Clay mineralogy, chemical and geotechnical characterization of bentonite from Beni Bou Ifrour Massif (the Eastern Rif, Morocco)



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Abstract: Bentonite clay mineral is widely present in the Gourougou Volcanic Massif and its satellites located in NE Morocco. It originated from the alteration of pyroclastic flows in shallow marine water in a lagoon lake environment (Ibourhardayn deposit). All studied samples were collected from that area and analysed accordingly in order to characterize and identify their components. Experimental techniques used included X-ray diffraction, Fourier transform infrared spectroscopy, X-ray fluorescence and the geotechnical characterization of the clay fraction and Atterberg limits. Granulometric analysis exhibited the presence of a clay fraction ($<2 \mu$ m) ranging from 9.2 to 32.4%. The geotechnical study showed that the bentonites studied were generally very plastic, with plasticity index values ranging from 19.4 to 46.6%, and are also characterized by very high liquidity limits of 37.3–67%. A high water retention capacity with water contents ranging from 8.2 to 40.7% indicated that Ibourhardayn bentonites have important swelling properties. Mineralogical results showed that all specimens were mostly composed of montmorillonite alongside other clay minerals. Some crystalline impurities were also detected by X-ray diffraction and Fourier transform infrared spectra.

Clay and clay minerals are considered as some of the oldest materials used by humans. In the modern world they are necessary for the manufacture of materials such as drilling fluids, ligands on casting moulds and precursor materials of organophilic clays, as well as for applications in vegetal and mineral oil decolouration and deodorization (Mannu *et al.* 2019). Owing to their low cost, abundance, high sorption properties and ion exchange potential, clays are good candidates as pollutant adsorbents. The classification of clay and clay minerals is based on the differences in their layered structures (smectites, illites, kaolinites and such like; Reeves *et al.* 2006; Mannu *et al.* 2019).

Bentonites consist essentially of a smectite clay mineral, which is composed of two silica sheets and one aluminium sheet (Fig. 1). The smectite

mineral is divided into two subgroups: trioctahedra (hectorite, saponite and stevensite) and dioctahedra (montmorillonite, beidellite and nontronite). This particular group of minerals is characterized by the substitution of Si⁴⁺ by Al³⁺, leaving uncompensated negative charges which are balanced by exchangeable interlayer cations (Na⁺, Ca²⁺, Mg²⁺, H⁺, etc.). Depending on the dominant exchangeable cations present, the clay may be referred to as calcium bentonite or sodium bentonite. Most bentonites are formed by the alteration of vitreous and pyroclastic ash flows, which are linked to explosive volcanism (Christidis and Scott 1997). Different bentonites are distinguished according to their mode of geological formation, chemical and mineralogical composition, grain size distribution, swelling and absorption rate, and geotechnical and textural

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O Water O Exchangeable cations



properties (Zhang 2019). Knowledge and understanding of these chemical and geotechnical properties is therefore important to target the most suitable application (Gupta *et al.* 2013; Miguel *et al.* 2019).

Bentonite deposits are distributed all over the world: the North and South American continents (Canada, Brazil), Africa (Morocco, Algiers, South African Union and Mozambique), Europe (UK) and the Eastern Mediterranean (Greece and Italy, etc.) and Australia (Western Australia, Perth). This study was conducted on bentonites originating from NE Africa, from the Beni Bon Ifrour Massif. The literature reports that these deposits were formed according to the hypothesis of the transformation of the volcanic ash and brecciated pyroclastic flow deposits (Ddani *et al.* 2005). This research aimed to study and characterize these bentonites.

Geological setting

Geographically, the Ibourhardayn deposit is part of the Beni Bou Ifrour Massif situated in the northeastern part of the Moroccan Eastern Rif Massif. The Ibourhardayn deposit is located about 30 km SW of the city of Nador. From a geological point of view, the Eastern Rif structurally represents a transitional phase between the Rifain orogen, of which it constitutes for the most part the so-called external zones (Intrarif, Mesorif and Prerif), and the middle-Atlasic front to which its southern units belong (Wildi 1983). The Beni Bou Ifrour Massif (Fig. 2) structurally belongs to the eastern native of the Mesorif zone of the Extra Rif Domain. This massif is mainly composed of sedimentary, volcanic and granodiorite rocks ranging from Mesozoic to Neogene (El Rhazi and Hayashi 2002) in age.

The Ibourhardayn deposit results from the alteration of volcanic ash and brecciated pyroclastic flows that have typical transport characteristics (Ddani *et al.* 2005). It consists of two powerful bentonite layers: the lower layer rests on Miocene marls and is covered by trachyandesite tuffs, and the upper layer in a thin volcanic ash (cineritic) facies surmounts the trachyandesite tuffs. These are hosted in a basement of sandy marl with biodetritic levels containing algae and bryozoans. Fossil fauna and flora are typical of shallow marine waters for lagoonlacustrine environments (Asebriy and Cherkaoui 1995; Ddani *et al.* 2005).

