USE OF INDUSTRIAL WASTES AS OPACIFIERS IN PORCELAIN TILE BODIES

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ABSTRACT

The present research was conducted to assess the feasibility of using two kinds of industrial wastes as opacifiers in porcelain tile bodies, as well as to define what pre-treatment would be required to prepare the wastes for such use.

The characteristics of the wastes were analysed, first, to determine their chemical and mineralogical composition, as well as their behaviour when subjected to heat, in order to identify any undesirable substances and to establish suitable conditions for removing these with simple methods. This allowed suitable materials to be obtained for use in porcelain tile compositions.

The effects were then studied of the incorporation of these pre-treated waste materials on porcelain tile characteristics. The results obtained indicate that the two waste materials used in this research have a significant opacifying capability, which makes them of great interest as possible raw materials for products that are not required to have maximum whiteness values. The only drawback detected in one of these wastes was that the porcelain tile composition needed to be slightly adjusted in order to ensure that its behaviour during firing did not change.

1. INTRODUCTION

Environmental policies regarding waste materials have gradually changed away from landfill management towards sustainable development, which seeks to coordinate a medley of issues such as climate change, prudent natural resource management and economic growth [1].

This concern for our environment, which on occasions combines with a shortage of certain raw materials, is encouraging research into the reuse of waste materials as an alternative supply for the same industrial sector that generated them initially or even for some other sector. Very often, the reuse of a certain waste product is hindered by the impurities or pollutants that it has picked up during the process, but that does not rule out the possibility of it being used in another sector, either directly or after a relatively simple pre-treatment.

The ceramic industry has made a remarkable effort to limit the amount of waste it generates and to attempt to reuse a large part of its processing waste, such as, for example, ground fired scrap [2], or porcelain tile processing sludge [3]. Numerous studies have looked at how to reuse waste products from other sectors as raw materials for the ceramic industry, using either the actual waste itself (one example would be slagsitall glass-ceramics obtained from metallurgy wastes [4]) or raw materials obtained by treating prime waste with relatively simple processes (an example of this would be the obtainment of ZnO from Zamak waste [5]).

Porcelain tile manufacturing calls for large amounts of zircon to be used as opacifying agent6, but the price of zircon has risen significantly in recent years due to the high demand and limited supply. One possible way of mitigating this problem would be to use waste materials as a substitute for zircon, at least for those products that only require moderate levels of whiteness. With this objective in mind, two waste materials from different sources were tested, one being an adsorbing agent from the cleaning of non-inflammable solvents at a chemical plant (waste W1), while the second material comes from the electronics industry, specifically from ferrite processing (waste W2). Both waste materials were selected for this study based on previous test results.

2. EXPERIMENTAL PROCEDURE

Chemical characterisation was carried out by means of wavelength dispersive X-ray fluorescence spectrometry (XRF), using a Philips model PW 2400 XRF instrument fitted with an Rh white fluorescent tube. The samples were prepared as fused beads using a Philips PERL'X3 instrument. Mineralogy characterisation was carried out on the powder samples by means of X-ray diffraction (XRD) using a BRUKER Theta-Theta D8 Advance diffractometer, comparing the results with the JCPDS (Joint Committee for Powder Diffraction Standards) files. Particle size was analysed using a MALVERN MASTERSIZER 2000 and the Mie theory to interpret

the collected signal. The samples were dispersed in water combining the action of ultrasounds and a deflocculant (mixture of sodium hexametaphosphate and sodium carbonate). Thermal characterisation was performed using a METTLER model TG/SDTA 851e simultaneous thermal analysis instrument. The tests were conducted with a platinum crucible in dynamic air atmosphere, at a heating rate of 10ºC/min and peak temperature of 1000ºC.

