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Assessment of the influence of copper and zinc on the microstructural parameters and hydraulic conductivity of bentonites on the basis of SEM tests

Edyta Nartowska *, Tomasz Kozłowski, Jarosław Gawdzik

Faculty of Environmental, Geomatic and Energy Engineering, Kielce Univ. of Technology, Al. Tysiąclecia P.P. 7, 25-314, Kielce, Poland

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ABSTRACT

The aim of this study was to determine the influence of potentially toxic metals, such as Cu^{2+} and Zn^{2+} ions, on the microstructural parameters of bentonites and their hydraulic conductivity (K), calculated based on the empirical formulas for clays according to Hazen-Tkaczukowa (formula 1 based on granulometric parameters) and Kozłowski et al., (2011) (formula 2 based on microstructural parameters). Metal ions influence the microstructure changes of bentonites, which can lead to changes in the geotechnical parameters that are used in empirical K formulas. The research was carried out on model clays (SWy-3, Stx-1b and Slovak bentonite), which were modified by introducing Cu^{2+} or Zn^{2+} ions into the structure. A significant dependence was observed between an increase in the Cu^{2+} ion content in clay and an increase in the pore area. Therefore, the value of the hydraulic conductivity was estimated with the use of formula 2, which proved to be a useful tool for determining hydraulic conductivity in the case of bentonites contaminated with Cu^{2+} ions. In contrast, the effect of Zn^{2+} ions on the granulometric parameters was significant, and formula 1 proved to be useful tool for determining hydraulic conductivity in the case of bentonites contaminated with Zn^{2+} ions. The results showed that the behavior of bentonites saturated with Cu^{2+} and Zn^{2+} ions differed. Therefore, the authors believe that the empirical formulas of the hydraulic conductivity of the clays saturated with potentially toxic metals should be based on the selected clay parameters dependent upon the nature of the ion.

1. Introduction

Copper and zinc are two of the most common potentially toxic metals in the water and soil environment (Wuana and Okieimen, 2011). The maximum allowable content of these metals at a depth of 2–15 m, i.e. 1000 mg/kg of dry soil (Cu^{2+}) and 3000 mg/kg (Zn^{2+}) according to Polish law regulations, is present in industrial and transport-related areas. It is believed that higher concentrations in these soils pose serious hazards to water and soil (Gawdzik and Gawdzik, 2012). One of the potential sources of soil contamination with toxic metals is leachates from hazardous waste landfills. In this case, in addition to the environmental aspect, the influence of leachate on soil engineering properties, which affect its long-term functioning, is particularly important. Landfills are protected with a sealing layer, often with bentonite as a component. Bentonite has a high cation exchange capacity, owing to which after contact with leachate ion exchange can occur in the interlayer surfaces. A change in the chemical composition may lead to microstructural changes of bentonite, e.g. changes in porosity or interplanar distances. These, in turn, may change the engineering properties of clays, important for the proper functioning of a waste landfill. One of the most important engineering parameters is hydraulic conductivity (k), which, according to Council Directive (1999)/31/EC, should be smaller than $k \leq 10^{-9}$ m/s for hazardous waste. In addition to laborious laboratory procedures, this parameter may be estimated based on the empirical formulas for cohesive soils, which are based on their microstructural, granulometric, plastic or sorption parameters. Changes in the values of these parameters, as a result of exposure to the potentially toxic metals, may reduce or completely exclude any effectiveness in estimating the hydraulic conductivity.

Lange et al. (2005), Meril (2014) and Dutta and Mishra (2016) believe that bentonite hydraulic conductivity increases with an increasing concentration of potentially toxic metals, such as Cu^{2+}, Pb^{2+}, Zn^{2+}, in the solution. The authors (Arasan, 2010; Evangeline and John, 2010; Shariatmadari et al., 2011; Meril, 2014; Lu et al., 2015; Kobayashi

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* Corresponding author.
E-mail address: enartowska@tu.kielce.pl (E. Nartowska).

