Optimization of the sintering process of raw material wastes

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Abstract

The analysis of the mineralogical composition of most rock wastes shows the presence of a high percentage of minerals with SiO_2 and Al_2O_3, which could be used as raw materials for ceramic products. The main objective of this work is to recover wastes from one primary rock industry, utilised in the production of tiles and flooring, for the manufacturing of ceramics, using powder technology: pressing and sintering. The sinterability of the powders, with and without previous heat treatment, was studied in order to obtain a product with the best performance. Powders from different quarries after being uniaxial pressed at 40 MPa, or isostatic pressed at 170 MPa and sintered within the range 1150–1170°C present properties as follows: (a) hardness: 5.5–7.5 GPa; (b) transverse rupture strength: 55–94 MPa; (c) abrasion and erosion wear better than that of bulk to be drawn materials, and (d) water absorption of less than 0.5%. The results allow the conclusion that these wastes can be recovered and used successfully in the manufacture of ceramics with better performance than traditional tiles and flooring. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

During the manufacturing process of tiles and flooring from schist, from mining to their last machining operation, there are thousands of tons of wastes, which are presently unrecoverable. This creates several problems, involving the economic aspects of production (sometimes losses of over 50% of the raw material) and environmental aspects, i.e. thousands of tons of wastes usually end up in rivers or become part of the landscape as mountains of slurries.

Patents and open literature refer to the recovery process of these wastes in their direct application as additives of other products, or mixed with organic resins [1–4]. However, these applications are not enough for the enormous quantity of wastes produced in world quarries. The application of these wastes as raw material in the manufacturing of ceramic products could be a good alternative because it will mean greater consumption. For this to occur, it is important to study the thermal stability of the mineral components and to characterise the physical and mechanical behaviour of these complex materials.

Despite the great quantity of research work on the heat treatment of clays, little information is available concerning other raw materials from sedimentary and metamorphic rocks. The phase diagrams available [5] might be necessary information but are not sufficient for the understanding and establishment of sintering conditions. The aim of this research work is to optimise sintered schist wastes, taking into account the properties of the bulk material and those of traditional glazed tiles.

2. Experimental

The chemical composition of samples P and G (Table 1) were analysed using atomic absorption spectroscopy equipment, Perkin-Elmer 303, a UV/vis spectrophotometer, Perkin-Elmer λ2, and an electron microprobe Cameca SX50 (EDAX). X-ray diffraction was the technique utilized to determine the mineralogical composition. In this case a Philips diffractometer Xpert was used with a heating capacity of up to 1400°C with an anticathode of cobalt

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Table 1
Chemical composition of the samples

Oxides (%)	P	G
SiO$_2$	53.4–57.2	53.9–79.8
Al$_2$O$_3$	23.9–26.8	15.8–26.8
Fe$_2$O$_3$+FeO	7.9–11.6	5.4–10.8
Others oxides[a]	8.2–9.8	8.7–6.8
Loss of ignition	4.8–5.9	7.3–6.9

[a] TiO$_2$, MnO, MgO, CaO, Na$_2$O, K$_2$O, P$_2$O$_5$.

($\lambda K_{\alpha 1}$=1.78896 Å, $\lambda K_{\alpha 2}$=1.79285 Å). To analyse the diffractograms the ICDC patterns were used. The samples were also analysed with optical microscopy and scanning electron microscopy (Jeol T 330). Some samples from G were calcined at 1250°C and subsequently milled (these samples are identified as GC). The steps of the experimental procedure are summarised in Fig. 1. After sieving the samples under 100 μm, the powders of P and G samples were uniaxially compacted at 40 MPa and the GC samples were cold isostatically pressed at 170 MPa. The green parts were sintered at temperatures between 1000°C and 1200°C in order to determine their sintering behaviour through densification. The apparent density was measured using the Archimedes method and employing a sealant in order to occlude open porosity and real density, through a helium picnometer.

