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Research of Kosova Bentonite Through Difractometer Dust Analysis, ESR Spectroscopy and TDA and TGA Analysis

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Abstract: Experimental realization of this work we have done in natural and activated bentonite of Kosova. Diffractogram analysis shows that the natural bentonite of Karaçeva contains mainly montmorillonit mineral, while the clay mineral contained in the bentonite of Gushica and Kabash presents the structure of the mixed layers of mika and montmorillonit, respectively of ilit ore. To create specific statement of phase transformations of special mineralogical components during heat treatment of bentonite of Kosova were used analysis methods of TDA and TGA. Research by ESR spectroscopy have been undertaken to identify the positions of Fe^{3+} and Mn^{2+} ions in the structures of minerals present in various deposits in Kosova.

Keywords: *bentonite, research, dust diffractometer, TDA, TGA, ESR, spectroscopy, analysis*

Introduction

Bentonite are clay minerals, whose main component is montmorillonite. Kosovo has large reserves of bentonite. The geological researches conducted so far show that the localities of respective deposits are concentrated in two main regiona: in that of Kamenica with main deposit of Karaçeva and that of Vitia with deposits of Gushica, Sadovina and Kabash. Like other types of clay, also bentonite clays have sedimentary origin. They were created as a result of chemical and bacteriological impacts on feldspat and other natural materials with volcanic origin, such as granit, porfit, *etc*. (Grim, 1962; Stoch, 1974). The more significant physical-chemical properties which characterize bentonite clays are swell, adsorption, ion exchange and catalytic activity. Chemical and mineralogical structure of bentonite undergoes substantial transformation during their activation, by heating in the strong acids (Onal *et al*., 2002). Besides uses in drilling and in areas dealing with adsorptive skills, clays has found wide industrial application for ion exchange, such as their use for cleaning of wastewater, but also in agriculture to improve the quality of land. (EUBA, 2006; Amorim et al., 2004).

Material and methods

Table 1 presents all the investigated samples with signs and respective origins.

Difractometer dust analysis

X-ray analysis is method widely used for the characterization of the mineralogical composition of natural and processed samples (Atkins, 1992). Type of instrument: Philips, PW 1050 X-ray diffractometer.

TDA and TGA analysis

Thermal differential analysis (TDA) and thermo gravimetric analysis (TGA) are used as complementary methods for the characterization of the mineralogical composition of the investigated samples and quantitative determination of water for constitutional and carbonates in them. (Fotic et al, 1990; Grim, 1962) Type of instrument: ATD 67, Adamel-Lhormargy, condition of measurements: thermo element Pt/Pt Rh with 0,1 mV; rate of heating 10 ^{o}K/min; mass of standard sample 500mg.

ESR spectroscopy

The properties of basic structure and hyperfine structure of ESR spectra show strong information for determining the deep structure of the clay montmorillonite. (Atkins, 1992; Hanzhel, 1989). For this purpose they are used natural samples and processed samples.

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Type of instrument: Varian E-12 century line spectrometer.

Table 1. Overview of samples investigated naturally, activated and separated.

Sign of sample	Deposit, region	The origin of sample	Activated sample
1	Gushicë, Viti	Natural sample	Not activated
1a	"	Fraction ≤ 2μm	"
1b	"	Seperated montmorillonit	"
1c	"	Activated sample	10% HCl
1d	"	"	20% HCl
1e	"	"	30% HCl
1f	"	"	3% Na_2CO_3
1g	"	Fraction ≤ 2μm	10% HCl
2	Kabash,Viti	Natural sample	Not activated
2a	"	Fraction ≤ 2μm	"
2b	"	Seperated montmorillonit	"
2c	"	Activated sample	10% HCl
2d	"	"	20% HCl
2e	"	"	30% HCl
2f	"	"	3% Na_2CO_3
3	Karaçevë, Kamenicë	Natural sample	Not activated
3a	"	Fraction ≤ 2μm	"
3b	"	Seperated montmorillonit	"
3c	"	Activated sample	10% HCl
3d	"	"	20% HCl
3e	"	"	30% HCl
3f	"	"	3% Na_2CO_3
3g	"	Fraction ≤ 2μm	10% HCl

Results and Discussion

Table 2 summarizes the relevant data for natural bentonite of Kosova.