The opacifying capability of the waste materials was tested by incorporating them into a porcelain tile composition of white clay (UA-50/2), potassium feldspar (fine ground Turkish potassium feldspar), and kaolin (Arevi). Zircon was used as reference opacifier (micronised zircon from Mario Pilato Blat with a d_{50} = 1.6 µm). Before preparing the composition, the clay was dispersed wet in a 95%/5% acetone/water mixture using a concentric-crown stirrer at 5000 rpm (IKA Ultra Turrax T50). Finally, the various raw materials were mixed in the pre-set percentages and wet-milled with acetone for 10 minutes. The resulting suspension was then dried under infrared lamps. The powder thus obtained was formed into cylindrical test pieces (4 cm in diameter and about 7 mm thick) using a one-directional press with a moisture content of 5.5% (dry basis) and 400 kg/cm^2 pressure. The test pieces were dried at 110ºC in an electric lab oven with air recirculation. Once dry, they were weighed, their diameter was measured and bulk density calculated, whereupon they were fired in an electric laboratory kiln in a specifically-designed cycle with a heating rate of 25ºC/min before the samples were held for 6 minutes at maximum temperature. Once fired, they were re-weighed to calculate bulk density, firing shrinkage, water absorption and colour coordinates. Bulk density was measured using the mercury displacement method; firing shrinkage was assessed as the difference between dry and fired diameters, defining these parameters on a dry basis. Water absorption was calculated by measuring the gain in test piece weight when the pieces were immersed in boiling water for two hours.

The CIELab colour coordinates of the test pieces were measured using a MACBETH Color-Eye 7000A diffuse reflectance spectrophotometer, using a standard CIE D_{65} light source and CIE 10º standard observer, including ultraviolet and spectral ranges, as the measuring conditions.

3. RESULTS

3.1. Chemical characterisation.

Chemical analysis revealed significant differences between the two waste materials (table 1). W1 was mainly composed of aluminium and oxygen, together with small quantities of silicon and sodium, and as a characteristic trait, it was found to be free of chromophores, although it did exhibit significant loss on ignition. On the other hand, W2 mainly comprised zirconium, oxygen and hafnium together with smaller amounts of other elements, including typical chromophores such as iron and titanium.

Component	W1	W2
SiO_2	4.7	0.8
Al_2O_3	68.4	0.53
ZrO_2	-	95.2
Na_2O	2.86	0.06
K_2O	< 0.01	0.02
MgO	0.03	0.02
CaO	0.1	0.11
ZnO		0.28
Fe_2O_3	0.01	0.46
TiO_2	< 0.01	0.2
P_2O_5	< 0.01	0.02
Y_2O_3	-	0.17
HfO_2	-	1.9
LOI at 1000ºC	23.7	0.07
S Cl	0.22 0.03	- -

Table 1. Chemical composition of the waste materials (% by weight).

This chemical analysis indicated that neither waste material should be directly incorporated into a porcelain tile composition, since they both contained harmful substances, either for the process (adsorbed substances present in W1) or for the product end properties (chromophores present in W2). Therefore, pre-treatments were designed to remove or at least reduce the quantity of undesirable substances.

3.2. Pre-treatment of the waste materials.

Waste W1 was dark brown in colour due to the substances adsorbed superficially, which, depending on their properties, could have a negative effect on the porcelain tile process (by altering slurry stability, generating black core during firing, etc.). The thermal analysis of these waste materials revealed that the greatest weight loss detected in chemical analysis occurred in the range between 25ºC and 600ºC (figure 1), which may be divided into two sections:

- The first section corresponds to the elimination of moisture and any possibly volatile substances that might be weakly adsorbed (weight loss associated with an endothermic process).

- The second section corresponds to the combustion of adsorbed substances, of which there are possibly two types with differing ignition points (weight loss associated with an exothermal process with two peaks).

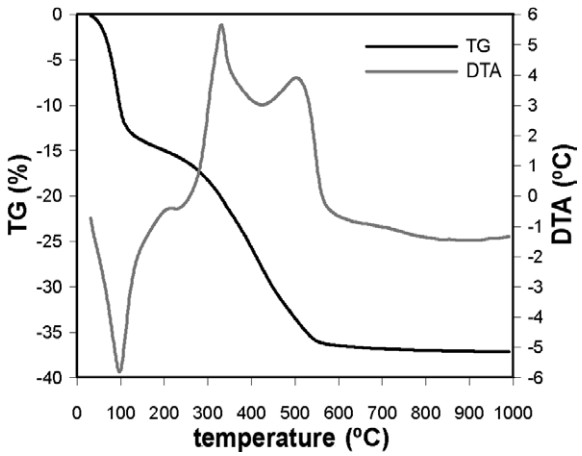

Figure 1. Curves of simultaneous heat analysis of waste material W1.

