
Physico - chemical and mineralogical characterization of a Moroccan bentonite (Azzouzet) and determination of its nature and its chemical structure

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Abstract: This study concerns the results of Physicochemical and mineralogical characterization of a Moroccan bentonite (bentonite Azzouzet) and determination of its nature and its chemical structure. Several techniques were used; in particular X-ray diffraction (XRD), scanning electron microscopy coupled with EDX microanalysis (SEM-EDX), differential thermal and gravimetric analyses (DTA-TGA) and finally infrared Fourier transform (FTIR) and X-ray fluorescence (XRF). The bentonite fine fraction (< 2 μm in size), was characterized by BET method for specific surface area, and a cation- exchange capacity. The X-ray diffraction analysis supplemented by gravimetric analysis showed that Azzouzet bentonite is primarily (smectite) (49 wt %) with the presence of feldspar (34 wt %), Quartz (5 wt %), magnetite (7 wt %) and amorphous iron oxide (3 wt %). It has a cation- exchange capacity of 73,3 meq/100g and a specific surface area by using surface area analyser and N_2 gaz was used as adsorbate under atmosphere of 31 m^2/g . The structural formula calculated for bentonite has shown that the montmorillonite has a high charge density. SEM-EDX, X-ray, chemical analysis and Infrared spectroscopy demonstrated that this montmorillonite contains iron Fe^{3+} in the octahedral sheet. The origin of the charge sheets is tetrahedral (Si_4) ($\text{Al}_{2.12}\text{Mg}_{0.15}$), with the montmorillonite character of the bentonite (15%) is present (less than 50% octahedral charge) with a phase rich in iron.

Keywords: XRD, (DTA-TGA) (SEM-EDX), FTIR, FX, Bentonite, Azzouzet, Montmorillonite, Morocco

1. Introduction

The important deposits of white and easily accessible Azzouzet clay in Morocco is located in the northern part, particularly in the Nador region (see map location of the deposit on Azzouzet Figure 1). The bentonites have been used in food technology such as bleaching earth, and clarification of mine, animal feed bond, and food additives [1-2-3].

In this paper, we report the results of physico-chemical and mineralogical study conducted on a clay samples (bentonite) taken from the Azzouzet deposits. The study focused on the determination of its nature and its chemical structure. These bentonites may contain other clay and non clay minerals as impurities, such as 2:1 layered, hydrated aluminium silicates belonging to montmorillonites which are dioctahedral smectites in which isomorphous substitution occurs. Aluminium and sometimes iron

substitutes for silicon in the tetrahedral sheet and iron or magnesium ions for aluminium in the octahedral sheet [4]. As a result of the isomorphous substitutions, crystalline order is reduced and structural imperfections arise. Often in the same deposit, a range of montmorillonite clays can be found with different isomorphous substitutions and variation in structural disorder.

Low iron montmorillonites are exemplified by the so called Cheto montmorillonites which are iron free. The Wyoming type montmorillonites are examples in which there is some replacement of the aluminium by iron. In beidellites, aluminium is partially substituted for silicon in the tetrahedral sheet. These differences in the dioctahedral structure are reflected in variations in the infrared spectra [5] and are characterised by the well resolved OH deformation bands at 915 cm^{-1} for AlAlOH and 840 cm^{-1} for AlMgOH , in the Wyoming montmorillonite this band occurs at 890 cm^{-1} for $\text{AlFe}^{\text{iii}}\text{OH}$.

