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Research of the Chemical Composition and Ion Exchange Properties of Karaçeva Bentonite

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Abstract: The value of pH varies depending on the activation of bentonite, by increasing the concentration of sulfuric acid, increases the acidity. With the rise of the pH value, we have a continuous increase of ion exchange capacity of bentonite, so high values of pH, we have a high capacity to exchange cations. The ion exchange capacity of natural samples of Karaçeva bentonite, varies according to the depth of drilling, with increase of the percentage of activation, have significant increase of ion exchange capacity for all investigated samples. By experimental measurements, it was found that the Karaçeva bentonite has good ion exchange properties.

Keywords: *natural bentonit, treatment, ion exchange capacity, ennoblement, pH*

Introduction

Mining raw materials are essential for the economic development of a country. In general, the clays which contain montmorillonit as the main mineral called bentonite. Chemical and mineralogical structure of bentonite undergoing the significant transformations, during their activation, by heating in strong acids (Onal & Sarikaya, 2002). The data for its application in the industrial developed countries, suggest that wider application include drilling and injections (50%), discharge (23%), bleaching and awakening (21%), while the other part consists on the multiple applications in the pharmaceutical industry, the application as filler in paper and rubber industry, as filler and additive in pesticides and animal feed, application as slowing in nuclear reactors, as catalysts in many processes of the chemical industry, as adsorbent in the food industry, *etc*. (EUBA, 2006; Alemdaroglu *et al*, 2003).

Cation exchange capacity is an important parameter, for the fact that clay minerals vary in their reactivity. (Karimi *et al*, 2011) In general, the smectites have high capacity to exchange cations. (Allen & Whitney, 2005). Cation exchange capacity is the measure of all cations adsorbed on the surface of clay and is usually expressed in milli-equivalents per 100 grams clay. (Borden and Giese, 2001). Besides use in drilling and in areas dealing with adsorptive properties, the bentonite have found the wide industrial application due to ion exchange, such as their use for the purification of waste water, but also in agriculture to improve the quality of land (EUBA, 2006; Amorim et al, 2004). Potentiometric titration applied to study the surface properties of many materials, including clay minerals (Amman, 2003).

Ennoblement of bentonite can be mechanical, acidic and basic. The results achieved by acid treatment, vary according to the type of clay used, its nature, the acid concentration, temperature and time of treatment (El Hechi et al, 2009). With acid treatment, the pore diameter of bentonite ranging from (2-6) nm, and specific surface area ranging from (200-400) m^2/g (Valenzuela *et al*, 2001). Acid treatment of montmorillonite results in the formation of nano-porous structure. (Vlasova *et al*, 2003)

Material and Methods

The researched deposits of bentonite, located in Karaçevë village, in the eastern part of Kosovo. To determine the geological reserves and quality of bentonite in the deposits of Karaçeva, there were three deep drilling. Chemical analysis of Karaçeva bentonite worked in natural samples and in samples enabled with 10 % H_2SO_4. For chemical analysis of natural samples, are used standard analytical methods, of their quantitative analysis. Determination are made with ICP-OES device. They are determinated these components: SiO_2, K_2O, Na_2O, CaO, MgO and Fe_2O_3. Acid activation is carried out with boiling of bentonite in the solution of sulphuric acid, with concentrations 10%, 20% and 30%

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during the 3 hours. The samples were activated with basic method, with the application of the standard method of basic activation with (1-5) % Na_2CO_3. After that, many of the properties of bentonite depends on the pH value, I have determined the pH of natural and activated bentonite in acidic and basic way.

In the context of this paper is used potentiometric titration method, a method that enables the identification of ion exchange capacity in different environments of acidity and basicity. The method is based on comparing the two titration curves of added acid and base, constructed on the basis of measurements conducted in the presence and in the absence of bentonite. To calculate the ion exchange capacity of bentonite, must first build the standard curve.

In a glass mixed 50 cm^3 sodium chloride with concentration of 0.2 M and 50 cm^3 water, without bentonite. This solution, firstly treated with portions of 1 cm^3 hydrochloric acid (HCl) with 0.1 M concentration and after each addition of hydrochloric acid, measured the pH value of solution.

The above procedure is repeated, but instead of hydrochloric acid, add 12 portions of 1 cm^3 NaOH, with a concentration of 0.1 M. From the data obtained, built the graph for bentonite and standard, where in the abscissa set the volume of NaOH, while in the ordinate set the pH value. The values of ion exchange capacity calculated from data derived from the graph and replacing them in the following equation:

$$IEC = \frac{(V_1 - V_0) \cdot C_{NaOH}}{m} \cdot 100$$

From the obtained results, built the dependency graph of pH from ion exchange capacity.

Results and Discussions

The obtained results of pH for natural bentonite and activated bentonite in acidic and basic way are shown in Table 1. The results of chemical analysis of the main components of Karaçeva bentonite, in its natural state and after activation with 10% sulfuric acid are presented in Table 2.