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et al., 2017; Oyediran and Olalusi, 2017; Li et al., 2019; Wang et al., 2019; Xu et al., 2019) agree as to the direction of changes in hydraulic conductivity of bentonites after exposure to landfill leachates, such as NaCl, KCl, $CaCl_2$, $MgCl_2$, $ZnCl_2$, $CuCl_2$, HCl, HNO3, NH_4Cl, CH_3COOH. Generally, the value of hydraulic conductivity increases. A number of publications indicate the possible significant impact of landfill leachate on the Atterberg limits and plasticity index (Harun et al., 2013; Sandhya and Shiva, 2017), granulometric composition (Tito et al., 2008; Krupskaya et al., 2017) and specific surface area (Meril, 2014; Krupskaya et al., 2017). The effect of the landfill leachate on these parameters still needs to be identified. The changes extend with increasing leachate concentration and time of interaction with the soil. The impact of leachate on soil parameters, although not yet fully understood, is widely discussed in the literature. There are few publications, however, in which authors could look for the causes of observed changes in soil parameters at the microstructural level. Some researchers claim that changes in the physicochemical parameters of soils may be caused by microstructural changes (Arasan, 2010; Meril, 2014; Dutta and Mishra, 2016; Krupskaya et al., 2017; Sandhya and Shiva, 2017). Others explain the change in geotechnical and structural parameters of bentonites in contact with the landfill leachate using the theories describing the Diffuse Double Layer (DDL). Clay particles are negatively charged. If clay particles come into contact with a leachate, positively charged ions in solution are attracted by them through electrostatic forces at the interface between the clay surface and soil solution. The presence of the DDL provides the clays with plastic properties, swelling, and reduced friction by separating soil particles. The double thickness of the layer decreases, thereby increasing the concentration of cations contained in the liquid holding to clay. Arasan (2010), Meril (2014) and Sandhya and Shiva (2017) find the decreased liquid limit and hydraulic conductivity in high plasticity clays due to synthetic leachate and salt solutions to be a result of DDL reduction. Researchers also observe a looser soil structure and the formation of various size aggregates. In the soft clays of Visakhapatnam, new minerals of kaolinite and chlorite group are formed with increasing percentage of leachate (Meril, 2014). Changes in geotechnical parameters of soils contaminated with leachate cannot always be explained by DDL theory, which mainly explains changes in plastic properties of soils. The soil-water system is complex and when in contact with leachate, its behaviour is simultaneously affected by a number of factors such as granulometric composition (Zhao et al., 2018), specific surface area (Krupskaya et al., 2017), exchangeable cation type (Kozłowski et al., 2014). It is assumed that each of them will contribute to the structural changes of the soil and to the changes in its microstructural parameters. This problem is being raised by a small group of researchers and is still not clarified. The findings of Zhang et al. (2016) show an increase in the number of pores in the 2 nm–6 nm range in contaminated clays, a loss of pores< 2nm and a decrease in the average pore size from 5 to 4 nm. The increase in the pore size in the range of 2–7 nm has also been described by Lu et al. (2015). Krupskaya et al. (2017) claim that the changes in structural parameters of bentonites contaminated with HCl and HNO_3 acids depend on montmorillonite content, leachate concentration, type and time of interaction. In general, these researchers observe a decrease in interplane distances (d_{001}) and an increase in total pore volume in bentonites with the highest montmorillonite content (97%) exposed to HCl for seven days. In bentonites containing 70% montmorilonite no changes of distance d_{001} were found, regardless of its HCl or HNO_3 contamination and the decrease in total pore volume occurred only in leachates of lower concentrations (<0.5 mol/l). The studies showed the increase in the number of pores above 5nm and the appearance of micropores (<0.1 nm) in clays saturated with 1M HNO_3 for 108 h.

Information on the microstructural parameters of contaminated soils provided in literature is scarce, and tests are carried out on different soils treated with leachates with various chemical compositions. The reported results usually represent additional studies, which don't typically focus on microstructural analysis. The authors conduct research mainly on synthetic leachate, acids and their salts. As a result, the complexity of the leachate composition, the presence of chloride ions (Frankovská et al., 2010) and the absence of studies on model soils make the interpretation of the results difficult and do not allow for reliable conclusions to be drawn on the impact of waste landfill leachate on soil microstructural parameters. In addition, the results in the studies mentioned above make it difficult to compare them in a way that can be trusted due to the lack of statistical analysis. Therefore, it seems justified to undertake research in assessing of the impact of potentially toxic metal ions on microstructural parameter changes. According to Wuana and Okieimen (2011), potentially toxic metals are the main source of pollution in the water and soil environment. Changes in the microstructural parameters of clays may changes their granulometric and sorption parameters, which are similarly used in the empirical formulas of hydraulic conductivity. The behavior of metal ions in the clay-water system differed. Due to this fact, the authors believe that when estimating the empirical hydraulic conductivity, in clays contaminated by potentially toxic metal ions, we should not use universal empirical formulas for cohesive clays. To our knowledge, no work has reported upon this. In addition, knowing the statistically significant relationships between metal ions and the microstructural, sorption and granulometric parameters of clays may, in the future, allow for the optimization of their sealing properties and provide protection against the negative effects of potentially toxic metal ions.

Herein, We presents a study on the influence of high levels of metals, such as copper or zinc, on the microstructural parameters and empirical hydraulic conductivity of bentonites. The experiments utilized three well-known source clays (sodium and calcium forms). Full-scale ion exchanges procedures were then conducted, and the homoionic forms of clays (copper and zinc forms) were obtained. The content of metals in the samples was determined using inductively coupled plasma optical emission spectrometry (ICP- OES) and microanalysis of the area from SEM photographs (% by weight). The parameters of the clays were determined before and after ion exchange, utilizing applicable procedures. The microstructural parameters were evaluated in Photoshop CS4 with a digital image analysis (NIA) overlay on the basis of SEM photographs. The following parameters were analyzed: the number of pores, the total pore surface area and circumference, the mean surface area and circumference of mesopores, micropores (0.1–2; 2–4; 4–10 μm) and ultrapores. The interplanar spacing d_{001} was determined with the use of the XRD method. The empirical hydraulic conductivity was evaluated on the basis of two formula based on the other parameters of clay (granulometric-formula(1) and microstructural parameters-formula(2)). Verification of the obtained results was performed with Statistica 8 software. In the result, the usefulness of the formulas was assessed, separately for the Cu^{2+} and Zn^{2+} forms of clays.