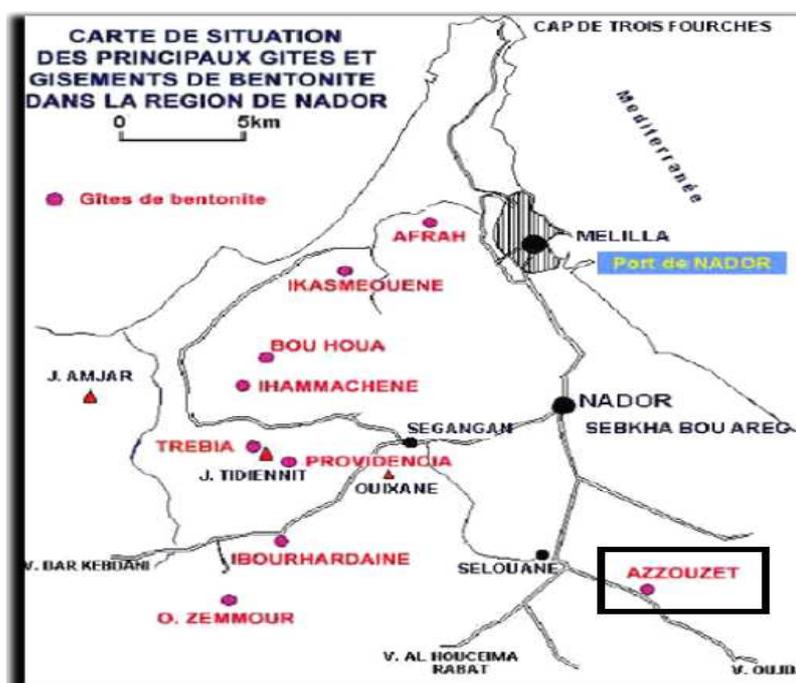


Figure 1. location map of bentonite Azzouzet.

2. Experimental Procedure

The crude clay as well its fine fraction (less than $2\mu\text{m}$ in size), which is isolated by sedimentation following the experimental procedure [19], have been investigated by means of X-ray diffraction (XRD), thermal analysis (DTA and TG), Infrared spectroscopy (IR), Fluorescence X (FX), Scanning electronic microscopy (SEM-EDX).

Since the mineral composition associated with bentonites is variable, we felt it necessary to use XRD analysis. Spectrometric analysis by SEM, EDX was performed at the Laboratory IFM NIS-materials chemistry at the University of Turin (Italy). This SEM-EDX can detect chemical elements. The joint use of the micrograph, the X-ray fluorescence spectrometry allowed us to obtain the most probable chemical composition of Azzouzet bentonite.

The X-ray analysis was performed by a diffractometer (45kv, 40mA whose technical characteristics are as follows: Type configuration PW3064, Goniometer type PW3050/60; rotating sample holder (spinner) type PW3064, using either a copper or a cobalt anticathode. The thermograms were realized by a XPERT-PRO operating under the following conditions: heating rate = $10^\circ\text{C}/\text{min}$, sample weight = 40 mg, atmosphere: air. The fine fraction the bentonite ($< 2\mu\text{m}$ in size), was characterized by a cation- exchange capacity (CEC = 73,3 meq/100g) and specific surface area ($31\text{ m}^2/\text{g}$) by BET. The procedure generally used for these measurements is based on multilayer adsorption theory of Brunauer, Emmet and Teller (BET) which is adapted to analysis of the adsorption of non polar gases on non-porous solid. To meet these accordingly, it is important to remove

any adsorbed gases by heating before measuring the adsorption isotherm of non polar gases (nitrogen).

Fourier transform infrared spectra (FTIR) of samples were obtained on a spectrometer with a DTGS detector and a KBr beam splitter, the KBr pressed-disk technique (1 mg of samples and 200 mg of KBr) was used, the spectra were recorded in the region $4000-400\text{ cm}^{-1}$.

3. Results and Discussion

3.1. Analysis XRD X-Ray

3.1.1. Associated Minerals

In some favorable cases, the associated minerals in the bentonite can be identified by their main peaks. Thus, as shown in the diffractogram presented in Figure 2 on the raw Azzouzet bentonite can easily identify:

- * the montmorillonite symbolized by Mt represents (49 wt %);
- * Feldspar symbolized by F whose main peak is located around 27.7° represents (34 wt %);
- * Quartz symbolized by Q whose main peak is located at 26.5° represents (5 wt %);
- * magnetite symbolized by M, whose main peak is located at 35.5° represents (7 wt %).

