Effect of waste glass (TV/PC cathodic tube and screen) on technological properties and sintering behaviour of porcelain stoneware tiles

Raimondo M., Zanelli C., Matteucci F., Guarini G., Dondi M., Labrincha J.*

CNR-Institute of Science and Technology for Ceramics, via Granarolo, 64, 48018 Faenza (Italy)

*Departamento de Engenharia Cerâmica e do Vidro-University of Aveiro, Campus de Santiago 3810-193, Aveiro (Portugal)

Abstract

In the last years, the reutilization of wastes in the production of building materials has been successfully pursued since it can reduce both the comsumption of natural resources and the cost of waste storage, protecting the environment from their harmful action. the In particular, in the industrialized countries, the possibility of recycling PC and TV wastes has been investigated and, notwithstanding their variable chemical composition and the high content of hazardous elements, i.e. Pb, Ba and Sr, their introduction into different ceramic matrix was pursued. In the present work, the effects of TV and PC cathodic tube and screen glasses additions to a porcelain stoneware body, in partial replacement of feldspar, were evaluated simulating the tilemaking process. Their presence allow to obtain good technological and mechanical properties, complying with the latest requirements of the industrial practice. Moreover, both glasses are able to modify the body sintering pattern with a different effectiveness degree.

Keywords: recycling, PC and TV waste glasses, porcelain stoneware, sintering.

1. Introduction

Nowadays, recycling processes became more and more important mostly due to the impressive increase in the production of wastes and to the growing attention at the environmental safeguard. In the modern society, the improvement of life and the technological development brought about a significant growth in the consumption of computer (PC) and TV-sets. The consequent increasing of wastes, coming from electronic and electrical devices, requires to make their recycling technically and economically feasible [1,2]. Actually, the level of the reutilization of both PC and TV wastes is about 5% of the total production, but the latest trend is moving towards an increasing of these levels; for this purpose, some recent investigations within the European countries [2] estimated the necessity to allocate about $1 \cdot 10^6 \, m^3$/year of TV glass wastes every million people.

The 85% of PC and TV wastes is made up of cathodic ray tubes and screen glasses, and, notwithstanding their particular chemical composition due to the presence of some hazardous elements, it has been demonstrated that their recycling on an industrial scale is possible [3].

In the literature, the reuse of different waste glasses has been throughly investigated [4-8], so that, in the latest years, they became a commercial alternative to the traditional raw materials (mainly clays and mineral sands) in composite bodies [9]. The use of waste glasses in the production of building materials has been successfully pursued since it can reduce both the consumption of natural resources and the cost of waste storage,

protecting the environment from their harmful action. Moreover, being the glass one of the predominant constituent of the vitrified ceramic bodies, i. e. porcelain stoneware in which it is formed in situ by the reaction of quartz and clays with feldspars, many authors considered this as the most suitable field for the potential recycling of waste glasses [10-14]. In fact, due to both the large amount of liquid phase (50-65%) developed during firing and the flexibility of the tilemaking process, glassy materials may be introduced into porcelain stoneware bodies without modifying significantly the manufacturing cycle.

Recently, some papers concerned the introduction of soda-lime waste glasses as raw materials for both ceramic bodies and glazes [9-12]. In porcelain stoneware bodies, where soda-lime glasses substitute feldspathic fluxes, additions up to 5wt.% do not bring about any significant change in the technological behaviour, and a reduction of the sintering temperature was rather observed [10-14]. On this basis, commercial fluxes have been developed as a mixture of feldspar plus different amounts of soda-lime glass and utilized for porcelain stoneware tiles [9].

However, since waste glasses present a variable chemical composition, their utilization can not be easily modelled; in particular, the recycling of TV and PC cathodic tube and screen glasses involves technological problems due to the high lead content and the great amount of Ba and Sr, respectively [2]. In the last decade, many authors exploited the possibility of fabricating high density bodies at relatively low temperature by mixing raw materials with TV and PC glass powders. Boccaccini et al. [15] studied the sintering behaviour of compact bodies, made from TV glass powder, obtained at relatively low temperature and suitable as tiles for radiation protection use. TV screen recycled glasses were also mixed by Minay et al. [16] with Al_2O_3 platelets to produce composite materials having enhanced mechanical and elastic performances, these bodies result candidate materials for wear and abrasion resistant applications. The reutilization of TV waste glass in the porcelain stoneware tiles has been recently investigated by Rambaldi et al. [17] which highlighted the strong fluxing power of the lead based glass, able to improve the formation of both liquid phase and mullite when present in low amount (<2%).

In this work, TV/PC cathodic tube and screen glasses were added to a typical porcelain stoneware body as partial substitutes of fluxes, in particular of sodic feldspar. Simulating the tilemaking process at a laboratory scale, it was appraised whether the waste glass additions determined any change in the technological and mechanical properties of both fired and unfired tiles, taking a waste-free porcelain stoneware body as a reference. In order to comprehend the effect of recycling glasses on the firing of fully vitrified products, particular attention was paid to a better understanding of the waste glass addition on the sintering behaviour of tiles as well as on the phase composition and chemico-physical properties of the liquid phase. With this aim, the progress of sintering was appraised by the quantification of the bodies microstructural modifications at different temperatures, calculating from time to time the correspondent kinetic parameters.

2. Experimental

Two different types of glass, coming from the recovery of TV/PC cathodic tube (C) and screen (S), were selected together with a porcelain stoneware body (V0) consisting of a mixture of ball clay, quartz sand, sodic and potassic feldspars. In the design of the porcelain stoneware formulations, the recycled glasses were introduced in the weight percentages of 5% (VC5, VS5) and 10% (VC10, VS10) in partial replacement of the sodium feldspar. In addition, a mixture containing 5% of each glass (VCS5) was also formulated (Table 1).

Raw materials were characterized from the chemical point of view by inductively coupled plasma emission (ICP-OES, Varian Liberty 200) on the solutions obtained by melting the samples with lithium tetraborate at 1200°C (Table 2).

All the bodies underwent a laboratory simulation of the industrial tilemaking process by:

- mixing and wet grinding in porcelain jar with dense alumina media for 20 minutes in a planetary mill;
- slip drying at 105 ± 5°C, powder deagglomeration and humidification with 7-8% water;
- uniaxial pressing (40 MPa) of 110 x 55 x 6 mm^3 tiles;
- drying in an electric oven at 105 ± 5°C;
- firing in an electric roller kiln at maximum temperatures from 1180 up to 1220 °C with a thermal cycle of 51 minutes cold-to-cold.

Technological properties were investigated on powders and slips as well as on unfired and fired tiles. For this purpose, it has to be pointed out that particular attention is necessary during the treatment of the cathodic tube wastes, because a rubber layer, usually present as antielectrostatic coating, could influence the rheological behaviour and, in particular, the slip viscosity.

Slips were characterized by weight/volume and water content by the gravimetric method, while particle size distribution (ASTM C958) and moisture content (ASTM C324) were determined on powders. Bulk density (ASTM C329), drying shrinkage (ASTM C326) and 3-points flexural strength (ISO 10545-4) were measured on dry tiles.

All the fired samples were characterized through the determination of firing shrinkage (ASTM C326), water absorption, open porosity (OP) and bulk density (BD, ISO 10545-3), 3-points flexural strength (ISO 10545-4). Specific weight (SW) and total porosity (TP) of both fired and unfired tiles were evaluated by He pycnometry (Micromeritics 1305) and by the ratio (1- BD/SW)·100, respectively. The closed porosity (CP) was calculated by difference: CP=TP–OP. CIE-Lab colorimetry (ISO 10545-16, Hunterlab MSXP-4000) of sintered tiles was also performed.

