JOURNAL OF MATERIALS SCIENCE 22 (1987) 2493–2496

Expanded materials from quartz–porphyrite sands

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Experiments on the preparation of glass from quartz–porphyrite sands showed the occurrence at about 1300° C of extensive bubble formation which cannot be easily removed on further heating at higher temperatures. This prompted us to exploit this process in the synthesis of expanded material. The research work was addressed to determining the origin of the bubble phenomenon in order to control the potential foaming at high temperature. The parameters controlling the production of cellular glass directly from quartz–porphyrite sands are presented and discussed. The results allow the preparation of polycellular vitreous material with a homogenous bulk distribution of SiO_2 microcrystals. The main features of the product are: bulk density in the range 720 to 980 kg m^{-3}; average bubble diameter 0.1 to 0.3 mm; thermal conductivity 0.19 to 0.28 W m^{-1} (° C)$^{-1}$; compressive strength 1.96 to 3.92 MPa.

1. Introduction

In the area of Trento quartz–porphyrite materials are commonly called "porphyry" and we shall use this name through all this work.

The peculiar layering and cracking of porphyry rocks in the Trento region allow the use of these rocks for route paving as small cubes, for inside flooring as smooth slabs, for bordering sidewalks and platforms and for decorating outside artworks. This high-quality exploitation of local quarries involves a 60 to 70% loss of the extracted crude material, with severe economical and environment problems due to the wide discharge areas of the discarded rocks.

The use of porphyry quarry litters has stimulated the private and public research organizations into finding suitable applications such as glass or glass raw materials, expanded products, abrasive materials, chamotte and other uses.

The present research was performed within this general scope, having as a target the preparation and characterization of expanded inorganic products starting from porphyry powders of quarry work wastes.

TABLE I Mean chemical composition and standard deviation (σ) of material from forty different porphyry quarries

Component	Composition (wt %)	σ
SiO_2	72.96	1.31
Al_2O_3	14.60	0.71
Fe_2O_3	1.82	0.25
TiO_2	0.28	0.08
Na_2O	1.70	0.94
K_2O	5.41	0.39
CaO	0.85	0.60
MgO	0.38	0.16
Other oxides	0.15	0.09
Wl*	1.83	0.58

*Weight loss due to carbonate reduction.

2. Experimental procedure

Samples of porphyry were collected from forty different quarries of the Albiano (Trento) area. The average concentrations of single oxide components were determined by X-ray fluorescence analysis (Philips PW 1220). The results and relevant standard deviations are reported in Table I.

Since the chemical composition is quite constant irrespectively of the particular quarry, further research was performed on samples from a single quarry whose composition is reported in Table II.

3. Results and discussion

3.1. Thermal behaviour

Porphyry foaming upon thermal treatment at high temperatures was immediately apparent from preliminary experiments. Even though the literature is rich both in publications and in patents [1–8], we had difficulty in identifying the foaming agent, because the foaming occurred at an unusually high temperature.

Fig. 1 shows the product heated at 1350° C for a short time by using a thin porphyry sand obtained by grinding. The phenomenon was studied by optical

TABLE II Chemical composition of the porphyry selected for present research

Component	Composition (wt %)
SiO_2	73.30
Al_2O_3	14.40
Fe_2O_3	2.41
TiO_2	0.24
Na_2O	2.40
K_2O	5.00
CaO	1.08
MgO	0.57
Wl*	1.21

*Weight loss due to carbonate reduction.

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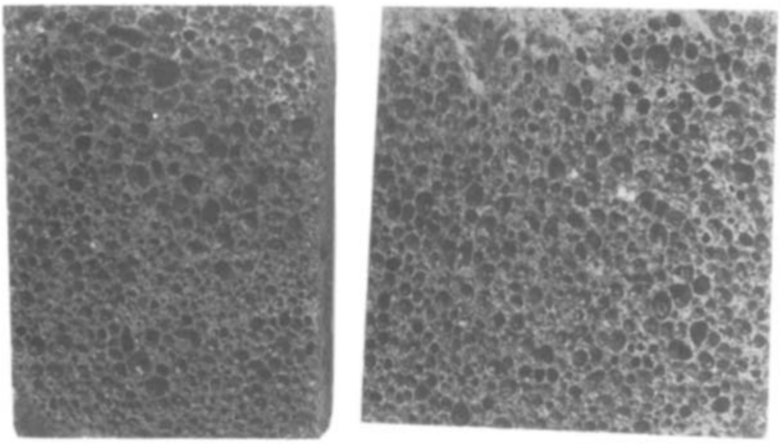

Figure 1 Foam structures obtained from porphyry powders.

microscopy, density measurements, differential thermal analysis (DTA) and thermal gravimetry (TG). The latter experiments were made at temperatures up to 1500° C using samples treated for 2 h at 200° C to eliminate the non-bonded H_2O.