The materials were tested mechanically: transverse rupture strength in a three-points bending test, hardness and wear resistance. The mechanical reliability of the transverse rupture strength, from the point of view of the Weibull modulus, was obtained through the method described by Molinari et al. [6]: 20 samples of dimensions 100 mm ×50 mm×3 mm were tested. The hardness of the materials was determined through the Mohs and Vickers scales. The materials that presented the best performance were subjected to the tests that are usually conducted on materials for construction: abrasion, erosion and water absorption. The abrasion test was conducted in accordance with the ASTM G 65-94 standard under the following conditions: speed of rotation, 200 r.p.m.; load, 130 N; number of rotations, 2000;
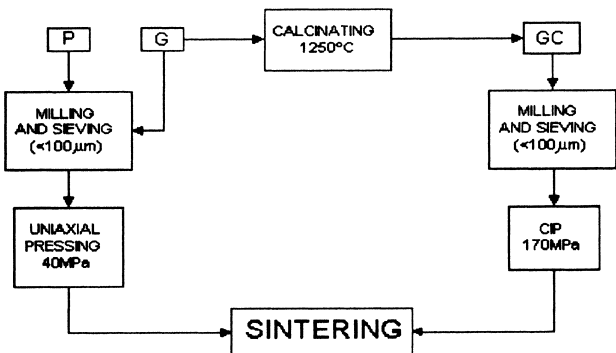
diameter of the wheel, 226.3 mm; width of the wheel, 13.6 mm; abrasion flux, 400 g/min; the results were compared with those of 14 different glazed ceramics. The erosion test was carried out using Air Jet Erosion Test Mach, experimental equipment made by Falex Corporation. Alumina was used as an erosive in the experiment. Water absorption was measured using the standard project of European Norms 1339/96.

3. Results

The chemical analyses of schist are presented in Table 1 (wt%). The principal components are silica, alumina and iron oxides. In Fig. 2 the variation of the density as a function of the sintering temperatures is shown. In the P and G samples, the results for temperatures of up to 1150°C are similar.

The transverse rupture strengths as a function of the sintering temperatures are shown in Fig. 3 and their reliability under the Weibull modulus parameter in Fig. 4. P, G and GC samples present the same value when sintered at 1150°C (80 MPa). At a sintering temperature of 1170°C, the bending strengths are maximal for P and G. However for the previously heat-treated samples, the bending strength decreases significantly with temperatures higher than
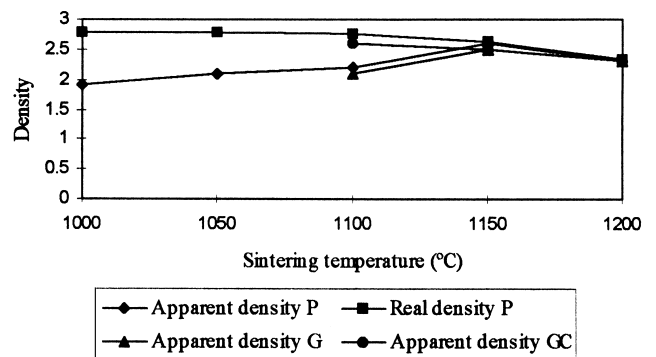

Fig. 2. Sinterability of the P, G and GC materials.

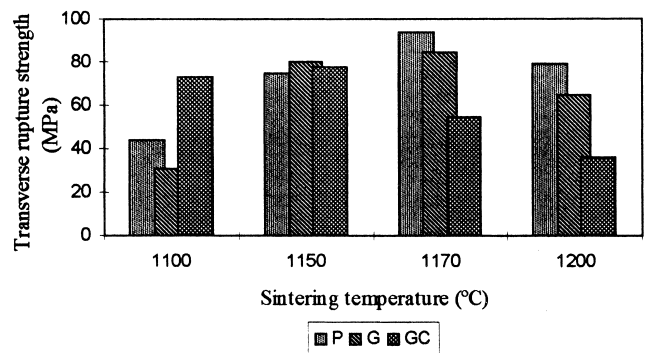

Fig. 1. Flow chart of the experimental process.

