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Production of glass-ceramics from coal ashes

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Abstract

Coal fly ashes produced by an extinguished power plant in the north of Portugal have been melted with addition of $CaCO_3$ and Na_2CO_3 to obtain glasses. One of the formulated compositions was selected for further studies and it was possible to manufacture glass-ceramics by crystallising the parent glass through adequate time–temperature schedules. The macroscopic appearance, microstructure, mechanical, thermal and chemical properties indicated that these materials are quite attractive for cladding applications, exhibiting in some cases better performances than the conventional ceramic tiles. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The burning of coal in thermal power plants produces significant amounts of ashes. A number of methodologies of treatment and recycling has been developed to minimize the harmful effects in the environment caused by the landfill disposal of solid wastes.[1–4] Coal ash is usually a valuable source of minerals containing SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO and other oxides. These oxides can provide a useful preliminary batch for the preparation of glasses by melting the coal ashes. Sometimes, small amounts of other ingredients are added to the batch in order to lower the glass melting temperature.

In the last few years waste vitrification has been considered an attractive procedure for the treatment of different types of solid wastes, either municipal or industrial[5]. It destroys the hazardous organics and immobilizes heavy metals and radioactive elements, and additionally, it provides volume reductions that can vary between 40 and 99%.[5–9] The vitrification process can be followed by adequate thermal treatments, which result in the obtention of glass-ceramics with higher chemical durability, mechanical strength and wear resistance than the original glasses.[10–13]

Glass-ceramics based on wastes can have different applications, such as wall-covering panels, floors and roofs in industrial and public buildings, interior facing of containers for the chemical industry and as road surfacing.[14–21] These glass-ceramics usually have an attractive appearance[20] similar to that of natural granites and marbles (japanese and bulgarian patents)[22,23] and are predicted to have service lifes between 20 and 45 years, provided they are not exposed to intensive impact.[16]

In Tapada do Outeiro, an extinguished coal power plant in the north of Portugal, about 10 wt.% of the burnt coal was converted into fly ashes. In 30 years life, the disposal of about 100,000 tons of ashes per year created a huge landfill which transformed a valley into a mountain.[24] With the aim of reducing the environmental impact caused by such landfill, several studies have been made with these ashes and some solutions have been proposed, such as colour removers of textile industry effluents[25] and road surfacing.[24]

In the present work fly ashes from the landfill at Tapada do Outeiro have been used to produce glass-ceramics. The coal ashes were melted with added pure $CaCO_3$ and Na_2CO_3 and the obtained glasses were submitted to adequate time-temperature schedules, giving rise to attractive dark green glass-ceramics, with suitable properties for application as covering materials.

To accomplish this study, techniques such as inductively coupled plasma spectrometry, X-ray diffraction,

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differential thermal analysis and scanning electron microscopy have been used. Determination of thermal, chemical and mechanical properties has been made according to internationally accepted standards.

2. Experimental procedure

2.1. Characterization of raw materials

Four lots of fly ashes, collected from different places at the disposal landfill, were used in this study. These lots, identified by the names BC, PC, B and C, exhibited different macroscopic aspects. All, except BC, contained small hard stones, which were crushed together with the ashes and included in the respective batches. The moisture content of the four raw materials was determined by heating small amounts of powdered ashes at 110 °C until constant weight.

All ashes were crushed in a mortar and stored at 110°C in large trays, before use. To ensure an efficient heat transfer a thickness not higher than 1 cm was kept in all trays.

Since the amount of carbon in coal ashes is not negligible, a calcination process is required before further studies. Following literature indications[5] the calcination temperature was fixed at 950°C. The duration of the calcination stage was estimated by thermal gravimetric analysis (TGA), using a heating rate of 10°C min^{-1} from 20 to 950°C, and holding at this temperature for 7 h, to determine the time from which weight losses were kept unchanged.

