

PORCELAIN TILE PYROPLASTIC DEFORMATION DURING FIRING AND POST-FIRING VARIATIONS IN PLANARITY

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ABSTRACT

In ceramic tile manufacture, porcelain tile is undoubtedly the product with the greatest commercial value, owing to its technical and aesthetic characteristics. Indeed, the last decades have witnessed a continuous increase in porcelain tile production worldwide and, as a result, a great differentiation in products in regard to compositions, sizes, thicknesses, and aesthetic effects, also achieved by means of glaze applications and decorations.

In view of such a variety of productive situations, one of the greatest technical difficulties lies in reconciling the foregoing with the need to obtain a material with almost zero porosity and good dimensional stability. In effect, porcelain tile is a product that is readily subject both to pyroplastic deformations in the vitrification stage during the firing process and to subsequent variations of planarity in the already fired material that is stored while awaiting polishing and/or squaring.

This study examines in detail the factors that determine the greater or lesser proneness to pyroplastic deformation of porcelain tile bodies and, in particular, the aspects relating to the body composition and processing parameters. The study presents several porcelain tile compositions in which an instrumental analysis was

performed of pyroplasticity, followed by experimental verification by fast firing in a roller kiln at different temperatures.

In addition, the variations in planarity over time of the finished products were evaluated as a function of the physico-mechanical and microstructural characteristics of the resulting materials; these variations were verified on the one hand on the basis of the cumulative stresses during the cooling stage and, on the other, by the possible hydration reactions of the fired ceramic material.

Finally, the experimental results are used to put forward certain recommendations to enhance porcelain tile dimensional characteristics with relation to body composition and to processing conditions, in particular with regard to the firing stage.

1. INTRODUCTION

The thermal treatment of ceramic products, generally known as firing, is known to be the production process stage that establishes, definitively and stably over time, all the finished product properties and technical requirements regarding shape, aesthetics, and functional aspects, such as water absorption, bending strength, coefficient of expansion, frost resistance, etc.

Different chemical and physical phenomena develop in this stage, which modify the composition and structure of the ceramic mass. In particular, thanks to the dissociation reactions of the clay minerals owing to the loss of water of the crystalline composition (in the thermal range between about 400 and 1000 °C), successive neo-formation phases (for example of metakaolin to mullite), and sintering/vitrification, the ceramic body takes on its well-known fired consistency.

Ceramic tile post-firing deformation may be attributed to two main features:

- Presence of residual stresses in the tiles

These stresses develop in the tiles independently of the applied force, and they arise particularly during the cooling stage. Indeed, this is when the edges and side surfaces of the ceramic tiles cool first, while the tile centre sometimes displays a very pronounced thermal delay (up a hundred degrees). The stresses are absorbed by the tile while it remains plastic and are then fully transmitted when the tile becomes rigid. This effect increases as tile size becomes larger; as a result, in view of the need to produce ever-larger tiles and slabs, the immediate and residual stresses in the tiles become very significant both in absolute and percentage terms.

- Formation of a glassy phase with little resistance to pyroplastic deformation

This effect depends to a large extent on the body composition and production process parameters, such as forming pressure, temperature, and firing cycle.

In the first case of deformation, the influence on production is evident: owing to the effect of stress release (which ends about 2–3 days after kiln exit, see Fig. 1), a dimensional variation is observed in the piece, which produces a change in planarity that does not fit well with the final finished product treatment operations (selection, rectification or edge-grinding, polishing/lapping).

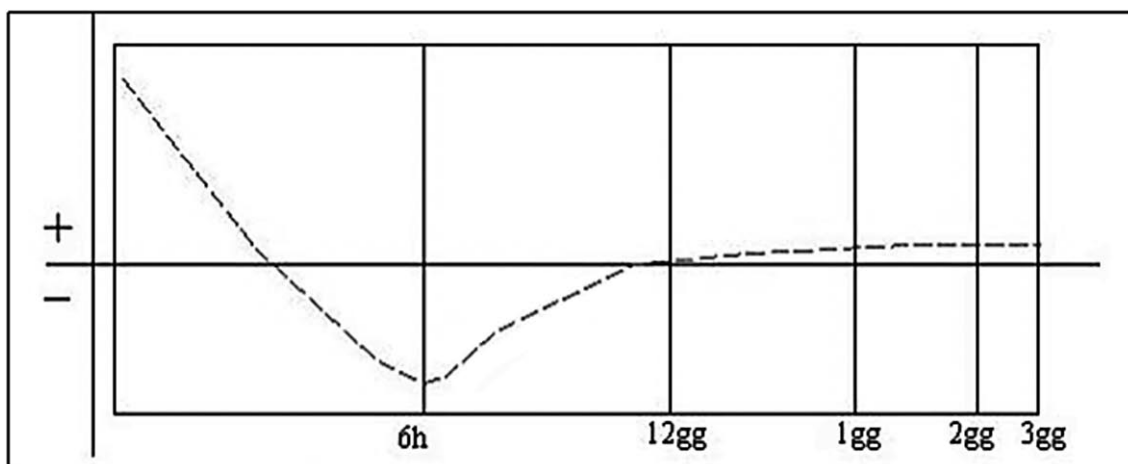


Figure 1. Average variation in tile planarity after firing (+convex -concave)

Residual stresses may be transient, if they cancel out by themselves, or permanent, if they remain for quite a long time.

