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## **CHARACTERIZATION, PROPERTIES AND MICROSTRUCTURE OF SPENT DRILLING MUD FROM THE POINT OF VIEW OF ENVIRONMENTAL PROTECTION\*\*\***

### **1. INTRODUCTION AND THE AIM OF THE INVESTIGATIONS**

Dynamic advances in the drilling technology applied to prospecting for oil and gas deposits are associated with growing volumes of drilling waste. The waste materials of this origin can be divided into two essential groups:

- 1) rock cuttings representing a fragmented mineral material derived from the rocks drilled through,
- 2) spent drilling muds of various types.

Utilization of the rock cuttings is not, generally, a serious environmental problem. The environmental problem appears in the case of spent water-based muds. They represent highly diversified, multicomponent and multiphase colloidal systems, consisting sometimes of several tens of chemical compounds and substances, both mineral and organic, the latter being various polymers and macromolecules that are derivatives of both natural biopolymers and synthetic organic substances [8, 11].

During drilling operations, the drilling mud is degraded by intensive mechanical processes and elevated temperatures as well as by a selective sorption phenomena taking place on surfaces of mineral components of the rocks being drilled through. Therefore, any research aimed at developing the technology of treating various drilling waste materials, their recovery and utilization must be preceded by combined investigations of the composition and properties of drilling muds. These very issues have been considered by the authors who concentrated particularly on studying the chemical composition, the mineral and phase content, and a specific microstructure of polymeric-mineral systems, in which interactions of substances of mineral and organic groups decide on the properties of spent drilling muds.

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## 2. STUDY MATERIAL AND THE METHODOLOGY OF ITS INVESTIGATIONS

Investigations were carried out on five samples of spent, water-based mud, representing various kinds of polymer-mineral systems and collected from wells located in Poland (Tab. 1).

**Table 1**  
List of analyzed samples spend drilling mud

| No. | Type of spent drilling mud               |
|-----|--|
| 1   | bentonitic                               |
| 2   | chloride – polymeric                     |
| 3   | potassium – polymeric                    |
| 4   | polymeric                                |
| 5   | chloride – polymeric, fourfold inhibited |
| 6   | bentonitic                               |
| 7   | potassium                                |

The methods of instrumental analysis applied are listed below.

### Structural and phase analyses

1. X-ray diffractometry (XRD) – a Philips APD X’Pert PW 3020 diffractometer, working on-line with the XRAYAN software and the ICDD (International Centre for Diffraction Data) database.
2. Fourier transformed infrared spectroscopy (FTIR) – a Bio-Rad 165 spectrometer.
3. Scanning electron microscopy (SEM) combined with spot chemical determination in microareas (EDS) – an FEI Quanta 200 FEG apparatus.

