

Article

The Effect of the Concentration of Copper Ions on the Unfrozen Water Content in Bentonites Measured with the Use of DSC Method

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Abstract: Studies on changes of unfrozen water content in calcium bentonite from Slovakia, with various concentrations of copper ions, were carried out using the method of differential scanning calorimetry (DSC). In this study, the influence of molar concentration of copper(II) chloride solution (1 M, 0.5 M, 0.25 M, 0.1 M), used to saturate clay, was analyzed, as well as the impact of copper ions contained in bentonite and how the copper concentration affects to changes of unfrozen water content versus temperature. The results suggest that new mineral phases originate in bentonite saturated with highly concentrated solutions due to the reaction with copper(II) chloride solutions. These minerals, identified based on XRD and SEM-EDS (X-ray Diffraction and Scanning Electron Microscopy with Energy Dispersive Spectroscopy) studies, are from the atacamite group. ANOVA (Analysis of Variance) has shown a statistically significant relationship between the unfrozen water content and the molar concentration of the solution used to saturate bentonite and between the unfrozen water content and the content of copper ions in the bentonite. The analysis of multiple regression has shown that the change of unfrozen water content in copper bentonites is related to the temperature change, specific surface, and the concentration of copper ions in the clay. An empirical equation was developed to estimate the content of unfrozen water at a given negative temperature in Cu-bentonites, in which the specific surface and copper ions concentration in the bentonite are the main parameters.

Keywords: copper concentration; molar concentration; clay minerals; unfrozen water; DSC; specific surface area; atacamite; clinoatacamite; salt concentration



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1. Introduction

When considering clay-water interaction, smectites are the most important minerals due to their expansive nature [1]. Bentonite is a swelling clay, the main mineral being from the smectite group—montmorillonite (2:1 type clay mineral). Montmorillonite has a variable space between the layers, which is occupied by exchangeable cations and water, thanks to which their specific surface area (S) is high. Exchangeable cations in clays are different to the ions added through reagents. The physicochemical properties of montmorillonites are closely related to the type of the main exchangeable cation [2]. Montmorillonite can adsorb water that does not freeze in a wide range of subzero temperatures. This is called unfrozen water. The properties of unfrozen water are similar to the liquids, ions, and dissolved substances moving freely in the water [3]. Research results [4] show that in STx-1b bentonite (from the Clay Mineral Society), the content of unfrozen water-determined NMR (Nuclear Magnetic Resonance) method at a temperature of $-20\text{ }^{\circ}\text{C}$ is on average 20–25%, depending on the main exchangeable cation. For comparison, in kaolin clay under the same conditions, the amount of unfrozen water usually does not exceed 3% [4].

The presence of substances dissolved in the porous water in clays determines the content of unfrozen water and its mobility, and the results of studies refer primarily to

the main exchangeable ions (Ca^{2+} , Mg^{2+} , Na^+ , K^+) [4,5]. Kruse and Darrow [4] analyzed the unfrozen water in cation-treated, montmorillonite clay (STx-1b) using the P-NMR method. The results indicated that the cation treatments have an effect on the unfrozen water content in the clay (STx-1b). The highest unfrozen water content was observed when treated with Na^+ cations, most likely due to the largest specific surface area of this clay. The same clay demonstrated a significant reduction in unfrozen water content after the K^+ treatment. In the case of the exchange of STx-1b with Ca^{2+} and Mg^{2+} ions, the changes in the unfrozen water content were not so significant, most likely because the source form of STx-1b is the calcium form, and calcium and magnesium cations show similar effect in the frozen clay-water system. Research by Nartowska et al. [6] show that in the case of bentonite with a copper concentration of 5428 and 7677 mg/kg of dry clay, the content of the unfrozen water (un_{Cu}) by the use of the ^1H -NMR method is lower than in the same clay unsaturated with copper ions in the temperature range between $-32\text{ }^\circ\text{C}$ and about $-3\text{ }^\circ\text{C}$. The differences in the unfrozen water content (un) increase as the temperature drops: $un_0 = 28\text{--}30\%$ and $un_{\text{Cu}} = 18\text{--}20\%$ ($T = -10\text{ }^\circ\text{C}$); $un_0 = 25\text{--}26\%$ and $un_{\text{Cu}} = 11\text{--}14\%$ ($T = -15\text{ }^\circ\text{C}$); $un_0 = 24\%$ and $un_{\text{Cu}} = 9\text{--}10\%$ ($T = -20\text{ }^\circ\text{C}$); $un_0 = 21\text{--}22\%$; and $un_{\text{Cu}} = 7\%$ ($T = -25\text{ }^\circ\text{C}$); $un_0 = 20\%$ and $un_{\text{Cu}} = 5\text{--}6\%$ ($T = -30\text{ }^\circ\text{C}$). Changes in the content of the unfrozen water in clay contaminated with copper ions in the presence of copper chlorides are not mentioned in the literature. Xiao et al. [7,8] reported that the freezing point of saline soils determined by the NMR method is closely related to the type of salt (sodium chloride, calcium chloride, sodium carbonate, sodium sulphate) and the size of the pores. The supercooling phenomenon delays the ice formation in the freezing process, thus leading to variation in the unfrozen water content in soil. The latest research by Xiao et al. [9] indicate that the unfrozen water content decreases as ice crystals form at the first stage of the phase transition, and further decreases as ice and hydrated salt precipitate at the second stage of the phase transition. A proper prediction of changes in unfrozen water content may be the basis for modelling processes to minimize the pollution in frozen clays [10]. Bentonites are widely used worldwide as an insulating material, e.g., in landfills of hazardous waste, where they can be exposed to the action of leachate containing copper chlorides or ions [11]. Based on their experiments, Podlech et al. [12] observed that the alteration of the smectite is mainly attributed to the nature of the bentonite, pore water chemistry, and temperature. These factors may cause mineralogical changes and affect the long-term performance of the bentonite barrier system. In addition, the interaction of corrosion products of copper-coated steel containers, in which nuclear fuels are gathered, with bentonite, may be a major problem [13]. Carlsson [14] showed that the soft samples, which consisted of water-saturated MX-80 bentonite mixed with 0.0001 M CuCl_2 solution, did not contain copper ions. The author of paper [13] found that the concentration is most likely too small for the physicochemical transformations of bentonite to occur. The information collected from the literature [15,16] shows that in an aerobic water-soil environment the copper chlorides can form $[\text{CuCl}_3]^-$ and $[\text{CuCl}_4]^{2-}$ complexes and also poorly soluble basic copper chlorides, such as atacamite. Additionally, King et al. [17] and Izosimova et al. [18] reported a significant influence of anions and cations concentration on the chemism of porous waters. The research team [18] confirmed that the smaller the amount of Cu^{2+} ions adsorbed on the sodium bentonite was, the higher was the initial concentration of copper chloride.

Scientific works regarding the impact of solutions with copper chlorides concentration on bentonites modifications are rare in the literature. The authors have not found a paper that determines the influence of copper ions concentration on the content of unfrozen water in clays. The previous authors' study [6], carried out using the ^1H NMR (Proton Nuclear Magnetic Resonance) method, suggested only that the content of unfrozen water in bentonites polluted with copper ions could be presented as a function of the metal concentration. The authors emphasized that, due to a possible occurrence of cations hydration in the ^1H NMR method, the research should be continued by means of another research technique, including the DSC. In addition, the studies should be carried out in

a wider range of copper ions concentration and in the same clay [6]. It is also necessary to consider [19] that in an actual water-clay system one can expect, within a certain small concentrations range, a reversal of the expected relationship and an increase in the content of unfrozen water with a decreasing concentration of the solution.

In this paper the authors evaluated the influence of the concentration of copper chlorides on changes in bentonite properties, including the chemical and mineral composition. In addition, the influence of molar concentration of copper(II) chloride solution, as well as the impact of concentration of copper ions in clays at the exchange sites on changes of unfrozen water content versus temperature, were studied. Monoionic Cu-forms of bentonite from Slovakia with various concentrations were prepared for studies. The content of unfrozen water was determined by means of the calorimetric method, using a DSC Q200 (TA Instruments, New Castle, DE, USA) instrument, at a temperature of $-23\text{ }^{\circ}\text{C}$. An empirical equation has been proposed to estimate the unfrozen water in clays polluted with copper ions, which uses the specific surface and copper ions concentration as parameters.

