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Development of a multipurpose tile body: Phase and microstructural development

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Abstract

In this study, an attempt was made in order to develop a multipurpose tile body using a single formulation. In order to achieve this, several body recipes were prepared using mainly local raw materials with clearly defined physical and chemical properties at different sieve residues and single fast fired under industrial conditions in the first part of the study. In the second part, the most suitable formulations with the corresponding sieve residues were determined and further fired at different peak temperatures under laboratory conditions in order to establish their vitrification ranges and optimum firing temperatures. The tested peak firing temperatures were varied at 20 °C intervals from 1120 to 1200 °C for multipurpose wall tile body and from 1140 to 1220 °C for multipurpose floor tile body. The physical and thermal properties of the fired bodies such as water absorption, linear firing shrinkage, bulk density and linear thermal expansion coefficient were measured. The vitrification behaviour of the multipurpose bodies was also evaluated using a double-beam optical non-contact dilatometer. Furthermore, the fired bodies were subjected to colour measurements. Particular consideration was given to the phase and microstructural evolution of the developed tile bodies. X-ray diffraction (XRD) was used to analyse the phases formed before and after firing. Scanning electron microscopy (SEM) in combination with energy dispersive X-ray spectroscopy (EDS) was further employed in order to observe the microstructural and microchemical characteristics of the fired bodies with respect to peak firing temperature. The preliminary experimental results showed that it was possible to obtain a multipurpose body with the properties in accordance with ISO-EN 10545.

Keywords: Firing; Electron microscopy; Thermal expansion; Tiles

1. Introduction

Ceramic tiles are commonly produced from a mixture of raw materials containing clay, flux, and refractory filler. Each raw material within the body formulation contributes differently to the final properties. A broad range of products varying in dimensions, dimensional tolerance, strength, apparent porosity, surface texture, decorative coatings, and overall quality are produced by the tiles industry. Since tile have high ratio of surface area to thickness, manufacturing process should be capable of achieving this shape in a highly productive manner. This type of tiles is usually obtained by wet grinding, dry pressing, fast drying and fast firing at suitable temperatures. Understanding and control of process steps in tile production has greatly improved within the recent years. In the relevant literature, several directions for further improvements have been mentioned. Among these directions: achieving better dimensional control, which is particularly more demanding for larger tiles, obtaining green granules with improved characteristics through dry preparation process, which is expected to enable lower running and production costs, and effective use of processing additives for improving process performance can be mentioned as important ones.[1] Moreover, the new research + development + innovation (R + D + I) lines, particularly relating to porcelain tile manufacturing technology, have also been suggested in areas such as in-press tile decoration and forming methods.[2]

Apart from the directions mentioned above, development of a multipurpose ceramic composite body suitable for both wall and floor tile production has already been reported. A monoporosa body composition cannot be fired at a higher temperature in order to obtain a vitrified product due to its rapid and uncontrolled melting. Moreover, a vitrified body cannot be properly

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Table 1
Chemical composition of the starting raw materials (wt.%)

Raw materials	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	L.O.I.[a]
Pegmatite (A)	75.5	14.9	0.65	0.2	1.13	–	3.48	1.9	2.2
Na-feldspar	67.9	18.7	0.39	0.48	1.27	0.37	9.65	0.65	0.6
Semi-plastic clay	62.1	23.2	2.35	1.14	0.14	0.58	0.17	2.13	8.2
Sandy clay	78.4	11.6	1.72	0.52	0.77	0.72	0.25	1.57	4.9
Magnesite	14.9	2.38	1.29	0.17	2.15	37.1	0.36	0.26	41.3
Ukrainian clay	63.9	23.6	0.9	1.26	0.25	0.5	0.39	2.36	6.7
Pegmatite (B)	71.5	17.0	0.79	0.74	0.15	–	0.07	1.83	8.0
Marble	0.42	0.21	0.06	0.02	54.6	1.36	0.03	0.03	43.3

[a] L.O.I. is loss on ignition.

used as wall tile, because its high firing shrinkage results in different sizes. On the other hand, a multipurpose body can fulfil the dimensional and mechanical requirements of both wall and floor tile through production in the same line. It has also been emphasized that the potential of such a body should be considered beyond its plant flexibility contribution, which improves the finished product quality, thus increasing profits, with the obvious possibility of improving the entire tile industry.[3]

There are around 22 ceramic tile manufacturing plants in Turkey and in 2003 these plants produced nearly 190 million square meters of tiles. Eight-four million square meters of this production was exported, which makes Turkey the fifth biggest exporter of the world.[4] Considering the expectation that the Turkish tile sector continues to expand, further studies both on the improvement and the development of tile formulations, mainly from the local raw materials, are necessary in order to make the producers advantaged in the world market while maintaining the capital and running costs at reasonably competitive levels as well. Keeping this in mind, the present study, which is a part of an extended research program, was designed in two sections: the first part involved developing a multipurpose tile body using a single formulation; the second part focused on firing behaviour of the multipurpose tile body in relation to its technological properties. A particular interest was given to crystalline phase and microstructural evolution upon firing. Glazing issue was, however, ignored in this part of the research program.

2. Materials and methods

The main raw materials employed to prepare the various formulations in this study are sodium feldspar from Cine region of Aydın/Turkey, two different pegmatites from Sogut region of Bilecik/Turkey, two different ball clays, one from Sile region of Istanbul/Turkey, and the other from Ukraine, and marble and magnesite from Eskisehir/Turkey. It is well known that characteristics of the raw materials used to prepare ceramic bodies considerably affect the ultimate product quality. In this respect, the chemical and some of the physical and firing properties of the starting raw materials were determined according to standard procedures and the results are reported in Tables 1–3. The experimental approach mainly consisted of a laboratory simulation of the tile-making process and characterization of both the semi-finished and finished products. Following the tests on the raw materials, different floor and wall tile formulations were prepared and compared with the standard formulations currently in production in a local tile company.

In the first part of the experimental study, several body formulations were prepared. Each mixture was wet-ground in a jet mill long enough until the residue on 63 μm sieve was reduced to required values. The obtained slips were first allowed to dry in an oven at around 110 °C, then deagglomerated and humidified (5–6 wt.% moisture content) and finally sieved down to 1 mm before forming. Rectangular samples of dimensions 66 mm × 15 mm × 4 mm were prepared by dry pressing at a

Table 2
Physical properties of the starting raw materials and formulations

Raw materials	Weight volume (g/l)	Time of flow (s)	Sieve residue on 63 μm (%)	Sieve residue on 180 μm (%)	Dry flexural strength (kg/cm^2)
Pegmatite (A)	1520	11	4.2	69.1	2.9
Na-feldspar	1513	12	4.1	1.9	2.5
Semi-plastic clay	1529	12	0.4	2.2	4.0
Sandy clay	1325	11	6.7	52.5	4.5
Magnesite	1490	–	0.5	28.0	7.6
Ukrainian clay	1525	45	0.4	0.5	4.0
Pegmatite (B)	1505	11	4.4	3.8	3.0
Marble	1510	10	1.5	4.4	2.5
Floor tile std.	1660	20	5.0	–	4.1
Multipurpose floor tile	1664	20	3.0	–	4.9
Wall tile std.	1673	20	3.3	–	4.0
Multipurpose wall tile	1672	20	5.5	–	4.1

Table 3
Firing properties (cycle: 1200 °C, 34 min) of the raw materials

Raw materials	Firing shrinkage (%)	Water absorption (%)	L.O.I.[a]	L^*	a^*	b^*
Pegmatite (A)	3.00	4.36	7.3	73.9	3.6	13.3
Na-feldspar	–	–	–	75.4	1.8	12.3
Semi-plastic clay	7.18	2.48	7.5	75.5	4.9	24.0
Sandy clay	5.21	4.43	7.6	69.9	5.8	20.6
Magnesite	23.45	6.69	39.9	85.4	1.9	19.0
Ukrainian clay	7.00	1.00	6.5	81.0	1.0	12.5
Pegmatite (B)	2.68	7.00	3.5	78.0	4.3	10.2
Marble	–	–	37.2	92.5	−0.6	4.9

