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CHARACTERIZATION OF BENTONITE IN KARAÇEVA DEPOSIT

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ABSTRACT

The objective of this paper is to research the reserves, lithological and chemical composition, percentage of montmorillonite and ion exchange capacity of bentonite in the Karaçeva deposit. Based on the calculations results of the geological reserves of the Karaçeva bentonite for different surface and thickness of the blocks, the total volume of bentonite reserves at the Karaçeva deposit is 832595.26 m^3. The chemical composition values of bentonite components vary for different composites. Based on the obtained results, Karaçeva bentonite is characterized by high SiO_2 content. The percentage of montmorillonite for different drilling depths ranges from (47.3-75) %. The value of ion-exchange capacity for different drilling depths ranges from (46 mmol M/100g) to (95 mmol M/100g).

Keywords: bentonite, chemical composition, ion exchange capacity, deposit, montmorillonite.

INTRODUCTION

In general, clays that contain montmorillonite as the main mineral are called bentonite. The chemical and mineralogical structure of bentonites undergoes significant transformations, during their activation, by heating to strong acids. [1]

Bentonites, which have more than 50 % of the cation exchange capacity, made up of sodium ions (Na^+), are called sodium bentonites, while calcium bentonites are those that have more than 50 % of the exchange capacity. of cations composed of calcium ions (Ca^{2+}). [2]

Potentiometric titration is applied to study the surface properties of many materials, including clay minerals. [3]

The method of adsorption of methylene blue is based on the replacement of cations in the external and internal structure of clay minerals with organic molecules.

The commercial importance of bentonites depends on the content of their clay and non-clay minerals. [4]

Non-clay minerals, mostly found in bentonites, are quartz, feldspar, zeolite, carbonate, sulfide, sulfate, oxides and hydroxides. [5]

The differences between clay minerals and the differences in their physical and chemical properties are due to the different combinations of octahedral and tetrahedral layers, as well as the electrostatic effects that chemical substitutions have on these layers. [6]

Cation exchange capacity is an important parameter, due to the fact that clay minerals vary in their reactivity. [7] In general, smectites have high cation exchange capacity. [8]

Cation exchange capacity is the mass of all cations adsorbed on the surface of clay and is usually expressed in milliquivalents per 100 grams of clay. [9] Mineralogical and chemical composition affects the properties of bentonite. Two types of bentonite exist: swelling bentonite which is also called sodium bentonite and non-swelling bentonite or calcium bentonite. [10]

Clay and clay minerals have atracted wide interest for application in various sectors including process industries, agricultural sectors, engineering and construction sectors, environmental remediation and water treatment. [11]

This is not only due to their abundance and inexpensiveness but also because of their physicochemical properties such as chemical and mechanical stability, larger specific surface area, higher charge density, layered structure, higher cation exchange capacity. [12]

MATERIALS AND METHODS

For the physico-chemical characterization of bentonites in the Karaçeva deposit, I have taken the representative samples of the composites in natural state, at different depths.

Three deep drillings have been carried out to determine the geological reserves and the quality of bentonites at the Karaçeva deposit. The first drilling was done to a depth of 25 meters, the second drilling to a depth of 33 meters and the third drilling to a depth of 24 meters. All drilling was done at a right angle of 90^0 and a diameter Φ=120 mm, the drilling was carried out without the use of solution.

In the map of the situation with a ratio of 1:1000, it is shown the order of all research works and the contouring of the surface, for the calculation of bentonite reserves (Figure-1).

The volume of bentonite and the sterile mass is calculated according to the equation:

$$V_P = S \cdot th_{average} \tag{1}$$

The total volume of bentonite and sterile mass at the Karaçeva deposit is calculated as follows:

$$V_P\,(m^3) = V_1+V_2+V_3+V_4+V_5+V_6 \tag{2}$$

$$V_{St}\,(m^3) = V_1+V_2+V_3+V_4+V_5+V_6 \tag{3}$$

The total volume of bentonite reserves is calculated according to the equation:

$$V_{reserves} = V_P - V_{St} \tag{4}$$

ARPN Journal of Engineering and Applied Sciences

Experimental research of bentonite samples at the Karaçeva field has been carried out using the following methods: fractional separation, chemical analysis, methylene blue method and potentiometric titration.

