\text{Eb} - \text{Em}) \times 100/\text{Eb};$$

whereas Eb = Extinction without sample (blank value), and Em = Extinction of the supernatant solution.

The measurements were repeated after four weeks and the mean of the CEC values was taken as final result.

4. Results

4.1. Bulk Mineralogy

The main minerals in the bulk samples were quartz, dolomite, calcite, K-feldspar and albite. In addition, the phyllosilicates muscovite, chlorite and kaolinite were detected in the bulk samples ([Table 1](#)). Sample “loess” contained the highest amount of carbonates, whereas sample “sand” had the lowest one. The percentages of the minerals were determined using a semi-quantitative method, hence an error of $\pm 10\%$ has to be taken into account. For the clay-loess mixtures and the clay-sand mixtures the quartz contents ranged between 24% and 53%, K-feldspar from 2% to 5%, albite between 3% and 12%, calcite between 1% and 12%, dolomite between 4% and 12% and the bulk clay minerals from 26% to 54% ([Table 1](#)). The quartz content clearly increases and the clay content decreases with the sand content for the clay-sand mixtures. For the clay-loess mixtures the trend is similar but not as pronounced.

4.2. Clay mineralogy

The clay fractions contained the minerals smectite, vermiculite, illite, kaolinite, and chlorite in varying amounts. The Mg-saturated “clay” sample ([Fig. 2](#)) showed a broad reflection at 14.2 Å, which belonged to smectite, vermiculite and chlorite. In addition, reflections of illite were present at 9.93 Å (001), 4.98 Å (002), and 3.33 Å (003). Vermiculite and traces of chlorite were also seen at 7.06 Å (002), 4.71 Å (003), 3.53 Å (004), and 2.88 Å (005). The reflections of kaolinite were located at 7.14 Å (001) and 3.57 Å (002). In the K-saturated sample, the (001)- reflection of smectite shifted to 11.3 Å and vermiculite to 9.95 Å. Saturation with Mg and glycerol expanded the smectite to 17.5 Å whereas vermiculite did not expand and kept its position at 14 Å. K + ethylene glycol saturation also expanded the smectite to 16.4 Å. The K-sample heated to 550 °C destroyed kaolinite, and smectite collapsed to 9.97 Å. Illite and chlorite kept their positions; chlorite was only present in traces. The quantification of the clay fractions gave 53% smectite, 8% vermiculite, 30% illite, 9% kaolinite, traces of chlorite for sample “clay”;

45% smectite, 31% illite, 12% kaolinite, 12% chlorite for sample “loess”; and 64% smectite, 7% vermiculite, 18% illite, 11% kaolinite, and traces of chlorite for sample “sand”;

In [Table 1](#) the clay mineral percentages recalculated to the bulk sample are listed. The amount of all clay minerals increased as the proportions of sample “clay” in the mixtures increased.

4.3. Total organic and inorganic carbon

The highest amount of organic carbon was measured in sample “clay” with 0.196 mass%, sample “loess” had a slightly lower amount of 0.093 mass%. Sample “sand” contained the lowest amount of organic carbon with 0.041 mass%. The highest amount of inorganic carbon was found in samples “loess” and “clay” with 2.102 mass% and 2.063 mass% respectively. Sample “sand” contained the lowest overall amount with 0.049 mass%.

4.4. Grain size distribution

Cumulative grain size distribution curves of the clay-loess mixtures (1:2, 1:1, 2:1) and the clay-sand mixtures (1:2, 1:1, 2:1), [Fig. 3](#), showed that the clay content decreased from sample “clay”- (48.5%) to “loess”- (23%) to “sand” (8.9%). The silt content decreased from sample “loess”- (64.8%) to “clay”- (49.5%) to “sand” (28.1%). The sand content decreased from sample “sand”- (63%) to “loess”- (12.2%) to “clay” (2%).