2. Materials and Methods

2.1. Materials

Bentonite from Slovakia (BSvk), which was subjected to ion exchange, was used for studies on changes of unfrozen water content in clays with various potentially toxic concentrations of copper ions. Table 1 presents the basic characteristics of clay samples, before the ion exchange ('0') and after ion exchange to copper ions ('Cu'), as a result of saturating the clay with copper(II) chloride solutions of various molar concentrations (0.1–1 M). The physicochemical properties of smectites depend on the location of cation substitutions in their 2:1 layer. The presence of various exchangeable cations makes it difficult to identify a specific smectite, and in order to prevent it, smectites are subjected to an ion exchange process to obtain their homoionic forms [20]. Only a sufficiently high concentration of copper(II) chloride can ensure that the basic exchangeable cations, such as Na, Ca, K, and Mg, are replaced with Cu ions to such an extent that copper becomes the main exchange cation. The molar concentration given by most authors, which ensures the efficiency of the ion exchange between the basic exchangeable cations, is 1 M [4,5,19]. The molar concentration of potentially toxic metals for which the ion exchange will be effective is not clearly defined in the literature and should be determined experimentally [6,18].

2.2. Methods

2.2.1. Determination of the Chemical Properties

The practical chemistry of samples was carried out by flooding the samples three times, in an air-dry state, with a mass of approximately 50 g, with 10 L solutions of copper(II) chloride of various molar concentrations (0.1 M, 0.25 M, 0.5 M, 1 M). Clays were flooded with an appropriate solution in 48 h intervals, after previous decantation. Soils were consecutively packed in membranes permeable to chlorine and placed in 20 L containers with permanent circulation of distilled water. The excess of chlorine was rinsed until the reaction characteristic of chloride ion (with AgNO_3) disappeared. Monoionic samples of bentonites were transferred to glass beakers and dried in the air to the soft-plastic state, then they were closed in jars and stored at room temperature for further studies. Details of the practical chemistry are available in the previous paper by the authors [6].

The metal contents in clays were determined by the ICP-OES method, with the use of an Optima 800 instrument (PerkinElmer company, Waltham, MA, USA). Prior to determinations the samples were appropriately prepared. Clays with a dry mass of 2 g were wet-mineralized with aqua regia in accordance with the PN-ISO 11466.

Additionally, a semi-quantitative analysis of the chemical composition of clays was carried out based on an area scan using an energy dispersive X-ray spectrometer (X-Max EDS system, Oxford Instruments, Oxford, UK). The order of magnitude of the energy of the X-ray quanta is suitable for the observation of atomic structures (the elemental composition) of substances from which they are emitted. Differences in the electronic

structure of the atoms make each of the elements excited in the sample send X-ray spectral series, differing from other energies of the individual lines. In contrast, the intensity of the line is proportional to the concentration of the given element in the sample [21]. The surfaces of the air-dried samples were covered with a thin layer of carbon to prevent electrification in a JEOL JEC-530 coater (JEOL company, Tokyo, Japan). Experiments were conducted with a JSM-7100F field emission scanning electron microscope (JEOL company, Tokyo, Japan), with 15 kV voltage applied. Photographs at a magnification of $\times 2000$ were analyzed. The SEM-EDXS (Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy) results indicated the main elements of clay, including the presence of chlorine in some samples, which was not detected by the method with AgNO_3 . This is possible because copper ions can form complexes with chlorides, leading to the formation of new mineral phases [22].

Table 1. Descriptive characteristics and the water contents of the samples.

Symbol	Description	Characteristics of the Samples		
		Water Content <i>w</i> . (%)	Mass of Water <i>m_w</i> . (g)	Mass of Dry Soil <i>m_s</i> . (g)
BSvk	Natural calcium bentonite from Stará Kremnička—Jelšovský Potok, Slovakia	125.0	4.05	3.24
		90.94	5.22	5.74
		54.46	1.77	3.25
		48.70	1.87	3.84
		70.06	3.44	4.91
BSvk 1 M 'Cu'		62.14	2.15	3.46
		58.64	2.85	4.86
		60.66	2.93	4.83
		59.20	3.57	6.03
		73.55	5.59	7.6
BSvk 0.5 M 'Cu'	Homoionic form of the bentonite from Slovakia saturated with copper ions of various concentrations	55.07	2.01	3.65
		55.79	2.12	3.8
		77.43	2.23	2.88
		69.52	3.33	4.79
		49.80	3.71	7.45
BSvk 0.25 M 'Cu'		64.11	2.43	3.79
		56.41	2.2	3.9
		56.06	2.22	3.97
		79.15	3.72	4.7
		58.88	3.68	6.25
BSvk 0.1 M 'Cu'		79.49	1.86	2.34
		78.64	3.83	4.87
		81.73	1.7	2.08
		66.56	2.01	3.02
		71.50	1.33	1.86

After saturation with copper(II) chloride at the given molar concentration of 1 M, 0.5 M, 0.25 M, and 0.1 M, respectively. The soils were purified of free chloride ions.

To confirm the non-existence of free chlorides in clays, the concentration of these ions was determined in water extracts using the Mohr method, consisting of titration with silver nitrate at the presence of chromate as an indicator (PN-ISO 9297:1994). Prior to determinations the samples were appropriately prepared: 2 g of clays were shaken for 24 h on a rotary shaker in 20 mL of distilled water (with conductivity of $0.06 \mu\text{S}\cdot\text{cm}^{-1}$). After shaking, the samples were filtered through a Whatman filtration paper until a clear solution was achieved.

For the assessment of clay activity in relation to water it is helpful to know the specific surface S (m^2/g) [23]. The specific surface area (S) was determined by the method using the water vapor sorption (WTC) in compliance with Equation (1) according to Stępkowska [23]. The sorption moisture w_{50} was determined at a relative water vapor pressure $p/p_0 = 0.50$

in the desiccator over a saturated solution of magnesium nitrate (V). Sorption lasts 10 days and the mass of clay is determined by drying at 220 °C.

$$S = 6 \times (w_{50} \times 5.85). \quad (1)$$

2.2.2. Determination of the Granulometric and Mineral Composition

Particle size distribution studies were performed by the ‘wet’ laser diffraction method with the use of a HELOS/BF SUCCELL device manufactured by Sympatec GmbH (Clausthal Zellerfeld, Germany). Use of the laser diffraction method as a standard test procedure for the determination of particle size distribution can provide reliable results, provided that consistent sample preparation is used [24]. No dispersant was used for the tests, as the type of dispersant may affect the results of the analysis, especially in clays, where the influence of substances dissolved in the pore solution is considered [25]. Before determining the particle size, the clay pastes, at a plastic consistency (after saturation in distilled water 48 h earlier) with a mass of approximately of 3 g, were dissolved in 50 mL of distilled water.

Determination of the mineral composition of the tested clays was carried out by X-ray powder method in the Bragg–Brentano geometry. X-ray images of all clays were recorded with a Bruker D8 advance X-ray diffractometer (Bruker, Berlin, Germany), a Johansson-type monochromator (Bruker, Berlin, Germany) to determine CuK α 1 radiation ($\lambda = 1.5406 \text{ \AA}$), and a LynxEye position-sensitive detector (Bruker, Berlin, Germany). The measurements were carried out at 2θ from 4.51° to 70° with 0.02° steps. The applied voltage was 3.540 kV with a 530-mA current. The values of interplanar distances obtained from X-ray images were used to identify the mineral phases included in the clays, based on the data contained in the International Center for Diffraction Data PDF-4+ database (ICCD, Newtown Square, PA, USA). X-ray diffractograms of the clays were subjected to semi-quantitative mineralogical analysis using Diffrac Eva V6 software (Bruker, Berlin, Germany). Semi-quantitative mineralogical analysis is based on the relationship between the intensity of the reflections coming from a given phase and the weight content of this phase. The integral intensity (the area under the peak) was used to measure the total intensity of the reflex. Mathematical curve fitting was used.

2.2.3. Determination of the Unfrozen Water Content

The calorimetric technique with the use of a calibrated DSC Q200 device manufactured by TA was chosen for the examination of the changes in the unfrozen water content at a given negative temperature. The DSC method seems to be more suitable than the $^1\text{H-NMR}$ method for the study of clay contaminated with copper ions, since it is very likely that the water molecules participating in the process of cation hydration are no longer partially “visible” for magnetic resonance [6,26].

Samples of clay paste weighing an average of 4–10 mg were placed in aluminum calorimetric hermetic pans with a diameter of 6 mm. The pans with the samples were weighed before and after the tests with an accuracy of 10^{-6} g. The research program consisted of freezing (at a rate of $-2.5 \text{ }^\circ\text{C}/\text{min}$ to a temperature of $-90 \text{ }^\circ\text{C}$) and heating (at a rate of $5 \text{ }^\circ\text{C}/\text{min}$ to a temperature of $20 \text{ }^\circ\text{C}$). The authors maintained the same experimental conditions as in the previous studies on model clays [27] and clays contaminated with copper ions [28] in order to validate the results of the studies. After the tests, the calorimetric lids were pierced and dried at $110 \text{ }^\circ\text{C}$ for 24 h in order to determine the water content (Table 1).

