Usability of Malatya Pyrophyllite in the Traditional Ceramic Industry

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Abstract. In the present study, the usability of the pyrophyllite in the traditional ceramic industry was investigated. The raw pyrophyllite was obtained in Malatya, Turkey. The characterization of the raw pyrophyllite and the prepared ceramics which were heated at the different temperatures in oven (800, 900, 1000 and 1100 °C) were done by XRF, XRD, FTIR, SEM and the main physical properties, like total shrinkage, water absorption capacity and compression strength were determined. As a result of experimental studies; the raw pyrophyllite had to be mixed with the feldspar and another clay (Unye clay) with having high plasticity in order to shape easily and a high water resistance. The optimum receipt was found as 70 wt % pyrophyllite, 20 wt % Unye clay and 10 wt % feldspar. The main properties of the obtained ceramics were specific white baking colour and high temperature resistance properties.

1. Introduction

Clays and clay minerals are used as raw materials in lots of industrial areas such as ceramics, petroleum industry, paper, paint and catalysis, etc. [1]. The application areas of clay minerals are directly related with their structure, composition, and physical properties [2].

Pyrophyllite, Al₄Si₈O₂₀(OH)₄, is a relatively rare clay mineral which is used in the manufacture of refractoriness, ceramics, fiber glasses, paints, rubbers, paper, porous materials and insulating materials [3]. In the literature, the raw pyrophyllite is used as an additive or substitute materials at different amounts (max. 20 wt.%) into a conventional porcelain mixture [4, 5].

The results show that the addition of pyrophyllite increases the strength and decreases the water adsorption ratio. In the present study, a particular application of local pyrophyllite clay deposit collected from Malatya, Turkey was characterized and investigated its potential applicability for traditional ceramic application.

2. Materials and methods

Pyrophyllite ore was taken from Malatya, Turkey and crushed and ground to 80–85 mass% passing 106 μm in a ball mill. Our preliminary investigation showed that the properties of the obtained ceramic structure which was produced from the raw pyrophyllite did not have high plasticity and was immediately decomposed in the water, so 20 wt % Unye clay and 10 wt % K-feldspar were mixed with the raw pyrophyllite. The elemental compositions of the raw materials were given in Table 1.
### Table 1. Element compositions of the raw materials

| Sample        | SiO₂ | Al₂O₃ | Fe₂O₃ | TiO₂ | CaO | MgO | Na₂O | K₂O |
|---------------|------|-------|-------|------|-----|-----|------|-----|
| Pyrophyllite  | 73.85| 21.82 | 0.39  | 0.53 | 0.06| 0.27| 0.80 | 1.62|
| Unye clay     | 84.58| 11.87 | 1.93  | 0.11 | 1.90| 1.78| 0.34 | 0.25|
| K-feldspar    | 71.26| 16.65 | 0.21  | 0.28 | 0.70| 0.35| 3.17 | 9.26|

Characterization and chemical structure of the pyrophyllite and the ceramic bodies were done by Spectro XEPOS, Rigaku Miniflex 600 with Cu Kα (40 kV, 15 mA, λ=1.54050 Å) XRD, Perkin Elmer Spectrum One FTIR-ATR and Leo Evo-40x VP Electron Microscope (Inonu University, Central Research Lab.). In order to determine and compare the linear shrinkage, the compressive strength and the water absorption ratio, ten flat test pieces (40 mm×40 mm×10 mm, material moistened up 7% water, per test piece in figure 1) were prepared using the only raw pyrophyllite and the mixture of the pyrophyllite (70 wt %), Unye clay (20 wt %) and feldspar (10 wt %) under the compaction pressure of 250 bars. After compaction, the test pieces were oven dried at 105 °C until constant weight and then fired at various temperatures (800 °C -1100 °C) for 2 h. Linear firing shrinkage and water absorption were determined by following the ISO 10545 and ISO-10543-3 standards, respectively [6, 7]. The formulas are given below;

\[
I = \frac{I_f - I_d}{I_d} \times 100
\]

\[
W_A = \frac{W_f - W_i}{W_f} \times 100
\]

where \( I \) is the linear firing shrinkage, \( I_d \) and \( I_f \) are the length of dried and fired samples, respectively. \( W_f \) and \( W_i \) are the weight of fired and starting samples, respectively.

