



## Research article

# The effects of potentially toxic metals (copper and zinc) on selected physical and physico-chemical properties of bentonites



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## ABSTRACT

The purpose of this study was to determine the effect of copper or zinc ions, absorbed by soil on its physical and physicochemical properties. The change in these properties may reduce the soil usefulness as a mineral protective barrier, for example, on hazardous waste landfills. Parameters such as granulometric composition, effective particle size  $d_{10}$ , empirical hydraulic conductivity, Atterberg limits, colloidal activity, specific surface area, sorption moisture content, and montmorillonite content were determined. The tests were carried out on model  $\text{Na}^+$  or  $\text{Ca}^{2+}$  samples of American bentonites (SWy-3, Stx-1b) and Slovak bentonite from Jelsový potok (BSvk), subjected to ion exchange for  $\text{Cu}^{2+}$  or  $\text{Zn}^{2+}$  ion. The content of elements was determined using inductively coupled plasma optical emission spectrometry (ICP-OES). Regression analysis showed a significant effect of  $\text{Zn}^{2+}$  ions on the reduction of sorption moisture content  $w_{95}$  and the increase in the hydraulic conductivity. Nearly complete negative correlation was obtained between the  $\text{Cu}^{2+}$  ion content and the specific surface area, sorption moisture content  $w_{50}$ , and montmorillonite content ( $R = -0.99$ ). It was observed that the significance of the influence of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions on specific clay properties differed, which indicates different behavior of these metals in the clay-water system. The different nature of clays contaminated with  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions justifies the need to continue research on other potentially toxic metals and to further search for prediction equations of the cohesive soil hydraulic conductivity based on soil parameters that are most frequently modified as a result of their impact.

## 1. Introduction

To be designated as bentonite, a soil must contain at least 70% montmorillonite a 2:1 layer of aluminum phyllosilicate clay. A layer is built from two sheets of silicon oxide tetrahedrons and one sheet of aluminum hydroxide octahedrons running parallel to each other. The interlayer space between the sheets is filled with water and exchangeable cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , etc.). The layer structure, as well as the small size of lamellar particles, determine the extremely high specific surface areas in these soils, owing to which the contact surface between the solid and liquid phases is the site of many physical and chemical phenomena. Water is strongly affecting with such clays, especially water related to the surface of particles known as “bound water”, which determines many physical properties of the soil, e.g. plastic limits, liquid limits. A part of this water, known as strongly bound water, corresponds to hygroscopic water ( $w_{95}$ ), which we can determine with use the Water Sorption test by Stepkowska (1977). Strongly bound water may remain in a liquid state even in very low negative temperatures of  $-70^\circ\text{C}$ , and this is

called unfrozen water. The amount of unfrozen water has an influence on leachate migration in the frozen clay-water system (Kruse and Darrow, 2017).

The specific properties of bentonites find their application in many industries. Researchers believe that bentonites are a cheap alternative for removing toxic metals from aqueous solutions such as  $\text{Cu}^{2+}$  (Turan and Ozgonenel, 2013; Tohdee and Asadullah, 2018),  $\text{Zn}^{2+}$  (Tohdee and Asadullah, 2018),  $\text{Ni}^{2+}$   $\text{Mn}^{2+}$  (Akpomie and Dawodu, 2015) and  $\text{U}^{6+}$  (Zahran et al., 2019). They are commonly used as mineral sealing materials for natural soils, which create barriers in landfills, including those with hazardous waste (Kozłowski et al., 2015; Krupskaya et al., 2017). Pursuant to the Regulation of the Minister of the Environment (Dz. U. [Journal of Laws] of 2013, item 523, as amended) and Council Directive 1999/31/EC, it is required that the landfill liner should have a suitable thickness, and the hydraulic conductivity ( $k$ ) should be smaller than  $1 \times 10^{-7}$  m/s for inert waste and smaller than  $10^{-9}$  m/s for other (including hazardous) wastes. Although the legislation does not impose additional criteria on the suitability of soils for layers of a mineral seal, many can be

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found in literature. Based on an analysis of the work of seven research teams, Łuczak-Wilamowska (2008) found that in addition to hydraulic conductivity, the most frequently applied parameters were: liquid limit, plasticity index, granulometric composition and clay mineral content. The data collected did not provide a definite answer as to the most optimal values of the soil parameters used for the mineral seal layers. Each of the research teams focused only on a few selected parameters. In addition, the authors presented divergent data with regard to, for example, the plasticity index, which according to different authors should be in the range between 7 to 10% (Daniel and Koerner, 1995), between 7 and 27% (Łuczak-Wilamowska, 1997), above 10% (EPA530-R-93-017), above 15% (Majer, 2005), above 20% (Jones et al., 1995) and below 20% (Widomski et al., 2018). It is important that this information can be used as a basis for further research in this field, but for a specific project. Literature provides only scarce information on the type and the parameter values of the bentonite used for the sealing of landfill sites. Cichy and Bryk (2006) recommended using the highest quality sodium bentonite, which contains more than 75% montmorillonite and has a specific surface area of more than 800 m<sup>2</sup>/kg. In turn, Evangeline and John (2010) and Naka et al. (2016) indicated that calcium bentonites may be more resistant than sodium bentonites to the chemical components contained in waste, and their ease of exchange in the environment with Na<sup>+</sup> ions may lead to similar permeabilities in both soil types. All the criteria presented are intended to provide, *inter alia*, geotechnical stability of deposited waste and reliable operation of the landfill for at least 30 years from the date of its closure (Dz. U. [Journal of Laws] of 2013, item 523, as amended). Regardless of the sodium or calcium form of bentonite and the selection of the criterion of its suitability as mineral sealing materials (hydraulic conductivity, liquid limit, plasticity index, granulometric composition, clay mineral content, etc.), numerous studies indicated that the contact of bentonite with landfill leachates can modify, to varying degrees, the previously mentioned engineering parameters.