2. Materials and methods

2.1. Testing materials

The research was carried out on the model samples of American clays (SWy-3 and Stx-1b) and Slovak bentonite from Jelsovy Potok, which were modified by introducing Cu^{2+} or Zn^{2+} ions into the structure. The procedure of preparing homoionic forms of bentonite were performed according to the Kozłowski et al. (2014) study. Two homoionic forms (Cu^{2+}, Zn^{2+}) were obtained from source clays by repeated saturation of the soil with an appropriate chloride and subsequent purifying from chlorine anion by diffusion, until the elimination of the characteristic reaction with silver nitrate. The clay pastes were then air-dried at room temperature.

2.2. Testing methods

After the ion exchange, the content of metals in the samples were determined using inductively coupled plasma optical emission spectrometry (ICP- OES*)* and microanalysis of the area from SEM photographs (% by weight). The last experiment was conducted with a Quanta FEG

Table 1

The concentrations of selected metals in clay samples.

Cations	Methods	SWy-3 form			Stx-1b form			BSvk form		
		„0’’	Cu^{2+}	Zn^{2+}	„0’’	Cu^{2+}	Zn^{2+}	„0’’	Cu^{2+}	Zn^{2+}
Cu	ICP-OES*	12.8	11221	109.47	8.97	5427.5	52.3	6.28	7676.9	39.55
	EDXMA**	0	2.8	0	0	5.08	0	0	3.81	0
Zn	*	163.66	83.2	44463	73.68	92.96	16153	64.54	95.61	17857
	**	0	0	39.69	0	0	31.04	0	0	36.12
Na	*	8282.4	405.3	994.91	1970.3	362.74	885.1	1151.2	412.57	1204.6
	**	1.2	0.17	0	0.26	0	0	0.2	0	0
K	*	1126.6	414.4	837.1	660.85	198.47	465.1	959.73	521.99	769.2
	**	0.42	0	0.19	0.2	0	0	0.4	0.28	0.23
Ca	*	10086	2028	4526	11802	1491.3	2985	11945	1598	2778
	**	1.06	0.22	0	1.4	0.6	0.12	1.63	0.18	0.01
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	388.8	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

“0” natural form of clay.

[*] Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) [mg/kg] dry of soil.

[**] Energy Dispersive X-ray microanalysis (EDXMA) [% wag].

Table 2

The properties of clays.

Geotechnical properties	SWy-3 form			Stx-1b form			BSvk form		
	„0’’	Cu^{2+}	Zn^{2+}	„0’’	Cu^{2+}	Zn^{2+}	„0’’	Cu^{2+}	Zn^{2+}
Liquid limit LL[%]	519	146	104	142	136	101	165	154	119
Plastic limit PL[%]	35	42	54	44	50	73	46	52	61
Specific surface area S_{total} [m^2/g][a]	307.2	355.4	516.0	568.4	413.8	537.9	670.6	460.2	556.7
hygroscopic moisture w_{95} [%][a]	21.67	22.13	17.05	29.08	27.7	22.67	30.14	26.92	20.1
Clay fraction [%][b]	38.13	12.73	4.1	11.87	14.04	11.87	10.57	12.65	7.87
Empirical hydraulic conductivity [m/s][c]	1.52×10^{-10}	3.31×10^{-9}	8.74×10^{-8}	6.27×10^{-9}	2.28×10^{-9}	2.44×10^{-9}	$9.9x\ 10^{-9}$	3.65×10^{-9}	9.54×10^{-9}
Empirical hydraulic conductivity [m/s][d]	$3.95x\ 10^{-7}$	6.44×10^{-7}	1.86×10^{-7}	9.62×10^{-8}	6.75×10^{-7}	2.74×10^{-7}	$2.67x\ 10^{-7}$	$4.80x\ 10^{-7}$	$2.34x\ 10^{-8}$

[a] Water Sorption Test (WST) by Stępkowska (1977).

[b] Laser diffraction method.

[c] acc. to Hazena-Tkaczukowej formula (1).

[d] acc. to Kozłowski et al.(2011) formula (2).

250 scanning electron microscope at 30 kV voltage, applied using accessories for determining elemental composition (EDX-MA). ZAF correction and normalization were applied to correct the recorded intensity of X-rays due to differences in the chemical composition of the standard and the sample analyzed. SEM photographs were taken at 2,000 x magnification.. The results are shown in Table 1.

2.2.1. *Determining the geotechnical properties of clays*

The soil parameters useful for assessing the properties of soils as mineral protective barriers have been determined. The characteristics of plasticity were determined by the use of normal procedures (Casagrande's cup device and the rolling test for liquid limit (LL) and plastic limit (PL), respectively). The specific surface area and sorption properties were determined by the water sorption test (WST) according to Stępkowska (1977). Granulometric composition was determined by laser diffraction using a Sucell Helos/bf instrument. Empirical hydraulic conductivity was determined with the Hazen-Tkaczukowa Eq. (1). This formula is used for permeability prediction of clayey-sandy soils with a content of particles with a diameter $d < 0.001$ mm 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. The nine tested clays are characterized in Table 2.

$$k = \frac{0.0093}{a^2} d_{10}^2 \tag{1}$$

$k[\frac{m}{s}]$, where d_{10} is an effective grain size.

a [%] content of particle with diameter less than 0,001 mm.

