An impact of modifications on Dylągówka clay on the rheological properties of its water suspensions

Introduction

Smectites are highly fine-grained aluminosilicate minerals, mainly characterized by properties resulting from their layer structure such as a high cation exchange capacity, swelling in the water environment, a highly developed surface area and good sorption (Murray 2007). In water, they disperse into single layer units or small aggregates of such units (this occurs rapidly in Na-smectites), due to which they form suspensions that are stable (i.e. not settling) for a long time (Permien and Lagaly 1995). This is caused by the three-dimensional structure of the main clay components of the suspension, and results in an interplay of
attractive and repulsive forces between the positively charged edges and negatively charged surfaces of the layer units \((\text{Ferguson and Kemblowski 1991; Niu et al. 2015})\). With regard to the arrangement of the layer units, their interactions are of the edge-to-surface, edge-to-edge and surface-to-surface types. When the contribution of the first two types increases, the system is subject to gelification and the formation of the “house-of-cards” structure, which in the macro scale is manifested by elevated by the viscosity of the smectite-water system. Such structures can be totally or in part damaged by mechanical stress (e.g. agitation), which lowers the viscosity \((\text{Kretser et al. 1998})\). The surface-to-surface attraction is a reason of aggregating and the formation of layered components with their parallel arrangement in a range not exceeding 2 nm \((\text{Adams and McCabe 2006})\). Thus, the number of elements in the gel structure is limited and the shear strength of the suspension is reduced.

The processes of damaging the stable suspension when subjected to mechanical forces and the processes of its reconstructing when such forces cease to act are reversible and called thixotropy. Thixotropy can be evaluated using several methods. The simplest are those based on the determining the thixotropy coefficient, which is the ratio of the viscosity of the suspension remaining for a specified time in a standstill to the viscosity of the suspension after its agitation, and are measured using rotational rheometers. A more precise method involving more sophisticated devices involves measuring the thixotropy value, i.e. determining the area of the hysteresis loop on the flow curves that show the dependency between the shear stress \(\tau\) and the shear rate \(\gamma\). The loop is defined as the field contained between the flow curves for increasing and decreasing shear rates \((\text{Dolz et al. 2000})\). The area of the hysteresis loop is associated with the physical energy (thixotropic energy \(E_{\text{tix}}\)) necessary to overcome the viscosity resistance to the extent of damaging the initial structure of the system (thixotropy) or restoring it (antithixotropy or negative thixotropy) \((\text{Perret et al. 1996})\). The specific properties of water suspensions of clay minerals primarily result from the content of particles with colloidal sizes, i.e. lower than 1 μm, and also from the adsorption of water molecules on the clay layer units, due to which their platelets can slide and move when affected by external forces. Of the clay minerals, the highest capacity to form thixotropic suspensions is shown by smectites because of: the finest size of their particles (thus they have the highest number of particles in a volume unit); their minor, negative layer charge (compensated fully or partly by exchangeable cations occupying interlayer spaces); specific properties of their outer surfaces \((\text{Tombácz et al. 1989})\). For these reasons, smectites are widely used – most often after modification(s) – as components of drilling muds, molding sands, in the refining industries, in civil engineering, as mineral fertilizers, pet litters, for land reclamation, waste dump sealing, etc. \((\text{Murray 2007; Eisenhour and Brown 2009})\).

Within the smectite group, the Ca-containing variety dominates in nature. Its rheological properties are considerably worse than those of Na-smectite, due to the stronger interlayer forces of the former. These properties can be improved by exchanging the Ca cations with Na cations. A typical industrial method involves sodium activation, i.e., introducing a certain amount (to 5%) of sodium carbonate \(\text{Na}_2\text{CO}_3\) into the smectite material in the wet state. The process results in the transformation of the Ca- into Na-smectites, the latter with a con-
siderably better developed surface because of very low, if any, aggregation of their layer units (Wyszomirski and Lewicka 2005; Panna et al. 2015). Another common modification method is acid activation, in which inorganic acids (HCl, H2SO4) of various concentrations are used (Komadel 2003). The process is conducted at elevated temperatures (to around 80°C) in variable time periods, depending on the required transformation degree of the starting Ca-smectite material. The final product is H-smectite with hydrogen cations in the interlayer sites, but if the acid treatment is more aggressive, the smectite finally changes into a protonated silica gel. Both materials are characterized by considerably larger specific surface areas than their Ca-bearing predecessor (Pentrák et al. 2012).

