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EFFECT OF CYCLIC FREEZING ON MICROSTRUCTURE PARAMETERS OF MONOIONIC BENTONITES

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Summary: In this study the effects of cyclic freezing on microstructure of monomineral forms of bentonite were investigated. Samples of the non-frozen soil and the soil frozen were tested using scanning electron microscope SEM. The analysis of the photographs was conducted using Photo Shop CS4 software. Results obtained show that the microstructure of the frozen soil undergoes significant modifications. The analysis revealed increase in total area of pores. On the basis of statistical analysis it can be assumed that the specific surface area of bentonite depended on the type of exchangeable cation (Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}).

Keywords: bentonite, freeze-thaw, microstructure

1. INTRODUCTION

Bentonite is a rock which originates from the transformation of tuff and tuffite. It is white, yellowish or dark brown. It is fragile, monomineral or almost monomineral, consisting mostly of montmorillonite. In commonly appearing types of solid soil in Poland, this mineral is minor in terms of quantity, as a component of clay fraction [10], from which 70% of the Earth's crust is built [4]. Thus, we can easily relate our research to the natural conditions. Additionally, the usage of solid soil in industry and environmental engineering is rising from year to year. One of the main use of bentonite is the process of stabilizing boreholes and deep earthworks. It is also used as stabilizers, absorbents and plasticizers [19]. In the last years betonites, thanks to their particular expansive properties and high potential adsorptivity to water, are offered to be used in building guardrails while storing radioactive waste [17, 19]. In all of these applications the proper recognition of the microstructure has become a matter of great importance.

Since Poland joined the UE, the research of properties of the soil containing montmorillonite has become very important. It is related to the fact of wide usage of this soil in nature preservation: removal of toxic chemical compounds from the environment and reduction the spreading pollution in the soil, water and air [1]. Analogically, the analyses of many complicated processes which take place in the solid soil are not possible without learning the problem from the micro structural level.

There is rich literature on the interrelation between the soil properties: the mineral composition, microstructure and the physical-chemical features. The research of the soil structure has 20 years of history. Commonly to such analyses, scanning electron microscopes are used (SEM). In Poland, SEM firstly was used for this purpose by Grabowska-Olszewska [6, 7, 8, 9]. Thanks to the scanning electron microscopes, it is possible to observe the construction of soil and mutual setting of the smallest elements in the soil structure. In solid soil, separate molecules make primary structure. Primary elements create micro aggregates in the soil. The dimension, form, character of the area and the quantitative ratio are involved in the microstructure [4].

The soil microstructures are changed as a result of freezing. Choma-Moryl [3] believes that the largest changes are observed after 1- 3 cycles. Identification of this process becomes hard with bentonite, which has the accessible surface for water and interchangeable ions in interlamellar space [15]. As the composition of the sorption complex of montmorillonite determines many of its physical – chemical properties, in this research the impact of the cyclic freezing on the changes of parameters of the monoionic bentonite microstructure is analyzed.

Thanks to the specialized equipment used in SEM research and software used in the numerical analyses of the image (NIA) Photoshop CS4, the research presents a qualitative and quantitative identification of solid soil microstructures. The received data has been put through a statistical analysis in the program SAS 9.1. We have to consider the precision of the results, which depends on how the test pieces were prepared for SEM research. As we know, the preparation is a piece of a whole material [11]. We should look at it with objectivity. In this study, the samples used in SEM research have been prepared in a simplified way, that is why the microstructure analysis shown below has an approximate character.

2. CHARACTERISATION OF THE SOIL MATERIALS

For this study, four homoionic forms of bentonite were used (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}). The forms had been obtained from natural bentonite from Chmielnik in Poland by repeated saturation of the fraction less then 0.063 mm and subsequent purifying from solutes by diffusion.

The bentonite from Chmielnik has been widely documented as a model montmorillonite soil [5, 2]. The montmorillonite content determined by use of the Water Sorption Test [18] is 96% [14]. This is in accordance with results of DTA, DTG and RTG analysis, reported by Heflik [12], Grabowska-Olszewska [5], Budziosz [2] and Kłapyta [13]. The total cation exchange capacity C.E.C. is 112.7 mval/100 g. In the sorption complex, 87% and 12% are calcium Ca^{2+} and magnesium Mg^{2+} cations respectively.

The cation exchange was performed on the fraction < 63 μm by repeated saturation with 1 N solutions of appropriate chlorides. After twenty-four hours the samples were centrifuged. This sequence was repeated four times and then the excess of chlorine was washed up till the characteristic Cl^- reaction with $AgNO_3$ disappeared. Samples of monoionic bentonites were then moved to evaporating dishes and slightly dried up with infrared lamps to the soft plastic consistency. Such samples were stored in hermetic glass jars at 8°C and used in subsequent tests.

Soil properties are given in Tables 1-3.