2.2.2. *Determining the interplanar spacing d_{001} and microstructural parameters of clays*

The main purpose of the X-ray diffraction study was to determine 001 planes, i.e. the planes parallel to the surface of the sample. Dominant metal ions in the clay structure have an influence on the changes of interplanar spacing (Kozłowski et al., 2014). X-ray diffraction analysis was conducted using a Bruker D8 advance powder diffractometer in Debye-Sherrer geometry, Cu–K $_{\alpha1}$ radiation ($\lambda = 1.5406$Å) from a Johansson-type monochromator and a LynEye position-sensitive detector. The measurements were carried out at 2Θ from 4.51° to 70°. The applied voltage was 3,540 kV with a530 mA current. Phase identification was made based on the database PDF 4+, whereas an estimation of the individual phases was made using a semi-quantitative method in the Diffrac Eva program.

The experiments determining microstructural parameters were conducted with a Quanta FEG 250 scanning electron microscope with a 20 kV voltage applied. The air-dried samples (8–10 mm diameter) of the homoionic bentonites were analyzed. The surfaces of the samples were covered with a 40 nm layer of gold to prevent electrization and photographs at a magnification of 5,000 x were used to determine the quantitative pore space parameters. Exemplar microphotographs of the clay (SWy-3) modified by introducing Cu^{2+} or Zn^{2+} ions into the structure are shown in Fig. 1. The SEM photographs were analyzed with the Photoshop CS4–based Numerical Image Analysis (NIA) method. Since the lighter

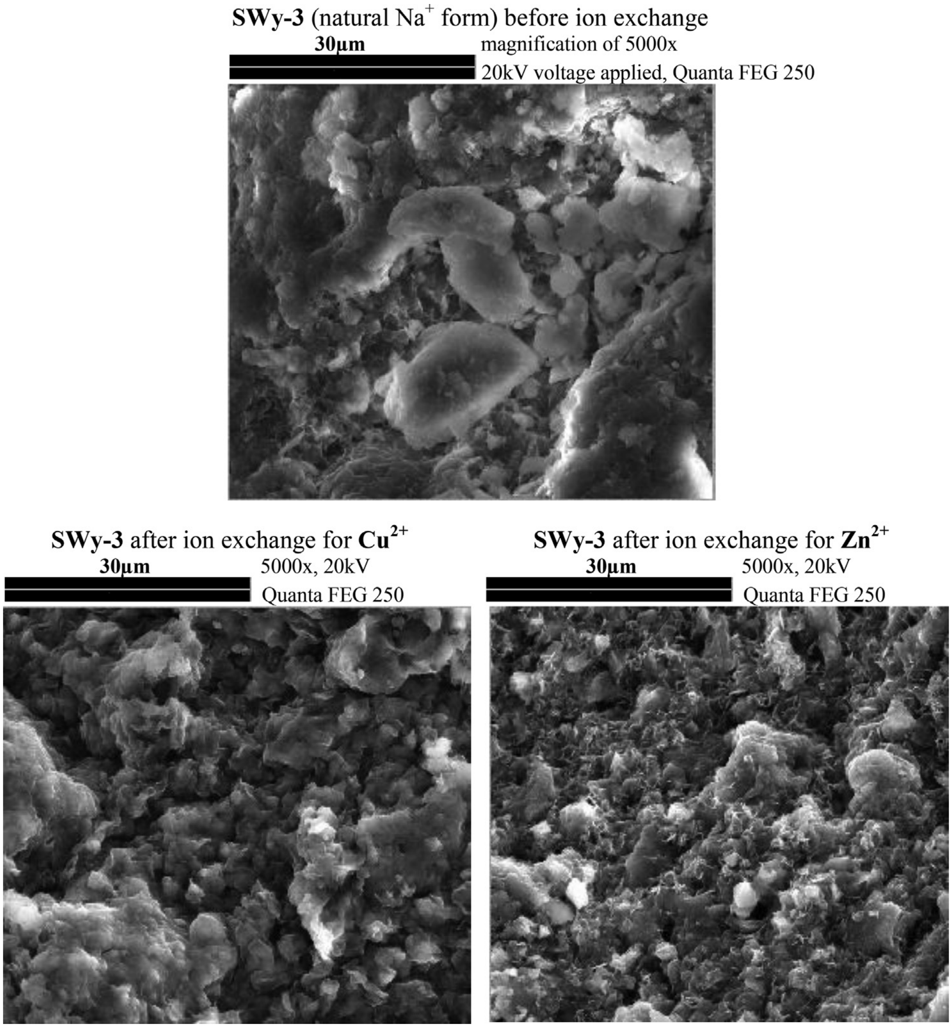

Fig. 1. SEM photographs of the natural SWy-3 bentonite and it's homoionic forms.

Table 3
The selected clay microstructural parameters.