Table 1. The determination of pH.

	pH			
Type of bentonite	**Sample 1**	**Sample 2**	**Sample 3**	**Average value**
Natural bentonite	8.25	7.80	7.95	8
Activated bentonite with 10% H_2SO_4	7.67	7.52	7.60	7.59
Activated bentonite with 20% H_2SO_4	7.10	7.14	7.05	7.1
Activated bentonite with 30% H_2SO_4	5.40	5.36	5.46	5.41
Activated bentonite with 1% Na_2CO_3	8.75	8.68	8.72	8.72
Activated bentonite with 2% Na_2CO_3	9.35	9.5	9.45	9.43
Activated bentonite with 3% Na_2CO_3	9.55	9.7	10.2	9.82
Activated bentonite with 4 % Na_2CO_3	9.70	9.8	10.2	9.9
Activated bentonite with 5% Na_2CO_3	9.75	9.96	10.34	10.02

Table 2. Comparison of the chemical composition of natural bentonite with activated bentonite by10% H_2SO_4

Components	**SiO_2 (%)**	**Al_2O_3 (%)**	**Fe_2O_3 (%)**	**MgO (%)**	**CaO (%)**	**Na_2O (%)**	**K_2O (%)**	**L. (%)**	**Humid (%)**
Drilling I-1	58.50	12.56	5.58	2.30	2.17	1.39	1.56	13.11	5.0
Drilling I-1 with 10% H_2SO_4	64.75	6.97	2.58	1.75	0.77	0.42	1.44	16.55	6.6
Drilling I-2	58.64	12.57	5.27	2.59	2.06	1.51	1.75	11.73	3.25
Drilling I-2 with 10% H_2SO_4	64.95	6.98	2.44	1.96	0.73	0.45	1.62	16.79	6.80
Drilling II-1	59.22	12.89	5.33	2.84	2.09	1.86	1.48	12.79	5.26
Drilling II-1 with 10% H_2SO_4	65.15	7.16	2.46	2.16	0.74	0.56	1.37	15.78	5.86
Drilling II-2	62.89	11.97	4.67	1.55	2.65	2.23	1.99	10.72	3.68
Drilling II-2 with 10% H_2SO_4	69.18	6.65	2.16	1.17	0.94	0.67	1.82	14.23	5.13
Drilling III-1	60.04	12.61	4.62	1.71	3.87	2.59	1.93	11.33	4.20
Drilling III-1 with 10% H_2SO_4	66.04	7.00	2.13	1.30	1.37	0.77	1.76	15.22	5.13
Drilling III-2	59.41	12.79	4.33	1.91	2.49	2.15	1.79	13.11	6.52
Drilling III-2	67.35	7.10	1.37	1.45	0.88	0.64	1.65	15.36	6.89

The results of the chemical composition of representative samples of Karaçeva natural bentonite, are presented in Table 3. The obtained results of ion exchange capacity of bentonite, for different values of pH are presented in Table 4. From the obtained values, build up the diagram of the dependency of ion exchange capacity of bentonite by pH of the solution (Figure 1).

Table 3. Chemical analysis of representative samples of bentonite.

Comp.	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	L. (%)	Humidity (%)
RS I	55.95	13.08	4.82	3.02	1.3	0.89	1.08	15.05	5.65
RS II	57.55	12.62	5.38	2.07	0.92	0.54	1.8	14.40	5.10
RS III	58.75	12.84	4.72	2.28	1.09	0.86	1.06	14.17	5.25

Table 4. Values of pH and ion exchange capacity of Karaçeva bentonite.

pH	4	4.5	5	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	10.5	11
IEC	16	19	22	24.5	26.5	29	31.5	33.2	35.4	37.8	42.6	48.4	55.3	66.5	74.6