The current authors investigated the changes of the rheological properties revealed by water suspensions of the clay-siliceous raw material from Dylągówka (for its closer characteristics, see Panna et al. 2014) exerted by its chemical modifications by sodium and acid treatments (their impact was analyzed in part by Panna et al. 2016). In contrast to frequent papers that deal with improvements of such properties resulting from changing the pH of the solutions or spiking them with various salts or liquidizers, the authors made their evaluation one step earlier, i.e. they first modified the raw material and only then studied the impact of the modification-related changes on the properties of the clay-water suspensions. A better understanding of the processes involved was obtained by using three samples differing in their mineral composition. So far, only a few published papers relate to the mineral composition and concentration of the solid phase (Keren 1989; Heller and Keren 2001; Penner and Lagaly 2001; Malfoy et al. 2003), which makes the performed observations particularly useful in the technology of various kinds of materials.

1. Experimental

1.1. Sample materials

The investigations were conducted on the clay-siliceous rocks from Dylągówka (SE Poland, Subcarpathian Voivodeship). Three samples (A, B and C, going downward) represent the deposit profile. Their detailed characteristics are given by Panna et al. (Panna et al. 2014) and the most important rock parameters related to the context of this paper have been compiled below (Table 1).

The starting samples (A, B and C) were dried and pulverized in a laboratory ball mill. Three of these (batch I) were sodium modified by adding 5% (in relation to the dry mass) of Na2CO3 into each, stirring the wet samples with a mechanical mixer, homogenizing for thirty days, renewed drying (at 105°C) and renewed milling. The sodium-activated derivatives are labeled as A1, B1 and C1. The other batch was also composed of three samples, whose 100 g milled samples were activated with a 10% solution of H2SO4 and homogenized for thirty minutes with a mechanical mixer. After retaining them for twenty-four hours in
a climatic chamber at 80°C and a relative humidity $H_r$ of 90%, they were dried and milled again. These derivatives are designated as A2, B2 and C2.

### 1.2. Methods

The rheological investigations were conducted with a Brookfield DV–III+ rheometer fitted with a thermostatic control TC 500 and working in the system of coaxial cylinders no. 29. The rheometer was used to measure the dependence between the shear stress or the apparent viscosity of a liquid and the shear rate; the respective functions were recorded with the Rheocalc for Windows software. The investigations on the thixotropic properties were conducted in the range of shear rates from 2 to 50 s$^{-1}$, within which, the changes of the clay-water system were recorded at every 4 s$^{-1}$ for a time of 30 s, whereas the determinations of the apparent viscosity were made at the constant shear rate 10 s$^{-1}$ for a period of 600 s.

The test suspensions were prepared by adding variable amounts of distilled water into the solid samples and stirring the mixture to attain the system viscosities in the range of 100–15,000 mPas. The content of solids in the suspensions ranged between 30 and 55%. The differences in the amount of water added were caused by the content and the type of smectite in individual samples as these two parameters determine the border at which the damp mass with the consistency of a paste alters into a suspension. For each sample, four tests were carried out in which the contribution of solids was changed stepwise by 2.5%. Next, the vessel with the suspension was left for 48 h to stabilize the clay-water system.