According to the majority of researchers, the action of leachate on the soil depends on its plasticity level (high or low plasticity clay), the soil-leachate interaction time and leachate concentration (Evangeline and John, 2010; Shariatmadari et al., 2011; Wuana and Okieimen, 2011; Meril, 2014; Krupskaya et al., 2017; Xu et al., 2019). Generally, changes in soil parameters increase with increasing exposure time to leachates such as NaCl, KCl, CaCl<sub>2</sub>, MgCl<sub>2</sub>, ZnCl<sub>2</sub>, CuCl<sub>2</sub>, HCl, HNO<sub>3</sub>, NH<sub>4</sub>Cl, CH<sub>3</sub>COOH and their increasing concentration (0.25–3 mol L<sup>-1</sup>). Meril (2014) reports that although the type of leachate is usually of secondary importance in developing soil parameters, it should not be ignored (Evangeline and John, 2010; Soumya and Sudha, 2016; Xu et al., 2019). Reports on the studies of the effects of landfill leachate are most often focused on the following bentonite geotechnical parameters: hydraulic conductivity (Arasan, 2010; Evangeline and John, 2010; Shariatmadari et al., 2011; Meril, 2014; Lu et al., 2015; Kobayashi et al., 2017; Oyediran and Olalusi, 2017; Li et al., 2019; Wang et al., 2019; Xu et al., 2019), Atterberg limits and plasticity index (Arasan, 2010; Evangeline and John, 2010; Shariatmadari et al., 2011; Harun et al., 2013; Meril, 2014; Sandhya and Shiva, 2017), granulometric composition (Tito et al., 2008; Harun et al., 2013; Meril, 2014; Kobayashi et al., 2017; Krupskaya et al., 2017; Sandhya and Shiva, 2017), specific surface area (Meril, 2014; Krupskaya et al., 2017). These authors agree as to the direction of changes in hydraulic conductivity and plasticity index of bentonites and their mixtures with sand (Soumya and Sudha, 2016) after the exposure to landfill leachate. Generally, the value of hydraulic conductivity increases, and the plasticity index decreases. The changes extend with increasing leachate concentration and time of interaction with the soil. The increased period of exposure to leachate alters the granulometric composition of bentonites. According to Krupskaya et al. (2017), large aggregates of different size form in the soil. Similar conclusions are included in the study by Sandhya and Shiva (2017), where, additionally, the formation of new minerals in the montmorillonite-illite group is reported. The effect of the landfill leachate on the specific surface area still needs to be identified. Krupskaya et al. (2017) reports that the specific

surface area in bentonites increases after 108 h of HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and HCl application. The main reason is its microstructural remodeling due to the layer charge reduction. The same tendency due to synthetic leachates is observed by Meril (2014) and is explained by the disintegration of soil particles and reduction of pore spaces and, as a result, an increase in the specific surface area. A literature review covering the last several years offers only partial answers to the probable change in the properties of bentonites due to leachate. The tests were carried out on soils with different initial values of the parameters and under varied experimental conditions (different leachate concentrations and types). Some issues remain unexplained or are poorly understood. The problem is still opened and requires further detailed research.

To my knowledge, no work has reported on the effects of potentially toxic metals, copper and zinc, on the granulometric, plastic and sorption parameters of bentonites, especially regarding homoionic (copper and zinc) forms of model source clays. The change in values of these parameters may reduce soil usefulness as a mineral protective barriers, e.g. on hazardous waste landfills. The author has not found any studies conducted on model soils that ensure comparability of the results indicating that copper or zinc ions present in a complex water-soil medium are responsible for the alteration of the physicochemical parameters of bentonites. In all the studies mentioned above, no statistical analysis was provided to verify the obtained results. In addition, the researchers studying the effect of potentially toxic metals on bentonites (Lange et al., 2005; Dutta and Mishra, 2016; Wang et al., 2019; Xu et al., 2019) examined the adsorption of metal ions in different solvents, e.g. copper(II) chloride or zinc(II) chloride. It seems that only full-scale ion exchange will allow the metal to be incorporated into the mineral structure and provide it with some stability that would not be disturbed by the procedures of determination of soil geotechnical parameters. Rinsing of the excess chlorine, which is part of the ion exchange procedure, will also prevent the clay properties from being affected. Frankovská et al. (2010) indicate that chlorine ions can have a significant effect on the permeability of bentonites.

Herein, I present a study on the influence of high levels of metals copper or zinc on the engineering parameters of bentonites, such as granulometric composition, effective particle size d<sub>10</sub>, empirical hydraulic conductivity, Atterberg limits, activity of clays, specific surface area, sorption moisture content and montmorillonite content. The experiments utilized three well-known source clays (sodium and calcium forms). Full-scale ion exchanges procedure were then conducted, and the homoionic forms of clays (copper and zinc forms) were obtained. The content of metals in clays was determined with the use of the inductively coupled plasma optical emission spectrometry method (ICP-OES). The engineering parameters were determined in clays before and after ion exchanged utilizing applicable procedures. Verification of the obtained results was performed with Statistica 8 software.

## 2. Materials and methods

### 2.1. Testing materials

The tests were carried out on model Na<sup>+</sup> or Ca<sup>2+</sup> samples of American bentonites (SWy-2, Stx-1b, respectively) and natural Ca<sup>2+</sup> Slovak bentonite from Stará Kremnička - Jelšový potok (BSvk), subjected to ion exchange for Cu<sup>2+</sup> or Zn<sup>2+</sup> ions. American bentonites were obtained from the Source Clays Repository of the Clay Mineral Society. Slovak bentonite were obtained from the ZGM Zębiec S.A. company – one of the largest importers of bentonites in Poland.