Leaching tests (DIN 38414-S4) were performed on both types of waste glasses (C and S) and on the samples fired at 1200°C in order to evaluate the inertization degree of waste glasses into the ceramic matrix.

The phase composition of stoneware tiles was quantitatively determined by RIR-XRPD method (Rigaku Miniflex, CuK$_\alpha$ radiation, 10-80° 2θ range, 0.02° stepscan) using CaF$_2$ as internal standard [18]. The chemical composition of the glassy phase was calculated on the basis of bulk chemistry and phase composition of the tiles, allowing the calculation of viscosity and surface tension of the liquid phase at high temperature [19-20].

The microstructure of the graphite coated surfaces of V0, VC10 and VS10 samples, fired at 1220°C, was also investigated through SEM micrographies obtained with a Leica Cambridge Stereoscan 360 instrument.

The sintering behaviour of waste added bodies was evaluated by isothermal and constant rate thermodilatometric analyses obtained by a hot stage microscope (Expert System, Misura 3). The isothermal tests were carried out at different maximum temperatures (heating rate 80°C/min to 1100, 1125, 1150, 1175 and 1200°C), allowing to calculate some kinetic parameters such as sintering rate and apparent energy of activation (Ea) [21-23]. The thermal cycle with a constant heating rate (40°C/min) up to 1200°C, plus 5 minutes soaking, was used to simulate the industrial firing.

3. Results and discussion

3.1 Semi-finished products
Slip properties and particle size distribution (Table 3 and Figure 1) of all waste glass added mixtures (VC, VS and VCS) are quite similar to those of the waste-free one (V0), complying with the latest requirements of the industrial practice. However, the median particle diameter slightly increases with the glass percentage, leading to the conclusion that the waste presence could somehow affect the grindability of porcelain stoneware bodies. An interference of soda-lime glass with slip rheology was effectively observed in porcelain stoneware bodies [6-7]. It is possible that the slightly coarser particle distribution of cathodic glass-bearing bodies should be due to the occurrence of rubber particles from the tube coating.

On the other hand, VC, VS and VCS semi-finished tiles present a slightly higher porosity (and a lower bulk density) than V0, with exception of the VC5 sample, whose data are practically unchanged with respect to the waste-free body. This circumstance can be probably explained by the higher working moisture of both V0 and VC5, that ensures a better powder compaction during pressing [8]. However, the slightly lower compaction degree of the VS bodies can be possibly ascribed to their different behaviour during pressing connected with their finer particle dimensions.

As already observed in the literature [8-11], mechanical resistance of dry tiles is improved by the recycled glass, especially when the screen glass S is added, though its trend does not correspond to the porosity differences. Probably, glass addition promotes local microstructural modifications, not detected by the measurements of a global property such as porosity, but which are able to enhance the product performance as a result of a mechanical stress.

On the whole, the characterization of the waste-added semi-finished products highlights their good technological and mechanical properties, which allow them to provide performances similar to those of the reference industrial bodies [4].

3.2 Firing behaviour
Waste glass added porcelain stoneware bodies behave in a different way during the firing cycle (Table 4). Generally, in the presence of waste glass C, the temperature of maximum shrinkage is shifted towards lower values. In particular, VC5 and VC10 bodies reach their maximum densification already at 1180°C, while their structural coarsening begins just after this temperature. Moreover, with the increasing of the waste glass percentage, the coarsening rate becomes very fast, as can be detected comparing the VC10 firing shrinkage at 1200 and 1220°C.

The maximum densification temperature, the linear shrinkage and the kinetic pattern of VS bodies depend on the waste glass percentage: VS5 presents the maximum densification degree at 1200°C, while VS10 is still contracting at 1220°C; moreover, in the 1180-1200°C range, the presence of a higher amount of waste glass seems to promote the body densification. The behaviour of VCS, which presents the highest shrinkage at 1200°C and the beginning of coarsening just after this temperature, is an average of that shown by the two other types of glass.

As far as water absorption and open porosity are concerned, at 1220°C all bodies present about the same value, but with a different trend from 1180 up to 1220°C due to their different densification kinetic. At 1200°C, the porosity of VC bodies is essentially made up by the closed pores, while, at the same temperature, VS bodies still preserve a residual amount of open porosity [21]. Generally, total porosity of waste added samples is higher than the value presented by V0 ones; besides, total porosity is higher in VS samples than VC ones. The trend of bulk density is consistent with these conclusions, even if a small

contribution to the higher density values of VC samples should be attribute to the presence of PbO.

The above mentioned circumstances are furtherly confirmed by the analysis of the SEM micrographies of figure 2, obtained on the samples fired at 1220°C. The presence in VC10 sample of a spherical closed porosity clearly stands out, being the structural coarsening already under way at this temperature. In addition, the irregular morphology of the porosity present in VS10 certifies that at 1220°C, in agreement with the firing shrinkage values, the densification is still in progress and that, notwithstanding all the porosity is practically a closed porosity, the bloating phenomenon does not already start.

The highest values of flexural strength do not belong to samples fired at the maximum temperature, but, in agreement with the densification pattern, the mechanical resistance reaches its maximum at 1180°C in the VC series and at 1200°C in the VS ones. Generally, the mechanical strength of fired tiles is lowered by the presence of the recycled glasses; however, all the waste glasses added samples show values of modulus of rupture satisfying the standard requirements (>35 MPa).

Waste glass additions also determined some variations of CIELab coordinates (Table 4); in particular, ΔE^* decreases with the firing temperature and, hence, with the amount of glassy phase as certified by the higher ΔE^* values presented by VC and VCS samples, presenting the highest crystalline/amorphous phase ratio. As far as the a* and b* parameters, VC bodies result darker when compared to V0; however, it results really difficult to explain these differences in terms of the nature or amount of the crystalline phases.

The results of the leaching test performed on the samples fired at 1200°C (Table 5) highlight the partial inertization of lead into the ceramic matrix; in fact, the amount of Pb found in the leachate is lower (of about 30%) when compared with its starting value in waste-glass C, also when the added percentage is up to 10%.

3.3 Phase composition

A typical porcelain stoneware is composed of quartz, mullite and plagioclase embedded in a very abundant glassy phase. Quantitative phase analyses of the ceramic tiles showed the trends of figure 3.

As the firing temperature increases, plagioclase (Figure 3A) melts very quickly, following a similar trend for all compositions, with a dissolution rate which seems to be a little bit lower just in the VS10 sample. Considering the amount of plagioclase with respect to the reference body V0 in the 1180-1220°C range, it results always higher in the VS samples and lower in the VC ones, with VCS5 presenting an intermediate content.

The amount of quartz in VS5 and VCS5 samples steadily decreases from 1180 up to 1220°C, while, in the case of VC5 and VS10 ones, its dissolution starts just after 1200°C (Figure 3B); this latter behaviour also belongs to V0 sample, whose total amount of quartz is, in any case, always higher than the modified bodies. For both VC and VS products, in fact, the presence of recycled glass from 5 up to 10% progressively reduces the total quartz amount.

The mullite content (Figure 3C) of all samples does not significantly change from 1180 up to 1220°C, even if a different influence of the waste glass typology on the mullite amount can be detected. In fact, waste-glasses C and S bring about, respectively, the occurrence of a lower or higher amount of mullite when compared to V0.