Fig. 2 shows a typical TG profile (Mettler Thermoanalyzer TA1). Two weight loss maxima are present at 500 and 730° C; these can be attributed to the decomposition of carbonates. The overall loss is 1.21%, in agreement with the literature values. The carbonate decomposition on heating was confirmed by weak acid attack on the crude material, which develops carbon dioxide whose chemical nature has been ascertained. Fig. 2 shows that above 900° C no further significant weight loss occurred.

The DTA curve (Fig. 2) displays a weak endothermic peak centred at 580° C, assigned to the alpha-quartz to beta-quartz transition, and two important endothermic effects at 1190 and 1300° C. The first peak at 1190° C may reasonably be attributed to feldspar melting, whereas the second one at 1300° C cannot be easily interpreted. On the other hand, since the latter falls within the temperature range where the foaming phenomenon is observed, we focused our attention on this 1300° C endothermic effect. It seemed conceivable to assign this effect to the Fe_2O_3 reduction reaction:

$$3Fe_2O_3 \rightarrow 2Fe_3O_4 + \tfrac{1}{2}O_2$$

which is an endothermic reduction process occurring above 1300° C (Ellingham diagram).

Indeed, the DTA profile of pure Fe_2O_3 (Fig. 3) shows a strong endothermic peak at this same temperature. This hypothesis was confirmed by DTA experiments carried out on samples of porphyry sands treated with warm concentrated HCl to eliminate the Fe_2O_3 content of the original specimen (Fig. 4).

In these cases no endothermic effects were found at 1300° C, and DTA of samples calcined at 900° C (Fig. 5) does not display any signal corresponding to carbonate decomposition. Fig. 6 compares the pictures of samples prepared by heating up to 1350° C for both the HCl-treated material, i.e. in the absence of Fe_2O_3,

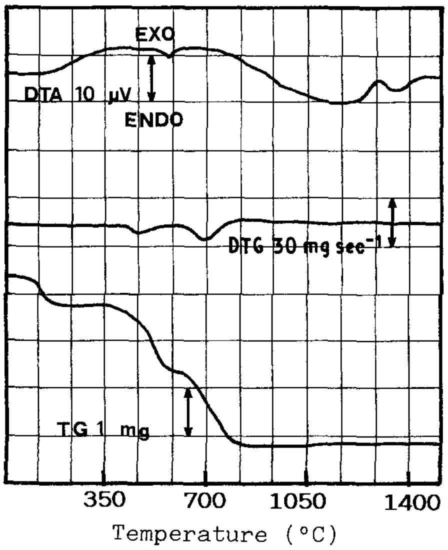

Figure 2 DTA/DTG/TG: porphyry powder (325 mesh, ASTM 11-70).

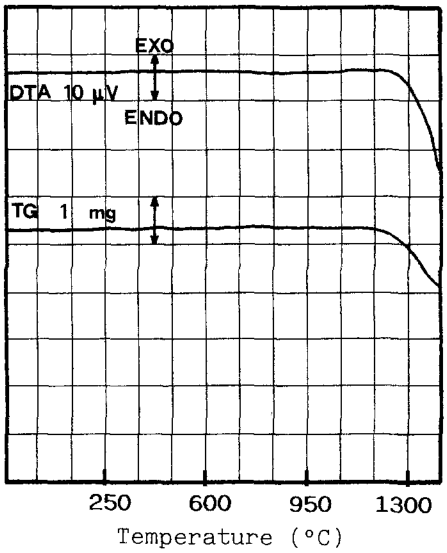

Figure 3 DTA/TG: haematite powder (325 mesh).

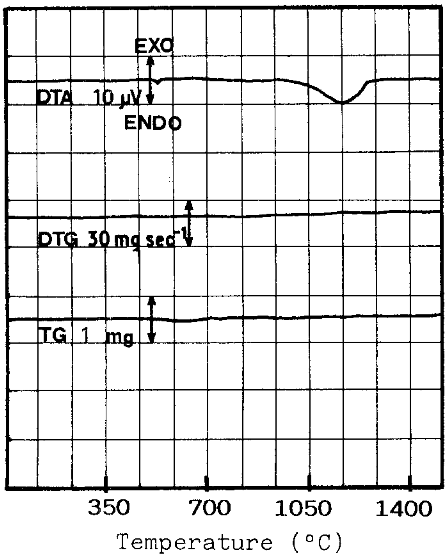

Figure 4 DTA/DTG/TG: porphyry powder (325 mesh) treated with warm concentrated HCl.

and the starting material: it is evident that foaming is absent once the iron oxide content is suppressed, ultimately supporting the idea that Fe_2O_3 reduction to Fe_3O_4 is responsible for the porphyry foaming. Further evidence for occurrence of the reduction reaction was obtained by mass-spectrometry analysis of the gas phase inside the bubbles of the expanded product. Mass spectrometry data indicate an O_2/N_2 ratio $= 9$, confirming that foaming is due to the free oxygen formed by the Fe_2O_3 reduction process induced by the high-temperature treatment.