### 2.2. Testing methods

#### 2.2.1. Chemical preparation of samples

The procedure of preparing homoionic forms of bentonite were performed according to the Kozłowski et al. (2014) study. Each 50 grams of bentonite was saturated with 10 liters of 1 mol L<sup>-1</sup> zinc or copper (II)

chloride solution. The solutes were hand mixed to obtain a homogeneous mixtures. Next, the solutions were allowed to stand for 48 hours. After that time, remaining the overlying water was carefully decanted. After saturation three times, the sediments formed after decanting were transferred into the chloride-permeable membranes, which were placed in containers with a mechanically forced circulation of demineralized water. The water in the containers was repeatedly changed. The rinsing operations were carried out until the disappearance of the characteristic reaction with AgNO<sub>3</sub> (duration on average for 40 days). The clay pastes were transferred to glass beakers and were then air-dried at room temperature.

Before proceeding with the analysis, the clays were subjected to drying at a temperature of 110 °C and then mineralization. A solution of nitro-hydrochloric acid (30 mL HCl (1.19 g/mL) and 10 mL HNO<sub>3</sub> (concentrated)) was poured into the samples with 2 gram of dry soil. Next, the samples were heated for 30 minutes under the watch glass and evaporated almost to dryness. The residue was dissolved in 25 mL of HCl (5% concentration). The cooled solution was filtered through a paper filter into a volumetric flask and supplemented with demineralized water to 100 mL. The determination of the content of metals in the clay matrices was done with the use of inductively coupled plasma optical emission spectrometry (ICP- OES).

### 2.2.2. Determination of soil parameters

The soil parameters useful for assessing the properties of soils as mineral protective barriers have been determined. These were parameters such as particle size distribution, effective particle size  $d_{10}$ , empirical hydraulic conductivity, Atterberg limits, activity of clays, specific surface area, sorption moisture content and montmorillonite content.

Particle size distribution (PSD) is a significant influencing factor with a lot of physical properties of soil (e.g. hydraulic conductivity) and the processes involved with it. The measurements were made using a HELOS/BF SUCELL laser granulometer to determine the percentage of particles in a size range of 0.2–87.5 μm. According to Cichy and Bryk (2006), this is the method recommended to determine the clay fraction in Skempton's Activity formula.

An effective particle size of  $d_{10}$  indicates the quantitative relationships between permeability and grain size distribution. It is a parameter used in empirical hydraulic conductivity equations.  $d_{10}$  values were calculated from grain size distribution curves.  $d_{10}$  is defined as the diameter at which 10% of the sample's mass is comprised of particles with a diameter less than this value.

Hydraulic conductivity was determined using the empirical Hazen-Tkaczukowa Eq. (1). This formula is used for the permeability prediction of clayey sand, sandy silt and sandy clay with a content of particles with a diameter less than 1 μm in an interval "a" between 2% and 20% (Kacprzak et al., 2010). This method was selected due to the fact that its assumptions can be met in the tested soils.

$$k = \frac{0.0093}{a^2} d_{10}^2 \quad (1)$$

**Table 1**

Content of elements in the dry soil matrix before and after ion exchange (for Cu<sup>2+</sup> or Zn<sup>2+</sup> ions), determined by the ICP-OES method [mg/kg dry of soil].

| element | SWy-3 (natural Na <sup>+</sup> form) |   | Stx-1b (natural Ca <sup>2+</sup> form) |   | BSvk (natural Ca <sup>2+</sup> form) |   |
|---------|--------------------------------------|---|--|---|--------------------------------------|---|
|         | before ion exchange                  | after ion exchange for<br>Cu <sup>2+</sup> Zn <sup>2+</sup> | before ion exchange                    | after ion exchange for<br>Cu <sup>2+</sup> Zn <sup>2+</sup> | before ion exchange                  | after ion exchange for<br>Cu <sup>2+</sup> Zn <sup>2+</sup> |
| Na      | 10086                                | 405.3    994.91   | 1970.3                                 | 362.74    885.1   | 1151.2                               | 412.57    1204.6  |
| Ca      | 8282.4                               | 2028    4526  | 11802                                  | 1491.3    2985  | 11945                                | 1598    2778  |
| Cu      | 12.8                                 | 11221    109.47   | 8.97                                   | 5427.5    52.3  | 6.28                                 | 7676.9    39.55   |
| Zn      | 163.66                               | 83.2    44463   | 73.68                                  | 92.96    16153  | 64.54                                | 95.61    17857  |
| Pb      | 26.01                                | 9.5    14.61  | 2.59                                   | 6.07    7.53  | 17.02                                | 17.93    17.5   |
| Ni      | 7.27                                 | 33.53    27.27  | 7.57                                   | 16.27    15.3   | 7.22                                 | 22.02    24.2   |
| Cr      | 11.24                                | 388.81    114.85  | 13.95                                  | 175.04    82.43   | 10.1                                 | 228.74    87.25   |
| Cd      | 0.37                                 | 0.95    0.67  | 0.25                                   | 0.03    0.42  | 0.27                                 | 0.63    0.61  |

$k \left[ \frac{m}{s} \right]$ , where  $d_{10}$  is a diameter at which 10% of the sample's mass is comprised of particles with a diameter less than this value,  $a$  is the content of particles with a diameter less than 1 μm.

The liquid limit (LL) was determined by the use of a Casagrande's cup device, and the plastic limit (PL) was determined by the use of rolling test (ASTM D4318-17e1). The Plasticity Index (PI) was calculated as the difference between the liquid limit and the plastic limit (PI = LL-PL). Next, the colloidal Activity of clay (A), as the ratio of the plasticity index to the clay fraction content obtained by laser granulometer, was determined.