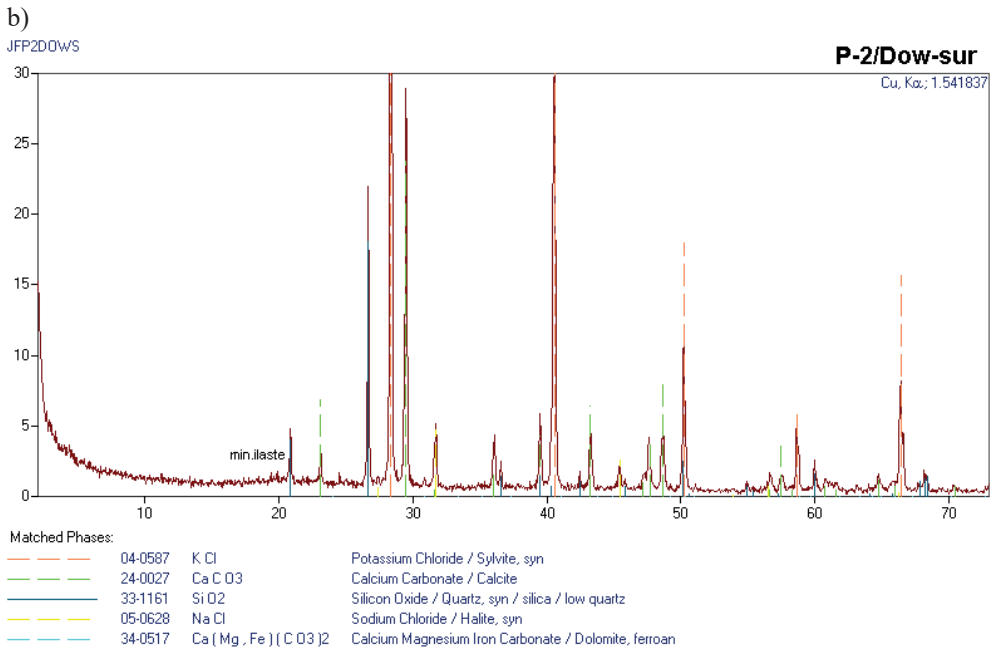
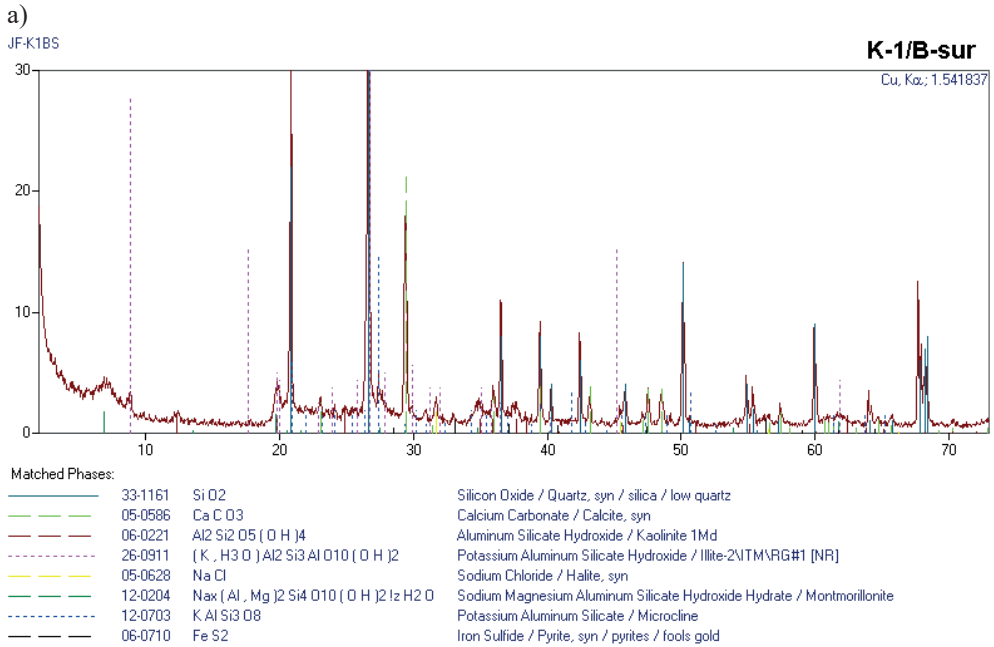
### Chemical analysis

Atomic absorption spectroscopy (AAS); induced coupled plasma spectroscopy (ICP) – using among others a Merc NOVA 60 and a Thermo Scientific ICE 3500 spectrometers.

## 3. RESULTS

### X-ray diffractometry

XRD analyses were carried out on the solid samples obtained after the evaporation of the water from spent water-based muds applying the powder the DSH method in the qualitative determinations. The X-ray diffraction analyses allowed for an unambiguous qualitative identification of all crystalline mineral substances, both insoluble and soluble in water. Selected X-Ray diffraction patterns of sample no. 1 and 4 are shown in Figure 1.



