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INVESTIGATING MINERALOGICAL AND PHYSIO-CHEMICAL PROPERTIES OF BENTONITE FOR WATER-BASED FLUIDS

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ABSTRACT

Bentonite is a well-known type of clay and the mineralogical and physio-chemical characterization of its suspensions is essential to be investigated. In this study, the mineralogical and Physio-chemical characterization of the nano-porous structure of four industrial-grade bentonite samples namely, B1, B2, B3 and B4 were investigated to determine their mineralogical properties for a specific industrial application. Instrumental analyses of samples using XRD, XRF and BET were investigated along with laboratory tests including swelling and sediment indices, surface area and cation exchange capacity as well in order to select the appropriate sample. XRF along with slurry pH shows alkali metal ions. The results indicate B4 has calcite impurity, 50 cP viscosity reading at 600 r/min, 6 value for yield point/plastic viscosity ratio and 39.05 wt% residue of diameter greater than 75 µm. B3 is the most suitable sample for water-based fluid utilization compared to B1, B2 and B4, which satisfies the best standard requirements.

KEYWORDS: Bentonite; Mineralogy; Montmorillonite; Swelling; Water-based

1. INTRODUCTION

Two different definitions are put forward by geologists for the word clay: the first refers to soil with particles smaller than 0.004 mm while another better known mineralogical term refers to a group of fine minerals with particular chemical composition. Bentonite is a clay mineral from smectite group with montmorillonite (Zhang et al., 2015) being the dominant phase comprising of one octahedral sheet sandwiched between two tetrahedral ones (Fig. 1). Montmorillonite, the main constituent of bentonite, is a nano-structured nano-porous mineral made from 2:1 (three) layer alominosilicate. As far as swelling characteristics is concerned in physio-chemical behavior of bentonite, it may be classified into two groups of swelling (sodium) and non-swelling (calcium) bentonites, both of which are being used in widely in various industries offering unique properties, including expandable layers, layer charge, base exchange capacity, thin flakes, surface area, absorption capacity, swelling capacity, viscosity and thixotropic (Chang and Leong, 2014).

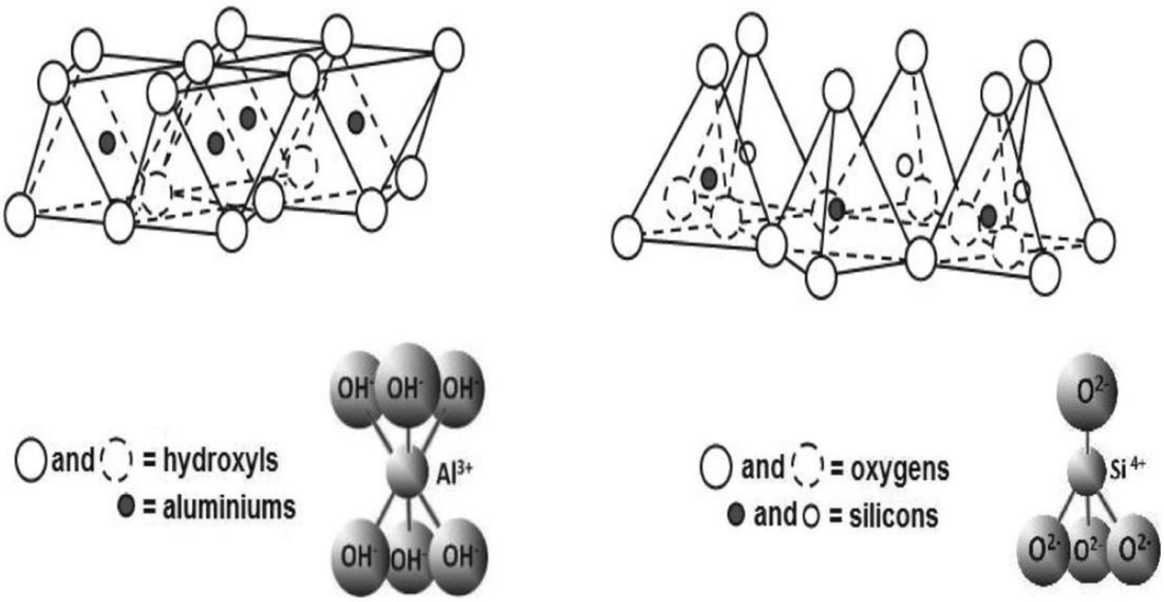

Fig. 1. Structure of octahedral sheet (left) and tetrahedral sheet (right) (Goh et al., 2011).

