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SWELLING PRESSURE OF NATURAL AND MODIFIED SMECTITE-BEARING CLAY RAW MATERIALS

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Abstract: Smectite clays, due to their barrier properties and swelling ability, are often applied for waterproofing purposes. A proper value of swelling pressure is one of the parameters, which must be met by the fillers used in hybrid waterproofing materials. The authors determined the swelling pressure of selected clay raw materials in their natural state and after chemical modification. This parameter was measured by the Komine method, as this procedure is more accurate than the standard edometric method. The authors introduced some changes in the method. The samples represent Krakowiec clays (Miocene) and a Triassic clay, collected in active pits of building clays, which are widely exploited in south Poland. The content of the smectite group minerals, determined from the sorption of methylene blue and copper(II) triethylenetetramine, ranges between 15 and 35%. Further characteristics of the clays were obtained with X-ray diffraction, chemical analyses (calcium carbonate content including) and pH measurements. It has been found that the activation of smectite clays with sodium lowers their swelling pressure as water penetrates easier the interlayer spaces of the smectites modified. This is important from the viewpoint of assessing the quality of bentonite fillers.

Keywords: *clay raw materials, swelling pressure, sodium activated smectites, waterproofing materials, Krakowiec clays, Triassic clay*

Introduction

Smectite-rich clays have been used in engineering since the second half of the 20th century. Initially, they were applied as a sealing additive in constructing river dams and other water plants. In 1970s it was established that the use of bentonites prevents penetration of various contaminants into the soil system. Two special examples of the effective use of the smectite-rich clays include their sorption abilities of heavy metals and radioactive elements in environmental engineering of dyes applied in the paint and textile industries (see, among others, Komine 2003; Gulgonul 2012; Janotka et al. 1996; Klapyta and Zabinski 2008). Based on such properties, clay rocks were utilized

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in Germany in the early 1980s in constructing barriers protecting disposal sites of hazardous waste (Koch 2002).

Currently, smectite-bearing materials are more often applied in civil engineering for waterproofing purposes. Besides pure bentonite granulates, a range of the products used in protecting buildings from water includes bentonite-containing mats, panels, tubes, putties and swelling tapes. The major feature made use of in such applications, is the capability of bentonite to adsorb polar compounds, water included, within smectite interlayers (Murray 2007). As a result, the distance between the smectite layers increases, the volume of an intergranular space of smectite-bearing clay gradually decreases, and the system becomes eventually sealed (Szarugiewicz 2007). Favorable properties of waterproofing clays depend mainly upon their content and type of the smectite group minerals (Panna et al. 2012). The most desirable are bentonite clays rich in montmorillonite. This mineral is common, but usually occurs in nature as the calcium-rich variety, whose sorption properties are inferior in comparison with those of the sodium-rich variety. However, the capability of exchanging interlayer ions, a typical feature of the montmorillonite group minerals, can be used to manufacture bentonites with better sorption properties by treating them with Na-bearing modifiers (Komadel 2003; Klapyta and Zabinski 2008). The modified smectite, which Ca^{2+} and Mg^{2+} ions has been replaced by Na^{+} ions, strongly swells if exposed to water as its aggregates disintegrate into single unit layers.

The capability of adsorbing water into the interlayer spaces of smectites results from many factors, which can be divided into two main categories: of the physico-chemical nature and of the mechanical nature. The first of them are associated with the structure of clay minerals. Due to the presence of not compensated total layer charges of these minerals, their interlayer spaces may be entered by exchangeable cations. The molecules of water that hydrate the exchangeable cations expand the layers to various distances. In addition, the concentration of cations in the immediate vicinity of clay particles becomes much higher than in pure water. A difference of the cation concentrations contributes to building up the osmotic pressure. As a result, water molecules move from the areas of a lower cation concentration to those where the cation concentration is higher until of the concentrations are equilibrated. The mechanical factors of the clay swelling process include, first of all, its time, load history, an effect of sample size, volume changes, temperature, surface pressure (Kulesza-Wiewiora 1982).

The authors assessed an impact of a soda (sodium carbonate) addition to smectite-bearing clays on their swelling pressure. The test materials represented clays from south Poland, containing smectite in the range from 15 to 35% and characterized by marked fineness.