Fig. 3. Transverse rupture strength of sintered P, G and GC materials for different sintering temperatures.
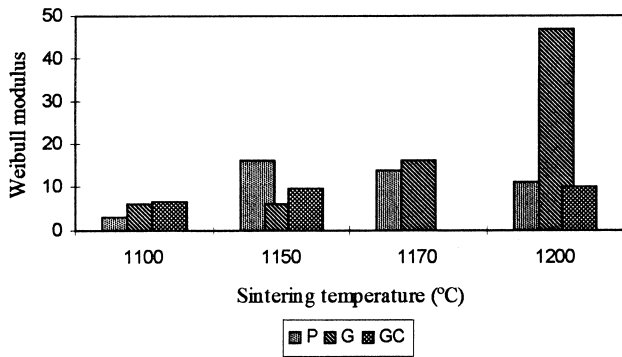
Fig. 4. Weibull modulus of sintered P, G and GC materials for different sintering temperatures.

1150°C. Also, after sintering at 1150°C, the Weibull modulus is normally higher than 10.

The variation of the Vickers hardness with sintering temperatures (Fig. 5) shows a maximum hardness at 1100°C for P samples and 1150–1200°C for G samples. In the Mohs scale the values for those temperatures are 7–8 hardness.

Figs. 6 and 7 show the results related to the wear behaviour of the materials under study. The comparison of the abrasion test results of the materials studied with those of 14 different ceramic glazed flooring tiles (T) are presented in Fig. 6. Fig. 7 reports the erosion rate of the P materials in
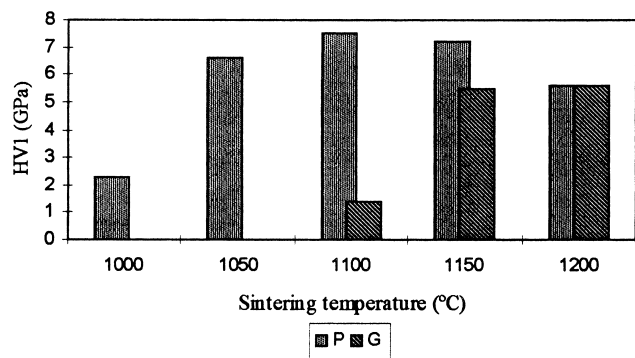

Fig. 5. Vickers hardness of sintered P and G materials for different sintering temperatures.
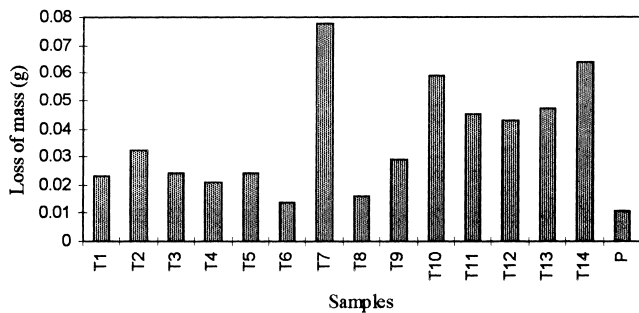

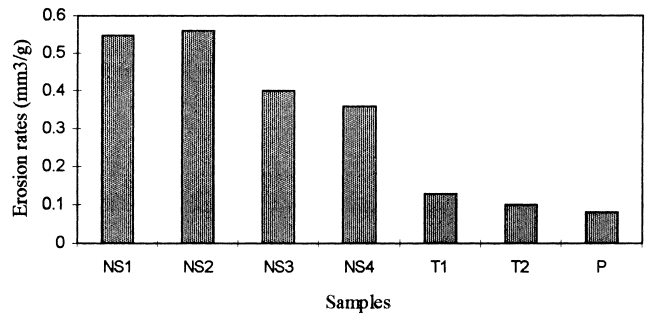Fig. 6. Abrasion results comparing sintered P materials with different ceramic flooring tiles (T).

Fig. 7. The erosion rate of sintered P materials in comparison with those of natural stone (NS) and ceramic flooring tiles (T).
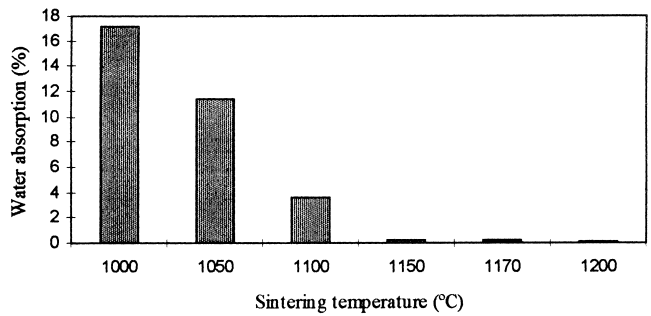

Fig. 8. Water absorption of sintered P materials for different sintering temperatures.

comparison with that of natural stone (NS) often used as paving, and two ceramic flooring tiles (T). In both cases the recovery product presents the best properties.