The chemical composition of the fly ashes after calcination was determined by Inducectively Coupled Plasma (ICP) optical emission spectroscopy in a Jobin Yvon JY 70 Plus equipment.

2.2. Preparation of ashes for vitrification

Amounts of about 50 g of each fly ash were heated in refractory sillimamite crucibles in a kanthal furnace at 1520°C for 2 h. Due to the high viscosity of the melts, which made pouring very difficult, they were quenched inside the crucibles, by plunging them into water. Pieces of the obtained frits were taken for X-ray diffraction (XRD) analysis in order to detect the presence or absence of crystalline phases.

With the aim of lowering the viscosity of the initial batch fluids, different amounts of modifier oxides were added by trial and error, essaying firstly the effect of Na_2O content and then the effect of $CaO + Na_2O$. Fly ashes from lot BC were chosen to test the effect of addition of modifiers on melting conditions. Na_2CO_3 and $CaCO_3$ were used as raw materials for Na_2O and CaO sources, respectively. A schematic representation of the methodology followed in the preparation of ashes for vitrification is shown in Fig. 1.

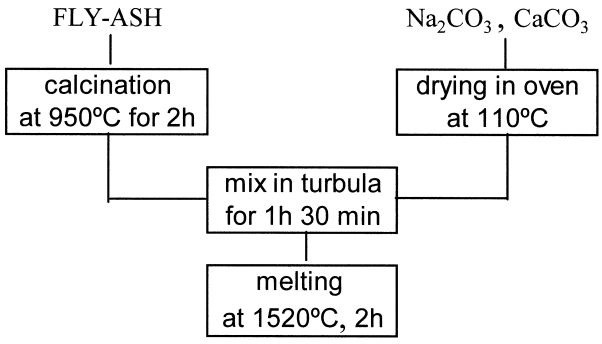

Fig. 1. Scheme of the experimental procedure for the melting of fly-ashes with flux addition.

2.3. Glass-ceramic synthesis

The obtained glasses were analysed by differential thermal analysis (DTA) in order to determine the transition temperature and to have an indication of the temperatures suitable for the precipitation of crystalline phases. DTA tests were performed on powdered samples with average grain size < 45 μm in a STA Linseis GmbH equipment. Samples were heated at 10°C min^{-1} from room temperature to 1000°C, in platinum crucibles, with calcined alumina as reference.

Based on the DTA results and on the definition of the exothermic peaks, glasses from lot PC were chosen for crystallization studies. Glass-ceramics were prepared from theses glasses by heating them at 5°C min^{-1} from room temperature to the temperatures suggested by the respective DTA curve, 800 and 870°C, with a 2 h stage at these temperatures. After this time the furnace was switched off and the heat treated materials were cooled to room temperature inside the furnace.

2.4. Characterization of glass-ceramics

The crystalline phases precipitated during the heat treatments were identified by XRD on powdered samples and the microstructure of the obtained glass-ceramics was observed by SEM on fractured samples etched with HNO_3 0.1 N for 10 s and gold covered before microscopic observation.

Other properties, such as density, bending strength, thermal expansion coefficient and chemical resistance were also determined. Density was measured using a helium pycnometer. The bending strength was determined from the 4-point bending strength test in a Shimadzu Universal Testing Machine model Autograph AG-A series, using eleven polished prismatic samples for each determination. Thermal expansion was evaluated by dilatometric analysis in a Linseis L75 dilatometer in which samples of $10 \times 5 \times 3$ mm^3 were heated at 10°C min^{-1} from room temperature to 700°C. The linear expansion coefficient was measured in the range

20–400 °C. For the evaluation of the chemical resistance of the glass-ceramics a standard procedure referred in the literature[20] was used. Following this procedure, 2 g of grained samples with average particle sizes between 0.3 and 0.5 mm were treated at 95C for 1 h in 60 cm^3 of leaching solutions (0.01 mol/l HCl and 0.01 mol/l NaOH). After washing and drying, the grained samples were weighed and the percentages of weight losses were calculated. The hydrolytic classes of the parent glass and of the obtained glass-ceramics were also determined following the standard DIN 12111.