The structural changes of the mineral phases resulting from sample modifications also have a significant impact on the rheological parameters of the suspensions and have been interpreted on the basis of infrared spectroscopy (IR). The IR analyses were carried out

### Table 1. Selected parameters of the clay-siliceous raw material sampled in the upper (A), middle (B) and lower (C) parts of the Dylągówka deposit

<table>
<thead>
<tr>
<th>Sample symbol</th>
<th>Smectite content (%)*</th>
<th>Other mineral phases**</th>
<th>Content of particles (%)***</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>opal, quartz, illite, kaolinite</td>
<td>&lt;1 μm</td>
</tr>
<tr>
<td>A</td>
<td>30</td>
<td>opal, quartz, illite, kaolinite, clinoptilolite, hematite</td>
<td>52.8</td>
</tr>
<tr>
<td>B</td>
<td>49</td>
<td>opal, quartz, illite</td>
<td>71.6</td>
</tr>
<tr>
<td>C</td>
<td>33</td>
<td>opal, quartz, calcite, kaolinite</td>
<td>42.8</td>
</tr>
</tbody>
</table>

* Determined using sorption of TETA Cu(II) (Perret et al. 1996).
** Determined using X-ray diffractometry.
*** Determined using particle size analysis with a X-ray SediGraph 5100 apparatus.
with a Fourier spectrometer Vertex 70v (Bruker Optics, Germany) in the wave range of 4000–400 cm⁻¹ at a resolution of 2 cm⁻¹ and a scan number of 126. Samples were prepared in the form of tablets pressed with KBr.

2. Results and discussion

2.1. Rheology

The results indicate that the values of apparent viscosity decreased proportionally to the increasing water to solid ratios of the suspensions (Figure 1). The dependence is described with the function which can be used to determine the viscosity of the suspension with a randomly selected content of the solid phase (Figure 2). This activity seems to be correct because of the high correlation coefficient R² of the fitted curves (about 0.98). The reverse operation can also be made, i.e., establishing the amount of the solid phase added to the suspension in order to attain its required viscosity under the conditions of a constant shear rate of 10 s⁻¹ and the time required to stabilize this viscosity (such a time used in the experiments was 600 s). As a result of this, the properties of water suspensions of clay raw materials can be compared to one another more accurately, while the impact of their phase composition and of their degree of smectite modification on the performance of these solutions in the course of rheological measurements can be determined.

The suspensions of the sodium-modified Dylągówka raw materials (particularly those less diluted) attained the stabilization of their structure after a much longer time than the
suspensions prepared from both the non-modified and the acid-treated samples (Figure 1). This results from the insufficient homogeneity of the clay-water system in which single layer units of smectite coordinate variable amounts of water layers. An initial structure of the mixture after its homogenization for forty-eight hours is disturbed or damaged by the rotation of the rheometer spindle. High viscosity of the clay-water system hampers the movement of solid particles, which only attain their arrangement concordant with the movement direction of the spindle after a long time and, as a result, form a new suspension structure and homogenize the system. The natural raw materials and their acid-modified derivatives are usually characterized by shorter times of stabilization as the water of the suspensions has a lower capability of penetrating the smectite layers (lower aggregation). Therefore, they have a limited capability of forming highly viscous suspensions at a relatively minor dilution of the system (Liang et al. 2010).

As the next stage of the experiments, for each of the suspensions, its concentration $c_{1000}$ required to attain the viscosity 1000 mPas at the shear rate 10 s$^{-1}$ was calculated from the values of the apparent viscosity established as described above. The parameter $c_{1000}$ was introduced in the case of comparing the possibilities of various types of raw materials to achieve higher viscosity with a low proportion of solids. This is not a determinant of a desired viscosity, e.g. for suspending drilling fluids. The calculated contents of the solids for the selected viscosity (Table 2) mean that a lowering of the dilution increased the apparent viscosity values, while an increase of the dilution decreased the apparent viscosity. The first factor controlling the amount of solids at which the suspension viscosity attains 1000 mPas is usually a smectite content of the rock. Therefore, sample A with its lowest smectite content (30%, Table 1) has the highest $c_{1000}$ value. However, the low $c_{1000}$ value of 38.3% for sample C results from its opal content (the highest of the three samples), as this mineral phase increases the sliding of clay mineral platelets in suspension (Bailey et al. 2014). For this reason, sample C has a lower content of the $c_{1000}$ solids even if related to sample B whose smectite content (49%) is the highest of the three samples tested.
Sodium activation (samples A1, B1 and C1) considerably increases the viscosity of the clay-water systems and thus lowers the $c_{1000}$ parameter. The reason for this is a dispersion of the smectite aggregates into single layer units, due to which, the mineral optimally fills the whole space within the suspension (Malfoy et al. 2003). The units are loosely distributed throughout the measuring vessel and form the structure of the “house-of-cards” type. In this case, smectite units most often build the surface-to-edge and the edge-to-edge layer aggregates.

