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The effect of fired scrap addition on the sintering behaviour of hard porcelain

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Abstract

The effect of the addition of porcelain fired scraps on the sintering, phase composition and properties of a hard porcelain was studied. Two ceramics were compared: a commercial triaxial porcelain labelled C-0 and one, where 15% of the mass of C-0 was substituted by scraps yielding a composition labelled C-15. The sintering was evaluated by the linear shrinkage, the water absorption and the variation of closed and total porosity, while the phase transformations were investigated by DTA-TG, dilatometry and XRD. Samples, sintered at 1350 and 1400 °C, were used for the evaluation of the Young modulus and the bending strength. The addition of the fired scrap had a positive effect on the quartz dissolution and on the formation of the liquid phase during the sintering. The sintering and the mechanical properties were improved by heat treatment in the 1300–1350 °C range. Above this temperature, a significant over-firing with a decrease of the mechanical properties was observed.

Keywords: A. Sintering; D. Porcelain; Waste

1. Introduction

Porcelain is a white, non-porous and partially transparent ceramic material, whose production started in China many centuries ago. Today, porcelain is produced in many countries and its technology is well known and described in different textbooks and papers [1–5]. Recently, a well-sintered tiling material, produced by a short firing cycle and known as porcelain stoneware, was developed [6]. However, the optimisation of the tableware porcelain and porcelain stoneware productions is still ongoing and many new works, discussing the ceramic structure [6–8] or the improvement of its properties [9–12], are published every year.

A consistent part of the new studies is related to the substitution of the traditional raw material in the composition (sand, feldspar and kaolin) with others, such as zeolite, corundum, bentonite, etc. [13,14], glass cullet [15–17] or waste products [18–20]. This latter aspect acquires particular importance due to the reduced availability of high quality raw materials. In this regard, the porcelain industry produces its own residues, part of which can be re-used in the production cycle; a typical example are the fired scraps of defected products [12,21,22]. Due to the requirement of using raw materials with very low iron oxides content, this possibility has particular importance for the production of hard porcelain. In this case, particular attention is paid to the rheological properties of the parent mass [21,22], because the addition of the waste might influence the forming process. This replacement, however, also leads to a variation of the phase composition of the green, which may influence the sintering process.

The present work investigates the effect of the addition of fired scraps on the densification process in a hard porcelain. Two ceramic compositions are compared: a typical commercial composition of kaolin, sand and feldspar and

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a second one, where part of the sand and part of the feldspar were substituted by fired porcelain scraps.

2. Experimental procedure

Fired porcelain rejects may be cannibalised in different manners. The simplest is the addition to an unchanged batch. This guaranties no variation of the total chemical composition but decreases the kaolin percentage, i.e. may influence the plasticity of the parent mass. This way is appropriate for a continuous production cycle and a relatively low percentage of scrap addition.

Another possibility is the replacement of only the non-plastic raw materials. This type of substitution varies the chemical composition, so that it is more suitable for a discontinuous production cycle. Since the single replacement of a filler increases the alkali oxides content and decreases the mechanical properties [12], it is more appropriate to simultaneously substitute part of the sand and part the feldspar.

In the present work, two porcelains, whose compositions are reported in Table 1, were studied. The first one, labelled C-0, corresponds to a commercial hard porcelain; in the second, labelled C-15, part of the sand and feldspar were replaced by fired scraps, milled under 63 μm in size, obtained by firing at 1350–1375 °C C-0.

The chemical compositions of the green and fired porcelains were analysed by XRF analysis (Spectro XEPOS), while BET specific surface of the parent powders were obtained by N_2 adsorption (ASAP 2000). The parent batches were prepared directly in a production plant using a discontinuous production cycle, as masses with water content of about 20 wt.% (calculated on dry batch). Then, the compositions were dried at 105 °C, crashed, milled and sieved at a grain size below 125 μm. After addition of 10 wt.% water and homogenisation, green samples with initial sizes of 10 mm × 10 mm × 8 mm (samples A) and 50 mm × 4 mm × 3 mm (samples B) were obtained by uniaxial pressing at 50 MPa. After drying at room temperature, the samples were heated at 5 °C/min up to different temperatures (1200, 1300, 1350, 1375 and 1400 °C), held for 1 h and cooled at 10 °C/min. The degree of sintering was estimated by the linear shrinkage, ΔL, related to the initial size of 50 mm (samples B), and by the water absorption, W, of samples A [3,4]. The experimental error was estimated as ±0.05% and ±0.03% for ΔL and W, respectively.

