

Effect of soda-lime glass on sintering and technological properties of porcelain stoneware tiles

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Abstract

The feasibility of waste glass recycling in ceramic tile production was assessed with special reference to fully vitrified products (porcelain stoneware). Soda-lime float or container glass was introduced, in replacement of sodic feldspar, in typical porcelain stoneware bodies (up to 10 wt.%) that underwent a laboratory simulation of tilemaking process, with a technological and compositional characterization of both fired and unfired tiles. Soda-lime glass had no significant effect on semi-finished products, but it influenced remarkably the firing behaviour, increasing shrinkage and closed porosity, decreasing open porosity and bulk density, and lowering mechanical and tribological performances. Waste glass promotes a more effective melting of quartz and a partial dissolution of mullite, leading to a more abundant and less viscous liquid phase, which accelerates the sintering kinetics. In conclusion, soda-lime glass can be used in small amounts (5% or less) with tolerable modifications of technological behaviour and performances of porcelain stoneware tiles.

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1. Introduction

In the last few years, due to the increased recovery of waste glass and to difficulties in separating light- and dark-colored types, the search for new recycling solutions has become mandatory. Many investigations have been addressed to reuse soda-lime glass to manufacture ceramic-like glassy products [1–7]. However, even if the technology to obtain glassy ceramics using waste glass is known, nowadays there are just a few industrial applications [8]. As a matter of fact, the standard requisites and the market trends are strongly oriented to the aesthetical and technical performances of traditional ceramic tiles, and glassy products do not match satisfactorily these requirements.

The aim of this work is to assess the feasibility of cullett glass reuse (soda-lime float and container glass) as a raw material in ceramic bodies for vitrified tiles.

For this purpose, porcelain stoneware tiles were selected for the following reasons:

- chemical compatibility of soda-lime glass and porcelain stoneware, since both materials are characterized by Na_2O and CaO as main fluxes [9,10];
- abundance of glassy phase (50–65%) in the finished products [9–11];
- flexibility of tilemaking process, which makes it possible to admix glass with other raw materials without modifying significantly the manufacturing cycle [11–14];
- continuously growing production worldwide [15] that makes porcelain stoneware tiles a potential receptor of huge waste amounts.

Porcelain stoneware bodies consist mainly of a mixture of ball clays, feldspars and quartz-feldspathic sands, often containing also glass-ceramic frits and pigments. This kind of tiles is obtained by wet grinding, dry pressing, fast drying, and fast single firing at maximum

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Table 1
Formulation of experimental bodies for porcelain stoneware tiles

Wt. %	Waste glass		Ball clays				Feldspathic materials				Quartz sand
	Container (B)	Float (L)	Westerwald	Devon	Ukraine 1	Ukraine 2	Albitite 1	Albitite 2	Aplite	Rhyolite	
V0	0	0	15	0	0	25	20	10	10	10	10
VC5	5	0	15	0	0	25	15	10	10	10	10
VC10	10	0	15	0	0	25	10	10	10	10	10
VF5	0	5	15	0	0	25	15	10	10	10	10
VF10	0	10	15	0	0	25	10	10	10	10	10
R0	0	0	0	20	20	0	15	20	10	0	15
RC5	5	0	0	20	20	0	15	15	10	0	15
RC10	10	0	0	20	20	0	15	10	10	0	15
RF5	0	5	0	20	20	0	15	15	10	0	15
RF10	0	10	0	20	20	0	15	10	10	0	15

Table 2
Chemical composition of raw materials

Wt. %	Waste glass		Ball clays				Feldspathic materials				Quartz sand
	Container (C)	Float (F)	Westerwald	Devon	Ukraine 1	Ukraine 2	Albitite 1	Albitite 2	Aplite	Rhyolite	
SiO ₂	71.70	71.92	61.06	48.90	57.00	57.20	66.30	69.20	71.00	72.00	92.50
TiO ₂	0.07	0.06	1.57	0.90	1.50	1.52	0.50	0.23	0.28	0.10	0.09
Al ₂ O ₃	2.10	1.22	25.24	33.70	28.00	27.90	17.90	18.60	16.00	17.00	4.50
Fe ₂ O ₃	0.23	0.36	1.20	1.10	0.85	1.04	0.50	0.13	0.70	0.80	0.25
MgO	2.07	3.95	0.46	0.00	0.60	0.60	3.00	0.07	0.80	0.40	0.19
CaO	9.68	7.45	0.18	0.00	0.40	0.38	1.20	0.56	1.20	0.10	0.06
Na ₂ O	12.90	14.15	0.18	0.20	0.60	0.48	8.00	10.40	1.40	0.60	0.01
K ₂ O	0.93	0.36	2.21	1.40	2.80	2.64	0.30	0.21	7.00	5.50	1.80
L.o.I.	0.00	0.00	7.90	13.50	7.50	7.68	3.00	0.54	1.50	3.50	0.60

temperature around 1190–1230 °C. Finished products exhibit excellent technical properties, especially mechanical strength, resistance to deep abrasion, frost resistance as well as chemical and stain resistance [9,10,16–19].

The feasibility of waste glass recycling in ceramic tile production has been appraised through laboratory simulations of the tilemaking process and technological characterization of both fired and unfired tiles. Tiles with addition of float or container glass were compared with waste-free porcelain stoneware in terms of technological, mechanical, and tribological properties. Particular attention was paid to sintering behavior, in order to comprehend the effect of soda-lime glass on phase composition and chemico-physical properties of the liquid phase formed at high temperatures.