Compared with the viscosities of natural samples, the acid activation increased the $c_{1000}$ parameter in the suspensions prepared of samples B2 and C2, whereas it decreased it in the suspension of sample A2. The negative impact of aggressive sulphuric acid on the rheological properties (more solids is required to attain the $c_{1000}$) is a result of leaching Mg and Al cations from the smectite octahedral sheet and lowering the negative smectite layer unit charge. In accordance with this, a number of exchangeable cations that compensate the negative charge decreases and the smectite grades into the protonated silica gel whose rheological properties are not so attractive as those of non-modified smectites (Pentrák et al. 2012). This is the case with samples B2 and C2: the amounts of them required to attain $c_{1000}$ had to be higher. An improvement in the rheological properties of the A2-based suspension was caused by the presence in the natural clay material of clinoptilolite (a zeolite), which was probably activated with acid as the first mineral phase (Yorukoglu 2012). The activation in question lowered the volume of the available acid, whose reaction with smectite must have been directed to the protonation of the interlayer surfaces and lowered the smectite

<table>
<thead>
<tr>
<th>Sample</th>
<th>Estimated contribution of the solid phase in the clay-water system sufficient to attain an apparent suspension viscosity of 1000 mPas ($c_{1000}$) (%)</th>
<th>Thixotropic energy $E_{th}$ determined for the $c_{1000}$ suspension (J/m$^3$)</th>
<th>pH [a.u.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>53.4</td>
<td>987</td>
<td>8.7</td>
</tr>
<tr>
<td>A1</td>
<td>45.8</td>
<td>560</td>
<td>9.5</td>
</tr>
<tr>
<td>A2</td>
<td>47.6</td>
<td>420</td>
<td>1.9</td>
</tr>
<tr>
<td>B</td>
<td>39.0</td>
<td>1,651</td>
<td>8.7</td>
</tr>
<tr>
<td>B1</td>
<td>34.3</td>
<td>1,768</td>
<td>9.4</td>
</tr>
<tr>
<td>B2</td>
<td>52.1</td>
<td>–130</td>
<td>2.0</td>
</tr>
<tr>
<td>C</td>
<td>38.3</td>
<td>433</td>
<td>8.3</td>
</tr>
<tr>
<td>C1</td>
<td>34.6</td>
<td>349</td>
<td>9.6</td>
</tr>
<tr>
<td>C2</td>
<td>50.2</td>
<td>154</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Sodium activation (samples A1, B1 and C1) considerably increases the viscosity of the clay-water systems and thus lowers the $c_{1000}$ parameter. The reason for this is a dispersion of the smectite aggregates into single layer units, due to which, the mineral optimally fills the whole space within the suspension (Malfoy et al. 2003). The units are loosely distributed throughout the measuring vessel and form the structure of the “house-of-cards” type. In this case, smectite units most often build the surface-to-edge and the edge-to-edge layer aggregates.
aggregation capability. As the H-smectites may accept up to four monomolecular water layers among their unit layers, the viscosity of 1000 mPas set in the experiment was attained with the addition of less solids because part of the water had been bound within the mineral structure of smectite.