Transient residual stresses cancel out spontaneously after suppression of the phenomenon that has created them. If a tile is subjected to a temperature difference, the hotter part expands with regard to the colder part, giving rise to stresses at the interface; after suppressing the temperature difference, the stresses also disappear. This only occurs if the material does not change during the creation of the stresses. The temperature gradient in cooling can be so high that it creates a stress that is able to generate dislocation movements (typical property of metallic materials, which allows them to deform at much lower temperatures than the melting temperature) with an ensuing lengthening of one part of the material with relation to the other. A permanent strain caused by the thermal gradient creates a permanent stress.

The stress does not remain if there is a viscous flow inside the material (as in the case of liquids). If a solid reaches a certain temperature, and thus acts as a viscous flow and not a dislocation, this movement cancels out the stresses. Another possible stress cancellation stems from the contribution of phase transformation that creates a change in volume.

Permanent residual stresses are not spontaneously cancelled out when the ceramic mass exhibits an elastic behaviour, i.e. too high a viscosity. If the temperature increases, this causes viscosity to decrease and the stress can drive a viscous flow that cancels it out. Materials such as glass, which at room temperature has a viscosity of 10^3 Poise, have 'geological' stress cancellation times.

That is only limited the stresses present in the body; to these stresses one would need to add those resulting from the dilatometric body-engobe-glaze fit.

In contrast, pyroplastic deformation produces a permanent strain in ceramic tiles, a defect that can already be observed at the kiln exit. In particular, a small collapse is noted at the tile edges in the sides at right angles to the roller axes (see

Figure 2) as an effect of the residence at peak firing temperature during maximum sintering. This type of defect is highly visible after tile installation; in fact grazing light produces a reflection on the surface of the tile that accentuates this deformation, which, measured with the appropriate instruments, is a few tenths of one mm.

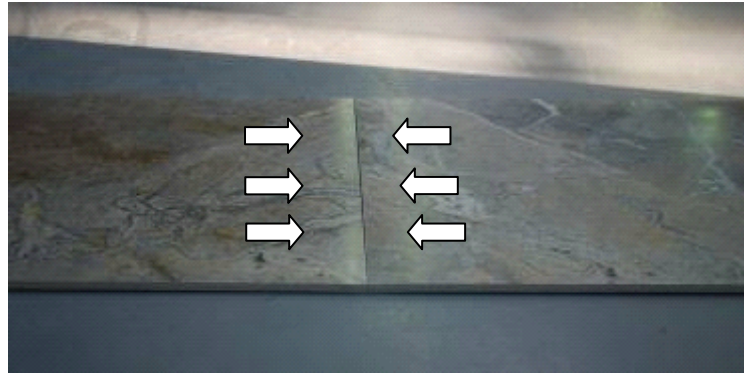


Figure 2. Defect of pyroplastic deformation in a finished product

2. EXPERIMENTAL PROCEDURE

The purpose of this study was to evaluate the variation of the raw materials proportions and the subsequent body composition with relation to the appearance or non-appearance of deformation phenomena. For this purpose, a number of formulations were prepared, in which the following parameters were varied:

- Variation of the quantities of clays/complementary materials
- Introduction of less fusible fluxes (increased proportion of K/Na)
- Reduction of refractory materials (reduction of free silica)
- Increase in the percentage of alumina.

PROVE RAW MATERIAL	BASE BODY	TEST 1	TEST 2	TEST 3	TEST 4	TEST 5
		-Clays +Com- plemen- tary ma- terials	-Comple- mentary materials +Clays	- Quartz + K feld- spar	-Sodium flux +Potas- sium flux	+Alu- mina +K feld- spar
	%	%	%	%	%	%
Plastic CLAY	30	22	30	30	30	30
Refractory CLAY	-	-	15	-	-	15
QUARTZITE	12	12	8	-	-	-
SODIUM FELDSPAR	58	66	47	58	40	40
POTASSIUM FELDSPAR	-	-	-	12	30	15

Table 1. Technological tests of the body compositions

The 'base' body consisted of 30% white-firing illitic kaolinitic clay, with high plasticity and a good degree of sintering; the remaining 70% was made up of sodium feldspar (58%), with a vigorous fluxing action in the mass, and quartz (12%), which contributed a useful 'structure' to support the mass during the vitrification/sintering phases linked to the thermal treatment cycle.