3. Results and discussion

3.1. Characterization of raw materials

The moisture contents of the four raw materials were 26% for fly ash BC, 20% for PC, 24% for B and 18% for C.

TGA results for the different coal ashes are given in Table 1. A typical TGA trace is presented in Fig. 2 for fly ash BC.

The adequate duration of the calcination process to be performed at 950 °C was indicated by the results in Table 1. For the coal ashes BC, PC and B a 2 h stage was considered sufficiently long to ensure an efficient elimination of carbon from the samples, while a 3 h stage was considered for ash C.

The chemical composition of the four ashes after calcination, as obtained by ICP, is given in Table 2. Minor components like Cu, Zn, Ni, Pb and Cr, were also found at percentages lower than 1%. As shown, SiO_2 and Al_2O_3 are the major components of the coal ashes, both representing, on the average, more than 86% in weight of the samples. This explained the high viscosity of the melts, and gave the first indication that addition of modifier oxides should be probably required for an adequate melting of the ashes.

3.2. Formulation of glass compositions

XRD analysis of samples from the frits obtained by quenching the molten coal ashes indicated that they were not amorphous, but all exhibited the presence of mullite, $3Al_2O_3{\cdot}2SiO_2$, together with cristobalite or quartz, SiO_2, in compositions PC and C. Fig. 3 represents the XRD traces of PC and B molten compositions. As expected, these results confirmed that the addition of fluxing agents should be necessary in order to achieve full vitrification of the coal ashes.

Since BC was the less heterogeneous coal ash, it was chosen to study the effect of additives on the melting behaviour, according to the experimental procedure

Table 1
TGA results of coal ashes

Coal ash	Weight loss on ignition (%)	Holding time at 950°C for constant weight loss
BC	12	1 h 10 min
PC	14	2 h 10 min
B	13.5	40 min
C	15	3 h 05 min

Table 2
Chemical composition (wt.%) of the fly ashes used

	BC	PC	B	C	Average
SiO_2	66.5	62.9	63.6	71.6	66.15
Al_2O_3	21.8	23.5	23.5	17.7	21.63
Fe_2O_3	6.66	8.06	7.48	6.6	7.20
CaO	0.35	0.38	0.41	0.31	0.36
MgO	0.74	1.1	0.84	0.71	0.85
TiO_2	1.06	0.94	1.01	0.86	0.97
P_2O_5	0.21	0.18	0.19	0.14	0.18
Na_2O	0.42	0.4	0.44	0.32	0.40
K_2O	2.08	2.41	2.4	1.65	2.14
Mn_3O_4	0.046	0.056	0.053	0.046	0.05

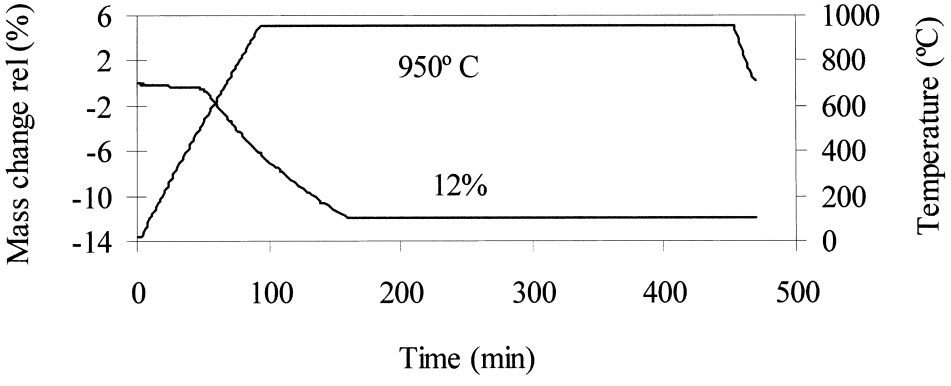

Fig. 2. TGA trace for fly ash BC.