Methods of investigations

Swelling parameters were determined in clays sampled *in situ* in the Ligota Dolna (Poland) deposit or in depositories of clay commodities used by three brickyards: Harasiuki, Przeclaw and Wola Rzedzinska (Poland). General characteristics of the clay materials were obtained using the following methods: analyses of the mineral and chemical compositions, measurements of cation exchange capacity, determinations of smectite and calcium carbonate contents.

The natural clays were modified into their sodium varieties by treating them with sodium carbonate in the amount from 0.5 to 2.5% (in increments 0.5%) relative to dry mass of the clay, followed by chemical activation, 30-day homogenization, and final drying and grinding of the modified clay samples. This procedure produced so-called swelling smectite powders. Their swelling pressure was determined using the method proposed by Komine (2004), but changed in details by the present authors. The changes involved preparing for pressure tests samples in the form of pellets and then measuring the pressure of the swelling pellets exerted on the piezometric sensor of a materials test frame device.

The pellets for the swelling pressure tests were prepared from 15 g of the smectite powders, pressed monoaxially at a pressure of 20 MPa in a steel cylinder with the diameter 60 mm. Then the pellets with the apparent density 1.60-1.65 g/cm^3 were placed into a die (Fig. 1) and positioned under a piston of the test frame. Next, distilled water was continuously supplied into the pellet trough steel, perforated rollers to initiate its swelling. The pressure inserted by the swelling sample (i.e. the pellet) onto the piezometric sensor of the test frame was finally measured. The test frame software records the pressure as a the function of time, due to which the maximum pressure value can be determined. From this value the swelling pressure of the sample is calculated.

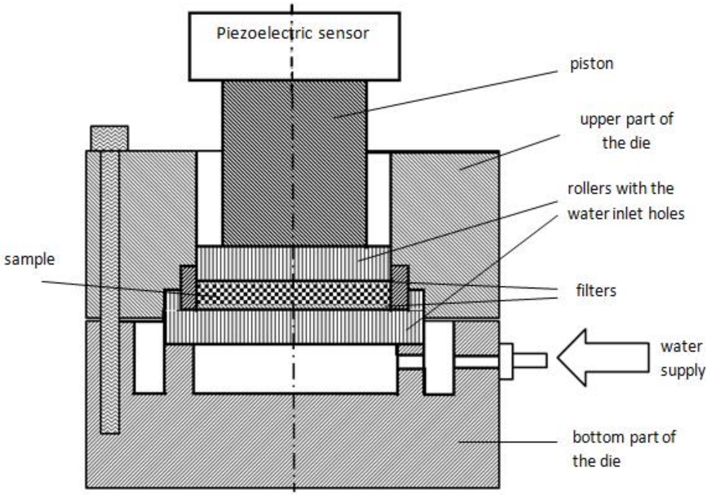

Fig. 1. Device for measuring the swelling pressure using a materials test frame

Characteristics of clay

The investigations were carried out on four samples representing the Miocene Krakowiec clays from the Carpathian Foredeep (Harasiuki, Przecław, Wola Rzedzinska) and the Triassic red clays (Ligota Dolna). The first of them are the essential raw materials of the building ceramics in south-east Poland, the other used in some brickyards located within the area of the Silesian-Cracow Monocline, i.e. between Kepno and Tarnowskie Gory (Wyszomirski and Galos 2005). These clay commodities, particularly the Krakowiec clays, are more and more often considered as starting materials in constructing the protection barriers that prevent various contaminants from penetration into soils (Branski 2007). The Krakowiec clays, occurring as grey, bluish-grey and dark grey varieties, in the engineering geology classification represent most often clays and silty clays. In places they contain more sandy inserts and admixtures of dispersed calcium carbonate (Pajak and Dobak 2008). The mineral and chemical characteristics of the clays considered are presented in Table 1.