2. Experimental procedure

Two wastes, coming from the recovery of float (F) and container glass (C), were selected together with two porcelain stoneware formulations (V0 and R0), both consisting of different mixtures of ball clays, quartz-feldspathic

sands, sodic and potassic feldspars. The float and container glasses were added to both mixtures in percentages of 5 and 10%, in replacement of the feldspathic component (Table 1).

Raw materials were characterized from the chemical (ICP-OES, Varian, model Liberty 200) and mineralogical (XRPD, Rigaku, model Miniflex) viewpoints (Table 2).

All bodies were experimented at a laboratory scale, simulating the industrial tilemaking process:

- wet grinding in porcelain jar with dense alumina media (18 h);
- slip drying (105±5 °C in oven), powder deagglomeration with hammer mill and humidification (5–6% water);
- dry pressing of 110.55.6 mm³ tiles (40 MPa);
- drying in electric oven (105±5 °C);
- firing in electric roller kiln (60 min from cold-to-cold at maximum temperatures from 1120 up to 1200 °C).

Technological properties were measured on both semi-finished and finished products. Slips were characterized

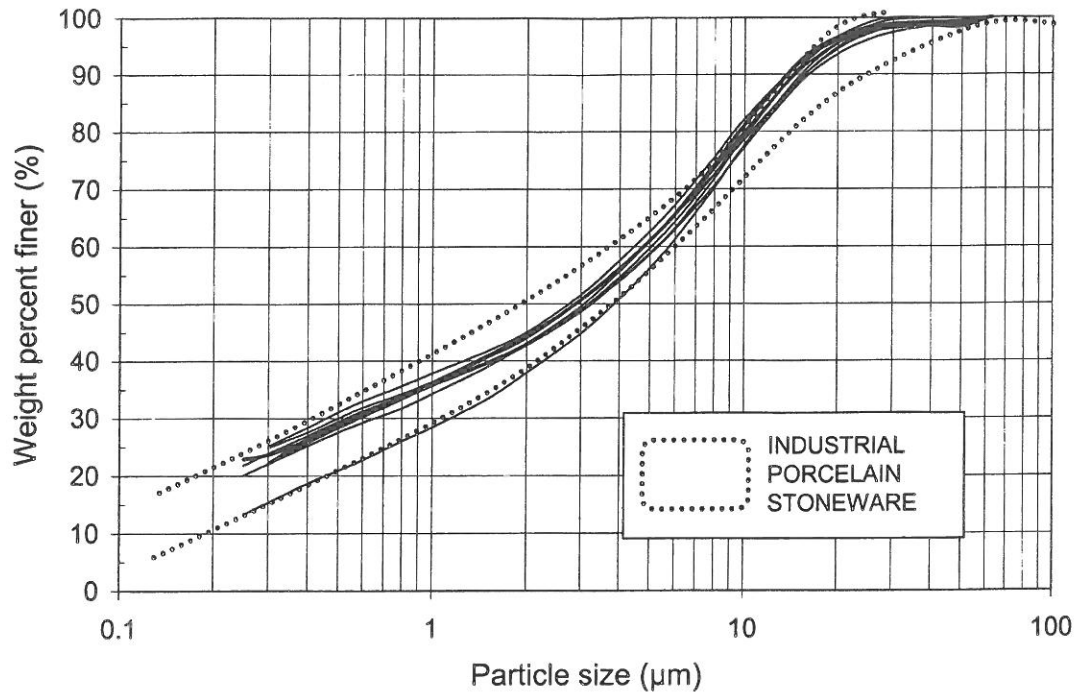


Fig. 1. Particle size distribution of porcelain stoneware slips: comparison between experimental and typical industrial bodies.

Table 3
Technological properties of semi-finished products

Product	Property	Unit	V0	VC5	VC10	VF5	VF10	R0	RC5	RC10	RF5	RF10
Slip	Water content	wt. %	35.7±0.2	36.6±0.2	35.4±0.2	35.4±0.2	35.1±0.2	36.6±0.2	35.8±0.2	35.9±0.2	34.6±0.2	35.9±0.2
	Weight volume	g·cm ⁻³	1.65±0.01	1.63±0.01	1.65±0.01	1.66±0.01	1.66±0.01	1.63±0.01	1.63±0.01	1.62±0.01	1.66±0.01	1.64±0.01
Powders	Median particle size	µm	2.9±0.2	3.2±0.2	3.2±0.2	3.8±0.2	3.4±0.2	3.1±0.2	2.8±0.2	3.2±0.2	3.2±0.2	2.9±0.2
	Working moisture	wt. %	4.7±0.1	4.9±0.1	6.6±0.1	4.4±0.1	4.5±0.1	6.0±0.1	5.9±0.1	5.2±0.1	5.4±0.1	5.6±0.1
	Compressibility	adim.	3.1±0.1	2.9±0.1	2.9±0.1	2.9±0.1	2.8±0.1	2.8±0.1	3.0±0.1	2.8±0.1	3.0±0.1	2.8±0.1
Green tiles	Pressing expansion	cm·m ⁻¹	0.7±0.1	0.8±0.1	0.7±0.1	0.7±0.1	0.7±0.1	0.7±0.1	0.7±0.1	0.7±0.1	0.7±0.1	0.7±0.1
	Modulus of rupture	MPa	1.1±0.1	1.1±0.2	1.1±0.1	1.0±0.1	1.1±0.1	1.1±0.1	1.1±0.1	1.0±0.1	1.1±0.1	1.0±0.1
Dry tiles	Drying shrinkage	cm·m ⁻¹	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	Modulus of rupture	MPa	2.2±0.2	2.3±0.1	2.9±0.4	2.3±0.1	2.6±0.3	2.9±0.3	2.2±0.4	2.6±0.2	2.7±0.2	2.6±0.2

measuring weight/volume and water content (gravimetric method), while particle size distribution (ASTM C 958), moisture content (ASTM C 324) and compressibility (mould depth/tile thickness ratio) were determined on powders. Green and dry tiles were tested for pressing expansion, drying shrinkage (ASTM C 326) and bend strength (ISO 10545-4).