Table 1
Initial compositions of the investigated porcelains (wt.%)

	C-0	C-15
Kaolin	52	52
Quartz	35	24
Feldspar	13	9
Scrap	–	15

Samples A were also used to evaluate the bulk, ρ_b, skeleton, ρ_s, and real, ρ_r, densities. ρ_b was estimated by a dry flow pycnometer (GeoPyc 1360), while ρ_s and ρ_r by He displacement Pycnometer (AccuPyc 1330), before and after crashing and milling the samples below 26 μm, respectively. The results were used to determine the total, P_T, and the closed, P_C, porosities:

$$P_T = 100\frac{\rho_r - \rho_b}{\rho_r} \tag{1}$$

$$P_C = 100\frac{\rho_r - \rho_s}{\rho_r} \tag{2}$$

GeoPyc 1360 [23] measures the ‘‘enveloped’’ volume of porous samples, placed in a chamber with compressed free-flowing dry medium. The used medium, named DryFlo, is made of tiny, rigid spheres and a small amount of dry lubricant. It cannot fill in the open pores so that the measured volume corresponds to the *bulk* density of the samples. The AccuPyc 1330 [23] is a gas displacement Pycnometer, which determines the ‘‘absolute’’ density by measuring the pressure change of He in a calibrated volume. When bulk samples are used, the evaluated volume corresponds to the mass volume and closed for He pores, while when powder samples are measured the *real* density is obtained.

The experimental errors associated in the evaluation of ρ_b, ρ_s and ρ_r were estimated as ±0.012 g/cm^3, ±0.003 g/cm^3 and ±0.002 g/cm^3, respectively, which correspond to an error of ±0.6% and ±0.2% for P_T and P_C, respectively.

The sintering process was studied by a Differential Dilatometer (Netzsch 402 ED) and by DTA-TG analysis (Netzsch STA 409). These experiments were carried out at 5 °C/min in the 20–1400 °C temperature range. By dilatometry, the thermal expansion curves of samples, sintered at different temperatures, were also obtained.

The phase analyses of the C-0 and C-15 porcelains, sintered at different temperatures, were made by X-ray diffraction (Philips PW1830 XRD apparatus and Cu Kα radiation). The quantitative analyses have been carried out by the combined Rietveld–Reference Intensity Ratio (R.I.R.) method [24,25]. A 10 wt.% of corundum (NIST SRM 674a) has been added to all samples as internal standard. The mixtures, ground in an agate mortar, have been side loaded into an aluminum flat holder in order to minimize the preferred orientation problems. Data have been recorded in the 5–140° 2θ range (step size 0.02° and 6 s counting time for each step). The phase fractions extracted by the Rietveld–R.I.R. refinements, using GSAS software [26] have been rescaled on the basis of the absolute weight of the corundum originally added to the mixtures as an internal standard, and therefore internally re-normalized.

Series of five B samples, sintered at 1350 and 1400 °C were used for the evaluation of the mechanical properties: the Young modulus was measured by means of the non-destructive resonance frequency technique (Grindosonic) while the bending strength was evaluated by a three point bending test with 40 mm outer span at a speed of 0.1 mm/min (SINTEC D/10).

3. Results and discussion

Table 2 reports the chemical analyses of the green and fired porcelains. The substitution of 11% quartz and 4% feldspar with 15% scraps does not vary the alkali content, while about 1.5 wt.% SiO_2 is substituted by Al_2O_3. The BET specific surfaces of both powders (8.3 m^2/g for C-0 and 7.7 m^2/g for C-15) are typical for tableware porcelain and porcelain stoneware [5,11,21].

The usual methods, used for the evaluation of the degree of sintering, are the linear shrinkage, ΔL, and the water absorption, W. These methods, however, give incomplete information about densification: W only measures the open porosity, while ΔL is a function of the initial green porosity, i.e. it may vary for different batches. In the present work, in order to obtain additional information about the closed porosity, density measurements were carried out.

The values of ΔL and W, after sintering at different temperatures, are presented in Table 3, together with the corresponding real, ρ_r, skeleton, ρ_s, and bulk, ρ_b, densities. Fig. 1 shows the variations of the total, P_T, and closed, P_C, porosity as a function of the temperature.

