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Physicochemical characterization of mixtures of the Miocene marl of Fez vicinity, cellulose and pozzolan

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Abstract

The clays form a very abrasive raw material in view of the new demands of the society in terms of sustainable development and energy saving we have developed materials based on marl, pozzolan and cellulose. This study aims at the physicochemical characterization of the Miocene marls of the Fez region in order to develop environmentally friendly building materials by improving the physico-chemical properties by adding different percentages of cellulose and Pozzolan. The marl was mixed with cellulose and pozzolan in the following percentages of 1%, 2%, 3%, 4% and 5% of the cellulose content and 10%, 15%, 20% and 25% of pozzolan in the samples tested. Complement tests were also performed. The geochemical analysis showed that there is indeed a change in the concentration of the main elements, relative to the raw marl.

The results of this work show that there is a change and improvement in the physicochemical properties of a new composite marl / pozzolan / cellulose.

1. Introduction

Clays and marl are very abundant at the earth's surface and generally consist of hydrous phyllo-silicates < 0.002 mm in size. They have long been exploited for a very wide variety of industrial applications (ceramics, ink, purify oils, tires, pharmaceuticals, paper, paint, petroleum industry, etc.)[1,2]. One of the main industrial applications of the clays is production of ceramics, which are derived from common, naturally occurring raw materials such as clay and sands of quartz and/or feldspar minerals. The best-known products are pottery, glass, brick, tile, china porcelain, and cement.

The ceramic industry in Morocco is one of the most important economic markets that has been rapidly growing since 1990 [3]. In the north region, extensive red firing clay deposits, which are currently being used for traditional pottery and brick productions are widely seen [4-5].The industrial use of clays in the Fes region (in ceramics, pottery, buildings, etc.) generates geotechnical problems in terms of material strength, cracking, intensity and permeability [6]. It is necessary to develop alternative processes making better use of the abundant resources of clay by suitable modification taking into account the excellent textural properties of these materials [7,8]. Practical applications in industrial and geotechnical activities are conditioned by better knowledge of physicochemical properties of selected marl deformations or malformations of finished products is a serious issue significantly limiting yields [9, 10].The clays are widely used for various needs by the local population in the region of Fez, for example in handcraft manufacture. However, there were no extensive R&D works reported so far; we can find just a few articles published in this field [4]. Doping clays with organic or inorganic compounds is among promising processes for clays upgrading. Promoting effects of doping agent produce physicochemical changes in properties of resulting composite material [11]. In addition, the mechanical

properties of the materials can be improved using inorganic additives such as pozzolan [12]. In particular, the use of pozzolan reduces the consumption of the clinker, contributing in a simple and economic way to solve environmental related problems [13].In this study, the pozzolan sample originated from the volcanic region of Ifrane (Middle Atlas) where is organic doping material consisted in a commercial cellulose powder. The cellulose has been selected in order to complement promoting effect of pozzolan by improving textural properties (such as porosity and mechanical resistance) as well as thermal resistance. The characteristics of these materials were also investigated in terms of their physical, mineralogical, chemical, and thermal properties. The objective of this work is to compare the physicochemical parameters of marl before and after doping with cellulose powder and pozzolan rock additive.