The chemical modifications of the Dylągówka clays also affect the magnitude and the shape of the hysteresis loop in the flow curves, which are a measure of the thixotropic energy $E_{tix}$. The determination of this energy was based on matching each of the curves of both increasing and decreasing shear rates $\gamma$ with the trend line which has the best fit of its correlation coefficient $R^2$, and then calculating the ratio of definite integrals in the range 2–50 s$^{-1}$ to establish the field $S$ between these curves: the field corresponds to the $E_{tix}$ value (Dolz et al. 2000; Stempkowska et al. 2007). The procedure of the energy calculation and the corresponding hysteresis loop are shown as an example for the suspensions prepared from the sodium-activated sample A1 (Figure 3). The suspensions with lower contents of the solids (40.0 and 42.5%) are characterized by the thixotropic flow within the whole measuring range. The denser suspension (45% solids) revealed a negative thixotropy for the shear rates from 2 to 14 s$^{-1}$, while at higher rates, its flow becomes thixotropic. The densest suspension

![Flow curves of the suspensions prepared from sodium-activated sample A1 with various amounts of the solid phase added. The directions of the increasing shear rates are shown with arrows. Exemplary equations of the trend line are given for the densest suspension.](image)

**Fig. 3.** Flow curves of the suspensions prepared from sodium-activated sample A1 with various amounts of the solid phase added. The directions of the increasing shear rates are shown with arrows. Exemplary equations of the trend line are given for the densest suspension.
(47.5% solids) showed negative thixotropy across the whole range. The same antithixotropy phenomenon was shown by the densest suspensions of all the samples, both the natural samples and those that were sodium- or acid-modified. It means that the structure of their suspensions was restored during shearing but then broke down when they were left motionless. Referring to the experiments conducted, it seems that in the dense systems either their water content was too low and the solids could not disperse evenly over the whole volume of the suspension, or the time of homogenizing the suspensions (48 h) was too short.

Based on the determined hypothetical values of the thixotropic energy for the suspensions with the apparent viscosity of 1000 mPas (the procedure was the same as that for the determinations of the $c_{1000}$ parameter), it has been found that these values of the sodium-activated suspensions are comparable to those of the suspensions prepared from non-modified clays but at considerably lower amounts of the solid phase. This is explained by a breakdown of larger smectite aggregates after introducing sodium cations onto the exchangeable positions and a more homogenous filling of the space within the whole suspension volume (Malfoy et al. 2003). Another observation is that at the viscosity set in the experiment is that the hysteresis field was considerably larger (in the range 1500 J/m$^3$) for samples B and B1, resulting primarily from their higher smectite contents. Acid activation of the Dylągówka clays results in a drastic lowering of the hysteresis loop fields in the point $c_{1000}$, which leads to a negative thixotropy with an energy of $-130$ J/m$^3$ for sample B2 (Table 2). It is an effect of changes in the structure of smectite exerted by the action of strong acid that lowers the overall charge of the smectite layer unit (Laird 2006).

The pH of the suspensions (Table 2) corresponds with the mineral composition of the clay raw materials and the manner of their processing. The clays rich in Ca, Mg-smectite are alkaline (pH in the range of 8.3 to 8.7), and their supersaturation with sodium carbonate increases the pH to approximately 9.5. The acid activation strongly reduces this parameter to a value of 2 for non-calcareous samples A2 and B2 and to 2.5 for sample C2, which is rich in calcite. A higher pH of the sample C2 results from a lesser amount of acid available, because part of it was consumed reacting with calcite and forming sulphate phases (e.g. gypsum). Additional determinations of the zeta potential confirm the stability of all the suspensions across a wider pH range and a partial destruction of the smectite structure causing a reduction of the layer charge. As a result of this, the investigations were focused on the structural changes of the smectite as they affect the rheological characteristics of the suspensions. The full results of zeta potential measurements have not been presented as they exceed the scope of this study.

### 2.2. Infrared spectroscopy

The infrared analyses (Figure 4) revealed that the smectite structural changes took place mainly in the acid-modified sample (B2). The 1031 cm$^{-1}$ major smectite absorption band was split into two components with maxima at 1041 and 1093 cm$^{-1}$, while the 834 cm$^{-1}$
band disappeared. The split means that at least part of the smectite was transformed into the silica gel with a three-dimensional arrangement of its ions, which results from the presence of Si–O vibrations. The same is confirmed by a small intensity decrease of the 519 cm\(^{-1}\) band, associated partly with the bending vibrations of the Al–O–Si domains. A small shift of the 1031 cm\(^{-1}\) band towards higher wave numbers is a result of minor rearrangements in the tetrahedral sheet of the smectite (Si and O are there in the tetrahedral coordination). The said disappearance of the 834 cm\(^{-1}\) band is attributed to the processes of leaching Mg\(^{2+}\) from the octahedral sheet of smectites, as this band marks the Al–Mg–OH vibrations (Madejová et al. 1998).

