GOSPODARKA SUROWCAMI MINERALNYMI – MINERAL RESOURCES MANAGEMENT

2025 Volume 41 Issue 1 Pages 141–161

DOI: 10.24425/gsm.2025.153176

WOJCIECH PANNA[1], WITOLD RECZYŃSKI[2], MAGDALENA SZUMERA[3],
SEBASTIAN PREWENDOWSKI[4], MARCIN GAJEK[5]

Sorption properties of selected clays from south-eastern Poland and their prospects for use in environmental protection

Introduction

Protecting the environment is one of the fundamental fields utilizing raw materials abundant in smectites. They are used, among others, as flocculants and layered barriers in waste disposal sites (Koch 2002; Ayari et al. 2005; Wyszomirski and Lewicka 2005; Justus Heyde 2020). In natural conditions, there are varieties of these resources with diverse chemical compositions resulting from isomorphic substitutions in the structure of the main mineral and ion exchange sorption of various interlayer cations (Churchman et al. 2006).

✉ Corresponding Author: Wojciech Panna; e-mail: wojpan3702@gmail.com

[1] University of Applied Sciences in Tarnów, Poland; ORCID iD: 0000-0002-6591-284X; e-mail: wojpan3702@gmail.com

[2] AGH University of Krakow, Poland; ORCID iD: 0000-0003-4751-8141; e-mail: wreczyn@agh.edu.pl

[3] AGH University of Krakow, Poland; ORCID iD: 0000-0002-5692-8161; e-mail: mszumera@agh.edu.pl

[4] AGH University of Krakow, Poland; ORCID iD: 0000-0002-2307-5588; e-mail: sebprew@gmail.com

[5] AGH University of Krakow, Poland; ORCID iD: 0000-0002-6020-8060; e-mail: mgajek@agh.edu.pl

Such a smectite structure causes it to be a reactive phyllosilicate undergoing reactions with various particles through ion exchange for hydrated organic and inorganic cations (Bobrowska and Szaniawska 2011). It endows the resources abundant in this mineral with, among other things, the ability to sorb hazardous chemicals, and is mainly related to the phenomenon of surface adsorption

When using clay raw materials, zeolites, and other fine-grained minerals for sealing purposes, two main issues are crucial: the retention of harmful components (e.g., liquids) due to their low conductivity through the material and the trapping of deleterious substances caused, among other factors, by sorption, precipitation, and redox reactions (Czurda 2006) – clay minerals sorb water and other polar fluids as well as cations. Water sorption leads to an increase in volume and the formation of a suspension. Toxic ions present in the suspension can be sorbed on the surfaces of clay plates, showing an electric charge mainly through ion exchange. These leachable ions are not permanently bound in the structure of the clay minerals but can participate in further chemical processes depending on the chemical environment (Helios-Rybicka et al. 1995). In many cases, the isolating layer of waste stored in a particular landfill may be permeable to separate water from solid substances. Depending on the functions performed, the waste encapsulation system differs in the materials used, which can be broadly represented by Figure 1.

The type of interlayer cations significantly influences the sorption properties (Ayari et al. 2007). Depending on the diameter of water-coordinated cations and their valency, smectites sorb them to varying degrees and undergo exchange for other cations. Na-smectites are the most desirable among all clay minerals used in mineral barriers. They exhibit a high swelling capacity and high sorption ability, especially concerning cations. As a result, they are practically impermeable and characterized by the ability to retain various types of pollutants (Czurda 2006). The material intended for barriers must meet many conditions,

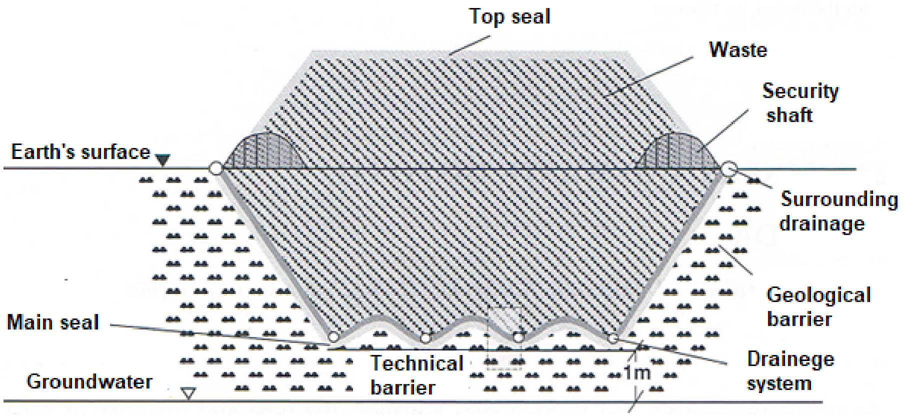


Fig. 1. A multilayer system for the hermetisation of pollutants. Its main parts are geological barriers in situ and technological barriers, including mineral layers and geomembranes (Czurda 2006)

Rys. 1. Wielowarstwowy system hermetyzacji zanieczyszczeń. Jej głównymi elementami są bariery geologiczne *in situ* oraz bariery technologiczne, w tym warstwy mineralne i geomembrany primarily low permeability to water solutions containing multiple harmful substances. This value is usually less than 10–9 m/s (Majer et al. 2007).

In Poland, an example of a raw material commonly used for such solutions is beidellite clay – containing approximately 70% of this smectite mineral – as a co-occurring mineral in the Bełchatów Coal Mine. It was used, among others, in the construction of mineral barriers at municipal waste and ashes landfills from the "Bełchatów" power plant, hazardous waste from the "Tarnowskie Góry" chemical plants, and industrial waste from the zinc smelter in Miasteczko Śląskie (Ratajczak et al. 2005). This study aimed to expand knowledge about the possibilities of using similar resources in southeastern Poland, with particular emphasis on the sorption of heavy metals.

1. Occurrence of smectite raw materials in Poland

In Poland, few raw materials are rich in smectites. The most common are bentonite clays. They occur in carboniferous formations, the clay-shale series of the Carpathian flysch, the Carpathian foredeep as a Miocene sediment, and weathered basalt rocks in Lower Silesia. Often, they also accompany coal deposits in Carboniferous sedimentary formations (Upper Silesian Coal Basin) and occur in the Świętokrzyskie Mountains in Devonian formations (Nieć and Ratajczak 2004). However, they are practically undeveloped due to the unfavorable geological situation, the small thickness of smectite layers, and economic and political-administrative reasons. Exploitation is carried out only in the Krzeniów deposit, where bentonites constitute weathering accompanying basalts (Brzeziński 2021).

There are also known occurrences of smectite raw materials of lower quality among Tertiary and Quaternary formations, such as reservoir clays (i.e., formed in reservoir lakes in the glacier foreland), Mio-Pliocene Poznań clays, and Miocene marine clays. These are most often beidellite varieties with relatively low sorption properties (Nieć and Ratajczak 2004).

Moreover, the clay seam deposit occurring in the Świętokrzyskie Voivodeship "Drugnia Rządowa" also seems interesting and prospective. The Drugnia Rządowa bentonite predominantly comprises highly crystallized montmorillonite with a pyroclast suite (biotite and quartz). However, it occurred only in layers no greater than 0.6 m (Górniak et al 2021). In addition, it is also worth mentioning the weathering deposits from the Rutki quarry near Niemodlin in the Świętokrzyskie Voivodeship. Clay layers consist of an enriched smectite-kaolinite mixture with a halloysite. Clay materials contribute to the high specific surface area of the deposits (up to 100 m^2/g) (Wyszomirski et al. 2024).

Of the raw materials mentioned above, in southeastern Poland, there are clay shales of the Carpathian flysch, bentonite clays of the Carpathian Foredeep, and clays of marine origin. These varieties of smectite raw materials, represented by Krakowiec clays, clinoptilolite-montmorillonite claystone, and clay shale from the Krosno Beds, were subjected to properties test sorption in this paper. The research was also extended to carrying out the processing of raw materials by sodium and acid activation.

2. Harmful impact of heavy metals on the natural environment

Due to the rapid development of industry, the danger of environmental pollution with heavy metals has significantly increased. Heavy metals include Cu, Co, Cr, Cd, Fe, Zn, Pb, Sn, Hg, Mn, Ni, and Mo (Ociepa-Kubicka and Ociepa 2012). The sources of pollution with these elements can be divided into natural and anthropogenic. The first is mainly related to processes such as the weathering of rocks, volcanic eruptions, forest fires, and evaporation of ocean waters. The latter sources related to human activity are much more dangerous. They include various industries, e.g., energy based on coal combustion, communication, chemicals and fertilizer, ore mining, and metallurgy (Kabata-Pendias and Pendias 1999).