The applications of different bentonites include: drilling mud, foundry mold, iron ore pelletizing, adsorbents, bleaching earths, animal feed bonds, barrier clays, catalysts, deodorizers, desiccants, detergents, emulsion stabilizers, fertilizer carrier, food additive, fulling wool, herbicide carrier, insecticide and pesticide carrier, medicines, water clarification, cat litter box, etc. (Chang and Leong, 2014).

Bentonite clay suspensions are of great industrial interest because of their colloidal and rheological properties and they are abundantly used as drilling mud in oil-producing countries such as Iran. In this work, the suitability of several local industrial types of bentonite has been investigated for this application according to OCMA and API standards by obtaining data regarding their yields, plastic viscosity, residues, and screen analyses. Instruments used include: XRD, XRF and BET. We have tried to emphasize on employing data regarding supplementary dry screen analysis in understanding size distribution and characterization of bentonite samples in this study.

2. MATERIALS AND METHODS

2.1. Materials and treatments

Four types of bentonite were analyzed using XRD (X-Ray Diffraction) and XRF (X-Ray Florescence) without activation or modification, in order to identify the dominant phase. These were called B1 (Chahkeshmir, Birjand, South Khorasan, Iran), B2 (Golkan, Gonabad, South Khorasan, Iran), B3 (Chah Golestan, Gonabad, South, Iran) and B4 (Booteh Gaz, Birjand, South Khorasan, Iran). The supplier of all samples was Iran Chemiral Company. Wet screen and organic content analysis (not mentioned here) were also carried out to determine the exact phases. Samples were first ground to less than 75 µm (US standard sieve mesh No. 200, Pars Sieve, Iran; ASTM E:11-70), before being dried to a stable mass.

2.2. X-Ray Diffraction (XRD)

Mineralogical structures of bentonite samples were evaluated by XRD using a STOE, STADIMP diffractometer with Cu-Kα (λ=1.541 Å) radiation at a scan rate of 0.02° (2θ), where patterns were collected from $2\theta = 2.010^\circ$ to $2\theta = 60^\circ$.

2.3. X-Ray Fluorescence (XRF)

Determination of the compositional metals was carried out using XRF, using an Oxford ED-2000 along with Xpertease software.

2.4. BET method (surface area)

BET specific surface area of the bentonites for Mesh No. 16 was carried out by means of a Quantachrome, NOVA 2000e series instrument. The experiment was performed at 77.3 K and at the relative pressures up to $P/P_0 \sim 0.95$. Before measuring the area however, moisture and gases such as nitrogen and oxygen adsorbed on the solid surface or held in the open pores were removed under reduced pressure at 100 °C for 8 hr.

2.5. Yield point and plastic viscosity

Yield Point (YP) is the initial flow resistance of the fluid or the stress required in order to move the fluid. In other words, YP is the attractive force among colloidal particles in drilling mud. In practice, YP and Plastic Viscosity (PV) are calculated as follows:

Yield Point (YP) = Reading from a viscometer at 300 rpm – Plastic Viscosity (PV) 1

Plastic Viscosity (PV) = Reading at 600 rpm – Reading at 300 rpm 2

Where YP and PV are expressed in lb/100 ft2 and cP (centipoise), respectively. However, rheological behavior should give a better understanding of the bentonite viscosity, which unfortunately could not be performed here, but will be given in future publications.

Drilling-grade bentonite should meet the requirements of International Standards such as API and OCMA whose physical specifications are listed in Table 1.

Table 1. API and OCMA grade bentonite physical specifications.

Requirement	API Standard	OCMA Standard
Suspension properties:		
Viscometer dial reading at 600 r/min	Min. 30	Min. 30
Yield point/plastic viscosity ratio	Max. 3	Max. 6
Residue, diameter > 75 µm	Max. mass fraction 4.0 %	Max. mass fraction 2.5 %

2.6. Dry screen analysis

Taking 100g of dried bentonite sample, sieves analysis was carried out using 5 sieves with Mesh number 150, 200, 270, 325 and 400, placed in descending order, respectively. The oversized weight percentage for each sieve and the undersized tray were then accurately weighed to determine the particle size distribution.

2.7. Wet screen analysis

This was carried out by adding 14g of bentonite sample to a beaker containing 350 ml of water and stirred by magnetic agitator for 15 min. 0.2 g of sodium phosphate (supplied by Merck) with molecular mass of 358.14 was then added to the suspension and further agitated for 5 min, before being transferred and washed gently in a mesh No. 200 sieve, with tap water. The retained oversized and sieve were placed in an oven for 2 hours at 110 °C and weighed accordingly (ASTM C 117, 1995; Yıldız et al., 1999).