The relative contents of montmorillonite, feldspar, Quartz and magnetite determined by volumetric dosage (attack with acid, solubilization, neutralization, precipitation and calcination ... etc), With :

$$100\% \text{ Raw Bentonite} = X\% \text{ montmorillonite} + Y\% \text{ Feldspar} + Z\% \text{ Quartz} + R\% \text{ Magnetite.}$$

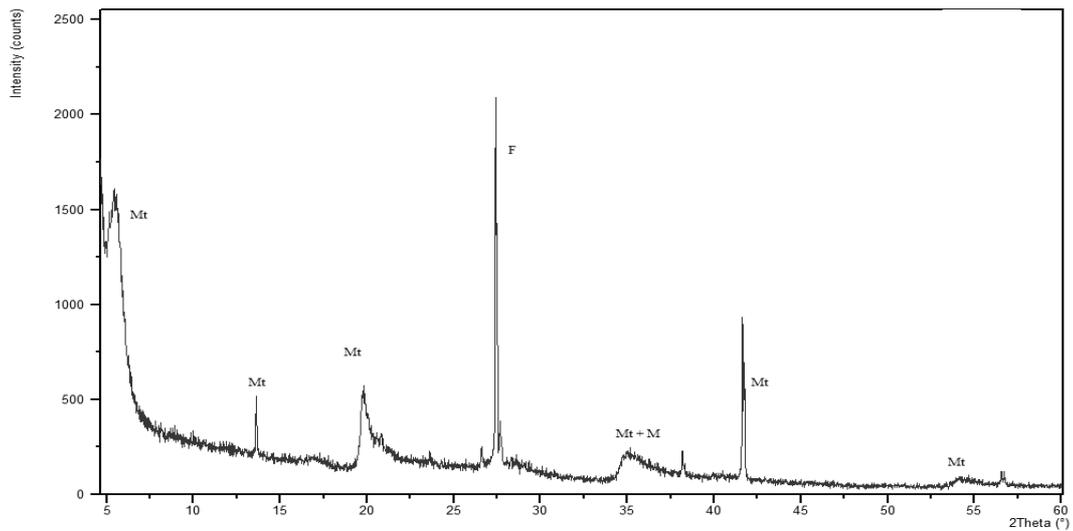


Figure 2. X-ray diffraction of powder Azzouzet bentonite.

3.1.2. Identification of Bentonite Azzouzet

For bentonite sedimented less than $2\mu\text{m}$ (Figure 3), allows an enrichment of bentonite minerals associated with fine particle size, namely montmorillonite, feldspar and silica.

The XRD analysis leads us to conclude that Azzouzet bentonite is indeed a well crystallized smectite (montmorillonite).

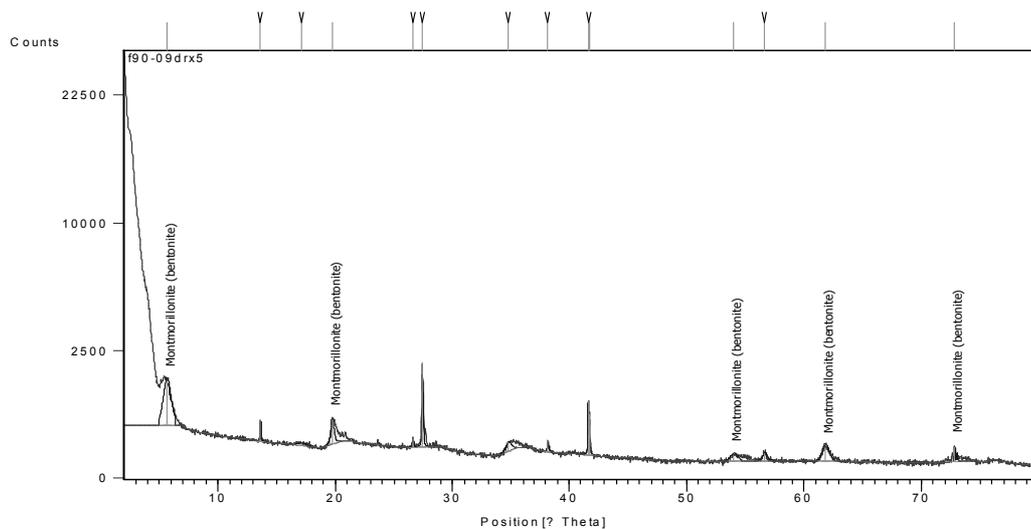


Figure 3. Diffractogram of sedimented fine fraction ($< 2\mu\text{m}$) of Azzouzet bentonite.