Analysis of the phase composition was conducted based on the thawing curves due to the phenomenon of supercooling, which becomes particularly significant in small samples [29,30]. Thermograms were obtained with the use of Universal Analysis 2000 software (TA Instruments, New Castle, USA). Calculations of the unfrozen water were carried out in accordance with the proven methodology, as demonstrated in the study by Kozłowski and Nartowska [27]. In order to extract the actual endothermic effects associated with melting, stochastic deconvolution was used, in accordance with Kozłowski’s assumptions [31].

The unfrozen water content, depending on the temperature $w_u(T)$, was calculated from Equation (2):

$$w_u(T_i) = w - \sum_{j=i}^n \frac{100 \times q(T_j) \times 1}{L(T_j) \times m_s}, \quad (2)$$

where, $w_u(T_i)$ is the unfrozen water content at temperature T_i as a percentage of the dry mass, w is the water content expressed as a percentage of the dry mass, $q(T_j) \cdot 1 = \Delta h_j$, Δh_j —change in the enthalpy within 1 K, m_s is the mass of the dry soil in the sample (g), and $L(T_j)$ is the latent heat of fusion of the ice at temperature T_j calculated according to the empirical equation given by Horiguchi (1985) [32] Equation (3):

$$L(T) = 7.3 \times T + 334, \quad (3)$$

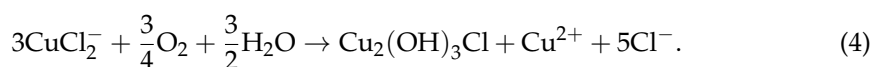
where $L(T)$ is the latent heat of fusion (J/g) of the ice at temperature T and T is temperature ($^{\circ}\text{C}$).

3. Results and Discussion

3.1. Properties of Bentonite (BSvk) after Chemical Modification

Table 2 presents properties of the BSvk bentonite, before ('0') and after the ion exchange ('Cu'), as a result of the clay saturation with the copper(II) chloride of various molar concentrations (1 M, 0.5 M, 0.25 M, 0.1 M), and then rinsing clays from free chloride ions.

The ICP-OES chemical analysis confirmed the effectiveness of ion exchange and the introduction of copper ions to the smectite structure. The results show that the process effectiveness was related to the initial molar concentration of copper(II) chloride solution. Izosimova et al. [18] made similar observations. When examining sodium bentonites, the authors observed that the amount of copper adsorbed on the bentonite significantly increased with the increasing molar concentration of copper chloride (0.025 to 0.125 mmol/L). The relationship was less significant, but still visible in the Al-bentonites. A supplementary SEM EDXS chemical analysis (Figure 1) has shown that copper is the main exchangeable cation in smectite. After saturation of clays with 0.1 M, 0.25 M, and 0.5 M solutions, small amounts of chlorine ions were found in the EDXS method, which were not discovered by the Mohr method. It may indicate the presence of new mineral phases, which originated due to a reaction with chlorine ions. Such a phenomenon was described by Standberg and Johansson [33] who found that, depending on the chloride concentration in the aqueous layer, copper ions can form chlorinated complexes of copper (CuCl_2^-), which in the presence of dissolved oxygen give rise to the formation of basic copper chlorides (atacamite, clinoatacamite) (4).



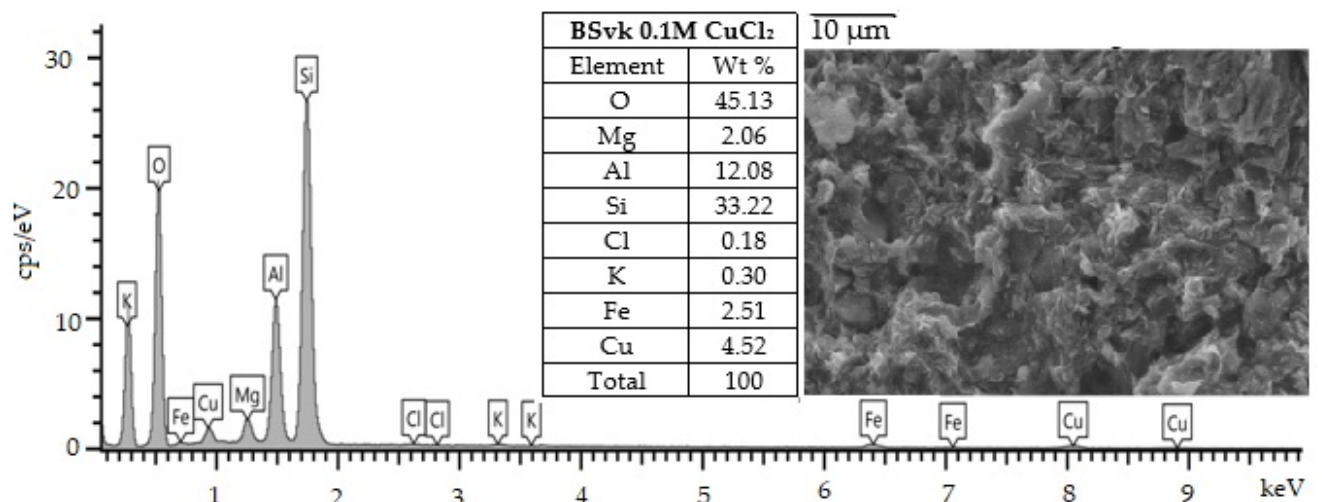
The performed X-ray diffraction patterns (Figure 2) revealed the existence of new mineral phases. They were identified as minerals from the atacamite (atacamite/clinoatacamite) group. The content of minerals from the atacamite group increased with a higher concentration of copper ions in the smectite. The increase in the crystalline phase of copper chlorides with the increase in copper ions was also confirmed by Han et al. [34], who examined the surface properties of the CuCl_2 /activated carbon (AC) catalyst for the synthesis of dimethyl carbonate at different copper contents. Figure 3 shows minerals, which crystallized after 30 days on leachate from the ion exchange of bentonites.

The modification of Ca-bentonite with Cu cations leads to a decrease in the interplanar spacing (d_{001}) of montmorillonite from 14.88 Å for the Ca-form to 12.31–12.48 Å for 'Cu' forms depending on the concentration of Cu cations. Results show that the higher the concentration of copper ions, the smaller the interplanar distance.

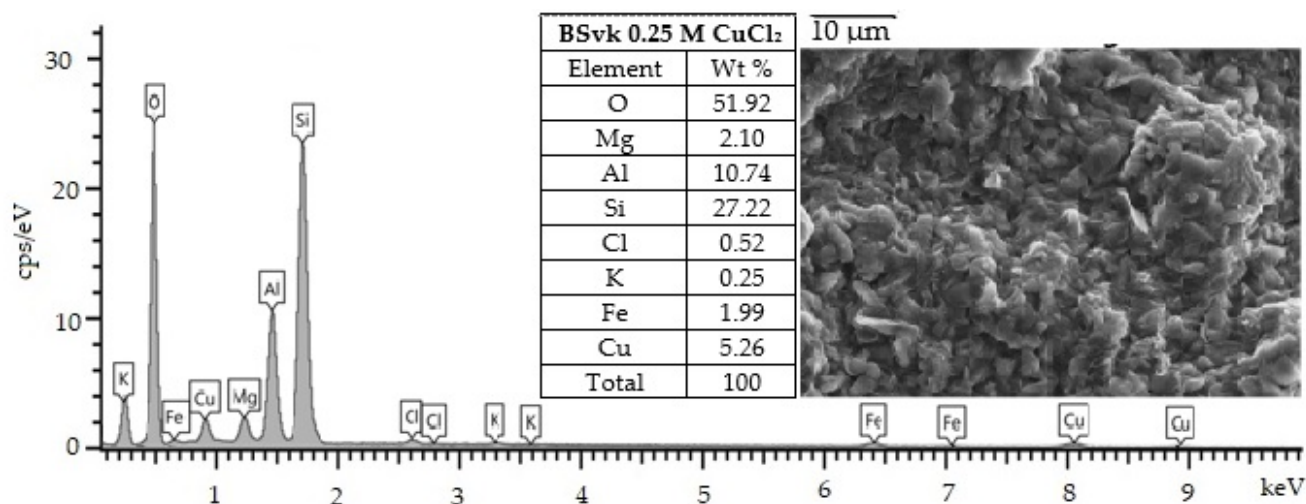
Table 2. Properties of the soils investigated in this study.