All fired samples were characterized measuring: firing shrinkage (ASTM C326); open porosity, water absorption and bulk density (ISO 10545-3); total porosity by the ratio between bulk density and specific weight (ASTM C329), while closed porosity by difference; modulus of rupture (ISO 10545-4). The resistance to deep abrasion (ISO 10545-6) and CIE-Lab colorimetry (ISO 10545-16, Hunterlab, model MSXP-4000) were determined only on fully sintered samples (fired at 1180 °C).

Furthermore, the phase composition of stoneware was quantitatively determined by RIR-XRPD using CaF₂ as internal standard (Rigaku, model Miniflex, CuK_α radiation). The chemical composition of the vitreous phase was calculated on the basis of bulk chemistry and phase composition. Viscosity [20] and surface tension [21] of the glassy phase at firing temperatures were estimated on the basis of its chemical composition.

3. Results and discussion

3.1. Semi-finished products

The particle size distribution (Fig. 1) and the characteristics of slips (Table 3) are very close to those of

Table 4
Technological properties of porcelain stoneware tiles (bodies series V)

Body	Firing temperature (°C)	Firing shrinkage (cm·m ⁻¹)	Water absorption (wt.%)	Open porosity (vol.%)	Closed porosity (vol.%)	Total porosity (vol.%)	Bulk density (g·cm ⁻³)	Specific weight (g·cm ⁻³)	Modulus of rupture (MPa)
V0	1120	4.8±0.1	4.3±0.5	9.6±1.0	1.2±0.1	10.8±1.1	2.26±0.01	2.53±0.01	46.7±2.0
	1140	6.1±0.2	1.5±0.1	3.6±0.3	2.9±0.3	6.5±0.7	2.37±0.01	2.53±0.01	53.5±3.1
	1160	6.7±0.1	0.3±0.1	0.8±0.1	0.6±0.1	1.4±0.1	2.41±0.01	2.44±0.01	61.2±2.9
	1180	6.7±0.1	0.11±0.07	0.3±0.2	2.2±0.2	2.5±0.3	2.42±0.01	2.45±0.01	52.5±3.2
VC5	1120	5.2±0.1	4.4±0.4	9.8±0.8	3.6±0.4	13.4±1.3	2.25±0.01	2.60±0.01	42.9±0.5
	1140	6.5±0.1	1.4±0.2	3.3±0.6	4.1±0.4	7.4±0.7	2.36±0.01	2.55±0.01	51.4±2.1
	1160	6.9±0.1	0.14±0.11	0.4±0.3	2.2±0.2	2.4±0.2	2.42±0.01	2.48±0.01	48.0±6.1
	1180	6.7±0.1	0.16±0.07	0.4±0.2	3.0±0.3	3.4±0.3	2.39±0.01	2.48±0.01	42.4±1.6
VC10	1120	5.3±0.1	3.1±0.4	7.1±0.8	4.9±0.5	12.0±1.2	2.28±0.01	2.59±0.01	43.7±1.5
	1140	6.5±0.1	0.7±0.2	1.7±0.4	3.3±0.3	5.0±0.5	2.37±0.01	2.50±0.01	51.7±2.3
	1160	6.5±0.1	0.3±0.1	0.7±0.3	3.0±0.3	3.7±0.4	2.39±0.01	2.48±0.01	42.9±1.1
	1180	5.8±0.2	0.2±0.1	0.5±0.1	3.7±0.4	4.2±0.4	2.32±0.01	2.43±0.01	38.2±1.4
VF5	1120	5.4±0.1	3.9±0.3	8.8±0.6	3.5±0.4	12.3±1.2	2.27±0.01	2.58±0.01	43.3±4.7
	1140	6.6±0.1	1.5±0.3	3.6±0.8	3.1±0.3	6.7±0.7	2.35±0.01	2.52±0.01	49.8±4.1
	1160	7.0±0.1	0.5±0.4	1.2±0.9	1.6±0.2	2.8±0.3	2.39±0.01	2.46±0.01	46.3±4.4
	1180	6.8±0.1	0.3±0.1	0.6±0.1	1.0±0.1	1.6±0.2	2.39±0.01	2.43±0.01	34.2±1.4
VF10	1120	5.6±0.1	2.7±0.4	6.1±0.8	4.5±0.5	10.6±1.1	2.30±0.01	2.57±0.01	46.2±3.0
	1140	6.7±0.1	0.4±0.1	1.0±0.1	3.4±0.4	4.4±0.4	2.40±0.01	2.51±0.01	56.2±5.0
	1160	6.7±0.2	0.07±0.02	0.2±0.1	2.7±0.3	2.9±0.3	2.40±0.01	2.47±0.01	44.9±2.0
	1180	6.3±0.2	0.11±0.03	0.3±0.1	3.6±0.4	3.9±0.4	2.34±0.01	2.44±0.01	42.8±2.3

industrial bodies, confirming that the presence of waste glass does not affect significantly the grindability of porcelain stoneware [16].