4.5. Atterberg limits

Sample “clay” absorbed the highest amount of water and hence displayed the highest value for the Atterberg liquid limit (LL) with

Table 1

Bulk and clay mineralogy of the clay-loess mixtures, and the clay-sand mixtures (in %). Please note that the values are semi-quantitative, with an error of $\pm 10\%$. K-Fsp = K-feldspar, bulk CM = bulk clay minerals; clay minerals in bulk sample: Verm = vermiculite.

| | Quartz | K-Fsp | Albite | Calcite | Dolomite | bulk CM | Smectite | Verm | Illite | Kaolinite | Chlorite |
|-----------|--------|-------|--------|---------|----------|---------|----------|------|--------|-----------|----------|
| Loess (L) | 38 | 3 | 12 | 10 | 12 | 25 | 11 | 0 | 8 | 3 | 3 |
| L-C 2:1 | 34 | 3 | 6 | 12 | 10 | 35 | 15 | 3 | 10 | 6 | 0 |
| L-C 1:1 | 41 | 3 | 6 | 12 | 8 | 30 | 15 | 3 | 9 | 4 | 0 |
| L-C 1:2 | 36 | 5 | 6 | 12 | 9 | 32 | 17 | 3 | 9 | 4 | 0 |
| Clay (C) | 24 | 2 | 5 | 10 | 8 | 51 | 27 | 4 | 15 | 4 | 0 |
| C-S | 27 | 2 | 3 | 7 | 7 | 54 | 36 | 4 | 11 | 4 | 0 |
| Sand (S) | 72 | 2 | 5 | 1 | 1 | 19 | 12 | 1 | 3 | 2 | 0 |
| S-C 2:1 | 53 | 4 | 9 | 5 | 4 | 26 | 16 | 2 | 5 | 2 | 0 |
| S-C 1:1 | 42 | 3 | 4 | 9 | 7 | 36 | 21 | 3 | 8 | 5 | 0 |
| S-C 1:2 | 41 | 2 | 5 | 9 | 7 | 38 | 23 | 2 | 9 | 3 | 0 |

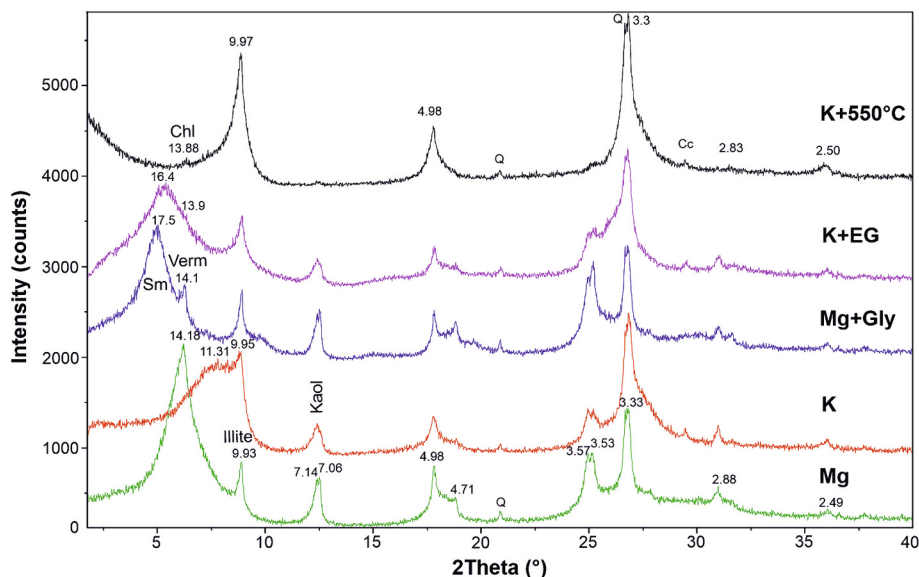


Fig. 2. X-ray diffraction patterns of the clay fraction of sample “clay”, saturated with Mg, K, Mg and glycerol, K and ethylene glycol, and heated to 550 °C; Sm = smectite, Verm = vermiculite, Kaol = kaolinite, Chl = chlorite, Q = quartz, Cc = calcite; d-values in Å.