Table 2. The summary results of TDA and TGA analysis of natural bentonite of Kosova

	Sample		
	Gushicë	**Kabash**	**Karaçevë**
Tv	160	170	140
Tq	570	590	500
Th	680	720	680
Tc	780	840	850
Tr	880	880	940
Tk	920	920	-
Wv	8,14	7,33	7,06
Wh	3,14	8,57	4,25
CO_2 (%)	4,00	5,60	-
$CaCO_3$ (%)	10,03	11,44	-
CaO (%)	5,83	6,65	-

Figure 1 illustrates the diffractograms of natural sample of the natural bentonite of Gushica deposit.

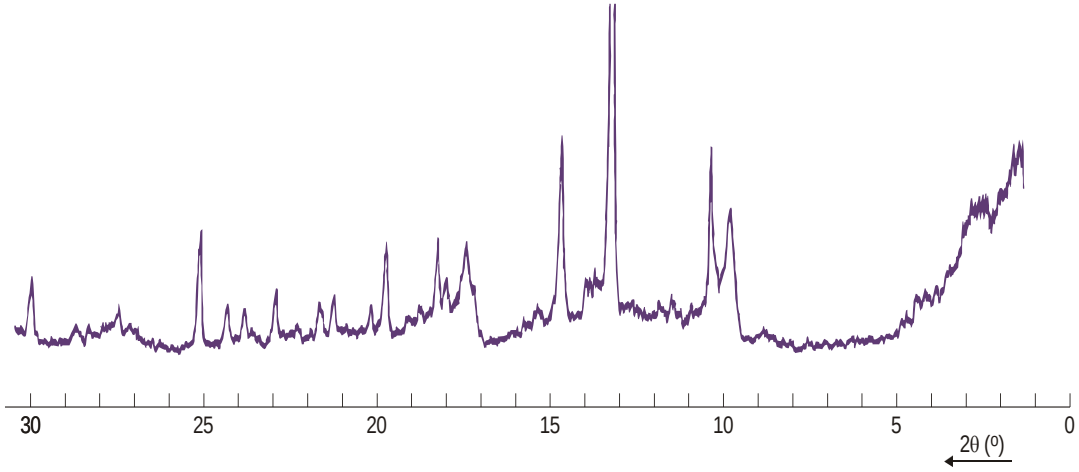

Figure 1. Diffractogram of natural sample of Gushica deposit.

Semi quantitative summarized presentation of relevant mineralogical analysis of natural and activated bentonite clay of Kosova is given in Table 3.

Table 3. Mineralogical setting of natural and activated bentonite of Kosova, based on the analysis of their diffractometric analysis

Sample	M	I	C	Q	D	F
1	♦♦	♦♦♦	♦♦♦	♦♦	♦♦	♦♦
1a	♦♦♦	♦♦♦♦	♦♦	♦	-	♦♦
1b	♦♦♦	♦♦♦♦	♦	-	-	♦♦♦
1c	♦♦	♦♦♦	-	♦♦	-	♦♦
1d	♦♦	♦♦♦	-	♦♦	-	♦♦
1e	♦♦	♦♦♦	-	♦♦	-	♦♦
1f	♦♦	♦♦♦	♦♦♦	♦♦	♦	♦♦
1g	♦♦	♦♦♦	-	-	-	♦♦
2	♦♦	♦♦♦	♦♦	♦♦♦	♦	♦♦
2a	♦♦♦	♦♦♦♦	♦♦	♦	-	♦♦
3	♦♦♦♦	♦♦	♦	♦	-	♦
3a	♦♦♦♦	♦♦	♦	-	-	♦
3c	♦♦♦♦	♦♦	-	-	-	-
3f	♦♦♦	♦♦	-	-	-	-