The specific surface area (S), sorption moisture ( $w_{50}$ ,  $w_{95}$ ) and montmorillonite (Mt) content were determined with the use of the water sorption test (WST) method according to Stępkowska (1977). This is a very useful method in clay-water systems, as water in the inter-packet spaces of clay minerals is measure. Thus, the WST method seems to be better describe the natural condition in clay-water system than the ethylene glycol monoethyl ether (EGME) adsorption or Brunauer–Emmett–Teller (BET) methods, where the inter-packet spaces is not available for water (Kumor, 1989; Kozłowski and Nartowska, 2013). The specific surface area of clays was determined with the use of the Eq. (2) according to Stępkowska (1977).

$$S = 6 \cdot (w_{50} \cdot 5.85) \quad (2)$$

$S \left[ \frac{m^2}{g} \right]$ , where  $w_{50}$  is the sorption moisture at a vapor pressure  $p:po = 0.5$  determined by drying at 220 °C.

### 2.2.3. Statistical treatments

To check whether the type of dominant cation (Na<sup>+</sup>, Ca<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>) has a significant effect on the physical and physicochemical parameters of clays, a multivariate analysis of variance (MANOVA) was performed with Statistica 8. The dependent variables were initially classified in three groups: sorption parameters (S,  $w_{50}$  and  $w_{95}$ , Mt), plastic parameters (PL, LL, PI, A) and granulometric parameters (clay fraction, silt fraction,  $d_{10}$ , diameter less than 1 μm, hydraulic conductivity acc. Eq. (1)). The significance ( $p < 0.05$ ) of dominant ions for the three groups was assessed. All  $p$  values are lower by several orders, which allows rejecting the null hypothesis about equal means. In addition, the near-zero value of Wilks' lambda confirms high discriminatory capacity of the model. To state clearly which mean values of particular soil parameters differ from each other, depending on the dominant cation, Tukey's post-hoc test was used. This test is recommended for comparing pairs of means and the amount of likelihood for a Type 1 error is smaller than in the least significant difference (LSD) test. The mean values of individual soil parameters were observed in groups determined by the type of dominant cation.

## 3. Results and discussion

The content of metals in the clay matrices of SWy-3, Stx-1b and BSvk after exchange for Cu<sup>2+</sup> and Zn<sup>2+</sup> ions differed (Table 1). Similarly, the

**Table 2**Sorpton, plastic and granulometric properties of the clays before and after ion exchange (for Cu<sup>2+</sup> or Zn<sup>2+</sup> ions).

| Property                 | SWy-3   |                          |                         | Stx-1b                  |                         |                         | BSvk                    |                        |                         |                         |
|--------------------------|---|--------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|------------------------|-------------------------|-------------------------|
|                          | Natural   | Cu <sup>2+</sup>         | Zn <sup>2+</sup>        | Natural                 | Cu <sup>2+</sup>        | Zn <sup>2+</sup>        | Natural                 | Cu <sup>2+</sup>       | Zn <sup>2+</sup>        |                         |
| sorption parameters      | Specific surface area S <sub>total</sub> [m <sup>2</sup> /g] <sup>a</sup> | 307.2                    | 355.37                  | 516.03                  | 568.37                  | 413.8                   | 537.95                  | 670.64                 | 460.19                  | 556.68                  |
|                          | Sorption moisture w <sub>95</sub> [%] <sup>a</sup>                        | 21.67                    | 22.13                   | 17.05                   | 29.08                   | 27.7                    | 22.67                   | 30.14                  | 26.92                   | 20.1                    |
|                          | Sorption moisture w <sub>50</sub> [%] <sup>a</sup>                        | 8.75                     | 10.12                   | 14.7                    | 16.19                   | 11.79                   | 15.33                   | 19.11                  | 13.11                   | 15.86                   |
| plastic parameters       | Mt content [%] <sup>a</sup>   | 34.65                    | 40.52                   | 61.08                   | 68.12                   | 47.82                   | 64.01                   | 82.40                  | 53.76                   | 66.54                   |
|                          | Liquid limit LL[%]  | 519                      | 146                     | 104                     | 142                     | 136                     | 101                     | 165                    | 154                     | 119                     |
|                          | Plastic limit PL [%]  | 35                       | 42                      | 54                      | 44                      | 50                      | 73                      | 46                     | 52                      | 61                      |
|                          | Plasticity index PI [%]   | 484                      | 104                     | 50                      | 98                      | 86                      | 28                      | 119                    | 102                     | 58                      |
| granulometric parameters | Skempton's activity A[-] <sup>b</sup>                                     | 12.69                    | 8.17                    | 12.2                    | 8.26                    | 6.12                    | 2.36                    | 11.26                  | 8.06                    | 7.37                    |
|                          | Clay fraction [%] <sup>c</sup>  | 38.13                    | 12.73                   | 4.1                     | 11.87                   | 14.04                   | 11.87                   | 10.57                  | 12.65                   | 7.87                    |
|                          | Silt fraction [%] <sup>c</sup>  | 61.87                    | 87.16                   | 95.43                   | 87.95                   | 83.72                   | 87.84                   | 89.43                  | 87.23                   | 92.13                   |
|                          | Effective particle size d <sub>10</sub> [mm] <sup>c</sup>                 | 0.0011                   | 0.0017                  | 0.0049                  | 0.0019                  | 0.0016                  | 0.0018                  | 0.0019                 | 0.0017                  | 0.0023                  |
|                          | Empirical hydraulic conductivity [m/s] <sup>d</sup>                       | 1.52 × 10 <sup>-10</sup> | 3.31 × 10 <sup>-9</sup> | 8.74 × 10 <sup>-8</sup> | 6.27 × 10 <sup>-9</sup> | 2.28 × 10 <sup>-9</sup> | 2.44 × 10 <sup>-9</sup> | 9.9 × 10 <sup>-9</sup> | 3.65 × 10 <sup>-9</sup> | 9.54 × 10 <sup>-9</sup> |

<sup>a</sup> Water Sorption Test (WST) by *Stępkowska (1977)*.<sup>b</sup> In this formula the clay fraction content obtained by laser granulometer.<sup>c</sup> Laser diffraction method.<sup>d</sup> acc. to Hazena-Tkaczukowej Eq. (1).

soil parameters changed (Table 2).

