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Application of the cation exchange capacity parameter (CEC) to the characterisation of the swelling capacity of lower Paleozoic, Carpathian Flysch and Miocene Carpathian Foredeep clay rocks

Cation exchange capacity (CEC) is closely related to the amount and type of clay minerals, which, due to their large specific surface area, are characterised by high ion exchange capacity. The CEC value is particularly strongly influenced by swelling minerals, such as: smectite, mixed-layered illite-smectite. The parameter of cation exchange capacity in conjunction with the analysis of clay minerals can be applied to the swelling capacity estimation of both highly diagenetic rocks such as shales from gas-bearing formations and less altered Miocene sediments of the Carpathian Foredeep and Flysch. The CEC parameter of an investigated sample is influenced by two factors: the total content of clay minerals and their swelling capacity determined by the content of smectite layers in the mixed-layered mineral illite-smectite (%S), the swelling capacity being the deciding factor.

Key words: cation exchange capacity, mixed-layered mineral illite-smectite, swelling of clays.

Wykorzystanie parametru pojemności wymiany kationowej CEC do charakterystyki zdolności pęcznienia skał ilastych dolnego paleozoiku, fliszu karpackiego i miocenu zapadliska przedkarpackiego

Zdolność wymiany kationowej jest ściśle związana z ilością i rodzajem minerałów ilastych, charakteryzujących się ze względu na wielkość powierzchni właściwej, dużymi zdolnościami jonowymiennymi. Szczególnie duży wpływ na wartość CEC mają minerały pęczniejące, takie jak: smektyt, mieszanopakietowy illit-smektyt. Parametr pojemności wymiany kationowej CEC w połączeniu z analizą minerałów ilastych może być wykorzystywany do określania zdolności pęcznienia skał ilastych zarówno mocno zdiagenezowanych, takich jak skały formacji łupków gazonośnych, jak i słabiej zmienionych osadów miocenu zapadliska przedkarpackiego i fliszu. Na wartość parametru CEC w badanej próbce wpływają dwa czynniki: sumaryczna zawartość minerałów ilastych i ich zdolności pęcznienia zdeterminowane przez zawartość pakietów smektytowych w minerale mieszanopakietowym illit-smektyt (%S), jak i sumaryczna zawartość minerałów ilastych, przy czym zdolności do pęcznienia są tutaj czynnikiem dominującym.

Słowa kluczowe: pojemność wymiany kationowej, minerał mieszanopakietowy illit-smektyt, pęcznienie iłów.

Introduction

Cation exchange capacity (CEC) is defined as the ability of clay minerals or soil to absorb cations in such form, that they can be easily exchanged for other cations present in an aqueous solution [3]. This parameter defines the amount of cations capable of exchange, and is usually expressed in milliequivalent weight per 100 g of rock [meq/100 g, mval/100 g].

Cation exchange capacity is closely related to the amount and type of clay minerals, which, due to the specific surface area, are characterised by high ion exchange capacity. The CEC value is particularly strongly influenced by swelling minerals, such as: smectite, mixed-layered illite-smectite and other mixed-layered minerals (for example chlorite-smectite, kaolinite-smectite). In this case the cation exchange is connected not only with the external surface of the minerals, but also with the internal interlayer surfaces. In the majority of siliciclastic rocks, swelling minerals are represented by the mixed-layered mineral illite-smectite [7]. The swelling capacity of the mixed-layered mineral illite-smectite is related to the content of smectite layers in its structure. With the progression of diagenesis, the amount of smectite layers decreases (they undergo a transformation into illite), therefore the swelling capacity of illite-smectite decreases.

The aim of the presented work was to estimate the possibility of application of the CEC parameter, to defining the swelling capacity of clay rocks displaying different degree of diagenetic changes.

