SINTERING MECHANISMS OF PORCELAIN STONEWARE TILES

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ABSTRACT

The sintering of porcelain stoneware tiles – a low porosity product with excellent technical performances produced in slabs up to 1 m^2 – is accomplished in roller kilns with fast cycles (<60 min) at maximum temperatures in the 1180-1240°C range. The main limit in further development of this product is its residual porosity, consisting of 2-8% closed pores, that is detrimental to its mechanical and tribological properties as well as the resistance to stains of polished tiles. Several industrial and experimental body formulations were studied by isothermal and constant rate optical thermodilatometry, quantitative XRPD, SEM and BET, in order to understand which mechanisms are active during the whole sintering path. In the initial stage, a strong reduction of specific surface occurs with negligible shrinkage, suggesting that surface diffusion is the leading mechanism below 1000°C. The main transformations are breakdown of clay minerals with formation of amorphous components, then over 1000 °C mullite and viscous phase. In the intermediate step, densification is accomplished with increasing rate from 1050 to 1200°C, being a viscous flow the basic mechanism. However, the maximum shrinkage at each temperature is not related to the amount of viscous phase, so densification seems to be mainly governed by viscosity of the liquid phase. In the final stage, a more or less conspicuous coarsening is observed, essentially over 1175°C, with development of coarse pores. Then a decreasing densification rate is contrasted by a coarsening mechanism, promoted by the wide range of pore and particle sizes of green compacts, and an important role is probably played by changes in the solubility of solids and gases in the liquid phase.

1. INTRODUCTION

Porcelain stoneware is a glass-bonded material with excellent technical performances for ceramic tiles, such as mechanical, wear, frost and chemical resistance. In the last decade, the growth rate of the global production of porcelain stoneware tiles increased more than other ceramic products; in fact, the technical properties of porcelain stoneware, coupled with even more improved aesthetic appearance, gave it a prominent role on the tile market[1].

Porcelain stoneware bodies consist mainly of a mixture of ball clays (30-40%), alkaline feldspars (40-50%), and quartz sands (10-15%). Their chemical composition may vary depending on the kind of fluxes (sodium or potassium feldspars) and their ratio, the possible use of sintering aids (i.e. alkaline-earth compounds, such as dolomite, talc or wollastonite) or glass-ceramic frits (e.g. $CaO-ZrO_2-SiO_2$, $CaO-MgO-SiO_2$, $BaO-Al_2O_3-SiO_2$ systems)[2-3].

The tiles are sintered by fast single firing (<60 minutes cold-to-cold, ≅1200°C of maximum temperature and 5-10 minutes soaking time) and the resulting phase composition consists of crystalline phases, both new formed (mullite) and residual ones (quartz, feldspars) embedded in an abundant glassy matrix.[4-5].

The main standard requirement for porcelain stoneware is a very low water absorption (<0.5% according to ISO 13006) that is largely fulfilled, being <0.1% in the products. In the industrial sintering process, a residual closed porosity cannot be completely removed – ranging usually from 2 to 8% - consisting of both small (<10 μm) spheroidal, gas-filled pores and irregularly shaped, coarser pores (up to 50μm) probably resulting from coalescence of smaller ones[6-7]. This is the main limit in further development of porcelain stoneware because is detrimental to the flexural modulus of rupture (max 80 MPa), Young's modulus (max 75 GPa), abrasion resistance (no less than 110 mm^3 of materials removed according to ISO 10545-6) and particularly resistance to stains of polished tiles.

The densification is achieved by particle rearrangement and viscous flow, occurring over 1100°C, with a linear shrinkage around 8 cm/m. Many sintering mechanisms are contemporarily active (melting, pore coalescence and coarsening, etc.) due to a wide range of pore and particle size in the green compacts, making difficult any efficacious design of the microstructure of porcelain stoneware. However, the densification appears to be rate-controlled by the strong dependence of melt viscosity on temperature and by the solubility of solids in the liquid phase. Nevertheless, in the final stage, coarsening and solubility of gases filling the closed pores become the most important phenomena affecting the microstructure[8].

The aim of this study is to understand better the mechanisms active during the whole sintering path of porcelain stoneware tiles, in order to achieve a phenomenological model of the process. In fact, notwithstanding the considerable innovation in the industrial firing technology (e.g. use of roller kilns, accurate control of temperature, great flexibility in time/temperature curves) the sintering process is still developed with an empirical approach (i.e. trial-and-error in the design of both sintering curve and body formulation). A scientific viewpoint is now necessary to accomplish any further material enhancement.

2. MATERIALS AND METHODS

Two samples of industrial bodies (ATP and AT) and five simplified compositions were studied: prevalently sodium (Na and NaB) or potassium (K and KB) and mixed sodium-potassium (NaK). Every body consists of a mixture of ball clay, quartz sand and sodium or potassium feldspars, with the bulk chemical composition listed in Table 1. These bodies were experimented at a laboratory scale, simulating the industrial tile making process, by mixing the raw materials, wet grinding in porcelain jar with dense alumina media (18h), followed by granulation and humidification with 5-6% water, uniaxial pressing (40 MPa) of 110 x 55 x 5 mm^3 tiles, then drying in electric oven at 105±5°C. All samples were characterized by isothermal and constant rate optical thermodilatometric analysis using a hot stage microscope (Expert System Misura). Isothermal tests were carried out at different maximum temperatures (heating rate 80°C/min to 1100, 1125, 1150, 1175 and 1200°C). Their interpretation allowed to calculate:

a) densification rates,
b) apparent energy of activation by Arrhenius[9],
c) the Avrami kinetic parameter[10].