46.7%. At 25.1% sample “loess” had a significant lower LL. It was not possible to analyze sample “sand” with the Atterberg method, because of lacking cohesion (Table 2). Looking at the loess-clay mixtures, the LL decreased from sample “clay” to samples L-C 1:2, L-C 1:1, L-C 2:1 to sample “loess” (Table 2). The plasticity index also decreased with decreasing clay content, from 21.1% for “clay” to 3.4% for “loess”. The sand-clay mixtures showed a similar behavior, the LL decreased from sample “clay” to samples S-C 1:2, S-C 1:1 and S-C 2:1. The plasticity index also decreased with decreasing clay content in the sand-clay mixtures from samples S-C 1:2 to S-C 1:1 and S-C 2:1 (Table 2).

4.6. Cation Exchange Capacity (CEC)

The highest mean values for the CEC were measured in sample “clay” with 19.2 mmol/100 g. The value of sample “loess” was significantly lower at 7.7 mmol/100 g. The lowest values were measured at 2.9 mmol/100 g for the sample “sand” (Table 2).

The loess mixtures showed a steady increase in CEC with increasing clay content in the mixtures. The increase of the CEC values with increasing clay content was even more pronounced for the sand-clay mixtures (Table 2).

The samples were analyzed in two runs and gave consistent results with standard deviations of ± 0.06 to ± 0.35 mmol/100 g with one exception. Sample “sand” had a higher standard deviation of ± 0.95 mmol/100 g.

5. Discussion

5.1. Mineralogical, chemical, and geotechnical properties of the landfill barrier materials

Samples “clay”, “loess”, and “sand” were collected from the two landfills “Kettlasbrunn” and “Mistelbach”. The samples were intended as test materials for the use in the construction of on-site artificial geological barriers. Mineralogical analyses highlighted small compositional differences between the samples: finer grained sizes correlated with lower amounts of quartz and feldspar. Sample “loess” contained the highest amounts of dolomite and calcite, also confirmed by the higher TIC values of the sample. The overall mineralogy of the 1:2, 1:1, 2:1-mixtures clay-sand and clay-loess confirmed the observation of the pure samples.

X-ray diffraction identified various clay minerals, specifically kaolinite, illite, chlorite, smectite, and vermiculite. Kaolinite, illite and chlorite, which are non-expandable, contrast with smectite and vermiculite, both expandable clays with significant interlayer reactivity and substantially greater surface areas (600–800 m²/g); (Heim, 1990; Jasmund and Lagaly, 1993; Ismadji et al., 2015; Awad et al., 2019). This means that reactants (inorganic and organic cations) can penetrate into the interlayer spaces and be bound there (Lagaly et al., 2013).

Quantification showed that smectite was the predominant clay mineral across all samples and mixtures, vermiculite was present in smaller amounts in all samples except for sample “loess”. It contained

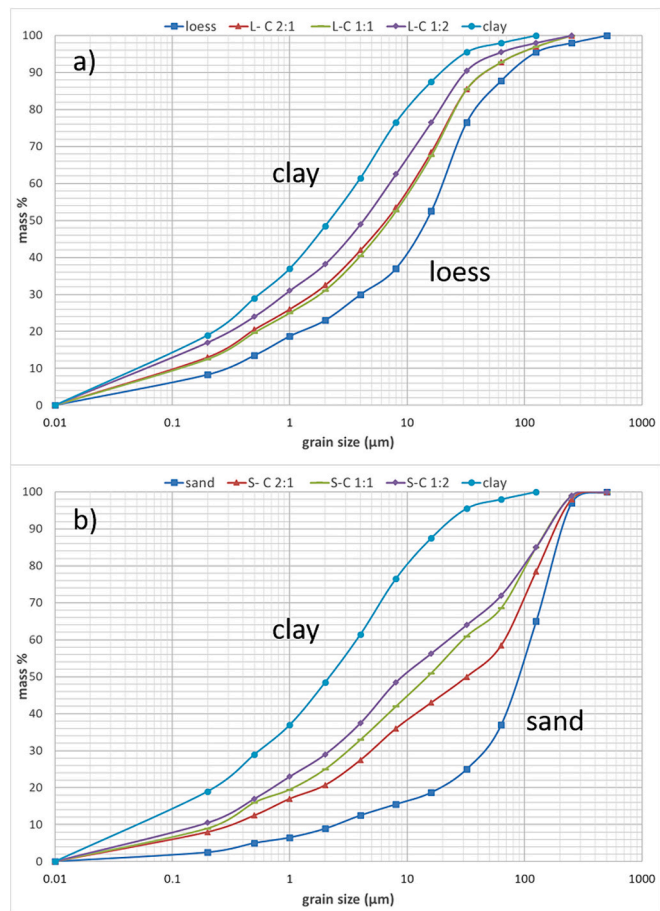


Fig. 3. Cumulative grain size distribution curves of the clay (C)-loess (L) mixtures (1:2, 1:1, 2:1) and the clay (C)-sand (S) mixtures (1:2, 1:1, 2:1).