Following this heat treatment, waste material W1 displayed a whitish colour, which was consistent with its low chromophore content. On the basis of this result, W1 was fired at 600ºC for two hours in an electric kiln to remove all organic matter, and the resulting whitish material was wet-ground in a ball mill with acetone and then dried, after which the resulting solid was collected.

Waste material W2 had a heterogeneous appearance, mainly consisting of light orange particles, with some darker-coloured particles. Apparently, the chromophores were concentrated in one fraction of the particles, possibly as part of ferrites, indicating that they should be separable by means of a magnetic field.

An initial magnetic separation was performed by dispersing the waste material in distilled water and dipping a high-intensity magnet into the suspension, thereby separating a large number of the black particles. Once free of the coarse magnetic fraction, the dry waste was ground in a tungsten carbide ring grinder and the crushed waste was then subjected again to magnetic separation, which led to removal of a very fine magnetic fraction, as well as another non-magnetic fraction, light orange in colour, which was collected as the end product of the separation process.

3.3. Characterisation of the treated waste.

After waste material W1 had been treated, it was found only to contain one crystalline phase, a low-crystallinity γ-alumina, whereas W2 was mostly made up of baddeleyite, together with a little zircon (figure 2). Both treated waste materials had a d_{50} of less than 10 microns (specifically 7.1 μm for W1 and 2.6 μm for W2), and were therefore coarser than the zircon used as reference (figure 3).

In view of their mineral composition, both materials could be suitable, in principle, for use as opacifiers in porcelain tile. W1 would tend to generate corundum particles during heat treatment, whereas the baddeleyite present in W2 would react

in part to create zircon. W1 would have the drawback of its lower refractive index (1.76 compared to 2.20 for zirconia or 1.96 for zircon), but this could be partially offset by its lack of chromophores compared with the treated W2, which possibly still kept a small quantity of iron and titanium, even after the magnetic separation of the ferrite fraction.

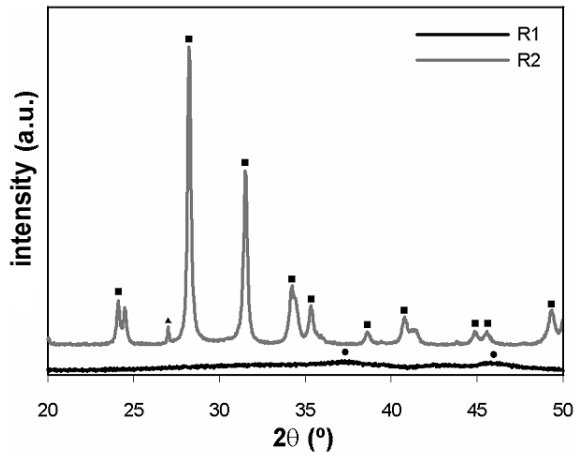

Figure 2. Detail of the diffractograms of the two treated and ground waste materials (• γ-alumina, ■ baddeleyite, ▲ zircon).

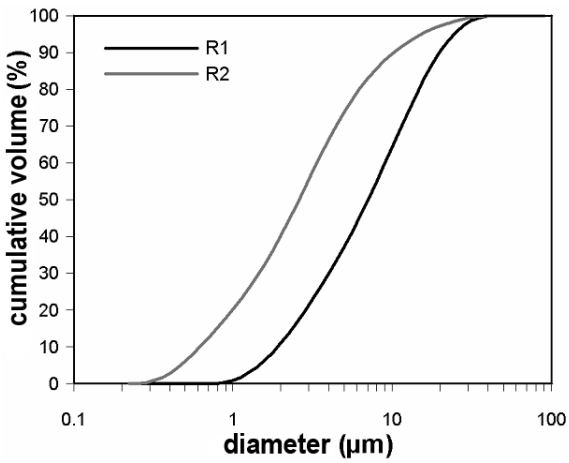

Figure 3. Particle size distribution of the two treated and ground materials.