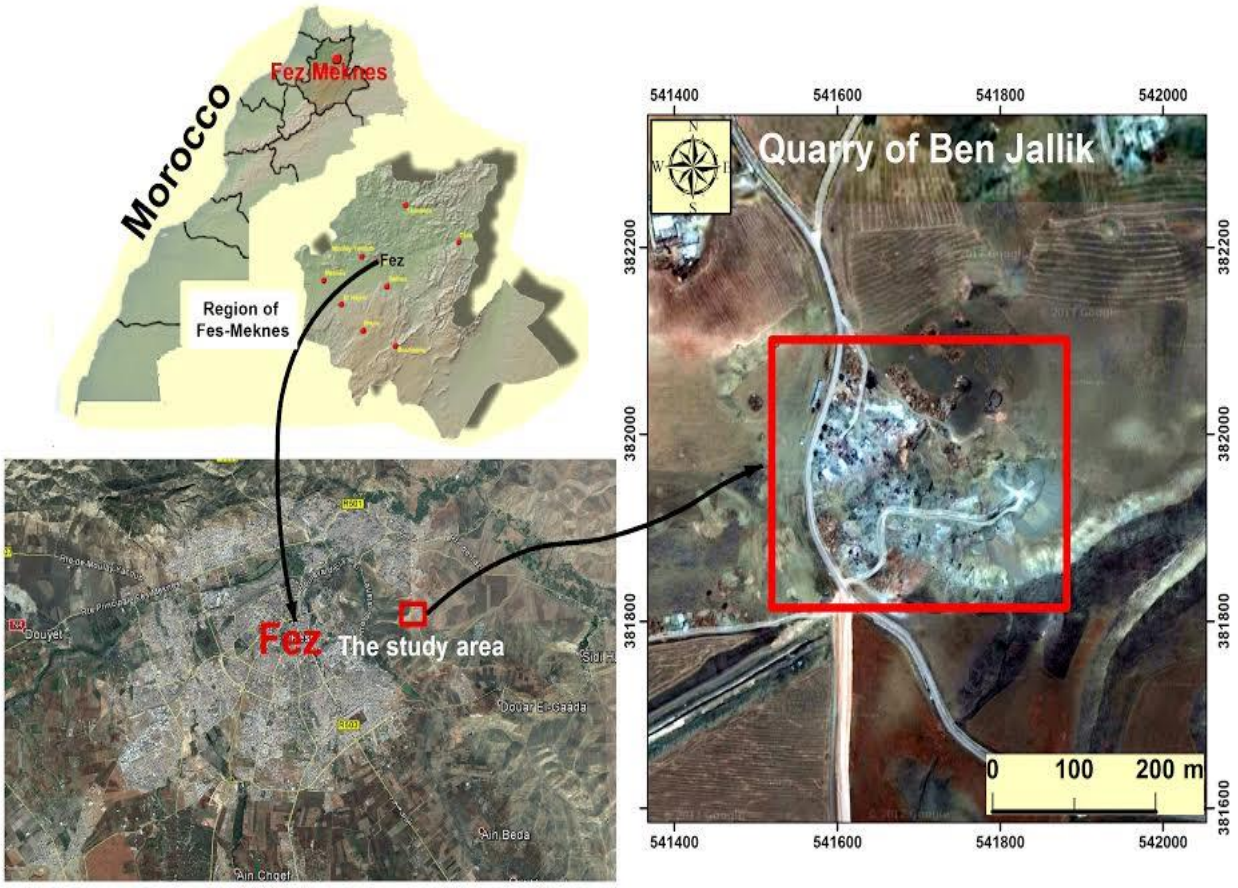

Figure 1: Location of the study area (Quarry of Ben Jallik, Fez)

2. Materials and methods

2.1. *Preparation of samples*

2.1.1. *Source of the marls*

The two raw samples denoted Bj1 and Bj2 were retrieved from Ben jellik, located in the eastern region of Fez (direction to Taza).

Before mixing with pozzolan and cellulose, the raw marls were crushed into small pieces by a mortar, dried at 50°C for 24 h, and then grinded until full homogenization of the size of their particles (less than 50µm).

2.1.2 *Preparation of mixtures marl / pozzolan /cellulose*

As a first step, pozzolan powder was prepared using a deep grinding of original rock. As reported in literature [14, 15], the use of pozzolan as an additive reduces the demand of the mixing water and improves the porous structure of the materials with decreasing the pore size. The Chemical composition of the used pozzolan is given in table 1.

Table 1: The chemical composition of pozzolan.

Elements	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Cr_2O_3	K_2O	Na_2O	SO_3	TiO_2	MnO_2	P_2O_5
Pozzolan	35,3	16,4	3,55	16,8	6,4	2,88	0,44	0,81	0,33	2,4	0,33	0,72

The used cellulose was a commercial powder of Sigma-Aldrich: Fluka cellulose (catalog code 22183). It was directly employed without further treatment.
The percentages of pozzolan and cellulose of the prepared mixtures marl / pozzolan / cellulose are given in table 2. The mixtures were prepared using a grinding apparatus equipped with mechanical mixer. The mixing duration was 15 min for each sample.