M → Montmorillonit (FDF: 7-330) Q → Quartz (FDF: 11-252)
I → Ilit (FDF: 7-25) D → Dolomit (FDF: 11-78)
C → Calcite (FDF: 5-058) F → Feldspat (FDF: 9-478)
FDF – Reference number in Powder Deffraction File
♦♦♦♦ dhe ♦♦♦ → main components
♦♦ → minor components
♦ → trace components
- → absent components

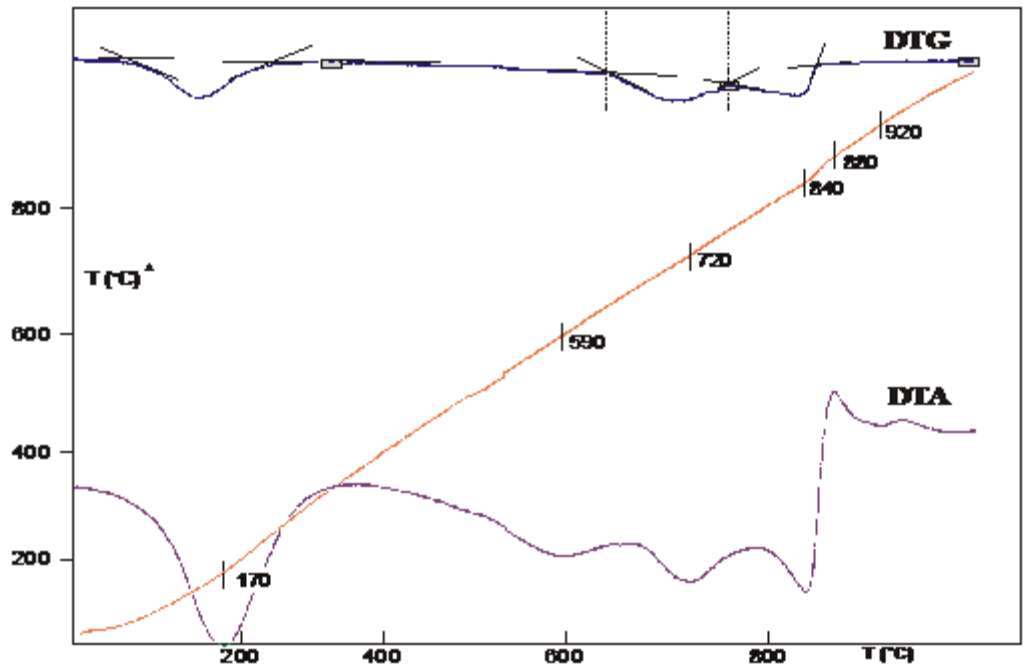

Figure 2. TDA and TGA diagrams of natural bentonite- Kabash deposit.

Mineralogical basic characterization of the natural bentonite by difractometer analysis is illustrated in Figure 3.