2.8. Sediment index

To obtain this index, 1.0 g of the original bentonite with known moisture content was added to 90 ml of distilled water in a beaker and stirred well. 10 ml ammonium chloride solution (NH_4Cl, 1 N) was then added to the mixture while stirred. The suspension was then transferred to a 100 mL graduated cylinder where the sedimentation volume was measured after 72 hours. Sediment index (S.I.) was calculated as follows (ASTM D 5890, 2002):

$$S.I. = \frac{V}{100-M} \times 100 \qquad 3$$

Where SI is Sediment index in mL/g, V is Sedimentation volume in mL and M is sample moisture in %.

2.9. Swell index

Two grams of dried bentonite was added to 90 mL of distilled water in a 100 mL graduated cylinder in 0.1g increments during approximately 30s for each increment, to ensure proper dispersion across the water surface in the cylinder. It took nearly 10 minutes before the 2.0 g sample was properly dispersed. The volume of resulting gel was measured after 16 hours and recorded as the swell index.

2.10. Methylene blue test

Specific surface area (SSA) was calculated using MB test as follows (Cokca, 2002):

$$SSA = \frac{1}{319.87}\,\frac{1}{200}\,(0.5N)A_V A_{MB}\,\frac{1}{10} \qquad 4$$

Where N is the number of MB increments added to the soil suspension solution, A_v is Avogadro's number (6.02×10^{23}/mol), and A_{MB} is the area covered by one molecule of methylene blue (typically assumed to be 130 Å^2).

3. RESULTS

3.1. X-Ray diffraction analysis

Fig. 2 illustrates the X-Ray diffraction pattern of the samples investigated. All samples show common peaks at 4.118˚, 7.999˚, 19.924˚ and 35.092˚ with large intensity.

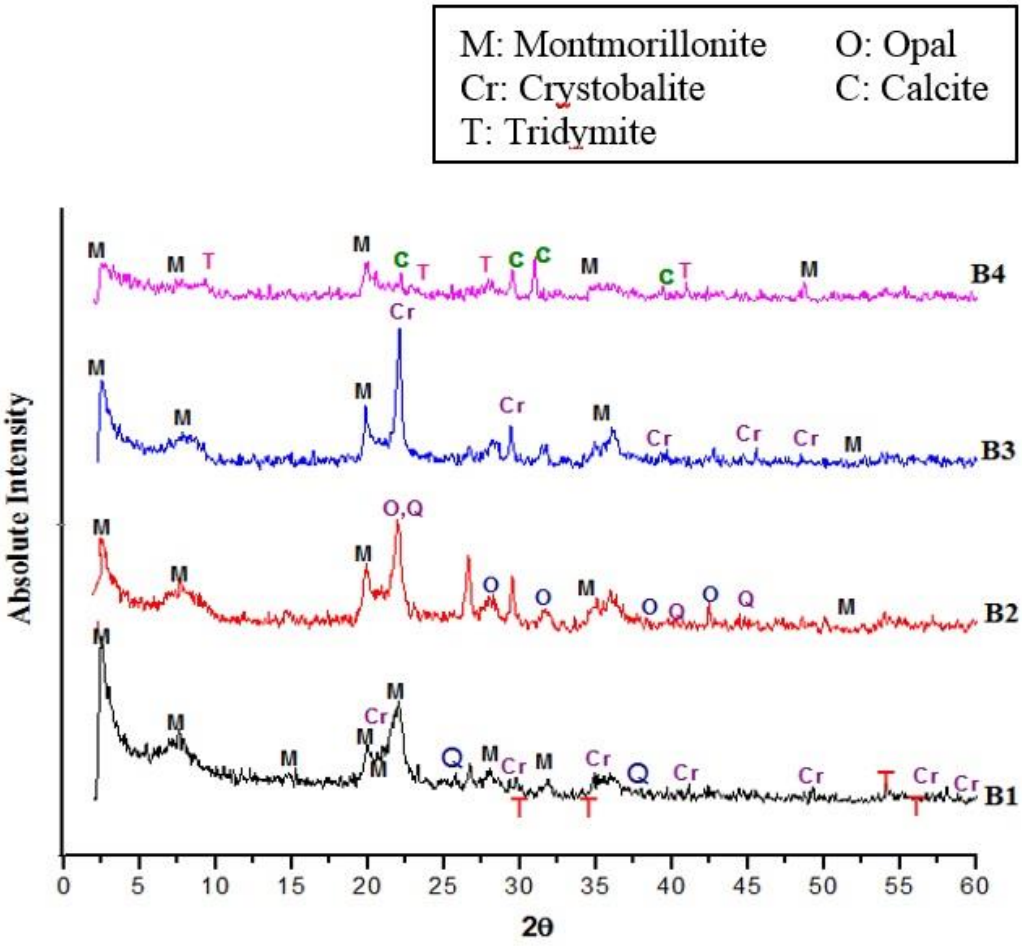

Fig. 2. XRD patterns of samples.