Table 2: Percentages of pozzolan and cellulose of the prepared mixtures.

Samples	% of pozzolan	% of cellulose
Bj1 raw sample 1	0%	0%
Bj1A	5%	1%
Bj1B	10%	2%
Bj1C	15%	3%
Bj1D	20%	4%
Bj1E	25%	5%
Bj2 raw sample 2	0%	0%
Bj2A	5%	1%
Bj2B	10%	2%
Bj2C	15%	3%
Bj2D	20%	4%
Bj2E	25%	5%

2.2 *Analytical methods*

2.2.1-*Chemical analysis (XRF)*

The quantitative chemical analysis of clays was performed by X-ray fluorescence spectrometry (WD-XRF) using the spectrometer Axios sequential brand Panalytical of the National Center for Scientific and Technical Research in Rabat, Morocco.
This analysis was conducted after grinding the material and pressing 10 g of each sample.

2.2.2. *Mineralogical analysis (XRD)*

X-ray diffraction analyzes were carried out using an X'Pert High Score PANalytical diffractometer, which is a direct optical coding goniometer with an operated working wavelength corresponding to copper Cu Kα = 1.54060 Å. The XRD patterns were performed in the range of 2θ between 10°and 80° with a step width of 0.06682.
This analysis was performed in the Innovation Center of Sidi Mohamed Ben Abdellah University in Fez, Morocco.

2.2.3. *Scanning electron microscopy (SEM)*

The purpose of the SEM was to identify the mineral components and morphology of the samples. Micrographs were performed for finely ground pellets (13 mm of diameter). The SEM analyzes were carried out using Hitch S-2500 microscope, which operates with an acceleration voltage of 16kv. It was performed in the Innovation Center of Sidi Mohamed Ben Abdellah University in Fez, Morocco.

2.2.4. *Fourier transformed Infrared spectroscopy (FTIR)*

The infrared spectroscopy was carried out using a Thermo-Nicolet spectrometer (AVATAR 320 AEK0200713) of the Innovation Center of Sidi Mohamed Ben Abdellah University in Fez, Morocco.
The spectra were performed in the range of 4000-400 cm^{-1}.

2.2.5. *Loss on ignition*

The loss on ignition allows knowing the quantity of the products likely to decompose or to volatilize during calcination. Measurements of loss on ignition were performed by using a WiseTherm type oven in Laboratory of Georessources and Environment of Sidi Mohamed Ben Abdellah University.

The raw marls and prepared mixtures were calcined with a gradual increase of temperature up to 1000°C for 1 hour, as described in previous works [17, 23]. The samples were cooled down to room temperature in a desiccator and then weighted. The loss on ignition has been determined by means of the following relationship:

$$LO.I = (W1-W2 / W1) * 100$$

W1: is the initial weight of the sample

W2: is the final weight of the sample

3. Results and discussion

3.1. *Chemical composition*

The chemical compositions of the studied samples provided by X-ray fluorescence are shown in the tables 3 and 4. It is noticed that silica, alumina and calcium are the major constituents of the two raw marls (Bj1 and Bj2) and the prepared mixtures. It is also the case of the used pozzolan, which contains also an important percentage of Fe_2O_3 (table 1).

Table 3: Percentages of the major elements in the Bj1 and mixtures of Bj1 /cellulose / pozzolan.

	SiO2	**CaO**	**Al_2O_3**	**Fe_2O_3**	**MgO**	**SO_3**	**K_2O**	**Na_2O**	**TiO_2**	**MnO_2**
BJ1Sample	45,1	9,94	12	5,54	2,71	2,6	1,25	1,2	0,546	0,0796
BJ1A	44,4	9,7	12,6	5,31	3,02	2,59	1,3	1,22	0,603	0,0787
Bj1B	39,9	8,65	11,6	5,7	2,94	3,24	1,16	1,05	0,66	0,0542
Bj1C	43,4	8,45	12,8	6,41	3,2	2,41	1,25	1,15	0,748	0,0855
Bj1D	42,4	8,27	13,7	6,55	3,24	2,5	1,09	1,12	0,842	0,088
Bj1E	42,2	8,,23	14,3	7,43	3,45	3,05	1,14	1,08	0,951	0,0703

Table 4: Percentages of the major elements in the Bj2 and mixtures of Bj2 /cellulose / pozzolan.