Table 1. Composition of the sorption complex, mval/ 100g of dry soil
! - form of bentonite

	B-Ca^{2+} !	B-Mg^{2+}	B-Na^+	B-K^+
Ca^{2+}	104,15	3,68	14,60	2,06
Mg^{2+}	3,50	105,22	5,72	2,65
Na^+	0,22	0,19	90,49	7,15
K^+	0,18	0,11	0,31	38,12

Table 2. Granulometric composition, %
!- form of bentonite

Fraction, mm	Preparation of suspension	B-Ca^{2+} !	B-Mg^{2+}	B-Na^+	B-K^+
>0,05	boiling with NH_4	2	5	0	2
0,002-0,05	boiling with NH_4	64	61	8	68
<0,002	boiling with NH_4	34	34	92	30
>0,05	vibration	5	3	0	2
0,002-0,05	vibration	61	65	12	80
<0, 002	vibration	34	32	88	18
Dispersion coefficient, %		100	94	96	60

Table 3. Sorption properties and specific surface
! - form of bentonite, w_{50}; w_{95}- moisture sorption a relative vapor pressure p/p_0=0,5; 0,95 respectively

Parameters	B-Ca^{2+} !	B-Mg^{2+}	B-Na^{+}	B-K^{+}
w_{50} after drying at 110°C, %	20,46	18,44	16,01	8,94
w_{50} after drying at 220°C, %	20,87	20,94	18,81	9,51
w_{95} after drying at 110°C, %	27,37	26,93	28,72	14,98
w_{95} after drying at 220°C, %	30,56	31,56	30,62	14,98
External specific surface S', m^2/g	122	122	110	56
Total specific surface S, m^2/g	732	732	644	336

3. LABORATORY PROCEDURE

The investigation of the possible microstructures modification due to cyclic freezing and thawing were carried out by use of the scanning electron microscopy SEM. Subsequently, the obtained photographs were processed using the Adobe Photoshop CS4.

The SEM experiments were carried out on air dried samples of 8-10 mm in diameter. Such a sample preparation in the case of soils in which contacts between structural units are stable, usually phase ones, lead to practically no microstructural changes during drying [10]. It was assumed that the soils used in the investigation, as not being composed of large quantities of clay fraction, can be numbered among such a category. The sample surface was obtained by chipping off [11]. The samples were broken and covered by a layer of gold of approx. 40 nm to prevent electrization. The observation of the surface of the fracture was made by scanning microscope JEOL JSM-5400 with applying voltage of 10 kV. As a rule,only surfaces parallel to stratification were examined. The photographs were taken at two magnifications: x1000 and x5000. The lesser magnification images were used to determine the quantitative pore space parameters, while the x5000 magnification images made it possible to characterize the microstructure qualitatively, among other things to determine the types of contacts.

The detail analysis was conducted by use of the Numerical Image Analysis NIA enabled by the Adobe Photoshop CS4 software. In SEM photograph of a clayey soil, darker areas correspond to pores and whiter areas – to mineral particles. Hence, a phenomenological analysis of such an image enables one to distinguish between pores and particles with a probability dependent on intensity of individual elements. The elements with intensity approximately equal to 0 are undoubtedly pores, while elements very bright, with intensity approximately near to 256, can be most certainly classified as particles. However, regions of pixels having intermediate values of intensity make serious problems. In such cases, a "manual" categorization of an element among pores or particles can prove strongly controversial. In the present tests, the tollerance was established experimentally for 28%. As the result, such pore data has been obtained as total surface, perimeter, height, width and the total number of pores. The additional values required to analysis (e.g. means or number of ultra/ micro pores) were calculated by use of Excel.

4. RESULTS AND ANALYSIS

4.1. Ca^{2+} bentonite

Differences in the microstructural parameters were found between natural and freezing Ca^{2+} bentonite (Tab. 4, Fot. 1).

Table 4. Microstructure parameters of bentonite Ca^{2+}

Microstructure parameters	the non-frozen soil	the frozen soil
Total pore area, µm^2	14,94	20,46
Average area, µm^2	0,05	0,07
Total pores perimeter, µm	211,44	250,21
Average perimeter, µm	0,7	0,9
Average height/width of the pore, µm	0,19/ 0,17	0,23/ 0,23
Total number of pores	301	278
Total number of ultra/ micro pores	272/ 29	238/ 40
The average ultra/ micro pores area, µm	0,01/ 0,41	0,01/ 0,45