The results concerning the test of water absorption in P materials as a function of sintering temperature shows that for a sintering temperature of 1150–1200°C the water absorption is nearly zero (Fig. 8).

4. Discussion

Taking into account the experimental results, it can be affirmed that samples densify easily for densities up to as close as 90% of the theoretical density 1. Using this as the main parameter, and looking at Fig. 2, these materials densify even at low temperatures (1100°C), considering the temperature at which conventional ceramics are fired. Thus one can deduce that these wastes can be processed just like ceramic materials.

In reality, the detailed study undertaken on structural phase transformations occurring in those materials as a function of temperature enabled the determination, through the analysis of the results of X-ray diffraction (Figs. 9–11) and chemical analysis by EDAX, the irreversible formation of hercynite, mullite and amorphous silica at above 1100°C. The irreversibility of the transformations that occur during the treatment at higher temperatures is shown also by the unchangeability of the X-ray diffractogram obtained at a
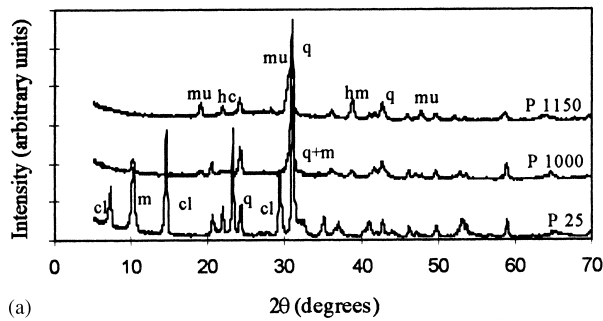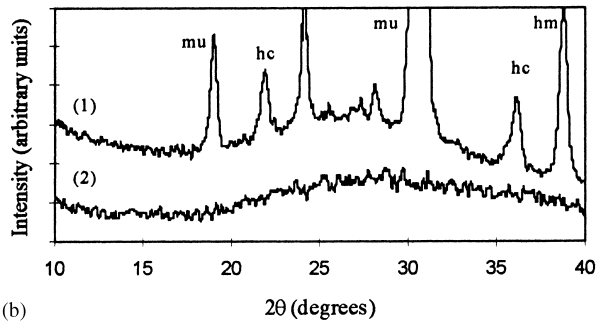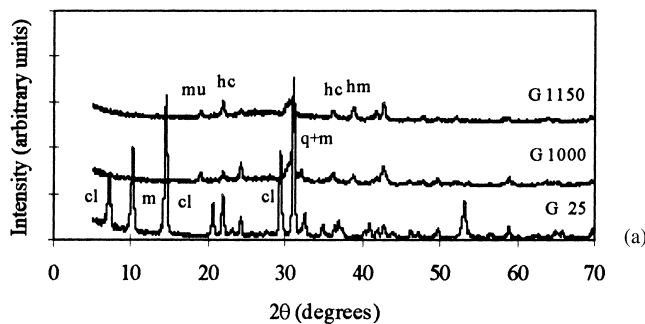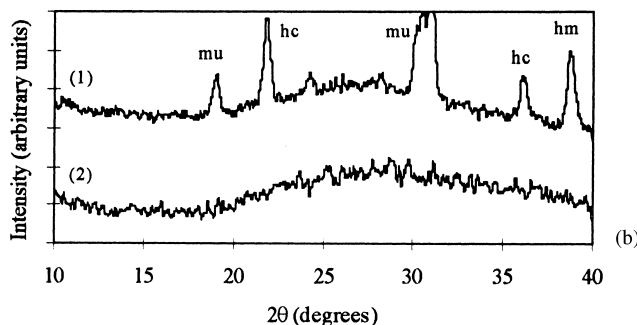
Fig. 9. (a) X-ray diffraction of P materials at different temperatures (q – quartz; m – mica; cl – chlorite; mu – mullite; hc – hercynite; hm – hematite). (b) Details of the P1150 diffractogram (1) and amorphous silica as standard (2).