Methodology

The research was carried out on groups of samples containing mixed-layered mineral illite-smectite with a varied smectite layers content (Figure 1). Both highly diagenetic rocks such as shales from gas-bearing formations of Lower Paleozoic from Baltic (K-1 and Op-2 boreholes) and Lublin (W-1 borehole) basins, and less altered Flysch mudstones (D-1 borehole) and Miocene sediments of the Carpathian Foredeep (Prz-267, 268, 273, 274 and K-1 boreholes) and were examined.

Measurements of cation exchange capacity (CEC) were conducted with the use of the cobalt hexamine method [1, 2, 5, 11]. The applied method is based on the measurement of the change in the indicator cation $Co[NH_3]_6^{+++}$ concentration, before and after introducing the cobalt hexamine solution to the sample.

$$CEC = 100w \frac{C_{wz} V_{wz} \left(1 - \frac{A_{pr}}{A_{wz}}\right)}{m_{pr}} \qquad (1)$$

where:

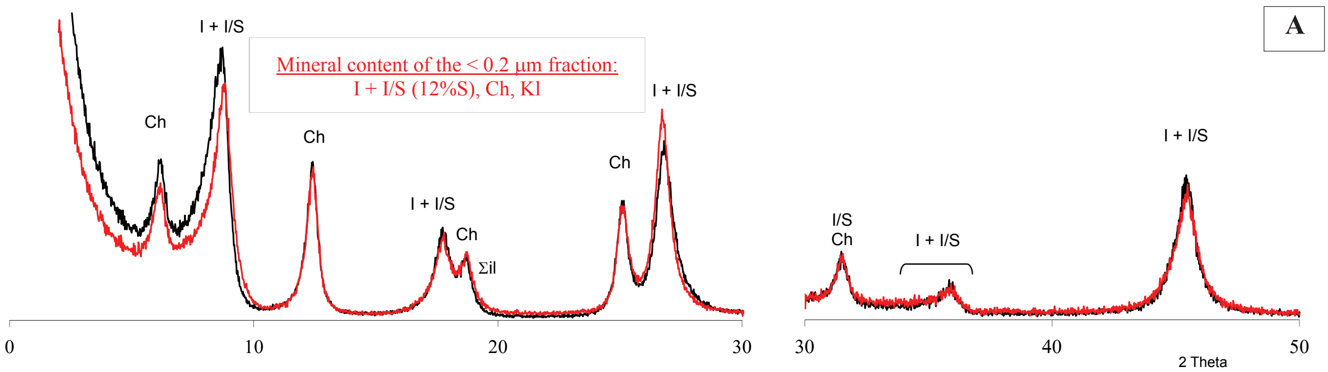
CEC – cation exchange capacity [mval/100 g],
w – valence of the indicator cation ($w = 3$ for cobalt hexamine),
C_{wz} – molar concentration of the cobalt hexamine solution [mmol/l],
V_{wz} – volume of the cobalt hexamine solution [l],
m_{pr} – sample mass [g],
A_{wz} – absorbance of the cobalt hexamine solution,
A_{pr} – absorbance of the cobalt hexamine after mixing with the measured sample.

The mineral composition of the rocks was established by X-ray quantitative analysis conducted in the Departement of Geophysical Well Logging INiG – PIB in Krakow [4]. The composition of the clay fraction was obtained by the X-ray analysis of the separated grain fraction < 0,2 μm. The mixed-layered mineral illite-smectite was characterized (establishment of the smectite layers content – %S) with the use of Środoń's methodology [6, 8, 9].

Results

The analysis of the relation between the CEC value and the smectite layers content in the mixed-layered mineral illite-smectite for all examined rocks

The correlation between the CEC value and the smectite layers content in the mixed-layered mineral illite-smectite was examined. Also the relation between the CEC parameter value and the total content of clay minerals was investigated. A clear correlation is visible between the swelling capacity of the mixed-layered mineral illite-smectite (the smectite layers content – %S) and the cation exchange capacity value (Figure 2). The lowest CEC values were obtained for the Lower Paleozoic shale samples containing the mixed-layered mineral I/S with a low smectite layers content (≤ 26%). Miocene rocks containing the mixed-layer mineral I/S with



