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CHARACTERIZATION, BENEFICIATION AND UTILIZATION OF THE CLAY FROM CENTAL BOSNIA, B&H

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ABSTRACT
Clay from deposit Bilalovac, Central Bosnia, was characterized by chemical, IR, XRD and DTA/TG analysis. The major mineral components are kaolinite, illite, muscovite and quartz. Raw clay may be used for pottery products and terracotta. Clay was beneficiated by wet method removing fraction over 20 µm. Beneficiation process increased content of kaolinite and decreased content of quartz. Beneficiated clay may be used for tiles, sewerage pipes, acid-resistant ceramic and stoneware, and even as refractory clay.
Key words: clay, beneficiation, mineral composition

1. INTRODUCTION
Technological, economic and demographic developments are speeding up the consumption of raw materials. This particularly applies to high grade raw materials, which have been used up more and more quickly and some will have soon become scarce. Beneficiation of low grade raw materials and their utilization can contribute to better use of resources and finding new reserves of raw materials. Clay is one of raw materials which usage for current and new applications will continue to grow. As a building material, it is used in the form of bricks and roof tiles. Other uses are in the making of refractories, manufacture of wall and floor tiles, porcelain, earthenware, pipe for drainage and sewage, etc. Clays are also of great importance in the paper, ceramics, plastics and cosmetic industries. Chemically, clays are hydrous aluminum silicates, usually containing non-clay minerals such as quartz, calcite, pyrite, talc and other impurities. Amount and kind of impurities vary greatly, and these strongly influence the uses of the various clay types. If clay doesn’t fit for final applications it needs to be processed through beneficiation process. Basically, clay beneficiation process includes removing certain types and amounts of non-clay minerals in order to improve some properties of clay. There are mainly two techniques used in industrial production, dry process and wet process [1]. Mostly, the aim of these methods is to decrease the content of quartz and ferrous minerals in clay [2]. In the dry process, the raw material is crushed to the desired size, dried, pulverized and air-floated to remove most of the coarse grit. The dry process is simpler but produces a lower quality product than the wet process. In wet processing clay is blunged to produce slurry, which is divided into coarse and fine fractions using centrifuges, hydrocyclones, or hydroseparators.

2. EXSPERIMENTAL
Bulk sample of the illite/kaolinite clay was collected from deposit “Bilalovac”, central Bosnia and Herzegovina. This bulk sample was subjected to testing before and after the beneficiation procedure. The characterization of clay is carried out with a number of experimental approaches in order to investigate all the relevant features. Roentgen - Fluorescent Analysis, RFA, (ARL 72000S) and Atomic Absorption Spectroscopy, AAS, (Perkin Elmer 3100) were used for determination of chemical composition of clay. Identification of clay minerals was carried out using IR spectroscopy (Spectrum One, Perkin Elmer) in wave number region between 4000 and 400 cm^{-1}. Also, in order to more

precisely determine mineralogical composition of clay, X–ray diffraction analyses was performed using Philips PW 1710 (Cu–Kα radiation with graphite monochromator) diffractometer. To investigate clay behavior during the thermal treatment, DTA and TG analyses were carried out by means of the Derivatograph Q1500D MOM Budapest apparatus. Clay samples were heated in air up to 1000°C with heating rate 10°C per minute. Beneficiated clay has obtained from dried and crushed up raw clay. Distillate water with 0.74 g/l sodium pyrophosphate was added into it and one hour stirring. According the Stoke's law and experimental conditions, the sedimentation time of grains over 20 μm was calculated. After that time the suspension with clay component bellow 20 μm was decanted and dried to finally beneficiated clay.

3. RESULTS AND DISCUSSION

Table 1 shows the chemical composition of the investigated clay before and after treatment, as well as the chemical composition of the residue after processing. Chemical analysis shows that the beneficiation reduces the amount of SiO_2, and increases the amount of Al_2O_3 which indicates an increase in the content of clay minerals, and reduce the content of quartz. Beneficiated clay has increased loss on ignition, probably due to increased amounts of kaolinite. Increased iron content in beneficiated clay indicates the presence of iron in the structure of clay minerals, as well as the possibility of the presence of certain fine grained iron minerals, probably limonite.