3.4. Test in porcelain tile.

To analyse the opacifying capability of the pre-treated waste materials, and their effects on porcelain tile behaviour during firing and tile end properties, 5% by weight opacifier was added to a porcelain tile reference composition (STD), and different tests were conducted using zircon and the two waste materials being examined (see table 2). In addition, a more fluxing reference composition was formulated to correct the undesirable effects that W1 had on the STD composition.

Raw material	STD	A	B	C	D
Clay	31.6	30.0	30.0	30.0	30.0
Feldspar	52.6	50.0	50.0	50.0	60.0
Kaolin	15.8	15.0	15.0	15.0	5.0
Zircon	-	5.0	-	-	-
Treated and ground W1	-	-	5.0	-	5.0
Treated and ground W2	-	-	-	5.0	-
Bulk density (g/cm^3)	1.880	1.910	1.813	1.942	1.791

Table 2. Tested compositions (percentage by weight) and bulk density of the unfired compacts.

The effects of incorporating these wastes into the STD composition on STD composition behaviour during the pressing stage can be inferred from the unfired

bulk density (ρ_a), where the test pieces were seen to behave like non-plastic materials, similar to zircon. The addition of W1 tended to reduce ρa compared with that of the STD composition, which could be due to the γ-alumina having a relatively low density, or to it hindering compaction as a result of its large particle size. On the other hand, adding W2 significantly increased ρ_a, even above that of the composition with zircon, which is consistent with the higher density of baddeleyite (4.68 g/cm^3 compared with 5.68 g/cm^3), which disguises any negative effect on compaction.

All five compositions behaved relatively similarly during firing, since the bulk density of the fired samples (ρ_{ac}) reached its peak in the same temperature range (1200ºC-1220ºC), except for composition B, whose maximum densification temperature was over 1220ºC (figure 4). In all cases, water absorption in the fired samples was less than 0.1% at the maximum densification temperature, which means that adding the waste materials did not imply increased open porosity in the fired piece (figure 5). Using the bulk density data of the fired samples versus firing temperature, the maximum densification temperature (T_{max}) was calculated, fitting the data to a third-degree polynomial equation and analytically calculating the position of the maximum. The T_{max} data enabled the values of the various properties of the porcelain tile composition at maximum densification temperature to be estimated by introducing the value of T_{max} in the fitting curves of the various properties versus temperature.

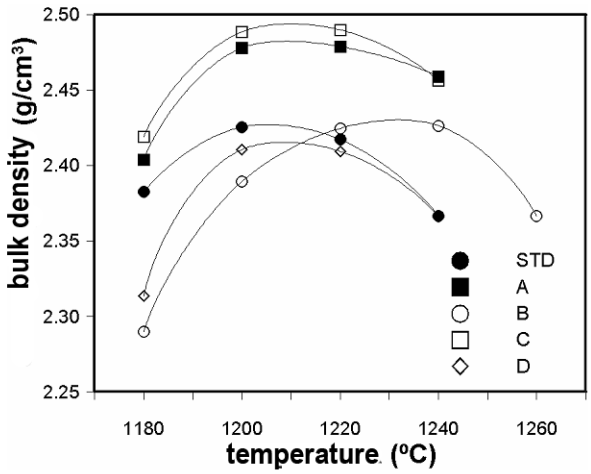

Figure 4. Evolution of bulk density in all five compositions against firing temperature.

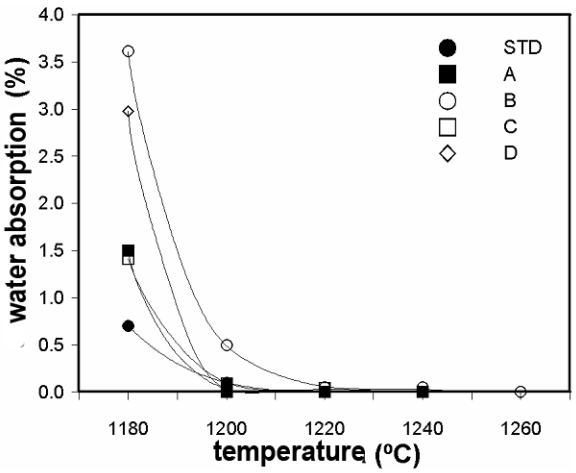

Figure 5. Evolution of water absorption in all five compositions against firing temperature.