The right evaluation of the porosity depends on the precise measurement of the real density. In some cases, ρ_r may be assumed as a constant, but in the porcelain, where the phase composition varies during the sintering, it must be obtained experimentally for each sample.

In C-0 and C-15, due to the increasing of the amount of glassy phase with temperature rise, the real density decreases. This is a consequence of the fact, that the glassy structure always has a lower density than the corresponding mixture of crystal phases. For example, ρ_r of the potassium feldspar, α-quartz and mullite have values of 2.54, 2.65 and 3–3.1 g/cm^3, respectively [3,27], while the densities of the glasses with feldspar, C-0 and C-15 compositions, estimated by the Appen method [28], were evaluated as 2.39, 2.35 and 2.36 g/cm^3, respectively. Some ρ_r decreasing may be also observed if re-crystallisation quartz-cristobalite occurs [3,29].

The results of the green samples show that the addition of fired scraps decreases ρ_b and increases ρ_r. This leads to a higher initial porosity of C-15 (28.9 ± 0.6%) with respect to C-0 (26.6 ± 0.6%) and indicates that the addition of reject decreases the compressibility. This is probably a result of the lower specific surface of the C-15 batch. This difference highlights that the same degree of the densification (i.e. the same total porosity) in C-15 will be attained with about 1% more linear shrinkage, than C-0.

Table 2
Chemical compositions of C-0 and C-15 green samples and porcelains (wt.%)

	Al_2O_3	SiO_2	K_2O	Fe_2O_3
C-0 green	24.89	63.65	3.16	0.43
C-15 green	26.38	62.30	2.99	0.46
C-0 porcelain	26.58	69.19	3.69	0.47
C-15 porcelain	28.21	67.47	3.52	0.49

The P_T and W values, obtained at 1200 °C, show that the densification process is in its initial stage: the porosity is only open with a value of about 14.5% for both composition; W values are also similar (5.95% for C-0 and 5.90% for C-15). This demonstrates that, regardless of the presence of an existent glassy phase in the scraps, at this temperature the waste addition does not improve the densification. This may be explained by the too high viscosity of the SiO_2-rich melt in the rejects.

At 1300 °C, the sintering is significantly improved and the transformation of open into closed porosity is observed: P_T decreases to 6.8% for C-0 and 5.3 % for C-15, while W to 0.96% and 0.87%, respectively. The highest densification degree of C-15, corresponding to 4.2% P_T is attained at 1350 °C, while sintering at 1375 and 1400 °C yields an over-firing, leading to increased closed porosity and decreased shrinkage. At the same time, the C-0 composition has the best firing temperature at 1375° C, with a total porosity of 5.5%; at 1400 °C C-0 shows over-firing.

The C-15 batch has a lower specific surface and the C-15 green has higher initial porosity. Nevertheless, this composition sinters better at 1300–1350 °C and shows over-firing at lower temperatures, respectively, C-0. This behaviour may be explained by the variations in the mineralogical compositions during heat-treatment.

In order to investigate the reactions taking place during the heat-treatment, the sintering process was studied in non-isothermal conditions by Dilatometry and DTA-TG [30,31]. Fig. 2 shows the dilatometric traces of C-0 and C-15, while

Table 3
Shrinkage, water soaking, bulk, ρ_b, skeleton, ρ_s, and real, ρ_r, densities of C-0 and C-15 after 1 h holding at different temperatures

	Shrinkage (%)		Water soaking (%)		Bulk density (g/cm^3)		Skeleton density (g/cm^3)		Real density (g/cm^3)	
	C-0	C-15	C-0	C-15	C-0	C-15	C-0	C-15	C-0	C-15
Initial	–	–	–	–	1.962	1.929	2.689	2.731	2.672	2.711
1200	5.83	7.22	5.95	5.90	2.234	2.241	2.589	2.602	2.616	2.625
1300	8.09	9.28	0.96	0.87	2.406	2.452	2.528	2.533	2.581	2.589
1350	8.24	9.95	0.15	0.02	2.413	2.460	2.473	2.488	2.559	2.567
1375	8.29	9.81	0.05	0.03	2.409	2.436	2.421	2.443	2.550	2.558
1400	7.58	8.39	0.04	0.04	2.368	2.363	2.378	2.372	2.542	2.550