Table 1. Chemical composition of clay "Bilalovac"

Component	Chemical composition (wt. %)		
	Before beneficiation	After beneficiation	Residue
SiO_2	63.6	53.4	74.2
Al_2O_3	22.3	30.1	15.5
Fe_2O_3	2.04	2.52	1.58
TiO_2	0.95	0.71	0.94
CaO	0.006	0.28	0.17
MgO	0.76	0.73	0.43
MnO	0.008	<0.01	<0.01
K_2O	4.66	4.16	2.88
Na_2O	0.5	0.7	0.4
ZnO	0.016	0.02	0.015
L.O.I.	4.98	7.26	3.02

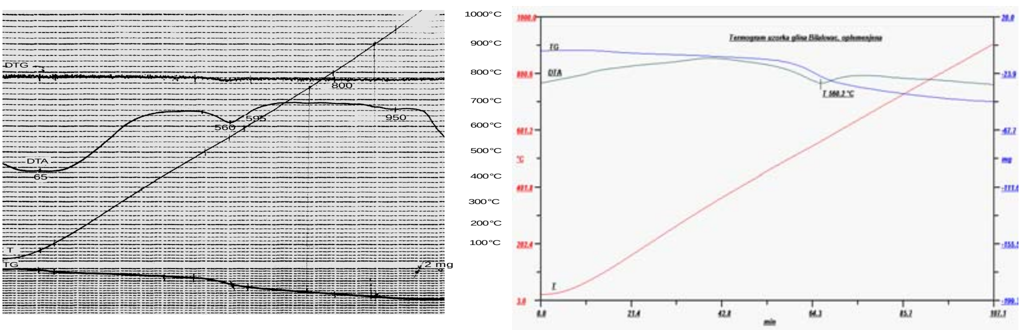

Figure 1. DTA/TG of the clay before and after beneficiation

DTA/TG analysis (Fig. 1), IR (Fig. 2) and XRD (Fig. 3) show that the main minerals in the clay are kaolinite, illite, muscovite and quartz. Two endothermic effects on DTA curve (before beneficiation) which are superimposed (560°C and 595°C) and weight loss in the temperature range 350-750°C indicated on TG curve are attributed to the removing hydroxyls that are lost as water at elevated temperature from the clay minerals illite and kaolinite. Because of their intensity these endothermic peaks cover much weaker endothermic effect of quartz transformation at 573°C.

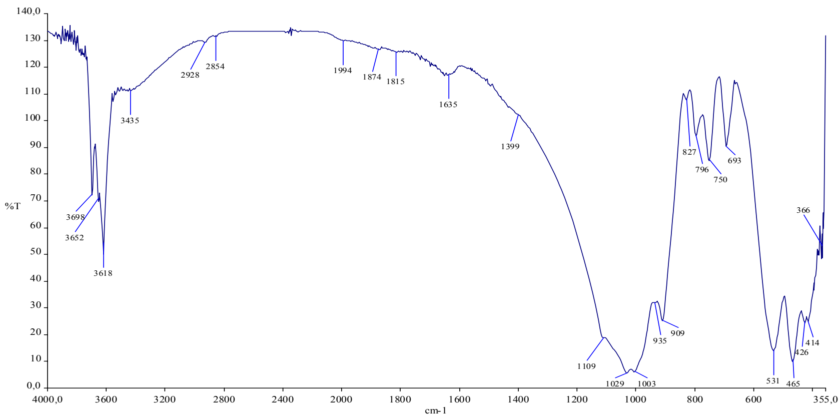

Figure 2. IR spectra of the clay

Thermogram of beneficiated clay (Fig. 1) also shows only a broad endothermic peak formed by overlapping dehydroxylation of illite and kaolinite and quartz phase transformation. Weight losses in temperature range 750-900°C result from the decomposition of muscovite, and losses in temperature range 110-350°C resulting from the combustion of organic matter and decomposition of limonite. In beneficiated clay these losses are higher in the temperature ranges up to 750°C. It may be presumed that there has been an increase in the amount of kaolonite and limonite. Comparative diffraction patterns (Fig. 3) also show a decrease in the amount of quartz and increase in the amount of kaolinite.

