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Porcelain stoneware obtained from the residual muds of serpentinite raw materials

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Abstract

The recycling of solid waste produced by the processing of natural raw materials and urban centres is one of the priorities of the European Community. As a means of reducing such waste, government agencies are encouraging the manufacture of alternative ceramic products. In the present work the possibility of using serpentinite muds from a quarry of dunite rocks to make ceramic products is explored. It was found that the ceramic blocks obtained after processing these muds present a very high fracture resistance, very low porosity with an optimum colour after firing, and an excellent polished surface, qualities which make them highly suitable for producing porcelain stoneware.

Keywords: Serpentinite silt; Physical and chemical properties; Porcelain stoneware

1. Introduction

The European Commission aims through its Framework Programme for Research and Technological Development to reduce the amount of pollutants (solid, liquid and gas)[1] by encouraging the recycling of solid waste as a raw material for industrial purposes.[2–5]

Porcelain stoneware is a ceramic product[6,7] which has become very popular and its use has spread enormously over the recent years. In addition to its great resistance to wear, porcelain stoneware has a number of other interesting properties, such as its ability to withstand chemical attack, extremely low values of water absorption and its excellent behaviour in frost and flexural tests.

Spain has a significant extraction industry of peridotite plutonic rocks[8–10] which are difficult to classify due to the diverse processes of serpentinisation by which they have been affected. Their main mafic components are olivine and minerals from the pyroxene and amphibole groups. The terms olivine, dunite and serpentinite are the main commercial names for such rocks, all of which contain olivine in varying proportions. Olivine, $(Mg,Fe)_2SiO_4$, is a solid solution of two minerals: forsterite ($MgSiO_4$) and fayalite (Fe_2SiO_4). Dunite is a rock rich in olvine (>90% volume) while serpentinite is a rock mainly composed of clay minerals from the serpentinite group – $(Mg,Fe)_3Si_2O_5(OH)_4$ – originating from the alteration of olivine or dunite rocks. Commercially, the term olivine is used to refer to materials with a MgO content of 45–50 wt.%, SiO_2 39–42 wt.%, F_2O_3 5–8 wt.% and losses due to calcination of 1–2 wt.%, while the term dunite–serpentinite refers to rocks with MgO contents of 35–45 wt.%, SiO_2 36–39 wt.% and with losses after calcination exceeding 8 wt.%. Worldwide, the main exploitable deposits of peridotite rocks are the ones of the serpentinite kind.

In this investigation, a detailed study regarding the physical and chemical properties (granulometry, mineralogy, chemical analysis, etc.) of serpentinite silts from a dunite rock quarry has been carried out in order to select the most adequate processing route to obtain dense ceramic products. The mechanical properties of the obtained materials as a function of temperature were studied in order to evaluate its use as porcelain stoneware.

2. Experimental procedure

2.1. Raw materials

Four samples of waste muds from the decanting ponds of a quarry of peridotite rocks (serpentinite–dunite) were taken from Mina David in Llandoy, in Cariño, La Coruña, NW, Spain,

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belonging to the company, Pasek, S.A. The muds were dried at 120 °C for 24 h and subsequently a granulometric analysis was carried out (Coulter LS 130 system). The results obtained were displayed on a Shepard diagram[12] using the Wentworth scale nomenclature[11] (sand > 62 μm; 4 μm < siltstone < 62 μm; clay < 4 μm).

The chemical composition of the muds was analysed by X-ray fluorescence in a Siemens SR-3000 spectrometer, with the exception of the sodium content which was analysed by atomic absorption spectrophotometry (AAS) in a ThermoJarrell Ash model IL-951 system.

Samples were ground in a ball grinder (alumina) down to 40 μm in order to make an X-ray diffraction analysis. X-ray diffraction powder patterns were obtained from 2° to 65° (2θ) in a Siemens Diffractometer model D-5000, fitted with a Cu anticathode and operating at 30 mA and 40 kV. Orientated aggregates were taken from the serpentinite muds in order that any clay minerals could be detected. In addition, the usual thermal and solvation treatments at 550 °C/2 h and 60 °C for 24 h, respectively, were carried out.