MANOVA of the major cation (Na<sup>+</sup>, Ca<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>) for the soil parameters (Table 3) showed that the type of dominant cation in the clays (SWy-3, Stx-1b and BSvk) has a significant effect on the behavior of their sorption, plastic and granulometric parameters.

### 3.1. The effect of Cu<sup>2+</sup> or Zn<sup>2+</sup> ions on sorption parameters of clays

Tukey's HSD test showed that the influence of Cu<sup>2+</sup> ions on the soil specific surface area was particularly significant in soils with the highest specific surface areas (S ~600 m<sup>2</sup>/g) and montmorillonite content (Mt ~75%), whereas the influence of Zn<sup>2+</sup> ions proved to be the most significant in soils with the smallest specific surfaces (S ~300 m<sup>2</sup>/g) and lowest montmorillonite content (Mt ~35%). Identical relationships were obtained for sorption moisture w<sub>50</sub>. It was also observed that in the above specific surface area ranges, the influence of Cu<sup>2+</sup> ions was as important as that of Na<sup>+</sup> ions (if S ~600 m<sup>2</sup>/g), and the influence of Zn<sup>2+</sup> ions as that of Ca<sup>2+</sup> ions (if S ~300 m<sup>2</sup>/g), which may indicate their similar behavior in the soil-water system, especially in plastic consistency (Table 4). Na<sup>+</sup> bentonite (SWy-3) and Cu<sup>2+</sup> form of SWy-3, Stx-1b and BSvk bentonites lower the specific surface areas than Ca<sup>2+</sup> and Zn<sup>2+</sup> forms of bentonites were observed. Thus, the statistical effect was more visible in soils if the specific surface area was high and a large decrease in the parameter value was observed. The specific surface area of Na<sup>+</sup> and Cu<sup>2+</sup> bentonites was probably related to their microstructural parameters

**Table 3**Multivariate tests of significance (MANOVA: Wilks' Lambda) of the major cation (Na<sup>+</sup>, Ca<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>) for the soil parameters.

|   | Value | F         | df | Error df | p     | significance |
|---|-------|-----------|----|----------|-------|--------------|
| <b>sorption parameters<sup>a</sup></b>      |       |           |    |          |       |              |
| Intercept                                   | 0.001 | 470.566   | 4  | 2        | 0.002 | **           |
| Major cation                                | 0.000 | 8.635     | 12 | 5.583    | 0.009 | **           |
| <b>plastic parameters<sup>b</sup></b>       |       |           |    |          |       |              |
| Intercept                                   | 0.001 | 753.205   | 3  | 3        | 0.000 | ***          |
| Major cation                                | 0.001 | 17.108    | 9  | 7.452    | 0.000 | ***          |
| <b>granulometric parameters<sup>c</sup></b> |       |           |    |          |       |              |
| Intercept                                   | 0.000 | 1.426E+21 | 4  | 2        | 0.000 | ***          |
| Major cation                                | 0.000 | 6.529E+07 | 12 | 5.583    | 0.000 | ***          |

Significant at the \*\*\*0.001 \*\*0.01 \*0.05 probability level; NS. not significant at the 0.05 probability level.

<sup>a</sup> S. w<sub>50</sub>-w<sub>95</sub>. Mt.<sup>b</sup> LL. PL. PI. A.<sup>c</sup> clay fraction. silt fraction. d<sub>10</sub>. d < 0.001mm. hydraulic conductivity.

and a decrease in the interplanar spacing (Nartowska et al., 2019). In contrast, the behavior of Zn<sup>2+</sup> and Ca<sup>2+</sup> forms of bentonites is probably related to a clay's physical parameters, not dependent on the

**Table 4**Tukey's HSD test of the major cation (Na<sup>+</sup>, Ca<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>) on the selected soil parameters\*.

| Values of the parameters               | Na <sup>+</sup>                  | Ca <sup>2+</sup> | Cu <sup>2+</sup> | Zn <sup>2+</sup> |
|--|----------------------------------|------------------|------------------|------------------|
| <b>sorption parameters</b>             |                                  |                  |                  |                  |
| S <sub>total</sub> [m <sup>2</sup> /g] | Error: MS within = 2315.1 df = 5 |                  |                  |                  |
| 307.2                                  |                                  | <b>0.012</b>     | 0.354            | <b>0.033</b>     |
| 409.79                                 | 0.354                            | <b>0.018</b>     |                  | 0.079            |
| 536.89                                 | <b>0.033</b>                     | 0.341            | 0.079            |                  |
| 619.51                                 | <b>0.012</b>                     |                  | <b>0.018</b>     | 0.341            |
| w <sub>95</sub> [%]                    | Error: MS within 6.917 df = 5    |                  |                  |                  |
| 19.94                                  | 0.937                            | <b>0.0362</b>    | 0.152            |                  |
| 21.67                                  |                                  | 0.181            | 0.606            | 0.937            |
| 25.583                                 | 0.606                            | 0.421            |                  | 0.152            |
| 29.61                                  | 0.181                            |                  | 0.421            | <b>0.0362</b>    |
| Mt [%]                                 | Error: MS within 40.951 df = 5   |                  |                  |                  |
| 34.651                                 |                                  | <b>0.013</b>     | 0.402            | <b>0.039</b>     |
| 47.371                                 | 0.402                            | <b>0.018</b>     |                  | 0.086            |
| 63.877                                 | <b>0.039</b>                     | 0.317            | 0.086            |                  |
| 75.262                                 | <b>0.014</b>                     |                  | <b>0.018</b>     | 0.317            |
| <b>plastic parameters</b>              |                                  |                  |                  |                  |
| LL [%]                                 | Error: MS within 122.63 df = 5   |                  |                  |                  |
| 519                                    |                                  | <b>0.000</b>     | <b>0.000</b>     | <b>0.000</b>     |
| 153.5                                  | <b>0.000</b>                     |                  | 0.849            | <b>0.023</b>     |
| 145.33                                 | <b>0.000</b>                     | 0.849            |                  | <b>0.033</b>     |
| 108                                    | <b>0.000</b>                     | <b>0.023</b>     | <b>0.033</b>     |                  |
| PI [%]                                 | Error: MS within 179.57 df = 5   |                  |                  |                  |
| 484                                    |                                  | <b>0.000</b>     | <b>0.000</b>     | <b>0.000</b>     |
| 108.5                                  | <b>0.000</b>                     |                  | 0.800            | <b>0.013</b>     |
| 97.33                                  | <b>0.000</b>                     | 0.800            |                  | <b>0.019</b>     |
| 45.33                                  | <b>0.000</b>                     | <b>0.013</b>     | <b>0.019</b>     |                  |
| <b>granulometric parameters</b>        |                                  |                  |                  |                  |
| Clayey fraction content [%]            | Error: MS within 6.4571 df = 5   |                  |                  |                  |
| 38.13                                  |                                  | <b>0.001</b>     | <b>0.002</b>     | <b>0.000</b>     |
| 13.14                                  | <b>0.002</b>                     | 0.834            |                  | 0.174            |
| 11.22                                  | <b>0.001</b>                     |                  | 0.840            | 0.544            |
| 7.9467                                 | <b>0.000</b>                     | 0.544            | 0.174            |                  |
| <b>d &lt; 1µm fraction content [%]</b> |                                  |                  |                  |                  |
| 8.38                                   |                                  | <b>0.002</b>     | <b>0.003</b>     | <b>0.002</b>     |
| 3.0183                                 | <b>0.003</b>                     | 0.513            |                  | 0.750            |
| 2.4733                                 | <b>0.002</b>                     | 0.938            | 0.750            |                  |
| 2.1325                                 | <b>0.002</b>                     |                  | 0.513            | 0.938            |