Analytical methods

Ten bentonite samples (Ib1-Ib10) were collected systematically with a 10 m pitch over the entire deposit (Fig. 3). Indeed, across the sampling points for samples Ib_1-Ib_{10} the contact with the ground moves away and the volcanic tuff mass becomes important. The Ibourhardayn bentonites were first oven-dried at 48°C for 24 h; then the samples were characterized by X-ray diffraction (XRD), particle size distribution, sedigraphy, bulk density (G_s) , liquid limit (LL), plastic limit (PL) and shrinkage limit (W_s) . The crystalline phases were identified by XRD using an XPERT-PRO diffractometer, operating at a voltage of 40 kV and an intensity of 30 mA with radiation (Cu), on the powdered sediments following the normal procedure for clay analysis (Moore and Reynolds 1989). The determination of mineral



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Fig. 2. Location map showing the region of Beni Bou Ifrour Massif within the structural areas of the Rif, northeastern Morocco. After Villand (1966).

phases was performed using X'pert HighScore based on the ICDD database. The minerals present in the studied samples were determined in a semiquantitative manner (\pm 5%) according to Cook *et al.* (1975). The intensity of the main diffraction peak of each mineral was measured and corrected by a multiplicative factor (Cook *et al.* 1975). Fourer transform infrared spectroscopy (FTIR) provides valuable information on absorbed water molecules and structural hydroxyl groups of clay minerals (Khatem 2017). The latter technique was performed using a Shimadzu FTIR-8400S spectrometer over a range of 400–4000 cm⁻¹. The samples were packaged as dispersion in a dry KBr tablet, which often complements and supplements XRD analysis.

The particle size distribution of particles with a diameter greater than 75 μ m was obtained by wet sieving using a series of sieves in decreasing order (from 4750 to 75 μ m). Particles >75 μ m were put into the water with a few grams of (NaPO₃)₆ to dissociate the possible agglomerates. For particles with a diameter less than 75 μ m, it was determined by sedigraphy with the SediGraph III device, in accordance with standards (ASTM D422-C958-E1617; Laboratory Prove, Geotechnical Centre of the University of Siena). The determination of the calcium



Fig. 3. View of the Ibourhardayn deposit in Beni Bou Ifrour region.

carbonate (CaCO₃) content was determined by the calcimetric method using Bernard's calcimeter protocol according to the French standard NF P 94-048 and confirmed by XRD analysis. The organic matter was determined by the loss on ignition (Heiri *et al.* 2001). The swelling index was performed on 2 g of bentonite powder added to distilled water. After 24–48 h, the swelling volume was measured according to the methodology described by Qlihaa *et al.* (2016).

Colloidality was measured by suspending a given amount of clay, by adding 0.2 g MgO in order to allow deflocculation, after 5 min of agitation. The mixture was then placed in a graduated cylinder. After 24 h, the supernant volume V (ml) was measured (Gillot 1968). The particle density (specific gravity of the grains) was assessed by gas pycnometry, with helium on the powdered sample passing through a 1.00 mm sieve, using Micromeritics Accu-Pyc II 1340 V1.09. The values of the total specific surface area (S_{st}) were derived from the methylene blue test using Ngoc Lan's formula (Ngoc Lan 1977; Medjnoun 2014):

$$S_{\rm st} \,({\rm m}^2 \,{\rm g}^{-1}) = 21 \times VB \,(\% \le 2 \,\mu{\rm m})$$

where $VB \text{ (ml g}^{-1}) = V_{BM}/M$, VB being the value of methylene blue, V_{BM} the amount of methylene blue adsorbed and *M* the dry mass.

The plasticity was obtained by determining the Atterberg limits: LL and PL. The plasticity index (PI) was also calculated as the difference between LL and PL of the bentonites studied. To determine the liquidity limit, the Casagrande apparatus was used (ASTM D4318); this test consists of forming a 3 mm diameter rolled sample. The PL is obtained when, simultaneously, the rolled sample splits and its diameter reaches 3 mm (ASTM D3418 1983).

The shrinkage limit was undertaken in accordance with the standards ASTM D4943 (1990). Chemical analyses of the samples were performed using an X-ray fluorescence analyser.

Results and discussion

Particle size distribution

The analysed samples show a large variation in grain size distribution. Four grain size fractions were identified in each sample: clays, silts, sands and gravel (Table 1). The clay fraction ($<2 \mu$ m) ranged between 9.2 and 32.4%, the silt fraction between 33.5 and 46.8%, the sand fraction between 26.9 and 53.8% and the gravel fraction between 0.1 and 3.9%. The granulometric curve (Fig. 4) of Ibourhardayn