In order to estimate the actual phase composition at high temperature, the bodies underwent a water quenching:

- at different temperatures (1050-1200°C) and times corresponding to the maximum densification (Figure 1);
- at different times up to the maximum densification at 1200°C (Figure 2).

%wt	AT	ATP	NaB	Na	NaK	K	KB
SiO_2	72.73	73.89	71.04	70.00	69.66	69.31	65.18
TiO_2	0.60	0.54	0.22	0.72	0.67	0.63	0.23
Al_2O_3	18.76	17.50	20.98	21.27	20.96	20.65	24.98
Fe_2O_3	0.62	0.58	0.56	0.46	0.45	0.44	0.55
MgO	0.24	0.49	0.41	0.30	0.28	0.27	0.48
CaO	0.79	0.58	0.77	0.38	0.34	0.30	0.28
Na_2O	4.51	4.16	4.76	5.66	3.67	1.69	0.69
K_2O	1.74	2.27	1.25	1.21	3.96	6.71	7.62

Table 1: Chemical composition of industrial and simplified bodies for porcelain stoneware tiles.

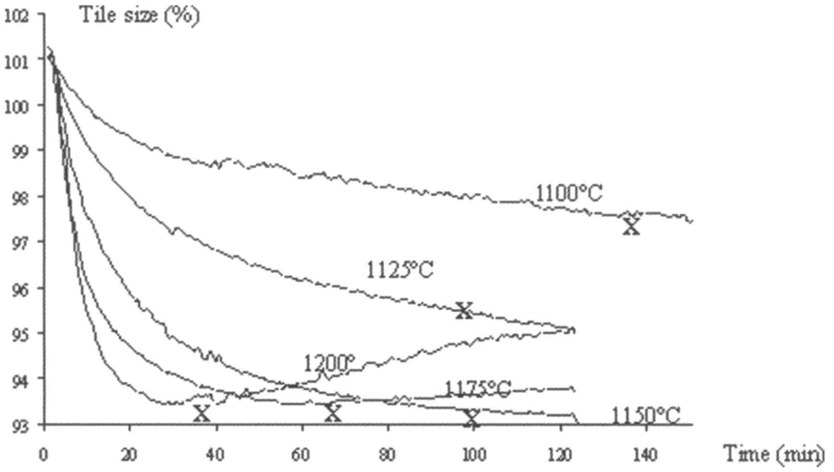

Figure 1: Isothermal densification curves for the industrial sample AT. The X symbols indicate for each temperature the time of maximum densification at which quenching was done.

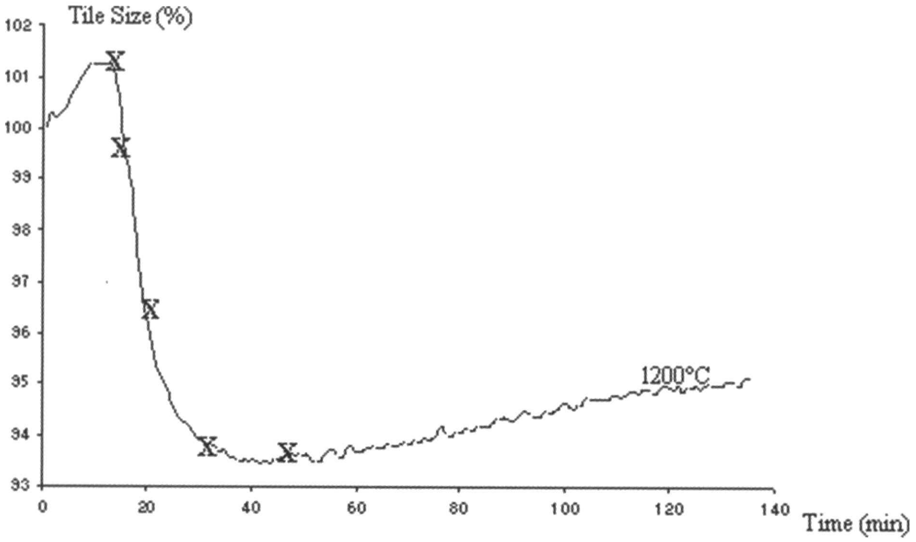

Figure 2: Isothermal (1200°C) densification curve for the industrial sample AT. The X symbols indicate the times of progressive densification at which quenching was done.

Green compacts were characterized by testing (Table 2): particle size distribution (photosedimentation, ASTM C 958), bulk density (geometrical method) and relative density (specific weight of powders by He pycnometry).

The quenched specimens were characterized analysing:

- phase composition by RIR-XRPD method, using CaF_2 as internal standard (Rigaku Miniflex, CuKα radiation);
- specific surface BET (Flowsorb II 2300 Micromeritics);
- microstructure through SEM observations (Leica Cambridge Stereoscan 360).

Some physico-chemical properties of the liquid phase –such as viscosity and surface tension at high temperature– were estimated on the basis of its chemical composition[11-12].

Property	Unit	AT	ATP	NaB	Na	NaK	K	KB
Median particle size	μm	5.6	6.0	6.6	3.5	4.2	4.0	4.9
Bulk density	g/cm^3	1.92	2.07	1.95	1.86	1.89	1.91	1.90
Relative density	1	0.738	0.796	0.750	0.721	0.735	0.726	0.725

Table 2: Physical properties of green bodies.