The glassy phase (Figure 3D) increases regularly with the firing temperature, with VC and VS samples showing the highest and the lowest content, respectively. The total amount of vitreous phase is proportional to the waste glass percentages just in the samples VC and for firing temperatures up to 1200°C. In the other cases, a similar quantity of glassy phase is developed independently of the waste amount.

Overall, the presence of waste glasses C and S brings about a modification of the crystalline/glassy phase ratio:

- The screen glass involves the persistence of mullite (9-10%) at temperatures of 1200-1220°C, independently of its relative amount in the starting formulations. The residual amount of plagioclase (8-9%) is larger when compared with all the others formulations, while the quartz dissolution rate seems to be lowered by increasing the waste glass percentage. On the contrary, the lowest quantity of glassy phase is developed;
- The cathodic tube is the most effective in promoting the formation of glassy phase, mainly at expenses of plagioclase, whose dissolution is practically complete at 1200°C. Its occurrence brings about a lower amount of mullite, but for VC10 at 1220°C, while an intermediate content of quartz is detected;
- The trends shown by the mineralogical transformations of VCS5 seem to confirm the opposite effect exerted by C and V-glasses, resulting often in an averaged behaviour.

3.4 Sintering behaviour

Constant rate thermodilatometry, showing the dimensional variations as a function of the temperature (figure 4), indicates that, after the structural expansion due to the clay minerals transformations, the body densification starts at different temperature, following a different kinetic. With respect to the V0 reference body, whose expansion is still in progress at 1000°C, the presence of both glasses bring forward the beginning of the densification (figure 4B).

The sintering rate of porcelain stoneware tiles, as more clearly detected by the isothermal curves of figure 5, where the dimensional variations have been reported as a function of the elapsed time, is somehow affected by the different recycled glass amount and typology; at 1200°C, which is the typical industrial firing temperature of porcelain stoneware, in a few minutes, VC5, VS5 and VCS5 samples already reach the maximum densification, with shrinkage values of about 8-10%. The presence of a higher amount of wastes reduces the final shrinkage and/or causes an elongation of the time necessary to achieve the same densification degree. Moreover, once the maximum densification degree is reached, VC and VS samples show an inversion of their sintering curves, with the consequent decrease of density due to the bloating phenomenon, which in turn is directly linked to the waste glass amount.

The sintering rate, calculated as the volumetric dimensional variation per unit time, obviously increases with the firing temperature, but has a different trend for the two glass typologies (Table 6): while glass C improves the sintering rate, expecially when present at the lower percentage, glass S has a more moderate effect and, at temperatures up to 1175°C, does not significantly change the sintering kinetics.

The addition of waste glasses involves a modification of the apparent energy of activation E_a (Table 6), strictly connected with the added percentage amount; according to these values, both cathodic and screen glasses at the lower percentage help the sintering kinetic through the lowering of the E_a. However, when their amount is up to 10%, and expecially for waste glass S, a noticeable increase of E_a values is observed. In the case of glass S, this is consistent with the densification behaviour previously described, while the E_a value calculated for VC10 sample is higher than expected on the basis of its densification pattern. For this purpose, some other factors, not easily identifiable at this stage, play a significant role.

Obviously, the chemico-physical properties of the glassy phase, summarized in table 7, vary according with the firing temperature, the percentage and typology of waste glasses. In particular, when recycling glass are present, it becomes reacher in SiO_2 and poorer in Al_2O_3, while Na_2O and K_2O content are, respectively, lower and higher.

These chemical variations bring about different values of the liquid phase viscosity; generally, it decreases with the glass additions which bring about the progressive

decrease of the Na_2O/K_2O ratio. Moreover, the influence of screen glass on these parameters seems to be the most effective.

The surface tension of the liquid phase, which in turn indicate its wettability capacity, is lowered by the waste glass additions, even if there are not significant variations with respect to the amount and glass typology.

4. Conclusions

TV/PC cathodic tube and screen glasses, added to a typical porcelain stoneware body, are able to partially replace the conventional industrial fluxes, without significant repercussions on the technological process. The waste glass presence, however, affects in some way the technical performances, the compositional properties and the firing behaviour of the added bodies.

The characterization of the waste added semi-finished and final products highlights their good technological and mechanical properties, which allow them to provide performances similar to those of the reference industrial bodies. In particular, the mechanical strength, even if generally lowered by the presence of the recycled glasses, show values of modulus of rupture satisfying the standard requirements.

The positive influence of the glass additions in promoting the densification stands out when the mineralogical composition and, above all, the sintering parameters are analysed. In the presence of waste glass C, the temperature of maximum shrinkage is shifted towards lower values (1180°C), when compared, respectively, with V0, VS5, VCS5 (1200°C) and VS10 (1220°C). As the maximum firing temperature increases up to 1220°C, the microstructural differences among the different samples easily come out. At this temperature (SEM micrographies of figure 2), the presence in VC10 of a spherical closed porosity clearly stands out, being the structural coarsening already under way. In addition, the irregular morphology of the porosity present in VS10 certifies that, at 1220°C, in agreement with the firing shrinkage values, the densification is still in progress and that, notwithstanding all the porosity is practically a closed porosity, the bloating phenomenon does not already start.

The effectiveness on the sintering rate exerted by waste glass C is greater as certifyied by the phase composition of the added bodies: cathodic tube, in fact, is the most effective in promoting the formation of glassy phase, mainly at expenses of plagioclase, whose dissolution is practically complete at 1200°C. The screen glass, indeed, involves the persistance of mullite (9-10%) at temperatures of 1200-1220°C, independently of its relative amount in the starting formulation, while the residual amount of plagioclase is larger (8-9%); on the contrary, the lowest quantity of glassy phase, when compared to waste glass C, is developed.

The sintering rate of porcelain stoneware tiles, as more clearly detected by the isothermal curves of figure 5, where the dimensional variations have been reported as a function of the elapsed time, is somehow affected by the different recycled glass amount and typology; at 1200°C, which is the typical industrial firing temperature of porcelain stoneware, in a few minutes, VC5, VS5 and VCS5 samples already reach the maximum densification, with shrinkage values of about 8-10%. The presence of a higher amount of wastes reduces the final shrinkage and/or causes an elongation of the time necessary to achieve the same densification degree. Moreover, once the maximum densification degree is reached, VC and VS samples show an inversion of their sintering curves, with the consequent decrease of density due to the bloating phenomenon, which in turn is directly linked to the waste glass amount.

The sintering rate shows a different trend for the two glass typologies: while glass C improves the sintering rate, expecially when present at the lower percentage, glass S has

a more moderate effect and, at temperatures up to 1175°C, does not significantly change the sintering kinetics.

The addition of waste glasses also involves a modification of the apparent energy of activation E_a: both cathodic and screen glasses at the lower percentage help the sintering kinetic through the lowering of the E_a. However, when their amount is up to 10%, and expecially for waste glass S, a noticeable increase of E_a values is observed.

The chemico-physical properties of the glassy phase vary according with the percentage and typology of waste glasses. In particular, when recycling glass are present, it becomes reacher in SiO_2 and poorer in Al_2O_3, while Na_2O and K_2O content are, respectively, lower and higher. These chemical variations bring about different values of the liquid phase viscosity; generally, it decreases with the glass additions, which bring about the progressive decrease of the Na_2O/K_2O ratio. Moreover, the influence of screen glass on these parameters seems to be greater.

Overall, the presence of both types of recycling glasses is able to positively affect the technical and physical properties of the added bodies, as a result of a modification of their sintering behaviour.