**Fig. 1.** X-Ray diffraction patterns of: a) sample no. 1 – bentonitic spent drilling mud; b) sample no. 4 – polymeric spent drilling mud

The list of phases of all analyzed samples spent drilling mud are shown below:

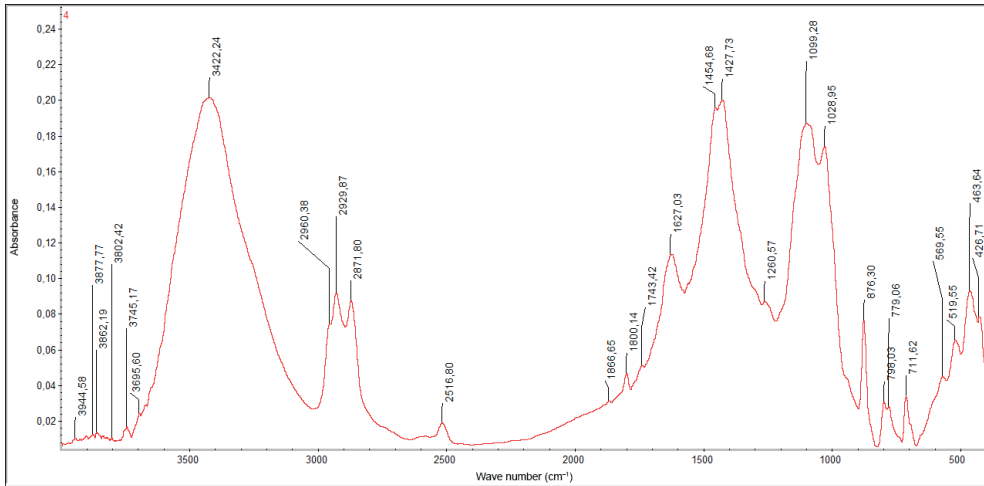
- 1) quartz, calcite, halite, K-feldspar, pyrite, illite, kaolinite, Na-smectite, amorphous phase,
- 2) halite, sylvine, calcite, quartz, illite, smectite, chlorite, kaolinite, dolomite, amorphous phase,
- 3) sylvine, halite, quartz, calcite, chlorite, kaolinite, illite, dolomite, a mineral of the illite-smectite type with the mix-layered structure, amorphous phase,
- 4) sylvine, calcite, quartz, halite, dolomite, clay minerals with a highly disorder structure as the reflection 020 is only visible, amorphous phase,
- 5) halite, quartz, calcite, chlorite, kaolinite, illite, barite, dolomite, amorphous phase,
- 6) calcite, quartz, dolomite, illite, chlorite, kaolinite, Na-smectite, amorphous phase,
- 7) barite, sylvine, halite, calcite, quartz, dolomite, kaolinite.

Comparing X-ray patterns of samples no 1 ( $C_{\text{org}} = 1.08\%$ ) and sample no. 4 ( $C_{\text{org}} = 11.56\%$ ) (Fig. 1), respectively, it can be seen that the basal 001 montmorillonite reflection is clearly marked, although diffused, in the case of the first sample while the same 001 reflection in the case of the other sample is absent, while a very weak 002 reflection is only observed. It can be thus inferred that shearing forces acting in the drilling processes break the smectite crystallites into single clay platelets or small domains composed probably by several platelets, that can adsorb the polymer chains both on the outer surfaces of the clay nanoparticles and on the inner surfaces (smectite interlayers). Specific clay-polymer nanostructures with the exfoliated or delaminated structures are formed as a consequence of these processes. The similar phenomena were observed in the course of synthesizing clay-polymer resin nanocomposites [10].

### Fourier transformed infrared spectroscopy

Fourier transformed infrared spectroscopy (FTIR) is an essential research tool particularly when a sample is composed of a mixture of crystalline, weakly crystalline and amorphous substances. It is just a case of the polymer-mineral systems represented by spent drilling muds: they contain crystalline mineral components, non crystalline organic polymers, and also products of mutual interactions of the two. Figure 2 shows FTIR spectrum of sample no. 4 (polymeric spent drilling mud).