Property	Before Ion Exchange		After Ion Exchange for Cu ²⁺			
	BSvk '0'	BSvk 1 M 'Cu'	BSvk 0.5 M 'Cu'	BSvk 0.25 M 'Cu'	BSvk 0.1 M 'Cu'	
Content of elements in the dry clay matrix—(mg/kg dry weight) ^a	Ca	11,945 ± 140	1598 ± 28	675.9 ± 22.8	328.1 ± 5.8	383.5 ± 4.9
	K	959 ± 9	522 ± 18	290.2 ± 5.0	280.7 ± 7.3	301.2 ± 6.1
	Mg	5348 ± 60	2819 ± 11	1091.2 ± 19.6	1088.7 ± 24.5	1003.1 ± 11.2
	Na	1151 ± 9	412.6 ± 4.8	167.8 ± 1.1	194.8 ± 1.9	132.9 ± 2.2
	Fe	3582 ± 46	4443 ± 32	4559 ± 65	4457 ± 75	4154 ± 70
	Cd	0.270 ± 0.002	0.630 ± 0.003	0.072 ± 0.001	0.114 ± 0.002	0.137 ± 0.003
	Cr	10.09 ± 0.11	22.88 ± 0.17	58.09 ± 0.85	35.73 ± 0.57	13.97 ± 0.11
	Ni	7.22 ± 0.21	22.02 ± 0.09	6.44 ± 0.40	2.41 ± 0.65	3.47 ± 0.13
	Pb	17.02 ± 0.01	17.93 ± 0.18	13.31 ± 0.84	14.53 ± 0.67	22.90 ± 0.29
	Zn	64.54 ± 0.69	95.61 ± 0.72	80.75 ± 2.03	78.72 ± 0.86	71.36 ± 2.13
	Co	1.26 ± 0.01	0.11 ± 0.06	0.08 ± 0.01	0.13 ± 0.02	0.12 ± 0.01
Specific surface area S (m ² /g) ^b	Cu	6.28 ± 0.06	7677 ± 70	28,773 ± 162	27,571 ± 90	23,284 ± 121
		671	460	203	189	183
Estimated mineralogical composition ^c		≈92% smectite (5% quartz, 3% biotite)		≈86% smectite (5% quartz, 3% biotite, 6% atacamite/ clinoatacamite)	≈87% smectite (5% quartz, 3% biotite, 5% atacamite/ clinoatacamite)	≈89% smectite (5% quartz, 3% biotite, 3% atacamite/ clinoatacamite)
	d ₀₀₁ for smectite (Å) ^c	14.88	12.48	12.31	12.34	12.38
Granulometric composition (%) ^d	0.002 < d < 0.063 mm	80.2	79.5	84	81.5	82
	d ≤ 0.002 mm	19.8	20.5	16	18.5	18

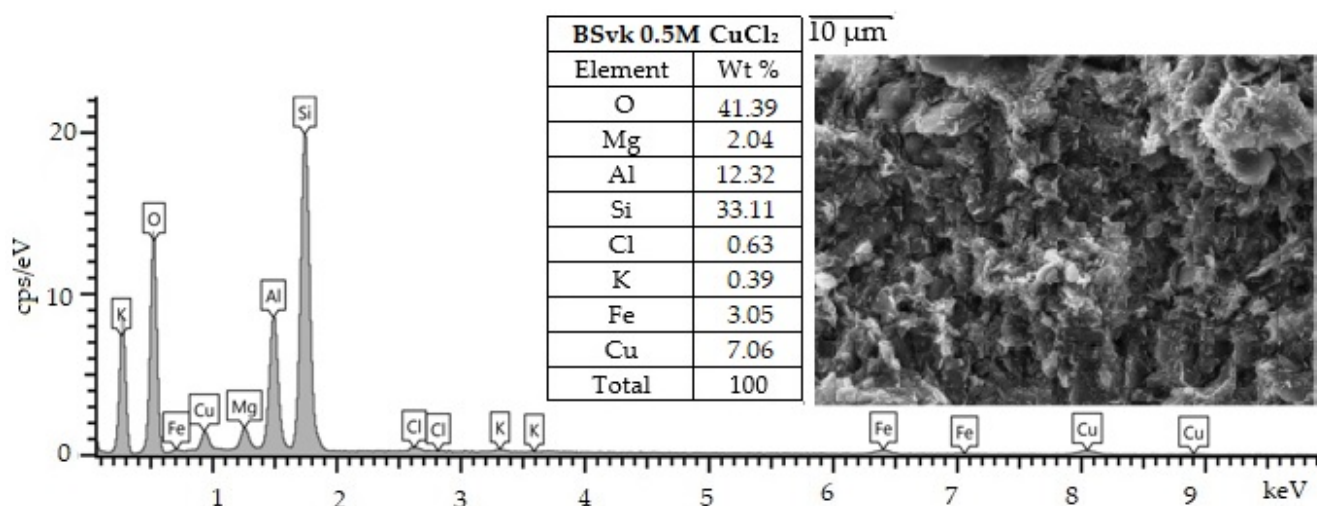
^a ICP-OES method; ^b Water Sorption Test (WST) by Stepkowska (1973); ^c XRD method; ^d Laser diffraction method; 0.1 M, 0.25 M, 0.5 M, and 1 M molar concentration of CuCl₂ used for ion exchange in BSvk bentonite; The content of free chlorine ions (Mohr's method PN-ISO 9297:1994)—below the level of the detection limit in each clay.



(a)



(b)



(c)

Figure 1. Morphology and SEM-EDX data of the BSvk bentonite samples saturated with copper(II) chloride solutions of different molar concentrations: (a) 0.1 M, (b) 0.25 M, (c) 0.5 M.

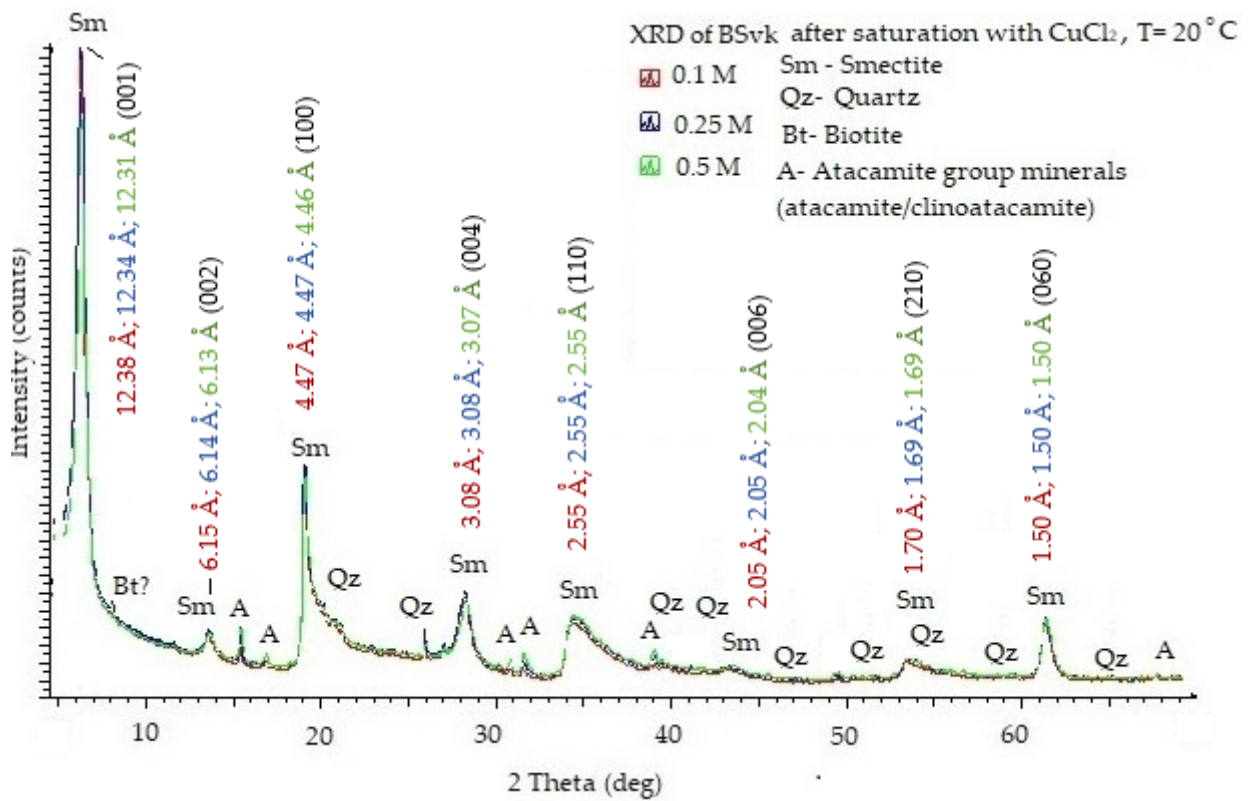


Figure 2. Powder XRD patterns of the bentonite BSvk samples after saturation with copper(II) chloride solutions of different molar concentrations: 0.1 M, 0.25 M, and 0.5 M.