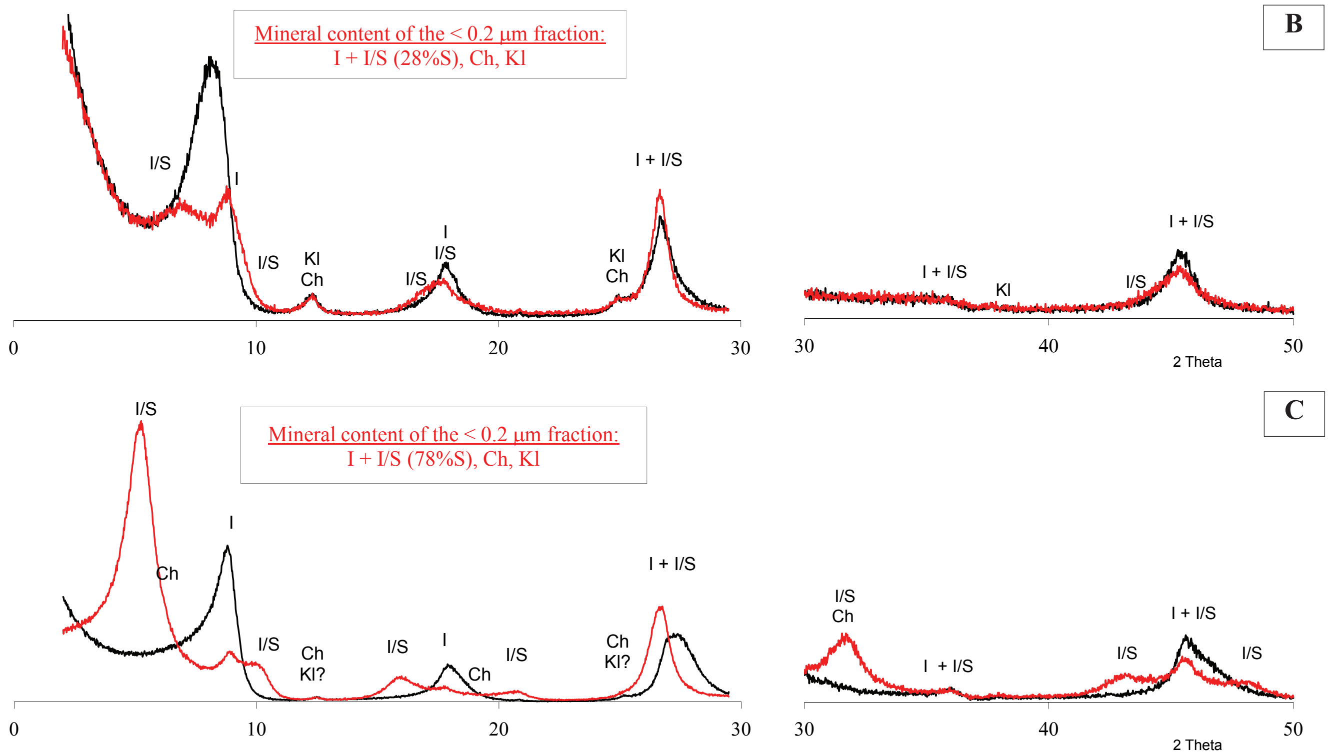


Fig. 1. X-ray diffractograms of the <0,2 µm grain fraction of the examined rocks containing the mixed-layered mineral illite-smectite with a varied amount of smectite layers; black line – air-dried sample, red line – glycolated sample, I/S – mixed-layered mineral illite-smectite, I – illite, Ch – chlorite, Kl – kaolinite. A – Silurian mudstone, B – Flysch mudstone, C – Miocene mudstone

a high smectite layers content (in most cases above 60%S) are characterised by significantly higher values of cation exchange capacity. Flysch rocks samples exhibit intermediate properties (Figure 2).