a
b

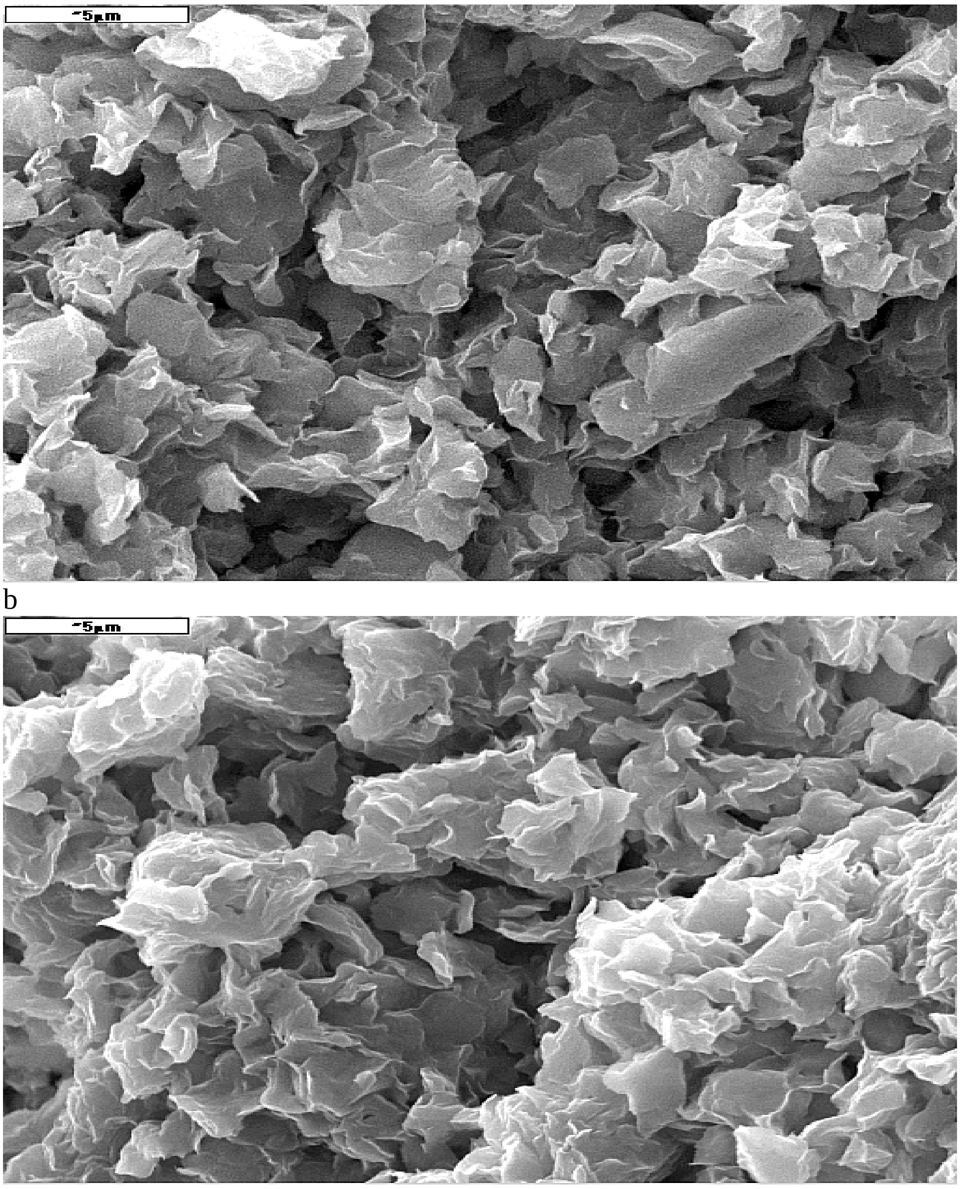


Photo 1. Microstructure of Ca $^{2+}$ bentonite: a- non-frozen b- frozen, magnification 5000x. Cellular microstructure with elements of the pseudo-globular structure. Microagregates are formed with isometric cell open diameter 2 µm . Contacts between microaggregates are of the face-to-face (F-F) and face-to-edge (F-E) type. Contacts between microaggregates are of the mixed, coagulation and phase type. There is no orientation of structural elements, intermolecular porosity is low.