	SiO2	**CaO**	**Al_2O_3**	**Fe_2O_3**	**MgO**	**SO_3**	**K_2O**	**Na_2O**	**TiO_2**	**MnO_2**
Bj2sample	42,9	9,74	13,2	4,53	3,54	0,534	1,5	1,4	0,55	0,0304
Bj2A	42,5	9,6	13,7	4,7	3,51	0,497	1,48	1,38	0,63	0,0575
Bj2B	42,3	8,59	13,7	4,8	3,49	0,447	1,63	1,29	0,657	0,0542
Bj2C	42,7	8,44	14,9	4,82	3,65	0,414	1,52	1,32	0,662	0,682
Bj2D	40,4	8,41	15,4	5,67	3,38	0,419	1,4	1,28	0,89	0,069
Bj2E	41,5	8,3	16,7	6,42	3,98	0,418	1,37	1,23	0,97	0,101

The obtained results reveal a significant alumina (Al_2O_3) and iron oxide (Fe_2O_3) enrichment and a decrease of SiO_2 concentration with increasing the percentage of pozzolan and cellulose. It is expected that this evolution of constituent's concentration could be probably due to the cation exchange between the components of the marls and those of the pozzolan [4]. Furthermore, the percentages of CaO and MgO suggest a probable presence of calcite and dolomite. As reported by Chossat J.C in a previous work [17], magnesium and calcium may be part of the interfoliar space and structure. On the other hand, the SiO_2 / Al_2O_3 ratio = 3.2 is higher than that of pure kaolin (SiO_2 / Al_2O_3 ratio =1.18) [24]. This result highlights the presence of free quartz in the samples.

3.2 *Mineralogical composition*

Figures 2 and 3 illustrate respectively the X-ray diffraction patterns of the raw marls Bj1 and Bj2 and that of the prepared mixtures with various percentages of pozzolan and cellulose.

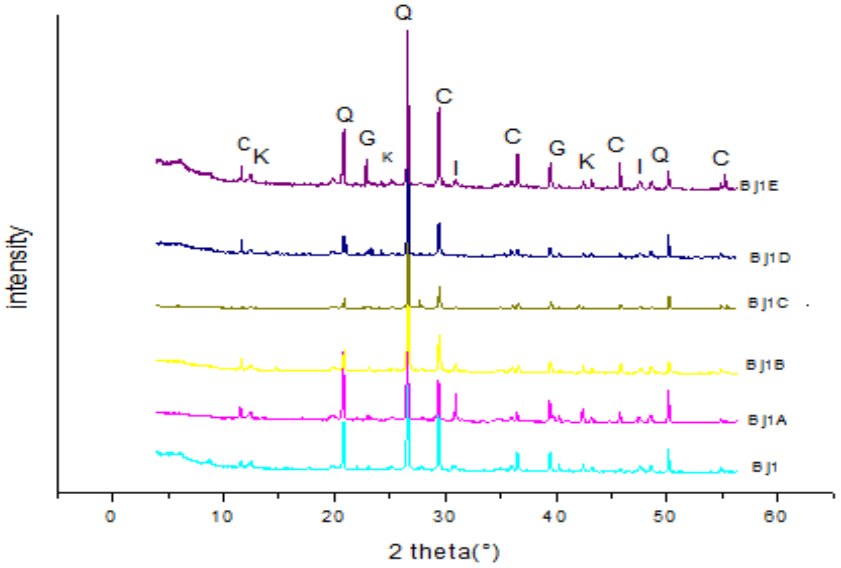

Figure 2: RX Diffractograms of the raw sample Bj1 and mixtures of Bj1 /cellulose / pozzolan.
Q: quartz; C: calcite; G: Gypsum I: illite; and K: kaolinite