[a] L.O.I. is loss on ignition.

pressure of 160 kg/cm^2 for wall tile body and 180 kg/cm^2 for floor tile body. Finally, tiles were single fast fired in a roller furnace under industrial conditions at different peak temperatures. Total firing times (cold-to-cold) for wall and floor tile bodies were 36 and 34 min, respectively. Amongst the different formulations, the multipurpose body ones with a sieve residue of 3.0% (floor tile) and 5.5% (wall tile) fired at 1200 °C and 1170 °C, respectively, were found to be the most suitable for further experimentation. Table 4 details the standard wall, floor and multipurpose tile body formulations investigated in the second part of the study. Note that the particle size distributions of the multipurpose bodies were obtained by wet sieve analysis. The particle size analysis of the as-received magnesite was, however, achieved using a Malvern laser diffraction instrument (Hydro 2000G, UK).

Considering the data obtained in the first part of the study, representative tiles from each multipurpose body composition were pressed at a specific pressure of 115 kg/cm^2 with dimensions of 100 mm × 50 mm × 6 mm. Further firings were ranged from 1120 to 1200 °C (wall tile) and from 1140 to 1220 °C (floor tile) at 20 °C intervals in order to establish their vitrification range and optimum firing temperature. The total firing time was 1 h with a soaking time of 5 min. All the firings were achieved in an electrical furnace (PLF 130/7, Protherm, Turkey) under laboratory conditions. The densification behaviour was described in terms of bulk density, water absorption and linear firing shrinkage. Breaking strength values of samples fired under industrial conditions were also measured using the three-point flexural method (Gabrielli S.R.L, Italy) with a lower span of 80 mm and crosshead speed of 1 mm/min. The vitrification behaviour of rectangular compacts of the bodies was studied using a double-beam optical non-contact dilatometer (MISURA, Expert System Solutions, Italy) according to the corresponding industrial firing profiles. In addition, linear thermal expansion coefficients of the industrially fired bodies were also determined using a Netzsch thermal dilatometer (402 EP, Germany) at a heating rate of 10 °C/min to 650 °C. Furthermore, the colour of fired bodies was measured using a UV–Vis spectrophotometer (Minolta 3600d, Japan) and the chromatic co-ordinates expressed as L^*, a^*, b^*.

Table 4
Formulation of the tile bodies (wt.%)

Raw materials	Floor tile std.	Wall tile std.	Multipurpose body
Pegmatite (A)	48.7	–	17.0
Na-feldspar	10.0	–	13.0
Semi-plastic clay	33.8	18.0	16.0
Sandy clay	6.0	44.0	19.0
Magnesite	1.5	–	3.0
Ukrainian clay	–	–	13.0
Pegmatite (B)	–	30.0	13.0
Marble	–	8.0	6.0

Qualitative determination of major crystalline phases present in green and fired tiles was achieved by X-ray diffraction (Rigaku, Rint 2000, Japan) on randomly oriented powdered samples (1.0 s/step, at scan rate 0.02° 2θ/s over a range of 5–55° 2θ). Microstructural observations were performed on both polished and fracture surfaces of some selected fired samples using a scanning electron microscope (SEM-Camscan S4 Series, UK) in both secondary (SE) and back-scattered (BE) electron imaging modes after sputtering with a thin layer of gold–palladium alloy in order to prevent charging. Polishing was carried out in accordance with the standard ceramografic procedures. Chemical etching was further employed to reveal the presence of certain crystalline phases by immersing the relevant samples in 10% hydrofluoric acid (HF) solution at room temperature for 20 s. Qualitative EDS (Oxford Inst. 5108 Link) analyses were performed simultaneously with microstructural observations in order to distinguish the various phases.

3. Results and discussion

3.1. Physical and thermal properties

Table 5 gives the particle size distributions of the multipurpose wall and tile bodies, obtained by wet sieve analysis. Furthermore, Table 6 presents some of the important properties of the investigated bodies fired at the relevant peak firing temperatures under industrial conditions in the first part of the study. A comparison of the standard wall and floor tile bodies with the multipurpose tile bodies was made according to the main technological properties measured. The L^*-value (lightness) of the multipurpose floor tile body is higher than that of the standard floor tile body. For the multipurpose wall tile body, the L^*-value is, however, slightly lower compared to that of the standard body. The multipurpose wall tile body exhibits lower values than the standard wall tile body. This is expected since there appears to be higher amount of glassy phase in the multipurpose body thus dissolving more free quartz into the melt. This assumption is

Table 5
Particle size distribution of the multipurpose bodies

Sieve size (μm)	Multipurpose wall tile body, mass on sieve (%)	CMPL (%)	CMPF (%)	Multipurpose floor tile body, mass on sieve (%)	CMPL (%)	CMPF (%)
125	0.28	0.28	100	0.36	0.36	100
63	5.29	5.57	99.72	4.06	4.42	99.64
45	6.62	12.19	94.43	5.85	10.27	95.58
32	6.65	18.84	87.81	6.81	17.08	89.73
−32	81.16	100	81.16	82.92	100	82.92
Total	100.0			100.0		

Table 6
Technological properties and chromatic co-ordinates L^*, a^*, b^* of the tile bodies prepared in the first part of the study

Formulation	Firing regime (°C-min.)	Firing shrinkage (%)	Water absorption (%)	CTE, 10^{-7} °C^{-1} (20–400 °C)	L.O.I.	Flexural strength (kg/cm^2)	L^*	a^*	b^*
Floor tile std.	1200–34	6.00	2.00	70.4	4.86	492.7	56.0	3.4	10.2
Multipurpose floor tile	1200–34	5.00	1.20	72.3	7.42	474.5	62.2	1.4	12.1
Wall tile std.	1170–36	−0.23	14.50	71.9	6.90	282.8	78.4	5.0	13.6
Multipurpose wall tile	1170–36	0.60	11.00	69.4	7.35	306.1	74.7	5.1	15.2

[*] Negative sign means expansion.

Table 7
Technological properties and chromatic co-ordinates L^*, a^*, b^* of the multipurpose wall tile body versus firing temperature

Peak firing temperature (°C)	Firing shrinkage (%)	Water absorption (%)	Bulk density (g/cm^3)	L^*	a^*	b^*
1120	0.19	12.2	1.88	78.6	5.6	15.2
1140	0.45	10.9	1.92	76.5	4.9	15.9
1160	1.27	9.4	2.03	74.7	4.2	16.6
1180	4.23	1.6	2.16	68.0	6.8	15.9
1200	4.57	0.7	2.25	65.8	1.6	14.9

also in line with the measured physical properties of the relevant bodies. Regarding thermal expansion behaviour, although the difference between the thermal expansion coefficients of the floor tile bodies is very similar to that between the wall tile bodies, the multipurpose floor tile exhibits a higher expansion. As can be assessed from the obtained values, by adjusting the formulation and its sieve residue carefully and firing at suitable peak temperatures, it was possible to obtain meaningful technological properties of both floor and wall tiles using a multipurpose body.