Heavy metals are sorbed to varying degrees by almost all components of clay rocks, and the sorption depends on their mineral composition. Clay minerals, amorphous iron, and manganese compounds are particularly active in sorption. An organic substance also plays a unique role in this process. As a surface phenomenon, the sorption depends on the specific surface area of the sorbent and, to a large extent, on its cation exchange capacity CEC (Sikora 1996). Because the sorption process is complex, sorption properties are determined empirically under specific conditions but should be as close to natural conditions as possible.

3. Research methodology

Tests of heavy metals sorption were performed using the static batch method. It involves introducing metal salts (with precisely known concentrations) and a known mass of the sorbent into a solution to prepare a suspension. After 24 hours of shaking, centrifugation separates the precipitate from the solution. In this solution, the equilibrium concentration of a given metal is determined using the AAS (Atomic Absorption Spectroscopy) method (Sikora 1996). The amount of metal adsorbed by a given substance is the difference between the initial and equilibrium concentration of the metal in the solution, which is converted into a unit of mass of the sorbent.

The research involved using 0.25 and 0.5 g of powdered raw materials (depending on the smectite content) in their natural state and after their modifications. The samples were quantitatively transferred to glass test tubes, and 10 ml of starting solutions were added. The concentration of the salt solutions depended on the chemical compound used for heavy metal elements (Zn, Ni, Cu, Cr), and they were selected experimentally. Therefore, sorption was performed using a 0.05% solution of $CuSO_4 \cdot 5H_2O$, a 0.1% solution of $ZnSO_4 \cdot 7H_2O$, a 12% $NiSO_4 \cdot 5H_2O$ solution and a 0.5% $K_2Cr_2O_7$ solution. Calibration curves of the content of these metals in standard solutions about absorbance were determined. In addition, the pH of the starting solutions was adjusted by adding a small amount of concentrated hydrochloric acid to determine the influence on the sorption properties of clay raw materials. The copper, zinc, nickel, and chromium content in solutions was determined using a Perkin Elmer HGA 600 spectrometer.

Moreover, Scanning Electron Microscope (SEM) observations were carried out to explain the impact of sodium and acid activation on clay samples. Microphotographs of the tested materials were made using a high-resolution Scanning Electron Microscope (SEM) Apreo 2S (Thermo Fischer Scientific, the Netherlands). The research was conducted in low vacuum mode using a secondary electron detector (LVD) to observe differences in the morphology of materials.

4. Research material

The Tertiary Krakowiec clays occurring in southeastern Poland were used for sorption tests, represented by samples from Harasiuki (1), Wola Rzędzińska (2) and Łukowa (3), clay-silica raw material from three levels of the Dylągówka deposit: sample 4A – from the upper, 4B – middle, 4C – lower part; clay shale (5) from the Krosno Beds (Figure 2). These samples show significant differences in the content of minerals with sorption capacity (including smectite), grain distribution and surface development. These parameters are presented in Table 1. Panna et al. (2014a, 2014b, 2015) present a more extensive sample analysis. The research was extended to include processing these raw materials by sodium

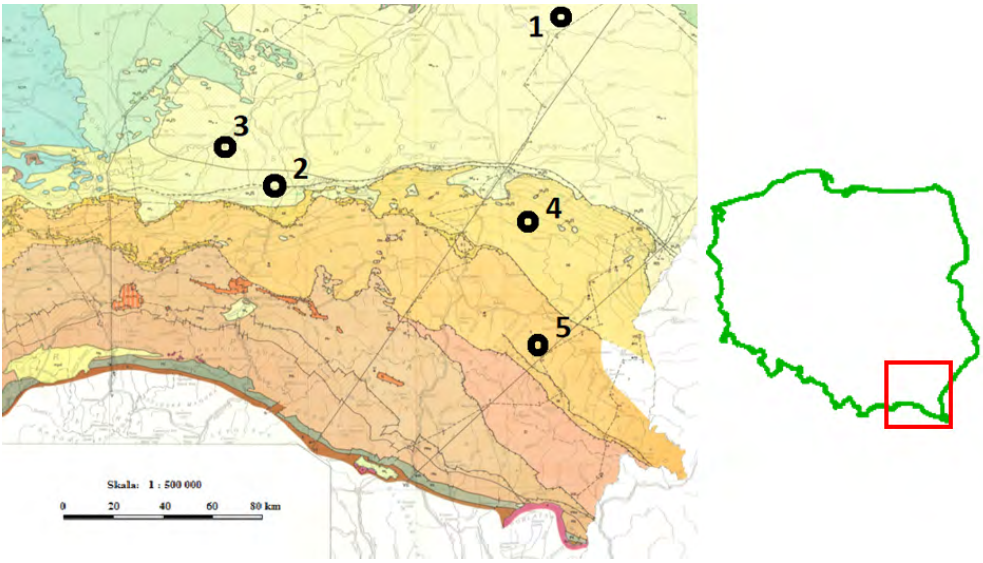


Fig. 2. Map of tectonic elements of Polish flysch Carpathians with the boundaries of their overlap (Żytko et al. 1989) and marked deposit locating, where the samples were collected
I – Subsilesian nappe, II – Skole nappe, III – Silesian nappe, IV – Dukla nappe, V – Magura nappe.
Deposits: 1 – Harasiuki, 2 – Wola Rzędzińska, 3 – Łukowa, 4 – Dylągówka, 5 – Wysoczany

Rys. 2. Mapa elementów tektonicznych polskich Karpat fliszowych z granicami ich nakładania się (Żytko i in. 1989) oraz zaznaczono lokalizację złoża, z którego pobrano próbki
I – płaszcz podśląski, II – płaszcz skolski, III – płaszcz śląski, IV – płaszcz dukielski, V – płaszcz magurski.
Złoża: 1 – Harasiuki, 2 – Wola Rzędzińska, 3 – Łukowa, 4 – Dylągówka, 5 – Wysoczany

Table 1. Selected parameters of investigated clay samples (Panna et al. 2014a, 2014b, 2015, Panna 2016)

Tabela 1. Wybrane parametry badanych próbek gliny

Parameter	Deposit						
	Harasiuki	Wola Rzędzińska	Łukowa	Dylągówka			Wysoczany
	1	2	3	4A	4B	4C	5
Grain content (%)[1]							
>1 µm	29	31	61	53	43	66	19
<0.5 µm	11	21	30	37	32	59	1
<0.2 µm	1	11	26	24	24	41	1
Median (µm)	2.5	2.9	0.6	0.9	1.6	0.2	6.9
Specific surface area[2] (m^2/g)	18	18	25	48	51	66	13
Smectite content (%)[3]	21	23	24	27	30	49	12
Occurrence of other minerals with increased content[4]	illite, quartz, chlorite, calcite, albite			opal-CT, zeolite, quartz, illite	opal-CT, illite, quartz	opal-CT, kaolinite, quartz, calcite	illite, chlorite, quartz, calcite, albite

[1] Determined using the sedimentation method.
[2] Determined using the BET method.
[3] Determined by the spectrophotometric TETA Cu(II) sorption method; in all case it is smectite of calcium-magnesium nature (confirmed by XRD method).
[4] Identified by X-ray diffraction method (XRD).

and acid activation. The preparation of samples for modification consisted of drying and grinding them in a laboratory ball mill "dry." The initial samples were subjected to sodium modification by adding Na_2CO_3 in 5% to each of them about the dry mass, physical activation of the moistened mass using a mechanical stirrer, homogenization for 30 days, and drying the obtained samples. The aim was to replicate the industrial processing of raw materials made from smectite. In the further part of the paper, numbers with the extension "as" were used for the samples obtained in this way, e.g. 1as, 4Aas, etc. Acid activation consisted of adding 100 ml of a 10% aqueous solution of H_2SO_4, 30-minute homogenization using a mechanical stirrer), keeping for 24 hours in a climatic chamber at a temperature of 80°C and relative humidity Hr = 90%, and – then – drying. In the further part of the paper, numbers with the extension "ak" were used for the samples obtained in this way, e.g. 1ak, 4Aak, etc.

5. Research results and discussion

Regarding the research carried out, it should be emphasized that the sorption of heavy metals is performed on samples of various mineral compositions, in which the increased sorption capacity is related to the presence primarily of smectite, as well as illite, kaolinite and chlorite, and non-clay minerals, such as opal, zeolite, and iron minerals (occurring additionally in the samples). Therefore, the assessment of the sorption capacity for copper, nickel, zinc, and chromium was presented using salt solutions with their natural pH and acidified to pH = 4. It should be noted that the tests were carried out only for experimentally selected concentrations of heavy metals. Therefore, it is only possible to make an indicative comparison of the results of sorption tests (about the clay raw materials used) with the sorption values of clay minerals listed, for example, in the paper of Helios-Rybicka (1995). However, it is impossible to determine the optimal conditions and the highest possible sorption value, which is determined by the experimental selection of the appropriate pH, sorbent concentration, temperature, and other parameters affecting the amount of substance absorption by the mineral components of the samples. These results significantly contribute to our understanding of the sorption capacity of various clay samples for heavy metals.