\***Bold** correlations are significant at p < 0.05.**MS:** Mean Square**df:** degrees of freedom.

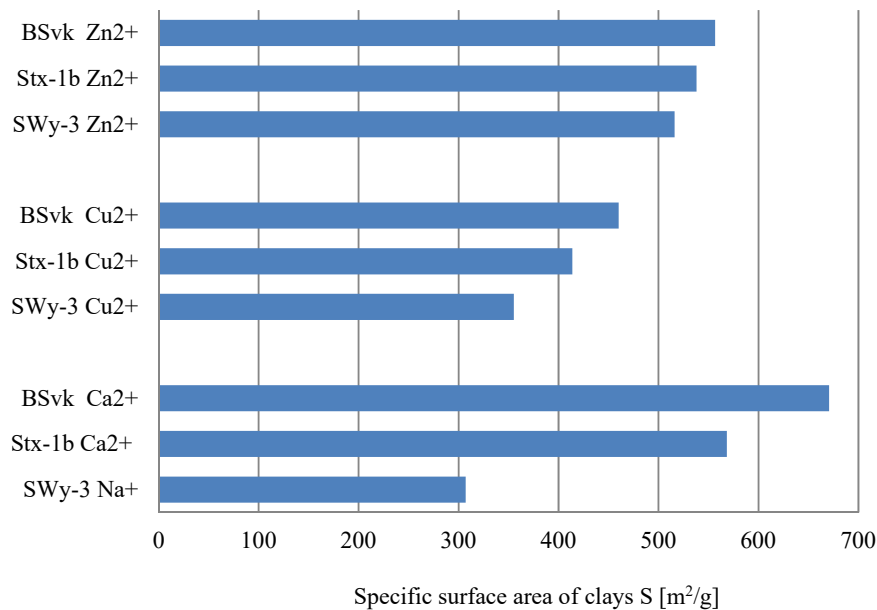


Fig. 1. Total surface area of clays depending on the type of dominant metal.

microstructure and the specific surface area of soil. Additionally, it was observed that the specific surface area of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  forms of bentonites SWy-3, Stx-1b and BSvk has a specific range, depending on the type of dominant metal but regardless of its initial form,  $\text{Na}^+$  or  $\text{Ca}^{2+}$  (Fig. 1).

Apparently montmorillonite can adsorb a well-defined amount of each ion into its layers. Some of the absolute amounts of adsorbed  $\text{Zn}^{2+}$  ions for a given metal concentration in the solution were provided by Helios-Rybacka and Kyziol (1990). However, due to the application of a more complex ion exchange process that allows the incorporation of trace metal ions into the mineral structure, it is difficult to refer to these values. In the case of sorption moisture  $w_{95}$ , significant relationships in Tukey's test was seen for  $\text{Zn}^{2+}$  ions in soils with the highest hygroscopic moisture ( $w_{95} \sim 29\%$ ). Additionally, a regression analysis was performed, which showed a significant decrease in hygroscopic moisture with increasing  $\text{Zn}^{2+}$  ion content in the soil (Table 5).

The effect of  $\text{Ca}^{2+}$  ions were significant for soils with the lowest hygroscopic moisture ( $w_{95} \sim 19\%$ ). This may indicate a different effect of  $\text{Ca}^{2+}$  and  $\text{Zn}^{2+}$  ions on the content of water strongly bound to the surface of the soil and thus on the unfrozen water content in the frozen soil-water system. The results indicate the need for further detailed research in this area. The unfrozen water content is a common parameter used in models for forecasting the depth and time of freezing and in modelling of heat

transfer in the soil-water system, which can help understand the behavior of clays contaminated with trace metals ions in the frozen environment (Kozłowski, 2004).