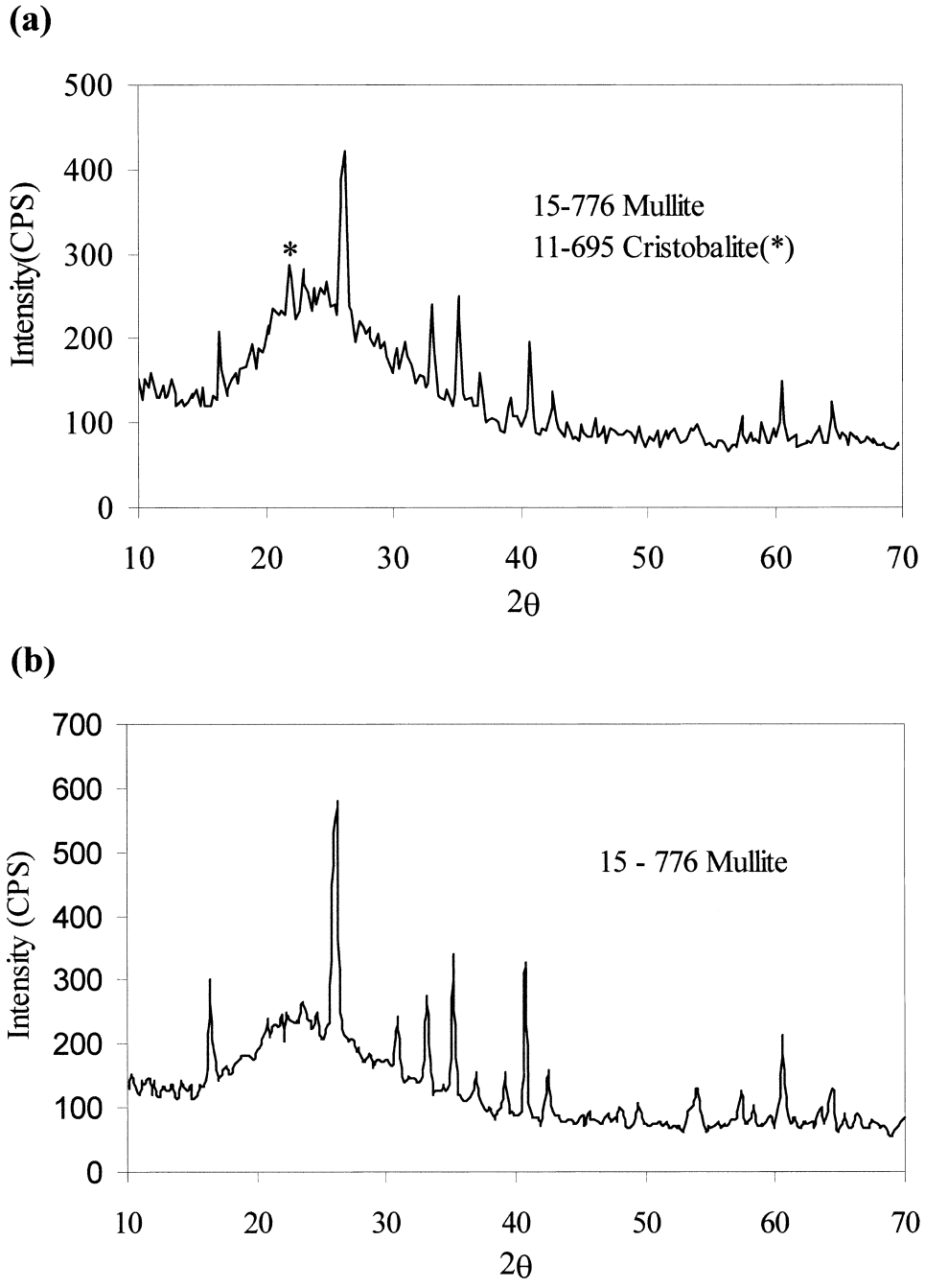

Fig. 3. XRD traces of PC (a) and B (b) molten coal ashes.

previously described. The obtained results are resumed in Table 3.

