Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of the European Ceramic Society 24 (2004) 83–92

www.elsevier.com/locate/jeurceramsoc

Use of soda-lime scrap-glass as a fluxing agent in a porcelain stoneware tile mix

A. Tucci[a,*], L. Esposito[a], E. Rastelli[a], C. Palmonari[a], E. Rambaldi[b]

[a]*Italian Ceramic Center, Via Martelli 26, 40138 Bologna, Italy*
[b]*Dipartimento di Chimica Applicata e Scienza dei Materiali, Facoltà di Ingegneria, Viale Risorgimento 2, Bologna, Italy*

Received 21 April 2002; received in revised form 3 February 2003; accepted 14 February 2003

Abstract

The study was directed towards determining the feasibility of using soda-lime scrap-glass as a fluxing agent in a porcelain stoneware tile mix. Both laboratory and industrial scale tests were carried out. Starting from a reference mix composition, different amounts (5–20 wt.%) of sodium feldspar were replaced with the same amounts of soda-lime scrap-glass. The soda-lime scrap-glass was added in the form of powder, prepared by wet grinding in a centrifugal ball mill. The rheological study of the resulting slips showed that increasing the amount of glass in the mix composition increased the viscosity but decreased the yield stress. Both the laboratory experiments and results of industrial trials showed that the only mix in which the soda-lime glass acted as a good fluxing agent, i.e. lowered the firing temperature, was the mix in which the scrap-glass replaced 10 wt.% of the sodium feldspar. This mix also showed better mechanical characteristics, attributed to enhanced microstructural homogeneity.

Keywords: Glass; Mechanical properties; Microstructure-final; Porcelain; Structure; Tiles; Wastes

1. Introduction

One of the most important problems regarding industrial and urban waste concerns its impact on the safety of people and the environment. The hazardous nature of some wastes requires that suitable treatments be found to render these materials inert. In addition, the use of non-hazardous wastes also needs to be carefully evaluated, taking into account the possibility of recycling them, not only in the processes of origin, but also in other industrial activities. Such recycling makes it possible to reach some important goals related to the storage of wastes, conserving limited supplies of natural raw materials and consequently, safeguarding the environment. To take advantage of the available opportunities and correctly use the wastes, it is necessary to understand whether or not they contain materials suitable for the processes and products for which they are to be used. As is well known, wastes can be divided into groups on the basis of their nature and characteristics.[1] Like natural raw materials, therefore wastes too can be identified and characterised to correctly predict their behaviour during processing and the effects on the final products. From the industrial point of view, it is also very important to define both the economical benefits and the quality of the products. In this regard, interesting opportunities are offered by the traditional ceramics industry. Different kinds of wastes have been incorporated into tiles and bricks, products in which microstructural homogeneity is not required. Important investigations have already been carried out on this topic,[2,3] and an interesting review has been published.[4,5]

The present work is focused on the possibility of using soda-lime scrap-glass in a mix for porcelain stoneware tiles. Porcelain stoneware is a product in which the synergy between manufacturing technology and physical–mechanical properties is particularly well developed with excellent results. Due to the high firing temperature ($>1200\ ^{\circ}C$), porcelain stoneware tile, an unglazed product, is characterised by very high density (water absorption $<0.5\%$). Since this product has excellent technical characteristics, such as good flexural strength, resistance to surface abrasion and stains, surface hardness

* Corresponding author. Tel.: +39-051-534015; fax: +39-051-530085.
E-mail address: tucci@cencerbo.it (A. Tucci).

0955-2219/03/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0955-2219(03)00121-3

and, in comparison with other classes of tiles, a high fracture toughness,[6] it can be used in those environments where high performance and reliability are required. For these reasons, the demand for porcelain stoneware tile has increased considerably. Indeed, in 2001[7] Italian production was higher than 309 million m^2. The natural raw materials used in the production of porcelain stoneware tiles, such as clays and feldspar, are usually purchased from a limited number of countries, for example, Germany, Turkey and Ukraine. For this reason, several countries have interest to reformulate the body mix composition, by partial replacement of one of the natural raw materials with a very cheap and readily available non-hazardous waste material consistent with the product. Such a solution can be considered viable only if the industrial process essentially remains unchanged and the quality and characteristics of the product do not decrease.

Taking into account these aspects, a non-hazardous waste, soda-lime scrap-glass, was chosen for this study. It is worth pointing out that based on 2001 data, it can be estimated that the annual use of glass (glass packaging) in Italy amounts to about 2.02 million tons, of which only 0.96 million tons are recycled.[8] The choice of this material was based on both the possible fluxing effect due to the presence of glass, and the potential matching to the vitreous microstructure of porcelain stoneware tiles. Considering the analogies between soda-lime glass and sodium feldspar, the composition of the body mix was reformulated, replacing part of the sodium feldspar with soda-lime scrap-glass. To quantify the suitability of this replacement and optimise the amount of scrap-glass to be used, the effects due to the reformulation were first investigated in laboratory experiments and then, on the basis of the laboratory results in industrial. The results obtained are discussed in terms of mix preparation, microstructure and physical–mechanical properties.

2. Experimental procedures

A formulation used for the industrial production of porcelain stoneware tile was selected as a reference body mix. It contains 45 wt.% of kaolinitic and illitic clays, 18 wt.% of sodium feldspar and 36 wt.% of feldspathic sand. The chemical analysis of the body mix, determined by inductively coupled plasma optical emission spectroscopy (ICP–OES Optima 3200 XL, Perkin-Elmer, USA) is reported in Table 1.

Starting from the reference body mix, denoted STD, different amounts, 5, 10, 15 and 20 wt.%, of the sodium feldspar were replaced with the same percentages of soda-lime scrap-glass. The average chemical compositions of the sodium feldspar and the soda-lime scrap-glass, determined by ICP–OES, are reported in Table 1.