The results of copper sorption tests at natural pH = 5.2 are presented in Figure 3. The test results, considering the content of smectite and other minerals with sorption capacity in the raw materials, showed a correlation with the test results of individual minerals presented in the paper of Helios-Rybicka et al. (1995). Due to the properties of smectite, the highest copper sorption value – in the order of 3,050–3,480 mg/kg – was demonstrated by the clay-silica mineral from Dylągówka (4A, 4B, and 4C), characterized by the highest content of this mineral. However, it should be noted that the test results do not correlate with the share of smectite in the tested samples. This is due, among others, to their increased illite content. Although this mineral has an almost 3-times lower sorption capacity compared to smectite (Helios-Rybicka et al. 1995), its large amount in the tested sample has a significant impact on the increased sorption value of Krakowiec clays (1, 2, 3) and Wysoczany shale (5).

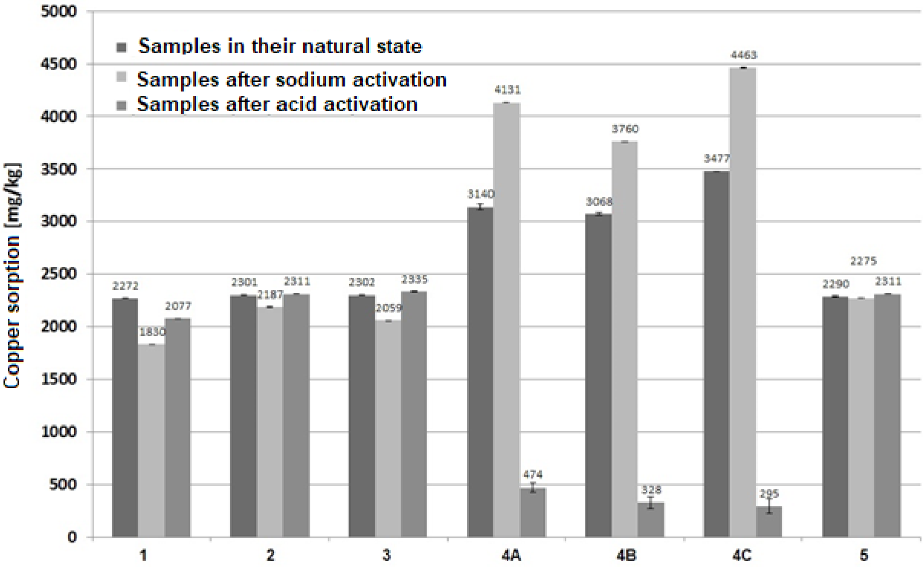


Fig. 3. Copper sorption on the tested clay raw materials in their natural state
and after chemical modification at pH = 5.2 of the initial solution
Deposits: 1 – Harasiuki, 2 – Wola Rzędzińska, 3 – Łukowa, 4 –Dylągówka, 5 – Wysoczany

Rys. 3. Sorpcja miedzi na badanych surowcach ilastych w stanie naturalnym
i po modyfikacji chemicznej przy pH = 5,2 roztworu wyjściowego
Złoża: 1 – Harasiuki, 2 – Wola Rzędzińska, 3 – Łukowa, 4 – Dylągówka, 5 – Wysoczany

However, it is worth remembering that its impact is very variable. This is due to its excellent chemical composition diversity and numerous isomorphic substitutions. Research has shown that the degree and type of isomorphic substitution can alter illite's physical and chemical characteristics, including its swelling, stability, and interaction with water and other chemicals (Gualtieri et. al 2008; Brown 2018). This makes illite's role in sorption processes complex and dependent on its specific composition and structural configuration, which can vary based on the source and the degree of alteration.

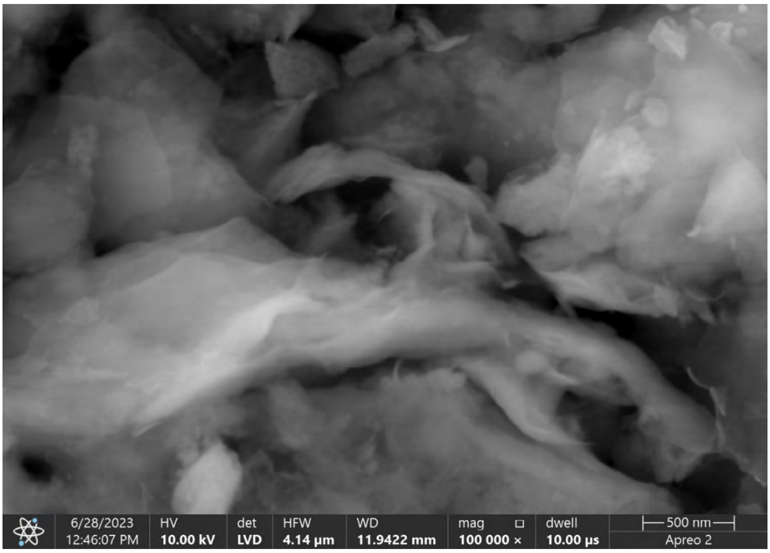
Sodium activation brought the desired effect only in the case of the raw material from Dylągówka (samples 4A, 4B, 4C), leading to an increase in copper sorption by almost 20%. It is primarily related to the reduced aggregation of smectite grains, which results from the weaker binding of the Na^+ cation in the structure smectite, which may be substituted by a heavy metal cation, in this case by Cu^{2+}. This thesis was confirmed by SEM microphotographs taken on a sample from the central part of the Dylągówka deposit (sample 4B) in its natural state (Photography 1) and after sodium activation (Photography 2), which in the case of microphotographs of the first sample (4B) it was observed that it was impossible to identify single smectite plates and in the case of the second (4Bas) – single plates of this mineral deposited on non-clay minerals. It correlates with observations compiled in other research papers (Bujdák et al. 2001; Komadel 2003), in which observations were made of changes in the degree of bonding of smectite plates using this most straightforward type of activation of smectite raw materials.

In the case of raw materials with less share of smectite, a slight decrease in sorption was noted after sodium activation, compared to samples in their natural state. It is most likely related to the pH of the sorption environment, which changes to alkaline (from the initial pH = 5.2). After its addiction into the vessel with the tested sample, the initial solution of copper sulfate changes the pH, which is related to the earlier activation of the raw material using Na_2CO_3. In the Krakowiec clays (samples: 1, 2, and 3) and in the Wysoczany shale (5), there is a much more significant amount of "free" Na_2CO_3, thanks to which the pH value is higher compared to that in the system with the raw material from Dylągówka (4A, 4B, 4C). How the amount of metal sorption changes with the pH of the solution also depends on whether a given metal is present in the solution as an independent cation or in the form of a compound complex (Bourg et al. 2003). Higher pH may favor an increased amount of complex anions, which significantly limits the sorption of copper. The highest sorption values are possible to obtain in pH conditions dominated by the Cu^{2+} cation, the presence of which favors ion-exchange sorption.

Acid activation significantly reduces the sorption capacity of the raw material from Dylągówka (samples 4Aak, 4Bak, and 4Cak). It is primarily influenced by the pores' surface sorption of sulfuric acid (VI). As a consequence, the pH of the copper solution decreases. It causes increased mobility of copper cations in the starting solution and makes it challenging to replace protons in exchangeable positions (Stumm and Morgan 1981). Therefore, copper (II) cations are not permanently bound in the structure. Another reason for reduced sorption on samples from Dylągówka (samples 4A, 4B, 4C) after acid activation is that there may be degradation of the smectite structure caused by too aggressive action of sulfuric acid (VI). In extreme cases, it may lead to the transformation of smectite into silica gel (Madejová et al. 1998; Komadel 2003). However, the SEM micrograph of sample 4B after acid activation (4Bak, Photography 3) proves that it did not significantly affect the shape of the grains.