References

1. Hermans, J. G. J. Peelen, R. Bei, Recycling of TV glass: profits or doom? Ceram. Eng. Proc., 2001, 2, 27-37.
2. Menad, Cathode ray tube recycling, Resources. Conservation and Recycling, 1999, 26, 143-154.
3. Cramer, F. Schmidt, Clasen R., S. Jasen, Recycling of TV-glass: problems and perspectives. Glastech. Ber., Glass Sci. Technol., 1995, 68 [C2], 191-196.
4. Lingart, Imitation natural material tiling using waste glass. Glass Technology, 1998, 39 [2], 42-43.
5. Rambaldi, A. Tucci, L. Esposito, Use of recycled materials in the traditional ceramic industry. Traditional Ceramics, 2004, [1-2], 13-23.
6. Manukyan, N. S. Davydova, Use of waste in the ceramic industry. Glass and Ceramics, 1996, 53 [7-8], 247-248.
7. Brown, K. J. D. MacKenzie, Ceramic composites from waste glasses. J. of Mater. Science, …
8. Brown, K. J. D. MacKenzie, Process design for the production of a ceramic-like body from recycled waste glass. Part 1. The effect of fabrication variables on green strength. J. of Mater. Sci., 1982, 17, 2164-2170.
9. Carbonchi, P. Danasino, R. Lorici, R. Riveriti, Impiego di fondenti additivati con vetro in un impasto da grès porcellanato. Ceramica Informazione, 2003, 426, 580-587.
10. Matteucci, M. Dondi, G. Guarini, Effect of soda-lime glass on sintering and technological properties of porcelain stoneware tiles. Ceramics International 2002, 28, 873-880.
11. 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.
12. Tucci, L. Esposito, E. Rastelli, C. Palmonari, E. Rambaldi, Use of soda-lime scrap-glass as a fluxing agent in a porcelain stoneware mix. J. of the Eur. Ceram. Soc., 2004, 24, 83-92.
13. Rambaldi, A. Tucci, L. Esposito, Glass recycling in porcelain stoneware tiles: firing behaviour. Process Engineering, 2004, 81 [3], 32-36.
14. Karamanov, M. Pelino, M. Slavo, I. Metekovits, Sintered glass-ceramics from incinerator fly ashes. Part II. The influence of particle size and heat-treatment on the properties. J. of the Eur. Ceram. Soc., 2003, 23, 1609-1615.
15. Boccaccini, M. Bücker, P. A. Trusty, M. Romero, J. M. Rincón, Sintering behaviour of compacts made from television tube glasses. Glass Technol., 1997, 38 [4] 128-133.
16. Minay, V. Desbois, A. R. Boccaccini, Innovative manufacturing technique for glass matrix composites: extrusion of recycled TV set screen glass reinforced with Al_2O_3 platelets. Journal of Materials Processing Technology, 2003, 142, 471-478.
17. Rambaldi, A. Tucci, E. Rastelli, L. Esposito, The use of waste glass as a raw material in porcelain stoneware tiles. In Proceedings IV Congresso VA.RI.REI., 2003, 24-27.
18. Dondi, B. Fabbri, M. Marsigli, Applicazioni al metodo "Matrix –flushing" all'analisi di fase quantitativa di laterizi e terracotta. Ceramurgia 1997.
19. Lakatos, L. G. Johansson, B. Skimmingskold, Viscosity temperature relations in the glass system SiO2-Al2O3-Na2O-K2O-CaO- MgO in the composition range technical glasses. Glass Techonol, 1972, 13, 88-95.
20. Cambier, A. Leriche, Vitrification materials science and techonology – A compresive treatment. Processing of Ceramics, 1996, 17B.

21. German, Sintering Theory and practice. 1996, The Pennsylvania State University…..
22. Cho, W. Schulze, et all, Crystallization kinetics and properties of nonstechiometric cordierite based thick film dielectrics. L. Am. Ceram. Soc., 1999.
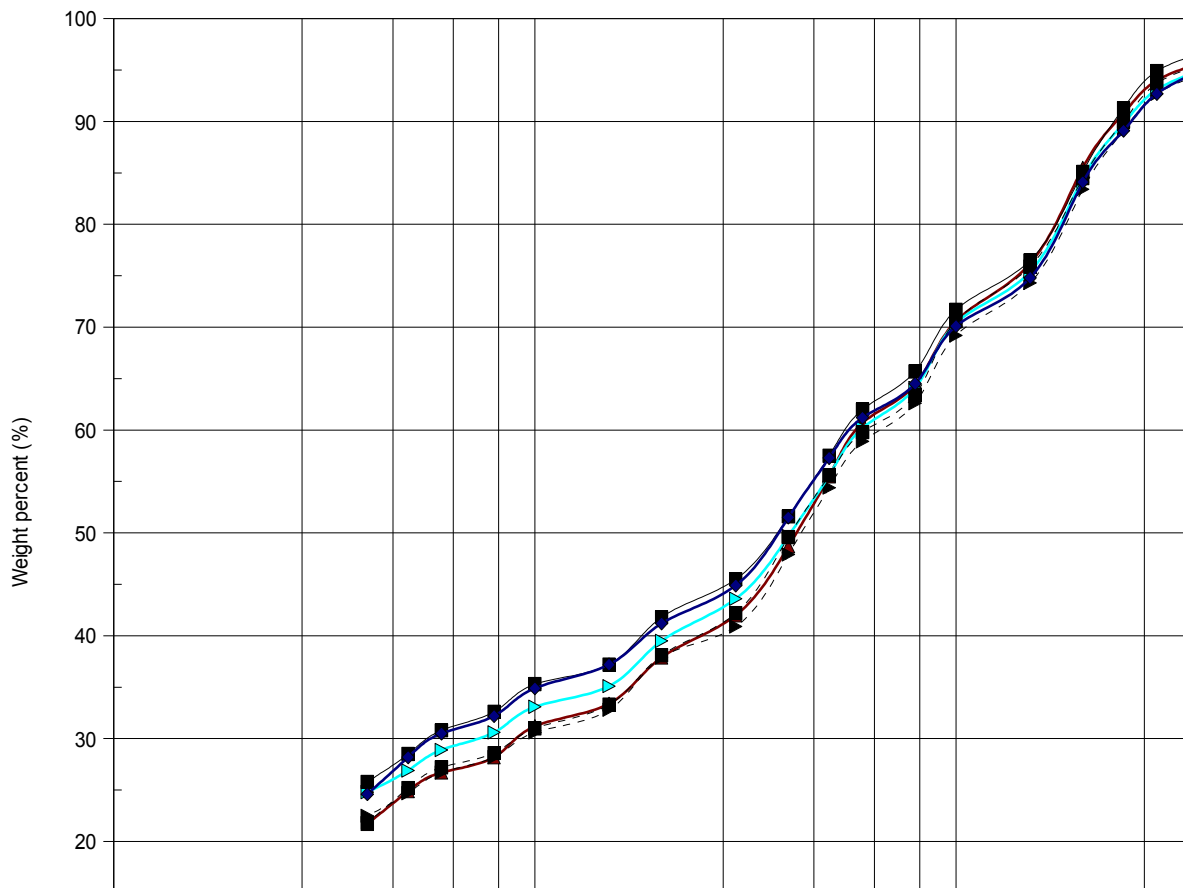23. Singh, Sintering of calcium aluminate mixes. British Ceramic Transaction, 1999.