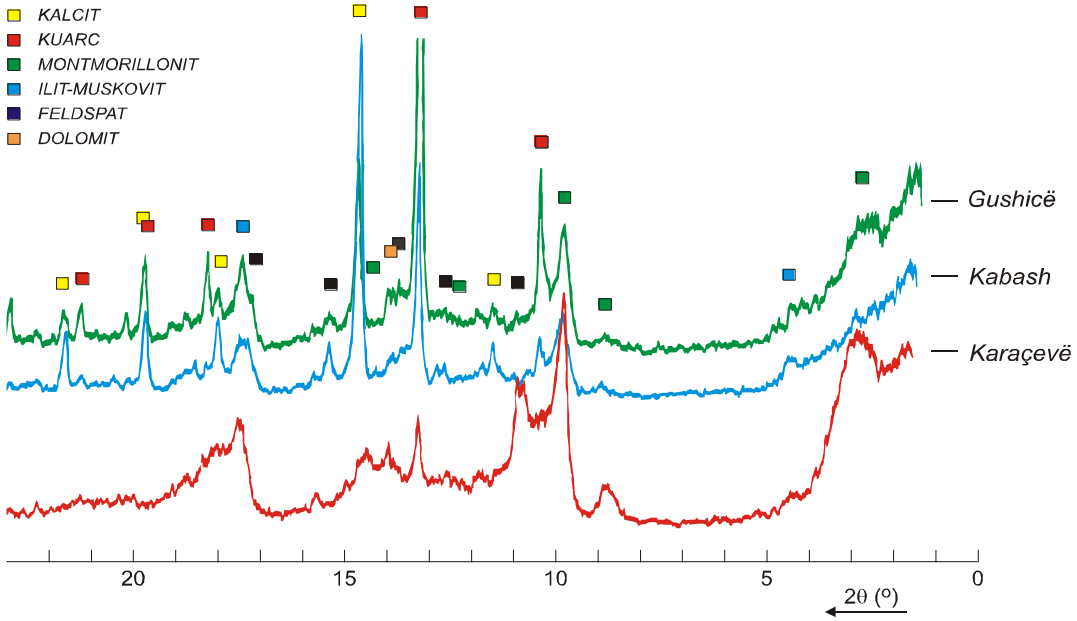

Figura 3. Comparison of diffractograms of natural bentonite of Gushica, Kabash and Karaçevë.

Figure 4 illustrates the impact of the degree of acid activation on mineralogical structure of Gushica bentonite.

The main conclusion from this figure is that acid activation causes the removing of calcite from bentonite.

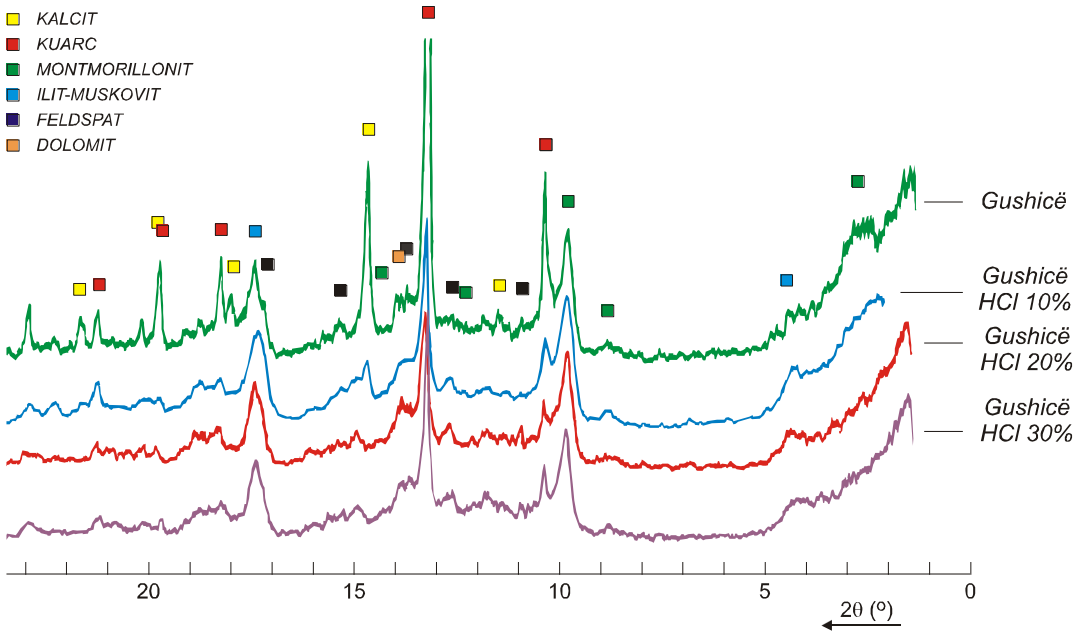

Figure 4. Comparison of the diffractogram of natural bentonite of Gushica with its activated bentonite with 10 % HCl, 20 % HCl and 30 % HCl.