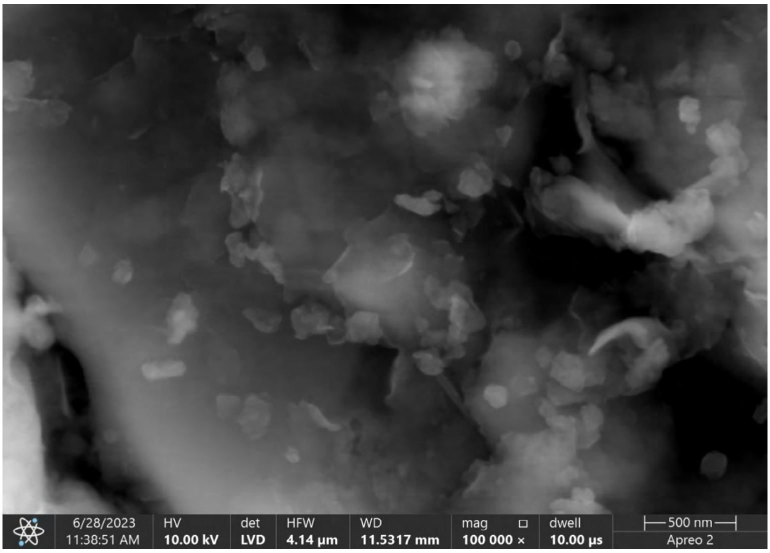
Nevertheless, a specific arrangement of smectite packets that are poorly aggregated (as in the case of the sample 4Bas) can be seen. It consists of the smectite plates being connected with non-clay minerals by their edges and located in a position that is not parallel to the surface of these minerals. It may mean that sulfuric acid (VI) has significantly degraded the structure of smectite, manifested by a reduction in charge of plates, which reduces the ability of parallel bonding of the plates with other minerals (Korichi et al. 2019). Therefore, only the positively charged edges of the smectite plates bind to non-clay minerals using electrostatic bonds (Photography 3).

The sorption value of Krakowiec clays (1, 2, 3) and Wysoczany shale (5) after acid activation (samples 1, 2, 3, 5) is practically unchanged – at the natural pH of the copper (II) sulfate solution – due to the reaction of the majority of sulfuric acid (VI) with calcite in during activation. The consequence of this reaction is the formation of gypsum crystals showing a regular cuboid shape on the nano-scale despite crystallization in a monoclinic system (Fusi et al. 2015). It was observed on a sample from the lowest part of the Dylągówka-Zapady deposit, containing calcite, as shown in the SEM micrograph in Photography 4.



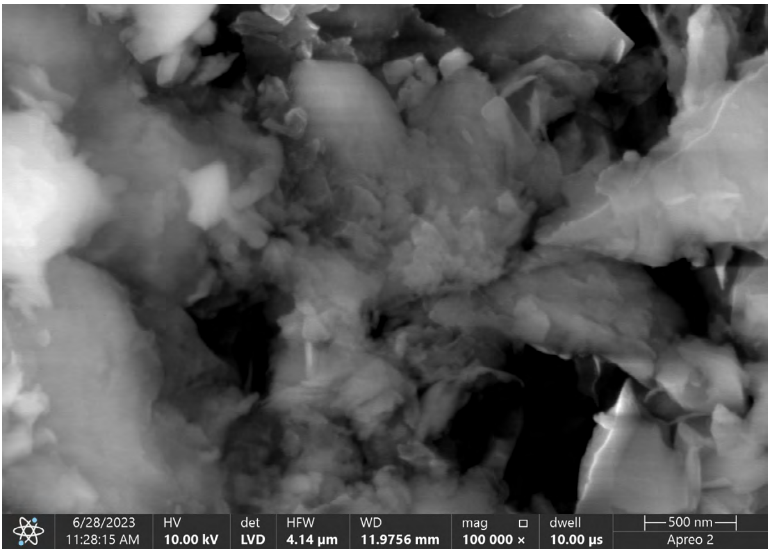
Phot. 1. SEM microphotograph of a sample of smectite-silica raw material from the middle part of the profile of the Dylągówka-Zapady deposit in its natural state (sample 4B)

Fot. 1. Mikrofotografia SEM próbki surowca smektytowo-krzemionkowego ze środkowej części profilu złoża Dylągówka-Zapady w stanie naturalnym (próbka 4B)



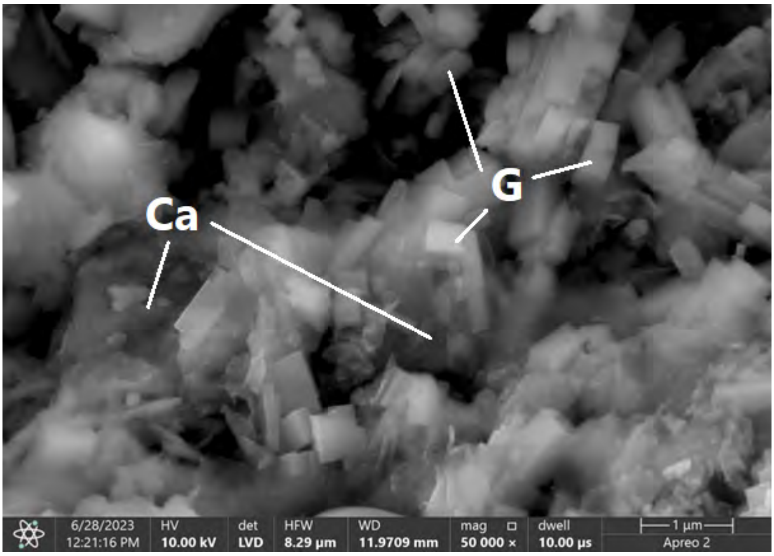
Phot. 2. SEM microphotograph of a sample of smectite-silica raw material from the middle part of the profile of the Dylągówka-Zapady deposit after sodium activation (sample 4Bas)

Fot. 2. Mikrofotografia SEM próbki surowca smektytowo-krzemionkowego ze środkowej części profilu złoża Dylągówka-Zapady po aktywacji sodowej (próbka 4Bas)



Phot. 3. SEM microphotograph of a sample of smectite-silica raw material from the middle part of the profile of the Dylągówka-Zapady deposit after acid activation (sample 4Bak)

Fot. 3. Mikrofotografia SEM próbki surowca smektytowo-krzemionkowego ze środkowej części profilu złoża Dylągówka-Zapady po aktywacji kwasem (próbka 4Bak)



Phot. 4. SEM microphotograph of a sample of smectite-silica raw material from the lowest part of the profile of the Dylągówka-Zapady deposit after sodium activation (sample 4Cak). Symbols: Ca – calcite, G – gypsum

Fot. 4. Mikrofotografia SEM próbki surowca smektytowo-krzemionkowego z najniższej części profilu złoża Dylągówka-Zapady po aktywacji sodowej (próbka 4Cak)

Acidification of the starting solution of copper (II) sulfate to pH = 4 (Figure 4) corresponds to the results of the determination for pH = 5.2 after acid activation (Figure 3). In samples with a lower calcite content, a decrease in the copper sorption value is observed as the pH decreases. Therefore, additional acidification of the solution causes a further reduction in sorption for samples from Dylągówka (4Aak, 4Bak, and 4Cak) to values below 100 mg/kg. In the case of Krakowiec clay samples from Harasiuki (sample 1) and Wola Rzędzińska (2), it also observed the disappearance of sorption due to the substitution of protons in sorption-active sites on the surface of clay minerals. Only samples from Wysoczany (5) and Łukowa (3) have such calcite content that the addition of acid does not cause a significant reduction in sorption due to its use in the chemical reaction of the decomposition of this mineral. Similar relationships were observed for nickel (II) and zinc (II) solutions with pH = 4. Due to these similarities, these results were not presented in this paper.

The results of nickel sorption tests (Figure 5) correlate with the results of copper sorption in terms of the relationship between smectite content and sorption capacity. However, the observed values are much higher. The raw material samples from Dylągówka are the most rich in smectite (1190A, 1190B, and 1190C); they show nickel sorption above 7,200 mg/kg in the case of samples after sodium activation. It does not correspond to the research results of Helios-Rybicka et al. (1996), indicating a similar value of copper and nickel sorption in