Taking as an example the spent drilling mud no. 4 (Fig. 2), the group analysis indicates that the sample is composed of considerable amounts of mineral phases: i.e., calcite (bands: 711, 876 and 1430  $\text{cm}^{-1}$ ), quartz (bands 779, 798 and 1099  $\text{cm}^{-1}$ ) and a clay mineral with the smectite structure (426, 463, 519 and 1028  $\text{cm}^{-1}$ ). They are accompanied by a significant amount of an organic polymer that strongly absorbs in the range: 3000–3600  $\text{cm}^{-1}$  (stretching  $-\text{NH}_2$  amide groups), 2800–3000  $\text{cm}^{-1}$  (strong multiples band from stretching vibrations of  $-\text{CH}_2$  and  $-\text{CH}_3$  groups), 1743  $\text{cm}^{-1}$  (a weak C = O) oscillations the carboxyl groups), 1672  $\text{cm}^{-1}$  (stretching of  $\text{COO}^-$  anions), 1427  $\text{cm}^{-1}$  (bendings vibrations of amide groups) and 1454  $\text{cm}^{-1}$  (bendings of  $-\text{CH}_2$  groups). This characteristic of the polymer substance points to the presence of a hydrolyzed polyacrylamide. Additionally, the analysis shows a considerable content of smectite, which has not been identified by the X-ray diffraction (comp. the X-ray pattern in Fig. 1).

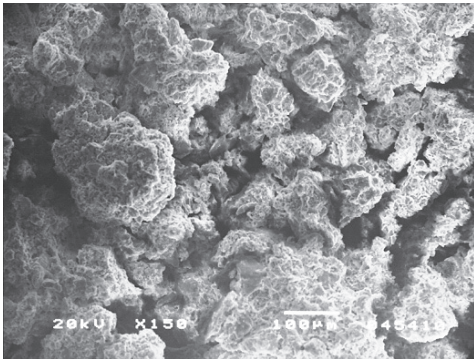


**Fig. 2.** FTIR spectrum of sample no. 4

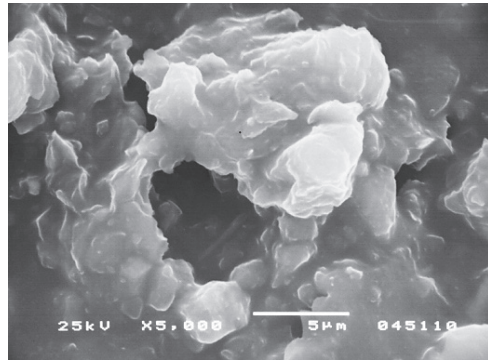
### SEM analysis

Scanning electron microscopy (SEM) was applied to solid samples of drilling muds dried at 50°C. The SEM electron micrographs of the selected sample Figure 3 reveal the features of a microstructure characteristic of the polymineral aggregates and agglomerates, which have been formed due to the interaction between the mineral and organic polymer substances.

a)



b)



**Fig. 3.** Electron micrographs SEM of sample no. 6: a) microstructure of agglomerates (grains) built with small aggregates; b) porous microstructure of montmorillonite aggregates

High amounts of organic polymers in spent drilling muds significantly affect the size of the aggregates being formed. Scanning images of the microstructure of the no 6 sample (whose  $C_{\text{org}} = 1.64\%$ ) visualize (Fig. 3a, b) the fabric of large agglomerates (grains) whose diameters range usually between 100 and 400  $\mu\text{m}$  (Fig. 3a). The agglomerates are built with much smaller aggregates (Fig. 3b), frequently showing the characteristic atoll-like arrangements composed of clay particles crosslinked with polymeric molecules.

## Chemical analyses

The results of chemical analyses point to considerable differences in chemical properties among the spent drilling muds considered. They are caused by several reasons: the variability of mineral composition of drilling muds, confirmed by the X-ray and infrared investigations; the variability of rocks within the profile being drilled through; the variability of the initial composition of the drilling muds; an amount of weighting agents (barite and others) in the drilling mud etc. The samples have been characterized by their chemical compositions, assayed in the solid matter separated from the spent drilling muds by the evaporation of water at 100°C (Tab. 2).