Table 2
Cation exchange capacity (CEC; in mmol/100 g), Atterberg liquid limits (LL; in %) and plasticity index (PI; in %) of the clay-loess mixtures, and the clay-sand mixtures.

| | CEC | LL | PI |
|-----------|------|------|------|
| Loess (L) | 7.7 | 25.1 | 3.4 |
| L-C 2:1 | 12.1 | 30.9 | 10.0 |
| L-C 1:1 | 12.6 | 34.2 | 11.3 |
| L-C 1:2 | 13.6 | 40.0 | 17.2 |
| Clay (C) | 19.2 | 46.7 | 21.1 |
| C-S | 18.7 | 44.4 | 22.7 |
| Sand (S) | 2.9 | n.a. | n.a. |
| S-C 2:1 | 8.3 | 25.3 | 5.1 |
| S-C 1:1 | 10.3 | 29.3 | 9.4 |
| S-C 1:2 | 13.7 | 38.3 | 18.1 |

n.a. = not analyzed.

chlorite instead of vermiculite; in all the other samples chlorite was only identified in traces.

Geotechnical investigations corroborated these mineralogical insights. Grain size analysis of sample “clay” showed high clay and silt sized grain fractions, while in sample “sand” the sand fraction predominated. Loess samples were notable for their silt content (Fig. 3).

Atterberg limits show medium plasticity in sample “clay” and the mixtures L-C 1:2, S-C 1:2, all other samples and mixtures are only slightly plastic (Table 2). This correlates with the presence of clay minerals, particularly the expandable varieties smectite and vermiculite.

Cation exchange capacity (CEC) increased proportionally with clay content in the pure samples or mixtures. This underscores the integral

relationship between CEC and clay mineralogy and content (Hepper et al., 2006). There are no prescribed CEC thresholds for barrier materials. However, Rowe et al. (1995) and Kabir and Taha (2004) suggest at least 10 mmol/100 g for artificial barrier application. Taking this threshold, samples “loess” and “sand”, and the mixture S-C 2:1 would not be adequate for an artificial geological barrier.

5.2. Correlation of Atterberg liquid limit (LL) and clay mineralogy

The intrinsic link between the Atterberg LL of various clay materials and their mineralogical composition is well-recognized (White, 1949; Schmitz et al., 2004; Polidori, 2007) and is critical for the design and subsequent performance of artificial geological barriers. This study underlines the direct correlation between the LL and the clay content. This is clearly shown in Fig. 4, where the bulk clay mineral contents of individual samples determined by XRD are plotted against their corresponding Atterberg LL. The correlation coefficient (R^2) of 0.73 confirms the assumption of a correlation between the Atterberg LL and the proportion of clay minerals. The extent to which Atterberg LL is related to the proportion of bulk clay minerals or to the presence of a specific clay mineral in the sample is also shown in Fig. 4. Although all clay types result in a positive correlation, vermiculite, smectite and illite show the most substantial R^2 values, ranging between 0.57 and 0.67. Kaolinite's minimal R^2 of 0.03 rules out any significant correlation with the Atterberg LL. The best relationship is established between Atterberg LL and the content of bulk clay minerals. As already stated in Schmitz et al. (2004), the overall presence of clay minerals is more important than the presence of a specific clay mineral. According to the correlations in Fig. 4, expandable clay minerals support a high value for Atterberg LL, but are not exclusively responsible for the high value.

5.3. Correlation of cation exchange capacity (CEC) and clay mineralogy

The determination of the CEC is based on the observation that clays have the ability to adsorb cations. This is due to the negative charge on the surface of clay minerals and the property of some clay minerals to swell and thus adsorb positively charged cations in their interlayers (Heim, 1990; Jasmund and Lagaly, 1993; Meunier, 2005).