Additional pieces of information have been provided by the bands of water associated with clay minerals and opal, and also with amorphous silica that was formed by the treatment of the sample with the strong acid. Elevated absorbance with the maxima at 1638 and 1701 cm\(^{-1}\) is caused by bending vibrations within the molecules of the water adsorbed and the water coordinated by interlayer cations, respectively (Frost et al. 2000). The 1701 cm\(^{-1}\) band disappears in the case of the sodium-activated sample (B1), in which the sodium cation coordinates only a single layer of water molecules in the air-dry state of the analyzed material. The sample after the acid modification has its water band at 1638 cm\(^{-1}\) diffused towards

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**Fig. 4.** IR spectra of clay rock from Dylągówka, representing the middle horizons of the deposit (sample B) and of the products of their modification depending on the temperature of thermal processing:

B1 – sample activated with 5% (by weight) of Na\(_2\)CO\(_3\); B2 – sample activated with 10% solution of H\(_2\)SO\(_4\)

**Rys. 4.** Widma iR skał ilastych z Dylągówki, reprezentujących środkowe poziomy złoża (próbka B) oraz produktów ich modyfikacji w zależności od temperatury obróbki termicznej:

B1 – próbka aktywowana 5% (wag.) Na\(_2\)CO\(_3\); B2 – próbka aktywowana 10% roztworem H\(_2\)SO\(_4\)
lower wave numbers due to a substantial amount of water, both this adsorbed and this proton-coordinated (even up to four water layers may be present) in the smectite structure. An elevated of the IR curve in the range 3200–3600 cm\(^{-1}\) confirms the relations between the water adsorbed (maximum at 3434 cm\(^{-1}\)) and coordinated (around 3200 cm\(^{-1}\)). This range is the widest in the acid-activated sample (B2), which can be explained by the presence of oxyhydroxides of aluminum, magnesium and silicon formed during the activation. All the samples show similar intensities of their 3631 cm\(^{-1}\) IR band, which is attributed to the stretching M–OH vibrations (Kloprogge et al. 2000).

The structural modifications have a substantial effect on the relationships between smectites and water. Despite coordinating within only one water layer by its sodium cations, the Na-smectite is capable of accepting substantial amounts of water among its layers due to lower interlayer interactions. The treatment with an aggressive acid transforms smectite into a silica gel and simultaneously lowers the layer charge. This is the reason for the rather inferior rheological properties of the acid-treated Dylągówka clays.

It should be noted that additional mineral phases present in the clays from Dylągówka can also affect the rheological properties of these raw materials. The presence of clay minerals other than smectite (i.e. illite and kaolinite) and especially such non-clay mineral phases as opal and zeolite may be an important factor. Their impact should also be considered but only in the future as due to its complexity, it is beyond the range of the current work.

**Conclusions**

The investigations have proved that an elevated content of opal in clay raw materials favors the formation of suspensions of high viscosity. Its presence results in better sliding of clay platelets within their layer aggregates and leads to their better dispersion. It corresponds with the observations of Bailey et al. (Bailey et al. 2014), who used colloidal silica as an additive to improve the rheological properties of clay raw materials. We have shown that such properties can also be controlled by the sodium activation of smectites as this process considerably increases the viscosity of the clay-water system and allows obtaining the suspension with a predicted viscosity at a much lower addition of the solid phase.

Activation that is too aggressive with strong acids leads to a partial damaging of the smectite structure and deterioration of the rheological properties of its water suspensions. In addition, the process lowers the zeta potential due to reducing the layer charge of smectites (Laird 2006). Acid activation also lowers the thixotropic energy, which has been confirmed in this paper. The process of sulphuric (VI) acid modification of smectite may be blocked if the smectite raw material also contains a significant amount of a zeolite or calcite due to sorption and chemical reaction with acid.