The results suggested that amounts of Na_2O higher than 15% could lead to adequate melts, since this modifier tends to lower the viscosity of the initial batch fluid increasing the workability of the melts. However, this indication was not followed because it is known that Na_2O-rich glasses are usually very unstable and exhibit low chemical durability. It was thus decided to use the combined addition of the fluxes Na_2O and CaO. Both materials, BC-15Na and BC-10Na10Ca, were analysed by XRD, and the results indicated that they were fully amorphous. The XR diffractogram of composition BC-10Na10Ca is shown in Fig. 4.

Assuming that for melting purposes the composition of the different lots is not significantly different, it was decided to add the same amount of 10% Na_2O + 10% CaO to all coal ashes. The obtained melts, corresponding to the compositions BC-10Na10Ca, B-10Na10Ca C-10Na10Ca and PC-10Na10Ca, were identified, for sim-

Table 3
Effects of different amounts of additive on the melting of coal ash BC

Amount of added oxides (wt.%)		Designation of melt	Effect on melting
Na_2O	CaO		
3	–	BC-3Na	Melt is very viscous and hardly poured out of the crucible
10	–	BC-10Na	Melt is very viscous and hardly poured out of the crucible
15	–	BC-15Na	Melt can be drained off from the crucible, and is reasonably workable
4	7	BC-4Na7Ca	Melt can be poured out of the crucible, but still very viscous
5	10	BC-5Na10Ca	Melt can be poured out of the crucible, but still very viscous
10	10	BC-10Na10Ca	Adequate viscosity for pouring and working the melt

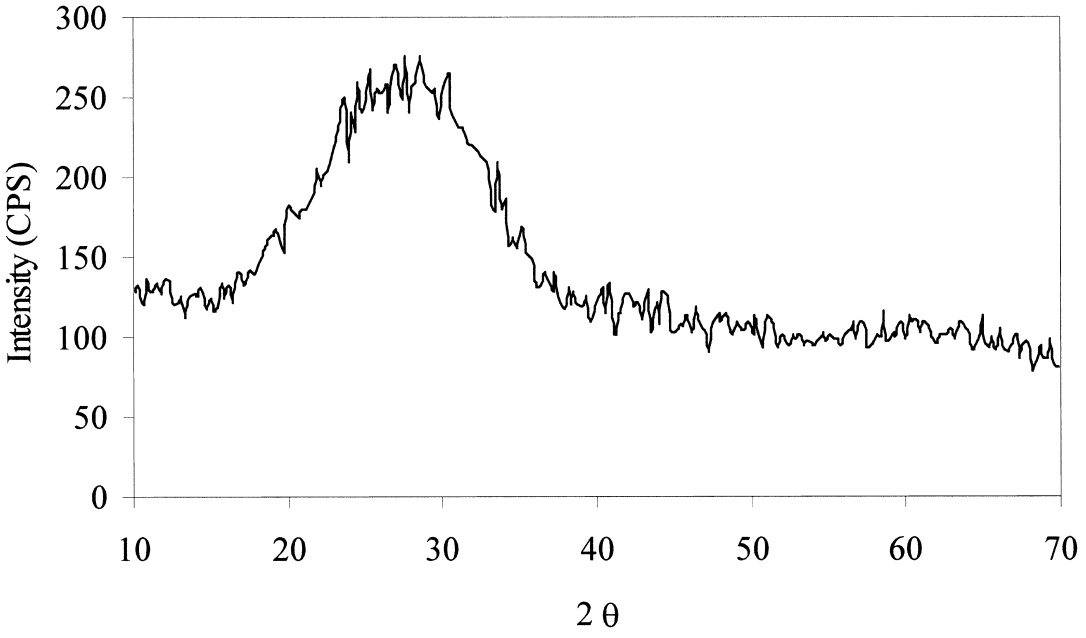

Fig. 4. XRD pattern of glass BC-10Na10Ca.

plicity, by the names of the respective lots, preceded by the letter M, meaning modified. XRD analysis confirmed the amorphous nature of all of them.