The compilation of the CEC value, smectite layers content in illite-smectite and the sum of clay minerals (Fig. 3) shows distinctly that the CEC value is influenced by both the swelling capacity of illite-smectite – smectite layers content (%S) and the total content of clay minerals; the swelling capacity being the dominating factor. As shown above (Figure 3) the CEC values in Miocene rocks are significantly higher than in gas-bearing shales, even though they contain a comparable or even lower content of clay minerals.

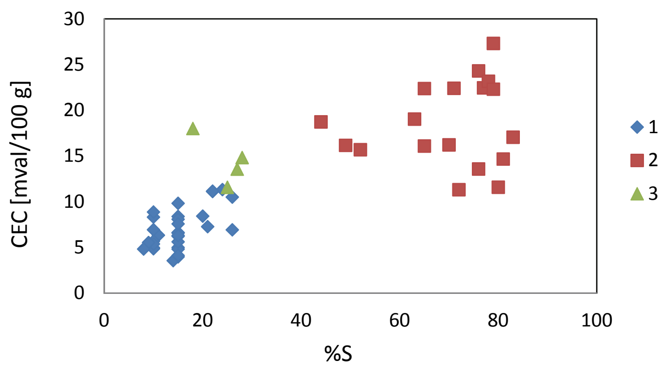


Fig. 2. Correlation between the cation exchange capacity (CEC) value and the smectite layers content (%S); claystones and mudstones: 1 – Lower Paleozoic, 2 – Miocene, 3 – Flysch

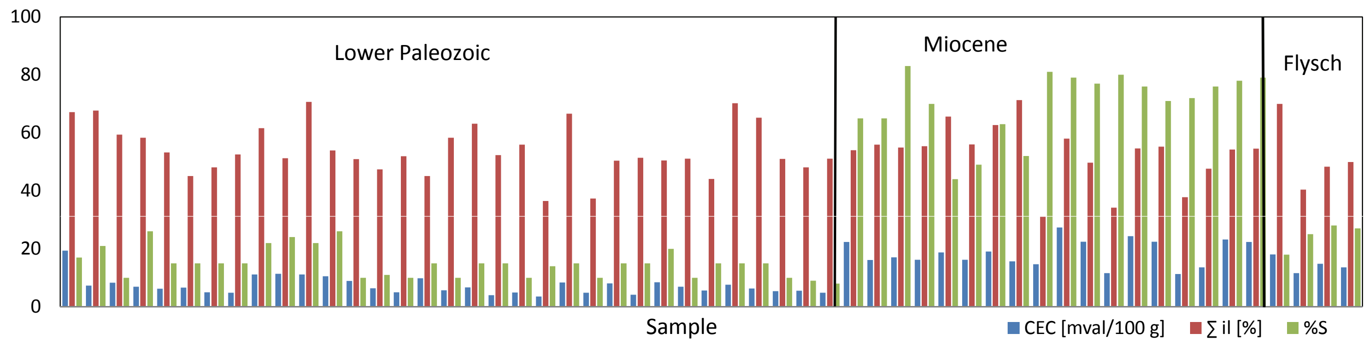


Fig. 3. Compilation of the CEC value, sum of clay minerals (∑ il) and smectite layers content in the mixed-layered mineral illite-smectite (%S) in claystones and mudstones of Lower Paleozoic, Miocene and Flysch

The analysis of the influence of clay minerals total content, on the cation exchange capacity value, taking into account the variety of the mixed-layered mineral, illite-smectite in the investigated samples

The influence of the sum of clay minerals on the cation exchange capacity value was examined separately for highly diagenetic Lower Paleozoic rocks and less altered Miocene and Flysch sediments, taking into account the variety of the investigated samples in respect to the smectite layers content in the mixed-layered mineral illite-smectite (Figures 4, 5, 10, 11).

Among the Lower Paleozoic rocks, two groups of samples differing in terms of the mixed-layered mineral illite-smectite properties (below 20% and above 20% of smectite layers S) were distinguished. As shown below (Figure 4), the samples containing more than 20% of smectite layers are characterised by higher cation exchange capacity values – in most cases above 10 mval/100 g, than the samples containing below 20% of smectite layers – in those rocks, the CEC value does not exceed 9 mval/100 g.