The T_{max} of the STD composition was barely altered by the addition of zircon or waste material W2, indicating that the interaction between these materials and the glassy phase generated during firing was very slight (figure 6). However, waste material W1 increased its T_{max} by 25ºC, which suggests that part of the aluminium oxide dissolves in the glassy phase, thereby increasing viscosity and thus shifting sintering to higher temperatures. This effect was corrected by the modification

used in composition D, where the increased feldspar/kaolin ratio led to a T_{max} within the same range as compositions A and C.

In the compositions with waste material W2 or zircon, ρ_{ac} was clearly higher than in the other compositions (figure 6), which can be attributed to the dominant effect of the higher density of the added opacifiers. In the other three compositions, however, very similar ρac values were obtained, which shows that the effect of sintering can offset the significant differences in ρa in the unfired pieces. However, this means that fired linear shrinkage will undergo significant alterations depending on the opacifier used (figure 7). Adding zircon or W2 led to minor changes, a slight increase in the former case and a slight decrease in the latter. However, the compositions that contained W1 displayed significantly higher linear shrinkage values than the rest, a phenomenon that in both cases may be related to the lower compactness of the unfired piece.

The luminosity values for the fired samples indicated that the three compositions containing the waste materials were situated in an intermediate position in the range of six units, with compositions STD and A at either end (figure 7). It should also be noted, however, that the composition containing W2 yielded a slightly higher L* value than the two compositions containing W1.

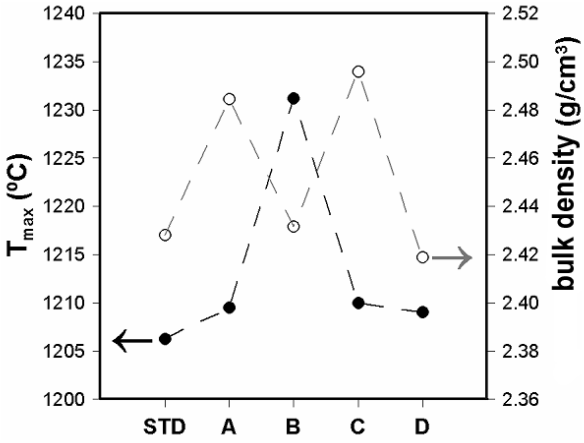

Figure 6. Estimated maximum densification temperature and bulk density for the five compositions.

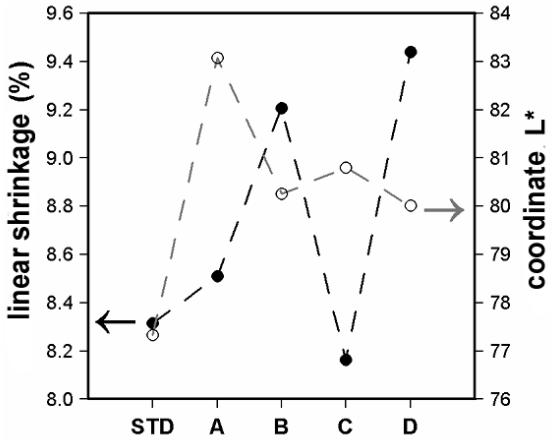

Figure 7. Estimated linear shrinkage and L coordinate at maximum densification for all five compositions.*

The red component was the one that presented the lowest variation range, indicating that it was scarcely influenced by the tested opacifiers or by changes in the reference composition (Figure 8). It should also be noted, however, that the four compositions with opacifiers yielded lower values compared with those of the STD composition, although the compositions containing zircon or W2 had slightly higher a* values than the two compositions with W1.