During the first test, the quantity of clays/complementary materials was modified in favour of the latter, obtaining a marked increase in the flux content in the mass.

In the second experiment, the clay portion of the body was significantly increased, leading to the presence of a greater alumina contribution in the general chemistry of the mass ceramic, with smaller quantity of quartz and sodium flux.

In the third and fourth tests, the same quantity of clays/complementary materials was maintained as in the initial base body. The only variant was the progressive replacement of the quantity of quartz with a potassium flux, which was to contribute to the formation of a more viscous and less deformable glassy phase.

In the last test, the clay and the potassium feldspar phase content were simultaneously increased with relation to the initial body composition.

In addition to the compositional variables, the influence of different process parameters was evaluated throughout the study, such as:

- sintering degree (low/high)
- firing cycle (fast/slow).

With regard to the stress load present in the fired materials at the kiln exit (t_0), precise measurements were performed of the planarity of fired tiles sized 600x600 mm, at three different times:

- a) $t_0 + 4h$
- b) $t_0 + 24h$
- c) $t_0 + 36h$

The determination of the pyroplastic deformation was carried in the laboratory using a Flexa hot stage microscope (see photo detail in Figure 3); small bars of the body were prepared with a fixed length and thickness (85 and 8,5 mm respectively), which were subjected to thermal treatment with typical industrial firing gradients, using the peak sintering temperature determined previously by means of a complete technological characterisation of the bodies fired with a semi-industrial process.

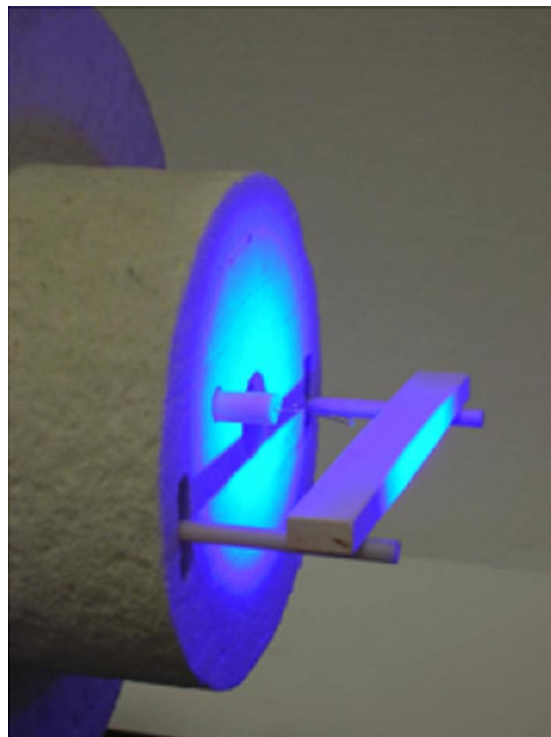
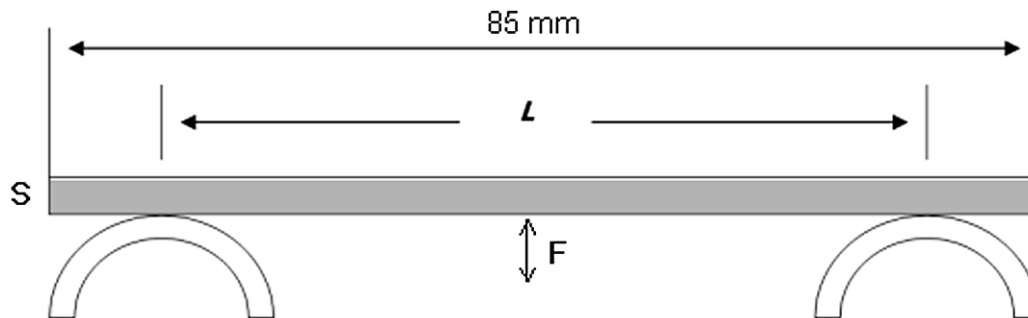


Figure 3. Detail of the Flexa hot stage microscope

Considering the value obtained and the thickness of the bar, the following formula was applied:

$$DEF = 4 \times S^2 \times F / 3 \times L^2$$

where:



S = thickness in mm (before firing)

F = measured value of bar curvature in mm

L = support span (between supports) of the sample in mm.

With this method, the evaluation is independent of the thickness used in the test, since the formula allows (with discreet verified credibility) a comparable value to be obtained for different thicknesses.