Table 1. Card ASTM (American Society for Testing and Materials) of montmorillonite (bentonite Azzouzet).

Pos. [2Th.]	Height [cts]	FWHM [2Th.]	d-spacing [Å]	Rel. Int. [%]	Tip width [2Th.]	Matched by
5.6761	1015.96	0.6691	15.57038	53.60	0.8029	00-003-0015
13.6195	301.56	0.0669	6.50178	15.91	0.0803	
17.1422	26.00	0.8029	5.17280	1.37	0.9635	
19.7338	343.90	0.2676	4.49894	18.14	0.3212	00-003-0015
26.6066	94.95	0.1004	3.35035	5.01	0.1204	
27.4094	1895.40	0.0669	3.25402	100.00	0.0803	
34.7234	83.07	0.5353	2.58354	4.38	0.6424	
38.1801	111.31	0.1004	2.35722	5.87	0.1204	
41.6293	826.95	0.0612	2.16774	43.63	0.0734	
41.7474	535.92	0.0612	2.16726	28.27	0.0734	
53.9970	35.25	0.6528	1.69682	1.86	0.7834	00-003-0015
56.6444	44.60	0.3264	1.62363	2.35	0.3917	
61.7764	101.30	0.4896	1.50049	5.34	0.5875	00-003-0015
72.8431	110.54	0.0816	1.29741	5.83	0.0979	00-003-0015

The plug ASTM 03-0015 indicates that the bentonite in question is a montmorillonite, From these, we calculated the content of the montmorillonite our mesh density D, taking as the value of 2.11, a value obtained by fitting densitometric developed in the laboratory which takes into account the porosity of the bentonite, The molecular weight

$$(2.60 \text{ SiO}_2, 1.38 \text{ Al}_2\text{O}_3, 0.21 \text{ CaO}, 0.10 \text{ MgO}, -0.28 \text{ Fe}_2\text{O}_3, 0.02 \text{ K}_2\text{O}, 1.20 \text{ H}_2\text{O})_n \quad (1)$$

The calculated molecular weight W_{cal} would equal the weight measured W_{mes} that if we give the value $n = 1.54$.

$$4 \text{ SiO}_2, 2.12 \text{ Al}_2\text{O}_3, 0.32 \text{ CaO}, 0.14 \text{ K}_2\text{O}, -0.18 \text{ MgO}, 0.16 \text{ Fe}_2\text{O}_3, 1.60 \text{ H}_2\text{O} \quad (2)$$

3.2. Analysis by SEM-EDX and XRF

EDX microanalysis shows at a first look qualitatively the structural elements of clay, namely silicon, aluminium, elements of substitution of aluminium (Mg^{2+} , Fe^{3+}) and oxygen, and the interlayer cations. Once these elements are characterized, it is important to measure them quantitatively and qualitatively. EDX microanalysis results listed in Table 2 correspond to particles of raw bentonite figure 4a, the corresponding energy spectrum is that of Figure 4b and the Fine fraction less than $2\mu\text{m}$ Figure 4c.

X-ray fluorescence (XRF) of sedimented fine (less than $2\mu\text{m}$) Azzouzet bentonite shows a significant percentage of silicon oxide (SiO_2) and aluminum oxide (Al_2O_3), and a

thus measured is:

$W_{\text{mes}} = 540.46\text{g/mol}$, From the number of ions million shown in last column of Table 2 and taking into account the number of water molecules assayed ($1.20 \text{ H}_2\text{O}$) during thermal analysis (DTA-TGA), one can write:

The contents of the cell would be:

low percentage K_2O (Table 3) which approves that it is a bentonite which belongs to the families of montmorillonite.

Table 2. Results of chemical analysis on raw bentonite Azzouzet.