The ground dry mud was isostatically pressed at 200 MPa to provide the green cylinders used to obtain the dynamic sintering curve on a Bähr type 802 dilatometer. The final temperature of the test was 1250 °C with a heating rate of 5 °C/min.

Finally, a DTA–TG curve (heating rate 5 °C/min) of the ground dry serpentinite muds was obtained.

2.2. Processing

The dry powder with a degree of humidity of 5% was uniaxially pressed at 400 kg/cm^2 in order to obtain 41 mm diameter and 6 mm thick cylindrical disks. These disks were thermally treated in a laboratory furnace from 1050 to 1200 °C at a heating rate of 5 °C/min. The holding time at the maximum temperature was 1 h.

The physical properties of the fired samples, such as apparent density, open porosity and absorption capacity, were measured according to the Spanish UNE 61-033-90 standard.[13]

The mechanical properties were analysed employing machined samples with the following dimensions: 3 mm × 4 mm × 40 mm. The four points bending method test was performed at room temperature in an Instron universal testing machine (model 8562).

The fired and polished samples, previously coated with a thin layer of gold, were subjected to a microstructural examination in a scanning electron microscope (SEM) (Zeiss, DSM 942-model) equipped with a X-ray microanalysis probe from Oxford (Link Isis II).

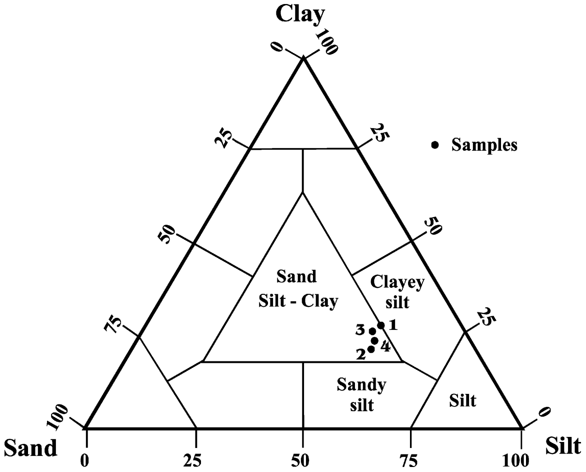

Fig. 1. Graphical representation of the granulometry from serpentinite mud samples (after Shepard diagram[13]).

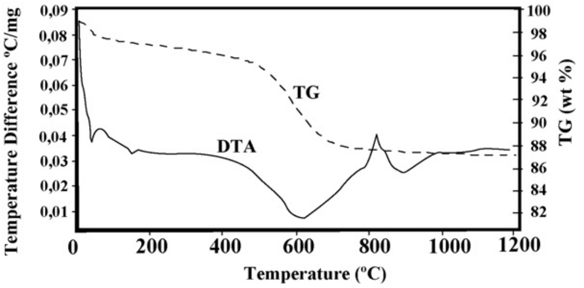

Fig. 2. DTA/TG curve of the serpentinite mud raw material.

3. Results and discussion

The results of the granulometric analyses of the silts "as received" are shown in Fig. 1. In accordance with their location on the Shepard diagram,[12] they are classified as sand-silt-clay materials. The powder used to make the ceramic bodies had the following granulometry: 90% volume of the material had a particle size of less than 70 μm with a mean value of 28 μm.

Table 1 shows the chemical composition of the analysed samples. The mineralogical composition of the silts studied is as follows:

(a) Non-clayey minerals: forsterite (majority), minerals of the pyroxene group (enstatite) and of the amphibole group (actinolite, tremolite, magnesian hornblende).