Figure 1. Particle size distribution of porcelain stoneware bodies.
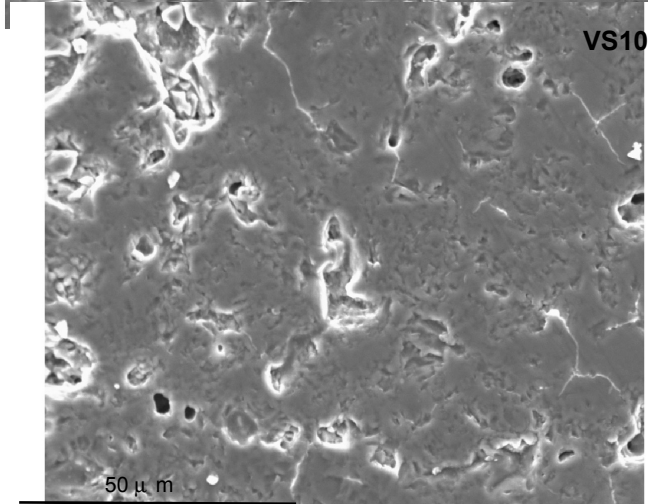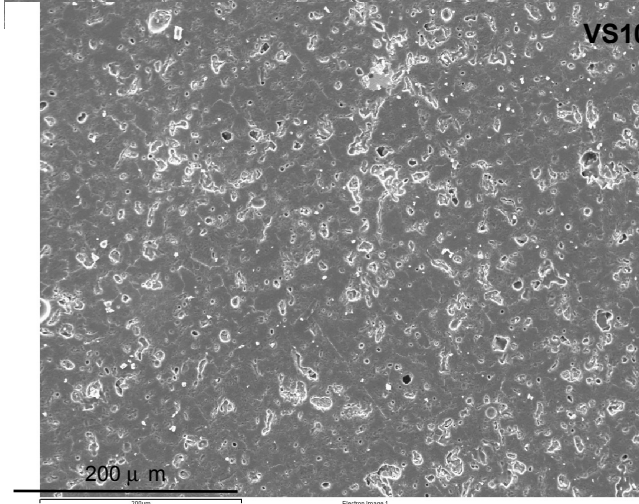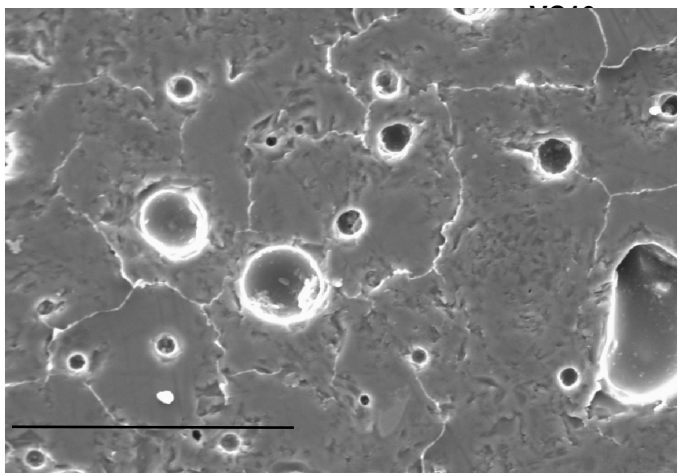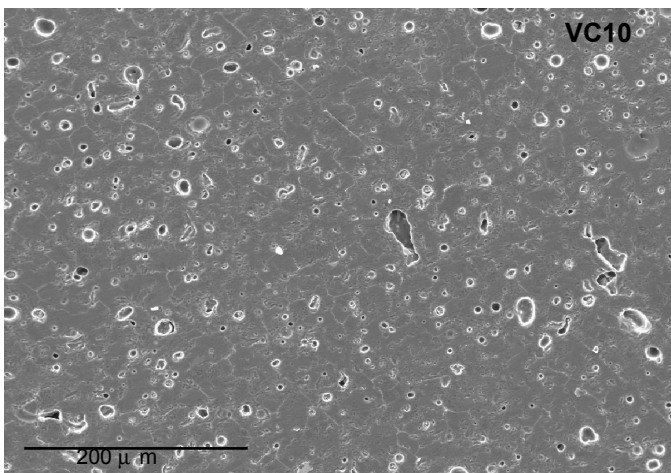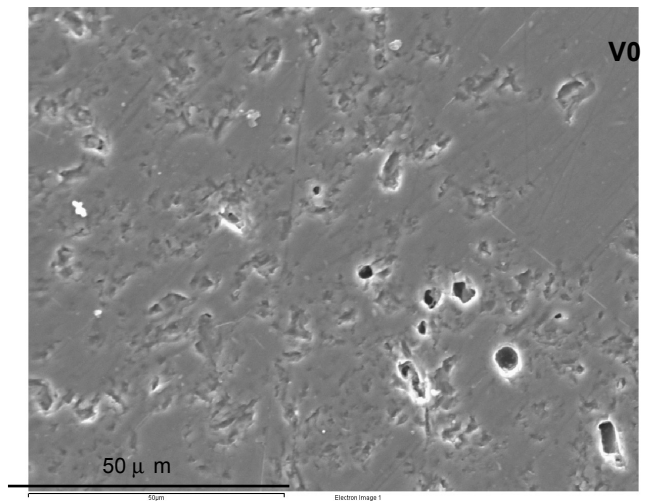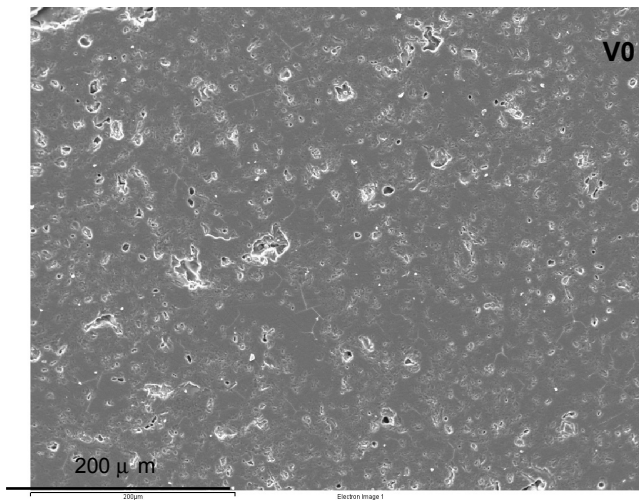
Figure 2. SEM micrographies of the V0, VC10 and VS10 samples, fired at 1200°C.

