Recycling of chromium-rich leather ashes in porcelain tiles production

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Abstract

Leather residues derived from shoes industry are often incinerated in winter times to warm the working ambient, giving rise to the production of chromium-rich ashes that put environmental problems on its disposal. The power of these ashes as colouring and fluxing agent for industrial porcelain tile formulations and the effects of incorporating different amounts on water absorption and bending strength were evaluated in the present work along a broad sintering temperature range of 1120–1180 °C. The experimental results revealed that the incorporation of these wastes can result in porcelain tiles with superior properties, in terms of water adsorption, density and bending strength. The results also showed the possibility of using these wastes as colouring agents to obtain broad range tonality products from cream to dark brown, depending on the added amount of leather ashes in the formulation and on the sintering temperature. The observed improvements of the final properties of the material and the ability of chromium-rich ashes to replace expensive pigments show that their incorporating in porcelain tiles formulations is a smart way of recycling this environmental dangerous leather derived waste.
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1. Introduction

Clay-based ceramic formulations generally feature high heterogeneity due to the wide range of the composition of natural clays used as raw materials in their fabrication. For these reasons there is tolerance for incorporating several kinds of wastes replacing natural raw materials, even in considerable percentages.[1–7] Traditional ceramic industries consume huge amounts of diminishing mineral resources.[8–10] This fact is another reason to consider interesting the use of such industries to incorporate inorganic potential harmful residues, even in small proportions, just to clean the environment. The correct recycling of wastes has clearly beneficial environmental and economical impacts,[11–15] while high temperature firing can turn wastes, which contain hazardous components, into inert and safe for the health products.[4,16]

Portugal is one of the main European producer and exporter of leather shoes. The production of leather residues is estimated to be around 10,000 t/year only in Portugal.[17] The Portuguese shoes industry is concentrated in certain regions in north of the country and the geographical concentration of these industries represents risks to the environment.[17]

The transformation of animal skin into hide requires a series of chemical and mechanical treatments. Chromium salts are the most widely used substances in the treatment of the skin. The skins treated with chromium salts exhibit good mechanical resistance, and a better hydrothermic resistance in comparison with the skins treated with vegetal substances. This chromium salts are characterized by a high rate of penetration into the interfibrillar spaces of the skin. Thus, the final resulting leather comprises some of this chromium.[18]

The deposition of huge quantity of leather wastes is obviously a potential danger to public health due to the possibility of oxidation of the comprised chromium(III) into toxic chromium(VI). This type of chromium has been shown to have serious toxic and carcinogenic effects even in very small concentration. Some forms of Cr(VI) are known to cause nasal polyps, septum deviation and respiratory tract cancer via inhalation exposure and with lung, skin and bladder cancer via ingestion.[19–23]

Shoes industries have enormous additional costs to remove the produced wastes. These costs are related to transport and deposition in land deposits or other destinations, besides the negative environmental impact. To mitigate these costs and take advantage of the high calorific power of leather

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(4500–5000 kcal/kg),[24–25] some shoes producing plants often incinerate part of leather residues in warming the working ambient in the colder season, giving rise to the production of chromium-rich ashes that put environmental problems on its disposal.

This work investigates the potential of chromium-rich ashes as colouring and fluxing agent for industrial porcelain tile formulations. The aim is a multifold one and includes: (i) reducing the environmental impact derived from landfill of a dangerous waste; (ii) to regard the chromium-rich ashes as a colouring agent to replace commercial pigments that are expensive and therefore reduce the production costs; (iii) to explore the fluxing role of chromium oxide to reduce the sintering temperature; (iv) maintenance, or if possible, improvement of the final properties of porcelain tiles (lower water absorption and higher bending strength).

The produced materials were evaluated in the frame of the ISO standard 13006, Group B-I, which is directed to the porcelain tiles consolidated by dry pressing, whereby water absorption must be less than 0.5% and the three point bending strength should be higher than 35 MPa.[26,27] For comparison purposes, the commercial porcelain tile formulation referred as K was used as reference material.