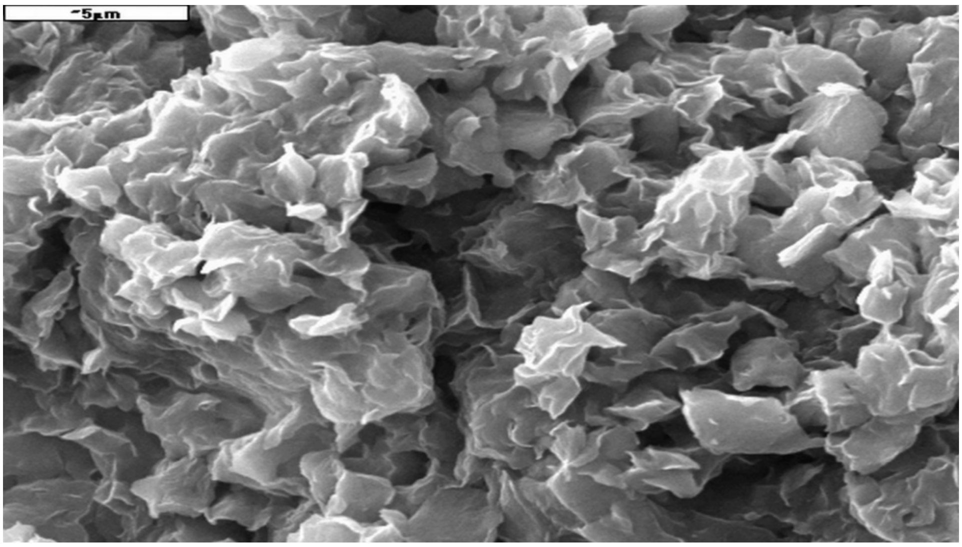
4.2. Mg^{2+} bentonite

Differences in the microstructural parameters were found between natural and freezing Mg^{2+} bentonite (Tab. 5, Fot. 2).

Table 5. Microstructure parameters of Mg^{2+} bentonite

Microstructure parameters	the non-frozen soil	the frozen soil
Total pore area, µm^2	12,05	22,31
Average area, µm^2	0,09	0,1
Total pores perimeter, µm	131,24	245,91
Average perimeter, µm	0,965	1,06
Average height/width of the pore, µm	0,22/ 0,44	0,29/ 0,25
Total number of pores	136	232
Total number of ultra/ micro pores	119/ 17	191/ 41
The average ultra/ micro pores area, µm	0,01/ 0,62	0,02/ 0,46

a



b

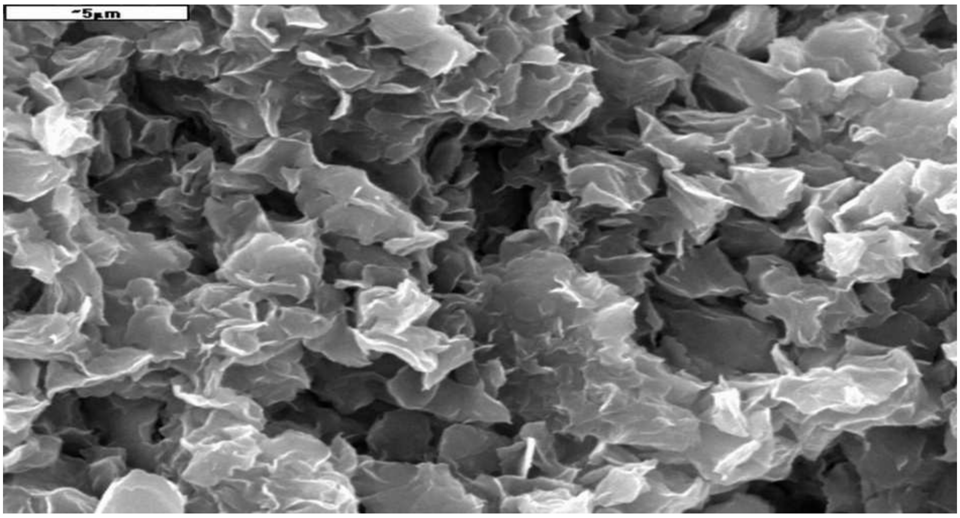


Photo 2. Microstructure of Mg $^{2+}$ bentonite: a- non-frozen, b- frozen, magnification 5000x. Cellular microstructure with elements of the pseudo-globular structure. Microaggregates are formed with isometric cell open. Contacts between microagregates are of the face-to-face (F-F) and face-to-edge (F-E) type. Contacts between microaggregates are of the mixed, coagulation and phase type.

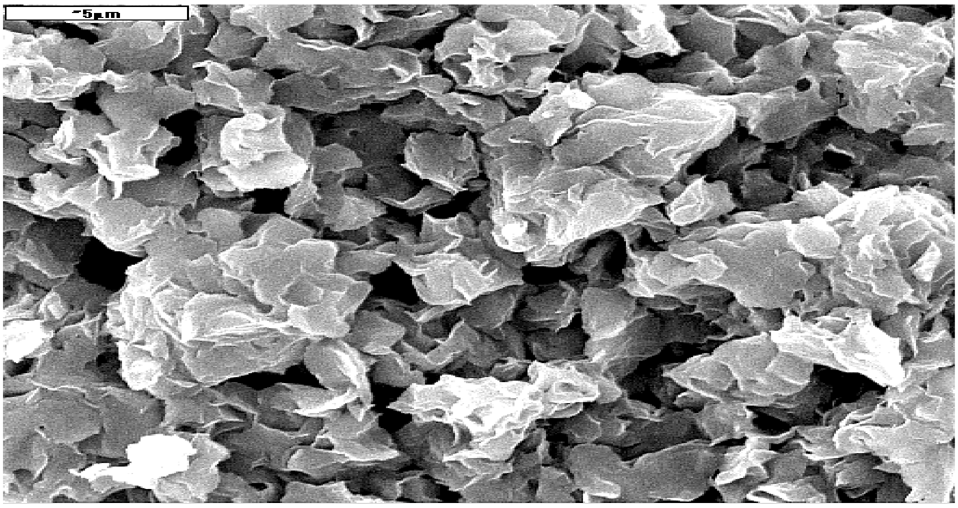
4.3. K^+ bentonite

Differences in the microstructural parameters were found between natural and freezing K^+ bentonite (Tab. 6, Fot. 3).