**Table 2**

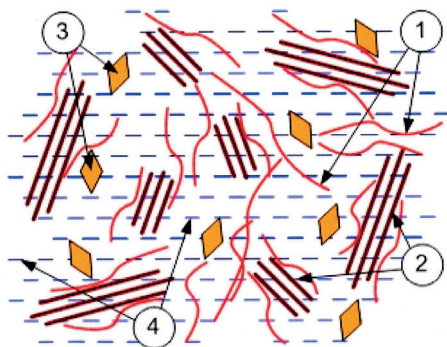
Chemical composition of solid phase samples obtained after evaporation of H<sub>2</sub>O from water-based spent drilling muds – main components

| Components<br>[wt.%]           | Samples |       |       |       |       |       |       |
|--------------------------------|---------|-------|-------|-------|-------|-------|-------|
|                                | 1       | 2     | 3     | 4     | 5     | 6     | 7     |
| SiO <sub>2</sub>               | 46.10   | 34.40 | 40.57 | 25.12 | 36.60 | 25.40 | 23.30 |
| Al <sub>2</sub> O <sub>3</sub> | 17.20   | 18.25 | 15.88 | 13.11 | 13.40 | 6.32  | 8.10  |
| Na <sub>2</sub> O              | 1.65    | 3.50  | 0.66  | 1.01  | 1.52  | 0.85  | 0.72  |
| K <sub>2</sub> O               | 0.50    | 4.62  | 4.76  | 6.83  | 1.80  | 0.40  | 1.43  |
| MgO                            | 1.47    | 4.59  | 5.36  | 5.96  | 6.08  | 2.05  | 1.30  |
| CaO                            | 12.45   | 7.27  | 4.60  | 13.38 | 7.40  | 27.90 | 7.50  |
| Fe <sub>2</sub> O <sub>3</sub> | 5.08    | 2.84  | 7.72  | 1.49  | 4.15  | 3.69  | 1.85  |
| BaO                            | 0.37    | 0.66  | 0.81  | 0.09  | 3.06  | 0.40  | 19.50 |
| SO <sub>3</sub>                | 2.45    | 1.20  | 1.35  | 1.12  | 3.20  | 1.60  | 16.24 |
| MnO                            | 0.02    | 0.08  | 0.06  | 0.03  | 0.08  | 0.02  | 0.04  |
| CO <sub>2</sub><br>(carbonate) | 5.69    | 2.73  | 2.64  | 10.68 | 5.11  | 21.89 | 5.77  |
| C <sub>org</sub>               | 1.08    | 6.86  | 8.30  | 11.56 | 6.01  | 1.64  | 5.12  |
| N                              | 0.026   | 0.266 | 0.118 | 0.063 | 0.393 | 0.042 | 0.327 |
| L.O.I. 950°C                   | 5.40    | 11.15 | 7.24  | 9.30  | 11.60 | 7.73  | 8.31  |

The contents of elements have been expressed as oxides with two exceptions. One is the organic carbon ( $C_{org}$ ) content, expressed in the elementary form as it indicates an amount of polymer substances in the studied material, while another one is nitrogen (N) content, which is to some extent also an indicator of some nitrogen-containing polymers, for instance of polyacrylamid.

#### 4. DISCUSSION

The combined investigations of the spent water-based drilling muds which involved a range of analytical methods, have allowed for better recognition of the nature of these composed, polymer-mineral hydrogels with colloidal properties. The results clearly indicate that it is mainly the mechanism of mutual interactions between colloidal mineral particles, first of all clay minerals, and organic polymer substances, that decides upon the specific physical and chemical properties of these colloidal waste materials. X-ray diffractometry and Fourier infrared spectroscopy have revealed that a deep transformation of the microstructure of clay crystallites (mainly smectites) proceeds in the course of drilling. The alterations begin from a degradation of parallel-stratified clay crystallites and result initially in the formation of a partly delaminated turbostratic structure of clay minerals. In the next stage, the splitting of the clay quasi-crystals takes place, under the influence of organic polymers reacting with separate clay platelets *via* various type of thus creating a clay-polymer nanocomposite microstructure, in which delaminated clay platelets crosslink the polymer chains (comp. Fig. 4).