2. Materials and experimental procedure

Chromium-rich ashes derived from the incineration of leather residues were received from Basílius, a shoes industry located in *S. João da Madeira*, Portugal. Since the as-received ashes presented some incomplete burned materials, they were first calcined at 900 °C for 1 h using a heating rate of 5 °C/min. The calcined ashes were then passed through a 500 µm sieve to remove most of the impurities (burnt wood, metallic nails, etc.) and then dry milled in a fast ball mill for 15 min. The particle size distribution was determined using light scattering apparatus (Coulter LS 230, UK, Fraunhofer optical model) and the crystalline phases were detected by XRD (Rigaku Geigerflex D/Mac, C Series, Cu Kα radiation, Japan).

Chromium-rich ashes were added to a commercial porcelain tile composition in different proportions as reported in Table 1 (the batch named K, without ashes, was also prepared for comparison purposes). The batches were mixed by mechanical stirring in aqueous media to obtain a good homogenization and then dried at 110 °C in an electrical oven, followed by deagglomeration in a mortar. Cylindrical pellets with 20 mm diameter and about 5 mm thickness were consolidated by uniaxial pressing (48 MPa for 1 min). Sets of rectangular sectioned bars with

Table 1
Batch formulations

Formulation	Leather ashes (wt.%)	Commercial formulation (wt.%)
K	0	100
K-1	1	99
K-3	3	97
K-5	5	95
K-10	10	90

about 50 mm × 5 mm × 5 mm were also prepared using the same pressure to evaluate the three point bending strength. The pellets and the bars were fired in electrical laboratory furnace at several sintering temperatures from 1120 to 1180 °C (1 h soaking time at the sintering temperature, using a heating–cooling rate of 5 °C/min).

Water adsorption was determined according to the ISO standard 10545-3 Group B-I, by measuring the weight gain of dried pellets after immersion into boiling water for 2 h followed by 3 h cooling.[28] Several types of characterization were conducted during the process. Density of samples was determined by the Archimedes method by immersion in ethyleneglycol. The three-point bending strength was measured in Shimadzu Autograph AG 25 TA machine at 0.5 mm/min displacement. The reported values are the average of 16–20 measurements. The shrinkage upon firing was also measured.

The CIELab method was used to evaluate colour differences.[29,30] This method developed by Commission International de l'Eclairage (CIE) gives an exact numerical specification of human vision. Colours are measured in terms of their tristimulus values and are used to calculate the CIE L^*, a^*b^* (CIELab) colour space values. Each particular colour has a unique location defined by its Cartesian coordinates with respect to the L^*, a^*, b^*. The L^* coordinate is related to lightness and covers a range from white (100) to dark (0) along a grey scale. The a^* and b^* coordinates are related to Hering's opponent theory: a^* gives the location on red-green scale and b^* gives the location on the yellow-blue scale.

Colorimetric colour coordinates of samples were measured using Minolta (CR300, Japan) colorimeter. The colorimetric parameters L^*, a^* and b^* for each sample were recorded and colour difference (ΔE^*) was calculated according to $\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$. The values ΔL^*, Δa^* and Δb^* correspond to the difference of each parameter recorded for the two samples that are being compared.

Microstructure observation at polished and etched surfaces (immersion in 2 vol.% HF for 4 min) was made by scanning electron microscopy (SEM, Hitachi S-4100, Japan, 25 kV acceleration voltage), and elemental analysis of commercial formulation and leather ashes was accessed by energy dispersion spectroscopy (EDS) under point analysis mode.

3. Results and discussion

The particle size distributions of the commercial tile porcelain composition (K) and of leather ashes are reported in Fig. 1. It can be seen that leather ashes comprise smaller particles in comparison to commercial porcelain tile formulation. After calcination and sieving, the ashes presented some aggregates which confer to the powder the aspect of coarser grains but these aggregates were easily destroyed by dry milling.