The X-ray diffraction diagrams (Figure 2) show the presence of the following peaks:

- 2θ = 20.2 °, 26.69 °, 50.40 ° characteristics of the quartz phase.
- 2θ = 10.78 °, 29.5 °, 36.98 °, and 55.26 ° characteristic of the calcite phase;
- 2θ = 23.64 °, 39.58 ° characteristics of the .gypsum phase
- 2θ = 13.78 °, 24.9 °, 44.98 ° characteristics of the kaolinite phase;
- 2θ = 32.64 °, 47.58 °, and 51.30 ° phase characteristics. Illite.

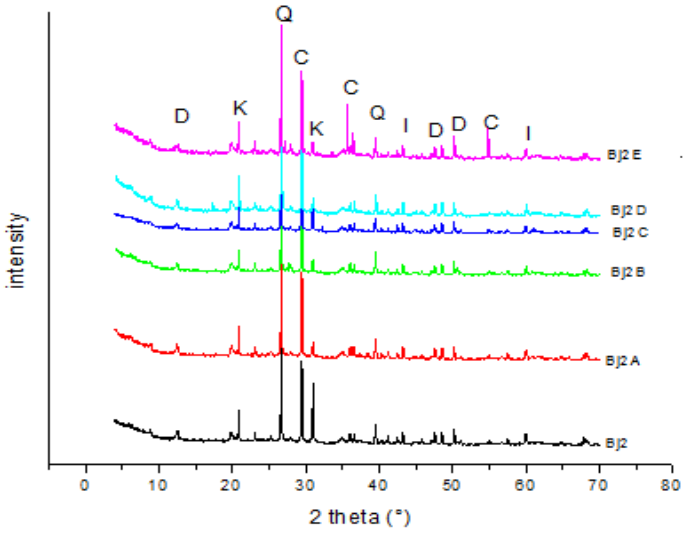

Figure 3: RX Diffractograms of the raw sample Bj2 and mixtures of Bj2 /cellulose / pozzolan
Q: quartz; C: calcite; D: Dolomite I: illite; and K: kaolinite

The X-ray diffraction diagram (Figure 3) shows the presence of the following peaks:

- 2θ = 26.69 °, 39.2 °, characteristics of the quartz phase;
- 2θ = 29.68 °, 35.4 °, 56.98 ° characteristics of the calcite phase;
- 2θ = 12.64 °, 48.69 °, and 51.22 ° characteristics of the dolomite phase;
- 2θ = 43.78 °, 61.22 ° characteristics of the illite phase;
- 2θ = 21.62 °, 32.58 ° phase characteristics. Kaolinite.

The X-Ray diffractograms (figures 2 and 3) highlight the predominance of silica in the crystalline form of quartz and the presence of calcite, kaolinite and illite in the samples. It is known that these minerals are suitable for the manufacture of ceramic products with high quality.
The diffractograms show also the presence of a small amount of gypsum in Bj1 and that of dolomite in Bj2.
On the other hand, a continuous and positive correlation between the increasing of the pozzolan and cellulose contents and the evolution of peaks intensity related to quartz and calcite is also shown by the X-Ray diffractograms (figures 2 and 3). These results highlight that there is a good crystallization of quartz with increasing the contents of pozzolan and cellulose.
So, there is an evidence of mineral crystallization changes that occur when pozzolan and cellulose are added to the raw marls.

3.3. *Scanning electron microscopy (SEM)*
The microphotographs obtained by SEM measurements are given in Figures 4 and 5.