Table 1
Average chemical composition, in wt.%, of the body mix, the sodium feldspar and the soda-lime scrap-glass used in this investigation

Oxides	Body mix	Sodium Feldspar	Glass
l.i.	5.30	0.64	–
SiO_2	66.10	69.81	70.50
Al_2O_3	21.20	17.74	1.00
TiO_2	0.49	0.06	0.05
Fe_2O_3	0.63	0.30	0.16
CaO	0.99	1.31	8.98
MgO	0.29	0.19	3.81
K_2O	2.16	0.59	0.28
Na_2O	3.23	8.93	14.26
PbO	–	–	0.11
BaO	–	–	0.10

The samples prepared were designated STD5, STD10, STD15 and STD20, indicating the percentages of sodium feldspar replaced, 5, 10, 15 and 20 wt.%, respectively. To facilitate its incorporation into the mix, the scrap-glass was wet ground in a centrifugal ball mill and then the required amounts were added to the other raw materials. The samples of both the reference body mix and modified mix compositions were prepared by dispersing the powders in an aqueous slip, 70 wt.% solid with 1 wt.% of the deflocculating agent "Fluicer S035" (Ceramco, Zwischer & Schwarz Group, Geramny), and finally milled for 1 h in a ceramic jar mill until a residue of about 0.2% on a 45-μm screen was obtained.

The rheological characterisation of all the slips was carried out on fresh samples, using a RS 50 HAAKE (Germany) rheometer (control rate and control stress), equipped with a plate-plane sensor. In order to start the rheological measurements at the same conditions, the slurries were first subjected to pre-shearing at 1000 s^{-1} for 60 s and maintenance of an equilibrium phase at 0 s^{-1} for 180 s. The equilibrium phase is important in order to rebuild the original structure of the particle in the slurry, which is destroyed during the pre-shearing. In this way, the rheological history of the slurry is cancelled, all the samples are in the same rheological conditions and their behaviours can be compared. The flow curves were obtained in the mode control rate, in order to evaluate the variation of viscosity in shear rate conditions. The yield stress was measured from tests conducted in the control stress mode, by gradually increasing the stress from 0 to 200 Pa in 300 s.

The particles size distribution of the slips were determined using a laser particle size analyses (MASTERSIZER 2000, Malvern UK).

The slips were dried in a oven at 120 °C for one night, the dried cakes were then crushed and sieved to pass through a 125-μm screen to obtain suitable powders for pressing. The test specimens, in the form of discs for the firing tests, and bars for the mechanical tests, were pre-

pared by adding 6 wt.% water to the sieved powders and uniaxial pressing at 52 MPa. The sintering behaviour was evaluated by firing the discs in a laboratory electric gradient furnace, following eight firing schedules reaching different maximum temperatures in the range 1180–1280 °C, at regular intervals of 20 °C, with a soaking time of 40 min and natural cooling to room temperature. The firing cycle was of about 2 h.

The sintering behaviour of the fired test pieces was evaluated on the basis of the linear shrinkage and water absorption. Determination of the water absorption was carried out using the ISO 10545-3 test method for ceramic tiles.

The mineralogical compositions of the starting body mixes and fired samples were determined by X-ray diffraction analysis.

The bulk porosity and pore size distribution of the fired samples were evaluated by analysing suitable specimens with an optical microscope, in reflected light and clear field, connected with an image analyser system (Qwin, Leica, Germany). The pore size is expressed as the diameter of the circle having the same area as that of the pore. The samples analysed were prepared by embedding with an acrylic resin and by polishing them with a laboratory bench grinder-polisher (Leco Co., VP-150, USA) equipped with diamond grinder discs, using six stages in sequence with the abrasive grain size in the range 60–2 μm.

The microstructure of the fired samples was studied by observing both fracture and polished surfaces surfaces with a scanning electron microscope, SEM, (Jeol, T330, Japan), equipped with an energy dispersion X-ray attachment, EDS, (Noran, USA).

The flexural strength was determined on specimens in the form of bars, 70×10×6 mm. At least 20 specimens were tested using a universal testing machine (MTS, 10/M, USA), in three-point bending fixture, 60 mm support span and with a crosshead speed of 5 mm min^{-1}. The modulus of elasticity was also evaluated, using an extensometer applied in correspondence to the middle of the surface of the specimens subjected to tensile stress. The average flexural strength, σ, was calculated and Weibull's modulus, m, was evaluated via the least squares method and linear regression analysis, adopting $P_n = (I-0.5)/N$ as the probability estimator.[9]

3. Results

The flow curves in control rate mode are reported in Fig. 1. Due to non-Newtonian behaviour of the ceramic suspensions, the experimental data are better fitted with use of the Bingham model, for which viscosity is the slope of the straight line of Eq. (1):

$$\tau = \tau_0 + (\mathrm{d}\gamma/\mathrm{d}t)\eta \quad (1)$$

where τ_0 is the calculated yield stress (Pa), $(\mathrm{d}\gamma/\mathrm{d}t)$ is the shear rate (s^{-1}) and η is the viscosity (Pa s). The regression coefficient for each curve was greater than 0.99. The calculated viscosity values are reported in Table 2. The presence of glass in the slips causes an increase in viscosity, which increases as the amount of glass increases. This was related to the decreasing particle size, as detected for the slips with glass. Silicate glass is less hard than feldspar, so for the same milling condition, the grain size distribution for the modified slips is finer than for the STD slip, as experimentally detected (Table 3). Furthermore, the observed increase of viscosity could also be caused by a different ionic effect

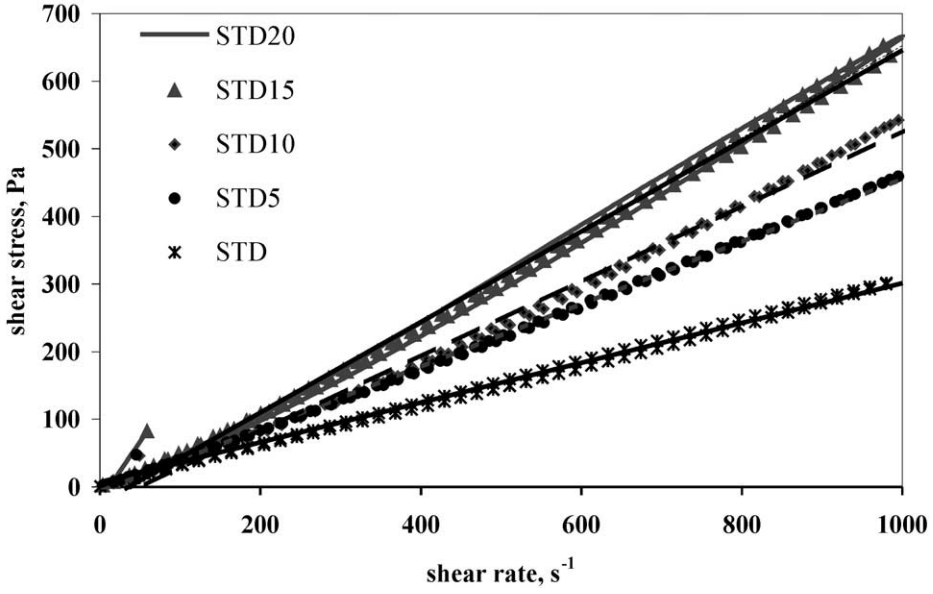


Fig. 1. Flow curves for the slips.