Element	% Weight	% Atomic	% oxide	Formulae	Number of ion
Ca K	1.38	1.62	3.11	CaO	0.21
Mg K	2.09	1.92	2.78	MgO	0.10
Al K	11.91	9.75	15.43	Al_2O_3	1.38
Si K	28.93	21.08	52.83	SiO_2	2.60
K K	1.23	0.71	0.31	K_2O	0.02
Fe K	3.65	2.92	3.35	FeO	0.28
O	48.42	62.49			8.00
Total	100.00				
Number of Cations					4.59

Table 3. Characterization by Fluorescence X of bentonite Azzouzet sedimented less than $2\mu\text{m}$.

Compounds	SiO_2	Al_2O_3	MgO	Na_2O	CaO	SO_4	K_2O	L.I.*
Content.%	53.44	17.32	3.66	1.01	1.75	0.04	0.28	14.23

*L.I : Loss on ignition at 1000°C .

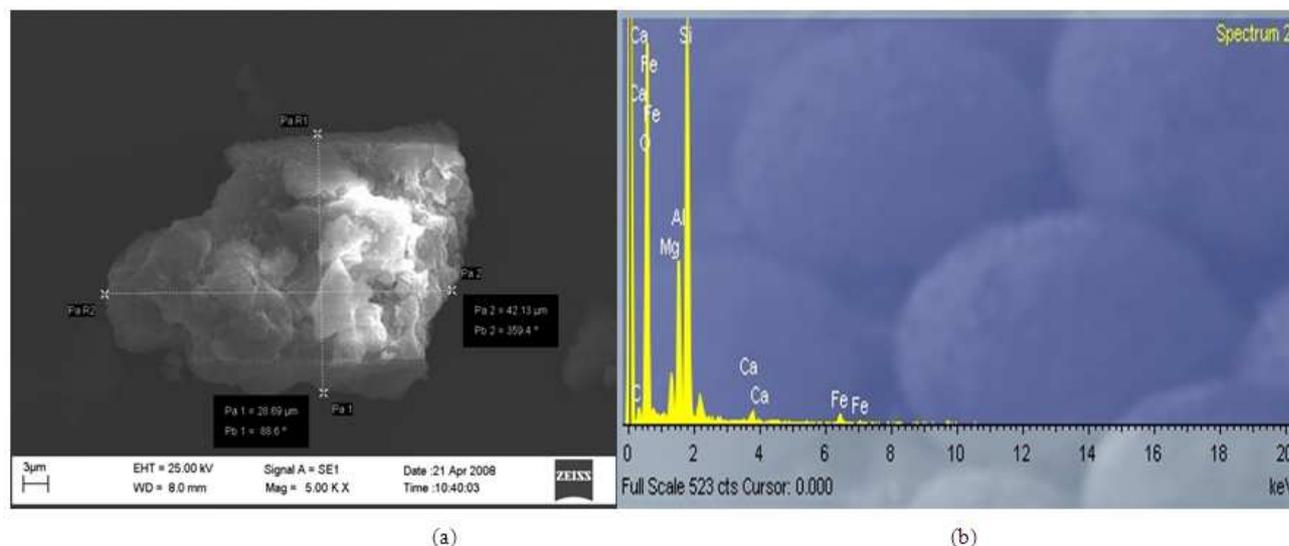


Figure 4. Micrometer particle of Azzouzet bentonite analyzed (a) and Energy spectrum of the particle analyzed (b).

3.3. Thermal Analysis

This is primarily a complementary method to X-ray diffraction. TGA-DTA is very useful, especially in the case of clay groups characterization.

Firstly the weight loss recorded in the thermogravimetric analysis weight of gross Azzouzet bentonite involves three steps as shown in Figure 5. A first loss between 25°C and 150°C , a second between 550°C and 750°C , the third between 800°C and 950°C .

Figure 5 shows a first endothermic peak at 100°C. We initially attributed flash interlayer water which represents about 13.50 % by weight of the clay [11-12].

The endothermic reaction that occurs in the range 550°C-750°C is due to the progressive departure of water molecules bound to interlayer cations (4,79% weight loss). This loss corresponds to the equivalent of 1.20 H₂O ($0.0479 \times 2.11 \times 215.4 / 18 = 1.20$). This water structure may be eliminated without destroying the clay network. Indeed sedimented Azzouzet bentonite (< 2µm) heated at 600°C could be rehydrated at room temperature.