Fig. 3. Quantitative phase analyses of the ceramic tiles: (A) plagioclase; (B) quartz; (C) mullite; (D) vitreous phase.
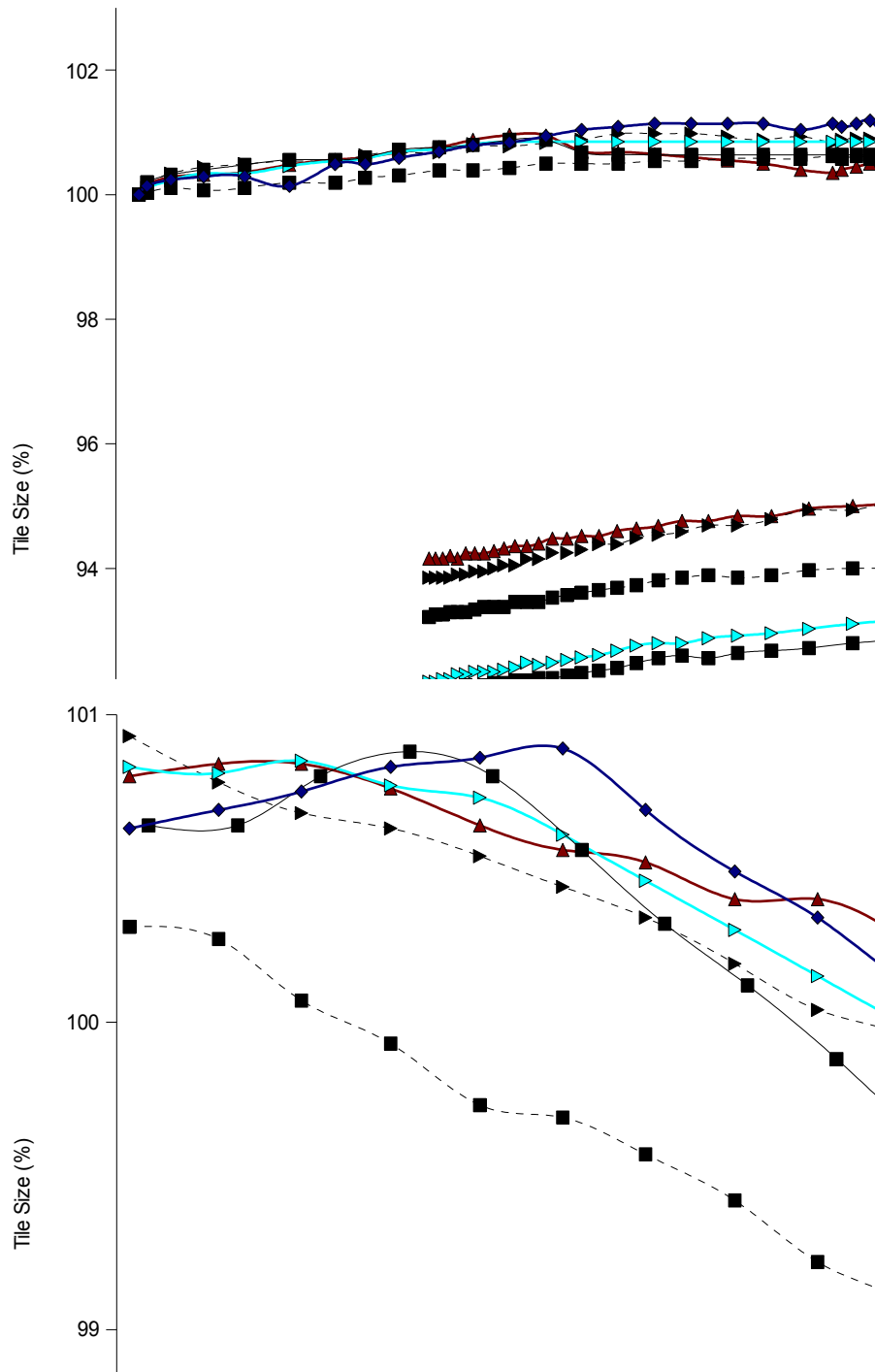
Figure 4. Firing behaviour of porcelain stoneware bodies in an industrial-like cycle.
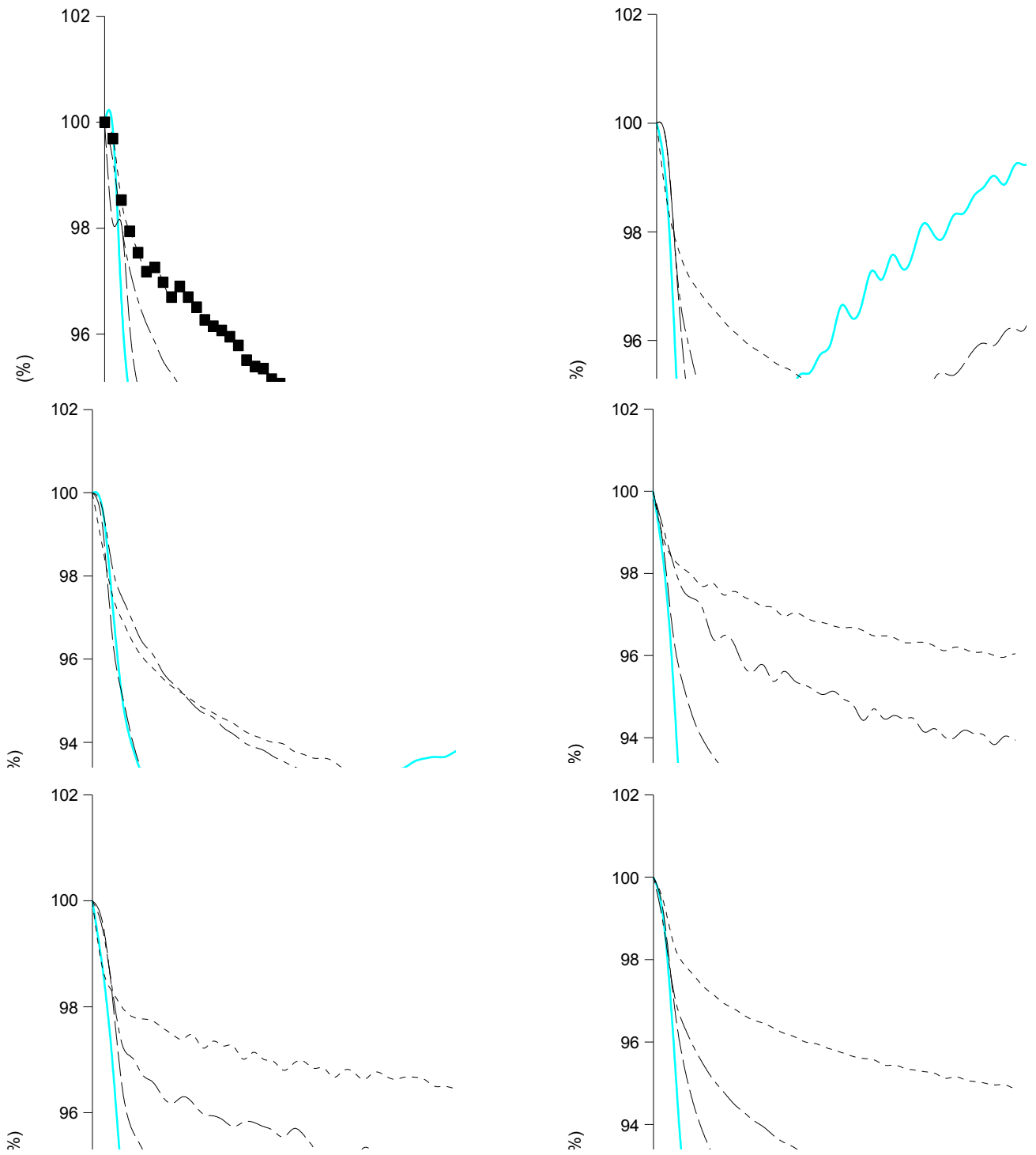
Figure 5. Isothermal curves (heating rate 80°C/ min to 1100, 1125, 1150, 1175, 1200°C) of porcelain stoneware bodies.