Further firings, carried out in order to establish both maturing range and optimum firing temperatures of the multipurpose tile bodies, show that the amount of change in the studied physical properties up to 1160 °C is small (Tables 7 and 8). However, above this temperature, a considerable increase in firing shrinkage and a corresponding decrease in water absorption (directly related to the open porosity) values can be observed, the evolution of the physical properties being more pronounced for the floor tile body. This is expected since the letter has a lower sieve residue over 63 μm compared to the wall tile. The importance of particle physics on kinetics and reaction paths during firing has already been discussed in the literature.[5] It has been suggested that in order to achieve fired homogeneity, diffusion distances should be minimised. Increasing the number of contacts between particles of different mineralogical species enhances the probability that desired reactions occur. Apart from the importance of average particle size and size distribution, it has also been reported that the size, shape and composition of crystalline phases formed during firing are largely controlled by the extent of mixing of starting raw materials.[6] Furthermore, maximum sintering temperature and soaking time should be emphasized as other important parameters for degree of densification. Den-

Table 8
Technological properties and chromatic co-ordinates L^*, a^*, b^* of the multipurpose floor tile body versus firing temperature

Peak firing temperature (°C)	Firing shrinkage (%)	Water absorption (%)	Bulk density (g/cm$^{3)}$	L^*	a^*	b^*
1140	0.68	11.3	1.99	78.7	5.4	15.2
1160	1.45	9.9	2.07	74.7	4.6	16.6
1180	4.73	1.7	2.17	69.8	2.4	16.4
1200	6.09	0.1	2.27	58.9	0.5	12.5
1220	6.15	0.03	2.31	56.5	0.4	11.2

sification at higher temperatures is rate-controlled by the strong dependence of melt viscosity on temperature and by the solubility of solids in the liquid phase, mainly free quartz. On the other hand, it can be remarked that quartz dissolution is the slowest process during firing of such products, and it helps to maintain a higher melt viscosity, even with increasing temperature, which prevents pyroplastic deformation. Maximum firing temperature can be defined by coarsening and solubility of gases filling the closed pores accompanied with a more or less pronounced expansion, called bloating.[7] On the whole, the magnitude of the foregoing physicochemical transformations can vary considerably, depending on the characteristics of the raw materials employed and the complex interplay between them.

According to available studies in the literature, it is the current trend to employ flux-forming additives, both natural (feldspars, nepheline syenite, zeolites, spodumene, etc.)[8–12] and synthetic (including industrial wastes such as waste glass and fly ash) in order to reduce the peak firing temperature and soaking time of triaxial whiteware bodies and thereby reducing the cost of energy without compromising productivity and product quality.[13–17] These additives may, however, produce a rapid rise in the amount of liquid phase in a short time–temperature interval during sintering, thus providing a narrow firing range and a risk of pyroplastic deformation to the ware unless a careful control of formulations is achieved. In addition to the fluxing action of relevant oxides (Na_2O and K_2O), the investigated multipurpose body contains higher amount of MgO compared to the standard tile formulations, originating from the magnesite in the formulation (Table 4). As stated earlier, it is a local material and is mainly magnesium carbonate with a small amount of dolomite, as detected by XRD analysis. Another important property of this material is its fine particle size (mean particle size of around 2.3 μm). The influence of MgO-containing fluxes, such as talc, magnesite, dolomite and chlorite, as sintering promoters, on the vitrification behaviour of different compositions has also been studied by several authors. It has been reported that the concurrent presence of alkaline and alkaline-earth elements promoted the development of a less viscous liquid phase which improved the densification kinetics as long as it was operated within defined limits of composition and firing regime.[18–23] It is also possible that addition of the local magnesite with such fine particle size helps improving the dry mechanical strength to allow the mechanical manipulation of the tile without risk of rupture (Table 2). As referred above, controlling shrinkage on firing is one of the important considerations to achieve a high quality level. Apart from addition of free quartz, high dimensional stability required in fast-fired wall tile manufacture is commonly realised using various calcium containing materials in appropriate amounts such as chalk, limestone, marble, wollastonite and dolomite.[24–28] Considering the fact that both the standard wall tile and the multipurpose bodies in the present investigation involve certain amount of marble in their formulations, it is important to comment briefly on its behaviour during firing. It has been reported that the presence of calcium carbonate ($CaCO_3$) modifies the reactions and affects the formation of the liquid phase. During preheating, the $CaCO_3$ decomposes to CaO accompanied by the evolution of CO_2 outside the structure of fired bodies between 800 and 900 °C. It should be noted that the decomposition happens with slow thermal rates, i.e. <10 °C/min. Then, the free CaO reacts with the amorphous phase (metakaolinite), which quickly diminishes at increasing firing temperature. Thus, the formation of crystalline phases, namely gehlenite as an intermediate phase and anorthite, occurs to a great extent at the expense of the metakaolinite. Free silica appears to be less involved in the formation of new phases and so wollastonite does not arise. The series of reactions with the formation of small liquid phase volume, as expected, result in the body having high porosity.[29–32]

Achieving little or no moisture expansion is an important consideration for wall tile bodies. Otherwise, expansion of fired bodies in contact with moisture causes problems with flatness levels which, over the time, may lead the tiles to come loose or the glazes to fracture. The larger the tile the greater the tension. According to the literature, carbonates, particularly calcite, are effective in decreasing moisture expansion. It has also been mentioned that the influence of crystalline phases such as anorthite in reducing moisture expansion is greater than the role of porosity in some wall tile formulations.[25] However, the moisture expansion measurements of the tile bodies using autoclave treatment were not included in the present study.

It is known that porosity decreases mechanical strength by effectively reducing the materials cross sectional area. Pores can concentrate stress and reduce the flexural stress necessary to the rupture. The best criterion to indicate the reduction of porosity is bulk density. Generally, the higher the bulk density the higher the modulus of rupture (MOR). MOR is the most widely used method to characterise the mechanical behaviour of traditional ceramic bodies due to its simplicity and is calculated by the three- and four-points methodologies.[33,34] With reference to Tables 7 and 8 once again, it is expected that the firing temperatures that gave the highest values of bulk density for both bodies be also expected to provide the maximum flexural strength values. Apart from the effect of degree of densification on flexural strength, it is also important to consider the effect of type, morphology and amount of crystalline phases formed during firing. It has been reported that increased strength and toughness in clay–quartz–feldspar triaxial compositions can be partially explained with increased secondary mullite content and randomly interwoven nature of high-aspect-ratio mullite needles in a glassy matrix (mullite hypothesis).[35] On the other hand, little attention has been paid to the role of other crystalline phases, such as anorthite, in strengthening whiteware bodies although tri-dimensional dispersion of anorthite crystals in an aluminosilicate matrix has been shown to be beneficial to the overall mechanical strength.[26,30] The results on the breaking strength obtained from the industrially fired samples are given in Table 6. As can be seen, the strength of the multipurpose wall tile body is higher compared to that of the standard wall tile body, thanks to its better densification. On the other hand, there does not seem to be major difference in the strength values of the standard and multipurpose floor tile bodies. It is worth mentioning that a standard deviation of the presented data regarding the technological properties of the investigated bodies is needed to make such comparisons more reliable.

Tables 7 and 8 also set out the values of the chromatic coordinates of the multipurpose tile bodies with increasing peak temperature. It can be observed that L^*-value decreases as both bodies approach vitrification at higher temperatures. This is probably due to increased intensity of colour forming oxides such as Fe_2O_3 and TiO_2 present in the raw materials at such temperatures. Moreover, the decrease in L is higher for the multipurpose floor tile body where a higher amount of glassy phase is expected. Indeed, it has been shown that reducing the quantity of these oxides in a standard porcelain tile composition raises the degree of whiteness in the fired product, in other words; co-ordinate L^* increases and co-ordinate b^* (yellowness) decreases. However, at the same chromophore impurities content, the final whiteness of a vitrified body depends on the nature and proportion of the phases developed during firing. For example, it was indicated that the mullite structure can accommodate Fe^{3+} ions in the form of a solid solution, producing additional whitening.[2] It is worth mentioning that small variation in the chromatic coordinates of the multipurpose tile bodies may be attributed to the differences in the corresponding firing regimes.