Both reactions endo / exo in sequence, located in the

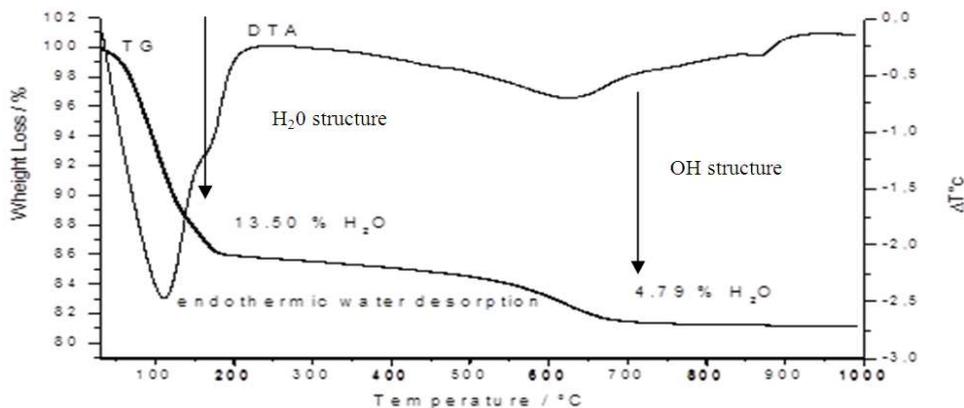


Figure 5. Curves of differential and gravimetric thermal analyses of raw Azzouzet bentonite.

3.4. Infrared Analysis

The infrared absorption spectrum of Azzouzet bentonite sedimented at room temperature (Fig. 6) shows:

- Two absorption bands in the region 3480 -1639 cm⁻¹ due to water molecules [14-15].
- Bands occurring at 3612 cm⁻¹ correspond to AlAlOH stretching vibrations of smectites [13].
- Absorption bands in the region 1220-1000 cm⁻¹ due to SiO group corresponding to the tetrahedral environment of the inner layer TOT [16].
- Three absorption bands in the region 1000 - 800 cm⁻¹ due to isomorphous substitutions of Al-MOH type corresponding to the internal environment of the octahedral layer TOT where M can be Al, Fe, Mg [17-18-20].
- Two absorption bands in the region 650-430 cm⁻¹ due to isomorphous substitutions TOT type corresponding to the tetrahedral environment of the inner layer TOT where T can be Al, Si [6-14-15].

Thus the phenomenon of dehydration that occurs in the range 25-630°C can be distinguished:

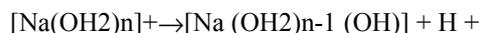
* The free water molecules located between the layers TOT characterized by bands located at 3480 cm⁻¹ (stretching vibration) ν (H₂O) and to 1639 cm⁻¹ (bending vibration) δ (H₂O). It should be noted that these frequencies are similar to the frequencies of water molecules in the liquid state. DTA-TGA curve of Figure 5 shows that this type of water molecules in the free state desorb instantaneously to 100°C.

* Bounds of water molecules on the surface layer TOT

range 700°C- 950°C are due to the departure of structural OH groups (4,79% loss in weight). This loss is the equivalent of 1.09 OH molecules ($0.0479 \times 2.11 \times 215.4 / 17 = 1.28$). This suggests that in the range 700°C- 950°C montmorillonite partially abandons its old structure while retaining its original network. As for the peak located around 900°C, we can attribute it to the amount of iron in the octahedral sites [10]. the portion of the curve above 900 ° C, which reflects phase changes after destruction of the structure is quite variable. It first appears quartz (α) or (β) and spinel, cristobalite then, finally, mullite and cordierite at 1300 ° C.

are characterized by a band located at 3612 cm⁻¹ (stretching vibration). DTA-TGA curve of Figure 5 and the infrared spectrum of Figure 6 show that this type of water molecules desorb gradually and eventually disappear around 640° C.