On the other hand, values of compressibility, pressing expansion, drying shrinkage and bend strength are similar each other, being the small differences mainly due to limited variations in the process parameters, particularly the moisture content (Table 3). The addition of a soda-lime glass does not modify sensitively the technological behavior during pressing and drying, in agreement with data of literature [16].

3.2. Firing behavior

The soda-lime glass has different effects on firing behaviour depending on the type (float or container) and sometimes on the composition of the porcelain stoneware (Tables 4 and 5).

In general, firing shrinkage increases with the amount of recycled glass, which tends to fasten sintering, as bodies with 10% waste begin to soften and reduce their shrinkage after firing at 1180–1200 °C. The values of bulk density are quite similar, though the reference bodies are in general slightly denser than glass-bearing samples.

The occurrence of 5% waste does not substantially change the values of water absorption and open porosity, which decrease sensitively when 10% soda-lime glass is added, particularly in bodies V, confirming some data of literature [16]. On the other hand, waste glass seems to foster the persistence of larger amounts of

closed porosity; this tendency is particularly conspicuous in bodies containing 10% float or container glass.

The flexural resistance of reference bodies is systematically higher than that of mixtures containing waste glass, as previously registered by Esposito et al. [16]. In fully sintered products (i.e. fired at 1180–1200 °C) this difference is around 5–10 MPa. Considering the tribological properties, the behaviour of bodies with 5% waste glass is very close to that of reference materials, while the addition of 10% glass produces an increased amount of material removed (Table 6): from 120–130 mm³ to 140–150 mm³ (bodies V) or from 130–140 mm³ to 150–160 mm³ (bodies R).

Moreover, soda-lime glass causes a slight darkening of color (ΔE around 1–2 for 5% addition; ΔE around 2–4 for 10% addition). This variation consists mainly in a decrease of lightness (L^*), while the differences in a^* and b^* parameters are limited to a general reduction of yellowness and redness in waste-bearing tiles (Table 6).

In summary, soda-lime glass seems basically to accelerate the densification process, increasing the firing shrinkage and decreasing the open porosity in respect of reference bodies, especially when glass addition is as high as 10%. At all events, this accelerated kinetics brings about the formation of a larger amount of closed porosity and, consequently, slightly lower values of bulk density. This circumstance can to a large extent explain the lowered mechanical and tribological performances of tiles containing waste glass. However, the conspicuous differences between the modulus of rupture of

Table 5
Technological properties of porcelain stoneware tiles (bodies series R)

Body	Firing temperature (°C)	Firing shrinkage (cm·m ⁻¹)	Water absorption (wt.%)	Open porosity (vol.%)	Closed porosity (vol.%)	Total porosity (vol.%)	Bulk density (g·cm ⁻³)	Specific weight (g·cm ⁻³)	Modulus of rupture (MPa)
R0	1120	5.9±0.1	4.3±0.2	9.8±0.5	3.5±0.4	13.3±1.3	2.26±0.01	2.61±0.01	38.8±2.0
	1140	7.2±0.1	1.7±0.1	3.9±0.3	2.4±0.3	6.3±0.6	2.36±0.01	2.52±0.01	46.8±2.3
	1160	7.8±0.1	0.2±0.1	0.4±0.2	3.8±0.4	4.2±0.4	2.41±0.01	2.52±0.01	48.7±1.9
	1180	8.0±0.1	0.05±0.04	0.1±0.1	2.8±0.3	2.9±0.3	2.42±0.01	2.49±0.01	40.8±3.6
	1200	7.8±0.2	0.10±0.03	0.2±0.1	5.6±0.6	5.8±0.6	2.42±0.01	2.57±0.01	37.8±1.0
RC5	1120	5.9±0.1	4.4±0.4	9.9±0.8	0.8±0.1	10.7±1.1	2.24±0.01	2.51±0.01	40.0±0.7
	1140	7.2±0.2	1.6±0.3	3.8±0.7	3.0±0.3	6.8±0.7	2.34±0.01	2.51±0.01	44.0±1.6
	1160	7.9±0.1	0.13±0.05	0.3±0.1	3.1±0.3	3.4±0.3	2.39±0.01	2.47±0.01	41.5±2.4
	1180	7.8±0.2	0.07±0.02	0.2±0.1	2.4±0.3	2.6±0.3	2.40±0.01	2.46±0.01	39.1±2.6
	1200	8.0±0.1	0.07±0.03	0.2±0.1	3.6±0.4	3.8±0.4	2.40±0.01	2.50±0.01	33.6±0.9
RC10	1120	5.6±0.1	4.5±0.2	10.1±0.4	4.3±0.4	11.9±1.2	2.23±0.01	2.53±0.01	36.2±0.9
	1140	6.9±0.1	1.9±0.1	4.5±0.2	3.7±0.4	8.2±0.8	2.32±0.01	2.53±0.01	42.9±2.4
	1160	7.4±0.2	0.2±0.1	0.5±0.1	4.6±0.4	5.1±0.5	2.39±0.01	2.52±0.01	45.7±1.9
	1180	7.5±0.1	0.07±0.02	0.2±0.1	4.2±0.4	4.4±0.4	2.38±0.01	2.49±0.01	38.0±3.9
	1200	7.6±0.2	0.10±0.05	0.2±0.1	2.9±0.3	3.1±0.3	2.40±0.01	2.48±0.01	33.8±1.1
RF5	1120	5.3±0.1	5.2±0.1	11.5±0.2	1.7±0.2	13.2±1.3	2.22±0.01	2.56±0.01	35.8±1.5
	1140	6.7±0.1	2.3±0.4	5.3±0.8	4.6±0.5	9.9±1.0	2.32±0.01	2.57±0.01	40.9±2.2
	1160	7.4±0.1	0.3±0.1	0.7±0.2	4.8±0.5	5.5±0.6	2.39±0.01	2.53±0.01	45.8±3.1
	1180	7.5±0.1	0.08±0.04	0.2±0.1	4.8±0.5	5.0±0.5	2.40±0.01	2.53±0.01	37.3±1.1
	1200	7.7±0.3	0.18±0.14	0.2±0.1	5.7±0.6	5.9±0.6	2.41±0.01	2.56±0.01	36.9±1.5
RF10	1120	5.9±0.1	4.9±0.2	10.9±0.5	1.9±0.2	12.8±1.3	2.20±0.01	2.52±0.01	35.8±1.9
	1140	7.4±0.1	1.8±0.2	4.1±0.4	4.0±0.4	8.3±0.8	2.31±0.01	2.52±0.01	40.7±2.0
	1160	8.3±0.1	0.18±0.03	0.4±0.1	4.8±0.5	5.2±0.5	2.38±0.01	2.51±0.01	39.7±1.2
	1180	8.0±0.1	0.07±0.05	0.2±0.1	5.9±0.6	6.1±0.6	2.36±0.01	2.51±0.01	36.6±0.6
	1200	8.3±0.3	0.08±0.03	0.2±0.1	5.0±0.5	5.2±0.5	2.38±0.01	2.51±0.01	30.0±3.1