Table 1
Formulation of experimental porcelain stoneware bodies

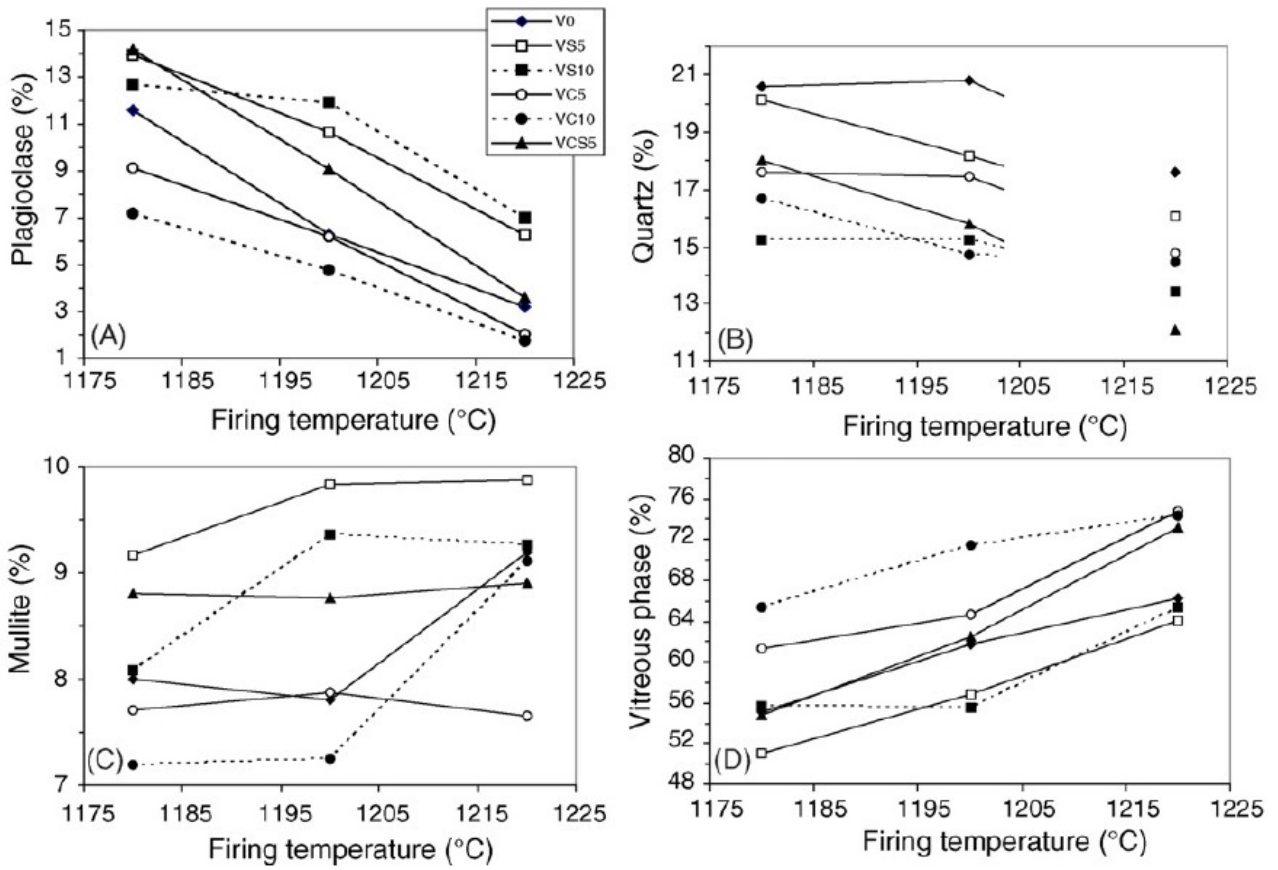| wt. %	V0	VC5	VC10	VS5	VS10	VCS5
Ball Clay	40	40	40	40	40	40
Quartz sand	10	10	10	10	10	10
Na-Feldspar	40	35	30	35	30	30
K-Feldspar	10	10	10	10	10	10
Cathodic tube glass	-	5	10	-	-	5
Screen glass	-			5	10	5

Table 2
Chemical composition of raw materials

wt.%	Quartz sand	Ball Clay	K-Feldspar	Na-Feldspar	Cathodic tube glass (C)	Screen glass (S)
SiO_2	94.5	58.0	67.6	69.2	51.6	62.7
Al_2O_3	3.1	27.0	18.0	18.6	3.6	2.3
TiO_2	0.1	1.5	0.0	0.2	0.1	0.4
Fe_2O_3	0.2	0.9	0.1	0.1	0.1	0.1
MgO	0.2	<0.1	0.3	0.1	1.9	0.3
CaO	0.1	<0.1	0.1	0.6	3.8	1.0
Na_2O	0.1	0.2	2.8	10.4	6.1	7.4
K_2O	1.5	0.2	10.8	0.2	7.5	7.1
ZrO_2	<0.1	<0.1	<0.1	<0.1	0.2	1.9
Sb_2O_3	<0.1	<0.1	<0.1	<0.1	0.2	<0.1
ZnO	<0.1	<0.1	<0.1	<0.1	0.1	0.2
SrO	<0.1	<0.1	<0.1	<0.1	0.7	7.6
BaO	<0.1	<0.1	<0.1	<0.1	0.8	8.4
B_2O_3	<0.1	<0.1	<0.1	<0.1	0.1	<0.1
PbO	<0.1	<0.1	<0.1	<0.1	23.1	0.4
Li_2O	<0.1	<0.1	<0.1	<0.1	0.1	0.1
L.o.l.	0.4	7.4	0.3	0.5	<0.1	<0.1

Table 3

Technological properties of semi-finished products

Product	Property	V0	VC5	VC10	VS5	VS10	VCS5
Slip	Water content (wt.%)	65.4 ± 0.2	65.5 ± 0.2	65.4 ± 0.2	65.3 ± 0.2	64.6 ± 0.2	64.8 ± 0.2
Powders	Weight/volume (g·cm^{-3})	1.65 ± 0.0	1.64 ± 0.0	1.65 ± 0.01	1.66 ± 0.0	1.63 ± 0.01	1.63 ± 0.01
	Median particle size (μm)	2.8 ± 0.1	3.0 ± 0.1	3.3 ± 0.1	2.7 ± 0.1	3.1 ± 0.1	3.2 ± 0.1
	Working moisture (wt. %)	7.6 ± 0.1	8.0 ± 0.1	7.4 ± 0.1	7.3 ± 0.1	7.2 ± 0.1	7.3 ± 0.1
	Specific weight (g·cm^{-3})	2.63 ± 0.0	2.63 ± 0.0	2.65 ± 0.01	2.63 ± 0.0	2.63 ± 0.01	2.62 ± 0.01
Dry tiles	Bulk density (g·cm^{-3})	1.96 ± 0.0	1.96 ± 0.0	1.95 ± 0.02	1.94 ± 0.0	1.93 ± 0.01	1.94 ± 0.01
	Total porosity (vol.%)	25.2 ± 0.1	25.5 ± 0.1	26.2 ± 0.1	26.3 ± 0.1	26.7 ± 0.1	26.0 ± 0.1
	Drying shrinkage (cm·m^{-1})	0.42 ± 0.0	0.38 ± 0.0	0.45 ± 0.02	0.38 ± 0.0	0.42 ± 0.05	0.45 ± 0.03
	Modulus of rupture (MPa)	2.4 ±	2.7 ±	2.4 ± 0.5	3.5 ±	3.4 ± 0.3	2.9 ± 0.6