### 3.2. The effect of $\text{Cu}^{2+}$ or $\text{Zn}^{2+}$ ions on plastic parameters of clays

In the case of plastic parameters, Tukey's HSD test showed statistically significant differences for the liquid limit and plastic index. The effect of  $\text{Cu}^{2+}$  ions was significant in the clays with the highest and lowest liquid limits and plastic indexes, LL  $\sim 519\%$ /PI  $\sim 484\%$  and LL  $\sim 108\%$ /PI  $\sim 45.3\%$ , respectively. The first observation is important as indicating a possible adverse interaction between  $\text{Cu}^{2+}$  ions and the sealing soils that usually have high liquid limits. The influence of  $\text{Zn}^{2+}$  ions was found to be significant for all the soils under analysis (SWy-3, Stx-1b and BSvk) within the entire range of LL and PI values. No statistically significant differences were obtained for the plastic limit, which may indicate that the dominant ion has no influence on the soil in the solid state in the non-frozen system. Surprisingly, no significant differences in colloidal activity were observed. This is a parameter considered by some authors (Rowe et al., 1995) as important in terms of choosing bentonite for sealing waste landfills. In the context of the Tukey's test results obtained, it is necessary to conduct tests on a larger number of samples to assess the suitability of this parameter for use in selecting mineral sealing barriers in landfills.

Table 5

Multiple regression analysis between the  $\text{Zn}^{2+}$  ions and effective diameter  $d_{10}$ , hydraulic conductivity  $k$  calculated in accordance with the Hazen-Tkaczukowa Eq. (1) and hygroscopic water content  $w_{95}^*$ .

| independent variable $\text{Zn}^{2+}$   |                             |              |                                   |                    |               |              |              |
|---|-----------------------------|--------------|-----------------------------------|--------------------|---------------|--------------|--------------|
| dependent variable  | the unstandardized beta (B) | Std. error B | the standardized beta ( $\beta$ ) | Std. Error $\beta$ | t test value  | p-value      | significance |
| R = 0.911 R <sup>2</sup> = 0.83 adj. R <sup>2</sup> = 0.81 Std. error of estimate: 0.0005 |                             |              |                                   |                    |               |              |              |
| Intercept   |                             |              | <b>0.002</b>                      | <b>0.000</b>       | <b>8.396</b>  | <b>0.000</b> | ***          |
| $d_{10}$  | <b>0.911</b>                | <b>0.156</b> | <b>0.000</b>                      | <b>0.000</b>       | <b>5.847</b>  | <b>0.000</b> | ***          |
| R = 0.885 R <sup>2</sup> = 0.78 adj. R <sup>2</sup> = 0.75 Std. error of estimate: 0.0000 |                             |              |                                   |                    |               |              |              |
| Intercept   |                             |              | 0.000                             | 0.000              | -0.050        | 0.962        | NS           |
| $k$   | <b>0.885</b>                | <b>0.176</b> | <b>0.000</b>                      | <b>0.000</b>       | <b>5.035</b>  | <b>0.001</b> | **           |
| R = 0.756 R <sup>2</sup> = 0.571 adj. R <sup>2</sup> = 0.51 Std. error of estimate: 3.128 |                             |              |                                   |                    |               |              |              |
| Intercept   |                             |              | <b>26.105</b>                     | <b>1.222</b>       | <b>21.36</b>  | <b>0.000</b> | ***          |
| $w_{95}$  | <b>-0.756</b>               | <b>0.248</b> | <b>0.000</b>                      | <b>0.000</b>       | <b>-3.052</b> | <b>0.018</b> | *            |

\***Bold** correlations are significant at  $p < 0.05$ .

Significant at the \*\*\*0.001 \*\*0.01 \*0.05 probability level; NS. not significant at the 0.05 probability level.



The new research would confirm the assumption of some resistance of soil activity to the interaction of selected trace metal ions, for example,  $Zn^{2+}$  ions, particularly in sodium bentonites. Despite no statistical impact of dominant ions, in  $Na^+$ SWy-3, the soil activity was found to remain at the similar level after the exchange for the  $Zn^{2+}$  ion. In  $Ca^{2+}$ -bentonites (Stx-1b and BSvk), the drop in activity was observed after the exchange for the  $Zn^{2+}$  ion. Regardless of the initial form of bentonite  $Na^+$  (SWy-3) or  $Ca^{2+}$  (Stx-1b and BSvk), the exchange for  $Cu^{2+}$  reduced the soil colloidal activity.

### 3.3. The effect of $Cu^{2+}$ or $Zn^{2+}$ ions on granulometric parameters of clays

Tukey's HSD test showed a statistically significant influence of  $Cu^{2+}$  and  $Zn^{2+}$  on clay fraction determined from laser diffraction method solely in the case of clay  $Na^+$ SWy-3 with the highest clay fraction content (clay fraction ~38.13%). These observations confirm that such soils are especially susceptible to the action of toxic metals, as found by Helios-Rybicka and Kyziol (1990), whose studies revealed that the toxic metal contents in the clay fraction was higher than in the silt fraction of bottom sediment. The particles finer than  $2\mu m$  that have the highest content of montmorillonite absorb toxic metal ions due their high cation exchange capacity (Turan and Ozgonenel, 2013; Akpomie and Dawodu, 2015; Kozłowski et al., 2015; Krupskaya et al., 2017). The most popular empirical model of hydraulic conductivity estimation for clay-sand soils (equation 1) is based on the effective diameter  $d_{10}$  and the content of particles with diameter less than  $1\mu m$ . Tukey's HSD test states that the type of dominant ion ( $Na^+$ ,  $Ca^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ) has no statistical significant effect on the effective diameter  $d_{10}$ . Thus the hydraulic conductivity of cohesive soils cannot be based on only this one parameter. It is known that bentonites with dominant  $Na^+$  ion have particularly low permeability (Cichy and Bryk, 2006). The effect of the ion on hydraulic conductivity seems obvious. The parameter proposed by Hazen-Tkaczukowa (equation 1) (the content of particles with  $d < 1\mu m$ ) and used in the Tukey's HSD test proves to be statistically significant for  $Na^+$  ion in each of the groups under analysis. The influence of  $Cu^{2+}$  and  $Zn^{2+}$  is significant in the soils when the content of such particles is the highest and reaches more than 8% (Table 4).  $Na^+$  SWy-3 is such a soil. It seems that hydraulic conductivity estimated using those two parameters adequately describes the behavior of selected cohesive soils, especially those whose ions affect the change in  $d_{10}$  value. The regression analysis results showed statistical significance influence of the  $Zn^{2+}$  content on effective diameter and empirical hydraulic conductivity according to Hazen-Tkaczukowa (equation 1) (Table 5).