Sample	${\rm Ib}_1$	Ib_2	Ib_3	Ib_4	Ib_5	Ib_6	Ib_7	Ib_8	Ib_9	Ib_{10}
Percentage gravel (60.00–2.00 mm)	0.4	0.5	0.2	0.2	0.2	0.1	0	3.9	0.3	0.6
Percentage sand (2.00–0.06 mm)	37.7	53.8	41.7	26.9	35	43.9	42.8	45.2	30.9	47.4
Percentage silt (0.06–0.002 mm)	39.7	33.5	38.8	40.5	36.9	38.7	35.3	41.7	46.8	40.6
Percentage clay (<0.002 mm)	22.2	12.2	20	32.4	27.9	17.3	21.9	9.2	22	11.4
D_{10}	< 0.001	0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.002	< 0.001	0.001
D_{30}	0.005	0.016	0.008	0.002	0.002	0.007	0.005	0.013	0.005	0.012
D_{60}	0.031	0.173	0.088	0.012	0.028	0.096	0.089	0.168	0.021	0.143
Uniformity coefficient C_{u}^{*}	>31.1	144.629	>8.09	>12.6	>28.75	>96.20	> 89.24	67.31	>21.07	95.276
Curvature coefficient C_{c}^{*}	I	1.239	I	I	I	I	I	0.418	I	0.651

Table 1. Grain size distribution of samples from Ibourhardayn deposit

 $C_{\rm u} = {\rm D}_{60}/{\rm D}_{10}; \ C_{\rm c} = D_{30}^2/(D_{10} \times D_{60})$



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Fig. 4. Cumulative curves of the all Ibourhardayn bentonite samples.

bentonite is uniform; this revealed a significant percentage of particles between 1 and 2 μ m. This fraction represents colloidal particles.

The data collected from the granulometric analysis of these samples were plotted on a ternary diagram according to the clay–silt–sand relationship using the Italian classification AGI (Italian Geotechnical Association, 1994). The Ibourhardayn bentonites exhibit two types of texture, either a sandy clay or a silty clay texture (Fig. 5).



Fig. 5. Ternary diagram of all the Ibourhardayn samples following the relation between sand, silt and clay. After the Classification AGI, 1994.

Physico-chemical parameters

The CaCO₃ contents of all Ibourhardayn bentonite samples were low (3-6%), except for Ib₃, which was about 16% by weight (Table 2). The values of organic matter content were quite low (less than 2%) with the exception of Ib_1 and Ib_2 . The total organic carbon at low concentrations did not exceed 1.25% and the total inorganic carbon values ranged from 0.2 to 3.5%. The Ibourhardayn bentonites have fairly high range of natural moisture contents (W%). from 8.2 to 40.7%. These variations in natural moisture content may be related to the amount of fine or clayey elements contained in the samples analysed. Therefore, the value of the moisture content was significant in all samples. This explains the hygroscopic nature and confirms the high value of the porosity, demonstrating that the samples are considered very porous. All samples indicated mild alkalinity with pH values between 6.67 and 9.29 owing to the presence of alkali carbonates and bicarbonates or silicates. These soluble and basic salts are generally associated with the composition of clay. The colloidality values varied between 42 and 58% and this parameter is quite important. The colloidal character reflects the coating of each clay grain with a double layer of water-soluble ions of opposite charges. Consequently the colloidal character may be due to strong ionization and the fineness of the particles involved in the original formation of the bentonite (Olihaa et al. 2016). The volume of the solid did not exceed 7 ml/2 g for all samples tested. From the volume of solid result, it can be concluded that the Ibourhardayn bentonites have significant swelling properties. In the literature the volume occupied by the solid is in the order of 5-7 ml for calcium bentonite. On the other hand, for sodium bentonites, significantly higher values are reported, ranging between 9 and 26 ml (Dixon et al. 1996).

Textural properties

The G_s , total pore volume and specific surface area, characterizing the textural properties of the samples, are presented in Table 3. The clay activity A_{CB} is the ratio between the value of methylene blue determined according to standard NF P 94-068 and the C₂ content of particles of dimensions less than 2 µm according to standard NF P94-057 (Bel hadj ali 2013). The Ibourhardayn samples have a value of methylene blue of between 11.69 and 71.56, corresponding to a clav activity from 1.19 to 1.61. These results show that the bentonites are inactive and the $A_{\rm CB}$ values vary in the interval (0.45 (Ib₅) < $A_{\rm CB} < 3.02$ (Ib₃)). The $G_{\rm s}$ values of all of the clay samples were very similar, ranging from 2.6065 to 2.6550 g cm^{-3} . This range is similar to the results of Maghnia bentonite observed by Kouloughli (2007) from northwestern Algeria.

The surface area of the Ibourhardayn bentonites ranged from 315 to 735 m² g⁻¹. The value of the specific surface area of the Ib₄ sample was *c*. 735 m² g⁻¹ (Table 3); comparing our results with the literature we find that the clays of the smectite family vary in an interval 700 m² g⁻¹ S_{st} (Smectite)–840 m² g⁻¹. We deduced that it is only possible to use the Ib₄ sample characterized by a significant amount of smectite.