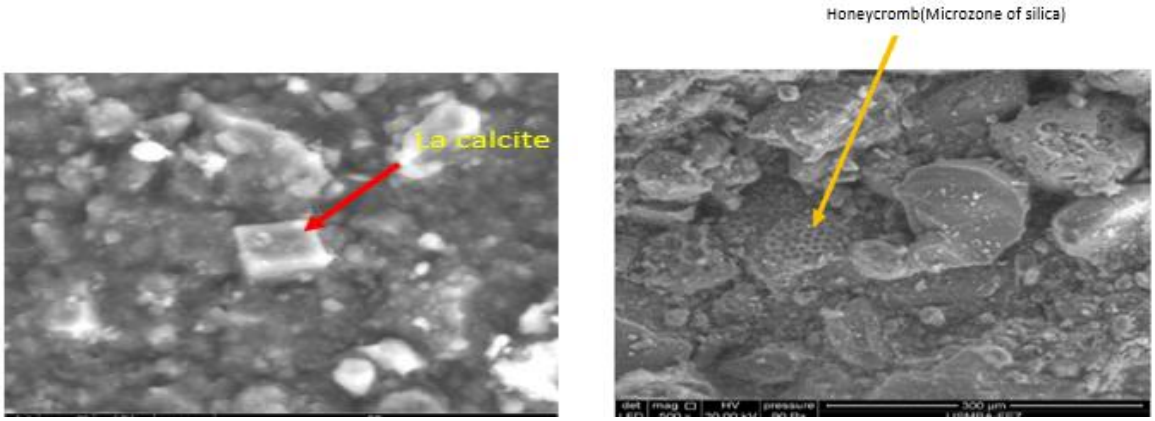

Figure 4: Micrographs of Bj1 raw marl

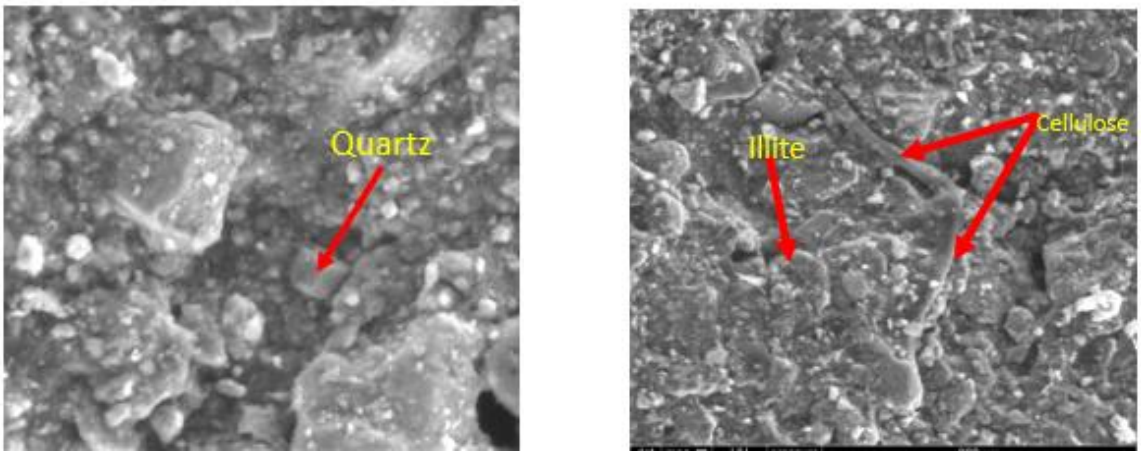

Figure 5: Microphotographs of a mixture of Bj1 /cellulose / pozzolan.

The crystallization of calcite in the form of visible aggregates [9] is shown in figure 4. The obtained micrographs highlight the presence of calcite, quartz and illite minerals which confirm the obtained results by the X-Ray diffraction analysis. The presence of quartz and illite could confer to the prepared materials suitable properties for the ceramic industry [19].

Figure 4 shows the presence of silica microzone primarily as a structure made of sponge or honeycomb which confirm the predominance of silica in the samples as stated by XRD analysis.
On the other hand, the impregnation of the cellulose in the clay layers is clearly shown in figure 5. It is also noted that increasing of the cellulose percentage induces a good dispersion and intercalation of the fibers within the matrix of clay. This result suggests that the prepared materials could present very interesting mechanical, thermal and morphological characteristics. In fact, Demir et al. [18] have reported that the increase of the cellulose content influences positively the resistance of the material and its thermal and morphological characteristics.

3.4. *FTIR spectroscopy*

The IR spectra of the studied materials are shown in figure 6.