The effective diameter  $d_{10}$  and hydraulic conductivity increased with increasing  $Zn^{2+}$  content in the soils (Stx-1b, BSvk and SWy-3, respectively). That fairly low increase in hydraulic conductivity (from  $k = 1.52 \cdot 10^{-10}$  to  $k = 8.74 \cdot 10^{-8}$  m/s) violates the limit value of  $k \leq 10^{-9}$  m/s for the sealing of hazardous waste landfills stipulated in Council Directive 1999/31/EC. These observations are particularly worrisome, considering the results showing that the effect of  $Zn^{2+}$  is most significant on  $Na^+$  SWy-3 (Tables 2 and 4), and sodium bentonites are highly recommended for sealing landfills and waste disposal sites (Cichy and Bryk, 2006). In terms of the results obtained, sodium bentonites seem to be less resistant to the increase in hydraulic conductivity due to  $Zn^{2+}$ . Assumptions of better resistance of  $Ca^{2+}$  bentonites to landfill leachate have been previously reported by Evangeline and John (2010) and Naka et al. (2016).

In the light of the results, it seems necessary to raise the issue of parameters most often given as a criterion for the selection of bentonites for sealing of landfills. These are montmorillonite content and the specific surface area. It should be noted that  $Na^+$ SWy-3 has the smallest specific surface area and montmorillonite content among the studied soils and yet it has the highest colloidal activity (Table 2) additionally confirmed by the highest adsorption of  $Cu^{2+}$  or  $Zn^{2+}$  ions from the soils under test. This is explained by the special nature of  $Na^+$  SWy-3, which most montmorillonite accumulates in the clay fraction. In their experiments, Chipera and Bish (2001) evaluated the content of montmorillonite for particles

less than  $2\mu m$  to be 95% (XRD). To sum up, the specific surface area and content of montmorillonite do not always reflect the real nature of clay. Colloidal activity seems to be a better parameter, which, in turn, indicates the presence of clay minerals such as montmorillonite (Cichy and Bryk, 2006), regardless of in which of the finest fractions it is accumulated. This requires further research towards finding the most optimal parameters of the sealing material for potentially toxic metal hazards. Given that the characterization of the influence of individual  $Cu^{2+}$  or  $Zn^{2+}$  ions on soil parameters showed different behavior of these ions in the soil-water system. This work presents no relationships between other trace metals such as lead, nickel, chromium, cadmium and soil parameters, because the performed analyses did not reveal their significant impact. The reason may be their very low concentration in the clay-water system (Table 1). However, significant correlations were found between chromium ion and sorption parameters ( $R = -0.99$ ), nickel ion and the plastic limit ( $R = -0.91$ ), and others. The research needs to be continued with respect to clays with other major exchangeable potentially toxic metal cations.

## 4. Conclusions

1. The results obtained demonstrate the significant effect of dominant cation ( $Na^+$ ,  $Ca^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ) in the bentonite on select groups of its sorption, plastic and granulometric parameters, respectively.
2. It was observed that the significance of the influence of  $Cu^{2+}$  and  $Zn^{2+}$  ions on specific clay properties differed, which indicates different behavior of these metals in the clay-water system. These changes are likely to be visible already at the microstructural level, which requires the continuation of research.
3. In general, an increase in the specific surface area was observed in the  $Na^+$ -SWy-3 bentonite and a decrease in  $Ca^{2+}$ -Stx-1b and -BSvk bentonites was observed after replacement with  $Cu^{2+}$  and  $Zn^{2+}$  ions.
4. The results of regression analysis showed a considerable reduction in hygroscopic moisture with an increase in  $Zn^{2+}$  content in the soil. The results indicate the need for assessment in the frozen system, due to the fact that the zinc ions may have an effect on the content of unfrozen water, the quantity that is used in heat transfer models for the water-soil system.
5. A drop in LL and PI after replacement with  $Cu^{2+}$  and  $Zn^{2+}$  ions was observed. The drop was twice as high in the case of  $Zn^{2+}$  ions.
6. Colloidal activity seems to be a better parameter than the content of montmorillonite and specific surface area in the assessment of the usefulness bentonite as adsorbents of copper and zinc ions. This research should be continued.
7. In the natural sodium bentonite (SWy-3), a several-fold decrease in clay fraction content was observed after replacement with  $Cu^{2+}$  and  $Zn^{2+}$  ions. Observations confirm the assumptions about such soils being particularly exposed to potentially toxic metals. It is in the smallest fraction that the most clay minerals, which adsorb metals, are found.
8. Regression analysis showed the impact of an increase in  $Zn^{2+}$  content in the soil on the increase in effective diameter  $d_{10}$  and hydraulic conductivity calculated according to the Hazen-Tkaczukowa Eq. (1). No such relationship was found for  $Cu^{2+}$  ions. However, after the analysis of the results it cannot be excluded that the calculation of the hydraulic conductivity according to another equation whose parameters will correlate significantly with the  $Cu^{2+}$  ion content, will show a significant decrease in hydraulic conductivity. Such a parameter is, for example, specific surface area ( $R = -0.99$ ), which is related to the microstructural parameters of the soil.
9. The different nature of clays contaminated with  $Cu^{2+}$  and  $Zn^{2+}$  ions justifies the need to continue research on other potentially toxic metal ions and to further search for prediction equations of the cohesive soil hydraulic conductivity based on soil parameters that are most frequently modified as a result of their impact.

## Declarations

### Author contribution statement

E. Nartowska: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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### Competing interest statement

The authors declare no conflict of interest.

### Additional information

No additional information is available for this paper.

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