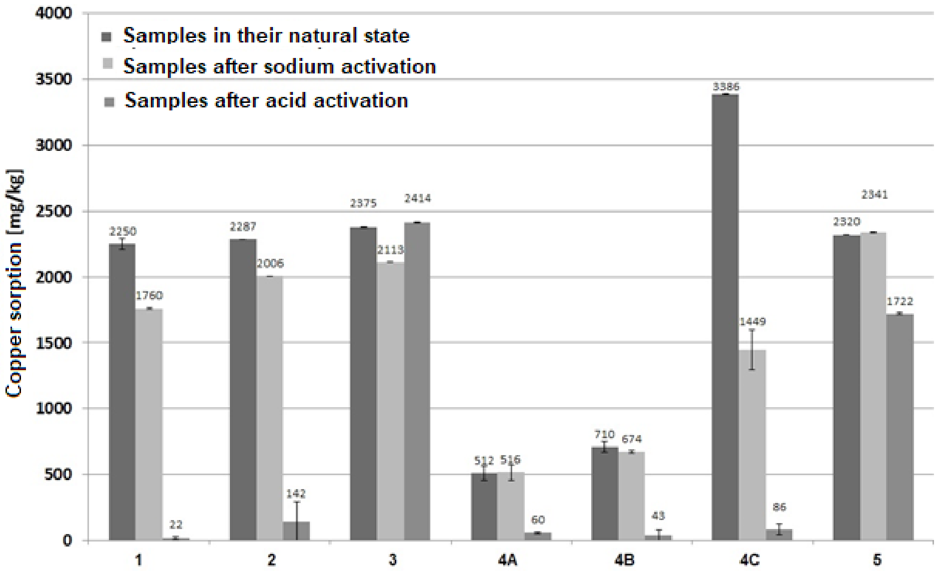


Fig. 4. Sorption of copper on the tested clay raw materials in their natural state and after chemical modification at pH = 4 of the starting solution
Deposits: 1 – Harasiuki, 2 – Wola Rzędzińska, 3 – Łukowa, 4 – Dylągówka, 5 – Wysoczany

Rys. 4. Sorpcja miedzi na badanych surowcach ilastych w stanie naturalnym i po modyfikacji chemicznej przy pH = 4 roztworu wyjściowego
Złoża: 1 – Harasiuki, 2 – Wola Rzędzińska, 3 – Łukowa, 4 – Dylągówka, 5 – Wysoczany

smectites. The reason for this may be the phenomenon of ion complexation. Most likely in an aqueous solution of sulfate copper at pH = 5.2, the Cu^{2+} cation, best sorbed on clays, is present in smaller amounts (Figure 3). The nickel (II) cation, in a solution at pH = 7.3 (Figure 5), is incorporated into the interlayer spaces of smectite on the principle ion exchange. Therefore, an increased sorption value of nickel from the sulfate solution is observed. Loosening the structure of smectite by introducing sodium cations, which – as we know – is easily exchangeable, causes a significant increase in sorption also in the case of Krakowiec clays (samples: 1, 2 and 3) and the Wysoczany shale (5).

The high value of nickel sorption may also be related to the phenomenon of substitutions in the structure of smectite. Ni^{2+} – bound in the interlayer spaces based on physical interactions – shows some stability due to compensating the negative charge of the plates. Nickel cations, due to the ionic radius of approximately 0.63 Å, can diffuse into the smectite network and occupy free spaces in octahedra or isomorphically substitute cations with similar ionic radii (e.g., Mg^{2+} – 0.66 Å and Fe^{2+} – 0.64 Å; according to Shannon 1976). Therefore, it may influence the sorption value in addition to physical sorption-chemisorption (Kou et al. 2000).

The sorption value on clay samples in the case of zinc (Figure 6) strongly depends on their illite content. Due to its increased content, Krakowiec clays show a slightly lower (only

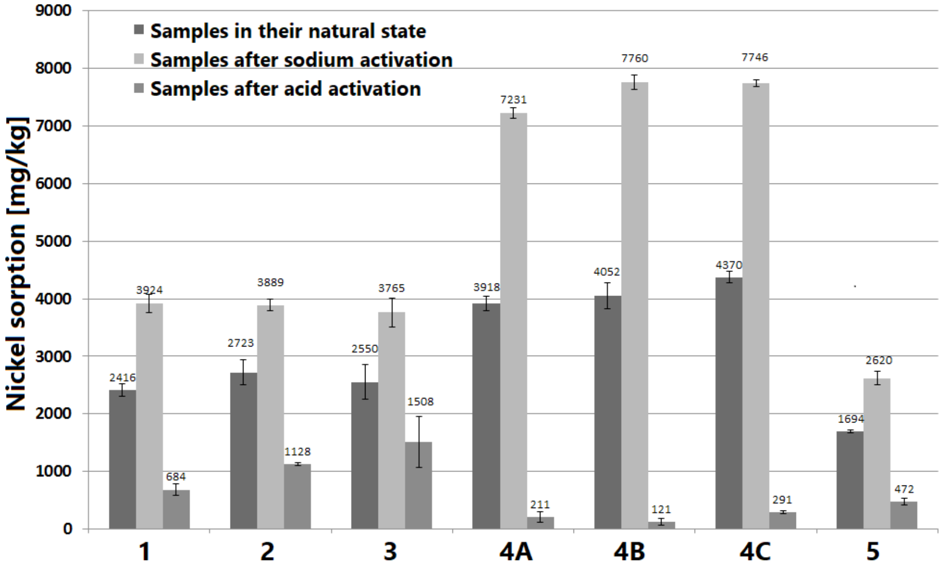


Fig. 5. Sorption of nickel on the tested clay raw materials in their natural state
and after chemical modification at pH = 7.3 of the initial solution
Deposits: 1 – Harasiuki, 2 – Wola Rzędzińska, 3 – Łukowa, 4 – Dylągówka, 5 – Wysoczany

Rys. 5. Sorpcja niklu na badanych surowcach ilastych w stanie naturalnym
i po modyfikacji chemicznej przy pH = 7,3 roztworu wyjściowego
Złoża: 1 – Harasiuki, 2 – Wola Rzędzińska, 3 – Łukowa, 4 – Dylągówka, 5 – Wysoczany

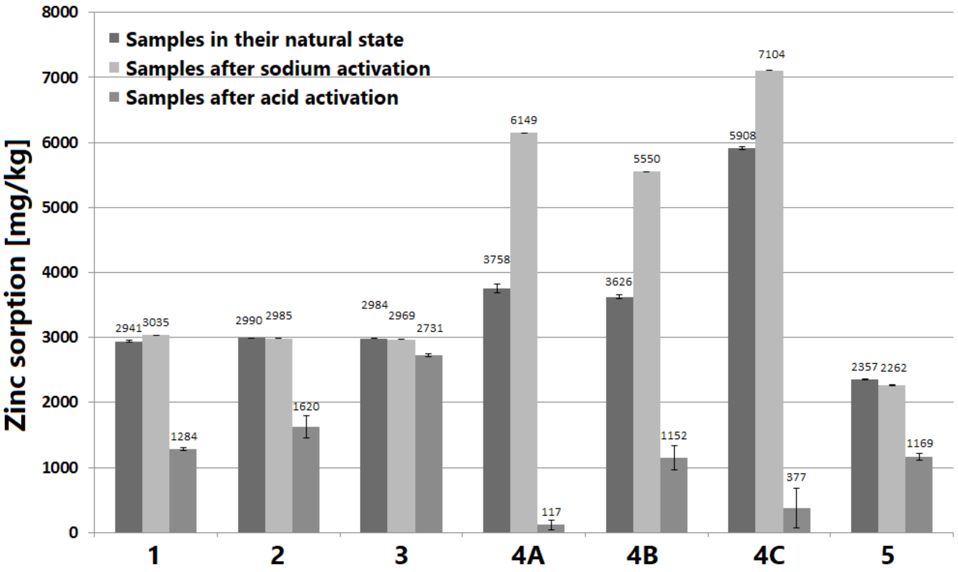


Fig. 6. Sorption of zinc on the tested clay raw materials in their natural state
and after chemical modification at pH = 6.6 of the initial solution
Deposits: 1 – Harasiuki, 2 – Wola Rzędzińska, 3 – Łukowa, 4 – Dylągówka, 5 – Wysoczany

Rys. 6. Sorpcja cynku na badanych surowcach ilastych w stanie naturalnym
i po modyfikacji chemicznej przy pH = 6,6 roztworu wyjściowego
Złoża: 1 – Harasiuki, 2 – Wola Rzędzińska, 3 – Łukowa, 4 – Dylągówka, 5 – Wysoczany

by approx. 700 mg/kg) sorption of this heavy metal compared to samples from the upper part of the Dylągówka deposit (samples 4A and 4B). The measurement results prove the similarity of the sorption mechanism of zinc and copper (Helios-Rybicka et al. 1996). It is confirmed by similar sorption values on sodium-modified samples and samples in their natural state. No improvement in the sorption capacity characterizes the Krakowiec clays as a result of this activation. It is most likely dependent on the mobility of these elements and the ability to complex their ions in appropriate pH conditions. Therefore, despite the improvement in the sorption capacity of smectite as a result of introducing it into its interlayer spaces, sodium cation, which is more easily exchanged for Zn^{2+} than, e.g., Cu^{2+}, sorption is reduced due to the presence of zinc in larger, most likely negative ionic complexes of this metal. In turn, samples of clay-silica raw material from Dylągówka show a significant increase in sorption after introducing sodium cations into the interstitial spaces. It is primarily due to the minor change in pH towards alkaline due to the ion exchange sorption of Na^{+}.