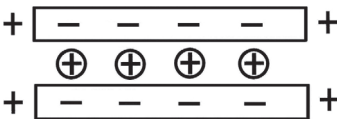
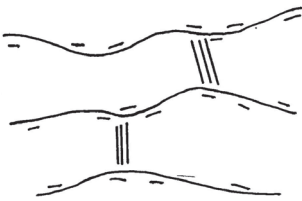
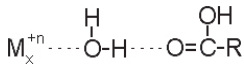
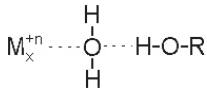
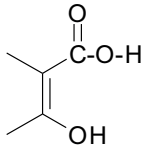
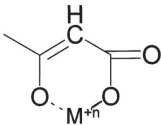


**Fig. 4.** Simplified model of exfoliated clay-polymer nanocomposite microstructure of water-based spent drilling muds  
1 – polymer chains, 2 – clay platelets, 3 – non clayey crystals, 4 – water solution

Combining knowledge on the surface properties and reactivity of the functional groups on clay minerals [2, 3, 6, 7] as well on the chemistry, structure and active centers configuration on the surfaces of selected groups of organic polymers and macromolecules [9, 13], it will be possible to predict most probable interactions between the two types of substances [1, 4, 5, 8, 12]. The results of the mentioned works could be applied into the explanation of the mutual interactions between the components in the organo-mineral spent drilling mud colloid systems (see Tab. 3 – reactions 1–5).

**Table 3**

Interaction between organic polymers and minerals particles in the waste drilling mud colloid systems

| Active sites of organic polymers   | Active sites of mineral components  | Mutual interaction in organo-mineral colloid systems   |
|--|---|--|
|  <p>Negatively charged polymer chains due to presence of anionic groups (e.g. <math>-\text{COO}^-</math>, <math>-\text{O}^-</math>)</p> |  <p>Microstructure of clay minerals:<br/> <math>-</math> negatively charged clay platelets,<br/> <math>+</math> positively charged crystal edges,<br/> <math>\oplus</math> exchangeable cations in the interlayers</p> |  <p>Clay platelets as cross-linking agents between the polymer chains</p>  |
| <p>Carboxylic <math>-\text{COOH}</math> groups of organic polymers</p>   | <p>Hydrated multivalent metal cations, hydroxymetal complexes or metal hydroxides on the clay platelets surfaces</p>  |  <p>Hydrogen bonding <i>via</i> water bridges</p>  |
| <p>Phenolic or alcoholic <math>-\text{OH}</math> groups of organic polymers</p>  | <p>Hydrated multivalent complexes on the clay platelets and exchangeable cations in the smectite interlayers</p>  |  <p>Interaction in which the bonding between <math>\text{H}_2\text{O}</math> molecule and <math>\text{OH}</math> groups are of the short-range hydrogen bond type. Intercalation of low-molecular polyglycols</p> |
| <p>Polymer containing two or more donor groups</p>    | <p>Polyvalent metal cations located in the clay interlayers or on the broken-bond surfaces</p>  |  <p>Chelate ring formation</p>   |
| <p>Aromatic rings in the structure of polymers able to react <i>via</i> <math>\pi</math> electrons</p>   | <p>Some metallic cations (e.g. <math>\text{Fe}^{\text{III}}</math>) located in the clay interlayers or on the broken-bond sites</p>   | <p>Sorption <i>via</i> <math>\pi</math> interactions with the organic radical cations formations</p>   |



## 5. CONCLUSIONS

1. The authors have elucidated a usability of structural and phase investigations combined with chemical determinations in the case of the samples of spent, water-based drilling muds, collected from drilling sites in various areas of Poland. An advanced analysis of such highly complex, polymer-mineral colloidal systems requires applying the following mineralogical methods: X-ray diffractometry XRD – mainly to identify the mineral and phase composition of the crystalline substances representing the solid fraction of drilling muds; infrared transformed Fourier spectroscopy FTIR – mainly to determine infrared-active groups of organic polymers and also to support phase analyses; and scanning electron microscopy SEM – to determine the microstructure of solid components; that must be complemented by instrumental methods of chemical assaying.
2. The authors have recognized a role of the high-molecular organic polymers, which in reaction with highly dispersed domains of clay minerals (mainly smectites) form delaminated or exfoliated polymer-mineral nanocomposites. Such nanocomposites control, among others, the microstructure and stability of spent drilling muds.
3. Combined investigations on the chemical and mineral composition as well as properties of water-based mud have a fundamental meaning for the studies on the management of those materials in the natural environments.

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