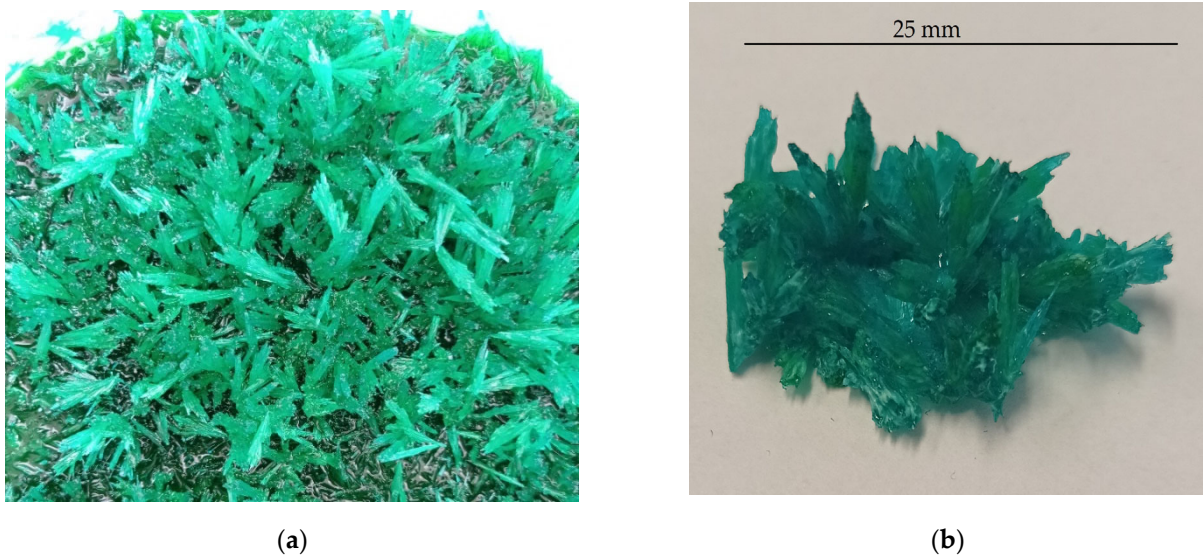


Figure 3. Macro photography of a mineral that crystallizes on the leachate from the bentonite ion exchange process, identified as an atacamite group mineral. (a) atacamite group mineral that crystallizes on the leachate (b) atacamite group mineral.

3.2. Influence of Chemical Modification of Bentonite on the Unfrozen Water Content

Figure 4 shows, for selected samples of BSvk bentonite, before ‘0’ and after the ion exchange into copper ions ‘Cu’ with various concentrations, how the content of unfrozen water changes versus temperature.

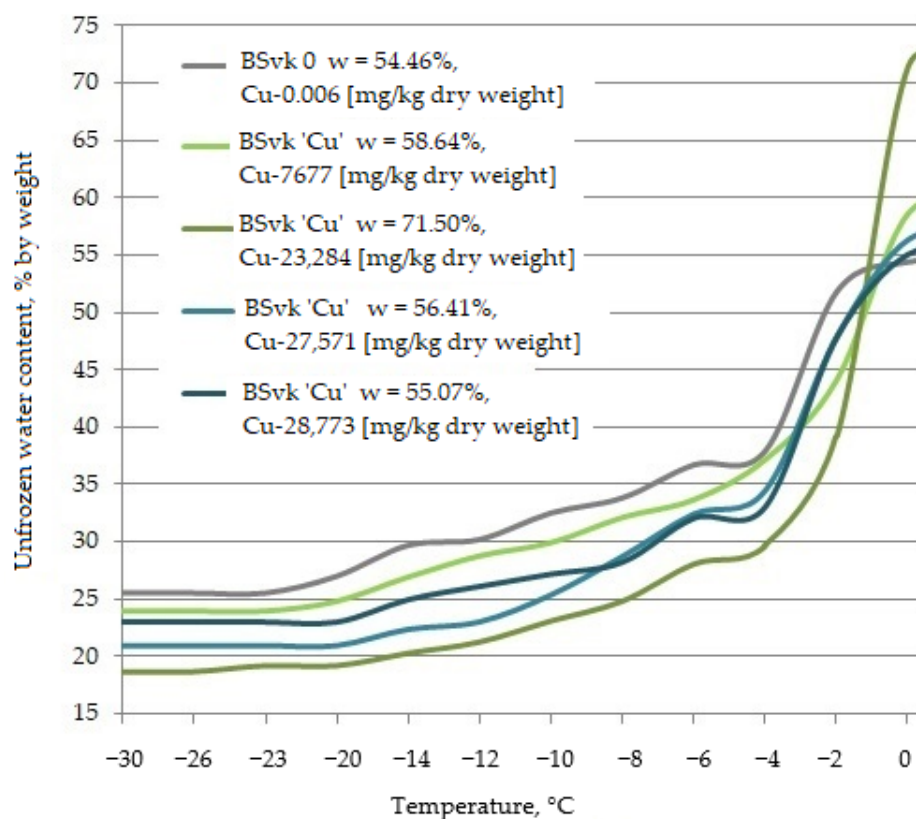


Figure 4. Curves of unfrozen water content versus temperature for selected samples of BSvk bentonite, before the ion exchange '0', and after saturation with copper ions 'Cu' of various concentrations.

It has been observed (Figure 4), that the content of unfrozen water undergoes change versus the concentration of copper ions in the soil. These observations were statistically significant ($p < 0.05$). To evaluate the statistical significance of the molar concentration of the CuCl_2 solution, a single factor the ANOVA (Analysis of Variance) was carried out, which is based on 180 observations (Table 3).

Table 3. Univariate tests of significance of molar concentration of the solution (CuCl_2) for the unfrozen water content.

The Unfrozen Water Content	Sum of Squares	Degrees of Freedom	Mean Square	F-Test Value	p-Value	Statistical Significance
Intercept	130,664.4	1	130,664.4	3148.061	0.000000	
Solution Molar concentration	1171.6	3	390.5	9.409	0.000008	***
Error	7305.1	176	41.5			

Significant at *** 0.001 probability level.

3.2.1. The Effect of the Molar Concentration of the Solution

Table 3 presents a significant relationship ($p < 0.01$) between the average content of unfrozen water and the molar concentration, used to saturate the clay. An average content of unfrozen water in a given clay, irrespective of temperature, grew with the increasing molar concentration ($0.1 \text{ M} < 0.25 \text{ M} < 0.5 \text{ M} < 1.0 \text{ M}$) and with the increasing specific surface of the clay (Figure 5). The increase in the specific surface with the increasing molar concentration has been explained below. The increase in the content of unfrozen water with the growing specific surface was discussed in many articles [3,6].

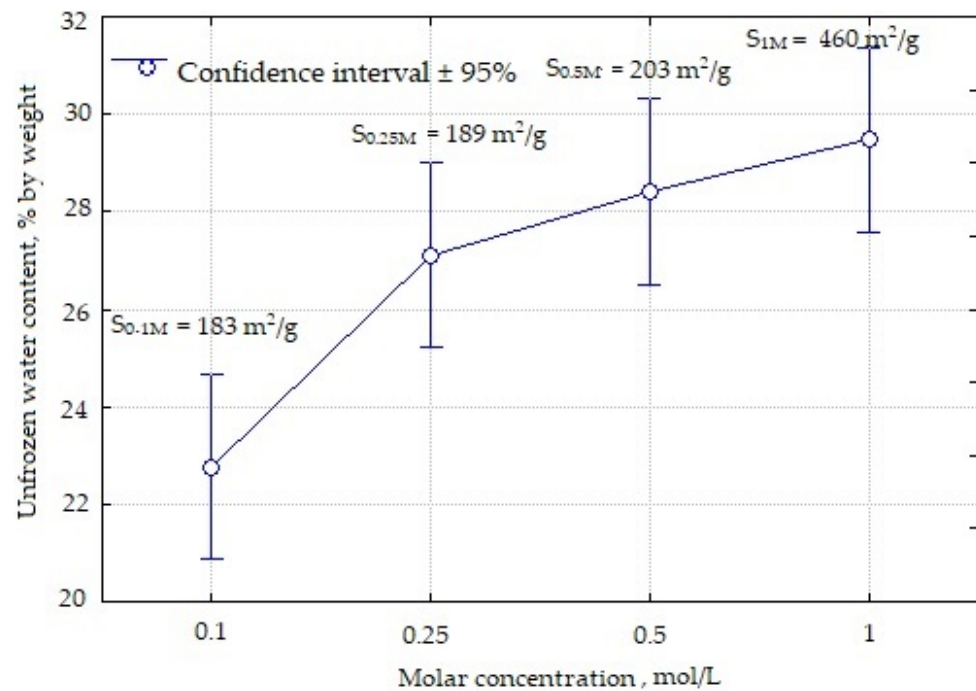


Figure 5. Average contents of unfrozen water in BSvk 'Cu' bentonites versus the molar concentration of the solution (0.1–1 M CuCl₂) used for Cu ion exchange.