![Figure 1. The photographs of the ceramic bodies at different temperature](image)

3. Results and discussions

The XRD pattern of the raw material showed the main structure as pyrophyllite (figure 2). Depending on the temperature, it can be seen that the intensities of diffractions of d(002) and d(004) decreased...
and nearly disappeared at high temperature of 1100 °C. On the other hand, the intensity of the main peak (006) drastically increased. This situation is observed in the literature [8] and explained the transformation of the pyrophyllite. Besides, the layered framework of the pyrophyllite is same in dehydroxylated structure. Dehydroxylated pyrophyllite decomposed into amorphous SiO₂ and mullite (950–1100 °C) [9]. The IR spectra of the raw pyrophyllite and the ceramic tile heated at different temperature are given in figure 3. The band at 3662 cm⁻¹ which was observed on the IR spectrum of the raw material was associated with the stretching vibrations of Al₂OH [10] and this band nearly disappeared on the IR spectra of the ceramic tile, meaning that some OH groups were removed depending on temperature [8]. On the other hand, the spectra showed that the main structure was not totally change, just the bands position shifted. It meant that the main structure was well-ordered and just the bands were merged at high temperature.

The scanning electron microscopy (SEM) image of the raw pyrophyllite in figure 4.a indicates the laminated structure and irregularly shaped particles and large size distribution and stacked clay mineral layers. It could be seen that depending on the heating process, the glassy structure started to occurred and increased with increasing the temperature. In addition, aforementioned, the pyrophyllite decomposed into amorphous SiO₂ and mullite (900–1000 °C, figure 4. b and 4. c, respectively) and mullite needles and vitrification were seen on the ceramic tile heated at highest temperature of 1100 °C (figure 4d). This behaviour was expected due to the smelting and transformation point of pyrophyllite, causing the low water adsorption, high strength and linear shrinkage.

![XRD Patterns](image)

**Figure 2.** XRD patterns of the raw pyrophyllite and ceramics heated at different temperature

The total shrinkage depending on temperature of the flat pieces was determined and the results are given in figure 5. The all experiments were triplicate. It can be seen that the shrinkage percent increased and the water adsorption decreased while increasing the temperature. The XRD patterns and SEM images of the samples proved that the main structure of pyrophyllite was dehydroxylated and the vitrification structure increased with increasing temperature. Therefore, the increased in total shrinkage and the decreased in the water adsorption were expected. The same trend is observed in the literature. Mukhopadhyay et al. [4] mentioned that the fired shrinkage increased and the water adsorption decreased with increasing pyrophyllite content due to the vitrification effect of the pyrophyllite.
Figure 3. IR spectra of the raw pyrophyllite and the ceramic tile heated at different temperature

Figure 4. SEM images a) of the raw pyrophyllite, b) the ceramic tile heated at 900 °C, c) 1000 °C, d) 1100 °C
The variation of compressive strength depending on the temperature indicated that the compressive strength of the obtained ceramics increased from 8.007 MPa (±0.878 MPa) to 8.905 MPa (±0.561 MPa). This is a good agreement with the results obtained the total shrinkage and the water adsorption. The compact structure caused the high compressive strength.

4. Conclusions
Ceramic bodies were prepared from the raw pyrophyllite and the mixture of the pyrophyllite, Unye clay and feldspar. The highest strength, fire shrinkage and lowest water adsorption ratio were obtained for the ceramic produced from the optimum mixture of 70 wt % of pyrophyllite, 20 wt % of Unye clay and 10 wt % of feldspar. With increasing the firing temperature to 1100 °C, the glassy form occurred into the ceramic structure and this filled the interstices among particulates increasing fire shrinkage and decreasing water absorption ratio. Given the low cost of pyrophyllite, production of pyrophyllite containing ceramic may prove economical. Due to its comparatively low strength, it was determined that during raw material preparation pyrophyllite can be a provide energy and time saving product, due to its specific and extremely white baking colour and high temperature resistance.

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