Mineralogical composition

Mineralogy by XRD. The results of the XRD on disoriented powder of the 10 bentonite samples collected are shown in Figure 6 and Table 4. They are mainly composed of montmorillonite (M) (1.64% for Ib₂ to 39.96% for Ib₄), which is present in all samples. The first peak is located at a spacing of 12 Å at \mathbf{d}_{001} reflection; this shows that the natural bentonite is in the form of calcium. The other three

Sample	Ib_1	Ib ₂	Ib ₃	Ib ₄	Ib ₅	Ib ₆	Ib ₇	Ib ₈	Ib ₉	Ib ₁₀
Total CaCO ₃ content (wt%)	3	4	16	9	4	5	8	3	4	6
Total MO content (wt%)	2.51	2.08	1.92	0.86	0.52	0.92	0.22	0.03	0.04	0.012
Total organic carbon (wt%)	1.255	1.04	0.96	0.43	0.26	0.46	0.11	0.015	0.02	0.000006
Total inorganic carbon (wt%)	0.2	3.23	0.37	0.22	0.27	0.28	2.99	0.22	1.06	3.05
Water content (<i>W%</i>) PH IG (%)* <i>C</i> (%)*	40.6 6.67 7.97 44	8.2 7.59 3.58 47	40.7 9.29 5.91 48	15.54 9.13 5.94 58	9.69 8.1 6.2 56	31.71 8.7 7.1 45	11.3 9 5.03 43	15.94 9.22 4.55 42	21.86 8.33 5.33 51	32.85 7.72 5.83 50

Table 2. Results of physico-chemical parameters of bentonite from Ibourhardayn deposit

* IG (%), swelling index; C (%), colloidality.

Sample	$G_{\rm s}({\rm g/cm^3})$	$V(\mathrm{cm}^3)$	$V_{\rm p} ({\rm cm}^3{\rm g}^{-1}) \pm 0.05$	VBS	$A_{\rm CB}$	$S_{\rm st} ({ m m}^2{ m g}^{-1}) \pm 5$
Ib ₁	2.6120	2.6704	0.1821	71.56	1.61	315
Ib ₂	2.6550	3.2245	0.1883	11.69	1.19	525
Ib ₃	2.6065	2.8510	0.1813	60.54	3.02	630
Ib ₄	2.6395	2.8001	0.1861	26.94	0.83	735
Ib ₅	2.6482	3.0688	0.1874	12.68	0.45	630
Ib ₆	2.6435	3.2231	0.1867	41.33	2.38	630
Ib ₇	2.6347	3.0516	0.1854	16.32	0.74	525
Ib ₈	2.6326	2.8413	0.1851	15.72	1.71	525
Ibo	2.6363	3.0934	0.1857	25.84	1.17	420
Ib ₁₀	2.6360	2.8737	0.1856	34.35	3.01	525

Table 3. Textural properties of the bentonite samples

* G_{s} , Bulk density; V_{p} , total pore volume; V, volume; VBS, value of methylene blue; A_{CB} , clay activity; S_{st} , specific surface area.

peaks are located at 4.45 Å (\mathbf{d}_{001}), 2.567 Å (\mathbf{d}_{200}) and 1.501 Å, 1.49 (\mathbf{d}_{060}). The \mathbf{d}_{060} reflection for the samples (Ib₁, Ib₃, Ib₅, Ib₆, Ib₇, Ib₈, Ib₉ and Ib₁₀) located at 1.49 Å indicates the dioctahedral character of the smectite (Inglethorpe et al. 1993; Kumpulainen and Kiviranta 2010). The plagioclase feldspar group with calcium pole is manifested by anorthite peaks (An) (8.57-85.07%), an albite sodium pole (Alb) (33.95-73.37%) and orthoclase K-feldspar (K-Fd) (11.36-32.63%). In particular, Ib₈ is characterized by sanidine variety. Cristobalite represents 4.85-71.71% of the raw materials, with the exception of Ib₄ and Ib₃. A moderate amount of calcite (6.7-35.23%) was detected by XRD analyses; this confirms the results obtained by Bernard calcimetry. Secondary minerals that contained less than 10% were also detected, including hematite (Hm; 4.11-8.44%), magnetite (Mg; 0.25-8.85%), quartz (Qz;

0.55–7.43%), volkonskoite (VI; 0.73–4.53%), siderite (0.65–4.14%), anatase (0.41–1.08%), muscovite (Mv; 0.104–1.5%), zeolite (natrolite; 1.08–4.56%) and ekmanite (0.71–3.27%). The presence of crystalline phases in the form of impurities including phillipsite d = 5.07 Å (Ph), gypsum d = 7.5 Å (Gp) and dolomite d = 2.87 Å (Dl) is also noted.

Fourier transform infrared spectroscopy. Figure 7 shows FTIR analyses performed in the 400–4000 cm⁻¹ range of Ibourhardayn bentonite samples. The presence of clay phase absorption bands and crystalline impurities is noted. All samples are characterized by very strong multiple absorption of montmorillonite (Khenifi 2010); these bands are observed from 3620.39 to 3439.08 cm⁻¹ (Ib₁), from 3620.39 to 3433.29 cm⁻¹ (Ib₂), from 3626.17 to 3433.29 cm⁻¹ (Ib₃), from 3626.17 to 3452.58 cm⁻¹



Fig. 6. Bulk mineral composition of the bentonite samples.