3. RESULTS AND DISCUSSION

The firing behaviour of porcelain stoneware tiles is characterized by three main steps, as can be seen in a typical constant rate curve (Figure 3):

- initial stage, corresponding to small size variations, extending usually up to 1050-1100°C;
- intermediate stage, accounting for most densification, usually in the 1100-1200°C range;

- final stage, where a more or less pronounced expansion occurs, due to a coarsening effect.

During each of these stages, several phase transformations occur, involving:

a) decomposition of clay minerals,
b) partial melting of feldspars-quartz eutectic compositions,
c) formation and solution/precipitation of mullite,
d) progressive dissolution of quartz in the liquid phase in absence of feldspars.

In particular, the breakdown of clay minerals brings about the formation of amorphous phases (e.g. metakaolinite) that around 1000 °C are converted to mullite + silica (from metakaolinite) or mullite + K-rich liquid phase (from illite).

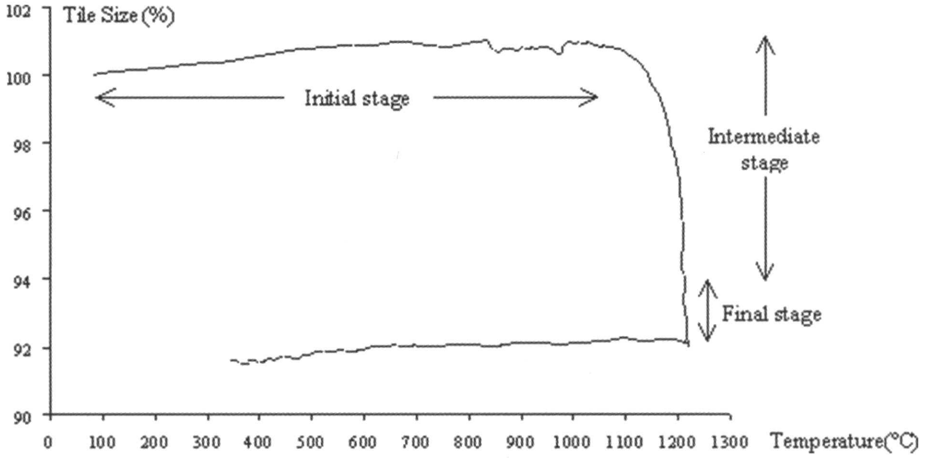

Figure 3: Example of constant rate sintering curve of an industrial sample of porcelain stoneware tile.

3.1. INITIAL STAGE

For the study of the early stage of sintering, an industrial body was quenched after firing at 900°C or 1000°C from 20 minutes to 24 hours of soaking time. The main sintering mechanism was evaluated by comparing the evolution of specific surface area (with respect to the value S_0 of the unfired body) versus linear shrinkage (Fig. 4).

A strong reduction of specific surface was found already at the lowest temperature for the shortest time (i.e. 900°C – 20 min) coupled with a negligible expansion. The specific area reduction increases progressively up to 93%, while the linear shrinkage is always below 1%. This trend of linear shrinkage to specific surface suggests that the leading mechanism for sintering at temperature below 1000°C is surface diffusion[12].

For higher temperatures, a viscous mass transport begins with a relevant shrinkage (3.5% at 1000°C for 24h) with just a limited further drop of specific surface (96%). The main transformation during the firing up to 900-1000°C is the clay minerals decomposition, giving rise to the formation of an amorphous phase and successively of primary mullite. There is a clue of a limited development of a feldspathic melt starting approximately from 900 to 1000 °C. (Table 3). In fact, a considerable amount of amorphous phase is formed, to a large extent after metakaolinite (mullite is not found yet) and an initial fusion of feldspar-quartz eutectics.

At 900°C it is evident a stabilization of the phase composition with increasing time, which represents a possible equilibrium condition. At 1000°C, the formation of mullite occurs together with a significant increase of liquid phase, which brings about the formation of about 20% of a feldspar-rich eutectic.

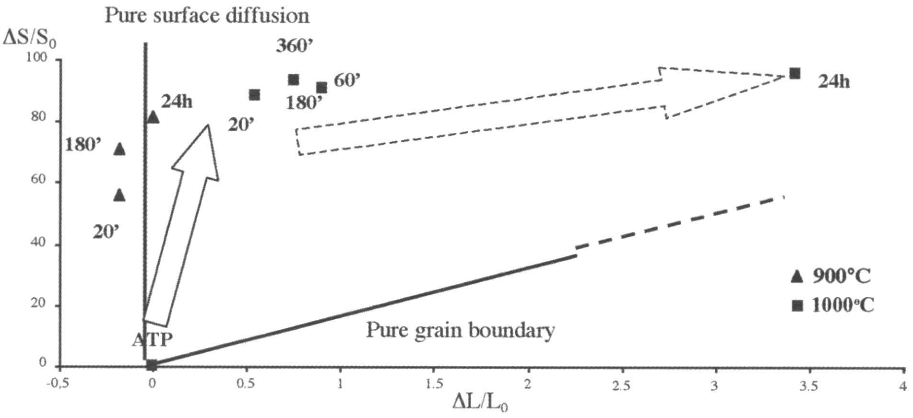

Figure 4: Relationship between linear shrinkage ($\Delta L/L_0$) and reduction of specific surface area ($\Delta S/S_0$)[13].