Figs. 1 and 2 represent the sintering behaviour of the standard and the multipurpose tile bodies obtained by using a double-beam optical non-contact dilatometer, an equipment specifically designed to reach a high heating rate to reproduce industrial firing cycles. Consequently, it allows precise determination of the best firing profile for any porcelain stoneware composition without the problem of mechanical dilatometers (i.e. the contact of the micrometer above the softening temperature modifies the measurement).[36] In the figures, all the graphs were plotted with time on the x-axis and both temperature and sintering percentage on the y-axis. The derivative of the sintering curve (dy/dT) is also presented on the graphs in order to identify certain critical temperatures, called as "flex" points, corresponding to the maximum amount of expansion, fastest sintering rate and end of sintering. According to the dilatometric curves of the standard and multipurpose wall tile bodies in Fig. 1, both show expansion up to around 900 °C (first flex point) prior densification occurs. The derivative sintering curve of the standard body reaches the zero line at 1167 °C (second flex point) with slight expansion. Almost the same second flex temperature was found for the multipurpose body. Similar temperature and expansion values (first flex point) were also found from the representative dilatometric curves of the standard floor and the multipurpose floor tile bodies before densification (Fig. 2). The maximum sintering rates were achieved almost at the same temperature, 1200 °C (second flex point), for both bodies. During the dwell period, both bodies continued to shrink and reached values of 3.6% for standard body and 3.0% (third flex point) for the multipurpose body near the end. It should be stressed out that the most important parameter to focus during studying thermomechanical behaviour of such bodies is not the total amount of shrinkage, but the sintering rate. The differences in terms of size stability and attitude to develop deformations during firing are controlled by the sintering rate. In fast firing, if the sintering rate is very high, then the heat transfer mechanisms create big differences in temperature among side and centre, even among corners and sides of the tiles and under the worst conditions, these stresses may lead to unrecoverable plastic deformation.[37] Taking this knowledge into account, the above data illustrates that the multipurpose bodies exhibit similar sintering rate to their standard counterparts.

3.2. Phase analysis

The main crystalline phases of the green body disappears during firing and are replaced by new phase development as shown by the XRD patterns of the standard and multipurpose tile bodies fired under industrial conditions (Figs. 3 and 4). The presence of quartz, plagioclase and mullite is easily detectable in the spectra. It is known that most of the reactions occurring during firing of traditional tile bodies are kinetically governed processes that do not reach thermodynamic equilibrium, since the industrial firing cycles are as short as half-an-hour. This explains the common occurrence of crystals of quartz and feldspars that have not been entirely transformed in the fired bodies. Another important observation in Figs. 3 and 4 is that the intensity of main reflections from plagioclase on the patterns of multipurpose tile bodies enhanced (marked with arrows) indicating crystallisation of a new phase. For the purposes of description, plagioclase feldspars are ubiquitous and represent the commonest rock forming minerals. They consist of solid solutions of albite ($Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2$) and anorthite ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$) in all proportions at all temperatures; expressed in another way, the substitution of CaAl in the lattice in place of NaSi results in a complete gradation between the two end members of the plagioclases.[38] Consequently, formation of a new phase with an intermediate composition between anorthite and albite is expected in the standard wall tile and the multipurpose tile bodies containing considerable amount of marble. To be more specific, considering the firing temperatures involved, crystallisation of a calcium rich phase, probably anorthite, is more likely. Indeed, the reflections marked with arrows in Figs. 3 and 4 coincide with the triclinic anorthite standard (JCPDS No.: 41-1486), which has the main peaks near the albite ones (JCPDS No.: 009-0466).

According to the XRD spectra of the green multipurpose wall and tile bodies, they both initially contained illite, kaolinite, quartz, plagioclase and calcite (Fig. 5). An overall examination of the typical XRD spectra of the multipurpose floor tile body fired under laboratory conditions showed that quartz is again one of the main mineral species as the unreacted residue of excess quartz present in the body (Fig. 6). The improved baseline due to the presence of a large amount of glassy phase with the increase with the firing temperature is noticeable on the spectra. Furthermore, it may also be expected that the quartz dissolution into the melt for the multipurpose floor tile body at higher thermal levels is greater, although no clear diminution of quartz reflections is appreciable in Fig. 6. In addition, change in the intensity of the plagioclase reflections is evident (marked with arrows) such that the rise in the firing temperature result in the development of characteristic anorthite peaks. In order to illustrate trends in albite disappearance and anorthite development, however, a detailed XRD study is required.

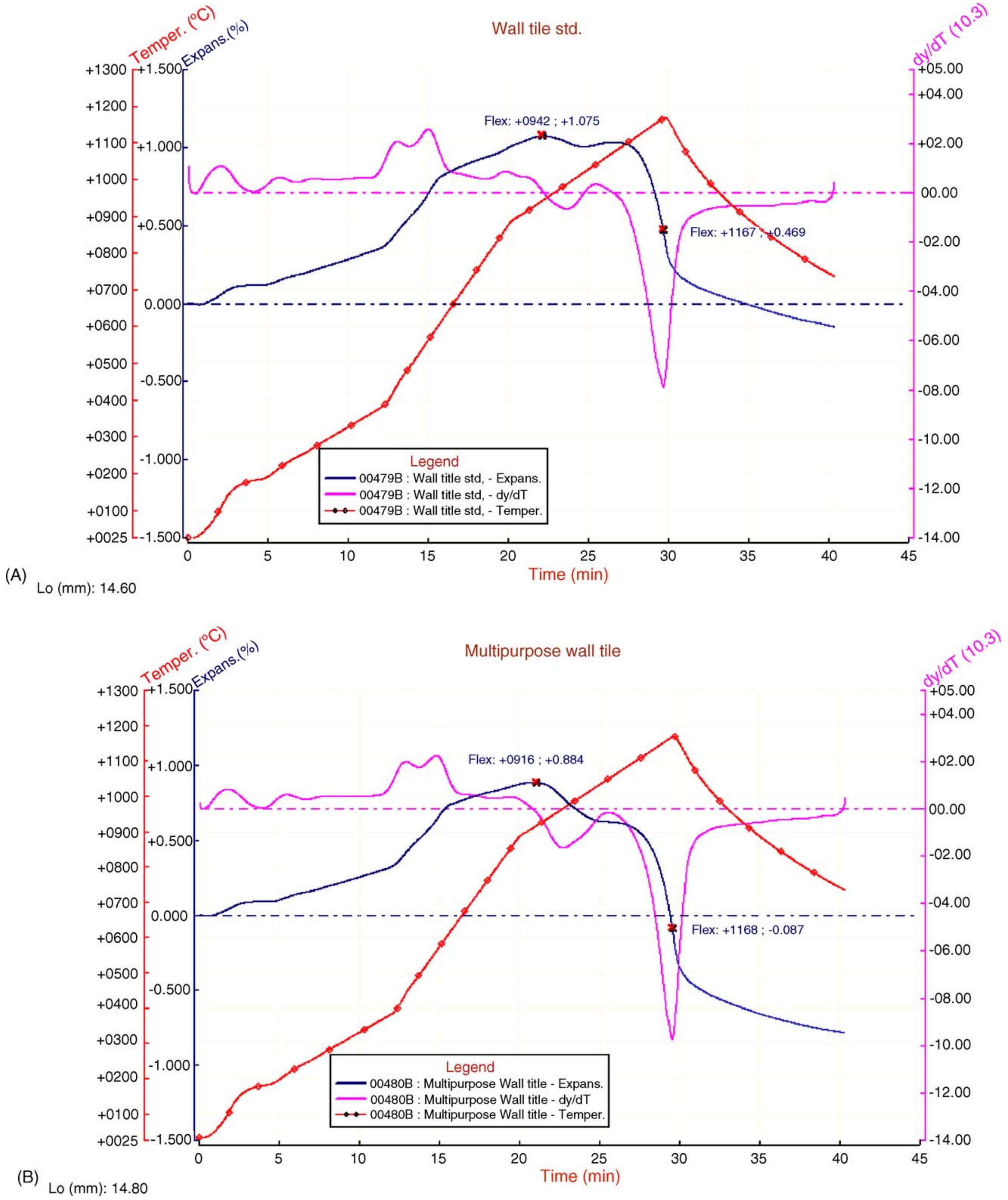


Fig. 1. Dilatometric curves of the standard (A) and the multipurpose wall tile body (B).