The analyzed samples show the lowest sorption capacity for chromium (VI) (Figure 7). This is probably related to the phenomenon of complexation (formation of chromium ionic complexes of large sizes and often with a negative charge), which means that in smectites it may be exclusively sorbed on the edges of their plates (does not enter the interlayer spaces) (Helios-Rybicka et al. 1995). Therefore, chromium sorption on the tested samples is low. At pH = 5.9, only sample 4A is characterized by an increased value of approximately 320 mg/kg. It may be related to the small content of zeolite in this sample (Mozgawa and Bajda 2005). In addition, the relatively high sorption of chromium (concerning the analyzed samples) may be influenced by the content of iron and manganese oxyhydroxides (Kłapyta and Żabiński 2008). MIR spectra and increased iron content (determined based on chemical analysis) may indicate their particular share in samples of Krakowiec clays (samples 1, 2, and 3) and shale from Wysoczany (5). The results of these analyses are presented in the papers of Panna et al. (2014a, 2014b, 2015), and Panna (2016).

Unlike the sorption of copper, nickel, and zinc, in the case of further acidification of the starting solution, the sorption capacity for chromium (VI) significantly improves, especially in the case of sodium-activated samples from Dylągówka (Samples 4A, 4B, 4C; Figure 8). This may be related to a much more favorable pH, obtained due to the transfer of some sodium ions into the solution. In the case of the remaining samples, the pH change was probably too significant, and the low acidic reaction did not produce the desired result.

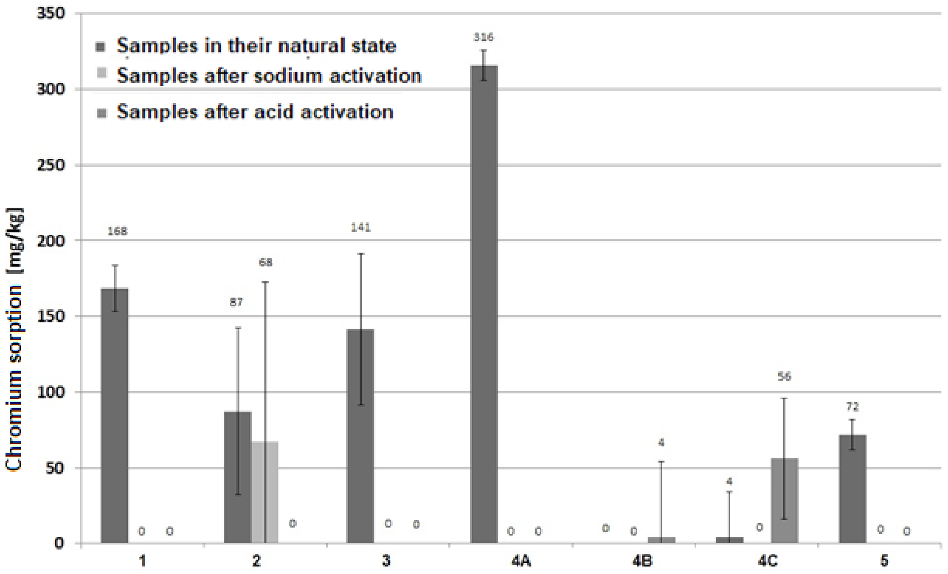


Fig. 7. Chromium sorption on the tested clay raw materials in their natural state
and after chemical modification at pH = 5.9 of the initial solution
Deposits: 1 – Harasiuki, 2 – Wola Rzędzińska, 3 – Łukowa, 4 – Dylągówka, 5 – Wysoczany

Rys. 7. Sorpcja chromu na badanych surowcach ilastych w stanie naturalnym
i po modyfikacji chemicznej przy pH = 5,9 roztworu wyjściowego
Złoża: 1 – Harasiuki, 2 – Wola Rzędzińska, 3 – Łukowa, 4 – Dylągówka, 5 – Wysoczany

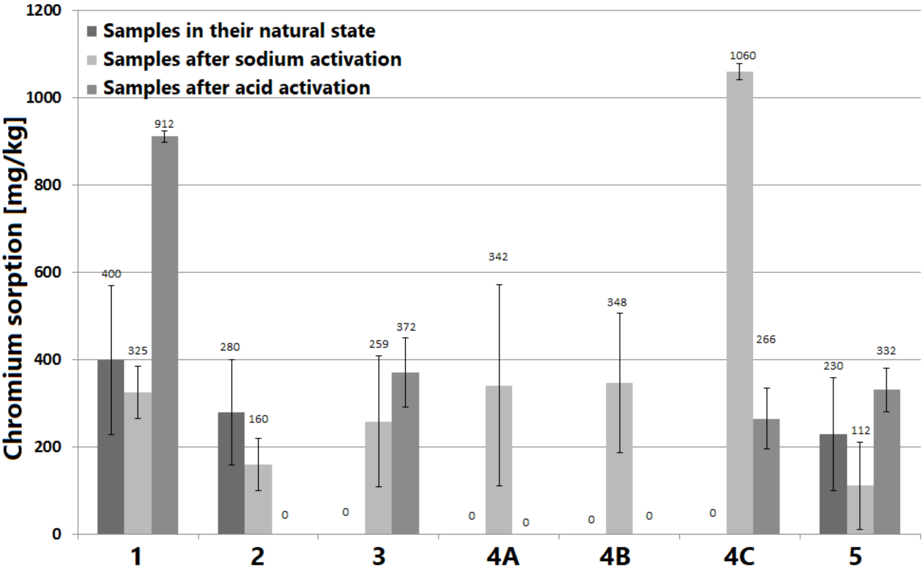


Fig. 8. Sorption of chromium on the tested clay raw materials in their natural state
and after chemical modification at pH = 4 of the initial solution
Deposits: 1 – Harasiuki, 2 – Wola Rzędzińska, 3 – Łukowa, 4 – Dylągówka, 5 – Wysoczany

Rys. 8. Sorpcja chromu na badanych surowcach ilastych w stanie naturalnym
i po modyfikacji chemicznej przy pH = 4 roztworu wyjściowego
Złoża: 1 – Harasiuki, 2 – Wola Rzędzińska, 3 – Łukowa, 4 – Dylągówka, 5 – Wysoczany

Conclusions

Based on the sorption tests carried out for heavy metals, it can be concluded that the analyzed samples have an increased ability to bind them partially. The clay-silica mineral from Dylągówka (samples 4A, 4B, and 4C) can be considered a medium-quality sorbent, which absorbs copper, nickel, and zinc to a large extent. In the case of this raw material, adding sodium cations into the interstitial spaces of smectite improves the sorption of all the above-mentioned heavy metals. Differences in sorption values concerning the type of sorbed metal depend primarily on the pH of the sorption environment. In general, however, the tests carried out confirm the correctness of the increasing sorption capacity of smectite concerning heavy metals in the following order: $Pb^{2+} \approx Cd^{2+} < Cu^{2+} < Zn^{2+} < Mn^{2+} < Ni^{2+}$ (Abollino et al. 2008). This relationship is met primarily for sodium-modified samples in which smectite content exceeds 30% (samples: 4Aas, 4Bas, and 4Cas).

In addition to ensuring a more excellent dispersion of smectite stacks in the aqueous environment, attention should be paid to the change in pH to alkaline as a result of the transfer of some sodium ions into the solution (both from inter-stack positions and from unreacted Na_2CO_3). As a result, it is impossible to compare the tests mentioned above' results with those experiments carried out at constant pH = 6.5 by Helios-Rybicka et al. (1995). In general, the values given by these authors are much lower, both in the case of natural samples and after sodium modification. The amount of sorption generally increases with the increase in the pH of the solution. It is related to the surface charge of the clay mineral packets. The surface becomes less damaging at a lower pH. It is due to the formation of positively charged sites due to proton sorption at the edges of the octahedral layers. A more significant number is formed on the surface of positive charges at a lower pH, while negative charges remain unchanged. As a result, the total charge determining the ion exchange capacity gradually decreases as the environment's acidity increases (Stumm and Morgan 1981). Acid activation, due to the physical adsorption of a significant amount of acid in the pores and on the surfaces of clay minerals, causes a decrease in the pH of the initial solution, which leads to a significant reduction in sorption. In the case of the raw materials researched in this paper, acid activation worsens Cu, Ni, Zn, and Cr sorption properties.

The amount of metal sorption also depends on whether the metal is present in the solution as an independent cation or in the form of a complex combination. The best example here is the complex anion, which is attributed to a significantly low value of chromium sorption in the tested samples (Figure 8). The amount of its sorption changes with a change in pH, just like the amount of sorption of the ligand itself (Bourg et al. 2003). In addition, attention should also be paid to the concentration of the adsorbate itself. In the case of copper, nickel, and zinc compounds, low concentrations were used as heavy metals (due to the need to ensure the highest possible accuracy of analyses). According to Millward (1980), the sorption at low pH increases with dilution of solutions.