Table 6. Microstructure parameters of K^+ bentonite

Microstructure parameters	the non-frozen soil	the frozen soil
Total pore area, µm^2	26,56	29,39
Average area, µm^2	0,08	0,14
Total pores perimeter, µm	305,23	212,7
Average perimeter, µm	0,86	0,98
Average height/ width of the pore, µm	0,22/ 0,24	0,26/ 0,25
Total number of pores	353	217
Total number of ultra/ micro pores	307/ 46	193/ 24
The average ultra/ micro pores area, µm	0,01/ 0,495	0,01/ 1,12

a



b

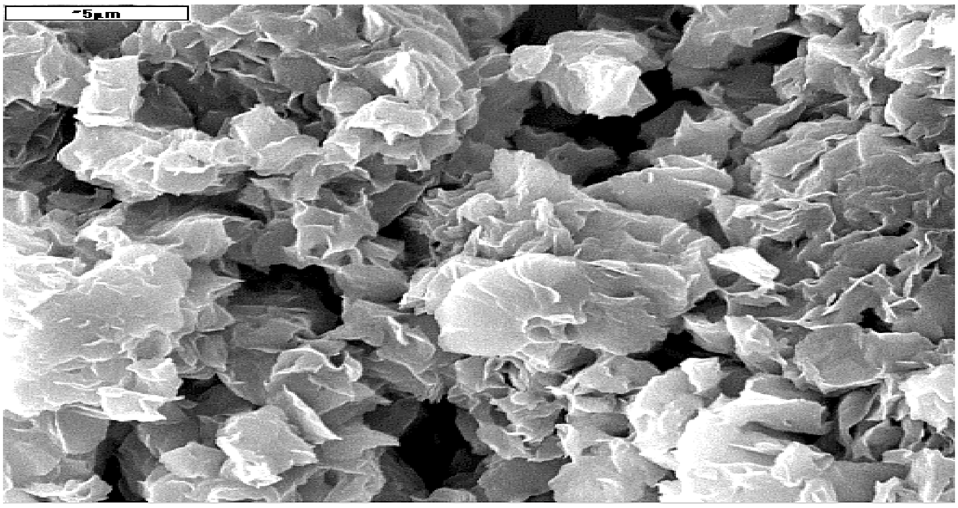


Photo 3. Microstructure of K^+ bentonite: a- non-frozen, b- froze , magnification 5000x. Cellular microstructure with elements of the pseudo-globular structure. Microagregates are formed with cells of different sizes. Contacts between microaggregates are of the face-to-face (F-F) and face-to-edge (F-E) type. Contacts between microaggregates are of the mixed, coagulation and phase type.

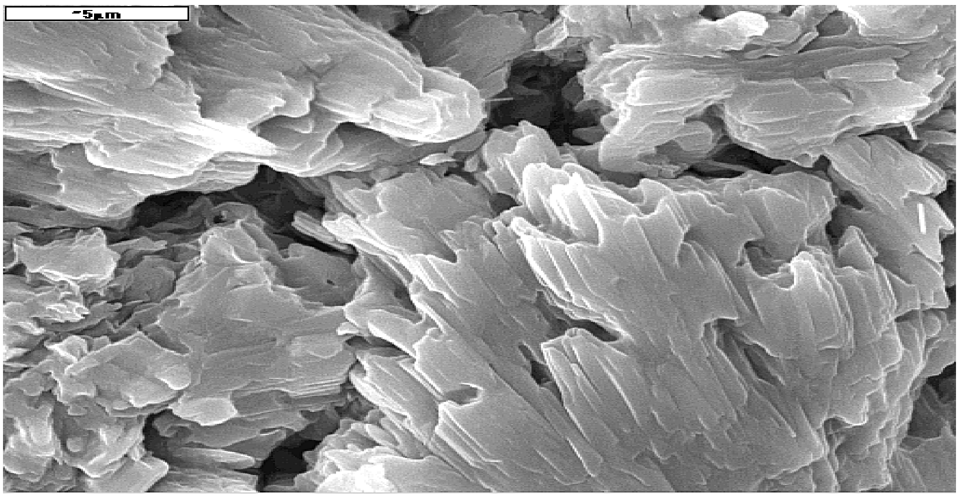
4.4. Na^+ bentonite

Differences in the microstructural parameters were found between natural and freezing Na^+ bentonite (Tab. 7, Fot. 4).

