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Research paper

Smectite-, silica- and zeolites-bearing raw materials (Hliník nad Hronom bentonite, Slovakia) - A new approach using integrated petrographic and mineralogical studies

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ABSTRACT

This paper presents the results of detailed petrographic and mineralogical studies of commercial bentonite from the Hliník nad Hronom deposit in Slovakia. The X-ray diffraction, optical microscopy, field emission scanning electron microscopy (FESEM), thermal analysis, infrared spectroscopy and chemical analyses revealed that the main component of the studied commercial bentonite is montmorillonite (47%) followed by opal-C/CT (20%), clinoptilolite (15%), biotite (3%), potassium feldspar and plagioclases (12%), and quartz (3%). Both the optical microscopy and FESEM studies demonstrated that the precursor of bentonite was ignimbrite composed of compressed, strongly deformed pumice fragments, which were moulded around pyroclastic grains such as biotite, plagioclase, quartz and fragments of volcanic rocks. The pumice fragments were locally cemented by microcrystals of potassium feldspars and subsequently replaced by montmorillonite, and opal-C/CT, less commonly by clinoptilolite. The specific surface area of the studied bentonite is about 50 m^2/g. Although bentonite from the Hliník nad Hronom deposit is recognized as a medium-quality raw material due to relatively low content of smectite, it can be valuable as a substance which integrates the properties of smectite-, silica- and zeolite-bearing raw materials.

1. Introduction

The Polish industry must import bentonite raw-materials due to the lack of the economically valuable domestic deposits. In last years, the main supplier was Slovakia from which over 45% of Polish bentonite demand was covered (Wyszomirski and Lewicka, 2005; Panna et al., 2012). Bentonites from Slovakia are utilized, among others, by the CERTECH company based in Niedomice near Tarnów. The CERTECH offers a wide spectrum of products (see *www.certech.com.pl*). Their production is based mostly on bentonites extracted in deposits located within the Central Slovakia Volcanic Field (CSVF) (Fig. 1), particularly the Kopernica deposit (Bahranowski et al., 2014; Górniak et al., 2016), subordinately also the Jelšowy potok deposit. In last years, the CERTECH has been utilizing also bentonite from the Hliník nad Hronom (HnH) deposit.

Bentonite from the HnH deposit has already been studied by Uhlík et al. (2012). Their results demonstrated rather medium quality of bentonite mined in 2008 due to relatively low contents of smectite (30–53 wt%) and high contents of low-crystalline silica (19–45 wt%). Variability of mineral composition together with diversified fabric are inherent features of bentonite deposits, particularly those hosted in large volcanic complexes of complicated geological history (see e.g. Christidis et al., 1995; Yildiz and Kuşcu, 2007; Christidis and Huff, 2009; Arslan et al., 2010; Çiflikli et al., 2013; Koutsopoulou et al., 2016). Some deposits reveal variability of contents and forms of occurrence of smectite, and accompanying components (e.g. Grim and Güven, 1978; Christidis and Dunham, 1993, 1997; Münch et al., 1996; Christidis, 2001). This is a result of diversified composition of pyroclastic precursors, their deposition conditions and post-depositional processes such as devitrification, vapor phase crystallization, and diagenetic transformations (e.g. Ross and Smith, 1961; Christidis et al., 1995; Münch et al., 1996). Generally, bentonites from the CSVF reveal lateral and vertical variability of mineral composition (Kraus et al., 1982, 1994; Górniak et al., 2016), hence, studies are justified on changes of bentonite quality during the mining operation.

This paper presents the results of detailed, petrographic and mineralogical studies of commercial bentonite from the HnH deposit mined in 2013. The research, aimed to assess qualitative and quantitative

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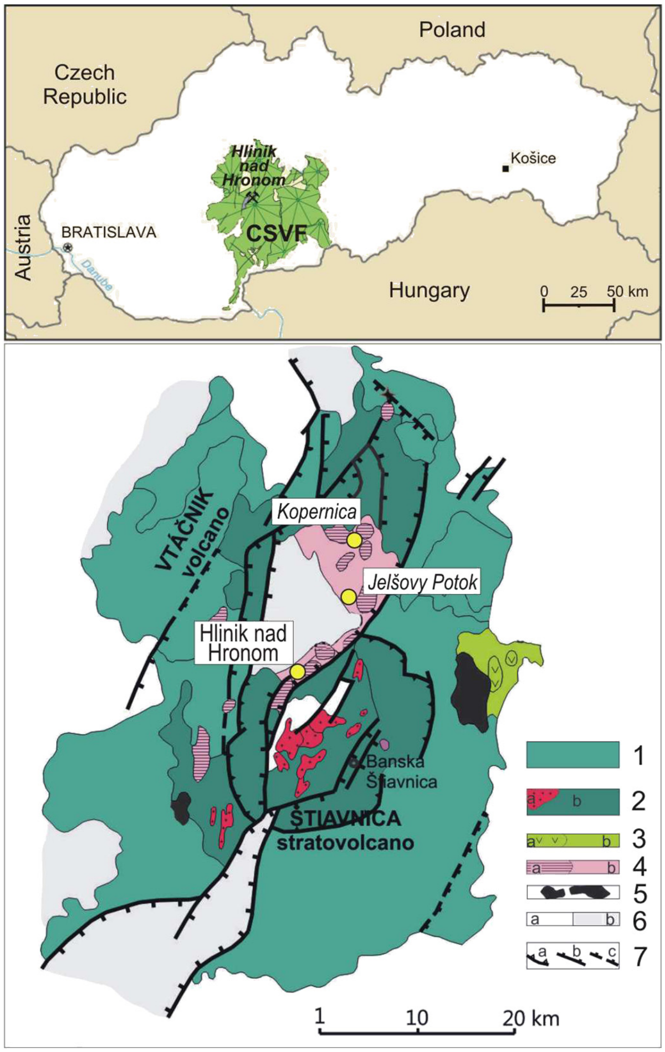