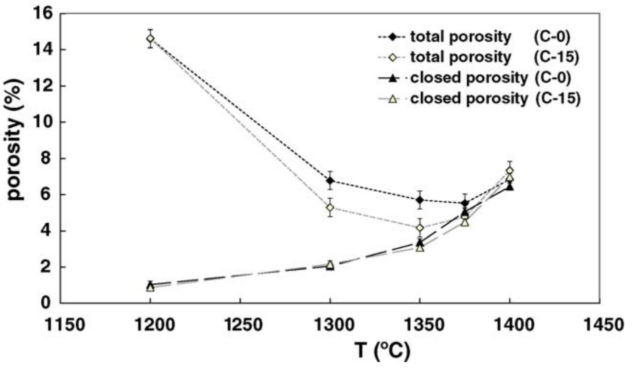

Fig. 1. Total and closed porosities of C-0 and C-15 as function of the temperature.

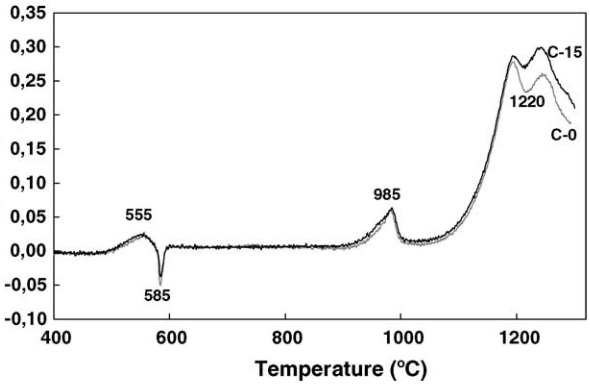

Fig. 3. Sintering rate of C-0 and C-15 compositions.

Fig. 3 plots the corresponding derivates (i.e. the sintering rate versus temperature). The two plots in Fig. 2 are similar up to 1150–1200 °C, while at higher temperatures C-15 sinters faster. At 550–600 °C and at 950–1100 °C, the samples show variations, related to the low-temperature phase transformations. The low-temperature shrinkage is more evident in C-15, probably, due to its higher initial porosity: ΔL values at 1100 °C are 0.1% and 0.5% for C-0 and C-15, respectively. At 1200 °C, the shrinkage is 2.9% for C-0 and 3.5% for C-15 (i.e. the difference remains similar), while at 1350 °C the C-15 shrinkage (10.3%) is significantly higher in respect of C-0 (8.4%). These results are in agreement with the P_T variations, presented in Fig. 1.

Fig. 3 shows that at 550–600 °C, as a result of the kaolinite de-hydration and metakaolinite formation, some shrinkage is observed, followed by a volume increase at 585 °C, due to the transformation of α-quartz in β-quartz. At 980–1000 °C, the transformation of the metakaolinite leads to new shrinkage [30] with a maximum transformation rate at 985 °C. The densification in both samples starts at 1100–1120 °C and up to 1170–1190 °C the sintering rate is similar. Then, the densification rate increases faster in C-15 and at 1250 °C its value is 20% higher than C-0. The observed decrease of the densification rate at 1220 °C in both ceramics is probably due to the beginning of formation of secondary mullite. Dilatometric traces with similar variations at 1210–1230 °C were also reported in other porcelain compositions [31].

The DTA results are shown in Fig. 4. The endo-effect in the 500–600 °C range is related to 7–7.5% losses in the TG traces and corresponds to the kaolinite dehydration, while the exo-peak at 990 °C to the metakaolinite transformations (i.e. the formation of spinel-type aluminosilicate structure and amorphous silica) [5,31]. The endo-effect, due to the feldspar fusion and the partial quartz dissolution, starts at about 1170–1190 °C. Notwithstanding the lower feldspar content in the batch, this endo-effect is more evident in C-15, highlighting that the milled porcelain waste accelerates the quartz dissolution. Taking the glassy phase already formed in the scrap into account, it may be inferred that the more intensive sintering in C-15, as well as the observed over-firing at lower temperatures, are due to the formation of a higher amount of liquid phase.

This assumption was confirmed by the XRD results of samples, sintered at 1350 and 1400 °C. The spectra are plotted in Fig. 5, while the quantitative results are summarised in Table 4. They show lower crystallinity in the C-15 samples and an increase in the amorphous phase with the temperature rise. It is also demonstrated that the increase in the glassy phase is due to the dissolution of quartz, while the mullite percentage remains constant. Similar results were reported by other authors [4,10,21].