The lowest metal concentration and the largest specific surface in the studied clays polluted with copper ions was obtained after the ion exchange for the most concentrated solution (1 M of copper(II) chloride). At first glance it seems inconsistent with expectations. However, such behavior is theoretically confirmed. The interaction of van der Waals forces with forces of ionic-electrostatic attraction, which occur at contacts of clayey particles during the procedure of ion exchange, is considered to be the cause. According to Van Olphen [35], an increase in the counter-ions concentration (≥ 1 M) results in the compression of a double layer around the flat surfaces of the particles, causing an increase in the forces of particles attraction. The surface density of charge then increases and the function of specific cations adsorption decreases [36]. In addition, the electrokinetic potential of the boundary surface of the particle in contact with 1 M solution is low (close to 0), due to which particles aggregate in larger clusters and form deposits of high porosity. At low concentrations of counter-ions, e.g., 0.1 M, a thick double layer originates, resulting in increased repulsion forces. The density of the surface charge is smaller, and the function of cations adsorption increases [35]. Therefore, in the clay subjected to the ion exchange with 0.1 M copper (II), a chloride solution with smaller specific surfaces and higher concentrations of copper ions are observed than after saturation with 1 M solution. It should be emphasized that the ratio of attraction and repulsion forces in the water environment is different for the various electrolyte concentrations and, so far, it has not been precisely determined. It is known that van der Waals forces decrease with increasing distances between particles, but this relationship is not linear and may be approximated to a parabola. So, it is possible to assume that distances between particles grow with a decreasing molar concentration of the solution as follows $1 \text{ M} > 0.5 \text{ M} > 0.25 \text{ M} > 0.1 \text{ M}$. Thus, the density of surface charge gradually decreases, and the specific surface of clays follows ($S_{1 \text{ M}} = 460 \text{ m}^2/\text{g}$; $S_{0.5 \text{ M}} = 203 \text{ m}^2/\text{g}$; $S_{0.25 \text{ M}} = 189 \text{ m}^2/\text{g}$; $S_{0.1 \text{ M}} = 183 \text{ m}^2/\text{g}$). The curve of cations adsorption goes up; however, the rise is not linear most likely due to ionic-electrostatic interactions between montmorillonite particles, which have a clear minimum [37,38].

3.2.2. The Effect of the Concentration of Copper Ions in the Clay

Figure 6 presents the relationship between average contents of unfrozen water versus copper concentration in the clay.

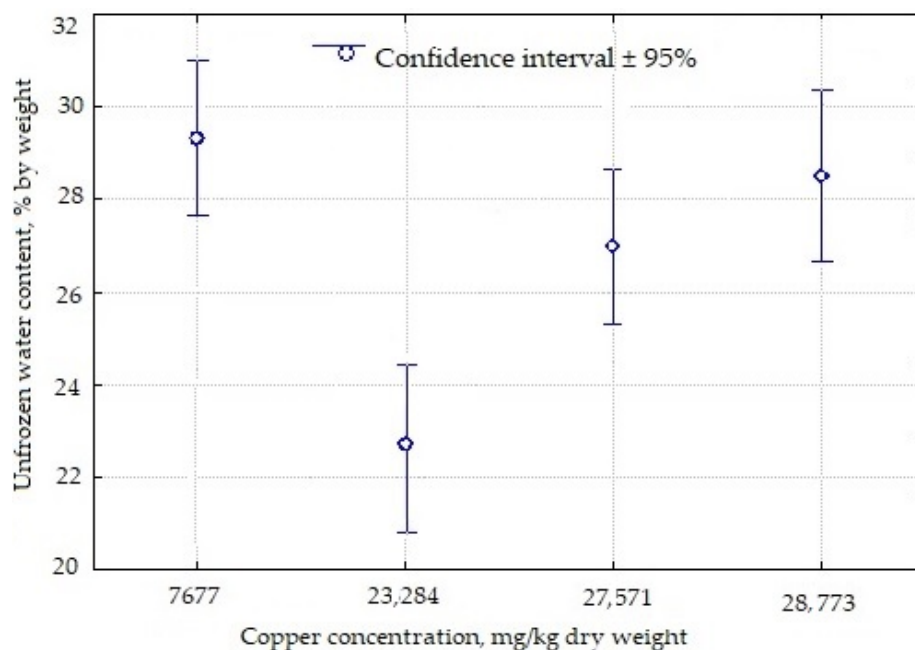


Figure 6. Average contents of unfrozen water in BSvk ‘Cu’ bentonites versus the concentration of copper ions in the soil, irrespective of temperature.

Looking for causes of observed variabilities, a multiple regression analysis was performed (Table 4), which has shown that a change of unfrozen water content in the studied soils has a significant relationship with the temperature change, specific surface, and copper ions concentration. As the temperature is the most important factor affecting changes in the unfrozen water content, further quantitative relationships of this water fraction with the copper concentration will be analyzed at defined temperatures (Table 4).

Table 4. Multiple regression analysis between the temperature, the specific surface area, and the unfrozen water of the soil in selected temperatures in the temperature range (−23 °C to −2 °C).

	The Unstandardized Beta (B)	Std. Error B	The Standardized Beta (β)	Std. Error β	t Test Value	p-Value	Significance
N = 180 Dependent variable: unfrozen water at the temperatures −23 °C. −20 °C. −14 °C. −12 °C. −10 °C. −8 °C. −6 °C. −4 °C and −2 °C							
R = 0.86 R ² = 0.73 adj. R ² = 0.72 Std. error of estimate: 3.63							
Intercept			0.273300	4.398521	0.06213	0.950526	
Temperature	0.767115	0.039492	0.789640	0.040652	19.42437	0.000000	***
Copper concentration in clay	0.984689	0.133673	0.802535	0.108946	7.36638	0.000000	***
Specific surface area of clay	1.169654	0.133673	0.068947	0.007880	8.75009	0.000000	***
N = 160 Dependent variable: unfrozen water at the temperatures −23 °C. −20 °C. −14 °C. −12 °C. −10 °C. −8 °C. −6 °C. −4 °C							
R = 0.90 R ² = 0.81 adj. R ² = 0.80 Std. error of estimate: 2.27							
Intercept			−0.333810	2.944228	−0.11338	0.909878	
Temperature	0.759655	0.035221	0.623249	0.028896	21.56848	0.000000	***
Copper concentration in clay	1.286717	0.123575	0.779045	0.074818	10.41248	0.000000	***
Specific surface area of clay	1.580003	0.127649	0.069188	0.005590	12.37774	0.000000	***

Significant at the *** 0.001 probability level.

Because the change of the unfrozen water content in the studied soils seems to be related to the temperature, copper ion concentration in the clay, and the specific surface of clay (Table 4), the authors have proposed an equation to estimate the unfrozen water in clays with high concentrations of copper ions (Equation (5)). It may be used for engineering purposes to predict the unfrozen water in soils contaminated with copper ions of a high concentration due to a good match of model parameters (R = 0.943). Table 5 presents the estimated parameters of model (5). In previous papers the authors reported a possible

influence of the copper ions concentration on the content of unfrozen water [28] and a significant relationship between the specific surface, porosity, and the concentration of copper ions [6]. An increase in the unfrozen water content with the growing specific surface seems to be obvious [3,27,39].

$$w_u(T_i) = a_1 + a_2 \cdot S + a_3 \cdot [Cu] + a_4 \cdot \ln \theta, \quad (5)$$

where $w_u(T_i)$ is the unfrozen water content at temperature T_i as a percentage of the dry mass. S is the specific surface area [m^2/g]. Cu is copper concentration in the clay [g/kg dry of soil], and θ is the temperature depression [K].