It should be noticed that mullite was not detected in the XRD analysis of the multipurpose bodies. Presumably, its amount is below the detection threshold of the method. Furthermore, it is known that the formation of anorthite decreases the amount of mullite, since the reaction between silica, alumina and calcium compounds to give anorthite occurs at lower temperatures with respect to the characteristic temperature for mullite formation. This is also in agreement with other studies on traditional bodies containing calcium compounds and with the phase diagram of the ternary $CaO–Al_2O_3–SiO_2$ system.[29–31] No newly formed

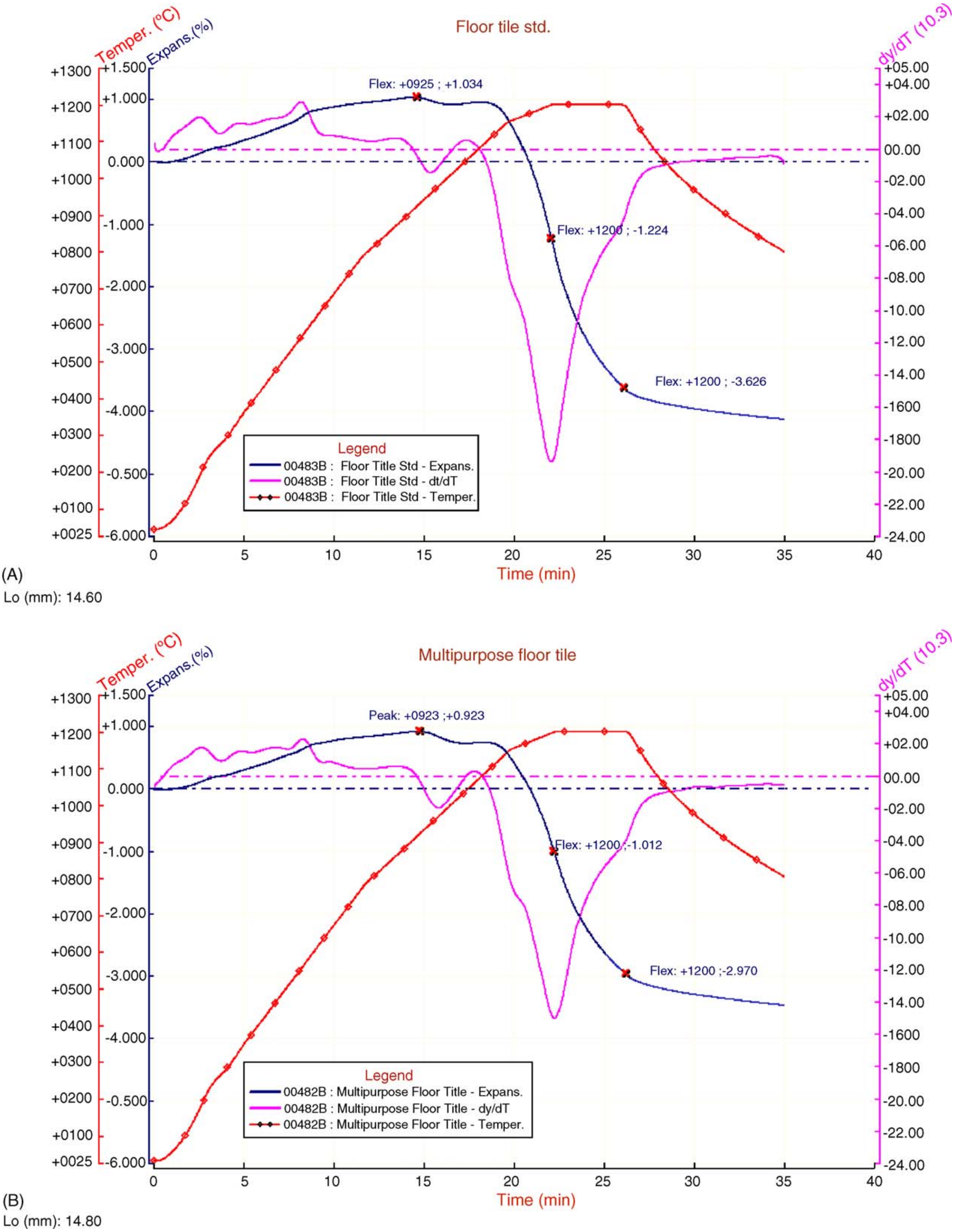


Fig. 2. Dilatometric curves of the standard (A) and the multipurpose floor tile body (B).

crystalline phase rich in magnesium was observed. This is an indication that magnesium resides in the liquid phase at the firing temperatures involved thus contributing early densification of the relevant formulations.

3.3. Microstructural analysis

BE images taken from the polished surfaces of the industrially fired standard and multipurpose floor tile bodies are presented

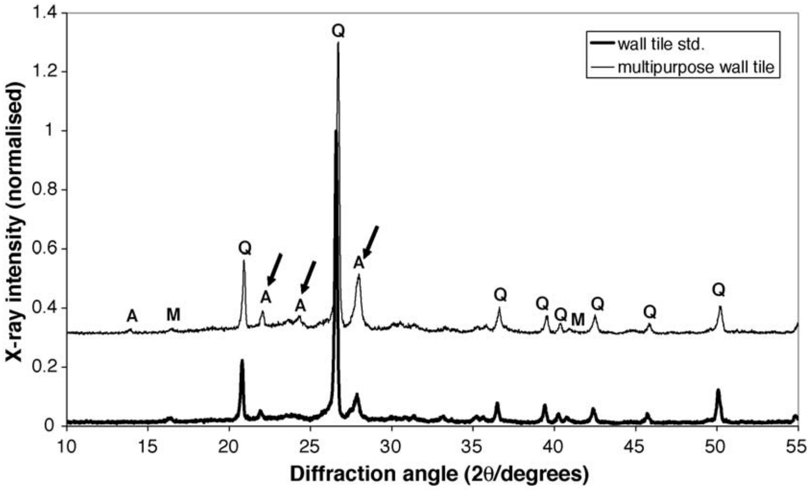


Fig. 3. XRD patterns of the standard and multipurpose wall tile bodies fired at 1170 °C under industrial conditions (A: plagioclase (albite, anorthite), M: mullite, Q: quartz).

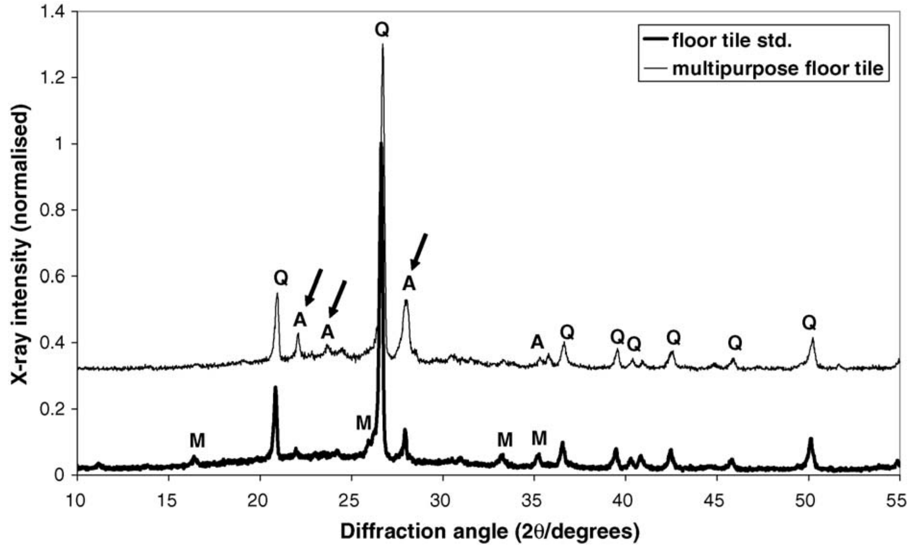


Fig. 4. XRD patterns of the standard and multipurpose floor tile bodies fired at 1200 °C under industrial conditions (A: plagioclase (albite, anorthite), M: mullite, Q: quartz).