Phase (wt %)	900°C 20 min	900°C 24h	900°C 3h	1000°C 20 min	1000°C 24h
Mullite	-	-	-	-	10.8±1.9
Quartz	37.5±1.5	27.1±2.8	27.6±1.0	32.8±1.5	23.2±1.1
Cristobalite	0.8±0.0	3.3±0.4	2.4 ±0.2	2.9±0.2	2.9 ±0.1
Plagioclase	32.0±0.5	22.8±2.4	23.6±1.5	23.1±0.9	13.8±0.1
K-Feldspar	4.8±0.3	-	-	-	-
Amorphous phase	25.0±1.8	47.0±3.0	46.0±2.8	41.0±3.3	49.0±4.1

Table 3: Phase composition of the industrial body ATP during the initial sintering stage (after quenching at 900 and 1000°C).

3.2. INTERMEDIATE STAGE

Approaching the intermediate stage of sintering, the seven samples underwent quenching from 1100 to 1200°C for soaking times corresponding to the maximum densification obtained from the isothermal curves.

The phase composition at the maximum densification does not change much for different sintering temperatures: there is just an increasing dissolution of quartz at higher thermal levels, with small variations in the amounts of mullite and glassy phase (Table 4).

The chemical evolution of the viscous phase is represented in the ternary diagram SiO_2-$NaAlSi_3O_8$-$KAlSi_3O_8$, which accounts for ≥95% of the bulk chemical composition of the porcelain stoneware bodies here considered (Figure 5). The graph indicates that –after the quick initial melting of feldspar-quartz eutectics– the main change in the chemistry of the viscous phase is a gradual enrichment in silica without relevant variations of the Na/K ratio. The sodium formulations exhibit often a narrower range of composition with respect to potassium bodies, resulting overall richer in silica.

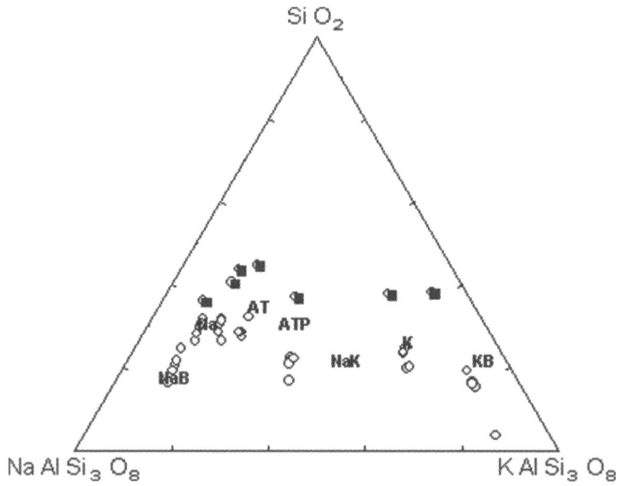

Figure 5. Plot of liquid phase compositions in the ternary diagram SiO_2-$NaAlSi_3O_8$-$KAlSi_3O_8$ at increasing temperatures (1100-1200°C) for time corresponding to the maximum densification. Black squares = bulk composition of the porcelain stoneware body.

Sample	Isothermal sintering to max densification										
	Temperature (°C)	Mullite	s.d	Quartz	s.d	K-Feldspar	s.d	Na-Feldspar	s.d	Vitreous phase	s.d
K	1100	11.7	1.1	18.6	1.5	0.3	0.1			69.4	4.7
	1125	13.7	1.5	17.4	1.7	0.4	0.1			68.5	3.5
	1150	10.7	1.9	15.0	1.2					74.3	3.8
	1175	9.4	1.4	13.4	1.2	0.6	0.1			76.6	1.8
	1200	10.8	1.4	13.7	0.8					75.5	4.8
Na	1100	12.0	1.3	12.0	1.4	0.7	0.1			75.3	4.5
	1125	11.9	1.1	14.3	1.3					73.8	4.1
	1150	12.4	1.1	18.0	1.6	0.9	0.1			68.7	6.5
	1175	13.7	1.7	13.1	0.8					73.2	5.4
	1200	16.3	1.6	14.2	1.2					69.5	5.1
NaK	1100	12.2	1.6	14.9	1.4	1.1	0.1	0.7	0.1	71.0	4.3
	1125	11.5	1.1	13.1	1.5	0.5	0.1	0.3	0.1	74.6	1.8
	1150	11.3	1.4	14.9	1.8					73.7	5.7
	1175	14.1	1.2	18.9	1.6	0.7	0.1	0.4	0.1	65.9	3.1
	1200	11.8	1.8	14.5	1.8	1.1	0.1			72.6	6.9
NaB	1100	10.0	1.1	12.2	1.2					77.8	5.0
	1125	11.8	1.3	13.6	0.8					74.6	4.2
	1150	9.2	1.4	17.4	0.7	0.9	0.1			72.5	7.3
	1175	10.3	0.7	13.4	0.9					76.3	6.2
	1200	11.3	0.5	14.9	0.6					73.8	6.1
KB	1100	12.1	0.8	25.8	0.6					62.1	1.0
	1125	12.0	0.8	19.9	1.5					68.2	0.9
	1150	12.1	0.4	18.1	0.5					69.8	7.6
	1175	12.8	0.6	17.8	1.0					69.4	4.8
	1200	12.5	1.1	16.0	1.1					71.6	7.5
AT	1100	10.5	1.7	20.3	1.2	5.4	0.1			63.8	1.5
	1125	9.2	1.3	16.6	0.6					74.2	5.9
	1150	8.0	1.5	15.0	0.8					77.0	5.2
	1175	9.9	1.1	15.6	0.8					74.5	5.5
	1200	7.2	1.1	14.5	0.3					78.3	7.8
ATP	1100	10.2	1.4	16.8	0.9	3.5	0.3			69.5	6.7
	1125	8.8	0.9	18.9	1.0	1.5	0.2			70.8	3.4
	1150	8.3	0.5	20.4	1.7	2.5	0.2			68.8	3.4
	1175	9.2	1.3	18.9	2.2	0.8	0.1			71.2	2.5
	1200	11.3	1.4	19.2	1.6					69.5	4.7