Table 2
Rheological parameters of the slips prepared from the different mixes tested

Slip	Viscosity, Pa s	Yield stress, Pa
STD	0.29	26.6
STD5	0.46	4.6
STD10	0.55	3.2
STD15	0.67	11.0
STD20	0.68	2.1

Table 3
Equivalent diameter, μm, corresponding to 10, 50 and 80% of the particle size distribution, for the tested slurries

Sample	d_{10}, μm	d_{50}, μm	d_{80}, μm
STD	1.57	6.61	22.24
STD5	1.50	6.30	21.23
STD10	1.48	6.07	19.58
STD15	1.47	6.05	19.00
STD20	1.45	5.69	17.85

acting in the slips containing the glass, for the presence of higher amounts of calcium and magnesium ions,[10] coming from the scrap glass.[11]

The Bingham model is not usually good for the evaluation of the yield stress, the extrapolated values are usually higher than the experimental ones.[12] Curves obtained in the control stress mode are better modelled by the power law equation.[13] Reported in Table 2 are the measured values of yield stress. The reference mix, STD, shows a value of yield stress considerably higher than that of the modified slips. In contrast, no meaningful differences are found for the slips containing different amounts of glass. This result indicates that the presence of the glass renders the network of particles inside the slips less structured.

Reported in Fig. 2a and b are the behaviour of the water absorption and linear shrinkage as a function of temperature, for the different compositions. The STD mix reaches a value of water absorption of 0.00% at the firing temperature of 1240 °C. The replacement of sodium feldspar with soda-lime scrap-glass resulted in a lower firing temperature only for the sample with 10 wt.% glass. The other compositions, STD5, STD15 and STD20 were more refractory than the reference composition, STD. The shrinkage (Fig. 2b) follows a similar consistent trend. The reference mix, STD, reaches its maximum shrinkage at 1240 °C, remaining rather constant also at higher temperatures. The STD10 mix shows the highest shrinkage, with its maximum in the range 1220–1240 °C. At higher temperatures, slight expansion of the STD10 sample (negative shrinkage) is observed. The other mixes, STD5, STD15 and STD20, reach their maximum shrinkage at about 1260 °C, followed by rapid expansion.

For the samples fired at 1220 and 1240 °C the bulk porosity, measured as the percentage of the area of the pores, and average pore radius are reported in Table 4. The reference material, STD, has the lowest porosity, while increasing the percentage of soda-lime scrap-glass caused a general increase in porosity, more evident in the STD15 and STD20 materials.

SEM analysis showed that the morphology of the pores in STD and STD5 is rather different. The STD material contains essentially isolated round pores (Fig. 3a) and STD5 is characterised by the presence of rather small pores, generally interconnected (Fig. 3b) as a result of incomplete densification. The microstructure of STD10 is very homogeneous for both firing temperatures, 1220 °C (Fig. 4a) and 1240 °C (Fig. 4b) with a rather smooth fracture surface, attesting to consistent development of the liquid phase during firing. The pores are always round and isolated, although in the sample fired at 1240 °C, they are larger than in the STD test piece. For the same range of firing temperature, the pores in the STD15 and STD20 materials are numerous and larger (Fig. 5).

The crystalline phases identified in all the samples fired at 1220 and 1240 °C, are quartz and albite, both residual minerals from the original raw materials, and mullite, formed during firing. For the compositions containing soda-lime scrap-glass some modifications in the intensity and position of the peaks in the X-ray diffraction patterns indicate the presence of a new phase, the amount of which increases with increasing percentage of glass and firing temperature (Fig. 6). This new phase is, very probably, anorthite sodian, which peaks, are very near to the ones of the residual albite, but the relative intensity is rather different.[14] Careful examination by SEM + EDS showed the presence of very fine particles enriched in calcium and completely lacking in the reference material, STD.

Table 4
Total pore area (%) and average pore diameter (μm) for the test pieces fired

Test piece	STD		STD5		STD10		STD15		STD20	
	%	μm	%	μm	%	μm	%	μm	%	μm
at 1220 °C	2.2	4.5	2.7	5.0	2.8	4.4	3.1	5.3	3.5	5.4
at 1240 °C	2.7	4.6	3.6	4.6	3.6	5.7	4.4	6.0	7.8	7.1