Table 6
Resistance to deep abrasion and color of fully vitrified tiles (fired at 1180 °C)

Body	Resistance to deep abrasion		Color CIE-Lab			
	Average volume removed (mm ³)	Standard deviation	L*	a*	b*	ΔE*
VO	123	1	67.2	3.1	13.0	
VC5	123	2	64.3	3.1	12.5	2.9
VC10	147	2	64.1	3.0	12.9	3.1
VF5	131	1	65.0	2.9	12.4	2.2
VF10	139	3	63.3	3.1	12.7	3.9
R0	139	2	72.5	2.3	11.4	
RC5	131	3	70.7	2.3	11.4	1.9
RC10	156	1	68.8	2.2	11.1	3.7
RF5	139	1	71.8	2.1	11.0	0.8
RF10	147	5	70.1	2.1	11.2	2.5

glass-bearing and glass-free tiles could be connected with both phase composition (e.g. lesser amounts of mullite) and microstructure, in particular flaws originated by the peculiar behavior of soda-lime glass, such as larger pores, glassy plaques, etc. [16, 22].

3.3. Phase composition

Porcelain stoneware contains quartz, mullite, plagioclase and an abundant vitreous phase. The quantitative

interpretation of X-ray patterns allows to outline the following trends in the 1100–1200 °C range (Figs. 2 and 3).

Plagioclase melts rapidly passing from about 10% (1100 °C) to few per cents at 1200 °C; however, there is more residual feldspar in waste-bearing samples than in reference bodies.

Quartz decreases slowly for increasing temperatures; the amount of residual free silica is inversely proportional to the addition of soda-lime glass, with the single exception of sample RF 10.

The percentage of mullite increases gradually with firing temperature, going from 7–10% (1100 °C) up to 12–20% (1180–1200 °C) as expected by literature data [10, 22]. At any event, the amount of mullite is slightly lower in samples containing waste glass; this trend is evident increasing the temperature, particularly in bodies R.

Vitreous phase increases regularly with firing temperature, showing a faster rate in glass-bearing bodies; the larger the addition of soda-lime glass, the more is the glassy component of tiles.

As a matter of fact, soda-lime glass seems to modify the equilibria between the co-existing glassy and crystalline phases in porcelain stoneware. Its relevant contribution of Na₂O and CaO promotes on one side a more effective melting of quartz and, on the other side, probably a lesser crystallization and/or a partial