		M*	An*	Alb*	Fd-K*	Sn*	Cr*	C*	Hm	Mg	Qz	Vl	S	At	Mv	Ph	Zl	EK	Gp	Dl	В
Ib1	<i>d</i> (Å)	12.19	3.21	_	-	-	-	-	2.2	-	_	_	_	-	-		_	_	_	_	_
	Weight (%)	4.35	85.07	-	_	_	-	-	8.44	-	1.06	-	0.65	0.41	_		_	_	-	_	-
Ib2	d (Å)	12.18	_	3.16	_	_	4.16	-	-	1.61	1.28	2.56	-	_	_	5.07	-	-	-	-	_
	Weight (%)	1.64	_	73.7	_	_	14.58	_	-	0.25	2.78	0.73	_	_	_	6.28	_	_	-	_	_
Ib3	d(Å)	12.87	_	_	3.27	_	1.79	2.97	_	_	1.56	2.57	2.81	1.87	_	-	_	_	7.52	_	_
	Weight (%)	20.88	_	_	22.6	_	9.18	35.23	_	_	4.81	1.49	4.14	1.08	_	-	_	_	0.53	_	_
Ib4	$d(\mathbf{A})$	4.45	2.04	_	_	_	1.74	3.12	_	_	1.27	_	_	_	9.68	-	_	_	_	_	_
	Weight (%)	39.96	8.57	_	_	_	31.3	6.7	_	_	7.43	4.53	_	_	1.5	_	_	_	_	_	_
Ib5	d(Å)	13.11	3.19	_	_	_	3.17	_	_	_	1.96	_	_	_	_	_	_	_	_	4.05	_
	Weight (%)	8.02	17.8	_	_	_	71.71	_	_	_	1.09	_	_	_	_	_	_	_	_	1.36	_
Ib6	d (Å)	13.6	3.16		3.21		1.79	_	_	_	1.3	_	_	_	9.82	_	1.62	_	_	_	_
	Weight (%)	15.34	56.04		20.3		4.85	_	_	_	1.34	_	_	_	0.62	_	1.43	_	_	_	_
Ib7	d(Å)	12.76	_	3.18	3.2	_	1.74	_	2.51		1.29	_	_	_	10.07	_	1.38	_	_	_	_
	Weight (%)	14.56	_	34	32.6	_	12.97	_	4.11		0.55	_	_	_	0.104	_	1.08	_	_	_	_
Ib8	d(Å)	12.57	_	_	_	3.26	1.79	_	_	2.52	1.34	_	_	_	9.7	_	1.61	6.33	_	_	_
	Weight (%)	33.45	_	_	_	11.36	36.27	_	_	8.85	4.9	_	_	_	0.65	_	1.21	3.27	_	_	_
Ih9	$d(\text{\AA})$	12.18	_	37	_	-	_	_	_	2.55	1.28	_	_	_	0.00	_	1.21	6 31	_	2.87	2.76
107	Weight (%)	9.98	_	73.4	_	_	_	_	_	6.23	1.02	_	_	_		_	4 56	0.71	_	$\frac{2.07}{3.04}$	1.05
Ib10	$d(\mathring{\Delta})$	12 20	32	-	_	_	_	_	_	2 57	1.02	1.68	_	_	_	_		0.71	_	5.04	1.05
1010	Weight (%)	26.2	68.47	_	_	_	_	_	_	4.53	_	0.79	_	_	_	_	_	_	_	_	_

Table 4. Representative mineralogical analyses for bentonites of Ibourhardayn deposit

Legend: M, montmorillonite; Qz, quartz; P, plagioclase; An, anorthite; Alb, albite; Zl, zeolite; Fd-K, k-feldspar; Sn, sanidine; Cr, cristobalite; C, calcite; Hm, hematite; At, anatase; EK, ekmanite; S, siderite; Vl, volkonskoite; Mg, magnetite; Dl, dolomite; Ph, phillipsite; Gp, gypsum; B, biotite; Mv, muscovite. * Main minerals.



Fig. 7. FTIR of the bentonite studied.

(Ib₄), from 3624.25 to 3433.29 cm⁻¹ (Ib₅, Ib₈), from 3626.10 to 3423.65 cm⁻¹(Ib₆), from 3616.53 to 3433.29 cm⁻¹ (Ib₇), from 3630.03 to 3431.36 cm⁻¹ (Ib₉) and from 3616.35 to 3427.51 cm⁻¹ (Ib₁₀). Between 3620 and 3640 cm⁻¹ the bands are attributed to the elongation vibrations of the binding of internal O–H groups in the structure of montmorillonite [*v*OH] at the level of the octahedral layer with two aluminium atoms located around 3620 cm⁻¹ (Ib₁), Ib₂); the peaks produced around 3626 cm⁻¹ (Ib₆) probably show the presence of magnesium in the structure of the bentonites analysed (Akcay and Yurdakoc 1999; Bouras 2003; Nayak and Singh 2007; Zahaf 2017).