This study investigates the relationship between CEC and both the presence of bulk clay minerals and individual clay mineral species. In Fig. 5, the CEC is plotted against the bulk clay mineral content determined by XRD, resulting in a correlation coefficient (R^2) of 0.88. Additional plots in Fig. 5 give a clearer understanding of individual clay mineral contributions to CEC. Consistent with the Atterberg LL, all clay types result in a positive correlation, vermiculite, smectite and illite show the most substantial R^2 values, ranging between 0.65 and 0.84.

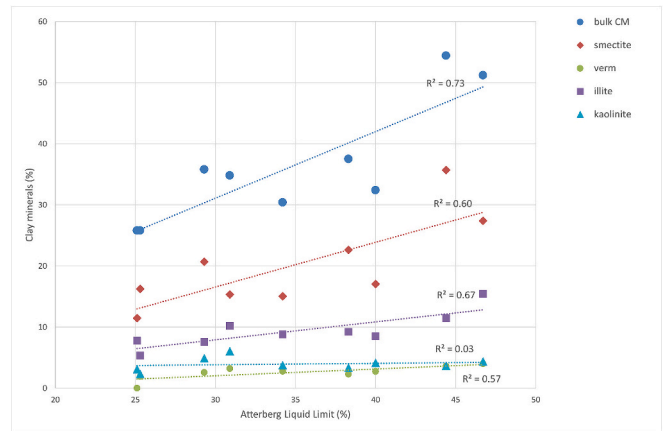


Fig. 4. Correlation of Atterberg liquid limit with bulk clay minerals (bulk CM) and smectite, illite, kaolinite, and vermiculite (verm).

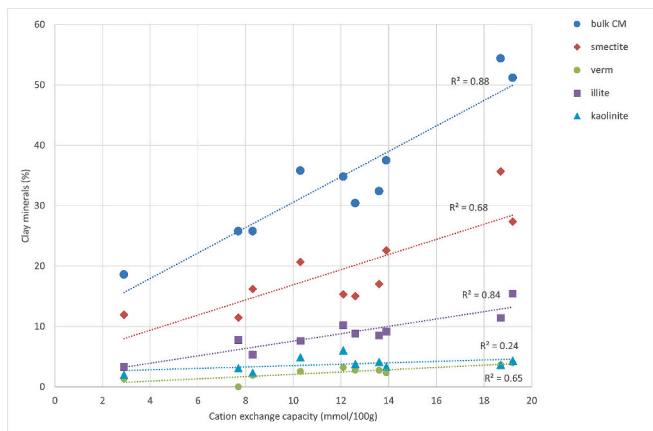


Fig. 5. Correlation of the Cation exchange capacity with bulk clay minerals (bulk CM), smectite, illite, kaolinite, and vermiculite (verm).

Kaolinite with an R^2 of 0.24, shows no direct relation to CEC. As expected when using semi-quantification, different qualities in correlation of CEC values with semi-quantitative clay mineral concentrations can be observed. Minerals with low CEC such as kaolinite have the poorest correlation, followed by illite and chlorite. The best correlations can be expected for smectite and vermiculite as these latter two minerals dominate the CEC values of the samples. However, Fig. 5 confirms that the presence of clay minerals is related to the CEC, regardless of the presence of a specific clay mineral.

Zeelmaekers et al. (2015) and Frederickx et al. (2018) studied the CEC in relation to the mineralogical composition of the Boom Clay. The Boom Clay is a potential host rock for radioactive waste and the CEC is related to the sorption potential of radionuclides to the host rock. They reported that the CEC could be used as an excellent proxy for the bulk-rock smectite content. Their method of calculating the smectitic content in the bulk rock directly from the CEC is: smectite content = $0.91 \times \text{CEC}$. For this, a CEC for an average charged smectite of around 100 mmol/100 g and a constant charge of 0.41 phuc for the smectite were assumed. When applied to the samples of this study, the CEC of the samples seems too low. Sample “clay” has a CEC of 19.2 mmol/100 g, calculated by this method, this would give a bulk-smectite content of 17.4%. However, sample “clay” contains 27% smectite (plus 4% vermiculite) in the bulk sample; according to the described method the CEC should be 29 to 34 (including vermiculite) mmol/100 g. This discrepancy can be explained in two different ways. One possible explanation could be the difference in methods used for the quantification of the clay minerals. This study used a semi-quantitative method developed by Schultz (1964) which works well for a relative comparison within a set of samples, Frederickx et al. (2018) used the “Sybilla” clay modeling software (© Chevron ETC), which overall results in more accurate data. The other explanation could be a higher layer charge of the smectites of the samples used in this study compared to the Boom Clay used by Frederickx et al. (2018). “In smectites with higher layer charge, swelling of layers is lower compared to smectites with lower layer charge, thus hindering the accessibility of incoming ions to the exchange sites” (Christidis, 2011).