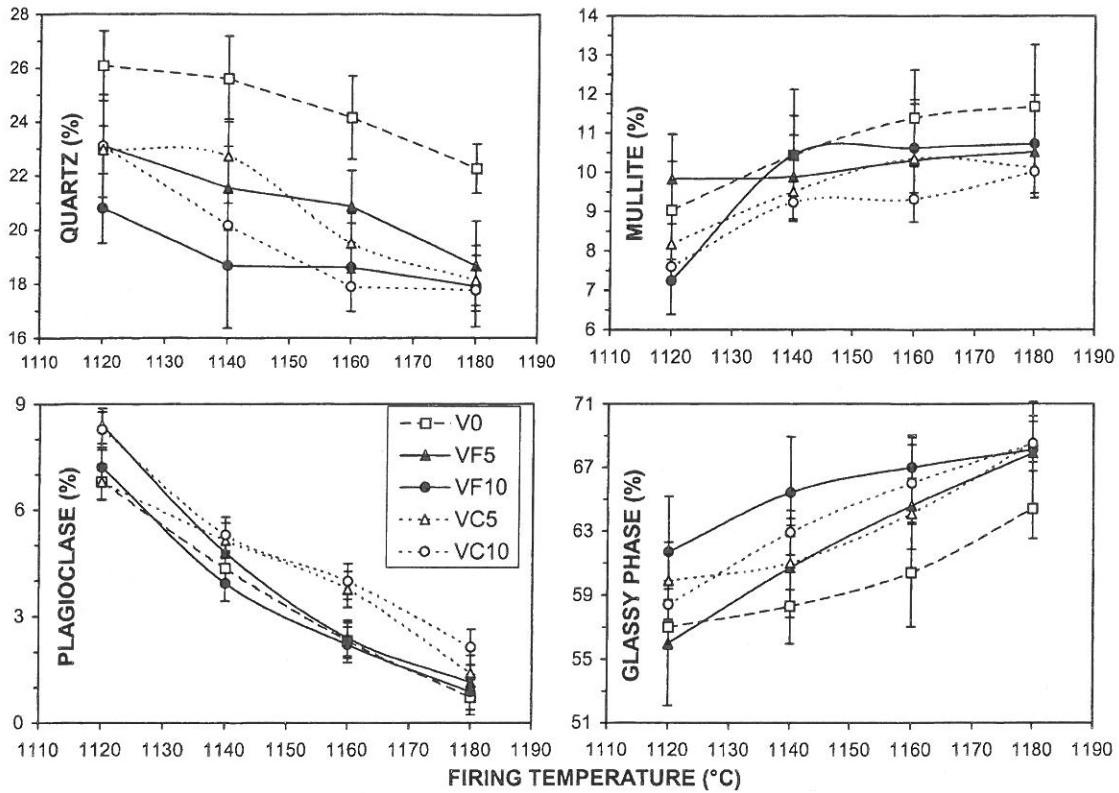


Fig. 2. Changes of phase composition in function of firing temperature (bodies series V).

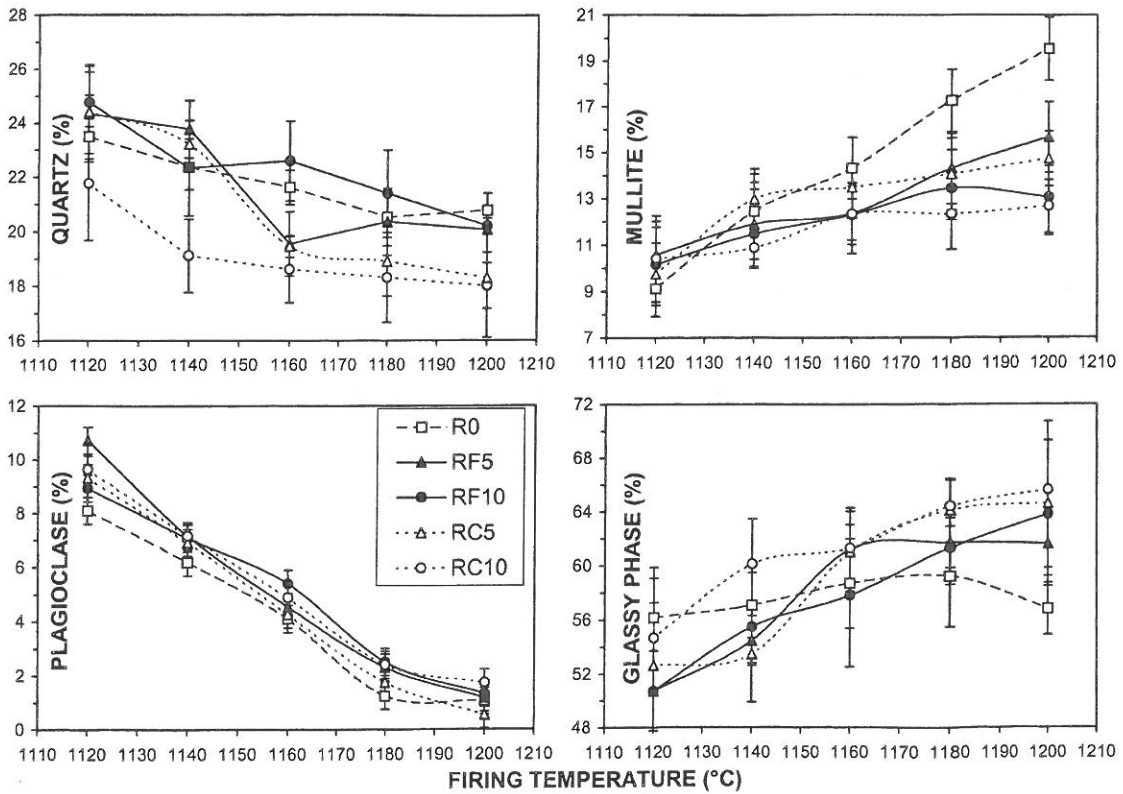


Fig. 3. Changes of phase composition in function of firing temperature (bodies series R).