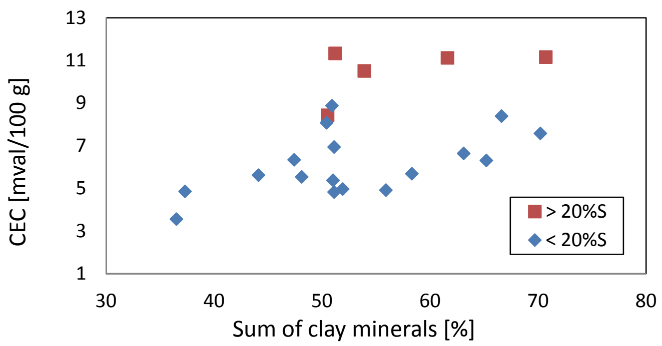


Fig. 4. Correlation between the value of the sum of clay minerals and the CEC value for shale rocks from gas-bearing formations taking into account the variety of the clay material; > 20%S, < 20%S – samples containing illite-smectite with the amount of smectite layers respectively higher and lower than 20%

In the samples containing illite-smectite of similar properties, a correlation was noticed between the total clay minerals content and the CEC parameter. An upward trend in the relationship between the CEC value and the sum of clay minerals is visible (Figure 5).

As in the case of the Lower Paleozoic rocks two groups of samples were distinguished among the less altered sediments (Miocene and Flysch claystones and mudstones). The groups are characterized by different properties of the mixed-layered mineral illite-smectite (below 70% and above 70% of smectite layers S) (Figure 6). The highest values of cation exchange capacity (above 20 mval/100 g) were obtained for the rocks containing the mixed-layered mineral illite-smectite with a high smectite layers content (above 70%) and at the same

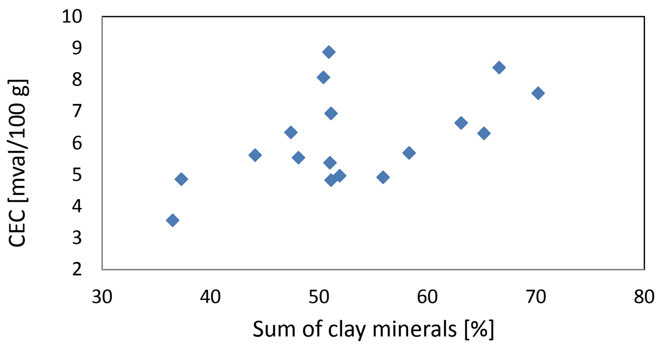


Fig. 5. Correlation between the value of the sum of clay minerals and the CEC value in mudstones and claystones of Lower Paleozoic containing illite-smectite with the smectite layers content lower than 20%

time, more than 50% of clay minerals. Rocks with a high clay minerals content, but characterised by a lower swelling capacity of illite-smectite exhibit lower CEC values (Figure 6).

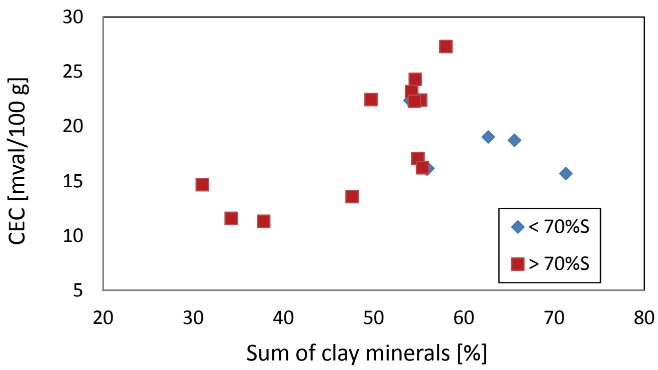


Fig. 6. Correlation between the value of the sum of clay minerals and the CEC value in Miocene and Flysch mudstones and claystones taking into account the variety of the clay material; > 70%S, < 70%S – samples containing illite-smectite with the amount of smectite layers respectively higher and lower than 70%