Fractional separation of bentonites is one of the enrichment methods with the montmorillonit component. For this purpose, standard methods have been used to separate fine fractions. Based on the Law of Stokes, for the laminar sedimentation of small particles, the required time has been calculated for the particles with a diameter of ≤2 μm, to pass the distance of 20 cm [13].

The chemical analysis of Karaçeva bentonites was performed on natural composite samples. The ICP-OES instrument was used for the chemical analysis of natural samples of bentonite composites. The process of mineralization of bentonite samples was carried out in the Berghof type microwave, according to the EPA-3052 method.

In the first phase, in order to selectively separate the bentonite quality layers, methylene blue research was performed.

The potentiometric titration method was used to determine the ion exchange capacity of bentonites.

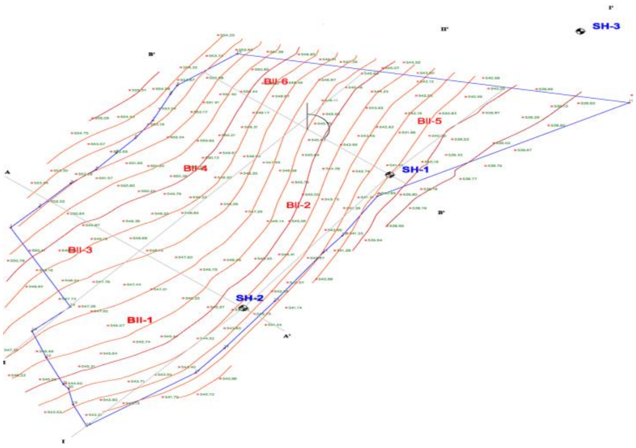

Figure-1. Map of the situation of the bentonite deposit in Karaçeva (1:1000).

RESULTS AND DISCUSSIONS

Table-1 presents the calculations results of the geological reserves of the Karaçeva bentonite according to equation (1), for different surface and thickness of the blocks.

Table-1. Calculation results of geological reserves of bentonite.

Block	S (m^2)	$th_{average\ b.}$ (m)	$th_{average\ st.}$ (m)	V_P (m^3)	V_{St} (m^3)
Block 1	6503.21	29.35	4	190869.21	26012.84
Block 2	7392.32	31.21	3.5	230714.31	25873.12
Block 3	2089.70	39.92	6.62	83420.82	13833.81
Block 4	6145.08	36.91	3	226814.9	18435.24
Block 5	1830.85	25	3	45771.25	5492.55
Block 6	6126.74	30	6.39	183802.2	39149.87

From the calculations made (Table-1), it results that the total amount of bentonite volume according to equation (2) is 961392.69 m^3, while the total amount of sterile mass volume according to equation (3) is 128797.43 m^3. The total volume of bentonite reserves according to equation (4) is 832595.26 m^3. Based on the results obtained from the table 1 shows that blocks 1, 2, 4 and 6 have higher amounts of bentonite compared to blocks 3 and 5.

In Tables (2-4) are presented the lithological composition of the Karaçeva deposit, for three drillings.

Table-2. The lithological composition of the Karaçeva deposit-Drilling I.

Quote (m)	Drilling depth (m)	Composition
538	(1-3)	Sterile mass
535	(3-6)	Bentonit mixed with quartz sand
527	(6-14)	Bentonit - green color
524	(14-17)	Bentonit compact, moisture free
523	(17-18)	Pure bentonite (dark yellow color)
520	(18-21)	Pure bentonite (dark yellow color)
517	(21-24)	Pure bentonite (dark yellow color)
516	25	Bentonite (dark blue color)

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Table-3. The lithological composition of the Karaçeva deposit-Drilling II.