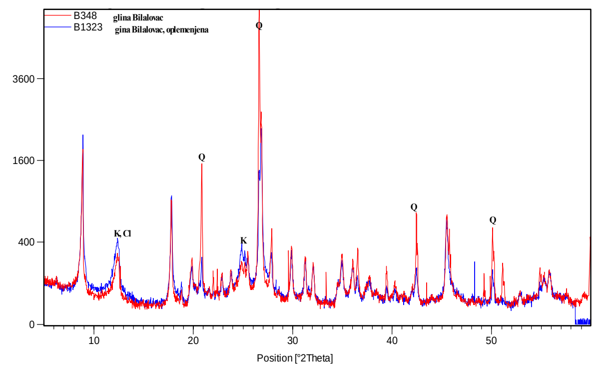

Figure 3. Comparative diffractogram of raw and beneficiated clay "Bilalovac" (Q – quartz, K – kaolinite, Cl – chlorite, Mu – muscovite, Il - illite)

Table 2. Chemical composition of clay minerals [8]

Oxide	*Chemical composition* (%)		
	Muscovite	Illite	Kaolinite
SiO_2	45,21	54,01	46,55
Al_2O_3	38,36	17,02	39,5
H_2O	4,07	12,03	13,96
K_2O	11,81	7,62	-
FeO	-	1,85	-
MgO	-	3,11	-

The approximate mineralogical composition of the clay was calculated on the basis of results obtained by chemical and thermogravimetric analysis. The main minerals identified in the clay "Bilalovac" are quartz, kaolinite, illite and muscovite. Chemical composition of minerals muscovite, illite and kaolinite is given in the table 2 [8].

The empirical formula of illite $K_{0,6}(H_3O)_{0,4}Al_{1,3}Mg_{0,3}Fe^{2+}_{0,1}Si_{3,5}O_{10}(OH)_2\cdot(H_2O)$ shows 4,61% of water and 7,42% structural hydroxyl groups in this mineral.
Equations for calculating the approximate mineralogical composition can be obtained by taking into account following data and assumptions [1]:
- Muscovite (M) releases hydroxyl groups in the temperature range 750-900°C. (Weight loss in this range is indicated by G 'and for raw clay is 0.95 % and for beneficiated is 0.96 %.)

- Illite (I) and kaolinite (K) release hydroxyl groups in the temperature range 350-750°C. (Weight loss in this range is indicated by G" and for raw clay is 3.29 % and for beneficiated clay is 6.02 %.)
- The content of free quartz (Q) is determined by subtracting parts that belongs to illite, muscovite and kaolinite from total SiO_2 obtained from chemical analysis.

$$M = G'/0.0407$$
$$I = (K_2O - 0.1181 \cdot M)/0.0762$$
$$K = (G'' - 0.0742 \cdot I)/0.139$$
$$Q = SiO_2 - 0.4655 \cdot K - 0.4521 \cdot M - 0.5401 \cdot I$$

Calculated mineralogical composition (Tab. 3) confirms an increase in the amount of kaolinite and reduction in the amount of quartz and illite, while amount of muscovite remained almost unchanged.

Table 3. Calculated mineralogical composition of clay

Mineral	Content of mineral (%)	
	Raw clay	Beneficiated clay
Illite	24.98	18.03
Muscovite	23.34	23.58
Kaolinite	10.33	33.68
Quartz	34.75	17.32
Other minerals	6.6	7.39
Illit+kaolinite	35.31	51.71

4. CONCLUSION

According to chemical and mineralogical analyses clay from deposit "Bilalovac" is illite/kaolinite type. Investigated clay doesn't contain unfavorable impurities limestone, magnesite, dolomite and gypsum and belongs to clays suitable for the manufacture of pottery and terracotta. Mineralogical study showed that the main mineral constituents of the clay are quartz, kaolinite, illite and muscovite. By simple beneficiation procedure it is possible to obtain clay with a higher percentage of kaolinite which gives the possibility for usage in the production of tiles, sewer pipes, acid-resistant ceramic and stoneware, and even as a refractory clay.

5. REFERENCE

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