It is recognized [7] that the compensation cations related to alkali can be linked to water molecules to form coordination spheres with the metal-oxygen character of ionicity. This fact suggests a close relationship between the hydration spheres of the type [Na(OH₂)_n]⁺ and OH groups of the absorption band located at 3612 cm⁻¹. We believe that the most probable reaction mechanism of the formation of these acid sites is of type:



The same way, the dehydroxylation phenomenon occurring in the temperature range of 600-800°C allows to distinguish two kinds of substitutions Al → M (M = Fe, Mg) in octahedral sites of internal slip bands whose TOT absorption are located at 920 cm⁻¹, 870 cm⁻¹ and 840 cm⁻¹ respectively attributable to the fragments Al-AlOH, Al-FeOH and Al-MgOH. We can therefore attribute the second endothermic peak located just visible around 615°C (see Figure 5) and the disappearance of around 615°C, two absorption bands located at 920 cm⁻¹ and 870 cm⁻¹ (see Figure 6) the partial release of structural OH groups.

The two absorption bands located at 452 cm⁻¹ and at 536 cm⁻¹ respectively are due to bendings vibration Si-O-Si and Si-O-Al on tetrahedral substitutions Si → Al. Taking into account these experimental observations given by the

infrared spectrum of Figure 6 and knowing that the montmorillonitic phase of Azzouzet bentonite is



This structural formula corresponds to montmorillonite having a character in the tetrahedral sheet of 15% (less than 50% octahedral charge). Since the chemical composition of aluminous smectites oscillates between a Cheto domain and a Wyoming domain [8], we felt it necessary to analyze the report MgO/Fe₂O₃ that cuts about membership in a particular field. Thus these authors found a report:

0.27 to 0.87 for Wyoming montmorillonite;

2.10 to 3.70 for montmorillonite Cheto;

Our experimental value of 0.83 which is led to believe that our Azzouzet bentonite is probably a Wyoming montmorillonite, where iron located in the octahedral sites is an iron rich- montmorillonite.

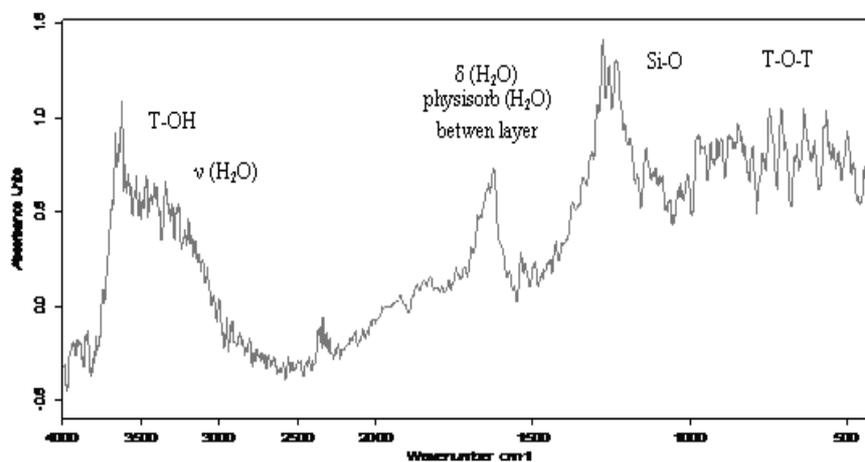


Figure 6. Infrared spectra of raw bentonite Azzouzet.

4. Conclusion

While in most of cases the diffraction is able to identify which group clay minerals (mica, smectite, vermiculite), it is however unable to distinguish clay minerals in the same group. It is in this kind of study that thermal analysis provide invaluable assistance to the X-ray diffraction.

Indeed, the thermal study of Azzouzet bentonite of northern Morocco allowed us to have cristobalite to 950°C. This led us firstly to classify the montmorillonite Azzouzet in Wyoming domain [8], on the other hand, other authors [9] showed that the exothermic reaction located around 830-850°C is a good criterion to distinguish in the field of montmorillonite. As for the peak located around 790-850°C, we can attribute it to the amount of iron in the octahedral sites [10]. We're in the presence of montmorillonite progresses to iron with lattice parameters remain constant but whose chemical compositions are variable with tetrahedral substitutions Si→Al and octahedral substitution Al→Fe.

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