The tests carried out with various concentrations of suspended Dylągówka clays have established that a high proportion of the solid phase promotes negative thixotropy. This also proves that there is a sound basis of for the application of the proposed methodology
of studying suspensions of clay raw materials and using the parameter $c_{1000}$ for an accurate comparison of rheological properties of clays, for example, in drilling techniques.

REFERENCES


AN IMPACT OF MODIFICATIONS AN DYLĄGÓWKA CLAY ON THE RHEOLOGICAL PROPERTIES OF ITS WATER SUSPENSIONS

Keywords

smectite-water suspensions, rheological properties, clay-siliceous rocks, modification of smectites

Abstract

This paper deals with the effects of modifications to clay-siliceous raw material from Dylągówka (Dynów foothills, SE Poland), which alter the rheological properties of its water suspensions. The investigations were carried out on three samples collected from various depths of the deposit as they considerably differ in their contents of smectite and other minerals. The samples were either modified with soda or activated with sulphuric (VI) acid and used to prepare their water suspensions with various contents of solids. The suspensions were subject to determinations of viscosity and flow curves.
Dependencies of three variables of the suspensions (rheological properties, mineral composition of the solid phase, and the modifications introduced) were assessed on the basis of: the contents of the solid phase in the suspensions required to obtain a viscosity of 1000 mPas; hypothetical, calculated thixotropic energy. These show that the amount of solids in the water suspension required to obtain the required viscosity is considerably lower in samples with higher contents of smectite and in those activated with sodium. In turn, the acid activation that partially alters smectite towards a protonated silica gel decreases the viscosity and thixotropy of the suspensions, which was confirmed in the studies of mid-infrared spectroscopy. The conducted studies provide important information needed in designing the mineral composition of drilling fluids and others applications.

**Wpływ modyfikacji surowca ilasto-krzemionkowego z Dylągówki na właściwości reologiczne jego wodnych zawiesin**

**Słowa kluczowe**

suspensje wodno-smektytowe, właściwości reologiczne, skały ilasto-krzemionkowe, modyfikacje smektytu

**Streszczenie**

W pracy przedstawiono wpływ modyfikacji surowca ilasto-krzemionkowego z Dylągówki (Pogórze Dynowskie, południowo-wschodnia Polska) na właściwości reologiczne jego wodnych zawiesin. Do badań przeznaczono trzy jego próbki pobrane z różnych głębokości złoża różniące się w znacznym stopniu udziałem smektytu i innych minerałów. Próbki te zostały poddane modyfikacji poprzez wprowadzenie sody (5%) i aktywacji kwasem siarkowym (VI). Sporządzono z nich wodne zawiesiny o różnym stężeniu fazy stałej i przeprowadzono na nich badania reologiczne polegające na określeniu krzywych lepkości i krzywych płynięcia. W celu wyznaczenia charakteru zmian we właściwościach reologicznych zawiesin wynikających ze zmiennego składu mineralnego próbek i z wprowadzonych modyfikacji oszacowano zawartość fazy stałej w zawiesinach potrzebnej do uzyskania zadanej lepkości 1000 mPas oraz ich hipotetyczną energię tiksotropową. Przedstawione w pracy rezultaty wskażują, że stężenie fazy stałej w wodzie, wymagane do uzyskania odpowiedniej lepkości, jest znacznie mniejsze dla próbek o wyższym udziale smektytu oraz dla próbek aktywowanych sodowo. Z kolei aktywacja kwasowa wywołująca w surowcu częściowe przejście smektytu w protonowany żel krzemionkowy powoduje zmniejszenie lepkości i tiksotropii zawiesin, co zostało udowodnione na podstawie badań spektroskopowych w środkowej podczerwieni. Przeprowadzone badania mogą być zatem pomocne w projektowaniu składu mineralnego płuczek wiertniczych i innych zastosowań wodnych zawiesin smektytowych.