3.3. Glass-ceramic synthesis

The DTA curves of the four modified melts are shown in Fig. 5.

All DTA patterns exhibit a smooth endothermic peak around 680°C, which was assumed to correspond to the transition temperature. Annealing of the glass samples for further studies (density, thermal and mechanical properties) was thus carried out at this temperature. After pouring the melts onto metal moulds the glass samples were transferred to a muffle at 680°C, kept at this temperature for 30 min and then slowly cooled to room temperature inside the muffle. The obtained samples have a smooth surface and a colour ranging from dark green to nearly black. After cutting and polishing

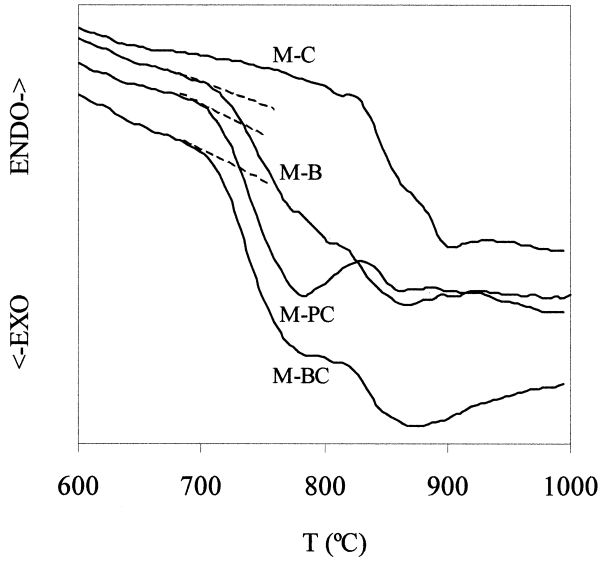

Fig. 5. DTA traces of modified glasses.

the samples exhibited an improved appearance, similar to malachite.

In the DTA traces two well pronounced exothermic peaks at 780 and 870 °C were found for glass M-PC. However, for the other compositions the definition of the peaks was not so clear. In order to get an efficient control of the heat treatment schedules, composition M-PC was selected for the crystallization studies.

This composition was heated at 800 and 870°C according to the time-temperature programme described in the experimental procedure and two glass-ceramics M-PC800 and M-PC870 have been obtained.

3.4. Characterization of glass-ceramics

X-ray diffractograms of the produced glass-ceramics are presented in Fig. 6. A calcium iron aluminium silicate, esseneite, $CaFeAlSiO_6$, was identified in the two glass-ceramics obtained after crystallization at 800 or at 870°C. As reported in the JCPD Standards[26], esseneite corresponds to a natural monoclinic crystal commonly resulting from the carbon combustion. A second phase, a sodium aluminium silicate, nepheline, $NaAlSiO_4$ has also precipitated at the highest temperature, together with esseneite.

SEM micrographs of both glass-ceramics are shown in Fig. 7. Bulk crystallization is evident at both temperatures, giving rise to quite homogeneous fine-grained microstructures.

At 800°C small crystals of average size below 100 nm have been formed, while at 870°C these crystals have grown to an average size which is twice the previous one. According to the XRD results, these precipitates were attributed to the esseneite phase. Although the X-ray diffractograms of the glass-ceramic obtained at the highest temperature indicated the presence of a second crystalline phase, this was not observed in the micrographs. An EDS analysis has been performed on the samples, aiming to find iron-free precipitates, like nepheline, but it was not successful.