3.2. X-Ray fluorescence spectrometry

Major constituents present in the bentonite samples obtained from the x-ray fluorescence analysis are shown in Table 2. As far as the most important constituents, i.e. Al_2O_3 and SiO_2 are concerned, the highest and the lowest values of Al_2O_3 in wt% terms are associated with samples B4 and B1, with 12.96% and 10.29%, respectively, while for SiO_2, these are 79.03% and 59.71% for samples B3 and B4, respectively.

3.3. Specific Surface Area measurement using BET method

The specific surface areas of four bentonite samples were determined by BET method illustrated in Table 3. The maximum (85.94 m^2/g) and minimum (36.02 m^2/g) surface areas are associated with samples B1 and B4, respectively. Bentonites are nano-structured and nano-porous minerals. Amongst the samples investigated here, the maximum and minimum average pore diameters belonged to samples of B3 and B4 having sizes of 8.153 nm and 5.983 nm, respectively. In addition, the minimum pore volume was obtained for sample B4 that shows the smallest pore diameter and was 0.05387 mL/g.

Table 2. Major constituents of samples.

Sample Constituents	B1	B2	B3	B4
Al_2O_3	10.29	11.02	10.77	12.96
CaO	2.58	4.11	1.89	10.63
Cl	0.34	0.2	0.35	0.11
Cr_2O_3	-	-	-	700 ppm
Fe_2O_3	1.52	2.38	3.66	7.54
K_20	0.39	0.61	0.17	400 ppm
MgO	1.29	1.45	1.48	2.71
MnO	300 ppm	250 ppm	-	650 ppm
Na_2O	0.68	0.54	0.55	-
P_2O_3	0.42	0.49	0.52	0.94
SiO_2	78.06	73.48	79.03	59.71
SO_3	4.21	5.34	1.13	3.23
Sr	350 ppm	450 ppm	250 ppm	500 ppm
TiO_2	200 ppm	0.14	0.25	1.26
ZrO_2	-	300 ppm	450 ppm	350 ppm

Table 3. Specific surface areas, average pore volumes and diameters.

Sample	Surface area, m^2/g	Pore volume, mL/g	Pore diameter, nm
B1	85.94	0.169	7.867
B2	42.20	0.08021	7.603
B3	38.26	0.0798	8.153
B4	36.02	0.05387	5.983

3.4. Yield point and plastic viscosity

YP indicates the ability of a drilling mud to carry cuttings to the surface. Frictional pressure loss is directly related to the YP. High YP values correspond to high-pressure losses while the drilling mud is being circulated. The results obtained in this work are shown in Table 4.

Table 4. Bentonite samples physical specifications.

Sample	Viscometer dial reading at 600 r/min	Yield point/plastic viscosity ratio	Residue of diameter greater than 75 µm
B1	5	0.5	6.77
B2	8	0.33	23.54
B3	60	4	15.62
B4	50	6	39.05

3.5. Dry and wet screen analyses

The results of these analyses are shown in Table 5 and 6. These experiments obtain grain size distribution and substances insoluble in water.

Table 5. Moisture content, pH, Wet screen analysis residue, cation exchange capacity.

Sample	Moisture (wt%)	pH	Wet Screen (wt%)	CEC (mEq/100g)	MB SSA (m^2/g)	Indices	
						Swell (mL)	Sediment (mL/g)
B1	13	8.8	2.2	56	440	5	16
B2	7	8.6	7.5	50	391	8	23
B3	6	9.4	1.1	72	563	28	75
B4	10	8.8	4.3	78	612	25	73

Table 6. The Dry (Granulometric) Screen analysis of bentonite samples.

Mesh No.	+140	-140+200	-200+270	-270+400	-400
B1	1.687	5.086	19.967	8.604	63.751
B2	10.169	13.174	31.178	9.014	35.376
B3	2.852	12.773	34.189	10.728	40.207
B4	15.236	23.813	6.864	6.864	31.045

The results of wet screen analyses are shown in Table 5. Table 5 shows that the maximum substance insoluble in water is for sample B2, 7.5% and its minimum is for sample B1, 2.2%.