The comparison of the results of sorption tests of the clay-silica mineral from Dylągówka and the Krakowiec clays proves that the sorption of metals is not a result of the smectite content. It is indicated, for example, by the relatively small difference between the sorption of copper on the sample from Dylągówka (4C), which is richest in smectite, and the sample from Harasiuki (1), which is approximately 1,200 mg/kg. It is influenced by phases other than smectite that have sorption capacity. In the case of Krakowiec clays (1, 2, 3), these are, in particular, clay minerals such as illite and chlorite, as well as organic substances and hydroxides of iron and manganese. Iron and manganese hydroxides are characterized by microcrystalline or X-ray amorphous nature and can absorb various substances. It may affect the sorption value of Krakowiec clays (1, 2, 3).

Sorption measurements of Krakowiec clays and Krosno shale samples from Wysoczany in their natural state and after various variants of chemical modification suggest the possibility of using them as mineral barriers due to the increased ability to sorb selected heavy metals. The former is characterized by a low filtration coefficient and appropriate parameters strength (Brański 1995). From the perspective of heavy metal sorption, sodium activation often enhances sorption properties, while acid activation generally diminishes them. Therefore, these treatments are not necessary for this material. The clay-silica raw material from Dylągówka (4) can be effectively utilized as a mineral sorbent for specific applications, which should be determined after conducting comprehensive physicochemical studies.

This study was carried out within the grant No. BAD-01/2024 obtained from the Academy of Tarnow.

The Authors have no conflict of interest to declare.

REFERENCES

Abollino et al. 2008 – Abollino, O., Giacomino, A., Malandrino, M. and Mentasti, E. 2008. Interaction of metal ions with montmorillonite and vermiculite. *Applied Clay Science* 38(3–4), pp. 227–236, DOI: 10.1016/j.clay.2007.04.002.

Ayari et al. 2005 – Ayari, F., Srasra, E. and Trabelsi-Ayadi, M. 2005. Characterization of bentonitic clays as adsorbent. *Desalination* 185, pp. 391–397, DOI: 10.1016/j.desal.2005.04.046.

Ayari et al. 2007 – Ayari, F., Srasra, E. and Trabelsi-Ayadi, M. 2007. Effect of exchangeable cations on the physicochemical properties of smectite. *Surface Engineering and Applied Electrochemistry* 43(5), pp. 369–378, DOI: 10.3103/S1068375507050110.

Bobrowska, M. and Szaniawska, D. 2011. Investigations of modified bentonites for use in environmental protection (*Badania modyfikacji bentonitów do zastosowań w ochronie środowiska*). *Inżynieria i Aparatura Chemiczna* 50(5), pp. 20–21 (*in Polish*).

Bourg et al. 2003 – Bourg, I.C., Bourg, A.C.M. and Sposito, G. 2003. Modeling diffusion and adsorption in compacted bentonite: a critical review. *Journal of Contaminant Hydrology* 61(1), pp. 293–302, DOI: 10.1016/S0169-7722(02)00128-6.

Brański, P. 1995. Prospects for the use of Miocene clays from the Carpathian Foredeep in environmental protection (*Perspektywy wykorzystania iłów mioceńskich zapadliska przedkarpackiego w ochronie środowiska*). *Przegląd Geologiczny* 43(6), pp. 493–496 (*in Polish*).

Brown, G. 1955. The effect of isomorphous substitutions on the intensities of (001) reflections of mica- and chlorite-type structures. *Mineralogical Magazine and Journal of the Mineralogical Society* 30(229), pp. 657–665. DOI: 10.1180/minmag.1955.030.229.06.

Brzeziński, D. 2021. Bentonites and bentonite clays (*Bentonity i iły bentonitowe*). [In:] Szuflicki, M., Malon, A. and Tymiński, M. (eds.), *Balance of Mineral Deposit Resources in Poland as of December 31, 2020* (*Bilans Zasobów Złóż Kopalin w Polsce wg stanu na 31 XII 2020 r.*). Warszawa: PIG-PIB, pp. 89–90 (*in Polish*).

Bujdák et al. 2001 – Bujdák, J., Janek, M., Madejová, J. and Komadel, P. 2001. Methylene blue interactions with reduced-charge smectite. *Clays and Clay Minerals* 49(3), pp. 244–254, DOI: 10.1346/CCMN.2001.0490307.

Churchman et al. 2006 – Churchman, G.J., Gates, W.P., Theng, B.K.G. and Yuan, G. 2006. *Clays and clay minerals for pollution control*. [In:] Bergaya, F., Theng, B.K.G. and Lagaly, G. (eds.), *Handbook of Clay Science*. Amsterdam-Tokyo: Elsevier, pp. 625–676.

Czurda, K. 2006. Clay liners and waste disposal. in Bergaya, F., Theng, B.K.G. and Lagaly, G. (eds.), *Handbook of Clay Science*. Amsterdam-Tokyo: Elsevier, pp. 693–701.

Fusi et al. 2015 – Fusi, L., Primicerio, M. and Monti, A. 2015. A model for calcium carbonate neutralization in the presence of armoring. *Applied Mathematical Modelling* 39(1), pp. 348–362, DOI: 10.1016/j.apm.2014.05.037.

Górniak et al. 2021 – Górniak, K., Szydłak, T., Wyszomirski, P., Gaweł, A. and Niemiec, M. 2021. Recently discovered thick bentonite bed hosted by the Lithothamnium Limestones (Badenian) in the Polish part of the Carpathian Foredeep: The evidence for volcanic origin. *Minerals* 11(12), DOI: 10.3390/min11121417.

Gualtieri et al. 2008 – Gualtieri, A.F., Ferrari, S., Leoni, M., Grathoff, G., Hugo, R., Shatnawi, M., Paglia, G. and Billinge, S. 2008. Structural characterization of the clay mineral illite-1M. *Journal of Applied Crystallography* 41, pp. 402–415, DOI: 10.1107/S0021889808004202.

Helios-Rybicka et al. 1995 – Helios-Rybicka, E., Calmano, W. and Breeger, A. 1995. Heavy metals sorption/desorption on competing clay minerals; an experimental study. *Applied Clay Science* 9(5), pp. 369–381, DOI: 10.1016/0169-1317(94)00030-T.

Heyde et al. 2020 – Heyde, J., Glaeser, S.P., Bisping, L., Kirchberg, K., Ellinghaus, R., Siemens, J. and Mulder, I. 2020. Smectite clay minerals reduce the acute toxicity of quaternary alkylammonium compounds towards potentially pathogenic bacterial taxa present in manure and soil. *Scientific Reports* 10, DOI: 10.1038/s41598-020-71720-5.

Kabata-Pendias, A. and Pendias, H. 1999. *Biogeochemistry of trace elements* (*Biogeochemia pierwiastków śladowych*). Warszawa: Wyd. Naukowe PWN (*in Polish*).

Kłapyta, Z. and Żabiński, W. (eds.) 2008. *Polish mineral sorbents* (*Sorbenty mineralne Polski*). Kraków: AGH (*in Polish*).

Koch, D. 2002. Bentonites as a basic material for technical base liners and site encapsulation cut-off walls. *Applied Clay Science* 21(1–2), pp. 1–11, DOI: 10.1016/S0169-1317(01)00087-4.

Komadel, P. 2003. Chemically modified smectites. *Clay Minerals* 38(1), pp. 127–138, DOI: 10.1180/0009855033810083.

Korichi et al. 2012 – Korichi, S., Elias, A., Mefti, A. and Bensmaili, A. 2012. The effect of microwave irradiation and conventional acid activation on the textural properties of smectite: Comparative study. *Applied Clay Science* 59–60, pp. 76–83, DOI: 10.1016/j.clay.2012.01.020.

Kou et al. 2000 – Kou, M.R.S., Mendioroz, S. and Muñoz, V. 2000. Evaluation of the acidity of pillared montmorillonites by pyridine adsorption. *Clays and Clay Minerals* 48(5), pp. 528–536, DOI: 10.1346/CCMN.2000.0480505.

Madejová et al. 1998 – Madejová, J., Bujdák, J., Janek, M. and Komadel, P. 1998. Comparative FT-IR study of structural modifications during acid treatment of dioctahedral smectites and hectorite. *Spectrochimica Acta Part A* 54(10), pp. 1397–1406, DOI: 10.1016/S1386-1425(98)00040-7.