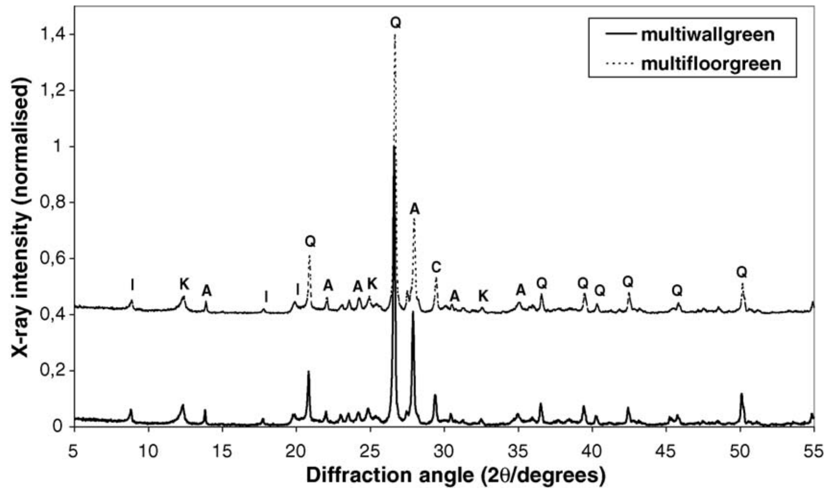


Fig. 5. XRD patterns of the green multipurpose wall and tile bodies (I: illite, K: kaolinite, Q: quartz, A: plagioclase (albite, anorthite), C: calcite).

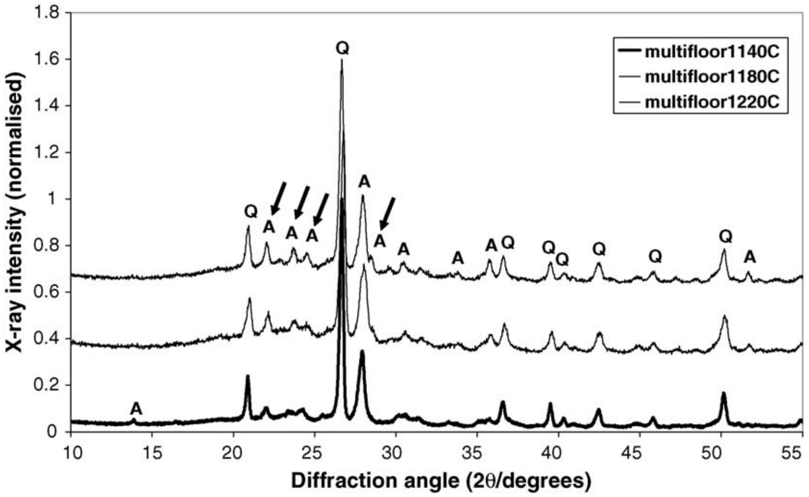
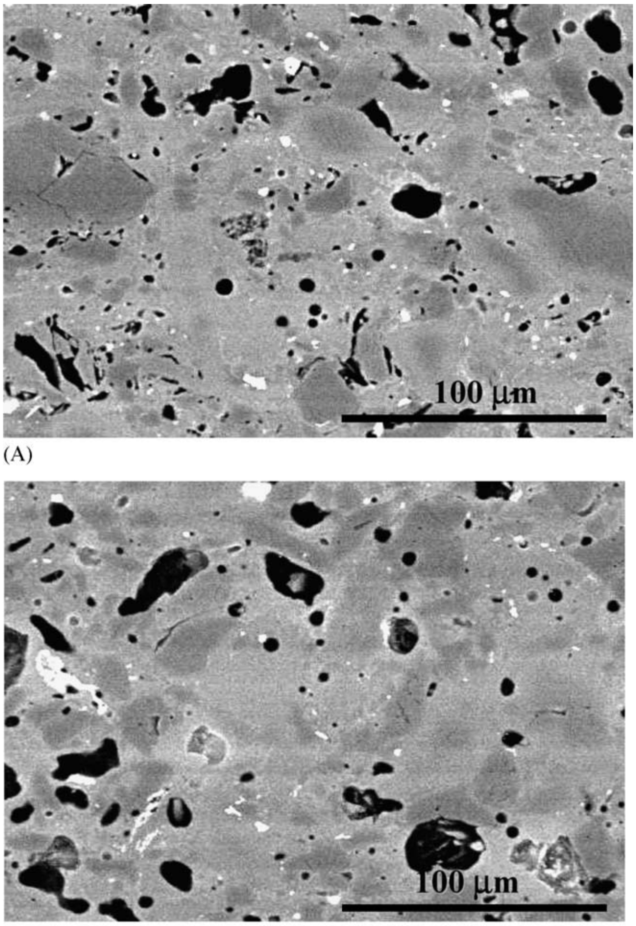


Fig. 6. XRD patterns of multipurpose floor tile body fired at 1140 °C, 1180 °C and 1220 °C under laboratory conditions (A: plagioclase (albite, anorthite), Q: quartz).

in Fig. 7. In back scattered mode, the areas with higher concentration of heavy elements appear brighter than the rest. Both bodies show a similar degree of densification. The main difference was, however, detected using EDX as the presence of calcium in the multipurpose body originating from the marble in the formulation. The polished surface of the multipurpose floor tile body fired at 1140 °C exhibits a large amount of porosity, represented as dark areas, with a variety of pore sizes, their irregular shape, and presence of particles with sharp edges can be taken as characteristics of the initial stages of vitrification (Fig. 8A). In addition, a typical SE image taken on the fractured surface etched with 10% HF solution for 20 s to selectively remove the glassy matrix shows some of the constituent crystalline phases (Fig. 8B). Here, attention should be paid at the presence of small spheroidal crystals forming clusters (marked with arrows) that contain mainly elements of calcium, aluminium, silicon and oxygen (Fig. 8C) so being attributable to anorthite, the main crystalline phase that appears during firing at high temperatures. The formation and physical characteristics of this phase have been previously treated and the existence of spheroidal as well as prismatic crystals of anorthite in porcelain and bodies has been reported.[26] Considering the morphology of the spheroidal crystals in Fig. 8B, anorthite is believed to be of primary formation.



(A)

(B)

Fig. 7. Typical BE images of the polished surface of the standard (A) and the multipurpose (B) floor tile bodies fired at 1200 °C under industrial conditions (quartz grains appear in dark gray).