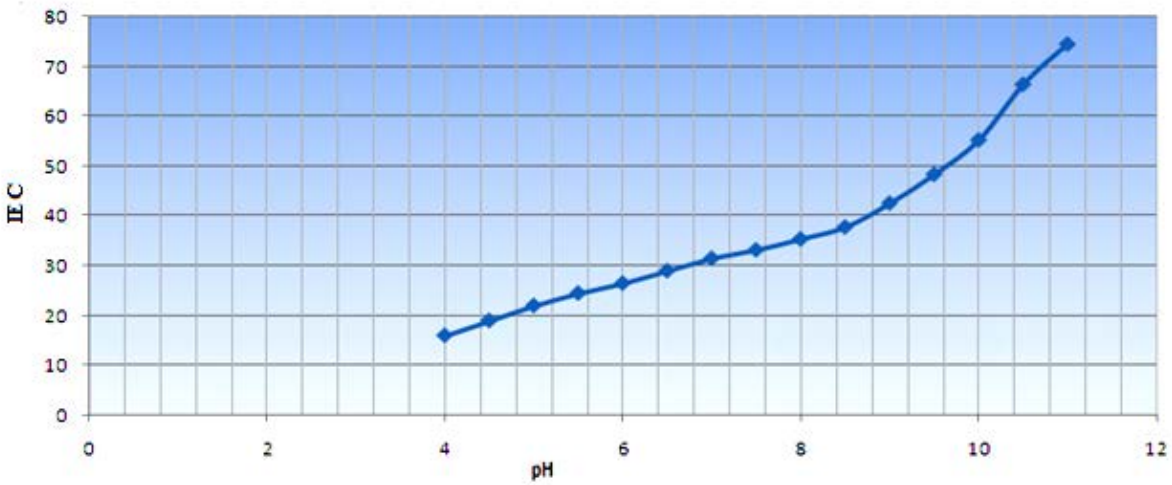

Figure 1. Dependency of ion exchange capacity by pH

Table 5 shows the results of the ion exchange capacity of bentonite at different depths from the deposit of Karaçeva. Table 6 shows the results of the ion exchange capacity (mmol/100g) for untreated bentonite and for treated bentonite in acidic way, with different percentages of sulphuric acid.

Table 5. Ion exchange capacity of bentonite at different depths

Signs of drilling	Depth (m)	Ion exchange capacity mmol/100g
Drilling I-1	(18-21)	90
Drilling I-2	(21-25)	95
Drilling II-1	(13-16)	78
Drilling II-2	(24-33)	85
Drilling III-1	(18-21)	80
Drilling III-2	(21-25)	90

Table 6. Results of the ion exchange capacity for natural and activated bentonite

Type of bentonite	IEC (mmol/100g)			
	Drilling I-2	Drilling II-2	Drilling III-2	Average value
Natural	95	85	90	90
a.b. with 10% H_2SO_4	106	97	103	102
a.b. with 20% H_2SO_4	128	121	125	124.7
a.b. with 30% H_2SO_4	131	125	128	128

From Table 1, shows that the value of pH varies depending on the activation of bentonite, by increasing the concentration of sulphuric acid increased acidity, in this case we have a decrease of the

value of pH from 8 at the sample of natural bentonite to 5.41 at the sample of activated bentonite by 30% H_2SO_4. With increasing of concentration of sodium carbonate, we have continued to increase the pH-value from 8 to sample of the natural bentonite, to 10.02 at the activated sample with 5% Na_2CO_3. From the table 2 shows that the content of components of the Karaçeva bentonite varies according to the depth of drilling, within the same source. The content of silicon dioxide of natural bentonite, varies from 58.50 % to samples of drilling I-1, up to 62.89 % to the sample of drilling II-2. During the acid activation process with 10% H_2SO_4, changing the chemical composition of bentonite, so that the content of components Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O and K_2O decreases, while the SiO_2 increases, for all investigated samples.

From the table 3 shows the chemical composition of representative samples of natural bentonite, not different much from the chemical composition of samples of natural bentonite, for special drilling. From table 4 shows that by raising the pH value, we have a continuous increase of ion exchange capacity of bentonite, so for high values of pH, we have high capacity to exchange cations. For pH value equal to 11, ion exchange capacity reaches the highest value (74.6 mmol/100 g). From the table 5 shows that the ion exchenge capacity of natural samples of Karaçeva bentonite varies by depth of drilling, the values of ion exchange capacity varies from 78 mmol/100 g at sample of drilling II-1 to 95 mmol/100 g, at sample of drilling I-2. From table 6 shows that increasing the percentage of activation, we have significant increase of ion exchange capacity for all investigated samples. The highest value of ion exchange capacity reached at sample of drilling I-2, activated with 30% H_2SO_4 (131 mmol/100g), while the lowest value of ion exchange capacity is at sample of natural bentonite of drilling II-2 (85 mmol/100 g). The average value of ion exchange capacity of natural and activated bentonite in acidic way, varies from 90 mmol/100 g for sample of natural bentonite, up to 128 mmol/100g for sample of activated bentonite with 30% H_2SO_4.

Conclusions

Based on the obtained results from experimental search, can conclude:

- The deposit of searched bentonite in Karaçevë contains the significant reserves of this mineral.
- The Karaçeva bentonite, possession very good ion exchange properties, and thermal stability, features that make be used in various field of industry.
- Acid activation, has changed the chemical composition and structure of Karaçeva bentonite.
- Acid activation, it has positive effect on improvement of ion exchange properties of bentonite.
- The values of ion exchange properties of Karaçeva bentonite, determinated with potentiometric titration, they are shown comparable with values encountered in literature.
- Natural and activated bentonite has shown the great ability of ion exchange capacity.
- The results of potentiometric experimental measurements has shown that ion exchange ability of bentonite varies with changing of pH value.

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