

## DIFFRACTOMETRIC X-RAY AND INFRARED STUDY OF A PORCELAIN-BENTONITE MIXTURE

H. BOUSSAK<sup>1</sup> & H. CHEMANI<sup>2</sup>

<sup>1</sup>Coatings Laboratory, Department of Materials and Environment, University of Science and Technology,  
M'Hamed Bougara, Boumerdes, Algeria

<sup>2</sup>Department of Materials Engineering, University of Science and Technology,  
M'Hamed Bougara, Boumerdes, Algeria

### ABSTRACT

Porcelain is a material produced by a process kaolinite clay, quartz and feldspar mixtures thereof. This material, usually used in tableware, parts for electrical system insulation, and also as removable prostheses and dental crowns, is endowed with high technology properties such as low water absorption, high flexural strength and excellent chemical resistance. Nevertheless, there is a rarity of high quality research focused on the effect of mullite growth in the technological properties of traditional porcelains. Four formulations of the porcelaine tableware were prepared in different percentage, from 0 to 15wt. % of calcic bentonite. Infrared (IR) analyzes are consistent with X-ray diffraction (XRD) results. They demonstrate the presence of vibration bands associated with the different phases detected in DRX. An evolution spectrograms profile is observed when the intensity of the laser radiation increases; it is probably related to a structural evolution and / or to the decomposition of the phases present in the sample analyzed. The intensity of the Al - OH and Si - O bond peaks in the IR which characterizes the 10wt. % bentonite mixture corresponds to the bands which designate the mullite phase, which is technically important.

**KEYWORDS:** Traditional Porcelains, Suspensions, Mineralogical Analysis, Bonds, Bentonite

### INTRODUCTION

Porcelain is a white ceramic material, non-porous and partially transparent, the production started in China centuries ago. Today, porcelain is produced in many countries and its technology is well known and described in various manuals and documents (Kingery, 1976, Reed, 1995, Hlavac, 1983, Gerasimov and Bachvarov, 1977, Carty and Senapati, 1998).

Porcelains are hard ceramics. They are obtained from a mixture of kaolin (55 wt. %), Feldspar (25 wt. %) and quartz (20 wt. %), firing at 950°C for the first time and between 300 and 1400°C the second time. The porcelain thanks to the kaolin has the particularity of remaining white after the firing (firing carried out in reducing atmosphere). At 1400 ° C., the porcelain finishes at the vitrification step (Bragança and Bergmann, 2004, Tulyaganov, Agathopoulos, Fernandes and Ferreira, 2006). Mullite ( $3Al_2O_3, 2SiO_2$ ) is considered to be the main crystalline phase in porcelain and responsible for their microstructure and mechanical properties. Mullite formation is dependent primarily on the nature and the proportion of kaolin used in the pure state it gives good results mullitisation. (Schneider, Okada and Pask, 1994). Moreover, the proportion and the nature of the quartz used in the porcelain composition influences the quality of the finished product.

The results obtained by (Diaz Rodriguez and Torrecillas, 2002; Garcia and Aguilar-Elguézaba, 2009; Andreola and Siligardi 2009) of the use of bentonite in the various formulations of ceramic pastes of wall tiles, bricks, ceramic tiles and porcelain stoneware are as follows: processes during firing are different from those of the classic formulation of kaolin. The bentonites consist of an octahedral sheet between two tetrahedral sheets with a high capacity for cationic change, therefore a large surface area of water absorption (Garcia and Aguilar-Elguézaba, 2009). Clay minerals have several functions: they confer plasticity and increase the firing time.

The objective of this study was to develop and characterize formulations of porcelain material containing Maghnia bentonite by physical analysis based on local raw materials. The results of the mineralogical and infrared characterizations are grouped together in the following.