Table 7
Chemical and physical properties of the glassy phase

Body		V0				VCS				VC10				VF5				VF10								
Firing	°C	1120	1140	1160	1180	1120	1140	1160	1180	1120	1140	1160	1180	1120	1140	1160	1180	1120	1140	1160	1180					
SiO ₂	cg·g ⁻¹	64.0	65.5	66.6	68.6	65.6	66.0	68.0	69.1	65.2	68.5	68.6	69.4	66.8	66.7	67.5	69.0	65.6	69.0	69.2	69.8					
TiO ₂		1.4	1.4	1.3	1.3	1.3	1.3	1.2	1.2	1.3	1.2	1.2	1.1	1.4	1.3	1.2	1.2	1.3	1.2	1.2	1.1					
Al ₂ O ₃		21.9	20.2	19.1	17.8	20.0	19.6	18.0	17.3	19.4	16.5	16.8	16.2	18.1	18.6	18.2	17.1	19.4	16.2	16.0	15.3					
Fe ₂ O ₃		1.3	1.3	1.3	1.2	1.2	1.2	1.2	1.1	1.2	1.2	1.1	1.1	1.3	1.2	1.2	1.1	1.2	1.1	1.1	1.1					
MgO		1.8	1.7	1.7	1.6	1.6	1.6	1.5	1.4	1.6	1.4	1.4	1.3	1.9	1.7	1.6	1.6	1.8	1.7	1.6	1.6					
CaO		0.6	0.8	0.8	0.9	1.2	1.3	1.3	1.4	1.7	1.8	1.9	2.0	1.0	1.2	1.2	1.3	1.4	1.6	1.7	1.7					
Na ₂ O		4.3	4.6	4.8	4.7	4.6	4.8	4.7	4.7	5.0	5.1	5.0	5.0	4.8	4.9	5.0	4.9	5.1	5.2	5.3	5.4					
K ₂ O		4.6	4.5	4.3	4.1	4.4	4.3	4.1	3.9	4.6	4.3	4.1	3.9	4.7	4.3	4.1	3.9	4.2	4.0	3.9	3.8					
Viscosity	MPa·s	22.0	12.8	8.3	5.7	16.6	11.1	7.4	5.2	13.7	8.1	6.2	4.4	15.5	10.6	7.4	5.2	15.2	8.5	6.0	4.2					
Surface tension	N·m ⁻¹	0.362	0.360	0.360	0.359	0.357	0.359	0.358	0.359	0.356	0.352	0.355	0.356	0.353	0.357	0.359	0.359	0.357	0.352	0.354	0.354					
Body		R0				RCS				RC10				RF5				RF10								
Firing	°C	1120	1140	1160	1180	1200	1120	1140	1160	1180	1200	1120	1140	1160	1180	1200	1120	1140	1160	1180	1200	1120	1140	1160	1180	1200
SiO ₂	cg·g ⁻¹	62.9	66.4	68.2	71.8	74.4	63.0	66.2	70.1	70.3	70.7	65.9	68.3	70.1	69.3	70.3	64.2	66.4	69.5	70.8	71.5	63.1	66.2	68.2	69.0	70.3
TiO ₂		1.2	1.2	1.1	1.1	1.2	1.3	1.2	1.1	1.0	1.0	1.2	1.1	1.1	1.1	1.0	1.0	1.3	1.2	1.1	1.1	1.1	1.3	1.2	1.1	1.0
Al ₂ O ₃		24.3	20.4	18.5	14.5	11.4	22.1	18.7	16.0	16.0	15.5	18.6	17.1	15.1	16.1	15.2	20.8	18.9	16.9	15.0	14.1	20.1	17.8	16.0	15.5	14.6
Fe ₂ O ₃		1.1	1.1	1.1	1.1	1.1	1.2	1.2	1.0	1.0	1.0	1.2	1.1	1.0	1.0	1.0	1.3	1.2	1.0	1.0	1.0	1.3	1.2	1.1	1.1	1.0
MgO		1.3	1.3	1.2	1.2	1.3	1.8	1.6	1.4	1.3	1.3	1.7	1.6	1.5	1.5	1.4	1.8	1.7	1.5	1.5	1.5	2.2	2.1	2.0	1.9	1.8
CaO		0.6	0.7	0.7	0.8	0.9	1.0	1.4	1.4	1.5	1.5	1.8	1.8	2.0	2.1	2.1	1.0	1.2	1.2	1.3	1.4	1.7	1.7	1.7	1.9	1.9
Na ₂ O		5.2	5.5	5.7	6.2	6.5	5.8	6.1	5.8	5.8	6.0	5.9	5.7	5.9	5.9	5.9	5.8	6.0	5.8	6.1	6.3	6.6	6.4	6.4	6.4	6.3
K ₂ O		3.4	3.5	3.4	3.3	3.3	3.7	3.7	3.2	3.1	3.0	3.8	3.4	3.3	3.1	3.0	3.8	3.5	3.1	3.2	3.1	3.6	3.5	3.4	3.2	3.1
Viscosity	MPa·s	17.5	9.0	5.6	3.1	2.0	14.7	7.4	5.1	3.7	2.6	11.3	7.7	4.8	3.7	1.5	14.0	8.2	5.6	3.5	2.5	12.1	7.9	5.2	3.6	2.7
Surface tension	N·m ⁻¹	0.368	0.360	0.358	0.350	0.344	0.364	0.357	0.354	0.356	0.357	0.356	0.355	0.353	0.358	0.358	0.360	0.358	0.357	0.354	0.353	0.361	0.357	0.355	0.356	0.356

dissolution of mullite, leading the liquid phase to a saturation in SiO₂, Al₂O₃, Na₂O and CaO, which fosters the stability of feldspar even at the highest temperatures (1200 °C).

3.4. Sintering

The chemical composition of the vitreous phase changes continuously with firing temperature. In particular, a progressive enrichment in SiO₂, Na₂O and CaO can be observed in all samples, with a relative decrease of Al₂O₃ and K₂O concentrations (Table 7).

In waste glass-bearing tiles, the vitreous phase contains more Na₂O and CaO (plus MgO in the case of float glass) with lower amounts of Al₂O₃, K₂O and sometimes SiO₂. These variations bring about a lowered viscosity of the liquid phase at sintering temperatures in the materials containing waste glass. These chemical fluctuations have little effect on surface tension, that nevertheless is systematically lower in glass-bearing tiles, with the exception of body R0 at 1180 and 1200 °C (Table 7).

On the whole, the presence of soda-lime glass contributes to accelerate the sintering kinetics, lowering appreciably the viscosity of the liquid phase. On the other hand, surface tension has just a modest effect on densification, since its values are higher or close to those of reference bodies at sintering temperatures (> 1160 °C).