Table 1. Some parameters of the clays under study

Sample	Deposit	Montmorillonite content [%] determined by sorption of:		Calcium carbonate content [%]	pH	CEC [mval/100g]
		methylene blue according to BN-77/4024-16	copper(II) triethylenetetramine according to Meier and Kahr (1999)			
640	Ligota Dolna	29	35	11.2	8.7	34
835	Harasiuki	17	23	9.2	7.9	20
839	Przeclaw	16	22	15.3	8.6	18
1187	Wola Rzedzinska	17	20	17.9	9.5	16

The highest content of montmorillonite, in the range of 35%, has been established in the Triassic clays from the Ligota Dolna deposit (Silesian-Cracow Monocline). The remaining three samples, representing the Krakowiec clays, contain about 20% smectite. These figures were obtained from the sorption of copper(II) triethylenetetramine. This method is more reliable than the method based on the sorption of methylene blue, as the latter gives correct determinations only in the case of samples, which smectite contents exceed 40% (Kosciowko and Wyrwicki 1996). All the samples reveal basic reaction, which results from the presence of fine-crystalline calcite and Ca,Mg-smectite. Isomorphic replacement of Al^{3+} ions, for instance by Mg^{2+} and/or Fe^{3+}, in the structure of smectites significantly affects their overall unit layer charge and, in turn, results in diversified CEC (cation exchange capacity) properties in clay samples with comparable smectite contents (Bobrowska and Szaniewska 2011).

Chemical analysis of major elements (Table 2) revealed an insignificant variability of the SiO_2 and Al_2O_3 contents in the Krakowiec clays, which is explained by small differences in their contents of main components, i.e., quartz and clay minerals. All the clay commodities studied are characterized by elevated amounts of magnesium and calcium, the elements being present as exchangeable cations in the structure of Ca,Mg-smectite, whereas in the case of calcium also in calcite. High contents of iron result from the presence of Fe^{3+} ions in the structure of montmorillonite, i.e. the most common smectite, and from the presence of hematite in the Triassic red clay from Ligota Dolna.

Table 2. The chemical composition of tested samples

Component	Content [%wt]			
	Ligota Dolna (640)*	Harasiuki (835)	Przeclaw (839)	Wola Rzedzinska (1187)
SiO_2	50.81	58.43	51.47	51.61
Al_2O_3	12.66	12.77	14.37	12.5
Fe_2O_3	5.39	5.22	5.58	4.86
TiO_2	0.76	0.69	0.71	0.64
MnO	0.15	0.09	0.14	0.14
MgO	2.82	2.41	2.97	3.34
CaO	9.53	5.22	7.05	7.96
Na_2O	0.35	1.01	0.77	1.00
K_2O	1.34	2.51	2.88	2.59
P_2O_5	0.11	0.17	0.13	0.13
LOI	16.35	11.9	14.01	13,99

* sample symbols are given in parenthesis

X-ray diffraction analyses (Fig. 2) showed that the clay from Ligota Dolna has the highest amounts of smectite as indicated by the intensity of the first, low-angle, distinctly broaden reflection with the d_{001} value ≈ 1.5 nm. Also in case of the remaining clays, the fields under their broad 001 reflections point to elevated amounts of smectite, whereas the diffusion of these reflections results from a typical, high fineness of smectite (Wyszomirski et al. 2005). The list of the X-ray identified clay minerals is supplemented by illite and kaolinite. The Miocene Krakowiec clays show also a considerable presence of chlorite, which is another clay mineral. The clay minerals listed above occur most probably as mixed-layer structures: chlorite/smectite, illite/smectite and chlorite/illite. Quartz and calcite are present in all the clays studied, and are accompanied in the Krakowiec clays by K-feldspars, plagioclases and dolomite.