The Ib₉ sample characterized by a less intense band is located at 3230 cm⁻¹, tuned to hydrogen from water bound to other water molecules in the interfoliar space of the montmorillonite (Khenifi 2010). The bands observed at about 3433 cm^{-1} are displayed the OH stretching (v_3) of the structural hydroxyl groups and the water present in the mineral (Mirzan et al. 2019). This indicates the possibility of a hydroxyl bond between the octahedral and tetrahedral layers (Silva et al. 2012; Ravindra Reddy et al. 2017). A very sharp and intense band present in all samples in the range $1635-1643 \text{ cm}^{-1}$ corresponds to the asymmetric (v_2) OH (deformation mode) of the interlayer water and a structural part of the mineral (Boufatit et al. 2007; Zaitan et al. 2008; Brahimi et al. 2015). The area around 1035.77–1105.21 cm^{-1} corresponds to the elongation vibrations of the Si-O bond in the tetrahedral structure (Zaitan et al. 2008), which is a characteristic of stratified montmorillonite silicate mineral and is attributed to the triple degenerate extension Si-O v3 (in the plane) (Ravindra Reddy et al. 2017). Generally in montmorillonite, these elongation vibrations appear at 1100 cm^{-1} in the case of sample Ib₁ but the other samples are characterized by lower frequencies linked to the presence in tetrahedral sites of trivalent ions (Al³⁺) substituted to silicon and ferric ions in octahedral sites located in clay minerals or quartz (Kumpulainen and Kiviranta 2010). Ib₃ and Ib₄ are characterized by small stretches located at 1433.11 cm⁻¹ is suitable for stretching CO₃, indicates the presence of carbonate impurities (Kumpulainen and Kiviranta 2010). The localized band from 914 to 918 cm⁻¹ corresponds to the AlA-10H vibrations assigned to clay minerals, either smectite or kaolin, present in all spectra of the samples (Akcay and Yurdakoc 1999). The weak band owing to AlMgOH at 844–840 cm⁻¹ is present in all samples. The bands located at 700 and 723 cm⁻¹ indicates Si-O stretching owing to the presence of quartz. Modes of Si-O and Si-O-Al of the clay minerals occurred at 621–624 cm⁻¹ (Ib₁, Ib₂, Ib₃ and Ib₄; Srasra et al. 1994; Ravindra Reddy et al. 2017). The small bands that are produced in the 466 cm^{-1} region correspond to Si-O-Al.

Geotechnical properties

Albert Atterberg in 1905 defined various physical constants comprising consistency limits for finegrained soils. The upper limit of viscous flow, the liquid limit, the sticky limit, the cohesion limit, the plastic limit and the shrinkage limit have all been defined as the Atterberg limits. The LL is defined by the water content, which in a soil corresponds to the limit between the semi-liquid state and the plastic state. It is an indicator of the binding property of a bentonite that will cause the flow of a bentonitewater mixture (Inglethorpe et al. 1993). The PL describes the quantity of water from a soil to the limit between the plastic state and the semi-solid state, marking the transition from the plastic state to the solid state with shrinkage, and the shrinkage limit is the transition from the solid state with shrinkage to the solid state without shrinkage (Table 5; Avenard 1961; ASTM D3418 1983).

Plasticity index. The plasticity of clay varies from one mineral to another and expresses its ability to deform when mixed with water. It is essentially dependent on the grain size, the type and structure of clay minerals and the presence of orgnic matter. Figure 8 shows that Ibourhardayn bentonites are highly plastic. The PI varies between $(19.4\% \text{ (Ib}_2))$ < IP < 46.6% (Ib₅)) and the PL (37.3% (Ib₂) <PL < 67% (Ib₄)). Bentonites are characterized by very high LLs $(37.3\% (Ib_2) < LL < 67\% (Ib_4))$. According to the literature two conclusions can be drawn. Firstly from the values of the PI the Ibourhardayn bentonites can be classified as very plastic. Secondly the liquid limit test can be a sensitive indicator of the response of a Ca-bentonite (100% < LL< 200%) or Na-bentonite (200% < LL < 750%). Therefore, from our results we conclude that the