This fact supports the hypothesis that at the foaming temperature, Fe_2O_3 is present and so available for thermal reduction to Fe_3O_4. However, it is possible that Fe_2O_3 is naturally present in a free form, since iron can be extracted by treatment of porphyry sands with any acid solution at pH 3.

3.2. Parameters for foamed material production and physical properties of the product

With the aim of getting a foamed product with mechanical and physicochemical features suitable for exploitation in building, the research was oriented to the achievement of uniform foaming. The occurrence inside single bubbles of a certain degree of vacuum, due to thermal contraction of the gas produced by the expanding process, can give a final product with good insulating properties and noise absorption or reflection features [9, 10].

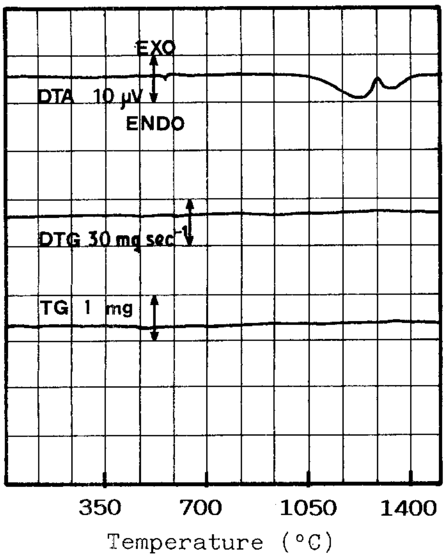

Figure 5 DTA/DTG/TG: porphyry powder (325 mesh) calcined at 900° C.

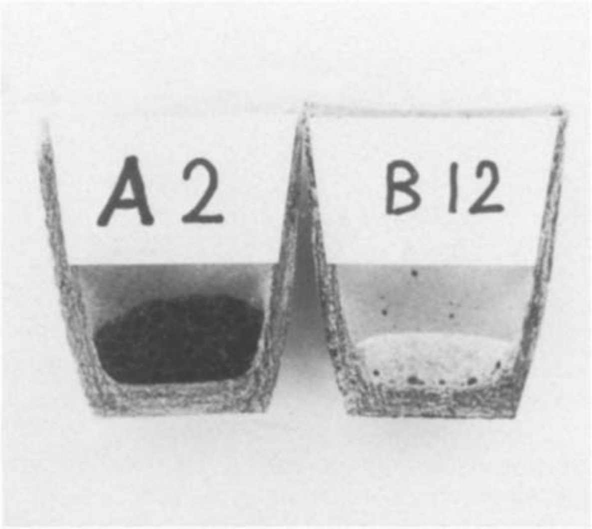

Figure 6 Porphyry powders (325 mesh) as-ground (A2) and treated with warm concentrated HCl (B12) after thermal treatment at 1350° C for 6 min.

The crude porphyry sand was mixed with the minimum amount of H_2O to obtain a medium which was poured and pressed in suitable stamps to achieve the desired shape. After drying, the cyclic thermal treatment of Fig. 7 was performed.

The following parameters were found to have an important effect on the foaming phenomenon:

(i) the particle size of used powders;

(ii) the residence time at a fixed temperature defined as the foaming temperature;

(iii) the viscosity reached by the thermal treatment; and

(iv) the Fe_2O_3 content and its distribution in the bulk.

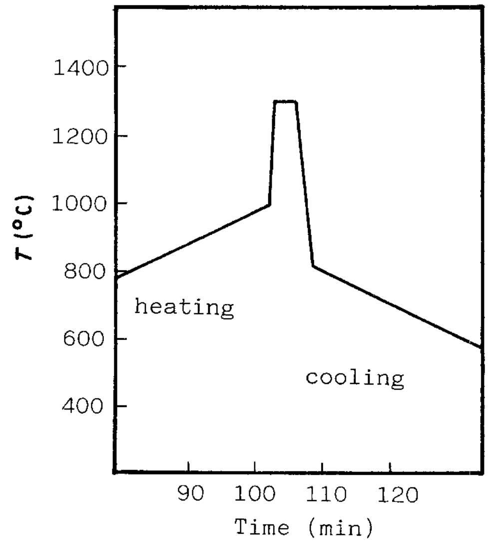

Figure 7 Thermal treatment cycle: heating rate up to 1000° C and cooling rate from 900° C are maintained at 10° C min⁻¹.