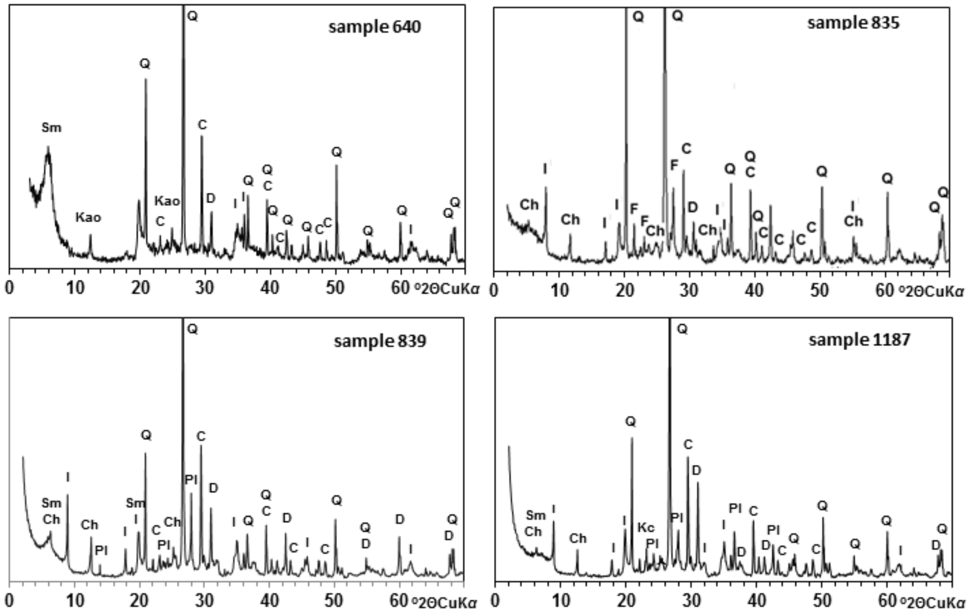

Fig. 2. X-ray patterns of studied clays from Ligota Dolna (sample 640), Harasiuki (835), Przeclaw (839) and Wola Rzedzinska (1187). Symbols: Sm – smectite, I – illite, Kao – kaolinite, Q – quartz, C – calcite, D – dolomite, Ch – chlorite, F – K-feldspar, Pl – plagioclase

Results of pressure experiments and discussion

The results of pressure experiments indicate that swelling pressure decreases with an increase of the sodium carbonate addition into the smectite-bearing clays. It is a result of different values of the Cartledge ionic potential of calcium and sodium ions, entering the interlayer spaces of smectites. X-ray analyses of the clay from Ligota Dolna (Fig. 3) indicate a gradual transition of Ca,Mg-smectite into Na-smectite in the clay activated. This process can be deduced from the shift the first, low-angle reflection of smectite from about 1.5 nm towards 1.25 nm which is accompanied by diffusion of this reflection and lowering its intensity. Such an X-ray pattern results from a considerable development of the specific surface of Na-smectite that took place due to disintegration of aggregates of this mineral into single unit layers after activation with soda.

Among not activated clays, the highest value of the swelling pressure shows the Triassic clay from Ligota Dolna (Fig. 4). This parameter reaches a value of above 600 kPa after water interaction lasting 1500 s. It is a result of the clay composition, i.e., a significant content of Ca,Mg-smectite that is prone to intercrystalline swelling. As the Krakowiec clays contain less smectite, their swelling pressure values are lower. In addition, a high value of the swelling pressure of the not activated clay from Wola Rzedzinska (sample 1187) may indicate a relatively low, negative resultant charge of its smectite unit layers. Laird (2006) showed that the intercrystalline swelling decreases when the layer charge increases.

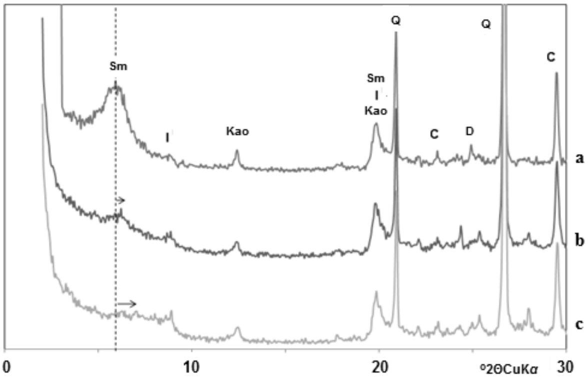

Fig. 3. X-ray patterns of the clay from Ligota Dolna (sample 640): a – air-dry state, b – after activation with 0.5% Na_2CO_3, c – after activation with 2.5% Na_2CO_3. Symbols: Sm – smectite, I – illite, Kao – kaolinite, Q – quartz, C – calcite, D – dolomite