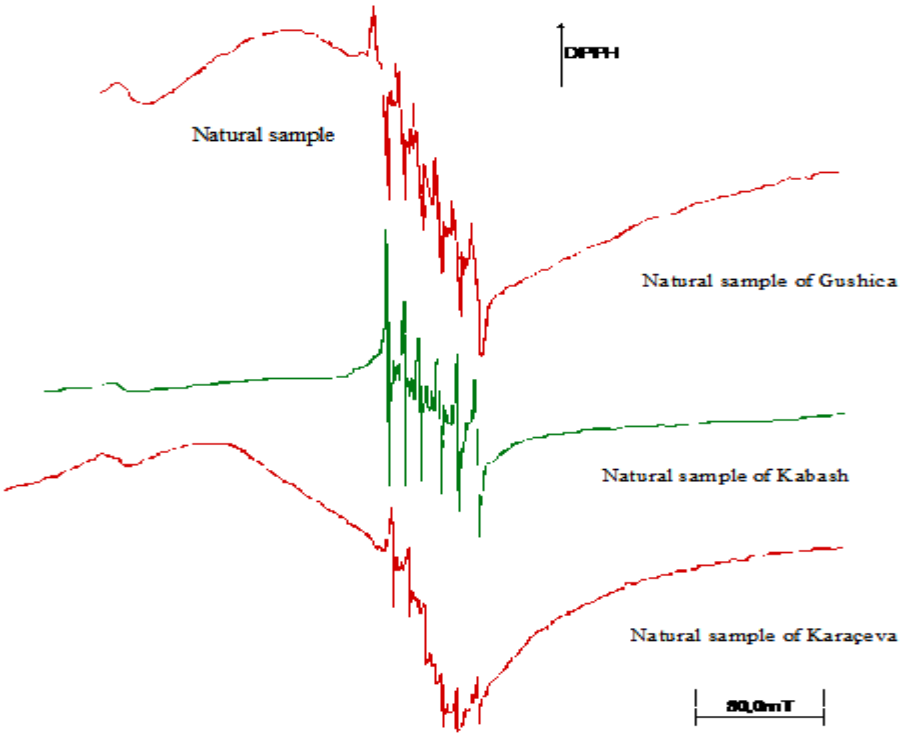

Figure 5. Comparison of ESR spectra of natural bentonites of Kosova.