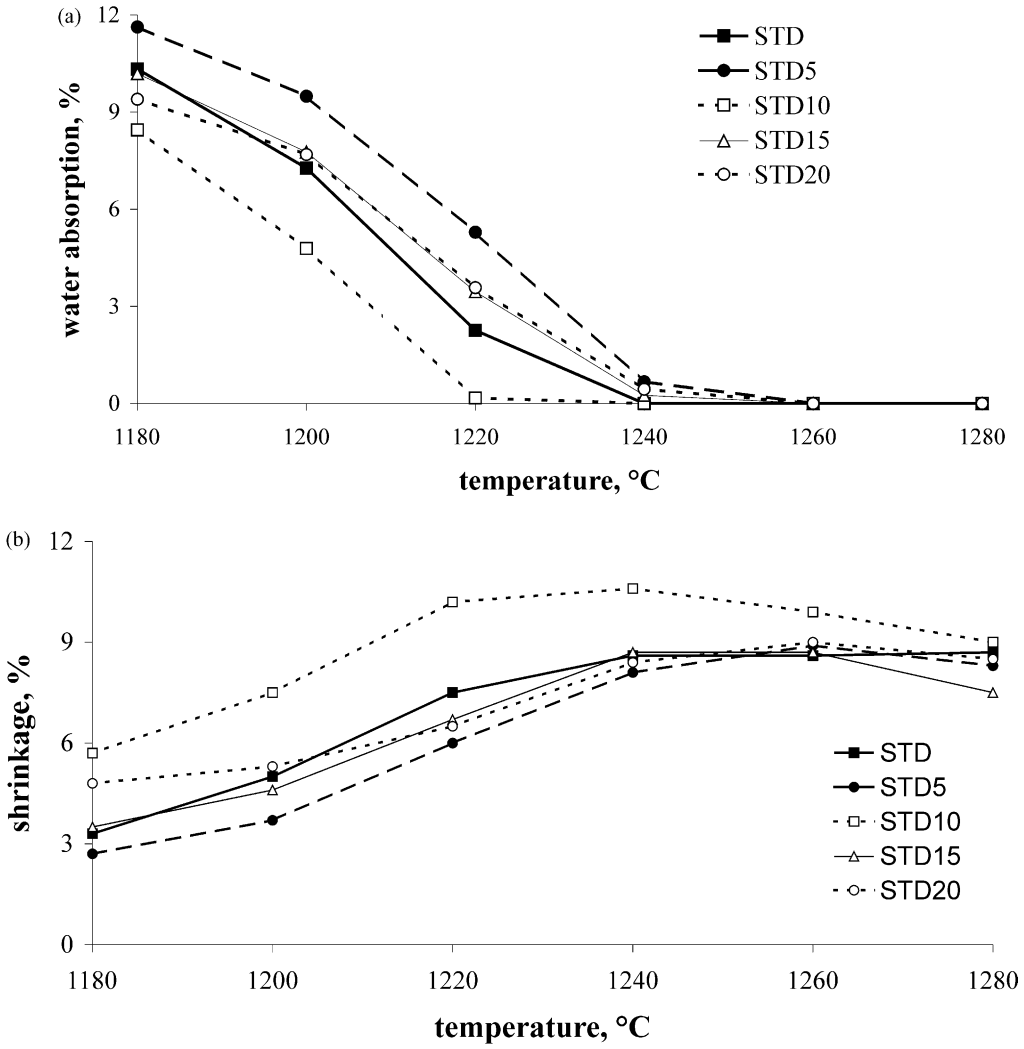
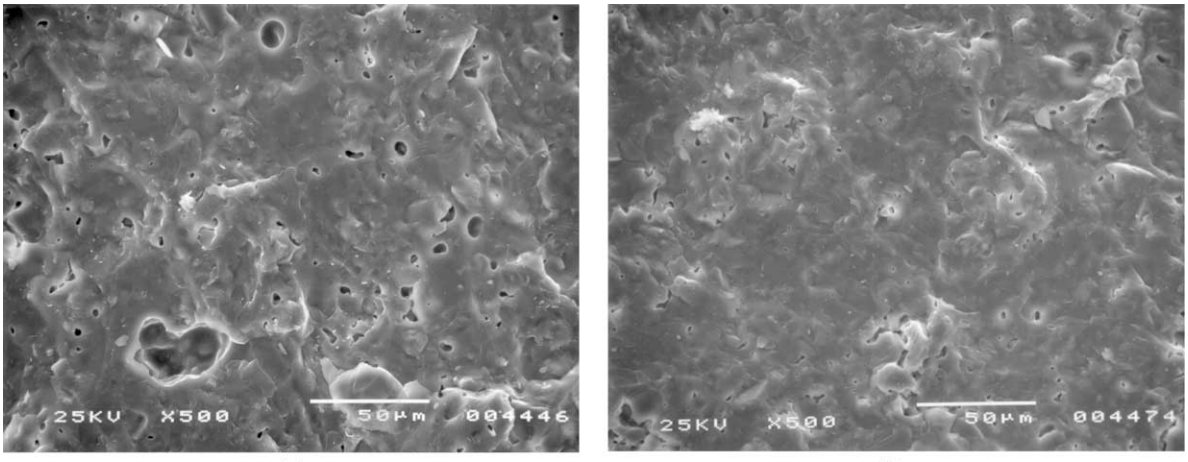
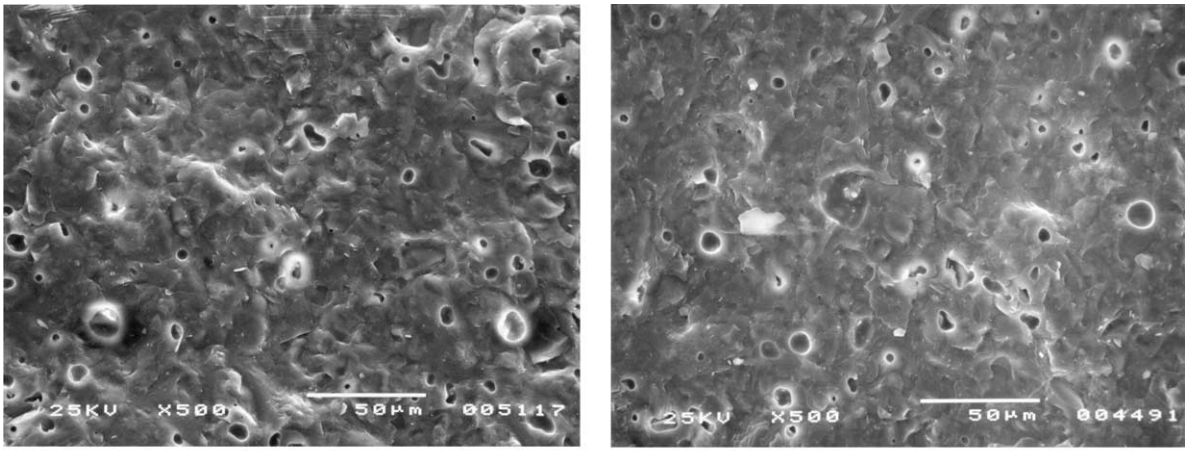


Fig. 2. Water absorption (a) and linear shrinkage (b) plotted vs. firing temperature.