 Table 5. Atterberg limits obtained for the studied samples

Sample LL PL PI W_s V_w (%) (%) (%) (%) (g cm ⁻³) Ib1 86.8 53.4 33.4 15.7 2.04 Ib2 56.4 37.3 19.4 23.5 1.88 1.88 Ib3 80 52.2 27.8 18.1 1.88 1.44 Ib4 105.6 67 38.6 12 2.11 1.55 Ib5 107.7 61.1 46.6 17.9 1.89 1.55 Ib6 90.7 44.8 45.9 15.5 1.87 1.57 Ib7 82 48.1 33.9 15.9 1.95 1.72 Ib8 69.9 44.9 25 31.5 1.72 1.59 85.7 56.2 29.5 11.1 2.06 1.50 Ib10 73.2 49.3 23.9 21 1.77 1.77							
Ib1 86.8 53.4 33.4 15.7 2.04 Ib2 56.4 37.3 19.4 23.5 1.88 Ib3 80 52.2 27.8 18.1 1.88 Ib4 105.6 67 38.6 12 2.11 Ib5 107.7 61.1 46.6 17.9 1.89 Ib6 90.7 44.8 45.9 15.5 1.87 Ib7 82 48.1 33.9 15.9 1.95 Ib8 69.9 44.9 25 31.5 1.72 Ib9 85.7 56.2 29.5 11.1 2.06 Ib10 73.2 49.3 23.9 21 1.77	Sample	LL (%)	PL (%)	PI (%)	Ws (%)	$V_{\rm w}$ (g cm ⁻³)	Ic
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Ib1	86.8	53.4	33.4	15.7	2.04	1.4
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Ib2	56.4	37.3	19.4	23.5	1.88	2.5
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Ib3	80	52.2	27.8	18.1	1.88	1.4
Ib5 107.7 61.1 46.6 17.9 1.89 Ib6 90.7 44.8 45.9 15.5 1.87 Ib7 82 48.1 33.9 15.9 1.95 Ib8 69.9 44.9 25 31.5 1.72 Ib9 85.7 56.2 29.5 11.1 2.06 Ib10 73.2 49.3 23.9 21 1.77	Ib4	105.6	67	38.6	12	2.11	2.3
Ib6 90.7 44.8 45.9 15.5 1.87 Ib7 82 48.1 33.9 15.9 1.95 1.95 Ib8 69.9 44.9 25 31.5 1.72 1.95 Ib9 85.7 56.2 29.5 11.1 2.06 1.91 Ib10 73.2 49.3 23.9 21 1.77	Ib5	107.7	61.1	46.6	17.9	1.89	2.1
Ib7 82 48.1 33.9 15.9 1.95 Ib8 69.9 44.9 25 31.5 1.72 Ib9 85.7 56.2 29.5 11.1 2.06 Ib10 73.2 49.3 23.9 21 1.77	Ib6	90.7	44.8	45.9	15.5	1.87	1.7
Ib8 69.9 44.9 25 31.5 1.72 15 Ib9 85.7 56.2 29.5 11.1 2.06 15 Ib10 73.2 49.3 23.9 21 1.77	Ib7	82	48.1	33.9	15.9	1.95	2.1
Ib9 85.7 56.2 29.5 11.1 2.06 3 Ib10 73.2 49.3 23.9 21 1.77	Ib8	69.9	44.9	25	31.5	1.72	2.2
Ib10 73.2 49.3 23.9 21 1.77	Ib9	85.7	56.2	29.5	11.1	2.06	2.2
	Ib10	73.2	49.3	23.9	21	1.77	1.7

LL, Liquidity limit; PL, plasticity limit; PI, plasticity index; W_s , shrinkage limit; V_w , maximum volumetric weight; I_c , consistency index.



Fig. 8. Plasticity map of Casagrande for the classification of fine-grained soils. CH, Inorganic clays of high plasticity; CL, mineral clays with low to medium plasticity; ML/OL, inorganic silts and very fine sands with very low plasticity and organic silts and silt–clay mixtures of low plasticity; OH/MH, organic silts and clays of medium plasticity to be raised and inorganic silts.

Ibourhardayn materials are of the Ca-bentonite type (Inglethorpe *et al.* 1993; Zeng *et al.* 2019). Consequently, the differences in the plasticity of the samples are due to the variation in grain size distribution (Table 1) and also the mineralogical composition. This is to say that samples with high clay content have a high plasticity, whereas the silt fraction (Ib₂) is characterized by relatively low plasticity. Consistency indices (I_C) vary in the range of 1.4–2.5,

and it is noted that all samples had $I_{\rm C}$ values greater than 1. From W < PL, with the comparison of the natural water content (*W*%) and plasticity and liquidity limits, it is deduced that the condition of all samples is hard or very stiff for the Ibourhardayn bentonites.

The shrinkage limit. Figure 9a shows the variation of the volume as a function of the water content of the



Fig. 9. (a) Volumetric shrinkage curve for the Ib_6 sample; (b) variation in volumetric weight according to water content.