Table 7. Microstructure parameters of Na^+ bentonite

Microstructure parameters	the non-frozen soil	the frozen soil
Total pores area, µm^2	6,59	7,32
Average area, µm^2	0,09	0,04
Total pores perimeter, µm	75,36	138,36
Average perimeter, µm	0,99	0,68
Average hight/ width of the pore, µm	0,27/ 0,26	0,19/ 0,18
Total number of pores	76	203
Total number of ultra/ micro pores	64/ 12	181/ 22
The average ultra/ micro pores area, µm	0,01/ 0,47	0,01/ 0,21

a



b

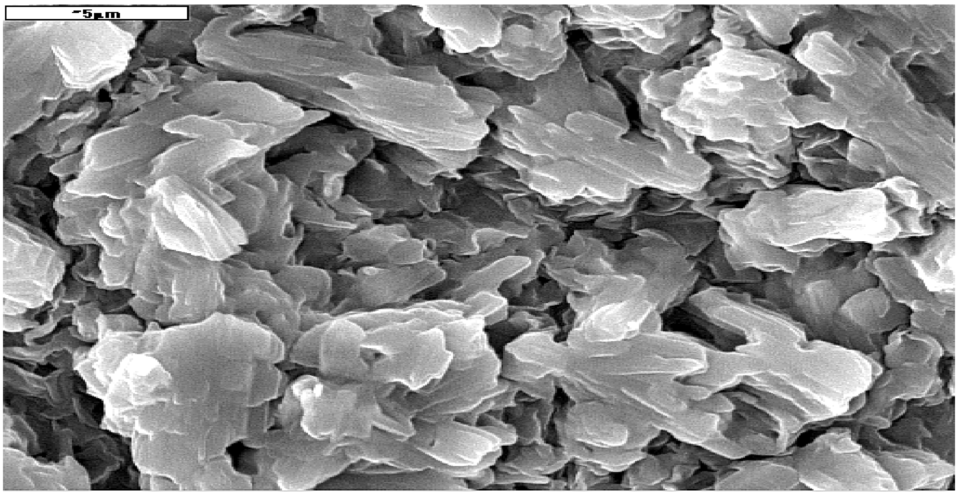


Photo 4. Microstructure of Na^{+} bentonite: a- non-frozen, b- frozen, magnification 5000x. Laminar microstructure of a high degree of microaggregates orientation, in diameter from 10 to 20 micrometers. Contacts between microagregates are of the face-to-face (F-F) type. The pore space is homogeneous. The pore space is formed mainly by intermicroaggregate pores, size 1.2 x 2.5 μm. There are slit and wedge-shaped pores extended according to stratification.

5. RESULTS AND DISCUSSION

The results of the SEM research presented above show that the process of cyclic freezing is followed by the growth in the total pore space on the sections, which are, as a matter of fact, SEM photographs. There also comes to changes in the distribution of micropores. Depending on the type of the primary renewable cation, the quantity of pores from particular ranges of diameters is subjected to change. At times, pores of certain diameters simply cease to exist replaced by the micropores with the diameters not observed in the system not subjected to freezing. Detailed modifications of microstructures in various types of bentonites before and after freezing are presented below.

5.1. Bentonite Ca^{2+}

Before freezing the isometric pores in intermicroaggregates with the diameters around 1-4 μm predominate as well as anisometric pores with the diameters 1,2 to 2,5 μm. The total area of the pores amounts to 14,94 μm^2, the pore perimeter is 211,44 μm. In the sample of non-frozen bentonite Ca^{2+} (Tab.4), 301 pores have been set apart, of which 90% are ultrapores with the average area of 0,01 μm^2, as well as the micropores with the average area of 0,41 μm^2 (10%).

After freezing, the total area of the pores has increased by 1/3, what may be a result of the growth in the quantity of micropores by almost 40% as well as the increase of the average of their area from 0,41 to 0,45 µm^2. Changes in the distribution of the content of the pore sizes also have become visible in decreasing the number of ultrapores by 12%. Their average area remains unchanged and amounts to 0,01 µm^2. In the frozen bentonite Ca^{2+} a certain dispersion of microaggregates and the growth in the quantities of single crystallites are observed.

5.2. Bentonite Mg^{2+}

Before freezing – intermicroaggregated isometric pores with diameters around 1-4 µm predominate as well as anisometric pores with diameters 1,2 to 2,5 µm. Interaggregated isometric pores have the diameter of around 5 µm. The total area of pores has amounted to 12,05 µm^2, the perimeter of 131,24 µm. In the microphotograph 119 ultrapores have been set apart with the average area of 0,01 µm^2 and 17 micropores with the average area of 0,62 µm^2. The average height (0,22 µm) and width (0,44 µm) of the pores point to the presence of anisometric pores.
After freezing the diameter of isometric pores has got diminished on average from 5 to 3 µm. The growth in the total area of the pores by more than 80% has been observed as well as the growth in the perimeter of the pore area by around 90%. The pores have got narrowed and have become regular, simultaneously their number has increased from 136 to 232. The changes have occurred in the distribution of the content of the pore sizes.
The number of ultrapores has increased with the simultaneous growth in the average area from 0,01 to 0,02 µm^2 as well as the number of micropores has increased by around 150% at the cost of decreasing in their average area by around 50%. Additionally, the dispersion of microaggregates, the growth in quantity of single crystallites and "unification" of microstructure, have been observed.