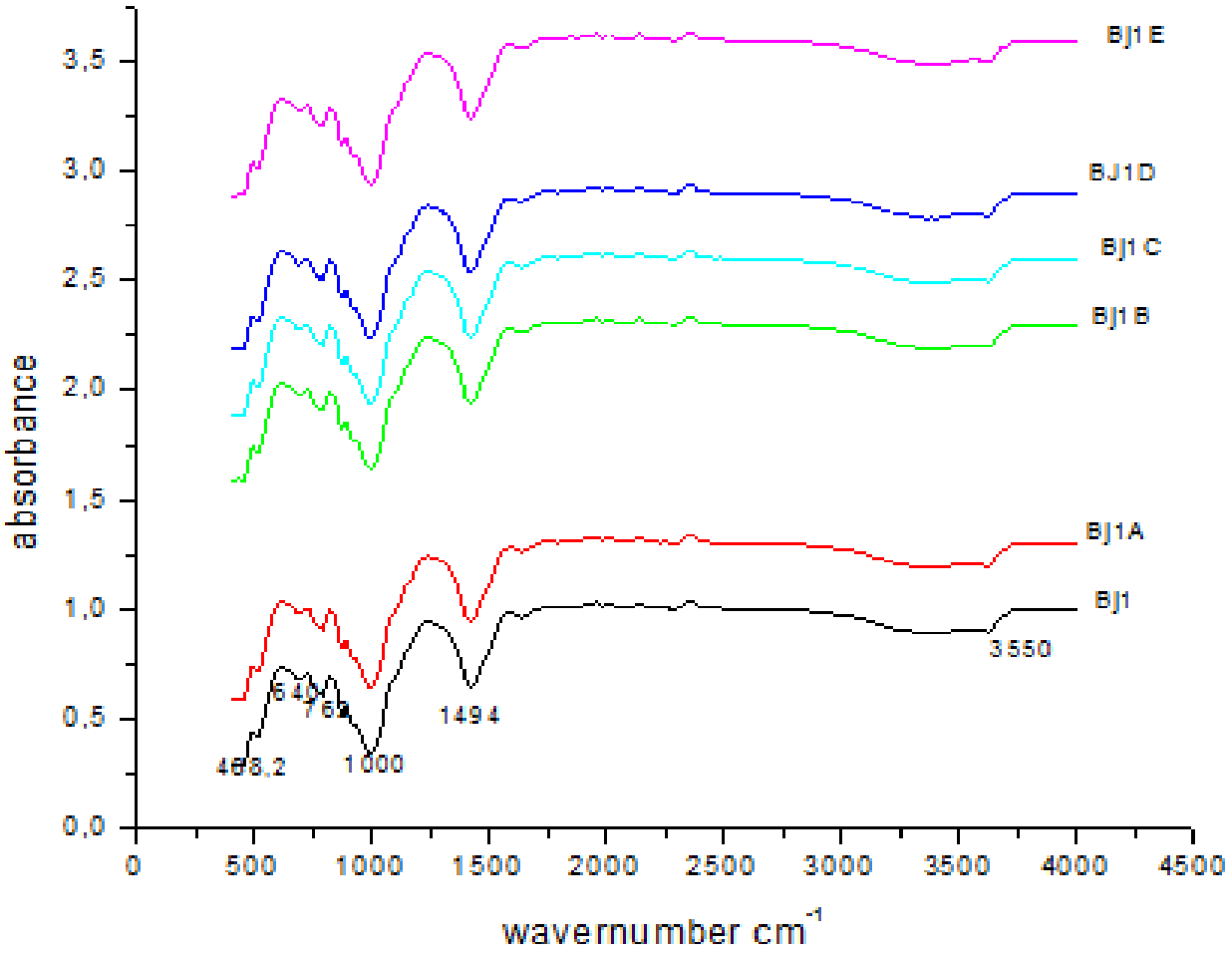

Figure 6: IR spectra of Bj1 and mixtures of Bj1 /cellulose / pozzolan.

Table 5 summarizes the main absorption bands found on the spectra of BJ1 and mixtures of Bj1 /cellulose / pozzolan.