Fig. 2 reports the XRD spectrograms of leather ashes before and after calcination at 900 °C. The non-calcined material is predominantly amorphous although some peaks can be identified such as calcite ($CaCO_3$), anhydrite ($CaSO_4$), rutile e anatase (TiO_2), calcium–aluminium–silicate ($Ca_3Al_2Si_2$) and quartz (SiO_2), being the peaks of quartz and rutile the most
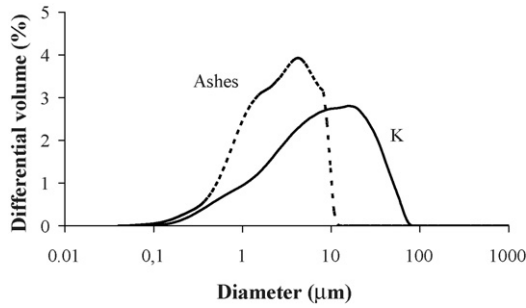
Fig. 1. Particle size distributions of powders of leather ashes and of commercial porcelain tile formulation.

intense ones. After calcination the material becomes predominantly crystalline with strong peaks for quartz and rutile. Calcite could not be detected, while the presence of hematite (Fe_2O_3) is evident. Cr-containing phases like chromite, chromium silicate and sodium-chromium oxide were also identified from the XRD spectrogram.

In order to evaluate the presence of chromium as well as other elements in leather ashes, EDS analysis was carried out. Fig. 3 reports the elemental composition of calcined leather ashes. The observation of the EDS plot reveals that the material comprises Fe and Cr. As expected, chromium is one of the dominant elements present in the ashes, due to leather treatment in earlier stages.[18]

The visual evaluation of the colour of the sintered samples showed that the colour varies from beige (formulation K) to dark brown with increasing of darkness as the amount of incorporated ashes increases at a given sintering temperature, or as the temperature increases for a given formulation. Chromium is a widely used element in ceramic pigment production. Brown colour can be obtained using pigments comprising oxides of Fe and Cr,[31,32] which are the most relevant elements detected by EDS analysis. This colour range is due to the presence of different contents of iron and chromium in the formulation resulting from the different amounts of leather ashes added to the batches.

It is not easy to detect relevant differences between K-5 and K-10 using direct visualization. This suggests that the colour will not change significantly for formulations with more than 5 wt.% of ashes. Fig. 4 shows the colour difference (ΔE) among samples for different sintering temperatures. It is clear that the colour
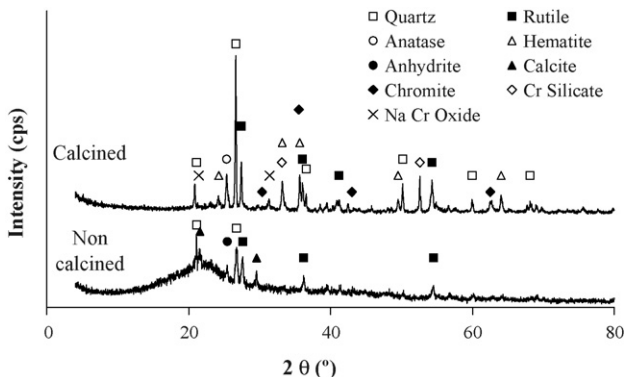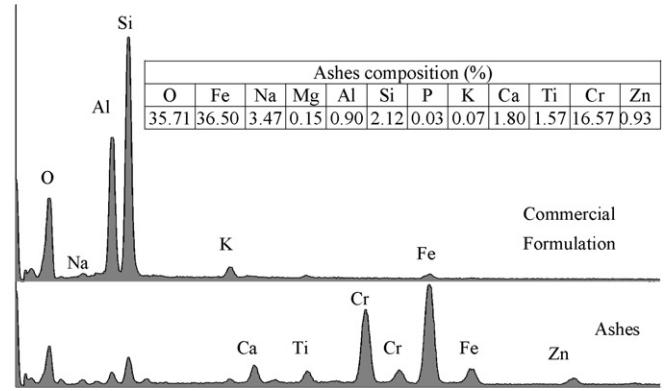

Fig. 3. EDS analysis of leather ashes and commercial porcelain tile formulation.

changes with sintering temperature are more significant for formulations with lower leather ashes concentrations. Formulations with higher ashes contents show little colour differences with sintering temperature.