Structural parameters	SWy-3 form			Stx-1b form			BSvk form		
	..0''	Cu^{2+}	Zn^{2+}	..0''	Cu^{2+}	Zn^{2+}	..0''	Cu^{2+}	Zn^{2+}
interplanar spacing d_{001}[a]	11.44	12.32	13.21	14.88	12.48	14.29	14.87	12.45	14.17
the pore total surface area[b]	306.6	753.3	576.2	201.5	617.3	317.5	182.5	487.6	22.87
the average area and perimeter of micropores[b]	0.22/1.29	1.26/6.72	1.08/6.64	0.58/4.65	1.15/7.11	0.66/5.4	1.36/7.17	1.37/7.97	0.29/3.29
the pore circularity[b]	0.245	0.238	0.277	0.315	0.202	0.259	0.283	0.22	0.342

[b] NIA method.
[a] XRD method.

areas on the SEM images of the soils correspond to the mineral particles, while darker areas – to the spaces between the particles, it is possible to identify pores and soil particles and to define the total number of pores, the total pore area and perimeter and the pore circularity. Additional values required for the quantitative analysis, such as the average surface area and perimeter of mesopores, micropores (0.1–2; 2–4; 4–10 µm) and ultrapores, were calculated using Excel. The pores were classified by size according to Grabowska-Olszewska (1990) on ultrapores <0.1 µm, micropores 0.1–10 µm and mezopores 10–1000 µm. The interplanar spacing d_{001} and selected microstructural parameters are shown in Table 3.

2.2.3. Determining the coefficient of permeability on the basis of the structural parameters of clays

Hydraulic conductivity (k_{SEM}) was determining according to Kozłowski et al. (2011). Researchers claim that there is a close relationship between the parameters determining the quantity, size and shape of the pores and the permeability coefficient. Researchers derived this parameter as a function of the areas and the hydraulic radii of micropores in the region of the analyzed section of microphotography, according to Eq. (2).

$$k_{10} = \frac{\sum A_i \cdot R_{h,i}^2}{A} \cdot 3,82235 \cdot 10^{-6} \tag{2}$$

where: A_i cross-section area of pore i, µm
A-area of the whole of analyzed region, µm
k-hydraulic conductivity at 10 °C, m/s
$R_{h,i}$- hydraulic radius of pore i, µm

Table 4
Multiple regression analysis between the cations determined by the ICP-OES method and the cations determined by the EDS method.

	the unstandardized beta (B)	Std. error B	the standardized beta (ß)	Std. Error ß	t test value	p-value
Dependent variable *$\mathbf{Cu^{2+}}$ $R = 0.81$ $R^2 = 0.65$ adj. $R^2 = 0.61$ Std. error of estimate:1.27						
Intercept			0.254	0.513	0.495	0.635
**$\mathbf{Cu^{2+}}$	**0.808**	**0.222**	**0.0003**	**0.0001**	**3.64**	**0.008**
Dependent variable *$\mathbf{Zn^{2+}}$ $R = 0.90$ $R^2 = 0.81$ adj. $R^2 = 0.784$ Std. error of estimate: 8.33						
Intercept			2.57	3.25	0.79	0.455
**$\mathbf{Zn^{2+}}$	**0.9000**	**0.164**	**0.0001**	**0.00019**	**5.488**	**0.00092**
Dependent variable* $\mathbf{Na^{+}}$ $R = 0.972$ $R^2 = 0.946$ adj. $R^2 = 0.938$ Std. error of estimate: 0.09						
Intercept			-0.0589	0.0398	-1.477	0.183
** $\mathbf{Na^{+}}$	**0.972**	**0.087**	**0.00015**	**0.000014**	**11.081**	**0.00001**
Dependent variable*$\mathbf{K^{+}}$ $R = 0.871$ $R^2 = 0.759$ adj. $R^2 = 0.725$ Std. error of estimate: 0.085						
Intercept			-0.132	0.074	-1.78	0.118
**$\mathbf{K^{+}}$	**0.871**	**0.1853**	**0.00049**	**0.000104**	**4.70156**	**0.00220**
Dependent variable* $\mathbf{Ca^{2+}}$ $R = 0.893$ $R^2 = 0.798$ adj. $R^2 = 0.769$ Std. error of estimate: 0.3						
Intercept			-0.107	0.164	-0.65	0.535
** $\mathbf{Ca^{2+}}$	**0.893**	**0.169**	**0.00012**	**0.00002**	**5.268**	**0.0011**

Bold correlations are significant at $\mathbf{p < 0.05}$.

[*] Energy Dispersive X-ray microanalysis (EDXMA) [% wag].

[**] Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) [mg/kg] dry of soil.

Table 5
Multivariate tests of significance (MANOVA) of the major cation (Na^{+}. Ca^{2+}. Cu^{2+}. Zn^{2+}) for the interplanar spacing.

d_{001}	SS	df	MS	F	p
Intercept	**1278.018**	**1**	**1278.018**	**8933.235**	**0.000000**
major cation	**11.787**	**3**	**3.929**	**27.464**	**0.001562**
Error	0.715	5	0.143		

Bold correlations are significant at $\mathbf{p < 0.05}$.

Hydraulic radius is defined as (3)

$$R_{h,i} = \frac{A_i}{U_i} \quad (3)$$

where: A_i cross-section area of pore i, μm; U_i is perimeter of pore i, μm.

At first approximation, the pores were identified manually as darker areas. Next, the optimum threshold values were obtained according to formula (4) by Kozłowski et al. (2011). The pores were identified as objects darker than the threshold value in each SEM microphotograph.

$$T_{opt} = a_1 \cdot (L_{mean})^3 + a_2 \cdot (L_{mean})^2 + a_3 \cdot L_{mean} + a_4 \cdot (\sigma_n)^3 + a_5 \cdot (\sigma_n)^2 + a_6 \cdot \sigma_n + a_7 \quad (4)$$

where: L_{mean} - mean grey level σ_n - standard deviation a_{1-6}- empirical parameters.

a_1 = -0,014329 a_2 = 2,335432 a_3 = -126,102 a_4 = -0,019976 a_5 = 1,127440 a_6 = -18,9358 a_7 = 2404,341.