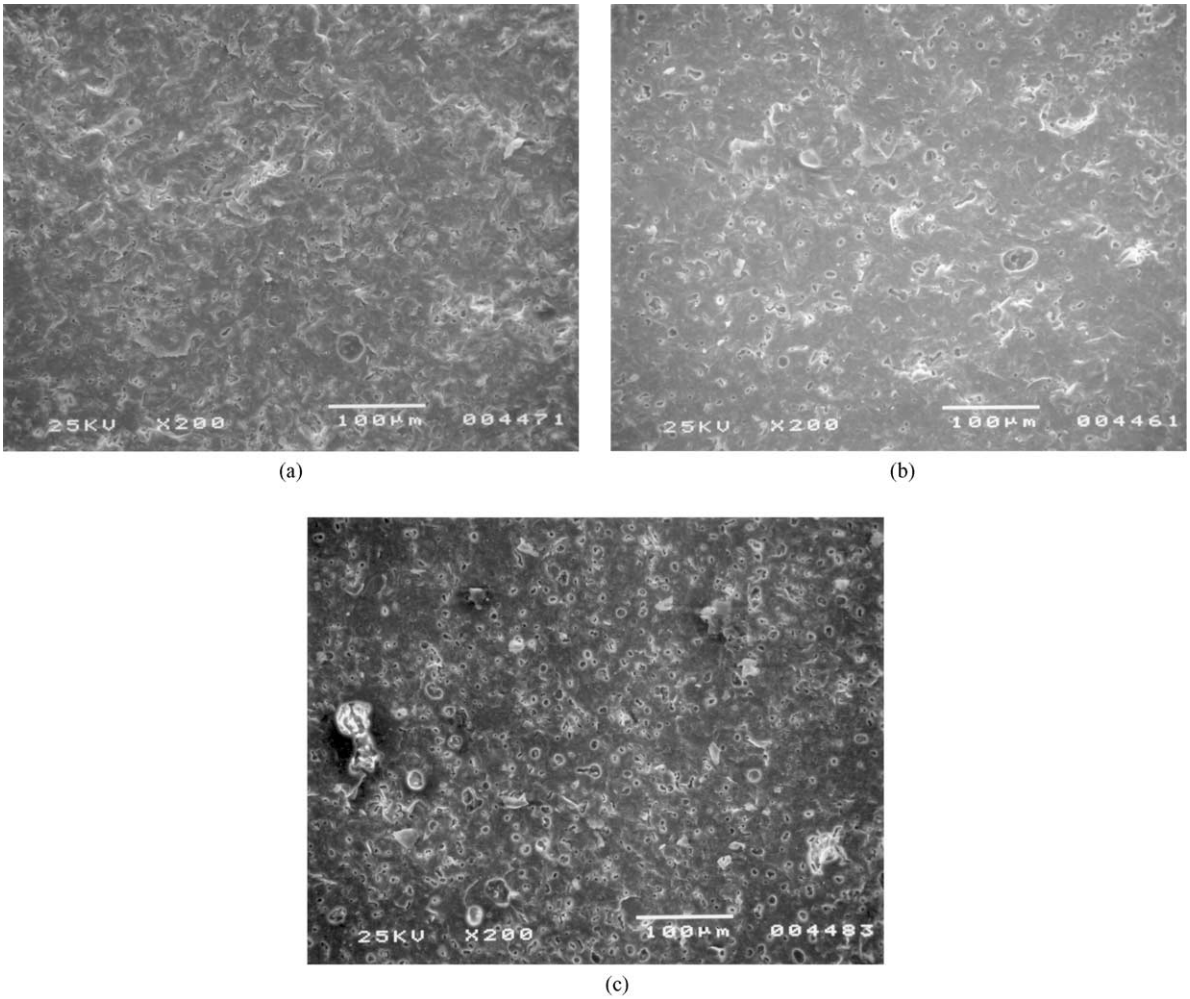
(a) (b)

Fig. 3. SEM micrographs of samples fired at 1240 °C, (a) STD and (b) STD5.



(a) (b)

Fig. 4. SEM micrographs of STD10 fired at (a) 1220 °C and (b) 1240 °C.



(a) (b)

(c)

Fig. 5. SEM micrographs of samples fired at 1240 °C, (a) STD, (b) STD15 and (c) STD20.

Mechanical characterisation was carried out only for those materials showing the lowest water absorption in the temperature range adopted in the industry for firing porcelain stoneware tile, 1210–1240 °C, Table 5. Because the reference material, STD, fired at 1220 °C can not be considered a porcelain stoneware, showing a water absorption of 2.26%, largely higher than the value requested, $<0.5\%$, by the International

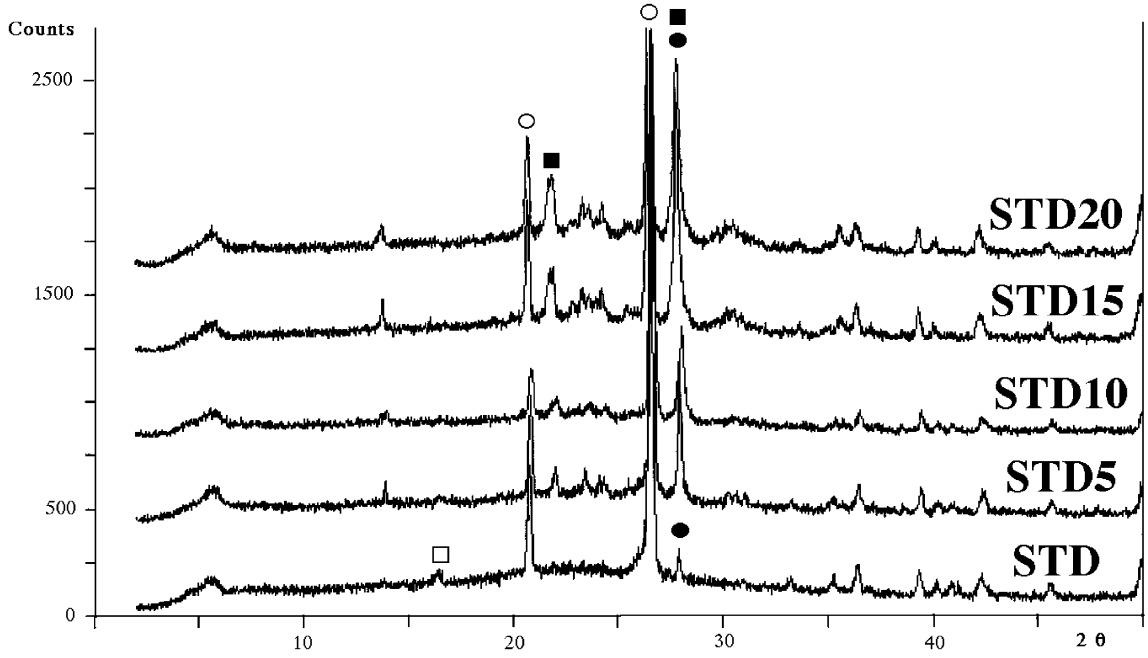


Fig. 6. XRD patterns of the samples, the standard one and the modified compositions, fired at 1240 °C. ○ quartz, □ mullite, ■ anorthite, ● albite.

standard,[15] its mechanical characteristics were not evaluated.