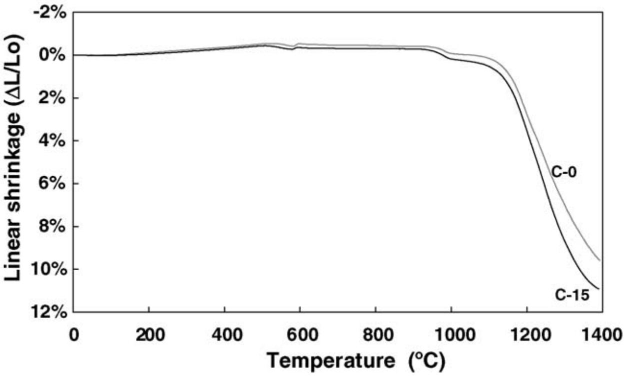

Fig. 2. Dilatometric traces of C-0 and C-15 compositions.

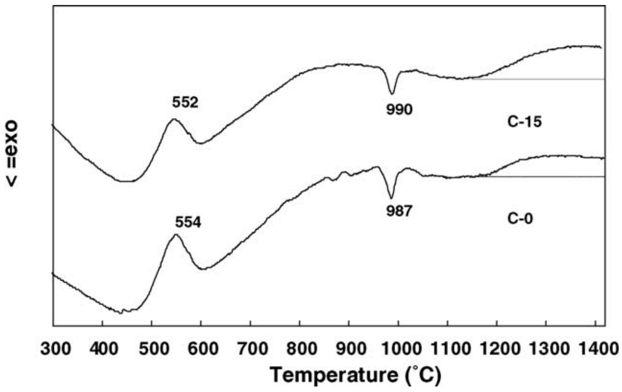

Fig. 4. DTA traces of C-0 and C-15 compositions.

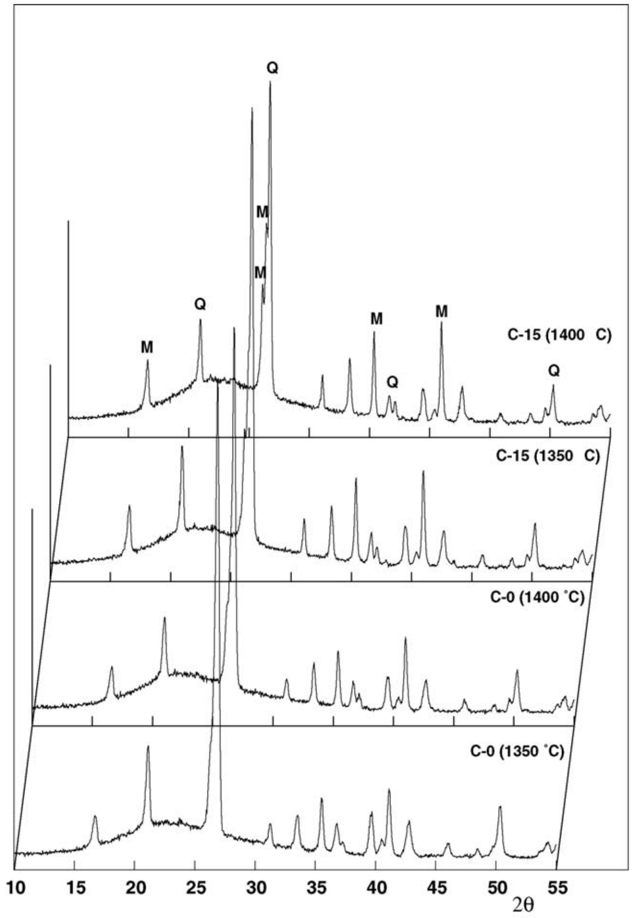

Fig. 5. XRD results of C-0 and C-15 porcelains, sintered at 1350 and 1400 °C.

The variation of the quartz amount may also be estimated by the changes of the thermal expansion coefficient, TEC, of final ceramics. Due to the high TEC of α-quartz ($15 \times 10^{-6}\,\mathrm{deg}^{-1}$) and the low ones of mullite ($5.3 \times 10^{-6}\,\mathrm{deg}^{-1}$) [3] and formed SiO_2-rich glassy phase ($4–5.5 \times 10^{-6}\,\mathrm{deg}^{-1}$) [28], the dissolution of the quartz leads to a decreasing of the thermal expansion coefficient. In fact, the samples, sintered at 1300 and 1400 °C have TEC (20–400 °C) of 5.72 and $5.26 \times 10^{-6}\,\mathrm{deg}^{-1}$ for C-0 and 5.51 and $4.84 \times 10^{-6}\,\mathrm{deg}^{-1}$ for C-15, respectively.