3. Results and discussion

The significant relationship between the content of the cations in the clays determined by using ICP-OES and SEM-EDS instruments were observed. Multiple regression analysis confirmed that we can predict the mutual behavior of these variables (Table 4). Comparative studies of these methods were carried out by Haley et al. (2006). Researchers claim that the SEM-EDS method can provide accurate concentration data for the basic cations (Al, Fe, Mg, Ca, K) occurring in soils. Haley et al. (2006) indicates that this is important to extend quantitative analysis to trace elements. In this study, the content of potentially toxic metals, such as copper and zinc, were determined by the ICP-OES and SEM-EDS method (Table 1). Additionally, the relationship between the content of cations (determined with two methods) and soil parameters was determined. It was surprising to obtain an identical Cu^{2+} ion correlation obtained by ICP-OES and SEM microanalysis with the soil microstructural parameters, which confirms the suitability of this method for determining toxic metal content for statistical purposes. These results are shown in the further part of this work.

Table 6
Tukey's HSD test of the major cation (Na^{+}. Ca^{2+}. Cu^{2+}. Zn^{2+}) on the the interplanar spacing d_{001}.

d_{001}	Na^{+}	Cu^{2+}	Zn^{2+}	Ca^{2+}
	Error: MS within = 0.14306 df = 5			
11.44		0.3614	**0.021865**	**0.00529**
12.41	0.3614		**0.018551**	**0.00503**
13.89	**0.0218**	**0.01855**		0.15573
14.87	**0.0052**	**0.00503**	0.15573	

Bold correlations are significant at $\mathbf{p < 0.05}$.

3.1. *The effect of Cu^{2+}or Zn^{2+} ions on clay interplanar distance d_{001}*

Variance analysis showed that the interplanar distances were dependent on the type of dominant cation in the soil (Table 5). To state clearly which mean values of interplanar distance differ from each other, depending on the dominant cation, Tukey's post-hoc test was used (Table 6). This test is recommended for comparing pairs of means as the amount of likelihood for a Type 1 error is smaller than in the least significant difference (LSD) test. Tukey's HSD test showed that the influence of Cu^{2+} and Na^{+} ions on the interplanar distance was particularly significant in soils with the highest interplanar distance (d_{001}~13,89 and 14,87), whereas the influence of Zn^{2+} and Ca^{2+} ions proved to be most significant in soils with the smallest interplanar distance (d_{001}~11,44 and 12,41). The correlation coefficient of the interplanar distance with the soil parameters is significant only in case of the specific surface area (S) and sorption moisture (w_{50}) (R = 0,94). Post-hoc test showed that the influence of Cu^{2+} ions on the soil specific surface area (**S**) was

Table 7
The correlations of the coefficient between Cu^{2+} and Zn^{2+} cations and the selected soil parameters.

	w_{50}	w_{95}	S	f_{cl}	f_s	d_{10}
Cu^{2+}	**-0.98**	0.39	**-0.98**	0.61	-0.60	-0.45
Zn^{2+}	0.59	**-0.85**	0.59	**-0.94**	**0.92**	**0.93**

Bold correlations are significant at $\mathbf{p < 0.05}$.
S- specific surface area of soil. $w_{50.}$ w_{95} –sorption moisture (WST) by Stępkowska (1977).
fcl/f s-clay/silt fraction by laser diffraction method. d_{10}-effective diameter.

Table 8

The correlations of the coefficient between Cu^{2+} and Zn^{2+} cations and the selected soil microstructure parameters.

	the pore total surface area	the average area of pores	the average perimeter of pores	the average area of micropores	the average area of ultrapores	the average area of mezopores	circularity
Cu^{2+}	**0.76**	**0.75**	0.49	0.6	-0.3	0.5	**-0.77**
Zn^{2+}	0.03	-0.14	0.18	-0.1	-0.12	-0.26	0.34

Bold correlations are significant at $\mathbf{p < 0.05}$.

ultrapores <0.1 µm micropores 0.1–10 µm and mezopores 10–1000 µm.

Table 9

Multiple regression analysis between the Cu^{2+} ions (determined with two methods) and the selected microstructural parameters of the soil.