Table 4: Phase composition of sintered porcelain stoneware tiles (wt%)

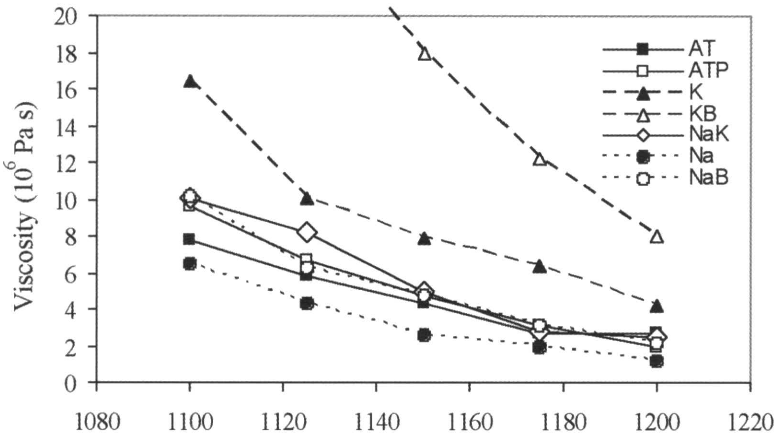

Figure 6. Calculated viscosity of the liquid phase in function of temperature.

There is an expected difference of viscosity between potassium and sodium liquid phases, being the K-rich melts more viscous – up to one order of magnitude – in respect of prevalently sodium and mixed Na-K ones. In contrast, some unexpected differences between sodium and sodium-potassium liquid phases arise, being the former only slightly less viscous than the latter at the sintering temperature (1200 °C). The viscous phase present in the industrial bodies here considered exhibits intermediate characteristics between sodium and sodium-potassium formulations. The viscosity decreases regularly with temperature, but this effect is more conspicuous in the K-rich phases, due to their wider chemical variations (Figure 6).

In all samples, the densification rate – attributable to a viscous flow filling the open porosity – increases rather regularly up to 1200°C, but the shrinkage reaches its maximum value already close to 1150°C and it does not vary much at higher temperatures (Figure 1). This behaviour is influenced by the volume changes consequent to the phase transformations, especially the melting of quartz plus feldspars eutectics brings about an increase in volume around 10% due to the lower density of the liquid phase.

However, for each sintering temperature, almost the same amount of vitreous phase was found, implying that the linear shrinkage is not proportional to the quantity of liquid phase produced.

The lower viscosity values of the liquid phase correspond to the larger shrinkage (Figure 7). This result suggests that the densification rate by viscous flow depends more on the viscosity values than on the amount of liquid phase made available during the process. Probably, the control of the densification rate – exerted by the solubility of the solid in the liquid phase – is not so strict as expected. A prominent role seems to be played by the strong dependence of viscosity on temperature.

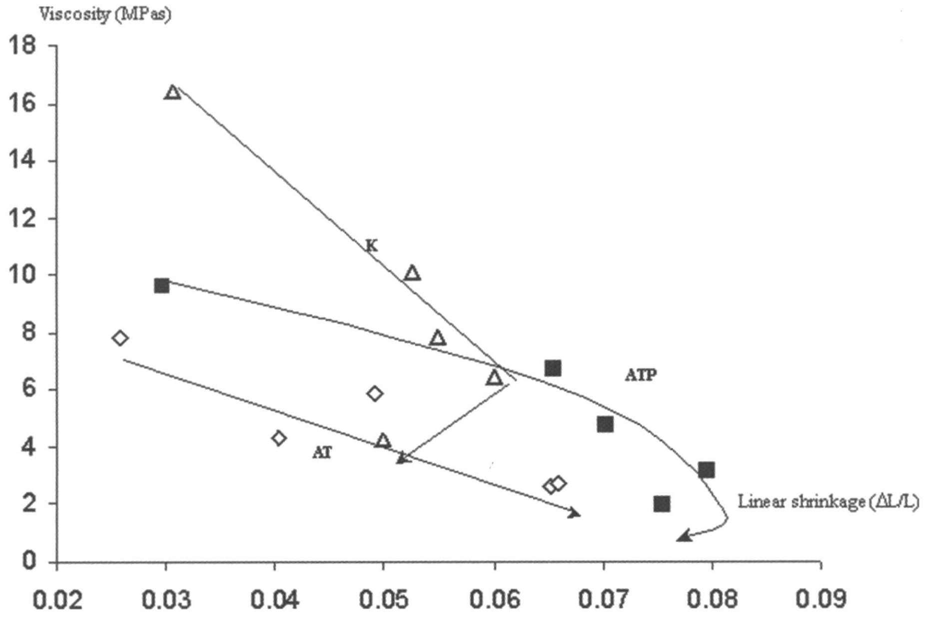

Figure 7: Relationship between linear shrinkage and viscosity of the liquid phase for samples ATP, AT and K.