5.3. Bentonite K^+

Before freezing the intermicroaggregated isometric pores with the diameters around 1-2 µm predominate as well as anisometric pores with the diameters 1,2 to 2,5 µm. The total area of the pores amounts to 25,56 µm^2, the periphery is 305,23 µm. In the microphotograph 307 ultrapores have been set apart with the average area of 0,01 µm^2 and 46 micropores with the average area of 0,495 µm^2.
After freezing, a lot of isometric pores with the measurement of 2-3 µm have emerged, occurring relatively more rarely before. Slight growth in total area of the pores has been observed (by around 10%) with decreasing the number of pores by around 40%. On the other hand, the number of ultrapores has decreased by around 40% with the unchanged average area, and the quantity of micropores

has decreased by around 50% at the cost of growth in their area by around 60%. Additionally a certain dispersion of microaggregates, the growth in quantity of single crystallites and "unification" of microstructure, as well as a general growth in measurements of micropores are visible.

5.4. Bentonite Na^+

Before freezing the total area of the pores has amounted to 6,59 μm^2. 64 ultrapores with the average area of 0,01 μm^2 have been set apart as well as 12 micropores with the average area of 0,47 μm^2.

After freezing the total area of the pores has increased only by 10%. A number of ultrapores has increased by around 300% with the unchanged average of their area. The growth has appeared in the quantity of micropores by around 90% with the simultaneous decrease in the average area by around 50%. The characteristic effect of the freezing is more than twofold decrease in the sizes of packages. The type of contacts has changed as well; beside former plane-plane contacts, considerable quantity of the plane-edge contacts type has arisen. Pore space has got enriched in isometric pores with diameters 1-2.5 μm, as well as anisometric ones with diameters 5 x 10 μm.

On the basis of obtained results, the statistic analysis has been carried out. For the assessment of the influence of the type of the mineral contained in bentonite as well as the method of freezing the samples (0- non-frozen sample, 1- frozen one time) on the average specific surface area S of the bentonite, bifactor analysis of variance has been applied. As the grouping variables were used the type of bentonite (4 values: Ca, Mg, Na, K) and the number of freezing-thawing cycles: 0 - not frozen, 1, 2, 5. At the first stage, the verification of zero hypothesis of the equality of the average values of S in groups determined on the basis of both considered factors, that is the type of bentonite as well as the number of cycles, has been made. For the verification of this hypothesis, the statistics F is applied, that is the quotient of the dispersion of the averages in groups determined on the basis of two factors simultaneously and the measure of dispersion of results within their group averages within particular groups. The obtained value for the statistics F less than 0,0001 is lower than the level of relevance 0,05. The zero hypothesis ought to be rejected. It denotes that at least two similar groups exist, in which the average values of the quality S differ relevantly. In the next stage the verification of hypotheses on the equality of the average values of the quality S in groups determined on the basis of one of the factors (type or freezing) was made. The research on the relevance of the effect of interaction between factors has been carried out, which is responsible for the differences between observed averages and these, which might be predicted only on the basis of primary effects. If the nature of interrelation between the levels of one factor and the dependent variable is approximate for the particular values of the second factor, then a relevant effect of interaction does not occur. It may be assessed on the basis of the chart of average values of S in considered groups. If the effect does not appear, then the differences in the average values of S for different groups are identical in the case of both considered freezings/ types. In such a case, the parallel segments appears in the chart.. An obvious deviation from the parallelism allows us to assume that a relevant effect of interaction occurs (Fig. 1).

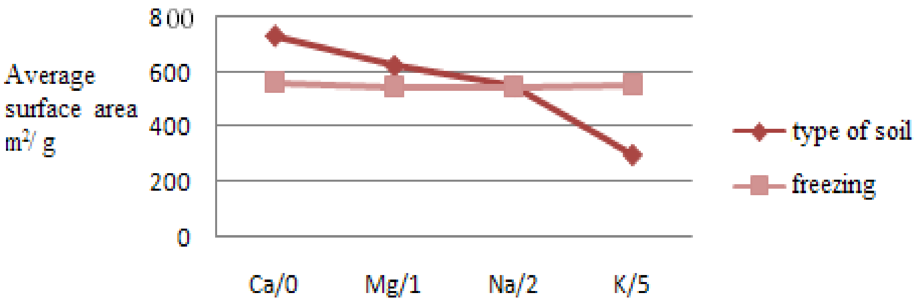


Fig. 1. The effect of interaction of factors affecting the surface area of bentonite.
not-frozen 1- once frozen 2- double frozen 5- five frozen