(b) Clayey minerals: mainly minerals of the serpentinite group (antigorite), together with minerals from the chlorite and the vermiculite group. This type of mineralogical association is

Table 1
Chemical composition (wt.%) of the analysed samples

Samples	SiO_2	Al_2O_3	Fe_2O_3	CaO	TiO_2	MnO	K_2O	MgO	P_2O_5	Na_2O	Ppc
Mud 1	39.81	3.83	6.65	3.111	0.194	0.188	<0.10	32.0	0.070	0.148	13.93
Mud 2	39.17	4.06	6.167	3.553	0.215	0.215	<0.10	31.85	0.079	0.146	14.48
Mud 3	39.13	4.31	6.351	3.327	0.220	0.172	<0.10	31.93	0.087	0.162	14.24
Mud 4	38.85	4.59	6.338	3.005	0.212	0.167	<0.10	32.36	0.120	0.159	14.16

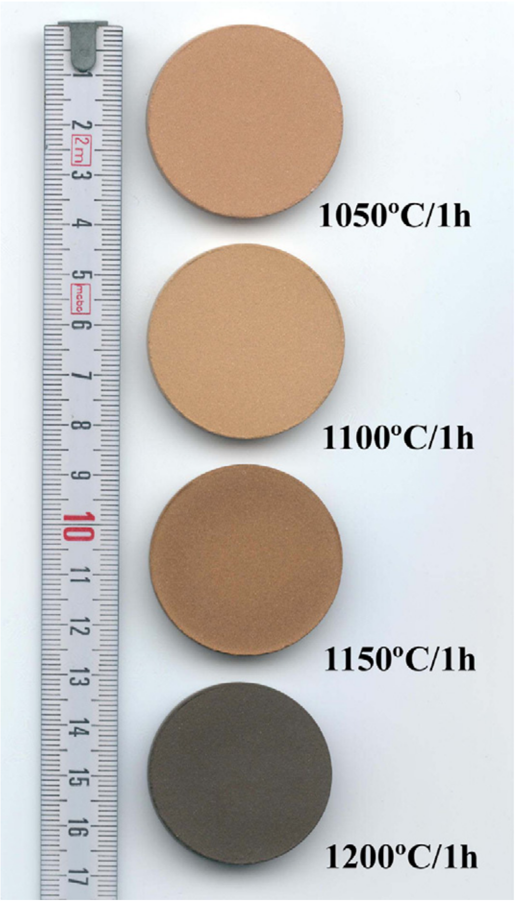

Fig. 3. Fired specimens of serpentinite muds at different temperatures produced by uniaxial pressing.

related to the surface meteorisation of the original dunite rock.[14]

The DTA/TG curves are shown in Fig. 2 and are clearly related to those obtained by X-ray diffraction. A weak endothermic peak can be observed below 100 °C as a result of the hygroscopic moisture of the mud. The marked endothermic peak during heating is principally caused by the presence of the serpentinite minerals (principally antigorite). Beyond 200 °C there is slight endothermic peak which reflects the loss of water from inside the vermiculite minerals.[15] At 653 °C, the removal of hydroxyl groups from the chlorite and serpentinite minerals takes place and, immediately afterwards at 823 °C, a well-marked exothermic peak due to structural reorganization within the serpentinite minerals (antigorite)[16] occurs.

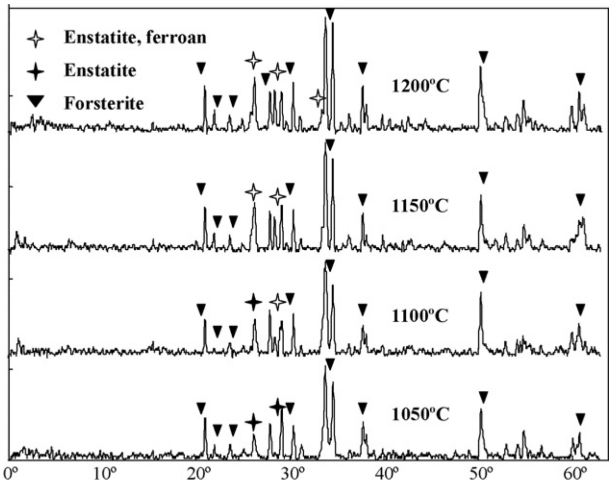

Fig. 4. XRD patterns of the fired ceramic samples at several temperatures between 1050 and 1200 °C.