Quote (m)	Drilling depth (m)	Composition
539	(1-4)	Sterile mass
535	(4-8)	Bentonit mixed with sand
531	(8-12)	Bentonite (blue to yellow color)
528	(12-15)	Bentonite (blue to yellow color)
525	(15-18)	Bentonite (blue to yellow color))
518	(18-21)	Pure bentonite (dark blue color)
519	(21-24)	Bentonite (dark blue color)
516	(24-27)	Bentonite (dark blue color)
513	(27-30)	Bentonite (dark blue color)
510	(30-33)	Bentonite (dark blue color)

Table-4. The lithological composition of the Karaçeva deposit-Drilling III.

Quote (m)	Drilling depth (m)	Composition
553	(1-3)	Sterile mass
550	(3-6)	Bentonit mixed with quartz sand
547	(6-9)	Bentonite (yellow to blue color)
545	(9-12)	Bentonite (blue to yellow color)
541	(12-15)	Impure bentonite (blue-yellow color)
538	(15-18)	Pure bentonite (dark-yellow color)
535	(18-21)	Bentonite (dark blue color)
532	(21-23)	Pure bentonite (yellow to blue color)

From the lithological composition of the Karaçeva deposit for the drilled I and III (Tables 2 and 4) it can be seen that in the shallow layers we have sterile mass and bentonite mixed with quartz sand, while from a depth of 6 m onwards the bentonite-rich layers are appear. From the lithological composition of the Karaçeva deposit for drilling II (Table-3) it can be seen that in the shallow layers we have sterile mass and bentonite mixed with sand, while from a depth of 8 m onwards the bentonite-rich layers are appear.

Table-5 presents the results of the percentage of montmorillonite for different drilling.

Table-5. Montmorillonite percentage for different drillings.

Drilling	Depth (m)	Average percentage of montmorillonite according to BM method (%)
D 1-1	(7-14) m	74
D 1-2	(15-17) m	52.05
D 1-3	(18-21) m	47.10
$D_{aver.1}$	(7-21) m	57.72
D 2-1	(15-18) m	75
D 2-2	(18-21) m	51.03
D 2-3	(21-24) m	47.3
$D_{aver.2}$	(15-24) m	57.78
D 3-1	(9-12) m	70.93
D 3-2	(12-15) m	71.2
D 3-3	(15-18) m	49.6
$D_{aver.3}$	(9-18) m	63.91

Table-5 shows that the percentage of montmorillonite varies according to the drilling depth.

The highest percentage of montmorillonite is reached in the drilling sample 2-1 (75 %), while the lowest value is reached in the drilling sample 1-3 (47.10 %).

VOL. 16, NO. 18, SEPTEMBER 2021 ISSN 1819-6608
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The average value of the percentage of montmorillonite, for the first drilling is 57.72 %, for the second drilling 57.78 %, while for the third drilling 63.91 %.

Based on the analysis, the chemical composition of the components of bentonite composites at the Karaçeva deposits has been determined (Table-6).

Table-6. Chemical compositions of composites in Karaçeva deposit.

Components	C I (%)	C II (%)	C III (%)	C IV (%)	Average value (%)
SiO_2	55.95	51.55	59.25	50.65	54.35
Al_2O_3	17.08	20.57	19.04	17.82	18.63
Fe_2O_3	4.82	7.15	4.72	6.00	5.67
TiO_2	0.58	0.98	0.58	0.74	0.72
CaO	1.30	0.92	1.09	2.07	1.345
MgO	3.02	2.07	2.58	2.94	2.65
Na_2O	0.89	0.54	1.28	0.33	0.76
K_2O	1.08	1.80	1.06	1.81	1.44
Losses	15.05	14.20	10.50	17.20	14.24

Table-7 presents the relevant reports for $SiO_2/\sum M_XO$ and SiO_2/Al_2O_3.

Table-7. Ratio $SiO_2/\sum M_XO$ and SiO_2/Al_2O_3 of composites.