Table 5. Parameter estimates and overall characteristics of the model given by Equation (5).

Parameter	Estimate	SE	t	p	Statistical Significance	Confidence Limits	
						Lower	Upper
a ₁	10.87651	2.259894	4.8128	0.000003	***	6.41257	15.34045
a ₂	0.06361	0.003936	16.1619	0.000000	***	0.05583	0.07138
a ₃	0.72401	0.054414	13.3056	0.000000	***	0.61653	0.83149
a ₄	−7.53268	0.244522	−30.8057	0.000000	***	−8.01568	−7.04968

*** Significant at the 0.001 probability level; For Equation (5) $R = 0.943$. $df = 156$ and standard errors of the estimate (SEEs) at -23 , -20 , -14 , -12 , -10 , -8 , -6 , and -4 °C are 1.39, 1.51, 1.46, 1.49, 1.52, 1.58, 2.06, and 1.63, respectively.

The proposed Equation (5) seems to describe better changes in the unfrozen water content in soils polluted with copper ions than the popular Anderson and Tice model, based on the specific surface [3]. It is proven by the lack of possibility to match the statistically significant parameters of the model. If the content of unfrozen water depends primarily on the specific surface and the copper ions concentration, one can presume that an appropriate type of water, depending on the exchangeable cation of bentonite, undergoes a phase transition. A strong relationship with the specific surface suggests that to a large extent the water adsorbed on the flat surfaces of crystallites undergoes a phase transition at $T \leq -4$ °C.

Table 6 summarizes the results of the unfrozen water content determinations at individual negative temperatures as a function of the molar concentration of the solution and the concentration of copper ions in the clay.

We observed that the unfrozen water content determined by the use of the DSC in BSvk 0 in the entire range of the tested temperatures is consistent with the previous results obtained with the $^1\text{H-NMR}$ method and the differences do not exceed 2% [6]. In the case of the same bentonite saturated with copper ions 'Cu' (1 M), the results of the unfrozen water content obtained by both methods differ. The differences in the content of the unfrozen water content are greater the lower the temperature is. In the temperature range from $T = -8$ to -2 °C, the differences are 2–5%, in $T = -10$ to -23 °C about 8–14%. The research seems to confirm the possible limitations of the $^1\text{H-NMR}$ method in determining the content of the unfrozen water in bentonites saturated with copper ions, due to the possible phenomenon of the cation hydration [6]. The results (Table 6) also show that at each negative temperature, the content of the unfrozen water increases with the increasing molar concentration of CuCl_2 used for the ion exchange in the clays. However, it should be kept in mind that chloride ions were only contained in bentonites saturated with 0.1–0.5 M solutions. In addition, this chlorine was not free but bound in the form of minerals from the atacamite group. Bing et al. [40] observed higher contents of the unfrozen water in saline soils and an increase in the unfrozen water content with an increase in the salt content. The latter is confirmed by our research. On the other hand, in our research, the content of the unfrozen water at any negative temperature is always higher in clays not subjected to ion exchange with copper. These results are difficult to compare due to the fact that we conducted the research in a more complex system, where copper chloride ions were bound in the form of a mineral.

Table 6. The average values of the unfrozen water content at a given temperature [°C] determined by the DSC method in BSVk 'Cu' bentonites with various concentrations.

The Molar Concentration of CuCl ₂ Used for the Ion Exchange Process in Clay	Copper Concentration in Clay [mg/kg Dry of Clay]	The Average of the Unfrozen Water Content [%] at a Given Temperature [°C]				
		−23	−20	−14	−12	−10
0	6.28 ± 0.06	24.23 ± 0.85	24.53 ± 0.85	27.03 ± 0.53	28.43 ± 2.06	29.14 ± 0.35
1 M	7677 ± 70	22.74 ± 1.65	22.98 ± 1.96	24.78 ± 2.05	25.91 ± 2.14	27.59 ± 2.08
0.5 M	28,773 ± 162	22.47 ± 1.44	22.61 ± 1.65	24.16 ± 1.60	25.21 ± 1.33	26.21 ± 1.94
0.25 M	27,571 ± 90	20.27 ± 1.18	20.27 ± 1.18	22.21 ± 0.67	22.99 ± 0.61	24.92 ± 0.47
0.1 M	23,284 ± 121	17.51 ± 1.38	18.94 ± 1.50	20.03 ± 1.77	21.47 ± 1.41	23.61 ± 1.12
		−8	−6	−4	−2	
0	6.28 ± 0.06	32.38 ± 1.24	35.12 ± 2.19	39.29 ± 0.98	44.61 ± 5.44	
1 M	7677 ± 70	30.43 ± 2.03	32.42 ± 2.21	37.31 ± 1.32	41.40 ± 4.07	
0.5 M	28,773 ± 162	28.15 ± 1.51	31.86 ± 1.44	33.24 ± 1.13	41.79 ± 8.82	
0.25 M	27,571 ± 90	27.68 ± 1.50	30.68 ± 2.01	33.95 ± 1.41	41.05 ± 6.61	
0.1 M	23,284 ± 121	23.61 ± 1.12	24.65 ± 2.34	28.91 ± 0.73	32.26 ± 5.24	

± Standard Deviation.

4. Conclusions

1. The higher the amount of copper cations in bentonite after the ion exchange of Ca-bentonite with the use of copper(II) chloride solution, the lower the solvent concentration;
2. In bentonite saturated with 0.1 M, 0.25 M, and 0.5 M solutions, new mineral phases originate due to the reaction with copper(II) chloride, which were identified based on the XRD and SEM-EDS studies as minerals from the atacamite group;
3. ANOVA (Analysis of Variance) showed a statistically significant relationship between the molar concentration of copper(II) chloride, used to saturate the clay, as well as the copper ions concentration in the clay, determined with the use of the ICP-OES method, and the unfrozen water content at temperatures below 0 °C;
4. The average content of the unfrozen water in copper bentonites increased with the increasing molar concentration of copper(II) chloride used to saturate the solid, following the sequence: 0.1 M < 0.25 M < 0.5 M < 1 M. These changes may be related to the increase of the specific surface of the clays in the same direction;
5. MLR (multiple linear regression) showed that a change of the unfrozen water content in the studied clays shows a significant association with the temperature change, the specific surface, and the copper content in the clay;
6. The content of the unfrozen water in ‘Cu’ bentonites, at temperatures ≤ -4 °C, may be estimated with the use of an empirical equation containing the specific surface and the copper concentration in the clay ($p = 0.001$, $R = 0.94$).

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References

1. Cruz, N.; Peng, Y.; Farrokhpay, S.; Bradshaw, D. Interactions of clay minerals in copper–Gold flotation: Part 1—Rheological properties of clay mineral suspensions in the presence of flotation reagents. *Miner. Eng.* **2013**, *50*, 30–37. [[CrossRef](#)]
2. Kumari, N.; Mohan, C. Basics of Clay Minerals and Their Characteristic Properties. In *Clay and Clay Minerals*; Do, G., Ed.; Intech Open: London, UK, 2021. [[CrossRef](#)]
3. Anderson, D.M.; Tice, A.R. The Unfrozen Interfacial Phase in Frozen Soil Water Systems. In *Ecological Studies (Analysis and Synthesis)*; Hadas, A., Swartzendruber, D., Rijtema, P.E., Fuchs, M., Yaron, B., Eds.; Physical Aspects of Soil Water and Salts in Ecosystems; Springer: Berlin/Heidelberg, Germany, 1973; Volume 4. [[CrossRef](#)]
4. Kruse, A.M.; Darrow, M.M. Adsorbed cation effects on unfrozen water in fine-grained frozen soil measured using pulsed nuclear magnetic resonance. *Cold Reg. Sci. Technol.* **2017**, *142*, 42–54. [[CrossRef](#)]
5. Darrow, M.M.; Guo, R.; Trainor, T.P. Zeta potential of cation-treated soils and its implication on unfrozen water mobility. *Cold Reg. Sci. Technol.* **2020**, *173*, 103029. [[CrossRef](#)]
6. Nartowska, E.; Kozłowski, T.; Kolankowska, M. Exchangeable cations (Cu²⁺, Zn²⁺) effects on unfrozen water content in clay-water system using ¹H NMR method. *Cold Reg. Sci. Technol.* **2021**, *192*, 103403. [[CrossRef](#)]
7. Xiao, Z.; Lai, Y.; Zhang, M. Study on the freezing temperature of saline soil. *Acta Geotech.* **2018**, *13*, 195–205. [[CrossRef](#)]
8. Xiao, Z.; Lai, Y.; You, Z.; Zhang, M. The phase change process and properties of saline soil during cooling. *Arab. J. Sci. Eng.* **2017**, *42*, 3923–3932. [[CrossRef](#)]
9. Xiao, Z.; Zhu, L.; Hou, Z. The change mechanism and a prediction model of unfrozen water content in sodium chloride soil. *Geoderma* **2022**, *419*, 115881. [[CrossRef](#)]
10. Ren, J.; Vanapalli, S.K. Effect of freeze-thaw cycling on the soil-freezing characteristic curve of five Canadian soils. *Vadose Zone J.* **2020**, *19*, e20039. [[CrossRef](#)]