Taking into account the measured values, K-5 and K-10 present a $\Delta E = 0.8$ and 1.3, respectively, along the sintering temperature range of 1120 and 1180 °C, while K shows $\Delta E = 9.1$ within the same temperature range. When $\Delta E < 1$, the colour differences cannot be distinguish by human eyes.[32] According to this statement one can say that the colour differences with temperature are negligible for higher ash content formulations. The standard commercial formulation shows bigger colour differences with sintering temperature which means more sensibility to sintering conditions. This experimental result demands that the industrial sintering temperature of the commercial formulation must follow good control to avoid temperature differences in order to preserve colour properties. Fig. 5 reinforces this observation. It is clear that the variation of colour with the sintering temperature is more significant for formulations with lower ash contents. In the plot b^*/a^*, the values of commercial formulation scatter more with variation of temperature. As expected, the L^* values (lightness) for leather ash-containing formulations are much lower than those of commercial formulation K and the scattering of L^* with sintering temperature is also larger in the case of this formulation.

Water absorption values can be an indirect way to evaluate the open porosity and densification level of the fired products.
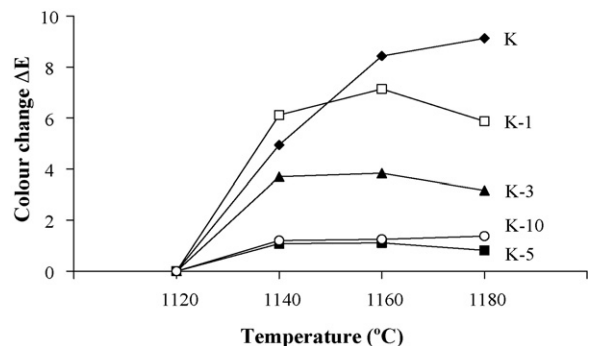

Fig. 2. XRD analysis of leather ashes before and after calcination at 900 °C.

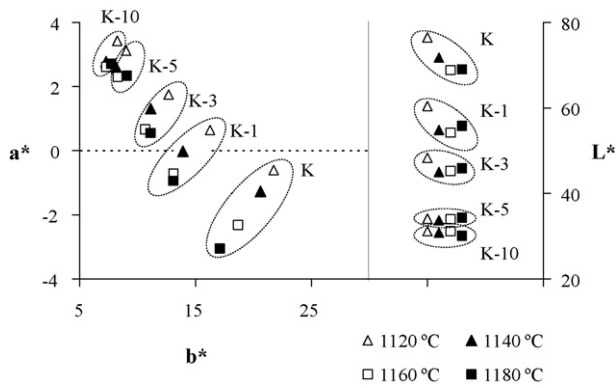Fig. 4. Evolution of colour difference (ΔE) between samples of each formulation with sintering temperature.

Fig. 5. Variation of CIELab parameters L^*, a^* and b^* with sintering temperature.

Fig. 7. Evolution of density with sintering temperature for different contents of leather ashes.

Fig. 6 presents the water absorption of the different formulations fired at different sintering temperatures.

Formulation K presents higher water absorption values for all sintering temperatures in comparison to the other formulations that show lower open porosity. For formulation K, water absorption steadily decreases as firing temperature increases reaching a minimum value of 0.32% at 1180 °C. The water absorption of the other formulations shows a first decrease followed by an increasing trend beyond 1140 °C due to an over-firing effect, but the values are systematically lower due to the fluxing effect of chromium-rich ashes, which seems to increase up to 5 wt.% (water absorption is as low as 0.11% at 1120 °C). The samples containing 10 wt.% become apparently more refractory again, at least at the lower sintering temperature. It is interesting to note that the lowest water absorption value (0.05%) is observed at 1140 °C for the formulations with added 3, 5 and 10 wt.% of chromium-rich ashes. This temperature is about 60 °C lower than the temperature used for firing the commercial formulation. This corresponds to a significant energy saving for the ash-added formulations in comparison to the optimal sintering temperature of the standard porcelain tile formulation. For all the samples and for $T \geq 1140$ °C, water absorption is always below the maximum value of 0.50% specified by the standard ISO 13006 Group B-I for porcelain tiles.