## **EXPERIMENTAL**

### **LOCATION OF RAW MATERIALS**

The different formulations of porcelain tableware (0, 5, 10 and 15wt. % of bentonite) were composed of kaolin from Djebel Debbagh, Guelma (Algeria) used in formulations tableware. The quartz comes from the area of Boussaâda (Algeria), the Feldspar from the area Bouira (Algeria) and the bentonite was calcined in a continuous roller kiln (heating to 973°K with a heating rate of 5°Ks<sup>-1</sup> and maintained at this temperature for 3min). To this is added a sodium tripoliphosphate (Na<sub>2</sub>P<sub>3</sub>O<sub>10</sub>, 6H<sub>2</sub>O) as a deflocculant (0.3wt. %) to improve the dispersion of the slurries.

### **MATERIALS AND METHODS**

This study concerns the chemical and mineralogical characterization of the raw materials used and the porcelain samples after elaboration. Mineralogical analyzes of the raw materials were carried out by XRD techniques using the analysis (Philips PW 1710, France) the wide-angle X-ray spectra were recorded with a D 500 diffractometer in progressive scan mode using radiation CuK $\alpha$  Ni-filtré (1,5406 Å). The IR spectra of the materials studied were recorded at the University of Tizi ousou (Algeria). The technique said DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) was used in a range of waves of between 400 and 4000 cm<sup>-1</sup> (in reflection) using a spectrophotometer of the type (Bruker IFS 55). The study was focused on the possibility of application of bentonite in the porcelain material; industrial tests were carried out to evaluate its possible use.

The standard composition of triaxial porcelain, defined as P0, was the formulation reference. Three formulations, with increasing amounts of bentonite (with respect to P0), designated from P1 to P3 (the number refers to the wt. % of bentonite in the batch), were produced in laboratory conditions via pouring and sintering. The mixtures were cast in rectangular plaster molds and dried at room temperature for 48 h at 105°C for 24 h. The samples were firing at temperatures of 1250, 1300, 1380 and 1400°C (heating and cooling rates 5°C/ min and 1 hour dipping at the highest temperature). The starting temperatures were chosen according to the respective liquidus temperatures of the systems SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-K<sub>2</sub>O.

**RESULTS AND DISCUSSIONS**

**Raw Materials and Porcelain Formulations**

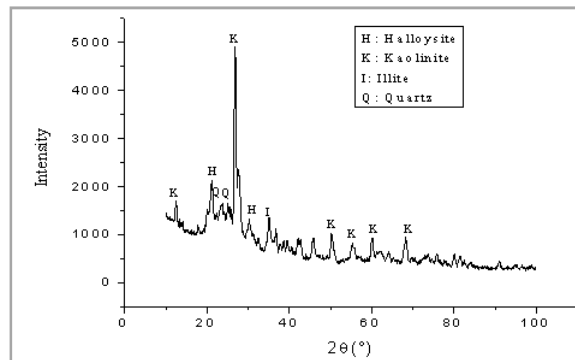
Table 1 summarizes the batch formulations and the chemical compositions of the porcelains (in wt. %). Bentonite was used in the three batch replacing feldspar that is normally used in traditional compositions. The main observations show the role of the bentonite as a fluxing agent.

**Table 1: Formulations (in wt. %) of the Model Porcelain P<sub>0</sub>, P<sub>1</sub>, P<sub>2</sub> and P<sub>3</sub>**

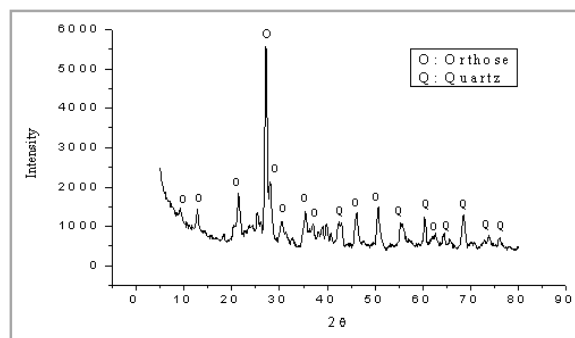
Raw Materials	Mass Percentages (wt. %)			
	P <sub>0</sub>	P <sub>1</sub>	P <sub>2</sub>	P <sub>3</sub>
Kaolin	55	55	55	55
Feldspar	25	20	15	10
Quartz	20	20	20	20
Bentonite	0	5	10	15