From the SEM investigation of the multipurpose floor tile body fired at 1220 °C under experimental conditions, the extent of vitrification with increasing peak temperature can be clearly observed (Fig. 9). As mentioned earlier, at higher temperatures liquid phase becomes progressively less viscous and is able to eliminate larger pores. The number of small pores thus decreases, while the larger pores become more isolated and start acquiring a rounded shape. In lower viscosity melts, gas bubbles can more quickly achieve their spherical equilibrium shape than in more viscous melts. Thus, the pore geometry in samples exposed to same heat treatment gives evidence to the relative viscosity of their melts and the degree of densification. From Fig. 9, it is also evident that the sharp corners of the quartz grains were somewhat rounded by surface tension forces and their partial solution into the glassy matrix during firing. Moreover, the presence of microcracking around and within the large quartz grains is clearly visible. Such microcracking is expected since differential stresses may arise as a result of the thermal

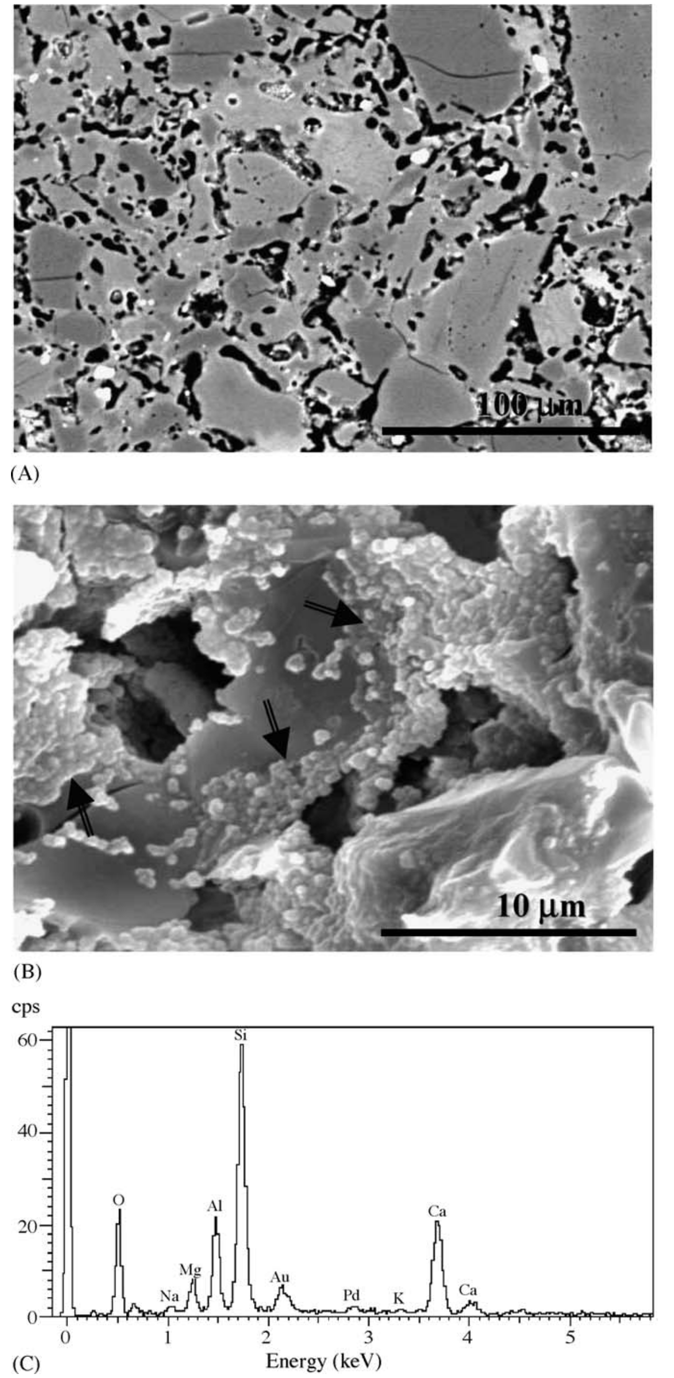


Fig. 8. A typical BE image of the polished surface of the multipurpose floor tile body fired at 1140 °C under laboratory conditions (A); SE image of the HF-etched surface of the multipurpose floor tile body fired at 1140 °C under laboratory conditions (B); EDS analysis of a cluster of spheroidal crystals in B (C).

expansion mismatch on cooling between the quartz grains and surrounding glassy matrix during the rapid displacive β- to α-phase transformation of quartz. The cracking severity largely depends on cooling rate. Such cracking may also be generated as a result of induced stresses during specimen preparation for microscopy such as grinding and polishing. Regarding the role of residual quartz in strengthening the structure of porcelain tile, there have been two mechanisms addressed in the literature. In the first place, the quartz crystals provide resistance to crack propagation by microcrack formation. In the second place, a crack deviation mechanism occurs in the vicinity of quartz grains.[39] However, there is still a conflict between researchers for the positive or negative influence of quartz on porcelain strength due to many interfering parameters.[40] Etching the multipurpose floor tile body fired at 1220 °C exposed small crystals embedded in glassy matrix (Fig. 10A) and elongated, lath-like grains, randomly oriented in glassy matrix mainly occurring near large pores (Fig. 10B). Fig. 10C depicts the representative EDX analysis obtained from one of these lath-like crystals consistent with anorthite. A similar occurrence was attributed to calcite decarbonation during firing, leading to higher local calcium concentration which favours the in situ anorthite formation.[41]

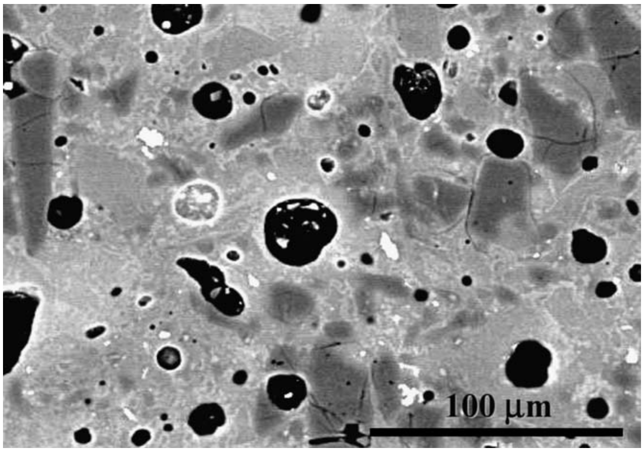


Fig. 9. A typical BE image of the polished surface of the multipurpose floor tile body fired at 1220 °C under laboratory conditions (quartz grains appear in dark gray).

Although XRD did not reveal mullite ($3Al_2O_3{\cdot}2SiO_2$) in the multipurpose bodies, SEM was further used to investigate its presence. According to the literature, mullite generally occurs in two morphologies: besides the well-known elongated needle-shaped mullite (also named as secondary mullite since it forms later in the firing process), it also occurs as a fine crypto-crystalline mass of scaly patches (primary mullite). Primary mullite is composed of aggregates of small mullite seeds. These are primary, as they form directly from the pure clay agglomerate relicts; secondary mullite is formed from the feldspar-rich melt by dissolution and recrystallisation. It is also known that primary mullite is susceptible to dissolution and recrystallisation in the presence of the increased silica content of the melt, which in turn is influenced by the dissolution of quartz. Furthermore, a third form of mullite has been reported to be present in porcelains containing α-alumina as filler and it is termed as tertiary mullite. Tertiary mullite is precipitated from alumina-rich melt formed from dissolution of the alumina filler but has been observed only in minor quantities. The size and shape of mullite crystals is to a large extent controlled by the fluidity of local liquid matrix from which they precipitate, and in which they grow, which itself is a function of its temperature and composition.[6] Secondary mul-