The flexural strength for the STD10 material fired at 1220 °C is rather high, with a value very near that of the STD material fired at higher temperature, 1240 °C. For STD10, the increase in firing temperature, from 1220 to 1240 °C, caused a decrease in flexural strength. Weibull's modulus, *m*, in the modified materials is always higher than in the reference material, STD, particularly evident for STD10 fired at 1220 °C.

The presence of soda-lime glass determines a decrease in Young's modulus. For STD10, the value of the modulus of elasticity is only slightly lower than that of the reference material STD.

4. Discussion

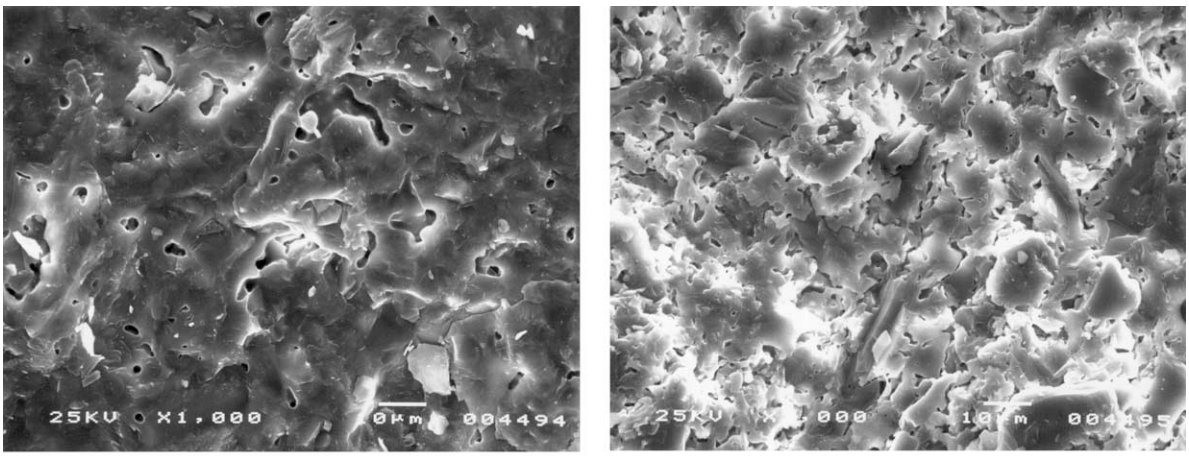
Replacing different amounts of the sodium feldspar, with soda-lime scrap glass in a porcelain stoneware tile mix, changes the amounts of the different alkalis in the mix. In particular, as the amount of sodium feldspar in the mix is decreased with corresponding increases in the amount of scrap-glass, the amount of calcium and to a lesser extent the amount of magnesium increases. In addition, the amount of alumina in the mix decreases. In a silica-based glass, the effect of replacing alumina with lime, in the temperature range used in the present investigation, does not cause a linear variation in the viscosity of the melted glass, but rather the viscosity first decreases and then rapidly increases.[16,17] The firing behaviours shown by the mixes tested can be attributed to the changes in composition resulting from the replacement of the feldspar with the scrap-glass, which in turn, led to differences in the viscosity of the liquid formed at the firing temperatures used to produce the porcelain stoneware tile.

Table 5
Physical–mechanical characteristics of the fired test pieces

Material	Water absorption (%)	σ (MPa)	E (GPa)	m
STD (1240 °C)	0.00	93.0	68.2	14.7
STD10 (1220 °C)	0.17	88.1	63.5	21.9
STD10 (1240 °C)	0.00	79.7	63.1	17.3

The STD5 body mix was found to be more refractory than the standard one, STD. The viscosity of the liquid phase is higher[16] and the capability of the liquid phase to wet and to react with the solid particles is less than for STD, thus explaining the presence of areas with interconnected porosity and higher refractoriness in the STD5 samples (Fig. 3).

For STD10, the mix composition is such that the amount and viscosity of the liquid phase allows vitrification of the sample at a lower temperature than with the reference mix, STD. Already at 1220 °C, the water absorption of the fired STD10 material is very low, 0.17% and the material is rather well sintered, only a few small pores are present (Fig. 7a). In contrast, at the same temperature the reference material, STD, has a water absorption of 2.26% with a microstructure characterised by narrow, but interconnected porosity (Fig. 7b). It is important to point out that tiles with a



(a) (b)

Fig. 7. SEM micrograph of the fracture surface of samples fired at 1220 °C, (a) STD10 and (b) STD.

water absorption >0.5%,[15] in this case the STD test pieces fired at 1220 °C, can not be considered to belong to the porcelain stoneware tile class.

In STD15 and STD20 the amount of alkaline earth ions is higher than in STD. The high viscosity of the liquid phase formed when STD15 and STD20 are fired means that filling of the inter-particle voids is more difficult, than for the STD sample and pools of high viscosity liquid form. The large gas bubbles that form during firing can be eliminated only with difficulty from the high viscosity liquid. All these factors contribute to reduce shrinkage (Fig. 2b) and slow densification (Fig. 2a). Furthermore, analysis of the X-ray diffraction patterns shows that for the materials with the highest amounts of glass, STD15 and STD20, the diffraction peaks of mullite are considerably less intense than those for the other compositions. This is essentially due to the lower alumina content in the liquid phase and higher viscosity that does not favour the formation of mullite. In this system, the crystallisation of some anorthite also could contribute to the depletion of mullite.[18]

The increased homogeneity of the STD10 material, fired at 1220 °C, is able to explain its rather good mechanical performance, in particular its narrow range of porosity that contributes to decrease the critical flaw dimensions. A decrease in the flexural strength is observed when STD10 is fired at 1240 °C which can be essentially attributed to bloating phenomena, causing an increase in the pores radius.