3.6. Swell and sediment indices

The results of the relevant experiments to achieve the swell and sediment indices explained above are listed in Table 5, where a direct relationship exist between the indices due to the montmorillonite content of bentonite samples.

3.7. M.B. test method

MB testing method allows measurement of both the SSA as well as the Cation Exchange Capacity (CEC) to be performed on the samples. Table 5 illustrates the MB test results for both SSA and CEC. Methylene Blue method has the advantage over BET in that it can also measure the internal as well as the external surface area of the samples. However, it is worth noting that the specific surface area obtained by the former is often much larger than that the latter.

4. DISCUSSION

XRD analysis revealed that common peaks of 4.118˚, 7.999˚, 19.924˚ and 35.092˚ are related to montmorillonite phase and other peaks may be attributed to impurities such as calcite, tridymite, opal and cristobalite. The existence of opal and quartz as the impurities in bentonites are clearly proved in our previous work (Ostovaritalab and Hayati-Ashtiani, 2019). Interestingly, as for various impurities in samples, calcite is the only phase apart from montmorillonite in sample B3. Concerning the highest % of montmorillonite, XRF analysis indicated that B4 has the highest amount of montmorillonite since the high amount of Al_2O_3 is mainly associated with montmorillonite (Daroughegi Mofrad et al., 2019). According to Table 2, sample B1 contains more the mineral component Na_2O and hence may be considered as Na-type montmorillonite, which explains its higher methylene blue cationic dye ($C_{16}H_{18}N_3S^+$) adsorption than that of calcium type, which in turn is responsible for the higher specific surface area measured by the BET method. Na-montmorillonite has larger face or planar surface of negatively charged surface than Ca-montmorillonite. Sample B1 has the highest external specific area while it also has the largest pore diameter and pore volume, confirming further that B1 is Na-montmorillonite.

To study the mobility of the exchangeable cations of interlayers is useful for the behavior of loosely surface bonded cations (Hayati-Ashtiani et al., 2011). The pH data could be used in determining the solubility of the exchangeable interlayer and loosely surrounded cations in bentonite. Upon dissolving in water, the released cations are hydrolyzed, leading to pH increase. Samples B3 and B4 showed the highest pH, which is expected considering their CECs results which are also high. The larger portions of cations in solution as well as their higher yields lead to higher viscosities and improving thixotropic properties, making it suitable for drilling fluid applications. The swell index values corresponded to the volume of hydrated samples were recorded in millimeters. Sample B3 and B4 also have the highest swelling index values since they release more exchangeable and loosely bonded cations in water resulting in higher swelling properties, as water molecules are soaked between the bentonite layers. One may therefor conclude that samples B3 and B4 are the most suitable ones for drilling fluid applications due to their superior pH, CEC, swelling index and yield. However, further investigations may be carried out to support this conclusion, which is behind the scope of the current study.

B1 and B2 have low viscosity, yield and Al_2O_3 content, and therefore may be classified as a bentonite with low clay minerals content montmorillonite. The yield results, XRD and XRF analyses indicate that B1 and B2 will not meet API and/or OCMA standard requirements for drilling mud applications. The nitrogen adsorption however, occurs on the external surface of fine particles, hence, the greater BET surface area of B1 amongst other samples. The results of XRD analysis indicate to us that the sample B4 has calcite impurity which is responsible for soaking water, justifying its higher swelling index value than other samples. As far as coarse and insoluble particles are concerned, these are present higher in B2 than other samples, explaining therefore, why its residue value is the highest and its viscosity is insignificant. Our tests have shown that B3 and B4 do meet the requirements of API and OCMA standards, as well as the wet screen analysis standards.

The moisture contents of all samples are consistent with the values in the API and OCMA standards. Sample B3 and B4 have high CEC and SSA compared to other samples and that they have higher viscosity and yield than others and meet adequately the API and OCMA standards requirements. Sample B3 satisfy the requirements of OCMA and API standards for moisture content, residue, viscometer dial reading at 600 r/min, yield point/plastic viscosity ratio. Therefore, this investigation showed that B3 is the most suitable sample for drilling mud amongst those studied here.

5. CONCLUSIONS

Experimental results on pH, CEC, yield, swelling index showed that samples B3 and B4 were more suitable for mud drilling than others. XRF analysis indicated that sample B4 contained the most montmorillonite percentage compared to others. Sample B3 is the most suitable sample for water-based fluid since it satisfies best the requirements of both OCMA and API.

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