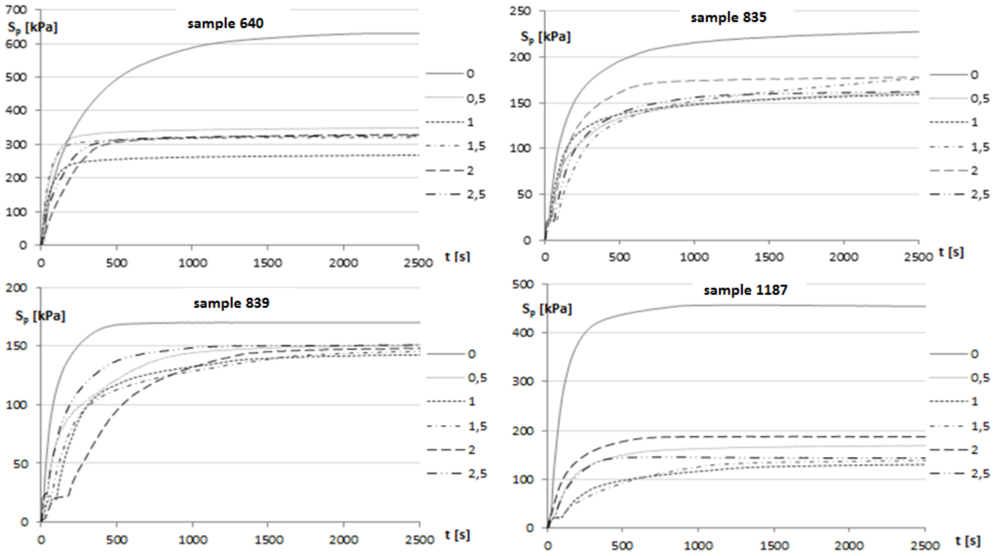

Fig. 4. Swelling pressure S_P of natural and activated smectite clays depending on the time of their water exposure. Samples: Ligota Dolna (640), Harasiuki (835), Przeclaw (839), Wola Rzedzinska (1187). Explanation: 0; 0.5; 1; 1.5; 2; 2.5 – the percentage content of Na_2CO_3 relative to the dry weight of samples

Sodium modification decreases the swelling pressure of the smectite-bearing clays, which is associated with the Cartledge ionic potential being almost twice as high for interlayer Ca^{2+} cations in comparison with Na^+ cations. So, the swelling pressure *Sp* of the samples activated with the highest content of soda (2,5%) varied in the range 150-300 kPa. In the case of Ca^{2+} cations, the interaction among smectite layers is much stronger due to this potential. Therefore, the smectite varieties containing calcium cations tend to form aggregates, which presence affects considerably intergranular swelling (Kulesza-Wiewiora 1982). The intercrystalline swelling results from the formation of an electric double layer between the interacting layers. The water entering the structure of smectites causes a considerable difference in concentration of the solutions separated by smectite layers. The interlayer solutions being in contact tend to equilibrate their concentrations, and the process results in a build-up of the osmotic pressure. This pressure takes higher values in the smectites, whose interlayer spaces are filled with cations with a high ion potential. An increase of the pressure is associated with strong interlayer reactions that hinder diffusion of migrating water molecules into consecutive interlayer spaces. In contrary, replacing Ca^{2+} by Na^{+} cations decreases the interaction forces within the electric double layer (Laird 2006). Making the structure of clay layers less compact results in easier diffusion of water molecules, which favors equilibrating cation concentrations and, finally, considerably lowers the swelling pressure of the modified smectite-bearing clay raw materials. Such lowering of the swelling pressure has been just established by the authors.

Summary

The authors have presented the method of measuring the swelling pressure of clay raw materials that extend their volume when being in contact with water. The investigations were carried on Polish clays with considerable smectite contents on the natural samples and after their chemical modification with Na_2CO_3. Laboratory tests have revealed lowering the swelling pressure of the clays as a result of such a modification procedure. The swelling pressure decreases despite the fact that the modification with soda enhances water adsorption among the smectite layers. It can be explained by diversified migration of water molecules in the interlayer spaces of smectite, which builds up the osmotic pressure. In the clays rich in smectite which contains in interlayer spaces cations with low ion potential (e.g. Na^{+}), equilibration of the concentrations of hydrating ions within the whole rock volume takes place under a much lower osmotic pressure than in case of the smectite varieties with bivalent cations (Ca^{2+} and Mg^{2+}). It was manifested in the tests by lower values of the swelling pressure of the clay samples modified with soda. This finding may be important when assessing the quality of bentonite fillers used in manufacturing of hybrid waterproofing materials.

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