Table 4
Results of Rietveld–R.I.R. quantitative XRD analysis (wt.%) for C-0 and C-15 samples

	1350 °C		1400 °C	
	C-0	C-15	C-0	C-15
Phases				
Amorphous	57.8(1)	61.9(1)	63.6(1)	66.2(1)
Quartz	21.0(1)	16.4(1)	16.5(1)	11.7(2)
Mullite	21.1(4)	21.6(1)	19.8(1)	22.0(1)
Total	99.9	99.9	99.9	99.9
χ^2	5.27	4.22	4.08	3.33
R_{wp}	0.060	0.053	0.052	0.048
R_p	0.044	0.039	0.039	0.036

Table 5
Mechanical properties of C-0 and C-15 after 1 h holding at 1350 °C and 1400 °C

	Young modulus (GPa)	Bending strength (MPa)
C-0 (1350 °C)	68 ± 3	57 ± 3
C-0 (1400 °C)	67 ± 4	56 ± 4
C-15 (1350 °C)	74 ± 4	67 ± 4
C-15 (1400 °C)	74 ± 2	59 ± 3

Table 5 summarises the bending strength and Young modulus of samples, sintered at 1350 °C and 1400 °C. The results are similar with standard deviations of the same order of magnitude as the differences between the four series. The characteristics of both C-0 series are practically identical. At the same time, the bending strength of C-15, sintered at 1350 °C has a maximum value, while the samples, held at 1400 °C, show some decreases. It may be concluded that the addition of scraps has a positive effect on the mechanical properties and that the variations of the properties are mainly related to the residual porosity.

4. Conclusions

At sintering temperatures below 1200 °C, the addition of fired scraps had no significant influence on densification. This may be explained by the high viscosity of the SiO_2-rich melt in the porcelain waste, which was already fired at 1350–1375 °C.

By raising the sintering temperature to 1300–1350 °C, the molten part of the scrap starts to participate in the dissolution of the quartz phase and in the densification process of the porcelain. As a result, the sintering is improved and products with lower porosity and higher mechanical properties are obtained.

At 1375–1400 °C, the percentage of liquid phase becomes too high, leading to over-firing and a decrease in the properties.

In conclusion, the addition of 15% porcelain scrap reduces the sintering interval, decreases the sintering temperature and helps to obtain better mechanical properties.

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References

[1] W.D. Kingery, Introduction to Ceramics, J. Wiley & Sons, New York, 1976.

[2] J.S. Reed, Principles of Ceramic Proceedings, J. Wiley & Sons, New York, 1995.

[3] J. Hlavac, The Technology of Glass and Ceramics: An Introduction, Elsevier, Amsterdam, 1983.

[4] E. Gerasimov, S. Bachvarov, Technology of the Ceramics Product, Technica, Sofia, 1977 (in Bulgarian).

[5] W.M. Carty, U. Senapati, Porcelain—raw materials, processing, phase evolution, and mechanical behavior, J. Am. Ceram. Soc. 81 (1) (1998) 3–20.

[6] T. Manfredini, G. Pellacani, M. Romagnoli, L. Pennisi, Porcelainized stoneware tile, Am. Ceram. Soc. Bull. 74 (5) (1995) 76–79.

[7] Y. Iqbal, W.E. Lee, Microstructural evolution in triaxial porcelain, J. Am. Ceram. Soc. 83 (12) (2000) 3121–3127.

[8] Y. Iqbal, W.E. Lee, Fired porcelain microstructures revisited, J. Am. Ceram. Soc. 82 (12) (1999) 3584–3590.

[9] C. Leonelli, F. Bondioli, P. Veronesi, M. Romagnoli, T. Manfredini, G. Pellacani, V. Cannillo, Enhancing the mechanical properties of porcelain stonewere tiles: a microsrtuctural approach, J. Eur. Ceram. Soc. 21 (2001) 785–793.

[10] O. Isik Ece, Z. Nakagawa, Bending strength of porcelains, Ceram. Int. 28 (2002) 131–140.