The increase in Weibull's modulus is further evidence of improved microstructural homogeneity, caused by the addition of glass. Since particularly high performances are required of porcelain stoneware tiles, the reliability of the product represents a very important parameter.

5. Industrial application

Industrial scale tests were carried out to verify the possibility of using soda-lime scrap-glass in a standard porcelain stoneware tile mix. On the basis of the results obtained in the laboratory tests, a small lot of tiles was produced on an industrial scale with the reformulated mix composition containing 10% of the soda-lime scrap-glass in place of the same amount of the sodium feldspar. Two different mixes were prepared using a pilot industrial process: (1) a reference mix denoted STD-I to distinguish it from that prepared in the laboratory and, (2) the corresponding modified composition, replacing 10 wt.% of the sodium feldspar with the same percentage of soda-lime scrap-glass, denoted STD-I + 10%.

The two mixes, 500 kg each, were prepared in a discontinuous mill with alumina linings and alumina grinding media, and then spray dried using pilot plant equipment. Reported in Table 6 are some characteristics of the slips and powders obtained in this step. Dry pressed ceramic tiles, 30×30 cm, were then manufactured. The tiles were fired in an industrial roller kiln, using a fast firing cycle of 46 min with a peak temperature of 1210 °C. These trials were monitored and no particular production problems were detected with either of the two mixes.

Some physical–mechanical characteristics of the tiles, considered interesting for the purposes of this study are summarised in Table 7. In particular, the water absorption and flexural strength were evaluated according to the test methods recommended in the International Standards ISO 10545-3 and ISO 10545-4, respectively. Furthermore, the modulus of elasticity was determined by subjecting, to three-point bending at the previously

Table 6
Technological characteristics of the industrial body mixes

Characteristic	Material	
	STD-I	STD-I + 10%
Milling residue,%	0.98	1.07
Slip density, g/l	1737	1726
Slip viscosity, °E	2.10	2.00
Moisture content of the powders,%	5.68	5.50

Table 7
Physical–mechanical characteristics of the fired tiles

Material	Water absorption (%)	Linear shrinkage (%)	σ_m (MPa)	E (GPa)
STD-I	0.39	7.6	55.6	53.2
STD-I + 10%	0.00	7.8	74.9	62.7

specified testing parameters, suitable specimens 70×28×8.5 mm, randomly cut from the tiles. At least 20 specimens for both products were tested. These further tests provided information on the homogeneity of the material.

It is interesting to note that, for the same firing cycle, the tiles obtained from the modified mix, STD-I + 10, are more compact, with 0.00% water absorption, and show a significant increase in flexural strength, about 33% in comparison with the value obtained for the STD-I tiles.

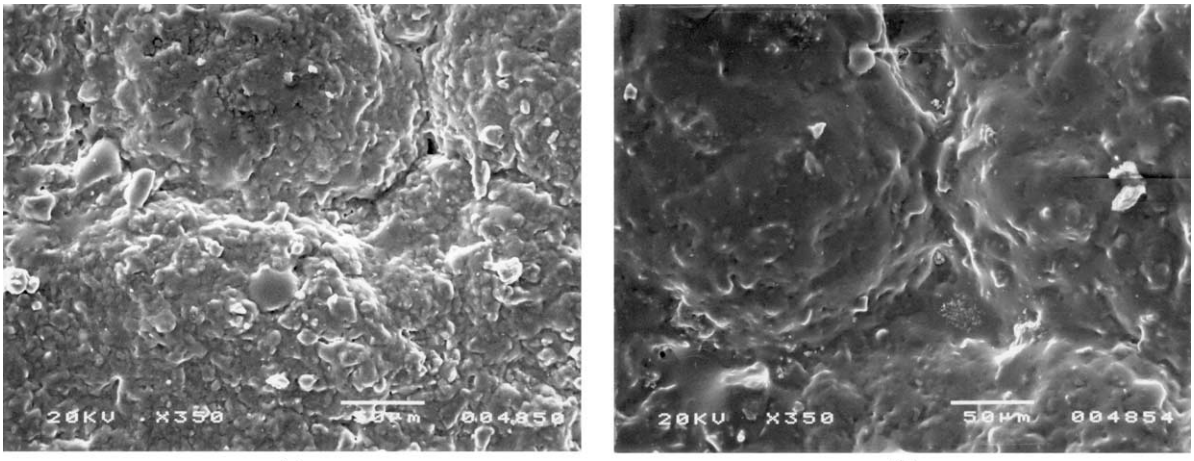
The proper surface of the STD-I + 10 tile, as observed by SEM (Fig. 8b) is much more vitrified, completely lacking in porosity, as compared with the same area of the STD-I tile (Fig. 8a). This is also confirmed by the analysis of the fracture surfaces. The reference tile shows many small, but interconnected pores (Fig. 9a) while the microstructure of the STD-I + 10 tile is very compact and characterised by few and small isolated pores (Fig. 9b). The observed increase in mechanical resistance for the modified composition is due to the enhanced microstructural homogeneity in terms of compaction and porosity. Replacing in a reference body mix for porcelain stoneware tile 10 wt.% of the sodium feldspar with soda-lime scrap-glass allows, under the same process conditions, a considerable reduction in water absorption and an increase in flexural strength. This aspect can also favour the cleanability of the working surface.[19,20]

6. Conclusions

In the present investigation, the possibility of replacing a percentage of the sodium feldspar with soda-lime scrap-glass in a standard porcelain stoneware tile mix was confirmed. The results of the laboratory tests showed that the replacement of 10 wt.% of the sodium feldspar with the same amount of soda-lime scrap-glass causes the following remarkable effects:

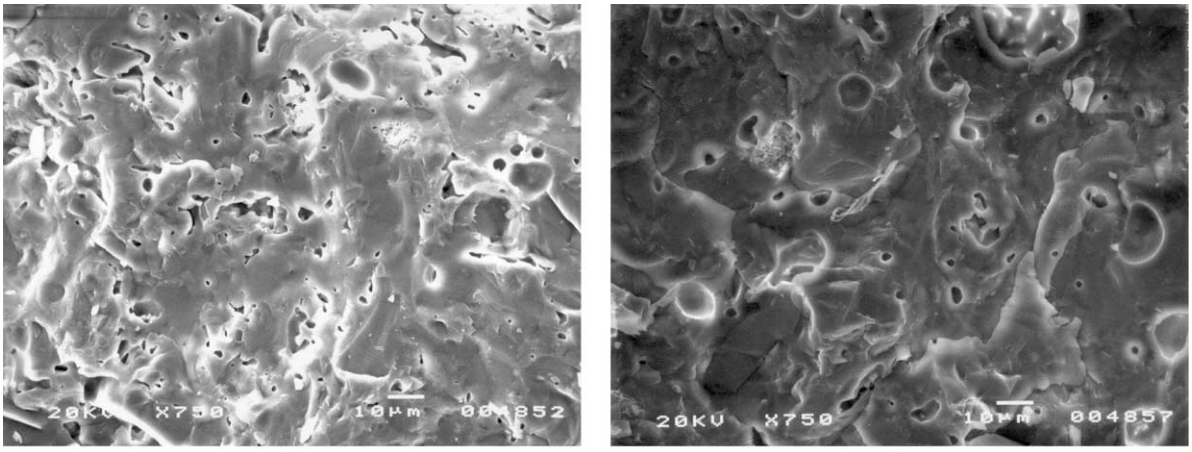
- a considerable decrease in firing temperature;
- an increase in mechanical resistance.

Preliminary industrial trials, carried out with the same porcelain stoneware body mix in which 10 wt.% of the sodium feldspar was replaced with the corresponding amount of soda-lime scrap-glass, confirmed the trend shown by the laboratory results. Taking into account the current market demand for porcelain stoneware tile, this aspect seems to be important for the possibility of improving the characteristics of a product, and at the same time finding a use for a waste material, the availability of which is increasing.



(a) (b)

Fig. 8. SEM micrographs of the surface of fired tiles from the industrial trials, (a) STD-I and (b) STD-I + 10.



(a) (b)

Fig. 9. SEM micrographs of the fracture surface of fired tiles from the industrial trials, (a) STD-I and (b) STD-I + 10.

Acknowledgements

The authors wish to thank Mr. S. Degli Esposti and Mr. D. Naldi for their contribution in carrying out the laboratory tests.

References

1. Martelon, E., Jarrige, J., Ribeiro, M. J., Ferreira, J. M. and Labrincha, J. A., New clay-based ceramic formulations containing different solid wastes. *Ind. Ceram.*, 2000, **20**(2), 71–76.
2. Mörtel, H. and Fuchs, F., Recycling of windshield glasses in fired bricks industry. *Key Eng. Mat.*, 1997, **132–136**, 2268–2271.
3. Pereira, D. A., Couto, D. M. and Labrincha, J. A., Incorporation of alumina rich residues in refractory bricks. *cfi/Ber. DKG*, 2000, **77**, 7 E21-E25.
4. Dondi, M., Marsigli, M. and Fabbri, B., Recycling of industrial and urban wastes in brick production—a review (part 1). *Tile & Brick Int.*, 1997, **13**(3), 218–225.
5. Dondi, M., Marsigli, M. and Fabbri, B., Recycling of industrial and urban wastes in brick production—a review (part 2). *Tile & Brick Int.*, 1997, **13**(4), 302–315.
6. Esposito, L., Timellini, G. and Tucci, A., Fracture toughness of traditional ceramic materials: a first approach. In *Proceedings of the 4th European Ceramic Society Conference Vol. 11*, ed. C. Palmonari. Gruppo Editoriale Faenza Editrice S.p.A, Faenza, 1995, pp. 221–230.
7. *Indagine statistica nazionale Industria Italiana delle piastrelle di ceramica—anno 2001*. Report by AssoPiastrelle, XXII Edition.
8. Private communication supplied by CO.RE.VE.
9. Balaba, W. M., Stevenson, L. T., Wefers, K. and Tackie, M. N., Probability estimators for Weibull statistics of the failure strengths of brittle powder compacts. *J. Mat. Sci. Let.*, 1990, **9**, 648–649.
10. Rossington, K. R. and Carthy, W. M. The effects of ionic concentration on the viscosity of clay-based suspensions. In *Science of Whitewares II*, ed. W. R. Carty and C. W. Sinton. The American Ceramic Society, 2000, pp. 199–211.
11. Pozzi, P., Comportamento reologico delle materie prime ceramiche. In *La reologia dei materiali ceramici tradizionali*, ed. P. Pozzi and C. Galassi. Faenza Editrice, Faenza, pp. 93–120.
12. Gutiérrez, C., Javier Sánchez-Herencia, A. and Moreno, R., Plastic or pseudoplastic? Methods for determining and analysing the yield stress of ceramic slips. *Boletin de la Sociedad Española de Céramica y Vidrio*, 2000, **39**(1), 105–117.
13. Albertazzi, A. and Rastelli, E., Valutazione del limite di scorrimento di barbottine ceramiche industriali con viscosimetro rotazionale. In *Proceeding of the 5th National Meeting of Applied Industrial Rehology, Viterbo 1997*, ed. University of the Study of Tuscia, 64.
14. Barbieri, L., Corradi, A., Lancellotti, I. and Manfredini, T., Use of municipal incinerator bottom ash as sintering promotor in industrial ceramics. *Waste Management*, 2002, **22**, 859–863.
15. International Standard ISO 13006.
16. Morey, G. W., *The Properties of Glass*. Reinhold Publishing Corporation, New York, 1954.
17. Doramus, R. H., *Glass Science*. Wiley, New York, 1973.
18. Iqbal, Y., Messer, P. F. and Lee, W. E., Non-equilibrium microstructure of bone china. *Br. Ceram. Trans.*, 2000, **99**(3), 110–116.
19. Tucci, A., Esposito, L., Malmusi, L. and Piccinini, A., Wear resistance and stain resistance of porcelain stoneware tiles. In *Proceedings of the 7th European Ceramic Society Conference*. Key Engineering Materials. 2001, Vol. 203–213, pp. 1759–1762.
20. Esposito, L., Tucci, A. and Palmonari, C., Surface morphology and resistance to stains of porcelain stoneware tiles. In *103rd Annual Meeting of the American Ceramic Society, Indianapolis*. 2001.