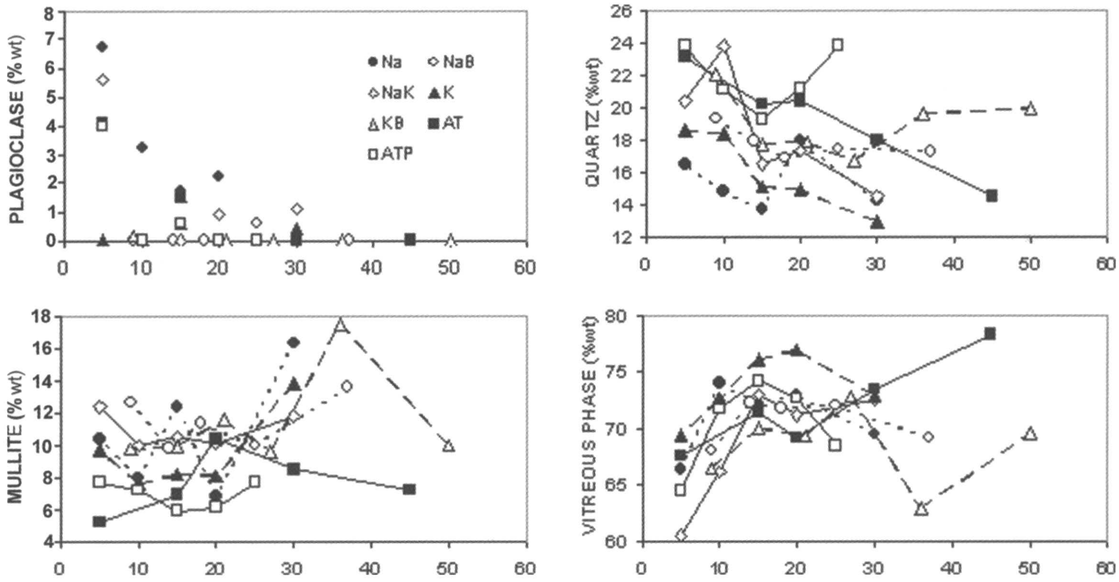

Figure 8. Phase transformations during the isothermal sintering (1200°C) of different porcelain stoneware bodies.

As a matter of fact, the melting process is very fast: 60-69% of liquid phase is already formed after 5 minutes and at the time of maximum densification (25 to 40 minutes depending on the body) its amount is just slightly increased to 69-78%. Feldspars are to a large extent fused after 5 minutes and the residual amount (4-7%) is completely dissolved within 15 minutes. The transformation rates of quartz and mullite are low and affected by many fluctuations: at all events, the amount of quartz tends to decrease, while that of mullite is slightly increased by 30-40 minutes soaking at 1200°C. Overall, the system seems to rapidly reach a sort of equilibrium, at which the liquid phase does not change significantly its composition (Figure 8).

Moreover, there are relevant differences among the various body compositions, both in terms of maximum shrinkage and densification rate (Figure 9).

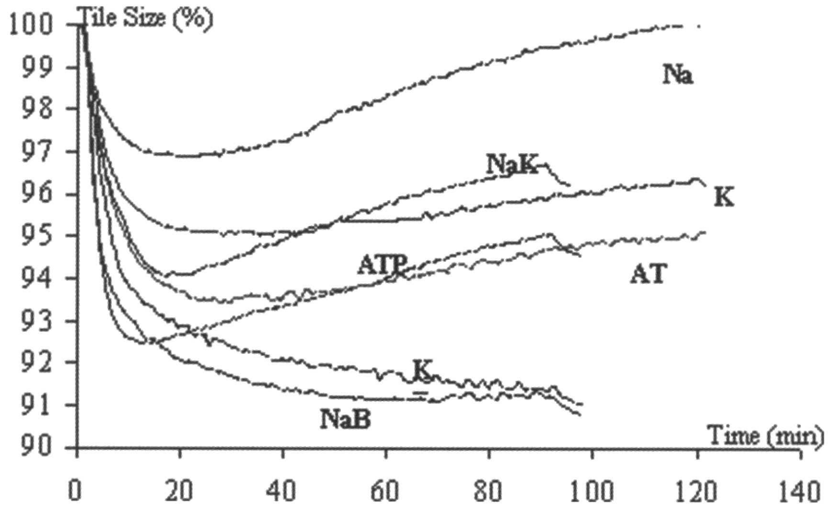

Figure 9: Isothermal curves at 1200°C for the different porcelain stoneware bodies.

Parameter	Unit	AT	ATP	NaB	Na	NaK	K	KB
Isothermal sintering rate (1200°C)	100 $(\Delta V/V_0)$ min^{-1}	2.38	4.36	4.63	1.52	2.00	2.04	2.49
Apparent energy of activation of initial densification (E_a)	kcal/mol	158.3	225.6	156.9	195.3	163.6	71.3	94.4
Avrami parameter (k)	1	0.0029	0.0250	0.0291	0.0072	0.0377	0.0069	0.0137

Table 5: Sintering rates and apparent energies of activation of initial densification

In particular, the sintering rates range between 1.5 and 4.6%/min ($\Delta V/V_0$) with the industrial compositions –containing also alkaline-earth oxides– that exhibit the faster ones (Table 5).Overall, the sodium-rich bodies are characterised by higher apparent energies of activation of the viscous flow, as these energy values seem to depend to a large extent on the Na/K ratio. The relationship with the kinetic parameter k is much less significant, probably because other variables –for instance the particle size distribution– play a critical role (Figure 10).