4. Conclusion

Soda-lime glass can replace conventional fluxes, such as sodic feldspar, in bodies for porcelain stoneware tiles, without relevant drawbacks in the technological process, but with some significant repercussions on the properties of finished products.

The presence of waste glass, in fact, does not remarkably change the technological behavior during grinding, pressing and drying. During firing soda-lime glass accelerates the densification process, with some positive effects (lower open porosity) combined with negative ones (higher values of shrinkage and closed porosity, lower values of bulk density, mechanical and tribological properties). These differences are limited and tolerable with the addition of 5% cullett glass, but become conspicuous when 10% waste is added.

Soda-lime glass seems to modify the equilibria between the coexisting glassy and crystalline phases: minor amounts of quartz and mullite as well as abundant vitreous phase. Moreover, the occurrence of waste glass improves sintering kinetics, lowering appreciably the viscosity of the liquid phase, though the effect on surface tension is probably modest.

References

- [1] I.I. Arkhipov, Z.O. Nemchenok, A.P. Rempel, Using waste for the production of ceramic tiles, *Glass and Ceram.* 36 (10) (1979) 588–589.
- [2] W.M. Brown, K.J.D. Mackenzie, Process design for the production of a ceramic-like body from recycled waste glass, *J. Mater. Sci.* 17 (1982) 2164–2183.
- [3] W. Liu, S. Li, Z. Zhang, Sintered mosaic glass from ground waste glass, *Glass Technol.* 32 (1) (1991) 24–27.
- [4] W.M. Brown, K.J.D. Mackenzie, Ceramic composites from waste glass, in: *Ceramics, Adding the Value, Proceedings of the International Ceramic Conference Austceram '92*, 1992, pp. 988–993.
- [5] R.V. Manukyan, N.S. Davydova, Use of waste in the ceramics industry, *Glass and Ceram.* 53 (7–8) (1996) 247–248.
- [6] Y. Lingart, Imitation natural material tiling using waste glass, *Glass Technol.* 39 (2) (1998) 42–43.
- [7] J.J. Blanc, Valorisation de déchets de verre dans les céramiques vitrifiées, *L'Industrie Céramique & Verrière* 953 (2000) 336–337.
- [8] R. Rambaldi, Recycled glass tiles, *Ceram. World Rev.* 9 (33) (1999) 234–239.
- [9] M. Dondi, B. Fabbri, T. Manfredini, G.C. Pellacani, Microstructure and mechanical properties of porcelanized stoneware tiles, in: *Proceedings of the 4th EUROCERAMICS*, 1995, vol. 11, pp. 319–326.
- [10] M. Dondi, G. Ercolani, C. Melandri, C. Mingazzini, M. Marsigli, The chemical composition of porcelain stoneware tiles and its influence on microstructural and mechanical properties, *Inter-ceram* 48 (2) (1999) 75–83.
- [11] G. Baldi, D. Biserni, D. Mazzini, D. Settembre Blundo, Vitreous stoneware: scientific and technical aspects of a new class of materials, *L'Industrie Céramique & Verrière* 967 (2001) 105–109 (in French).
- [12] G. Baldi, E. Generali, L. Rovatti, D. Settembre Blundo, Synthetic raw materials for bodies with a high whiteness index, *Ceram. World Rev.* 11 (42) (2001) 72–80.
- [13] A. Moreno, J. Garcia-Ten, V. Sanz, A. Gozalbo, J. Cabedo, R. Berge, J. Colom, S. Carmena, Feasibility of using frits as raw materials in porcelain tile compositions, in: *Proceedings of the 4th World Congress on Ceramic Tile Quality, QUALICER*, 2000, pp. 237–251.
- [14] A. Brusa, Porcelainised stoneware: evolution of production plants and devices, *Int. Ceram. J.* October (1999) 73–82.
- [15] P. Burzacchini, Porcelain tile, its history and development, *Ceram. World Rev.* 10 (37) (2000) 96–103.
- [16] L. Esposito, A. Tucci, C. Palmonari, Use of soda-lime glass as the fluxing agent in a porcelain stoneware tile mix, in: *Proceedings of the 7th European Conference on Advanced Materials and Processes EUROMAT*, 2001, no. 187.
- [17] G. Biffi, Porcelainized Stoneware, Gruppo Editoriale Faenza, Italy, 1996.
- [18] T. Manfredini, G.C. Pellacani, M. Romagnoli, Porcelainized stoneware tiles, *Am. Ceram. Soc. Bull.* 74 (5) (1995) 76–79.
- [19] L. Barbieri, L. Bonfatti, A.M. Ferrari, C. Leonelli, T. Manfredini, D. Settembre Blundo, Correlazioni fra proprietà microstrutturali e meccaniche nel grès porcellanato, *Ceramurgia* 25 (4) (1995) 187–190.
- [20] T. Lakatos, L.G. Johansson, B. Skimmingskold, Viscosity temperature relations in the glass systems, *Glass Technol.* 6 (1972) 88–95.
- [21] F. Cambier, A. Lérique, Vitrification, in: R.W. Cahn, P. Haasen, E.J. Kramer (Eds.), *Processing of Ceramics*, Vol. 17B, Part II, VCH Verlagsgesellschaft, Weinheim, 1996, pp. 123–144.
- [22] E. Sanchez, M.J. Orts, K. Garcia-Ten, V. Cantavella, Porcelain tile composition effect on phase formation and end products, *Am. Ceram. Soc. Bull.* 80 (6) (2001) 43–49.