5.4. Atterberg liquid limit (LL) and cation exchange capacity (CEC): A correlation analysis

Both the Atterberg LL and the CEC bear a correlation with the clay mineral content in the studied samples. The extent of correlation of the two methods is illustrated in Fig. 6. Here the CEC is plotted against Atterberg LL and the plasticity index. This comparative analysis shows positive, linear relationships between the variables of Atterberg LL and the CEC. Noteworthy R^2 values of 0.95 and 0.92 for the Atterberg LL and plasticity index, respectively, indicate a good correlation with the CEC.

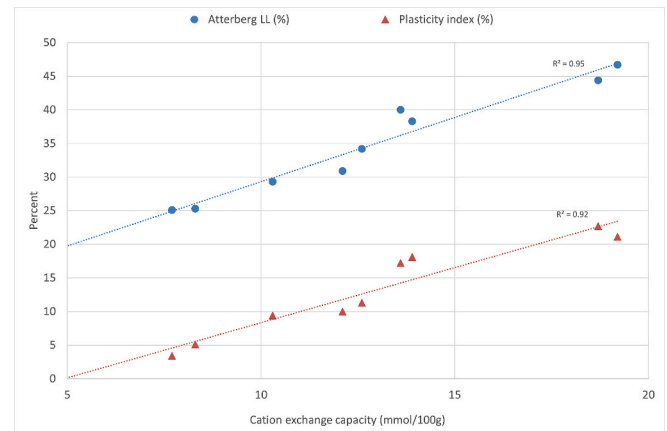


Fig. 6. Correlation of Atterberg liquid limit (LL) and plasticity index with cation exchange capacity.

Similar relationships between Atterberg LL and CEC are found in literature (Yilmaz, 2004; Mehta and Sachan, 2017; Spagnoli and Shimobe, 2019). This reinforces the hypothesis that increased CEC is indicative of higher Atterberg LL and plasticity index values and reflect a greater presence of expandable clay minerals. The cation exchange capacity is thus not only a measure of the reactive surface area of clays but also a reliable indicator of their geotechnical behavior.

5.5. Comparison: Atterberg liquid limit (LL), determination of the clay mineralogy based on X-ray diffraction and cation exchange capacity (CEC)

In this section, CEC is discussed as a potential alternative technique to determine sediment suitability for use as artificial geological barrier – a method which needs to be weighed against established laboratory methods, specifically the determination of the Atterberg LL and the analysis of clay minerals using X-ray diffraction. The distinguishing features of these three approaches, their variations in utility, and potential as tools for evaluating sediment characteristics and suitability for different applications within the geotechnical milieu are discussed in the following.

The Atterberg LL provides a direct correlation to the overall amount of clay minerals in the sample. Similar parallels can be drawn between the CEC and the proportion of clay minerals, denoting a significant relationship between the two. Furthermore, a clear connection between the Atterberg LL and the CEC is demonstrated, accentuating the crucial role of the clay mineral content in both of these methods.

Quantification through X-ray diffraction offers valuable insights into both the bulk and specific clay mineral content within the sample material, an advantage which is not obtained by the Atterberg LL and the CEC method. The Atterberg method produces additional data about the plasticity of the sediment that extend beyond the realm of clay mineralogy. The plasticity index is directly related to the permeability coefficient, which is crucial for the evaluation of a sediment as material for an artificial geological barrier. The CEC, on the other hand, indicates a measure of the ability of a sediment to adsorb cations.