The results of water absorption are consistent with the density measurements reported in Fig. 7. It can be seen that all formulations show higher density values upon sintering at
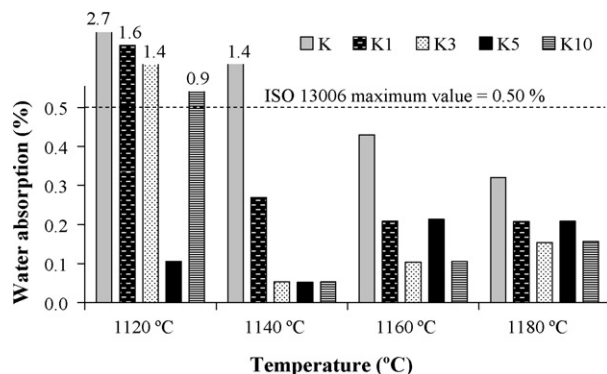
1140 °C, except sample K. Formulations K-5 and K-10 present higher density values even for sintering at 1120 °C. This can be attributed to: (i) the higher density of chromium/iron-rich ashes ($\rho Cr_2O_3 = 5.21$ g cm^{-3}; $\rho Fe_2O_3 = 5.25$ g cm^{-3}); (ii) to the fluxing effect of chromium-rich ashes. The over-firing phenomena for $T > 1140$ °C is confirmed especially for the K-5 and K-10 formulations that exhibit a noticeable decrease in density. At 1140 °C K-3, K-5 and K-10 exhibit their lowest water absorption and their highest density values. At temperatures higher than 1140 °C the density drops significantly while water absorption increases but less than proportionally. This can be explained by over-firing phenomena.

For K formulation a maximum density was achieved at 1160 °C. The somewhat lower density measured at 1180 °C is certainly due to the formation of an increasing amount of a less dense glassy phase. A small decrease in density does not necessarily mean an over-firing effect.

These results show that formulations with higher contents of chromium-rich ashes are more sensitive to sintering temperature as revealed by the steeper slope of the curves of Fig. 7.

The standard ISO 13006 Group B-I stipulates a minimum value of 35 MPa bending strength. The results of three-point bending plotted in Fig. 8 show that at the lowest sintering temperature only the formulations K-5 and K-10 overcame the specified limit. At 1140 °C, all the leather ash-containing formulations present values that are significantly above the minimum value required by the standard. The commercial formulation only qual-

Fig. 6. Dependence of water absorption on the content of leather ashes and sintering temperature.

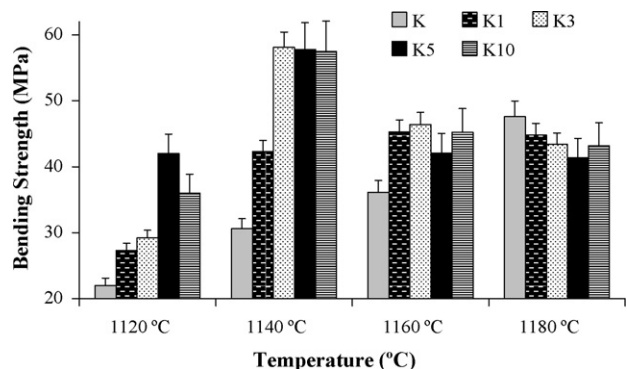Fig. 8. Dependence of bending strength on the content of leather ashes and sintering temperature.
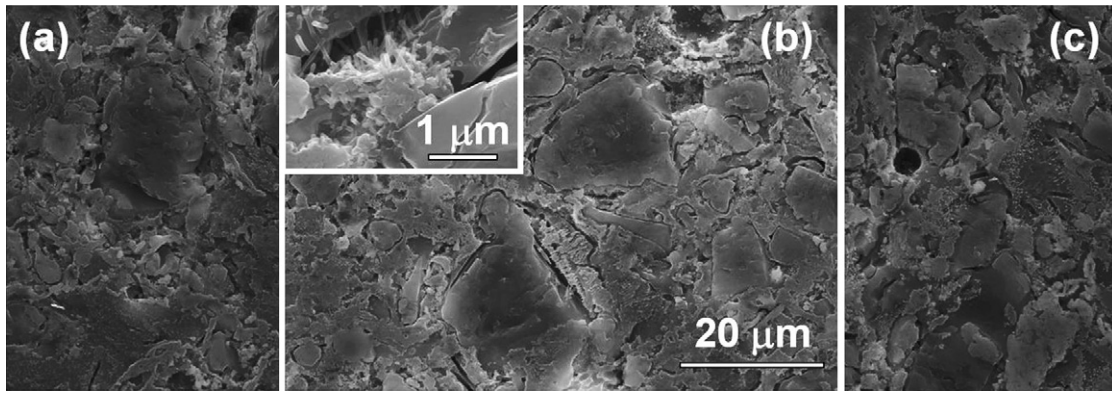
Fig. 9. SEM microstructures of K-10 samples sintered at: (a) 1120 °C; (b) 1140 °C; (c) 1180 °C. The same magnification was used in (a)–(c). The insert shows a higher magnification of the sample sintered at 1140 °C.