The yellow component was remarkable in all compositions, although its variation range was not as wide as for L* (figure 8). The STD composition and the

one containing W2 produced the highest values, the latter being slightly higher, while the other three compositions produced significantly lower values. Adding zircon led to the lowest b* value, whereas W1 gave slightly higher b* values for the two compositions to which it was added.

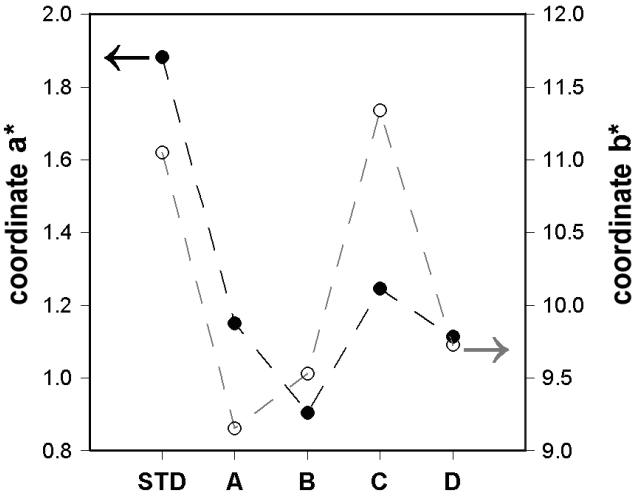

Figure 8. Estimated a and b* coordinates for maximum densification in the five compositions.*

Pre-treated waste material W1 can be used as an opacifier, since it is made up of relatively large aluminium oxide particles and is practically free of chromophores, so that adding it to porcelain tile increases luminosity significantly and reduces chromaticity to a slight extent. However, its usage requires formulation of more fluxing compositions in order to keep T_{max} within the standard range for porcelain tile. This phenomenon can be interpreted by considering the interaction of the Al_2O_3 particles with the glassy phase generated when the porcelain tile is fired, which causes its partial dissolution and therefore enriches the alumina content in the liquid phase, in turn giving rise to increased viscosity, delayed sintering and therefore a significant increase in the maximum densification temperature. This waste material was also observed to have a negative impact on pressing compaction, which does not lead to a significant drop in fired bulk density but leads to a noteworthy increase in fired linear shrinkage.

Pre-treated waste material W2 also acts as an opacifier, since it is mostly composed of zirconium oxide particles, though it also contains a small fraction of chromophore elements (especially iron). Consequently, adding it to porcelain tile leads to a significant increase in luminosity and a slight increase in b*. Its inclusion in porcelain tile compositions does not lead to significant alterations in properties such as maximum densification temperature or fired linear shrinkage, and the only significant effect noted was a notable increase in bulk density of the fired piece, which may be attributed to the high density of the waste material.

The results obtained indicate that both waste materials can be used as economical opacifiers in porcelain tile, especially in applications that do not require maximum whiteness, though each of them possesses specific characteristics which

may restrict – but not prevent - their possible use on an industrial scale. Should these materials be used in a porcelain tile plant, further research into the effect of particle size on their performance as opacifiers would be warranted, since it is very likely that there is a specific particle size distribution that maximises each one's opacifying capability and that would therefore allow them even more to closely approach the performance afforded by zircon.

4. CONCLUSIONS

The study shows that two industrial waste materials can be used as opacifiers in porcelain tile, provided they are subjected to simple pre-treatment processes to eliminate undesirable components. The waste adsorbent requires calcination at low temperatures to eliminate adsorbed organic matter, followed by grinding to adjust particle size. In the case of the waste material from the electronics industry, this pre-treatment can commence with grinding to separate the various types of particles present in it and to adjust particle size, followed by magnetic separation of the phases that contain most of the chromophores.

Both pre-treated waste materials behave as opacifiers in porcelain tile compositions, although they do not yet achieve the performance levels of zircon. Thus, they can only be considered as a zircon alternative in compositions that do not require maximum whiteness, which nevertheless account for a significant part of current industrial output.

From a technical point of view, no impediments have been found for using these waste materials as opacifiers, since in the worst-case scenario (incorporation of the adsorbent), the negative effects on the properties of the fired porcelain tile can be offset by simply adjusting the composition.

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