The obtained values of the level of relevance ($p < 0{,}001$) for the effect of the type of bentonite also support this hipothesis. In the case of this factor, the procedure of iterative comparisons has been applied. They determine the equality of the averages for each group pair defined on the basis of a considered factor. As opposed to T-Student's test, the risk of committing an error with the assessment of the relevance of differences between all compared group pairs is controlled. Comparisons on the level of p= 0,05 in considered groups (types of bentonite) have turned out to be relevant. The average values of S in the bentonites above differed. The Duncan Grouping confirmed this thesis. It disclosed 4 groups: A, B, C, D, to which the particular types of bentonite have been assigned. The analysis showed that the largest specific surface area occures in the bentonites Ca^{2+} and Mg^{2+}, while the smallest in the bentonite K^{+}. According to Grabowska-Olszewska [10], cations with a single electric charge i.e. Na^{+} and K^{+} form a single layer of water particles, at the higher water contents they may form a double one. Cations with the double electric charge, i.e. Ca^{2+} and Mg^{2+} have the tendency to form the double-layer complex with water. It causes changes in the interlamellar distances of montmorillonites. However, the relevant importance of the total humidity for the reaction of the system subjected to cyclic freezing, raises at this point. Authors did not find the work, in which the humidity would be the parameter taken into consideration in a research project. The second factor presented in the statistic analysis was the freezing. The average values of S in the groups determined by next levels of this factor does not differ relevantly. It has been also reflected in confidence levels for the next differences in the average values of the quality S. Each of the levels are 0, what means, that the equalities of the proper average values can not be excluded. Duncan Grouping revealed the same groups A. To sum up, it is difficult to determine explicitly an influence of cyclic freezing on the parameters of microstructure. Kumor [16] observed the decrease in the specific surface area in the bentonite MAD within around 10 first cycles and the growth within the next 10 cycles of freezing-defrosting. Yang et al. [20] had also been paying attention to multiplicity and ambiguity of the processes accompanying cyclic freezing**.**

6. CONCLUSIONS

The analysis of the obtained results allows us to draw the following conclusions:

1. Cyclic freezing significantly alters the values of such microstructural parameters, as specific surface area and pore size distribution.
2. Modification of microstructure due to freezing and thawing is dependent on the kind of the main exchangeable cation.
3. The results of ANOVA indicate that the effect of cyclic freezing and thawing on the specific surface area is less significant than the effect of the kind of exchangeable cation.

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WPŁYW CYKLICZNEGO ZAMRAŻANIA NA PARAMETRY MIKROSTRUKTURY MONOJONOWYCH BENTONITÓW

Streszczenie

Na skutek przemarzania mikrostruktury gruntów spoistych ulegają zmianie. Identyfikacja tego procesu staje się dość trudna w przypadku bentonitu, który ma dostępną dla wody i jonów wymiennych powierzchnię w przestrzeniach międzypakietowych. Ponieważ skład kompleksu sorpcyjnego montmorylonitu determinuje wiele jego właściwości fizyko-chemicznych w niniejszej pracy przedstawiono wpływ cyklicznego zamrażania na zmiany parametrów mikrostruktur bentonitów monojonowych. Badania składu fazowego prowadzono na próbkach iłów monojonowych, czterech bentonitów: B-Ca^{2+}, B-Mg^{2+}, B-Na^{+}, B-K^{+}. Materiał wyjściowy stanowił uznawany powszechnie za modelowy bentonit z Chmielnika. Badania wykonano przy użyciu elektronowej mikroskopii skaningowej SEM oraz metody numerycznej analizy obrazu NIA. Stwierdzono różnice wartości parametrów mikrostrukturalnych pomiędzy każdym z rodzajów bentonitów naturalnych i poddanych zamrożeniu. Wyniki badań SEM pokazują, że w procesie cyklicznego zamrażania następuje wzrost sumarycznej powierzchni porów na przekrojach, jakimi są w istocie fotografie SEM. Dochodzi również do zmian w rozkładzie mikroporów. W zależności od rodzaju głównego kationu wymiennego, ilość porów z poszczególnych zakresów średnic ulega zmianie. Niekiedy pory o pewnych średnicach wprost przestają istnieć; na ich miejsce pojawiają się mikropory o średnicach nieobserwowanych w systemie niepoddanym wcześniej zamrażaniu. Uzyskane dane zostały poddane analizie statystycznej w programie SAS 9.1. Wyniki przeprowadzonej analizy wariancji sugerują, że powierzchnia właściwa bentonitu jest zależna od rodzaju głównego kationu wymiennego (Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}).