ifies according to this criterion for $T \geq 1160\,°C$. The mechanical resistance of formulations with a content of chromium-rich ashes ≥ 3 wt.% tend to decrease as sintering temperature further increases beyond $1140\,°C$, due to the already mentioned over-firing effect. These results are in close agreement with the data of water absorption and density measurements reported in Figs. 6 and 7.

Fig. 9 shows the microstructure of formulation K-10 sintered at different temperatures (1120, 1140 and 1180 °C). The samples present typical features of porcelain tiles comprising a glassy feldspathic matrix containing disperse crystalline phases such as quartz and mullite. Quartz is apparently the major crystalline phase because the starting quartz particles tend to remain undissolved due to the fast firing cycle.[33] Taking this fact into account it is not surprising that one of the main microstructural features of K-10 samples is the presence of quartz grains, the dimensions of which tend to decrease as temperature increases beyond $1140\,°C$ due to partial dissolution in the glassy phase. The presence of iron and chromium in the ashes provides some auxiliary fluxing to the formulations and consequently the formation of higher amounts of glassy phase at lower temperatures. This mechanism promotes the sintering of the material at lower temperatures when compared to the commercial ash-free formulation K. In the insert picture related to sample K-10 fired at $1140\,°C$ also reveals details of the formed small secondary mullite crystals.

The over-firing effect of sample K-10 is illustrated in Fig. 10 through an increase of the size and volume fraction of closed pores as temperature increases due to some "boiling" and trapped gases effect, justifying the observed decrease in density. The material is apparently more compact at 1120 and $1140\,°C$, in good agreement with density and water absorption measurements. The maximum density observed at $1140\,°C$ suggests this temperature as the optimal one for sintering K-10 formulation. These experimental results support the advantages of incorporating leather ashes in porcelain tile formulation.

Fig. 11 compares the microstructural features of samples K, K-1 and K-10 after firing at $1140\,°C$ and their relation with measured water absorption values. The sample K shows a higher volume fraction of pores with sharp edges, characteristic of open

porosity in contrast with the relatively dense microstructures with more round shaped pores characteristic of closed porosity. At this temperature, the water absorption of sample K is almost three times higher than the maximum value stipulated in the standard, while sample K-10 shows a near-zero value. The microstructure and water absorption observed for sample K-1 reveal the strong effect that 1 wt.% of leather ashes has on the sintering behaviour of the commercial porcelain tile formulation.