	the unstandardized beta (B)	Std. error B	the standardized beta (ß)	Std. Error ß	t test value	p-value
Dependent variable: **circularity of pores** $R = 0.636$ $R^2 = 0.404$ adj. $R^2 = 0.32$ replaced as Std. error of estimate:0.0367						
Intercept			**0.282864**	**0.01477**	**19.15**	**0.0000**
**Cu^{2+}	-0.636241	0.2916	-0.000007	0.000003	-2.18	0.0654
Dependent variable: **circularity of pores** R = 0,773 R^2 = 0,597 adj. $R^2 = 0.540$ enter replaced as Std. error of estimate: 0.03019						
Intercept			**0.286873**	**0.012161**	**23.589**	**0.0000**
*Cu^{2+}	**-0.773278**	**0.239655**	**-0.016962**	**0.005257**	**-3.22663**	**0.0145**
Dependent variable: **the pore total surface area** $R = 0.755$ $R^2 = 0.570$ adj. $R^2 = 0.509$ Std. error of estimate: 166.74						
Intercept			**270.698**	**67.0439**	**4.037**	**0.0049**
**Cu^{2+}	**0.7553**	**0.24764**	**0.0418**	**0.01371**	**3.0499**	**0.0185**
Dependent variable **the pore total surface area** $R = 0.673$ $R^2 = 0.4529$ adj. $R^2 = 0.3747$ Std. error of estimate: 188.2						
Intercept			**282.58**	**75.813**	**3.727**	**0.0073**
* Cu^{2+}	**0.672986**	**0.279563**	**78.8934**	**32.77288**	**2.407**	**0.0469**
Dependent variable: **the average area of pores** $R = 0.752$ $R^2 = 0.566$ adj. $R^2 = 0.504$ Std. error of estimate: 0.09669						
Intercept			**0.1514**	**0.03900**	**3.88260**	**0.0060**
** Cu^{2+}	**0.75258**	**0.24889**	**0.000024**	**0.000008**	**3.023742**	**0.0193**
Dependent variable: **the average area of pores** $R = 0.746$ $R^2 = 0.5568$ adj. $R^2 = 0.4934$Std. error of estimate: 0.09806						
Intercept			**0.15160**	**0.0395**	**3.838**	**0.0064**
* Cu^{2+}	**0.746195**	**0.251621**	**0.050637**	**0.017075**	**2.9655**	**0.0209**

Bold correlations are significant at $\mathbf{p < 0.05}$.

[*] Energy Dispersive X-ray microanalysis (EDXMA) [% wag].

[**] Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) [mg/kg] dry of soil.

particularly significant in soils with the highest specific surface areas (S ~ 600 m^2/g), whereas the influence of Zn^{2+} ions was seen to be the most significant in soils with the smallest specific surfaces (S~300 m^2/g). The results indicates that in clays, the interplanar distance are consistent with the specific clay surface area and are dependent with regard to the dominant Cu^{2+} or Zn^{2+} cations.

Generally, our observations showed a decrease in interplanar distance d_{001} in Ca^{2+} bentonites after the exchange for the Cu^{2+} and Zn^{2+} ion. In addition, in the case of the Cu^{2+} form of bentonite the interplanar distance decrease was higher than the Zn^{2+} form. This can be explained by the Cu^{2+} ions having better correlations than the Zn^{2+} ions, with the clay surface area (Table 7). A higher decrease in the specific surface area of calcium bentonites after exchanging copper ions rather than zinc ions can be explained by the bigger copper ion radius; thus, the ability to exchange these ions in calcium bentonite is much smaller than in the case of zinc ions. A smaller number of cations with a larger ionic radius in the bentonite interlayer leads to an increase in the presence of large voids (thereby hydraulic conductivity) in this clays. Furthermore, no decreases in the interplanar distance were obtained for the Na^+ form of bentonite which had the smallest interplanar distance ($d_{001} = 11,44$). The results indicate that interplanar distances have specific ranges, depending on the type of dominant metal Cu^{2+} (d_{001}~12,5) or Zn^{2+}(d_{001}~14), but, regardless of its initial form-whether Na^+ or Ca^{2+}. Additionally, the obtained results confirms that a decrease in the interplanar distance does not indicate an increase in the surface area of bentonites - as was presented in the publication by Krupskaya et al. (2017). Of note, these researchers carried out their tests -on soils through the utilization of other leachates (inorganic acid solution). Therefore, it could be said that the type of leachate has influence on the changes of interplanar distance. Moreover, the trend differs. This research should be continued because the modification of structural characteristic can be used to simulate the behavior of engineered -barrier properties for industrial wastes (Krupskaya et al., 2017).

3.2. *The effect of Cu^{2+}or Zn^{2+} ions on clay microstructure parameters*

Limited information is currently available on the effect of leachate on soil microstructural parameters. The results of research by Zhang et al. (2016), Lu et al. (2016) and Krupskaya et al. (2017), however, indicate the need for further detailed work in this area. In this publication, the effect of Cu^{2+}or Zn^{2+} ions on the microstructure parameters of bentonite were determined. Herein, the following parameters were analyzed: the number of pores, the pore total surface area and perimeter, the mean surface area and the perimeter of mesopores, micropores (in the range between 0.1 to 2µm; between 2 to 4µm and 4–10µm) and ultrapores. The

Table 10

Multivariate tests of significance (MANOVA) of the major cation (Na^+. Ca^{2+}. Cu^{2+}. Zn^{2+}) for the hydraulic conductivity k_{SEM}.

*k	SS	df	MS	F	p
Intercept	**0.000000**	**1**	**0.000000**	**60.05203**	**0.000572**
****major cation**	**0.000000**	**3**	**0.000000**	**8.53376**	**0.020657**
Error	0.00000	5	0.00000		

Bold correlations are significant at $\mathbf{p < 0.05}$.

[*] Empirical hydraulic conductivity acc. to Kozłowski et al. (2011) Formula (2).

[**] Cation dominant in soil Na^+. Ca^{2+}. Cu^{2+}. Zn^{2+}

Table 11

Dunett's test of the major cation (0. Cu^{2+}. Zn^{2+}) on the the hydraulic conductivity k_{SEM}.

k_{SEM}	0	Cu^{2+}	Zn^{2+}
	Error: MS within = 0.0000 df = 6		
{1}		**0.028475**	0.612311

„0'' The control group was the natural form of bentonites.