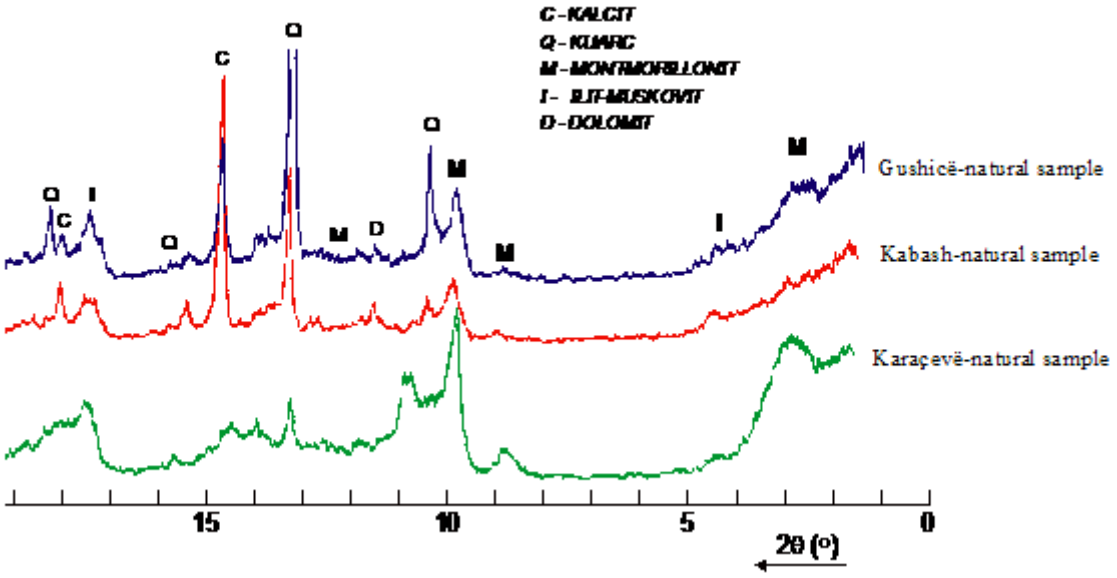

Figure 6. Diffractograms of natural bentonites of Kosova.

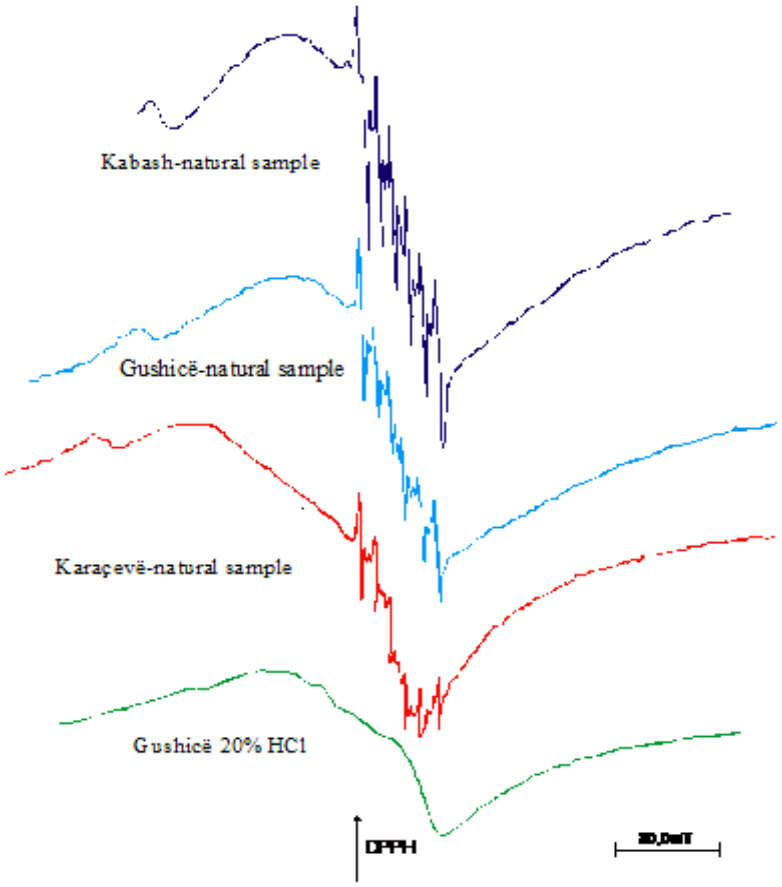

Figure 7. ESR-spectrograms of natural and activated bentonite of Kosova.

Conclusions

By analyzing the diffractograms of natural bentonite is found that:

- Mineralogical compositions of bentonite Gushica and Kabashi vary quite significantly from the composition of bentonite Karaçeva.
- Mineralogical compositions of bentonite Gushica and Kabashi are very similar to one another.
- Bentonite of Kabash and Gushicë containing in itself the greatest amounts of quartz and calcite than contain the Karaçeva bentonite.

- Bentonite of Gushica contains relatively large amounts of quartz, and bentonite of Kabash contain relatively large amount of calcite.
- X-ray diffraction and thermo gravimetric measurements have proven useful for the identification of the mineralogical changes during acidic and basic activation.
- It was found that acid activation causes the removal of the calcite from bentonite.

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