The commercial porcelain tile formulation K comprises feldspar and two types of clays. Theoretically, liquid phase should form at the eutectic temperature of potassium feldspar $(KAlSi_3O_8)$ and quartz (985 °C).[34,35] Amorphous silica, formed during the thermal decomposition of kaolinite, reacts with potassium feldspar. At high temperatures, quartz is dissolved in the liquid phase. For pure potassium feldspar, complete melting should take place at its melting temperature $\sim 1150\,°C$. It was also mentioned that the eutectic point of sodium feldspar and silica is $\sim 1062\,°C$, while the melting point of pure albite is $\sim 1118\,°C$.[36] As far as the fabrication and commercialization of porcelain tiles are concerned, this work has shown that incorporation of leather ashes in the batch and firing at $\sim 1140\,°C$ potentially result in superior porcelain tiles due to
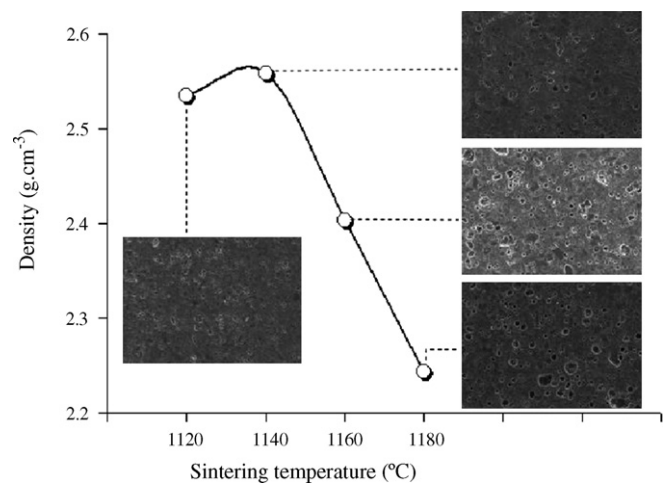

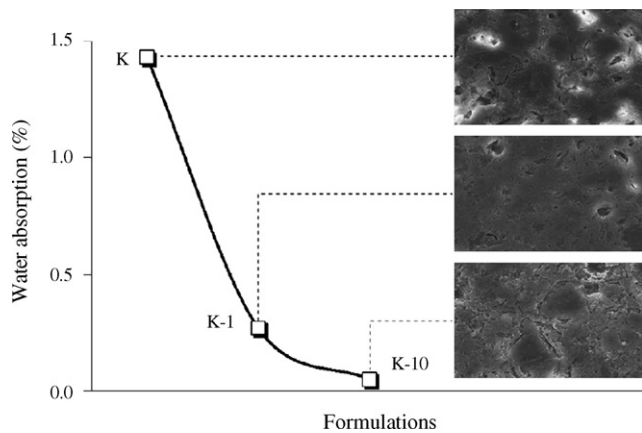Fig. 10. Microstructural evolution of K-10 samples with temperature.

Fig. 11. Microstructures of K, K-1 and K-10 sintered at 1140 °C and its relation with water absorption value.

its beneficial effects on density and water absorption. These effects derive from the fluxing roles of Cr and Fe oxides leading to mechanical strength >55 MPa and a near zero (∼0.05%) water absorption. The Cr and Fe oxides also act as colouring agents enabling to replace expensive Cr/Fe-based pigments.

4. Conclusions

The experimental findings of this work show the feasibility of incorporating potentially hazardous chromium-rich leather ashes in porcelain tile production as pigment and fluxing agent with the following interesting advantages:

1. The environmental threat bound to landfill due to the potential oxidation of chromium(III) into chromium(VI) is removed;
2. The chromium-rich ashes were proved to act as a colouring agent and can replace the expensive commercial pigments based on Cr/Fe oxides, therefore reduce the production costs;
3. The porcelain tile formulations with added chromium-rich leather ashes present maturation temperatures that are about 60 °C lower in comparison to the chromium-rich free composition;
4. The final properties of porcelain tiles fired at the optimal sintering temperatures are superior (lower water absorption, higher bending strength) in comparison to the chromium-rich free composition, being far better than the minimum values stipulated by standard ISO 13006 Group B-I.
5. Based on the above points, it must be concluded that the selection of porcelain tile formulations to host chromium-rich ashes is a wise choice to concomitantly solve environmental, economical and health problems while improving the materials properties.

Acknowledgments

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