Bold correlations are significant at $\mathbf{p < 0.05}$.

Table 12
Multiple regression analysis between the Cu^{2+} ions and the hydraulic conductivity of the soil k_{SEM}.

dependent variable k_{SEM}						
$R = 0.803339$ $R^2 = 0.64535$ adj. $R^2 = 0.59468977$ Std. error of estimate: 0.000						
independent variable	the unstandardized beta (B)	Std. error B	the standardized beta (ß)	Std. error ß	t test value	p-value
Intercept			**0.000000**	**0.000000**	**3.760223**	**0.007073**
Cu^{2+}	**0.803339**	**0.225086**	**0.000000**	**0.000000**	**3.569029**	**0.009109**

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

Table 13
The correlations of the coefficient between hydraulic conductivity (determined with two methods) and the selected soil properties.

R $p <$ 0.05	Cu^{2+}	Zn^{2+}	Surface area (S)	Sorption moisture (w_{50})	Clay fraction (f_{Cl})	Effective diameter (d_{10})
k_{SEM}	**0.96**	-0.69	**-0.97**	**-0.97**	0.67	-0.44
$k_{H\text{-}T}$	-0.38	**0.90**	0.25	0.25	**-0.88**	**0.99**

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

selected microstructural parameters are shown in Table 3. The correlations coefficient of Cu^{2+}or Zn^{2+} with the microstructural parameters were significant only in the case of the Cu^{2+} ion (Table 8). Furthermore, a significant dependence was observed between the increase in the Cu^{2+} ion content in the sorption complex and the increase in the total pore area and pore mean area and the decrease the circularity of pores. Additionally, the significant influence between Cu^{2+} ions (determined via two methods) with the soil microstructural parameters was evident (Table 9). With regard to the effect of Zn^{2+} ions on microstructural parameters, this was not significant. Most likely, the behavior of bentonites saturated with Zn^{2+} ions is more closely related to physical parameters, e.g., granulometric composition, than to physicochemical parameters dependent on the microstructurally dependent. These observations are possible in the lights of the obtained results-the correlation coefficient with the soil physical and physicochemical parameters (Table 7). Of note, the obtained results reveal the significant influence of the Cu^{2+} ions on the decrease of circularity of soil particles. This observation may indicate a change in the clay porosity. More research, however, is needed.

3.3. *The effect of Cu^{2+}or Zn^{2+} ions on clay hydraulic conductivity k_{SEM}*

The value of the hydraulic conductivity was estimated based on the relation between the pore area and pore hydraulic radii by way of the use of Eq. (2), (3) proposed by Kozłowski et al. (2011). The results are shown in Table 2. In our work, statistical analysis reveals the significant influence of the dominant cation (Na^+, Ca^{2+}, Zn^{2+}, Cu^{2+}) on hydraulic conductivity k_{SEM} (Table 10). To state clearly which mean values of hydraulic conductivity differ from each other, depending on the dominant cation (Cu^{2+} or $Zn^{2+)}$, Dunnett's post-hoc test was used (Table 11). The control group was the natural form of bentonites. The results indicate that the dominant Cu^{2+} ions have an influence on the change of hydraulic conductivity as determined via formula (2) put forth by Kozłowski et al. (2011). What is more, regression analysis showed a significant increase in hydraulic conductivity with increasing Cu^{2+} ion content in the soil (Table 12). Overall, the hydraulic conductivity formula of cohesive soils contaminated by Cu^{2+} or Zn^{2+} ions cannot be based on the same parameters. These ions have different natures and the hydraulic conductivity of these clays calculating accordance to empirical formulas (1) and (2) correlate with different soil parameters (Table 13). Finally, we hold that the hydraulic conductivity of soil contaminated by Cu^{2+} ions as estimated via formula (2) of Kozłowski et al. (2011) adequately describes the behavior of these cohesive soils.

4. Conclusion

- ➢ The identical Cu^{2+} ion correlation obtained by ICP-OES and SEM microanalysis with the soil microstructural parameters, confirms the suitability of this method for determining toxic metal content for statistical purposes.
- ➢ Variance analysis showed that the interplanar distances were dependent on the type of dominant cation in the soil (Na, Ca, Zn, Cu). In the case of dominant Cu^{2+} ions, the interplanar distance d_{001} decreased only in Ca^{2+} bentonites. We saw that observations are affected by the physicochemical parameters of these soils, such as sorption moisture content and specific surface area. It is, thus, probable that direction of changes of the interplanar distance is dependent on the type of leachate.
- ➢ A significant dependence was observed between the increase in the Cu^{2+} ion content in the sorption complex and the increase in the total pore area and pore mean area. formula (2) proposed by Kozłowski et al. (2011) is useful tool for determining the hydraulic conductivity in case of bentonites contaminated with Cu^{2+} ions. In contrast, the behavior of bentonites saturated with Zn^{2+} ions is more closely related to a clay's physical parameters, e.g., granulometric composition, than to physicochemical parameters dependent on the microstructure.
- ➢ The different behaviour 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 the 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.

T. Kozlowski: Conceived and designed the experiments; Analyzed and interpreted the data.

J. Gawdzik: Performed the experiments; Contributed reagents, materials, analysis tools or data.

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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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