Weight (%)	Ib_1	Ib ₂	Ib ₃	Ib ₄	Ib ₅	Ib ₆	Ib ₇	Ib ₈	Ib ₉	Ib ₁₀
Ca	16.77	22.2	17.45	_	16.65	14.01	17.18	16.06	14.66	15.56
Fe	43.08	44.36	37.41	91.6	49.43	30.93	47.11	45.62	50.18	46.34
Al	7.93	6.53	13.47	_	6.29	4.81	7.98	9.75	6.66	9.03
Si	17.81	12.21	18.24	_	11.73	7.94	12.55	13.68	14.11	13.9
Mn	0.68	3.31	0.66	1.1	0.99	0.18	2.12	1.28	1.46	1.15
Κ	5.53	5.96	5.13	_	5.46	4.06	4.74	4.94	4.93	4.63
Sr	0.57	_	0.39	_	0.85	0.68	_	0.65	0.33	_
Р	4.63	3.07	4.44	_	3.19	2.12	3.29	3.49	3.77	3.92
S	2.01	1.45	1.95	_	1.27	1.04	1.63	1.58	1.7	1.87
Th	0.11	0.07	0.099	0.42	0.047	0.033	0.081	0.11	0.12	0.12
Rb	0.07	_	0.06	_	_	_	0.054	0.055	0.03	0.059
Y	0.036	0.027	0.033	0.085	0.023	0.033	0.11	0.054	0.03	0.06
Mg	_	_	_	_	_	32.1	_	_	_	_
Zn	0.32	0.5	0.26	0.76	1.06	0.55	0.76	0.46	0.73	1.6
Sr	_	1.19	_	0.93	_	_	0.65	_	_	0.59
Ti	_	2.53	_	3.98	2.15	1.25	1.33	1.83	1.24	0.68
Pb	_	0.095	0.033	0.084	0.094	0.05	0.027	0.027	0.03	_
Zr	0.438	0.35	0.33	0.93	0.73	0.18	0.35	0.38	_	0.42
Мо	_	_	_	0.085	_	_	_	_	_	_
V	_	0.53	_	_	_	_	_	_	_	_
As	-	0.023	-	-	-	-	-	0.027	-	0.029

 Table 6. Chemical analysis of bentonite

material (shrinkage curve) for the initially saturated material. A dehydration test at different temperatures, 50 and 105°C, was carried out on the Ibourhardayn bentonite samples, deriving a moisture content of 8.2–40.7%. The W_s of Ibourhardayn bentonite varied from 11.1 to 31.5%. For an example, sample Ib₆ could be organized by two lines with an intersection corresponding to the same shrinkage limit of about 15.5%, which corresponds to a maximum volumetric weight of about 1.87 g.cm^{-3} (Fig. 9b). According to Altmeyer's method (1955), the swelling potential is based on a function of the shrinkage limit W_s and the critical potential (Ib₄, Ib₉), whose values vary from $10 < W_s < 12$. On the other hand, the samples have W_s % values of greater than 12 characterized by low potential (Djedid et al. 2001).

Chemical composition

From a chemical point of view, the data in Table 6 show that Ibourhardayn bentonites are characterized by high amounts of iron varying ranging from 30.93to 91.6%, typically associated with hematite (Fe₂O₃) and magnetite (Fe₃O₄), both identified by XRD analysis. The Si content varying between 7.94 and 18.24% is associated with the follwing minerals: quartz, silicate, cristobalite and feldspar. Samples are characterized by a medium content of calcium ranging from 14.01 to 22.2\%, which is attributed to calcite identified both by XRD analysis and by the Bernard calcimeter. On the other hand, the

aluminium content is between 4.81 and 13.47% and calcium is part of the mineralogical composition of montmorillonite (Na, Ca)_{0.3}(Al, Mg)₂Si₄O₁₀ $(OH)_2 \cdot (H_2O)$, as identified by XRD analysis and FTIR spectrum. Magnesium was identified only in sample Ib6 at 32.1%. Mg²⁺ ions can be substituted by Al^{3+} ions in the octahedral layers, which explains the decrease in aluminium content in sample Ib₆ offset by magnesium. The potassium content of 4.06-5.96% can be attributed to clav minerals, micas, as well as the role of charge deficit compensating for ions produced when replacing silicon by aluminium (Caillère et al. 1982; Parra et al. 1990). The low titanium content, from 0.68 to 3.98%, indicates the presence of anatase, TiO₂. Manganese ranges from 0.18 to 2.12% and can be attributed to ekmanite $(Fe^{2+}Mg_{0.4}Mn^{2+}{}_{0.3}Fe^{3+}{}_{0.3}Si_3AlO_{10}(OH)_2\cdot 02(H_2O)$ as identified by XRD analysis.

Conclusion

The Nador bentonite (Morocco) is diverse in terms of its clay and associated mineralogy. The mineralogical composition consists of a mixture of variable proportions of montmorillonite, anorthite, albite and orthoclase feldspar, with some calcite and impurities. The bentonites studied are generally composed of fine-grained particles with high plasticity with a low organic matter content. Chemical analyses on Ibourhardayn bentonite have shown the preponderance of the calcium percentage, which has allowed it to be classified in the category montmorillonite

pole calcium, which indicates that this bentonite has a very high water retention capacity and therefore a high swelling capacity. On the other hand, after comparing our results with those for bentonites from Maghnia (Algeria) (Bouras 2003; Boufatit et al. 2007; Kouloughli 2007; Benyounes et al. 2010; Youcef et al. 2011; Ben Hamouda et al. 2017), it is noticed that there is a similarity between these two bentonites, because of similarity of their geological setting, and consisting of a series of Cretaceous and Tertiary sediments with interlayer pyroclasts. The results obtained in this preliminary characterization study lead us to consider future research, focusing on the experimentation of these raw materials on a semi-industrial scale to evaluate in particular their use as absorbents.

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