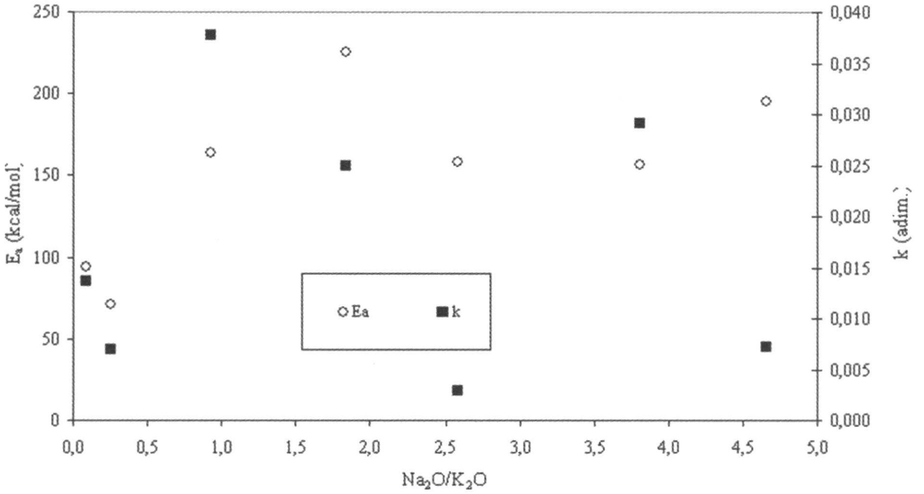

Figure 10: Correlation between the Na/K ratio of porcelain stoneware bodies with the apparent energy of activation of the viscous flow (E_a) and the Avrami kinetic parameter k.

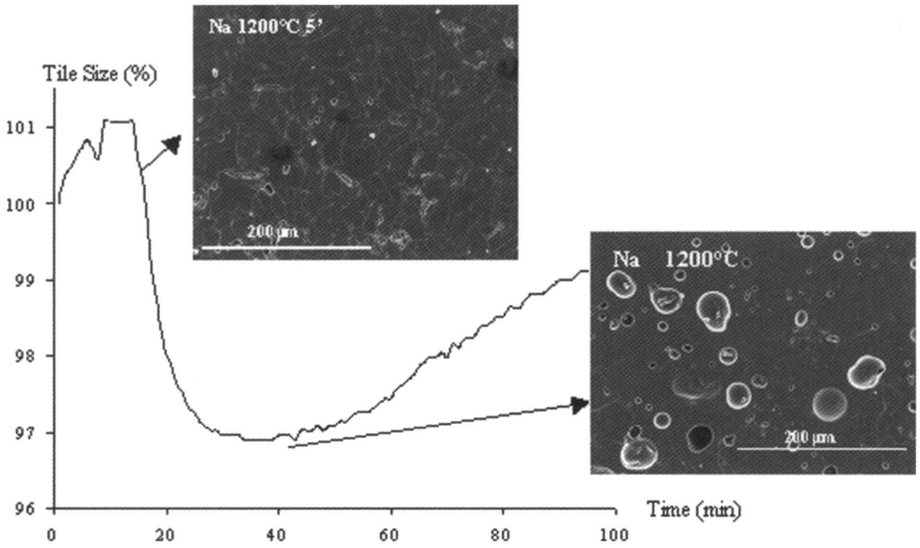

Figure 11: Example of coarsening during the isothermal sintering (1200°C) of porcelain stoneware (body Na).

3.3. FINAL STAGE

The final stage takes place over 1175°C and appears to be mainly characterized by constraints in pore removal. In fact the phase composition seems to reach an equilibrium and the only transformations are solution/precipitation of mullite and some dissolution of quartz in the liquid phase in all samples.

Coarsening and solubility of gases filling the closed pores become the most important phenomena affecting the tile microstructure. The porcelain stoneware bodies here studied, once the maximum density is achieved, tend more or less rapidly to expand with dramatic changes of pore size and microstructure. In some compositions, the coarsening of closed pores is well appreciable just after the maximum densification was achieved (Figure 11).

This phenomenon occurs with a different rate for the various bodies (Figure 12).

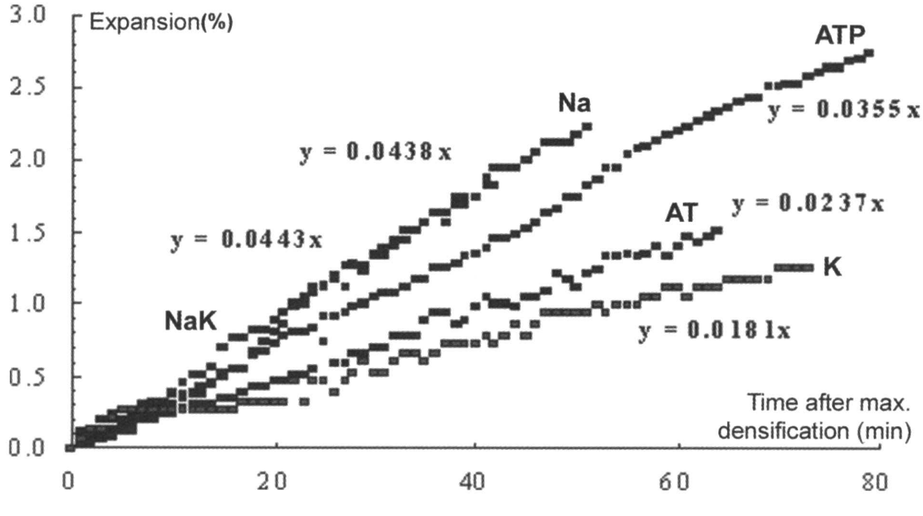

Figure 12: Correlation between the time after maximum densification and the expansion.