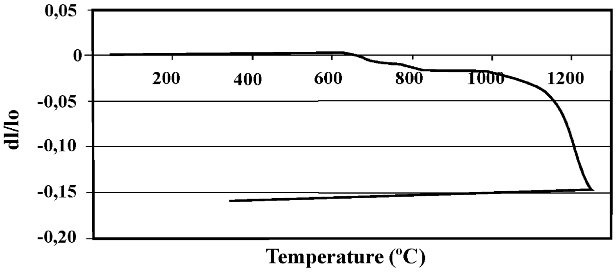

Fig. 5. Dynamic sintering curve of serpentinite mud powder.

Fig. 3 presents a general view of the fired samples at different temperatures. The chromatic development of the colours ranges from red tones for the tested samples fired at a low temperature (1050 °C) to a brown colour at the end of the test (1200 °C)

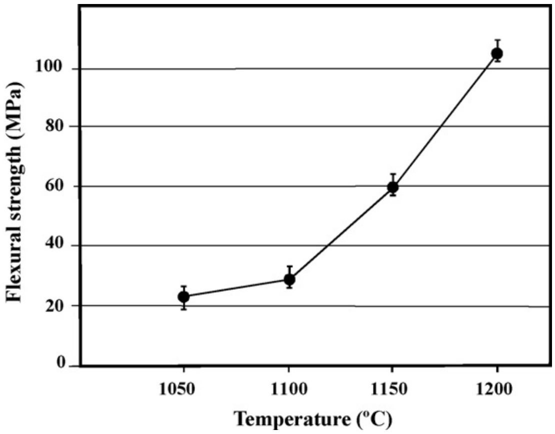

Fig. 6. Flexural strength graphic results from the fired samples at different temperatures between 1050 and 1200 °C.

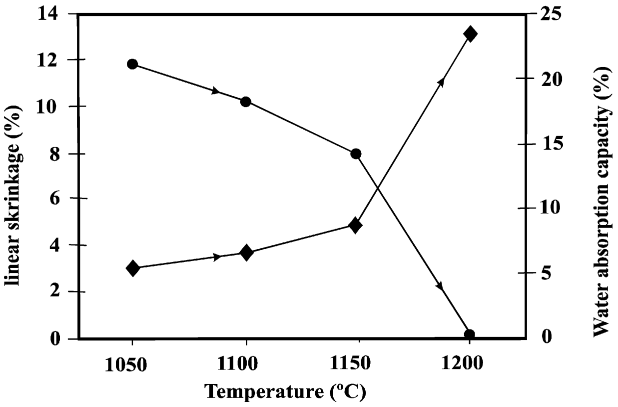

Fig. 7. Evolution of linear shrinkage and water absorption capacity of the sintered ceramic samples at several temperatures.