Components	SiO_2 (%)	$\sum M_XO$ (%)	Al_2O_3 (%)	$SiO_2/\sum M_XO$ (%)	SiO_2/Al_2O_3 (%)
C I	55.95	28.77	17.08	1.94	3.27
C II	51.55	34.03	20.57	1.51	2.5
C III	59.25	30.35	19.04	1.95	3.1
C IV	50.65	31.71	17.82	1.6	2.84
Average value	54.35	31.21	18.63	1.74	2.92

Based on the results of the Table-6, it can be seen that the chemical composition values of the bentonite components vary for different composites.

The highest value of SiO_2 is reached in composite III (59.25 %), the lowest value in composite IV (50.65%), while the average value is 54.35%.

The highest value of Al_2O_3 is reached in composite II (20.57 %), the lowest value in composite I (17.08 %), while the average value is 18.63 %. The highest value of Fe_2O_3 is reached in composite II (7.15 %), the lowest value in composite III (4.72 %), while the average value is 5.67%. The highest value of TiO_2 is reached in composite II (0.98 %), the lowest value in composite I and III (0.58 %), while the average value is 0.72 %. The highest value of CaO is reached in composite IV (2.07 %), the lowest value in composite II (0.92 %), while the average value is 1.345 %. The highest value of MgO is reached in composite I (3.02 %), the lowest value in composite II (2.07 %), while the average value is 2.65 %. The highest value of Na_2O is reached in composite III (1.28 %), the lowest value in composite IV (0.33 %), while the average value is 0.76 %. The highest value of K_2O is reached in composite IV (1.81 %), the lowest value in composite III (1.06 %), while the average value is 1.44 %.

Table-7 shows that the highest value of the $SiO_2/\sum M_XO$ ratio is reached in composite III (1.95 %), the lowest value in composite II (1.51 %), while the average value is (1.74 %). The highest value of the ratio Al_2O_3/SiO_2 is reached in composite I (3.27 %), the lowest value in composite II (2.84 %), and the average value of this ratio is 2.92 %. Table 8 presents the results of the ion-exchange capacity for different drilling depths.

Table-8. The ion exchange capacity of bentonites at different depths.

Drilling	Depth (m)	IEC (mmol M/100g)
D 1-1	(7-14)	95
D 1-2	(15-17)	89
D 1-3	(18-21)	48
D 1-4	(21-24)	78
D 1-5	25	71
$D_{aver.1}$	(7-25)	76.2
D 2-1	(15-18)	78
D 2-2	(18-21)	75
D 2-3	(21-24)	56
D 2-4	(27-30)	77
D 2-5	(30-33)	72
$D_{aver.2}$	(15-33)	71.6
D 3-1	(9-12)	76
D 3-2	(12-15)	46
D 3-3	(15-18)	88
D 3-4	(18-21)	80
D 3-5	(21-23)	61
$D_{aver.3}$	(9-23)	70.2

Table-8 shows that the ion-exchange capacity of bentonites varies according to the drilling depth. The highest value of ion-exchange capacity is reached at drilling 1-1 (95 mmol M/100g), while the lowest value at drilling 3-2 (46 mmol M/100g).

The average value of the ion-exchange capacity for the first drilling is 76.2 mmol M/100g, for the second drilling 71.6 mmol M/100g, while for the third drilling 70.2 mmol M/100g.

CONCLUSIONS

The bentonite deposit, explored in Karaçeva contains significant reserves of this mineral, respectively 832595.26 m^3. The largest amount of bentonites is found in blocks 1, 2, 4 and 6.

With drilling holes in this deposit, two bentonite layers were found, as well as many subbentonite layers. Karaçeva bentonite has very good ion-exchange properties and thermal stability.

The best values of ion-exchange capacity are achieved in the first drilling, while the lowest value at the third drilling.

Karaçeva bentonite is characterized by high SiO_2 content, indicating the presence of a large amount of montmorillonite, especially in the first and third composition.

Taking into consideration the length of the extension of the productive layers of bentonite in the Karaçeva deposit, then their thickness and the possibility of surface exploitation, as well as the quality of the raw material, this deposit is economically very important.

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