[11] E. Sanchez, M.J. Orts, J. Garcia-Ten, V. Cantavella, Porcelain tile composition effect on phase formation and end products, Am. Ceram. Soc. Bull. 80 (6) (2001) 43–49.

[12] G. Stathis, A. Ekonomakou, C.J. Stournaras, C. Ftikos, Effect of firing conditions, filler grain size and quartz content on bending strength and physical properties of sanitaryware porcelain, J. Eur. Ceram. Soc. 24 (2004) 2357–2366.

[13] R. Gennaro, P. Cappelletti, G. Cerri, M. Gennaro, M. Dondi, G. Guarini, A. Langella, D. Naimo, Influence of zeolites on the sintering and technological properties of porcelain stoneware tiles, J. Eur. Ceram. Soc. 23 (2003) 2237–2245.

[14] M.F. Abadir, E.H. Sallam, I.M. Bakr, Preparation of porcelain tiles from Egyptian raw materials, Ceram. Int. 28 (2002) 303–310.

[15] L. Tucci, E. Esposito, C. Rastelli, E. Palmonari, Rambaldi, Use of soda-lime scrap-glass as a fluxing agent in a porcelain stoneware tile mix, J. Eur. Ceram. Soc. 24 (2004) 83–92.

[16] S.R. Bragança, C.P. Bergmann, Traditional and glass powder porcelain: technical and microstructure analysis, J. Eur. Ceram. Soc. 24 (2004) 2383–2388.

[17] F. Matteucci, M. Dondi, G. Guarini, Effect of soda-lime glass on sintering and technological properties of porcelain stoneware tiles, Ceram. Int. 28 (2002) 873–880.

[18] P. Torres, H.R. Fernandes, S. Agathopoulos, D.U. Tulyaganov, J.M.F. Ferreira, Incorporation of granite cutting sludge in industrial porcelain tile formulations, J. Eur. Ceram. Soc. 24 (2004) 3177–3185.

[19] K. Dana, S. Das, S.K. Das, Effect of substitution of fly ash for quartz in triaxial kaolin–quartz–feldspar system, J. Eur. Ceram. Soc. 24 (2004) 3169–3175.

[20] F. Andreola, L. Barbieri, A. Corradi, I. Lancellotti, T. Manfredini, Utilisation of municipal incinerator grate slag for manufacturing of porcelainized stoneware tiles manufacturing, J. Eur. Ceram. Soc. 22 (2002) 1457–1462.

[21] S.M. Olhero, G. Tari, J.M. Ferreira, Feedstock formulations for direct consolidation of porcelains with polysaccharides, J. Am. Ceram. Soc. 84 (4) (2001) 719–725.

[22] I. Agote, A. Odriozola, M. Gutierrez, A. Santamaria, J. Quintanilla, P. Coupelle, J. Soares, Rheological study of waste porcelain feedstocks for injection moulding, J. Eur. Ceram. Soc. 21 (2001) 2843–2853.

[23] http://www.micromeritics.com.

[24] M. Bellotto, C. Cristiani, Quantitative X-ray diffraction Rietveld analysis of low temperature coal ashes, Mater. Sci. Forum 79–82 (1991) 745–750.

[25] A.F. Gualtieri, G. Artioli, Quantitative determination of chrysotile asbestos in bulk materials by combined Rietveld and RIR methods, Powder Diffr. 10 (1995) 269–277.

[26] A.C. Larson, R.B. von Dreele, GSAS: General Structure Analysis System LANSCE, MS-H805, Los Alamos National Laboratory, Los Alamos, NM, 1998.

[27] W. Deer, R. Howie, J. Zussman, An Introduction to the Rock-Forming Minerals, second ed., Longman Scientific & Technical, 1992.

[28] A. Appen, Chemistry of Glasses, Himiq, Leningrad, 1974 (in Russian).

[29] U. Mücke, Ch. Ullner, G. Nolze, Microsrtructure, internal stresses and fracture mechanics properties of quartzose silicate materials for whitewares, cfi/DKG 78 (7) (2001) 31–36.

[30] J. Blumm, Recent advanced in dilatometry, Am. Ceram. Soc. Bull. 79 (11) (2000) 64–68.

[31] M. Paganelli, Using the optical dilatometer, Am. Ceram. Soc. Bull. 81 (11) (2002) 25–30.