Fig. 1. Location of the Central Slovakian Volcanic Field (CSVF) and the Hliník nad Hronom deposit (after Uhlík et al., 2012, modified). Explanations: 1 – andesite stratovolcanoes; 2 – central zones of stratovolcanoes: intrusions (a), calderas and grabens (b); 3 – andesite extrusive domes (a) and breccias (b); 4 - rhyolite extrusive domes (a) and tuffs (b); 5 – olivine basalts; 6 – pre-volcanic basement (a) and post-volcanic sediments (b); 7 – caldera fault (a), other exposed (b) and covered (c) faults.

mineralogy of bentonite together with identification of the forms of its components and measurements of selected physical and chemical properties.

The new aspect of our paper is the assessment method of bentonite as a mineral raw-material based upon the latest petrographic tools applied in the studies on fine-grained rocks. Such attempt results from the request of bentonite producer, who expects not only the standard dataset, i.e., phase and chemical compositions, grain size distribution and textural features but needs also detailed information about forms of occurrence and mutual relationships between particular bentonite components. This information is crucial for new technological developments, especially those concerning the mineral processing of raw bentonite.

Another novelty is the petrographic technique, which has not been applied to the studies on Hliník bentonites, as yet. It integrates the microscopic methods: optical microscopy and high-resolution electron microscopy (FESEM), which enables the researcher to observe the bentonite component on various scales – from millimeters to nanometers. Moreover, in our observations we used the sister samples, i.e. thin sections and their polished equivalents. In comparison to "classic" SEM fracture surfaces, such method provides better understanding of mutual relationships between bentonite components.

2. Geological background

The HnH deposit is located in the Central Slovakia, in the northwestern part of the Štiavnica Mts., within the range of the Štiavnica stratovolcano; a huge (2000 km^2) structure within the CSVF (Fig. 1). According to Konečný et al. (2001) and Konečný and Lexa (2001a, 2001b), the Štiavnica stratovolcano is a complex eruptive center of long, complicated, multistage geological history. The center includes an andesitic volcano accompanied by a vast caldera, numerous subvolcanic intrusions and youngest rhyolitic extrusions and pyroclastics.

The CSVF is the most significant source of bentonite in the Western Carpathians. Here, the well-known Slovakian bentonite deposits Jelšový potok and Kopernica are located (Fig. 1). Similarly to these localities, the Hliník deposit is hosted in pyroclastic Jastrabá Formation (Sarmatian-Pannonian) (Kraus et al., 1982, 1994), which includes bentonitized rhyolitic tuffs forming a belt, about 700 m long, 100–200 m wide and 2–38 m thick (for details see Uhlík et al., 2012).

The Tertiary bentonites of the CSVF have formed under lacustrine conditions at the expense of volcaniclastic rocks (Kraus et al., 1982, 1994; Šamajová et al., 1992). Complicated geological history of the CSVF, which embraces multistage volcanic activity and fault tectonics (Konečný et al., 2001; Konečný and Lexa, 2001a, 2001b) implies variability of bentonite deposits, as noticed by Kraus et al. (1982, 1994), Šamajová et al. (1992) and Šucha and Kraus (1999). Bentonites show zonal variability: their mineral composition changes with the depth and depends on transformations of rhyolitic precursor in open or closed geochemical systems (Kraus et al., 1982, 1994; Šucha and Kraus,1999). A similar explanation, i.e., the progressive pore space sealing with the depth during alteration of volcaniclastic layers accompanied by changes in their mineralogical composition has already been proposed e.g. by Münch et al. (1996) for Mexican bentonite deposit. The CSVF bentonites contain montmorillonite accompanied by variable amounts of silica minerals and zeolites. Their origin is related to depth-controlled processes which transformed the rhyolitic precursor. Moreover, Šucha et al. (2001) and Stríček et al. (2006) advocate also weathering of bentonites as the source of silica.

3. Materials

The study material is representative of a supply of raw bentonite (about 10,000 metric tons) hauled from the Hliník nad Hronom bentonite deposit in Slovakia to the CERTECH company in Niedomice, Poland, in 2013. Each supplied portion of raw bentonite (several hundreds metric tons), was sampled in accordance with the routine procedure applied by the CERTECH. Precisely, from each portion 6 random samples were collected with the penetrator. Each sample weighted about 1 kg. Then, all 6 samples sampled were mixed, homogenized and reduced from about 6 to about 1 kg using the coning and quartering method. This sample was analyzed by CERTECH for physico-chemical properties including the content of montmorillonite, which was measured with the methylene blue sorption method, in accordance with the Polish Standard BN-77/4024-16 (photocolorimetric method).

Basing upon the results of physico-chemical studies, the CERTECH laboratory selected a sample of raw bentonite representative for the whole bentonite supply in 2013. This sample was our study material.

Bentonite sample supplied by the CERTECH to our Faculty laboratory (about 1 kg) was again homogenized and reduced to 100 g sample from which relevant portions were taken for analyses. Portions for qualitative X-ray diffraction (XRD), thermal analyses, IR-spectroscopy and chemical analyses were grinded in agate mortar and pestle down to several μm fraction. For XRD study of clay, fraction <2 μm was separated with the centrifugal separator. Moreover, lithoclasts were picked from sample studied for detailed microscopic and XRD investigations.