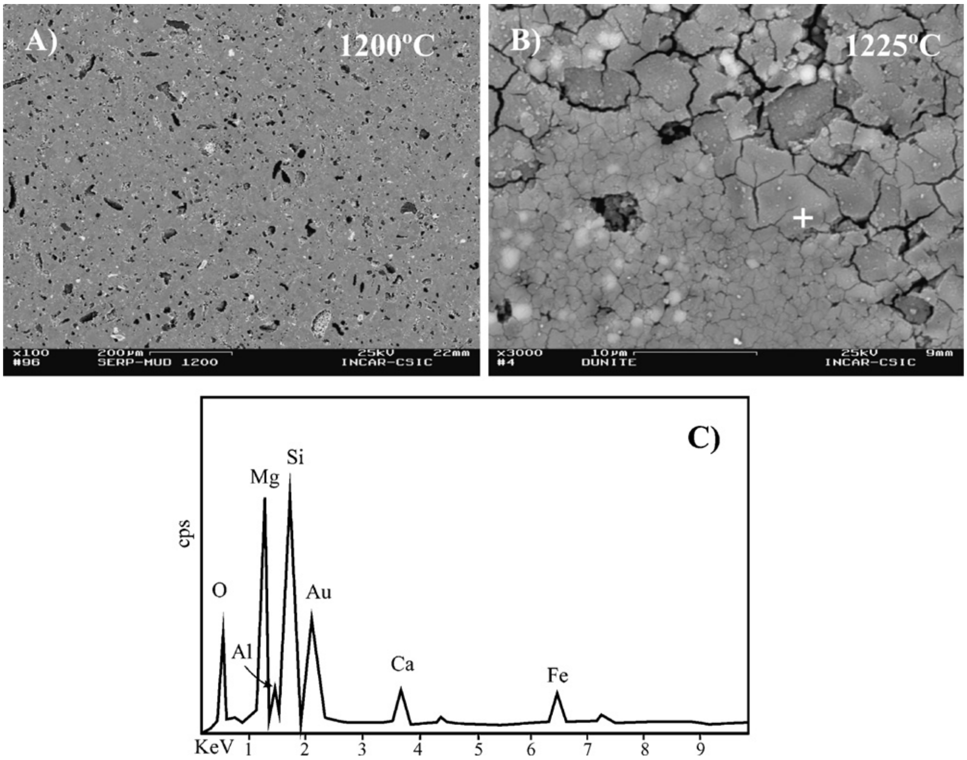

Fig. 8. (A) SEM image (secondary electrons) corresponding to the fired ceramic sample at 1200 °C; (B) SEM image (back scattered) corresponding to the sample sintered at 1225 °C, showing cracks due to swelling; (C) EDX analysis corresponding (white cross).

due mainly to the iron oxide content of the samples. Higher firing temperatures promote greater glass formation, which will darken metallic colouring oxides (as the iron oxide present in the muds).

Fig. 4 shows the mineralogical phase development as a function of temperature. Overall, only three phases appear between 1050 and 1200 °C: forsterite, enstatite and ferrous enstatite.[17] A ferrous enstatite phase appears at 1100 °C which stabilizes above 1200 °C.

The dynamic sintering curve of the isostatically pressed sample at 200 MPa can be seen in Fig. 5. The sintering stage starts at 600 °C as a result of the decomposition processes of the clayey minerals in the sample. A highly significant contraction occurs at about 1000 °C due to the acceleration of the sintering process caused by the presence of a large amount of liquid phase.

Improved physical and mechanical properties on fired samples are obtained at a sintering temperature of 1200 °C, with a holding time of 1 h. Above these temperatures (for example at 1225 °C), the samples swell due to the oxidation processes of the iron oxide[18] and the piroplasticity phenomena related to the high liquid phase content, mainly via the reaction of the clay minerals.

The results of the flexural tests, as a function of sintering temperature, are given in Fig. 6, while the variation of the linear contraction and water absorption capacity compared to temperature are shown in Fig. 7. Beyond 1050 °C, due to the reduction in open porosity, there is a drastic decrease in the capacity of the fired samples to absorb water, with values close to zero at about 1200 °C.

Fig. 8A shows the general microstructure of a polished sample taken from the ceramic pieces fired at 1200 °C. At this temperature the porosity is reduced and the micropores (elongated shape) are well distributed. Fig. 8B shows a high magnification SEM image were two different magnesium silicate phases with different transitional Fe contents are observed (dark and light). A third phase constituted by metals like Fe, Cr, can be observed as white spots in the micrograph.

4. Conclusions

Serpentinite waste muds from dunite quarries can be used as conventional raw materials in the ceramic industry. They possess good mineralogical, chemical, thermal, and mechanical properties which make them suitable for producing porcelain stoneware. During sintering and beyond 1150 °C, the studied composition starts to become dense with water absorption values approaching zero at 1200 °C (closed porosity), and the microstructure is mainly formed by two different magnesium silicate phases with different Fe contents. The mechanical resistance values obtained at this temperature are fairly high (average value of 110 MPa) whereas beyond 1200 °C a considerable swelling take place due to the expansion of the gases occluded at the heart of the samples.

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