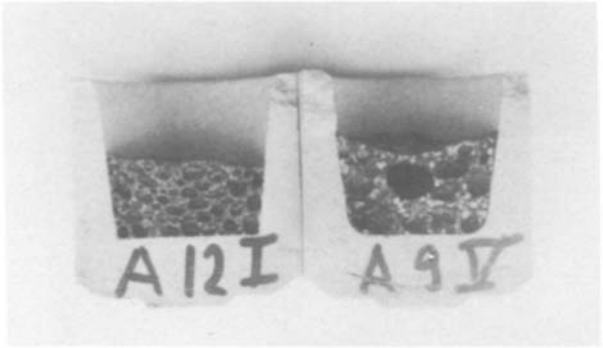

Figure 8 Foam structures obtained from porphyry powders of 325 mesh (A121) and 12 mesh (A9V).

Experiments at constant temperature (1350° C) show that the best distribution and homogenous shape of bubbles were obtained by lowering the mean particle size of the crude powders. Fig. 8 shows a typical good product prepared from a fine starting powder of size 325 mesh (ASTM E 11-70).

The relationship between the density of expanded material and the foaming temperature, at a constant residence time of 6 min, can be seen from the curve shown in Fig. 9. It is evident that the assumption of better foaming with increase of maximum heating temperature is incorrect; indeed, increasing the temperature above the so-called foaming temperature favours a viscosity decrease with consequent collapse of the bubbles.

The optimum Fe_2O_3 content, indispensable for bubble formation, was found to be from 2.9 to 2.1%. Larger percentages result in an increase of fluidification during the foaming process, leading to a final product with reduced bubble content and increased structural brittleness. Fe_2O_3 contents lower than 2.1% gave products with reduced foaming and higher densities owing to the lack of the chemical species responsible for the phenomenon.

The mechanical strength was found to be dependent on the density of the product. Fig. 10 shows the curves of compressive strength against density of final material for two series of samples obtained at different cooling rates. A different trend and a compression strength drop, observed for samples with higher cooling rates, may be attributed to the presence of a non-melted fraction of solid in the glass phase. Indeed, X-ray diffraction analysis (Philips PW 1050) of the expanded final product showed the presence of alpha-quartz (SiO_2) as small crystals which are present in the original porphyry powder and cannot be melted at the foaming temperature. This crystalline non-melted material may be responsible for important internal stresses as the material is rapidly cooled, ultimately resulting in a compression strength drop.

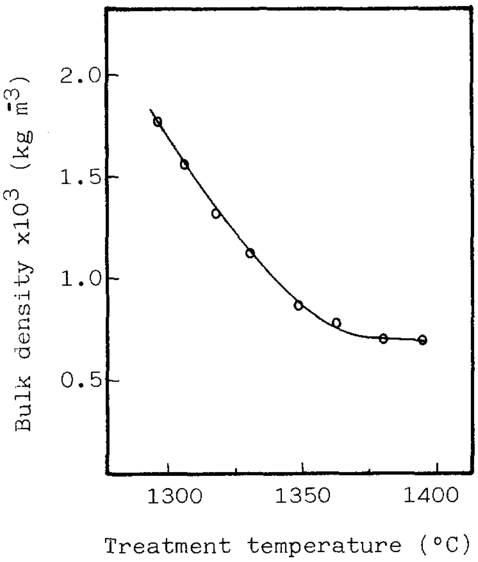

Figure 9 Bulk density as a function of treatment temperature for 6 min treatment time.

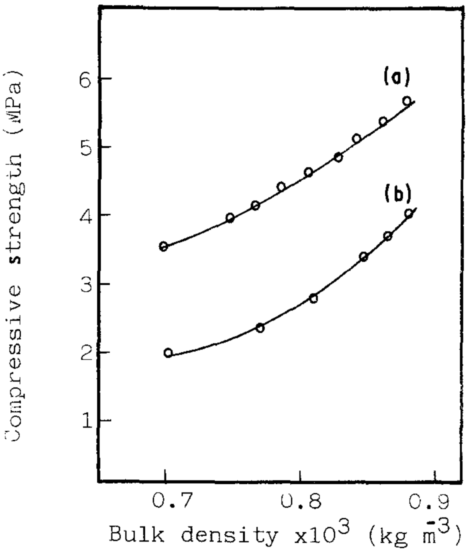

Figure 10 Compressive strength as a function of bulk density and cooling rate from 800° C: (a) $1° C\,min^{-1}$, (b) $10° C\,min^{-1}$.

Thermal conductivity was measured in the case of samples with density in the range 0.8 to 0.9 × $10^{-3}\,kg\,m^{-3}$: values fall in the range 0.18 to $0.28\,W\,m^{-1}\,(°C)^{-1}$.

4. Conclusion

The results indicate that it is possible to produce an expanded glass-like product using porphyry quarry litters as starting materials. The extension of the preparation procedure to any low-cost raw material of analogous chemical and physical composition seems quite promising and attractive, considering the valuable features of the final products.

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Received 18 August 1986
and accepted 15 January 1987