11. Wdowczyk, A.; Szymańska-Pulikowska, A. Differences in the Composition of Leachate from Active and Non-Operational Municipal Waste Landfills in Poland. *Water* **2020**, *12*, 3129. [CrossRef]
12. Podlech, C.; Matschiavelli, N.; Peltz, M.; Kluge, S.; Arnold, T.; Cherkouk, A.; Meleshyn, A.; Grathoff, G.; Warr, L.N. Bentonite Alteration in Batch Reactor Experiments with and without Organic Supplements: Implications for the Disposal of Radioactive Waste. *Minerals* **2021**, *11*, 932. [CrossRef]
13. Hall, D.S.; Behazin, M.; Binns, W.J.; Keech, P.G. An evaluation of corrosion processes affecting copper-coated nuclear waste containers in a deep geological repository. *Prog. Mater. Sci.* **2021**, *118*, 100766. [CrossRef]
14. Carlsson, T. *Interactions between Copper Corrosion Products and MX-80 Bentonite*; Working Report; Posiva Oy: Olkiluoto/Eurajoki, Finland, 2008.
15. Kosec, T.; Qin, Z.; Chen, J.; Legat, A.; Shoesmith, D.W. Copper corrosion in bentonite/saline groundwater solution: Effects of solution and bentonite chemistry. *Corros. Sci.* **2015**, *90*, 248–258. [CrossRef]
16. Kim, I.J.; Kwak, P.B.; Weitz, C.J. Specificity in Circadian Clock Feedback from Targeted Reconstitution of the NuRD Corepressor. *Mol. Cell* **2014**, *56*, 738–748. [CrossRef]
17. King, F.; Hall, D.S.; Keech, P.G. Nature of the near-field environment in a deep geological repository and the implications for the corrosion behaviour of the container. *Corros. Eng. Sci. Technol.* **2017**, *52*, 25–30. [CrossRef]
18. Izosimova, Y.; Tolpeshta, I.; Gurova, I.; Karpukhin, M.; Zakusin, S.; Krupskaya, V. Sorption of Cu²⁺ Ions by Bentonite Modified with Al Keggin Cations and Humic Acid in Solutions with pH 4.5. *Minerals* **2020**, *10*, 1121. [CrossRef]
19. Yong, R.N.; Cheung, C.H.; Sheeran, D.E. Prediction of Salt Influence on Unfrozen Water Content in Frozen Soils. *Eng. Geol.* **1979**, *13*, 137–155. [CrossRef]
20. Garcia-Romero, E.; Lorenzo, A.; Garcia-Vicente, A.; Morales, J.; Garcia-Rivas, J.; Suarez, M.J. On the structural formula of smectites: A review and new data on the influence of exchangeable cations. *Appl. Cryst.* **2021**, *54*, 251–262. [CrossRef]
21. Karina, T.-R.; Julio, B.-A.; Núria, F.; Antonio, F. Chapter, Ten—Metal and metal oxide nanoparticles: An integrated perspective of the green synthesis methods by natural products and waste valorization: Applications and challenges. In *Comprehensive Analytical Chemistry*; Verma, S.K., Das, A.K., Eds.; Elsevier: Amsterdam, The Netherlands, 2021; Volume 94, pp. 433–469; ISBN 9780323898812. [CrossRef]
22. Lopesino, P.; Alcántara, J.; De la Fuente, D.; Chico, B.; Jiménez, J.A.; Morcillo, M. Corrosion of Copper in Unpolluted Chloride-Rich Atmospheres. *Metals* **2018**, *8*, 866. [CrossRef]
23. Stepkowska, E.T. Simple method of crystal phase water. specific surface and clay mineral content estimation in natural clays. *Stud. Geotech.* **1973**, *2*, 21–36.
24. Fisher, P.; Aumann, C.; Chia, K.; O'Halloran, N.; Chandra, S. Adequacy of laser diffraction for soil particle size analysis. *PLoS ONE* **2017**, *12*, e0176510. [CrossRef]
25. Jaijel, R.; Goodman Tchernov, B.; Biton, E.; Weinstein, Y.; Katz, T. Optimizing a standard preparation procedure for grain size analysis of marine sediments by laser diffraction (MS-PT4SD: Marine sediments-pretreatment for size distribution. *Deep Sea Res. Part I Oceanogr. Res. Pap.* **2021**, *167*, 103429. [CrossRef]
26. Wang, H.; Shibue, T.; Komine, H. Hydration and dehydration of water of bentonite: A solid-state ¹H magic-angle spinning NMR study. *Chem. Phys.* **2020**, *536*, 110796. [CrossRef]
27. Kozłowski, T.; Nartowska, E. Unfrozen water content in representative bentonites of different origin subjected to cyclic freezing and thawing. *Vadose Zone J.* **2013**, *12*, 1–11. [CrossRef]
28. Nartowska, E.; Kozłowski, T. The Effect of Freeze-Thaw Cycling and the Initial Mass of Water on the Unfrozen Water Content of Calcium Bentonites Modified by Copper Ions. *Minerals* **2022**, *12*, 66. [CrossRef]
29. Teng, J.; Kou, J.; Yan, X.; Zhang, S.; Sheng, D. Parameterization of soil freezing characteristic curve for unsaturated soils. *Cold Reg. Sci. Technol.* **2020**, *170*, 102928. [CrossRef]
30. Kozłowski, T. Some factors affecting supercooling and the equilibrium freezing point in soil–water systems. *Cold Reg. Sci. Technol.* **2009**, *59*, 25–33. [CrossRef]
31. Kozłowski, T. A comprehensive method of determining the soil unfrozen water curves: 1. Application of the term of convolution. *Cold Reg. Sci. Technol.* **2003**, *36*, 71–79. [CrossRef]
32. Horiguchi, K. Determination of unfrozen water content by DSC. In Proceedings of the 4th International Symposium on Ground Freezing Sapporo, Rotterdam, The Netherlands, 5–7 August 1985; pp. 33–38.
33. Strandberg, H.; Johansson, L.G. Some aspects of the atmospheric corrosion of copper in the presence of sodium chloride. *J. Electrochem. Soc.* **1998**, *145*, 1093. [CrossRef]
34. Han, S.H.; Byung, G.L.; Byoung, S.A.; Dong, J.M.; Suk, I.H. Surface properties of CuCl₂/AC catalysts with various Cu contents: XRD, SEM, TG/DSC and CO-TPD analyses. *Appl. Surf. Sci.* **2003**, *211*, 76–81. [CrossRef]
35. Olphen, H. *An Introduction to Clay Colloid Chemistry*; John Wiley & Sons: New York, NY, USA, 1963; Volume 53, p. 230. [CrossRef]
36. Push, R. Microstructure Controls Physical Properties of Smectite Clay. *J. Earth Sci. Geotech. Eng.* **2019**, *9*, 63–98. Available online: <http://www.diva-portal.org/smash/get/diva2:1346212/FULLTEXT01.pdf> (accessed on 10 January 2022).
37. Jordine, E.S.A.; Bodman, G.B.; Gold, A.H. Effect of surface ions on the mutual interaction of montmorillonite particles. *Soil Sci.* **1962**, *94*, 371–378. [CrossRef]
38. Barshad, I. The effect of the interlayer cations on the expansion of the mica type of crystal lattice. *Am. Mineral.* **1950**, *35*, 225–238.

-
39. Jin, X.; Yang, W.; Gao, X.; Zhao, J.-Q.; Li, Z.; Jiang, J. Modeling the unfrozen water content of frozen soil based on the absorption effects of clay surfaces. *Water Resour. Res.* **2020**, *56*, e2020WR027482. [[CrossRef](#)]
 40. Bing, H.; He, P.; Zhang, Y. Cyclic freeze—Thaw as a mechanism for water and salt migration in soil. *Environ. Earth Sci.* **2015**, *74*, 675–681. [[CrossRef](#)]