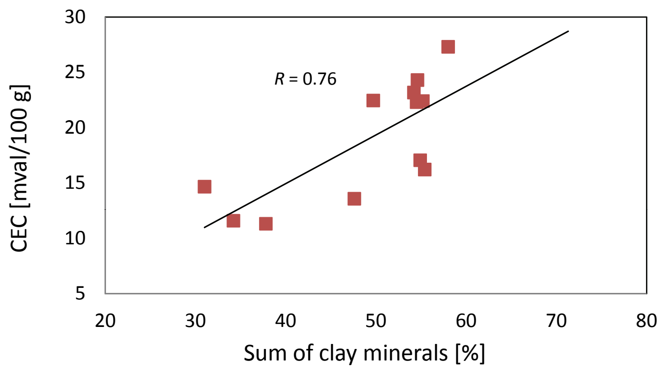


Fig. 7. Correlation between the value of the sum of clay minerals and the CEC value in Miocene mudstones and claystones containing the mixed-layered mineral illite-smectite with smectite layers content above 70%

In the case of samples containing illite-smectite with similar properties (characterised by more than 70% of smectite layers) a correlation between the CEC parameter and the total clay minerals content is visible. The cation exchange capacity (CEC) value distinctly increases with the increasing value of the sum of clay minerals (Figure 7).

Determination of the swelling capacity (reactivity) of the investigated rocks on the basis of the cation exchange capacity value

Cation exchange capacity value is one of the key parameters applied to establish the swelling capacity of clay rocks [10]. The authors indicate CEC values exceeding 20 mval/100 g as characteristic for swelling rocks, values from 10 mval/100 g to 20 mval/100 g for clay rocks of medium reactivity, and values below 10 mval/100 g as characteristic for non-swelling rocks.

In accordance with the above-mentioned classification, non-swelling samples (CEC < 10 mval/100 g, Figure 2) dominate in the group of highly diagenetic Lower Paleozoic claystones and mudstones. Among them, a small group of samples characterized by the CEC value higher than 10 mval/100 g can be distinguished. These samples, containing mixed-layered illite-smectite with more than 20% smectite layers (Figure 4), may be classified as clay rocks of medium swelling capacity. Most of the Miocene samples belong to the medium reactivity group (CEC value between 10 and 20 mval/100 g). Rocks of a high reactivity (CEC > 20 mval/100 g) were also distinguished, it is a group of samples containing mixed-layered illite-smectite with a high smectite layers content (above 70%) and at the same time characterised by a high total amount of clay minerals (above 50%) (Figure 6).

Summary and conclusions

The cation exchange capacity of an investigated sample is influenced by two factors: the sum of clay minerals and their swelling capacity determined by the smectite layers content in the mixed-layered mineral illite-smectite. The CEC value increases significantly with an increase in the smectite layers content. The lowest CEC values are found in the Lower Paleozoic samples, which, due to the high extent of diagenesis, contain the mixed-layered mineral I/S with a low smectite layers content, and therefore display low swelling capacity. Much higher values of cation exchange capacity are characteristic of the less altered Miocene rocks, containing mixed-layered I/S with a high smectite layers content. In rocks with clay minerals displaying similar properties. the total content of clays correlates also with the CEC parameter.

The investigated formations were characterised in respect to their swelling capacity on the basis of the CEC parameter value. The majority of Lower Paleozoic rocks belong to the group of low swelling capability, and the Miocene samples to the group of medium reactivity. A group of samples of high swelling capacity – Miocene rocks containing mixed-layered illite-smectite with a high smectite layers content (above 70%) and, at the same time, characterised by a high total content of clay minerals (above 50%) was distinguished.

The cation exchange capacity parameter in conjunction with the analysis of clay minerals can be applied to establish the swelling properties of clay rocks, both highly diagenetic such as shale rocks from gas-bearing formations and less altered Miocene sediments of the Carpathian Foredeep and Flysch.

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