Table 4

Technological properties of porcelain stoneware tiles

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$^{-3)}$)	Modulus of rupture (MPa)	Color CIE-Lab			
									L*	a*	b*	Δ E*
V0	1180	6.5 ± 0.1	1.5 ± 0.1	3.5 ± 0.2	3.4 ± 0.3	6.9 ± 0.7	2.36 ± 0.01	49.6 ± 2.0	80.4	2.4	11.6	ref.
	1200	6.8 ± 0.1	0.3 ± 0.1	0.7 ± 0.1	2.2 ± 0.2	2.8 ± 0.3	2.41 ± 0.01	49.9 ± 0.9	78.3	2.0	12.5	ref.
	1220	6.8 ± 0.1	0.1 ± 0.1	0.2 ± 0.1	1.5 ± 0.2	1.7 ± 0.2	2.41 ± 0.01	41.5 ± 9.2	76.8	0.7	12.5	ref.
VC5	1180	7.1 ± 0.2	0.3 ± 0.1	0.6 ± 0.2	3.6 ± 0.4	4.2 ± 0.4	2.41 ± 0.01	48.9 ± 1.7	77.6	2.2	13.5	3.3
	1200	7.0 ± 0.1	0.03 ± 0.02	0.1 ± 0.1	2.8 ± 0.3	2.9 ± 0.3	2.41 ± 0.01	45.8 ± 0.7	75.9	1.7	13.4	2.6
	1220	6.7 ± 0.1	0.05 ± 0.02	0.1 ± 0.1	3.0 ± 0.3	3.1 ± 0.3	2.37 ± 0.01	35.3 ± 8.3	76.6	0.3	14.4	1.4
VC10	1180	7.0 ± 0.1	0.03 ± 0.02	0.1 ± 0.1	4.2 ± 0.4	4.3 ± 0.4	2.42 ± 0.01	49.9 ± 0.3	75.9	2.1	14.3	5.3
	1200	6.8 ± 0.1	0.03 ± 0.02	0.1 ± 0.1	5.3 ± 0.5	5.4 ± 0.5	2.37 ± 0.01	41.4 ± 0.9	75.6	1.6	14.3	3.3
	1220	6.0 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	6.0 ± 0.6	6.1 ± 0.6	2.31 ± 0.01	31.0 ± 6.3	77.4	0.3	13.7	1.4
VS5	1180	6.4 ± 0.1	1.9 ± 0.2	4.5 ± 0.4	3.5 ± 0.4	7.9 ± 0.8	2.33 ± 0.01	43.3 ± 1.6	81.3	2.2	11.7	0.9
	1200	7.2 ± 0.1	0.4 ± 0.1	0.9 ± 0.2	3.6 ± 0.4	4.5 ± 0.5	2.39 ± 0.01	48.5 ± 0.7	79.3	1.6	13.1	1.2
	1220	7.0 ± 0.2	0.05 ± 0.02	0.1 ± 0.1	2.4 ± 0.2	2.5 ± 0.3	2.40 ± 0.01	40.7 ± 7.5	75.9	0.5	12.9	1.0
VS10	1180	5.1 ± 0.1	3.4 ± 0.4	7.6 ± 0.7	4.5 ± 0.5	١٢.١± ٠.٩	2.24 ± 0.02	36.9 ± 2.2	84.2	1.9	11.9	3.9
	1200	6.3 ± 0.1	1.4 ± 0.2	3.2 ± 0.4	4.4 ± 0.4	7.6 ± 0.8	2.32 ± 0.01	43.8 ± 0.6	76.7	1.8	12.3	1.6
	1220	7.0 ± 0.2	0.05 ± 0.01	0.1 ± 0.1	3.7± 0.4	3.8 ± 0.4	2.38 ± 0.01	34.9 ± 13.9	76.4	0.4	14.2	1.8
VCS5	1180	6.4 ± 0.1	1.1 ± 0.2	2.6 ± 0.4	5.0 ± 0.5	7.6 ± 0.8	2.33 ± 0.01	42.0 ± 1.3	78.3	2.0	13.7	2.9
	1200	7.2 ± 0.2	0.1 ± 0.1	0.2 ± 0.1	4.1± 0.4	4.3 ± 0.4	2.34 ± 0.01	48.4 ± 1.3	75.5	1.7	14.3	3.4
	1220	6.7 ± 0.1	0.04 ± 0.03	0.1 ± 0.1	4.6± 0.5	4.7± 0.5	2.35 ± 0.01	38.9 ± 1.5	76.5	0.5	13.8	2.0

Table 5
Leaching of lead from the two different glass typologies and the samples fired at 1200°C
(DIN 38414-4).

Body	Pb (mg·k^{-1})
V0	< 0.10
VC5	0.37
VC10	0.71
VS5	< 0.10
VS10	< 0.10
VCS5	0.23
Cathodic tube glass	9.97
Screen glass	0.22

Table 6
Shrinkage, sintering rate and apparent energy of activation of porcelain stoneware tiles

Parameter	Temperature (°C)	Sample					
		V0	VC5	VC10	VS5	VS10	VCS5
Shrinkage at maximum densification (cm· m^{-1})	1125	7.0	3.0	2.0	7.0	7.0	4.0
	1150	7.0	7.0	6.0	7.0	8.0	10.0
	1175	8.0	8.0	9.0	8.0	7.0	10.0
	1200	8.0	10.0	10.0	8.0	10.0	10.0
Sintering rate (min^{-1})	1125	2.4	2.9	2.4	2.3	1.9	1.7
	1150	2.9	5.1	3.7	3.1	3.0	2.1
	1175	4.0	4.5	4.5	4.2	4.2	4.0
	1200	4.0	7.0	5.6	5.8	4.5	5.2
(kJ/mol)		1241	861	1576	1078	2148	2169

Table 7

Chemical and physical properties of the glassy phase calculated at the different firing temperature

wt. % T(°C)	V0			VC5			VC10			VS5			VS10			VCS5		
	1180	1200	1220	1180	1200	1220	1180	1200	1220	1180	1200	1220	1180	1200	1220	1180	1200	1220
SiO_2	66.7	67.0	69.5	68.2	67.5	69.3	68.4	69.3	71.2	68.1	69.7	70.7	70.4	71.1	71.6	68.2	70.1	71.4
TiO_2	1.2	1.1	1.1	1.1	1.1	0.1	1.0	1.0	1.0	1.3	1.2	1.1	1.2	1.2	1.1	1.3	1.1	1.0
Al_2O_3	22.7	22.3	19.9	20.9	21.5	20.2	20.3	19.5	17.6	20.8	19.5	18.5	18.7	17.9	17.8	19.9	18.8	17.7
Fe_2O_3	0.8	0.7	0.7	0.7	0.7	0.6	0.7	0.6	0.6	0.8	0.7	0.7	0.7	0.7	0.6	0.8	0.7	0.6
MgO	0.1	0.1	0.1	0.3	0.3	0.2	0.4	0.4	0.4	0.1	0.1	0.1	0.2	0.2	0.1	0.3	0.3	0.3
CaO	0.3	0.3	0.3	0.6	0.6	0.5	0.8	0.8	0.8	0.4	0.4	0.4	0.4	0.4	0.4	0.7	0.6	0.6
Na_2O	5.9	6.2	6.4	5.5	5.7	5.7	5.2	5.3	5.5	5.4	5.5	5.8	5.0	5.1	5.3	5.0	5.2	5.5
K_2O	2.4	2.2	2.1	2.8	2.7	2.4	3.2	3.1	3.0	3.1	2.8	2.7	3.4	3.5	3.1	3.8	3.3	3.0
Viscosity (K·Pa·s)	8.4	5.8	3.2	6.7	5.3	3.5	6.2	4.2	2.5	6.6	4.3	2.8	5.4	3.6	2.7	5.8	3.9	2.6
Surface tension (N·m^{-1})	0.335	0.334	0.328	0.332	0.333	0.329	0.331	0.329	0.324	0.330	0.327	0.325	0.326	0.323	0.323	0.329	0.326	0.323