**Mineralogical Study of Raw Materials**

The (figures 1, 2, 3 and 4) show the X-ray diffraction patterns of the raw materials such as: Kaolin DD, feldspar, quartz and benonite clay. According to the results of the chemical compositions of the raw materials, the principal mineralogical constituents are: silica and alumina. The analysis shows a predominance of feldspar potassium in feldspar with a presence of the orthosis. Guelma kaolin contains a mixture of kaolinite and alloysite. The DRX spectrum of bentonite clay shows a predominance of montmorillonite with small amounts of crystalline impurities (non-clayey minerals) the presence of the quartz in small quantity limits the plasticity of the mixture, the presence of the calcite acts as a flux on the ceramic material during firing, traces of kaolinite and illite which increase the plasticity of the mixture.



**Figure 1: Diffractogram RX of the Kaolin (DD)**



**Figure 2: Diffractogram RX of the Feldspar**

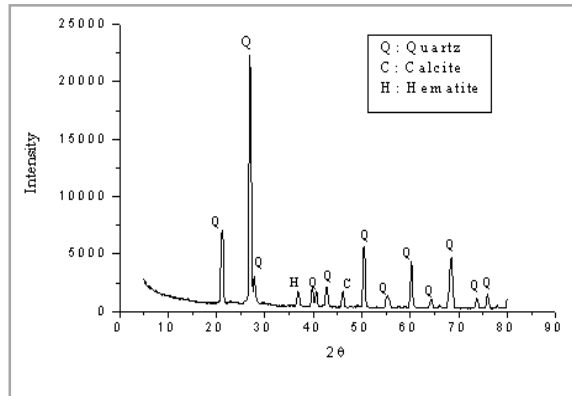


Figure 3: Diffractogram RX of the Quartz

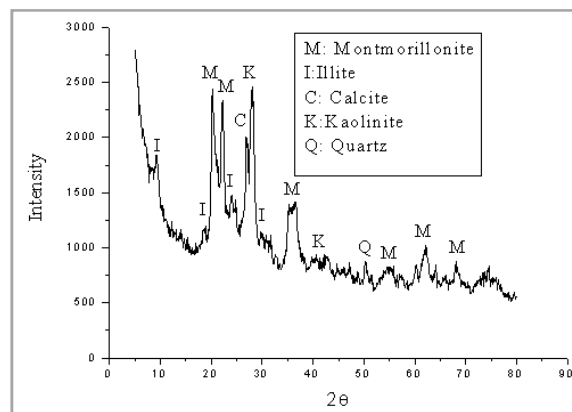


Figure 4: Diffractogram RX of the Bentonite

**INFRARED SPECTROSCOPIC STUDY**

To provide routine characterization of a clay mineral, it is useful to examine a sample measured with a KBr pellet. In figure 5 illustrates the absorption bands in the range 500-4000 cm<sup>-1</sup> existing in these materials after firing at 1250, 1300, 1380 and 1400°C. The analysis by infrared spectrometry makes it possible to identify the various chemical bonds belonging to the porcelain.