While there are clearly established standards and procedures both for the Atterberg method and the quantification of clay minerals, there is neither an official standard nor an established method for CEC determination.

The scope of application of the three methods also differs. The determination of clay mineralogy using X-ray diffraction and the determination of the CEC can be carried out on all sediments, regardless of their mineralogical and granulometric composition. Application of the Atterberg LL is constrained by grain size, as grains with a diameter of $>400 \mu\text{m}$ must be removed. If the proportion of clay in the sample is too

low, the Atterberg LL cannot be determined, like for sample “sand” used in this work.

In evaluating these techniques, it has to be noted, that all three methods are also subject to the experience of respective specialists. When determining clay mineralogy, this particularly applies to quantification. The reflection areas of the clay minerals needed for quantification are subject to the judgment of a specialist and are therefore subjective and not completely reproducible. Additional difficulties in quantification arise from the different degrees of preferred orientation of individual clay minerals (Dohrmann et al., 2009). Reproducibility also poses a common challenge for the Atterberg LL. This is explicitly mentioned in [ÖNORM EN ISO 17892-12 \(2020\)](#): “It is known that the test results are subject to the judgment of the laboratory technician and that certain fluctuations in the results can occur” ([ÖNORM EN ISO 17892-12, 2020](#)). In contrast, the CEC is methodologically less subjective, imposing fewer demands on individual judgments. An interlaboratory study, involving five different laboratories and four reference materials gave a very high precision of the Cu-trien method with a standard deviation of ± 0.7 to ± 2.1 mmol/100 g for CECs that ranged from 11 to 87 mmol/100 g (Dohrmann et al., 2012). This shows the accuracy and reproducibility of the method and supports the potential for the CEC to serve as an alternative for both the Atterberg LL and the associated clay mineral analysis.

Concerning potential risks of the methods, it must be mentioned, that the CEC method requires caution due to the toxic nature of the chemicals (Cu(II)-ethylenediamine complex) involved. This warrants careful adherence to laboratory safety protocols, unlike the relatively safer applications of Atterberg LL. Also, extensive safety requirements for radiation protection have to be fulfilled using X-ray diffraction for clay mineral quantification.

CEC is less time-consuming, with the preparation and execution taking only three hours for a batch of eleven samples. This is a stark contrast to the time requirements of an Atterberg LL and the preparation time and evaluation effort for X-ray diffraction analysis. Furthermore, the cost effectiveness of the CEC method further underscores its potential as a viable alternative.

As demonstrated, these correlations worked well on samples typically used for geological barriers, these were smectite-rich clays mixed with silt and sand in certain proportions. However, for mixtures with clays with a different mineralogical composition and grain size distribution further investigations need to be carried out to establish the application in a wider context.

In conclusion, the CEC emerges as an attractive alternative to both the determination of the Atterberg LL and the clay mineralogy via X-ray diffraction for this set of samples. It can thus be used as a potential substitute offering a practical and time- and cost-efficient approach to evaluating fine-grained sediments for geotechnical applications.

6. Conclusions

Test materials of different grain sizes (“clay”, “loess”, and “sand”) were collected from two landfills “Kettlasbrunn” and “Mistelbach” in Austria. The samples and their mixtures were intended for the use in the construction of on-site artificial geological barriers. The cation exchange capacity (CEC) using the Cu-trien method was determined and compared to the currently used tests defined in an Austrian standard – both Atterberg Liquid limit (LL) and clay mineral analysis using X-ray diffraction. The results showed that bulk clay mineralogy correlates well with the Atterberg LL ($R^2 = 0.73$) and the CEC ($R^2 = 0.88$) and that the two methods – Atterberg LL and CEC- correlate even better ($R^2 = 0.95$). This implies that the CEC is a valid alternative to the Atterberg liquid limit, which in itself is controlled by the mineralogical composition of the material. The key advantages of the CEC are speed, accuracy, reproducibility, cost-efficiency and its ease of use. Based on the results of this work, CEC is considered a feasible alternative for material characterization.

CRedit authorship contribution statement

Zora Alice Kumm: Writing – original draft, Methodology, Data curation. **Susanne Gier:** Writing – review & editing, Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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