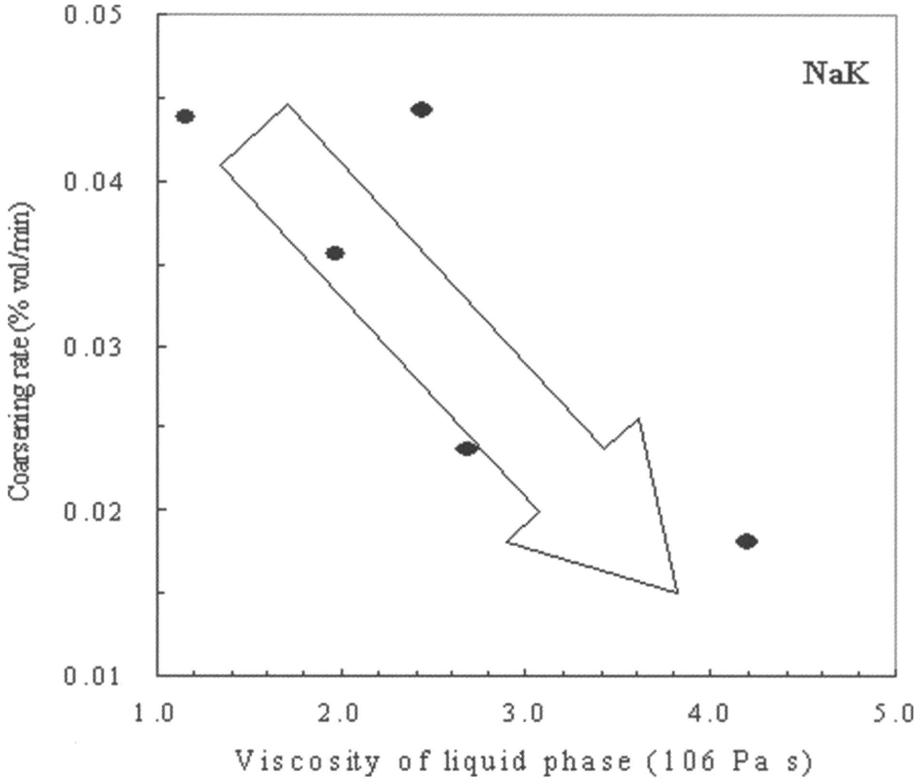

Figure 13: Correlation between the viscosity of the liquid phase and the coarsening rate of porcelain stoneware (body NaK).

The faster coarsening rates occur in the sodium-rich batches, so a fair dependence on the Na/K ratio of the liquid phase exists, though with the exception of sample NaK (Figure 13). The coarsening of microstructure is accompanied by a progressive deformation of the tile, due to an incipient slumping, whose origin is connected to the very large amount of liquid phase (> 70% weight) and to the consequent 'buoyancy' effects on residual crystalline grains.

Therefore, the amount of residual porosity in the final step depends on the contrasting effects of two competing mechanisms: a decreasing densification rate against an increasing coarsening rate.

4. CONCLUSIONS

Different mechanisms are active during the sintering of porcelain stoneware tiles and each of them is accompanied by a complex evolution of both phase composition and chemical composition of the liquid phase.

The most important are:

- surface diffusion, accounting for a strong reduction of specific surface with negligible shrinkage in the early stage (below 1000°C) where the main transformations involve the breakdown of clay minerals leading to the formation of amorphous components which, starting from about 1000°C, give rise to mullite and/or a viscous phase.
- viscous flow, responsible of densification occurring mainly in the 1100-1200°C range, which is promoted by the fast development, approximately over

1050°C, of an abundant liquid phase, whose composition corresponds to feldspars-quartz eutectics.

- pore coarsening, contrasting the decreasing sintering rate in the final stage (>1175°C) and resulting in swelling/bloating for prolonged firing.

The maximum densification achievable increases progressively in the 1050-1200°C range, while the melting of feldspars-quartz eutectics occurs already at 900°C and a large mass of viscous phase is present over 1000°C. However, the firing shrinkage is not proportional to the amount of liquid phase. This picture suggests that densification depends essentially on the viscosity of the liquid phase, which exhibits limited changes in composition with time and seems to be mainly affected by temperature.

The sintering rate is very fast up to 70-80% of pore removal, accounting for 2-5% volumetric shrinkage per minute at 1200°C. The apparent energy of activation for viscous flow is higher in sodium bodies (157-226 kcal/mol) than in potassium ones (71-94 kcal/mol).

Coarsening and solubility of gases filling the closed pores are the prevalent mechanisms affecting the tile microstructure in the final stage of sintering. Porcelain stoneware bodies tend to expand for prolonged firing, though this phenomenon occurs in the different bodies with a variable rate. In some compositions, a noteworthy pore coarsening appears just after the maximum densification was achieved. In this critical step, the amount of residual porosity seems to depend on the competing effects of decreasing densification rate against increasing coarsening rate.

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