Properties of glass-ceramics M-PC800 and M-PC870 are compared in Table 4. In the two last columns some equivalent results for commercial bricks and building tiles are shown.[27,28]

Hydrolytic class by the DIN 12111 standard was determined for the parent glass and for the respective glass ceramics. Durability of the glass corresponds to the second hydrolytic class and it turned into the first hydrolytic class after crystallization.

No significant differences are observed in density and linear expansion coefficient of both glass-ceramics. Typical values for commercial bricks indicate that the density of the obtained glass-ceramics can be 30–65% higher and linear expansion can be 10–120% higher.

Bending strength is lower for the glass ceramic M-PC800 than for the glass ceramic M-PC870. These findings seem to disagree with the SEM observations, since finer grained microstructures are usually responsible for higher strength values. However, the increased bending strength at 870°C can be explained taking into consideration the XRD results, which indicated that a second phase, not detected in the micrographs, precipitated at that temperature.

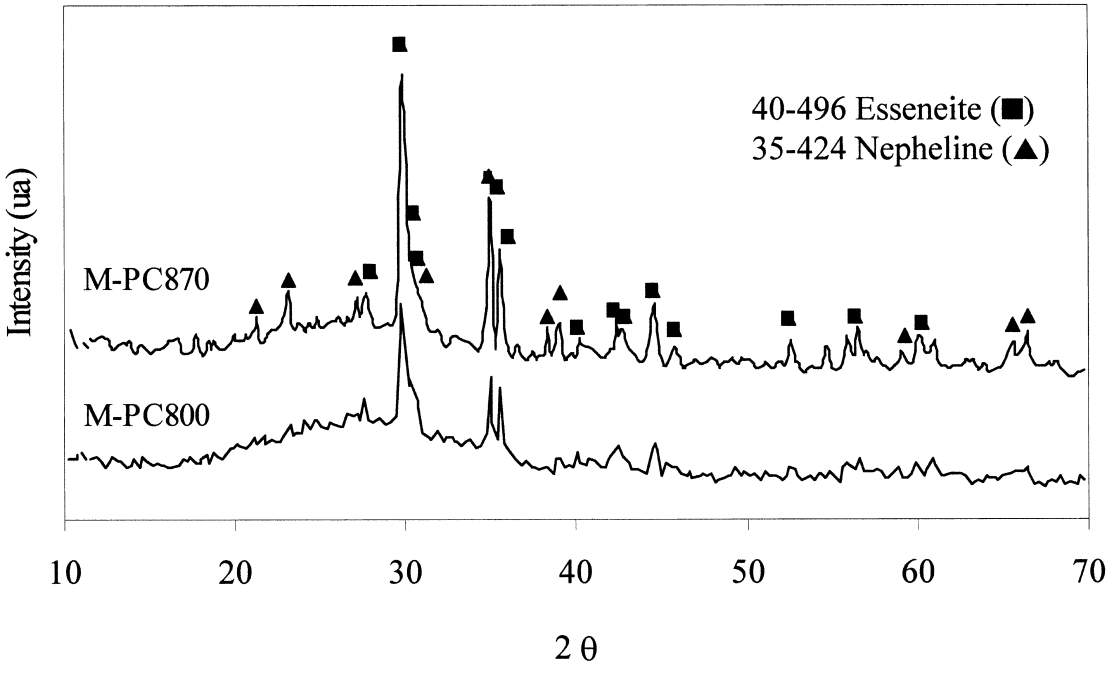

Fig. 6. XRD traces of the obtained glass-ceramics.