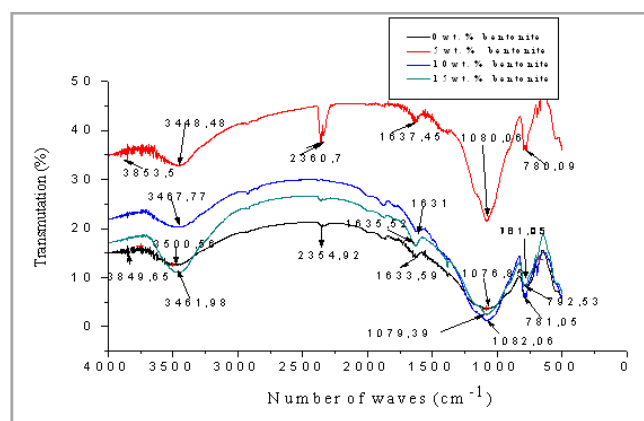


Figure 5: IR Spectra of the Porcelain Mixtures as a Function of the Addition of Bentonite

According to the results of the infrared spectra of the mixtures (5, 10 and 15wt. % of bentonite), several absorption peaks are observed, which characterize the good dispersion of the bentonite clay. In the porcelain

material, the following values, 1076.85, 1080.06, 781.05, 780.05, 792.53 $\text{cm}^{-1}$ , were successively characterizing the bonds: Al-OH, Si-O, which constitute the sheets of kaolin clays and bentonite.

These curves have several absorption bands. Each of them corresponds to vibrations of a functional group. For example, the large band observed in the neighborhoods of 3500.56, 3448.48, 3467.77, 3461.98  $\text{cm}^{-1}$  characterizes the OH elongation of water in compositions 5, 10 and 15wt. % bentonite (Savic Ivana, Stojiljkovic Stanisa, Savic Ivan, Sreten Stojanovic and Karl Moder, 2012).

Concerning the bands 2354 and 2360  $\text{cm}^{-1}$  of the percentages of bentonite at (0 and 5wt. %) respectively, corresponds to the triple bonds of nitriles (Madejova, 2003). The bands 1633.59, 1637.45, 1631 and 1635.52  $\text{cm}^{-1}$  of the percentages at (0, 5, 10 and 15wt. %) of bentonite respectively, attributed to the valence vibrations of the OH group of the water of constitution (F. Zibouche, 2009). Peaks correspond to large bands of 1076.85, 1080.06, 1082.06, 1079.39 $\text{cm}^{-1}$  of the bentonite percentages at (0, 5, 10 and 15wt. %) respectively, are characteristic of Si-O and Al-OH bonds characterizing the aluminosilicates and indicate, the formation of the mullite (Murray, 2000). These bonds are formed on the one hand by tetrahedral and octahedral vibrations of the oxygen and on the other, by the vibrations of the Si-O bond which are perpendicular to the layers of the silicates.

A high intensity of the Al - OH and Si - O bond peaks that characterize the 10wt. % bentonite mixture compared to the other mixtures corresponds to the bands which designate the mullite phase, hence the development of materials with high thermal resistance.

The presence of the bentonite clay in the ceramic materials increases the amount of the vitreous phase (mullite) which designates the refractory materials. In view of the cation exchange phenomenon characterized by calcium bentonite and which leads to the reduction of the pollutants found in the medium, the quantity of impurities is negligible in the 10wt. % bentonite material.

## CONCLUSIONS

All the materials studied have a sheet structure when they are raw and, after a heat treatment, more particularly above 1000 ° C, they are formed of a vitreous phase and this for the most part of the crystals. The use of bentonite clays in the ceramic industry for porcelain formulation is limited to 10wt. % bentonite content. The main reason for restricting its use is that bentonite induces flocculation of wet clay dispersions. The incorporation of different amounts of treated bentonite clay at different sintering temperatures led to the appearance of a mullite phase which is technically important.

Infrared (IR) analyzes are consistent with X-ray diffraction (XRD) results. They highlight the presence of vibration bands associated with different phases detected by XRD. An evolution of the profiles of the spectrograms is observed when the intensity of the laser radiation increases; it is probably related to a structural evolution and / or decomposition of the phases present in the analyzed sample. The intensity of the peaks of Al - OH and Si - O bonds in the IR, which characterizes the 10wt. % bentonite mixture, corresponds to bands which indicate the mullite phase

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