Majer et al. 2007 – Majer, E., Łuczak-Wilamowska, B., Wysokiński, L. and Drągowski, A. 2007. *Principles of assessing the suitability of cohesive soils in Poland for the construction of mineral insulation barriers* (*Zasady oceny przydatności gruntów spoistych Polski do budowy mineralnych barier izolacyjnych*). Warszawa: Instytut Techniki Budowlanej (*in Polish*).

Millward, G.E. 1980. The adsorption of cadmium by iron(III) precipitates in model estuarine solutions. *Environmental Technology Letters* 1(8), pp. 394–399, DOI: 10.1080/09593338009383993.

Nieć, M. and Ratajczak, T. 2004. *Deposits of bentonite and zeolite minerals* (*Złoża kopalin bentonitowych i zeolitowych*). [In:] Ney, R. (ed.), Mineral resources of Poland. Rock raw materials. Clay raw materials (*Surowce mineralne Polski. Surowce skalne. Surowce ilaste*). Kraków: MEERI PAS, pp. 101–116 (*in Polish*).

Ociepa-Kubicka, A. and Ociepa, E. 2012. *Toxic effects of heavy metals on plants, animals and people* (*Toksyczne oddziaływanie metali ciężkich na rośliny, zwierzęta i ludzi*). *Inżynieria i Ochrona Środowiska* 15(2), pp. 169–180 (*in Polish*).

Panna, W. 2016. *Properties of smectites and technological suitability of selected clay raw materials from south-eastern Poland* (*Właściwości smektytów a przydatność technologiczna wybranych surowców ilastych południowo-wschodniej Polski*). Rozprawa doktorska AGH w Krakowie. [Online:] https://winntbg.bg.agh.edu.pl/rozprawy2/11092/full11092.pdf (*in Polish*).

Panna et al. 2014a – Panna, W., Prosowicz, G. and Wyszomirski, P. 2014a. Assessment of smectite content in some clay raw materials based on spectrophotometric sorption tests (*Ocena zawartości smektytu w niektórych surowcach ilastych na podstawie spektrofotometrycznych badań sorpcyjnych*). *Chemik* 68(7), pp. 612–619 (*in Polish*).

Panna et al. 2014b – Panna, W., Wyszomirski, P. and Myszka, R. 2014b. Characteristics of the clayey-siliceous rock from the Dylągówka–Zapady deposit (Polish Flysch Carpathians) as a mineral raw material (*Charakterystyka surowcowa kopaliny ilasto-krzemionkowej ze złoża Dylągówka-Zapady (polskie Karpaty fliszowe)*). *Gospodarka Surowcami Mineralnymi – Mineral Resources Management* 30(2), pp. 85–102, DOI: 10.2478/gospo-2014-0012.

Panna et al. 2015 – Panna, W., Wyszomirski, P. and Myszka, R. 2015. Characteristics of the exploitation waste from the sandstone quarry in Wysoczany (Podkarpackie Voivodeship) (*Charakterystyka surowcowa odpadu eksploatacyjnego z kopalni piaskowca w Wysoczanach (woj. podkarpackie)*). *Zeszyty Naukowe IGSMiE PAN* 88, pp. 183–194 (*in Polish*).

Ratajczak et al. 2005 – Ratajczak, T., Jończyk, W. and Skórzak, A. 2005. Ecology and associated minerals on the example of the "Bełchatów" brown coal deposit (*Ekologia a kopaliny towarzyszące na przykładzie złoża węgla brunatnego „Bełchatów"*). *Górnictwo Odkrywkowe* 47(2), pp. 34–38 (*in Polish*).

Shannon, R.D. 1976. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica: Section A* 32(5), pp. 751–767, DOI: 10.1107/S0567739476001551.

Sikora, W.S. 1996. *Sorption of heavy metals by minerals and clay rocks* (*Sorpcja metali ciężkich przez minerały i skały ilaste*). [In:] Kościówko, H. and Wyrwicki, R. (eds.) *Methodology of research on clay minerals* (*Metodyka badań kopalin ilastych*). Warszawa-Wrocław: PIG, pp. 189–197 (*in Polish*).

Stumm, W. and Morgan, J.J. 1981. *Aquatic Chemistry*. Brisbane: John Wiley.

Wyszomirski, P. and Lewicka, E. 2005. Bentonite as a versatile industrial mineral for different markets (*Bentonity jako uniwersalny surowiec wielu dziedzin przemysłu*). *Gospodarka Surowcami Mineralnymi – Mineral Resources Management* 21(3), pp. 5–19 (*in Polish*).

Wyszomirski et al. 2024 – Wyszomirski, P., Szydłak, T., Zawadzki, T. and Baranowski, M. 2024. Basalt weathering crust from Rutki near Niemodlin (Opole Voivodship) – opportunities for its current utilization and remarks on its former use. *Gospodarka Surowcami Mineralnymi – Mineral Resources Management* 40(2), pp. 69–87, DOI: 10.24425/gsm.2024.150822.

Żytko et al. 1989 – Żytko, K., Zając, R. and Gucik, S. 1989. Map of the tectonic elements of the Western Outer Carpathians and their foreland 1:500 000. [In:] Poprawa, D. and Nemcok, J. (eds.), *Geological Atlas of the Western Outer Carpathians and their Foreland*. Warszawa: PIG.

SORPTION PROPERTIES OF SELECTED CLAYS FROM SOUTH-EASTERN POLAND AND THEIR PROSPECTS FOR USE IN ENVIRONMENTAL PROTECTION

Keywords

sorption of heavy metals, smectite raw materials, clay raw materials, activation of bentonites

Abstract

Due to the decline in the production of ceramic building materials (bricks, ceramic hollow blocks), alternative possibilities for managing clay raw materials and using equipment for their processing in production plants are sought. Therefore, the subject of this paper is the assessment of the suitability of selected raw clay materials from southeastern Poland for use as mineral sorbents. For this purpose, the following raw materials were used: Krakowiec clays, clay-silica raw materials from the Dynów Foothills, and Krosno slate in their natural state, as well as after sodium and acid activation. Sorption of copper, nickel, zinc, and chromium from their salts was carried out on the samples using the batch static method, aqueous solutions of experimentally determined concentrations. Experiments were performed using an AAS analyzer. The effect of the sorption environment was determined in conditions of changing pH.

It was found that the sorption of heavy metals depends to the greatest extent on pH and smectite content. However, it is also determined by the content of other mineral components, such as illite, kaolinite, opal, zeolite, iron, and manganese minerals. The influence of chemical modification of samples on sorption parameters and morphology of samples was also investigated. The latter factor was considered based on SEM micrographs. On their basis, prospects for developing the tested mineral raw materials for use as a medium-quality sorbent (clay-silica raw material) and in constructing mineral barriers (Krakowiec clays) were found.

WŁAŚCIWOŚCI SORPCYJNE WYBRANYCH IŁÓW POŁUDNIOWO-WSCHODNIEJ POLSKI I ICH PERSPEKTYWY WYKORZYSTANIA W OCHRONIE ŚRODOWISKA

Słowa kluczowe

sorpcja metali ciężkich, surowce smektytowe, surowce ilaste, aktywacja bentonitów

Streszczenie

W związku ze spadkiem produkcji ceramicznych materiałów budowlanych (cegły, pustaki ceramiczne) poszukuje się alternatywnych możliwości zagospodarowania surowców ilastych i wykorzystania urządzeń do ich przerobu w zakładach produkcyjnych. Dlatego też przedmiotem niniejszej pracy jest ocena przydatności wybranych surowców ilastych z południowo-wschodniej Polski do stosowania jako sorbenty mineralne. Do tego celu wykorzystano następujące surowce: gliny krakowskie, surowce ilasto-krzemionkowe z Pogórza Dynowskiego oraz łupki krośnieńskie w stanie naturalnym oraz po aktywacji sodowej i kwasowej. Na próbkach przeprowadzono sorpcję miedzi, niklu, cynku i chromu z ich soli metodą statyczną okresową, roztworami wodnymi o ustalonych doświadczalnie stężeniach. Doświadczenia przeprowadzono przy użyciu analizatora AAS. Określono wpływ środowiska sorpcyjnego w warunkach zmieniającego się pH.

Stwierdzono, że sorpcja metali ciężkich w największym stopniu zależy od pH i zawartości smektytu. Decyduje o tym jednak także zawartość innych składników mineralnych, takich jak illit, kaolinit, opal, zeolit, minerały żelaza i manganu. Badano także wpływ modyfikacji chemicznej próbek na parametry sorpcji i morfologię próbek. Ten ostatni czynnik uwzględniono na podstawie mikrofotografii SEM. Na ich podstawie stwierdzono perspektywy rozwoju badanych surowców mineralnych do zastosowania jako średniej jakości sorbent (surowiec ilasto-krzemionkowy) oraz do budowy barier mineralnych (gliny krakowskie).