Table 5: IR adsorption bands of raw sample [8, 22]

Frequency in cm $^{-1}$	**Attributions**
3550	Elongation vibrations of hydroxyl groups O-H of clay mineral
1494	Vibration due to the presence of carbonates
1000	(900-1200) cm-1 vibrations d'allongement de Si-O (Quartz)
760	Kaolinite
640	Vibrations des déformations of OH
468,2	Si-OH ou SiO (déformation) and/or Al-O (élongation)

The Absorption bands located at 1494 cm^{-1} are attributed to the presence of calcite [8, 21], which is also shown by the XRD, and SEM analyzes. Furthermore, the presence of quartz is confirmed by the absorption bands located at 1000 cm^{-1} [3]. This is in accordance with XRF, XRD and SEM results.
Regarding the presence of kaolinite shown by XRD, it is confirmed by the absorption bands located at 760 cm^{-1} [3, 8, 21]. In fact, Russel and Fraser [3] have reported that the band located in the range between 798 cm^{-1} and 750 cm^{-1} is one of the characteristic bands of kaolinite.

3.5. *Loss on Ignition*
The loss on Ignition of the samples increases progressively with increasing the percentages of pozzolan and cellulose (Tables 6 and 7). This loss of mass at 1000°C is mainly attributed to the loss of the adsorbed water and to the presence of carbonate and silicate minerals.

Table 6: The loss on Ignition of the BJ1 and mixtures of Bj1 /cellulose / pozzolan.

Samples	**Loss On Ignition (%)**
Bj1	13,4
Bj1A	14,7
Bj1B	14,9
Bj1C	14,7
Bj1D	15,5
Bj1E	15,7

Table 7: The loss on Ignition of the BJ2 and mixtures of Bj2 /cellulose / pozzolan.

Samples	Loss On Ignition
Bj2	18,4
Bj2A	18,5
Bj2B	18,7
Bj2C	18,7
Bj2D	19,4
Bj2E	19,9

Similar results were reported in literature for marls and clays. Mesrar [4] and Qlihaa & al. [16] have respectively apprehended the decomposition of fired marls and clays in similar conditions. They have reported that the loss on ignition is mainly attributed to the deshydroxylation of the phyllosilicate. Moreover, the loss on ignition could be also linked to the presence of calcite as confirmed by XRD and SEM.

3.6. *Discussion*

The analyzes carried out on raw marls (Bj1, Bj2) and mixtures of marl, pozzolan and cellulose show an evolution of the mineralogical composition with increasing the contents of pozzolan and cellulose. It is noted the predominance of free quartz that is proved by the high peaks of quartz in the X Ray diffractograms and by the presence of honeycomb in SEM micrograph. The raw marls and prepared mixtures contain also calcite, illite and kaolinite. The contents of these minerals increase with increasing of pozzolan and cellulose contents in the mixtures as shown by XRD analysis. Furthermore, evolution of crystallization of these minerals with increasing of pozzolan and cellulose contents is noticed. Thus, Bj1E and Bj2E present the best crystallization of minerals.
On the other hand, SEM analysis highlights the impregnation of the cellulose in the clay layers. The increase of the cellulose percentage induces a good dispersion and intercalation of the fibers within the matrix of clay.
All of these results suggest that the prepared materials could present very interesting mechanical, thermal and morphological characteristics. It is therefore expected that these materials can be used in the ceramic industry.

Conclusion

In the present work, the characterization of raw marls and mixtures of marl, pozzolan and cellulose at various percentages has been investigated. The obtained results reveal that the addition of pozzolan and cellulose to the raw marl induces a change on its chemical composition. The prepared mixtures contain more alumina (Al_2O_3) and iron oxide (Fe_2O_3) than the raw marls, which could improve the mechanical properties of the prepared mixtures.
The mixtures contain also minerals as quartz, calcite, illite and kaolinite. The contents of these minerals increase with increasing the contents of cellulose and pozzolan. So, it is expected that the addition of pozzolan and cellulose could improve the geochemical properties of the prepared mixtures.
In order to better exploit the prepared materials, it is suitable to carry out further research works on their mechanical, thermal, magnetic and electrical properties.

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