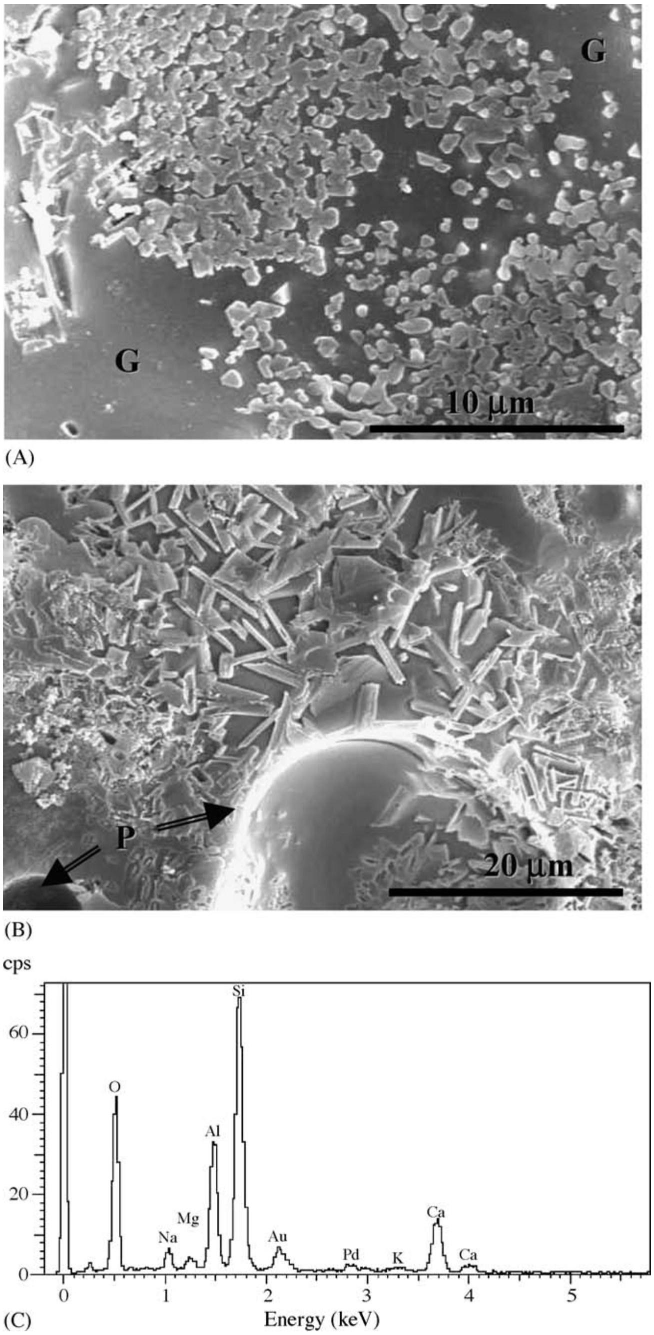


Fig. 10. SE images of the polished and HF-etched surface (A and B) of the multipurpose floor tile body fired at 1220 °C under laboratory conditions (G: glass, P: pore); EDS analysis of a lath-like crystal in B (C).

lite crystals, approximately <1 μm in size, are present in the multipurpose floor tile body fired at 1220 °C with characteristic needle-like morphology (Fig. 11A) and at places a strong *iso*-orientation as in Fig. 11B The EDX analysis shows the presence of mainly aluminium, silicon and oxygen elements (Fig. 11C). Mullite has a variable stoichiometry where the alumina-to-silica ratio ranges from 2.5 to 3.5. The similar amounts of aluminium and silicon in the EDX analysis may be due to signal interference from neighbouring areas making it possible to assume that the needle-shape crystals are mullite.

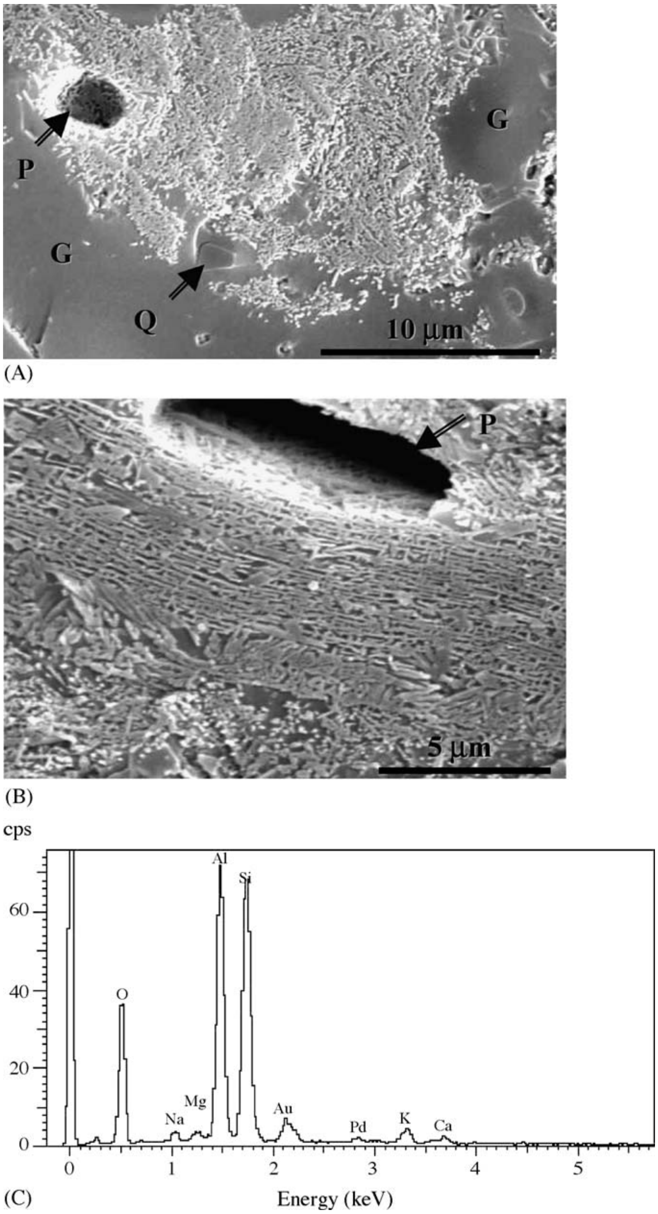


Fig. 11. SE images of the HF-etched fracture surfaces (A and B) of the multipurpose floor tile body fired at 1220 °C under laboratory conditions (G: glass, P: pore, Q: quartz); EDS analysis of a needle-like crystal in B (C).

4. Conclusions

As a result of the preparation of a series of body formulations at different sieve residues mainly from local raw materials and firing over a range of peak temperatures, a multipurpose body was produced, almost fulfilling the requirements of both wall and floor tiles in accordance with ISO-EN 10545. In particular, the sieve residues of 3.0% for the floor tile and 5.5% for the wall tile were close to the industrial ideal for a multipurpose body.

The vitrification behaviour of the multipurpose body was also appraised and it was found to be similar at both sieve residues. The optimum firing temperature ranges under laboratory conditions were from 1120 to 1140 °C (wall) and 1180 to 1200 °C (floor). It is worth restating that increased presence of magnesite, as a co-fluxing material, in the multipurpose body seems to accelerate the vitrification process. It was also shown that a large amount of information on the firing behaviour of the investigated bodies can be obtained from the non-contact dilatometer measurements. XRD spectra supported with the SEM investigation of selected fired samples indicated the presence of anorthite as newly formed and quartz and albite as residual crystalline phases, plus a small amount of mullite and glassy phase. The anorthite and mullite were observed to be tri-dimensionally dispersed in a silico-aluminate matrix.

To sum up, employment of the multipurpose body developed in this study seemingly has the potential to bring certain advantages in terms of production. Regarding possible single fast firing difficulties of $CaCO_3$ presence in the experimental bodies due to its decomposition in a wide temperature range, alternative calcium-containing raw materials that do not emit gas during firing, such as wollastonite ($CaSiO_3$), may be offered, although their cost restricts use to the most expensive products. Further modifications are also needed regarding body preparation, pressing variables, such as pressure and moisture content, and the firing conditions in order to obtain better values of the relevant technological properties and consequently to achieve the suitability of the new multipurpose body for industrial application.

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