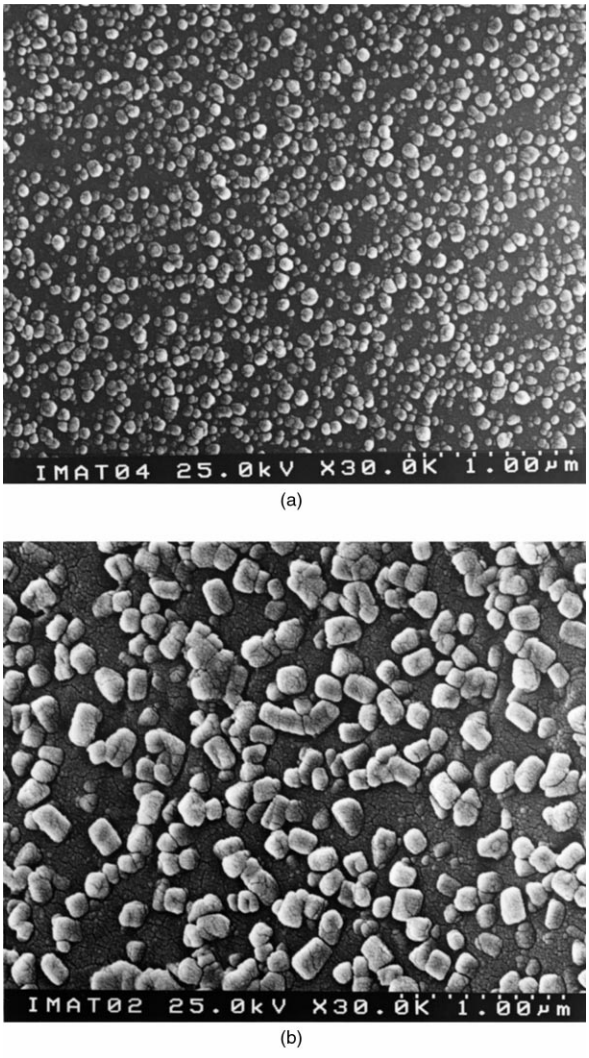

Fig. 7. SEM micrographs of glass-ceramics M-PC800 (a) and M-PC870 (b).

Chemical resistance of glass ceramic M-PC870 is higher than that of glass ceramic M-PC800. Again, the presence of two crystalline phases at 870°C can explain the observed behaviour. Although not clear from the micrographs, it is expected that the precipitation of a second phase decreased the amount of glassy matrix surrounding the crystalline grains. Since weight losses are usually attributed to the dissolution of the glassy matrix, this would lead to lower weight losses at 870 than at 800°C. More refined experiments to determine the amount of crystalline phases in both glass-ceramics are required to clarify the results. Although the literature does not exactly specify chemical resistance values for commercial bricks and tiles or for natural marbles and granites it should be noticed that the chemical durability of the obtained materials corresponds to that of glasses and glass-ceramics of high chemical resistance.[20]

Table 4
Measured properties of glass-ceramics M-PC800 and M-PC870. Typical values for commercial bricks and building tiles

	M-PC800	M-PC870	Brick	Building tiles
Density (g cm^{-3})	2.69	2.73	1.65-2.08	–
4-Point bending strength (MPa)	47.59[a]	67.02[b]	4.8–27.6	24–44
Linear expansion coefficient α_{20-400} (10^{-6} K^{-1})	9.57	10.1	4.5–9.0	–
Chemical resistance, wt.% loss in solutions				
0.01 mol/l HCl	1.08	0.58		
0.01 mol/l NaOH	1.06	0.56		

[a] Standard deviation = 6.00 (11 specimens).
[b] Standard deviation = 13.32 (11 specimens).

4. Conclusions

The formation of amorphous materials from coal ashes was accomplished at temperatures around 1520°C using Na_2O and CaO as fluxing additives. Adequate heat treatments on one of the formulated glass compositions showed that it was possible to bulk crystallize the glasses into fine-grained glass-ceramics, without addition of nucleating agents. Owing to their chemical, thermal and mechanical properties, and to their attractive appearance, similar to dark marble and malachite, it is suggested that a potential application for the coal ash-based glass-ceramics may be as low-loading bearing structural materials, that can be used for example in kitchen and laboratory benches, cooker plates and as cladding materials for walls, roofs and floors.

Acknowledgements

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