Fig. 10. (a) X-ray diffraction of G materials at different temperatures (q – quartz; m – mica; cl – chlorite; mu – mullite; hc – hercynite; hm – hematite). (b) Details of the G1150 diffractogram (1) and amorphous silica as standard (2).
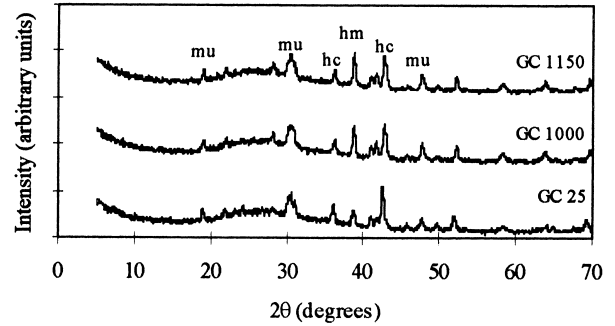

Fig. 11. X-ray diffraction of GC materials at different temperatures (mu – mullite; hc – hercynite; hm – hematite).

high temperature and also by those resulting from GC materials, previously treated at 1250°C (Fig. 11). The quantity of these phases is higher as the treatment temperature increases. During the evaluation of hardness, it was noted that at particular locations, the hardness values were significantly higher than the mean value (>10 GPa), which could be due to the presence of a very hard phase, spread over the matrix, that could be related to mullite. However, the SEM observation and the evaluation of the chemical composition by EDAX is not sufficiently clear in the identification of how these phases are distributed in the samples. For example at 1200°C the chemical analysis performed on different points of the sample only reveals three different typical chemical compositions: $3(Al,Fe)_2O_3 \cdot SiO_2$; $(Al,Fe)_2O_3 \cdot SiO_2$, which could be interpreted as two types of mullite or a mixture of mullite and hercynite; and $FeAl_2O_3 + SiO_2$ as hercynite with silica. These are not attached to a special phase micrography and could be present at close points of the same "phase".

The increase of amorphous silica with sintering temperature (Figs. 9 and 10) enables the conclusion that this phase serves as a binder, lodging into the pores available between the granules of the material, and being responsible for the increase in the mechanical behaviour of the samples, and the decrease in water absorption. In fact, from the studies undertaken on the absorption of water as a function of thermal treatment (Fig. 8) it can be concluded that the absorption only decreases significantly when the temperature during the treatment reaches a level higher than 1100°C, meaning after the clear formation of the amorphous phase.

Therefore, the mechanical behaviour of the heat-treated samples serves to prove that whilst the amorphous phase plays an important role in the densification process, mullite and hercynite can also play an active role in the process, although this is yet to be demonstrated.

The initially constant values of the mechanical resistance of the previously heat-treated samples (GC) show that this behaviour is related to phase transformations that occurred during the previous roasting. In fact, taking into consideration Fig. 11, it is verified that after previous heat-treatment, the phases present are similar to those that occurred during

the sintering of the P and G samples (>1000°C). However, the degradation of the bending strength for high values of sintering temperature, which can be related to an excess of the formation of silica during sintering, can be verified as being related to the temperatures of the treated powders. In effect, the excess of a fragile phase in the ceramic material could be responsible for the decrease in its mechanical properties.

Properties related to mechanical behaviour such as hardness, transverse rupture strength, abrasion and erosion wear, show higher values of reliability when compared with those of other traditional glazed ceramic products [7,8]. The excellent Weibull modulus should be highlighted, particularly for samples treated at 1150°C, especially when considering the Weibull modulus of 10, which is the goal for what are called advanced ceramics [9,10].

5. Conclusions

The technical properties of recovery wastes in relation to those of natural stone or other glazed or non-glazed traditional ceramics, are highly favourable. All of these properties reveal that the new materials have a wide range of applications and are highly competitive with most traditional ceramics presently on the market.

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