A statistical analysis conducted on the file of the tests performed in forgoing years was used to create Table 2, shown below, which details the evaluation ranges of the obtained values:

DEFORMATION (mm)	EVALUATION
<0,022	optimum
0,023–0,026	good
0,027–0,030	medium
0,031–0,034	sufficient
>0,034	low

Table 2. Evaluation table of pyroplastic deformation

3. RESULTS AND DISCUSSION

3.1. Deformation of the material over time

a. Influence of the sintering degree

The following diagram (Figure 4) shows the variation in planarity after firing when the material was fired with an intermediate degree of sintering; it may already be observed in these cases, in particular, that a low degree of sintering (corresponding to a water absorption of about 0,5÷1%) encourages notable finished product deformations; in particular the highly sodium glassy phases (test

1) increased the movement of material planarity while the optimum results were obtained with an increase in the clayey phase and the concurrent introduction of a mainly potassium fluxing phase (test 5).

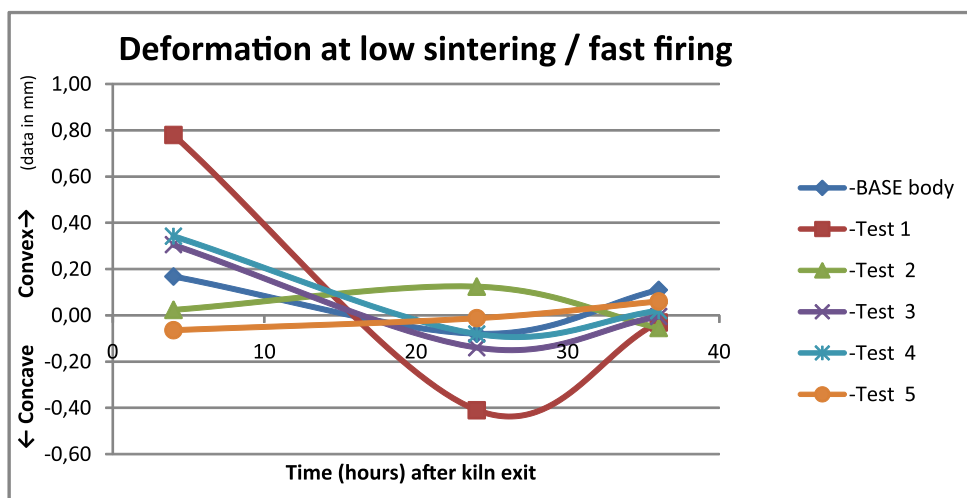


Figure 4. Deformation trend after firing: fast firing and low degree of sintering

In contrast, when a complete degree of sintering was reached (water absorption below $0,05 \div 0,1\%$), the general values of the planarity variation decreased considerably in absolute values (Figure 5).

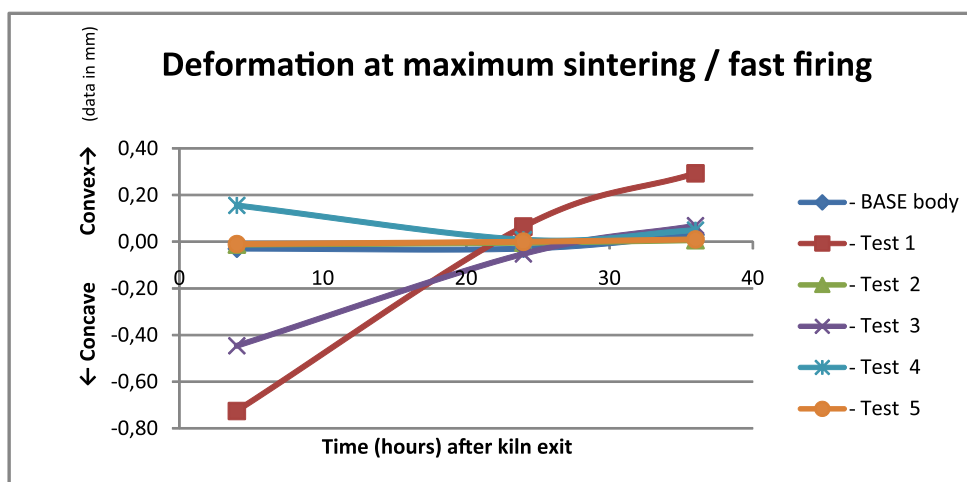


Figure 5. Deformation trend after firing: fast firing and complete degree of sintering

However, the worst results were observed to be maintained for the compositions with a pronounced sodium glassy phase content (test 1), while the best performance was found with the increase in clay and potassium feldspar with relation to the base mass.

b. Influence of the type of firing

The firing of the samples with a slower cycle (14 minutes more) than the foregoing cycle signalled a very important feature: the dimensional variation of finished product planarity decreased notably (see Figure 6).

Indeed, comparison with the graph in Figure 5 shows that, in all analysed bodies, the variation of planarity decreased significantly with time. This effect is very important and is related to the general lower thermal gradient in firing, in particular in cooling.

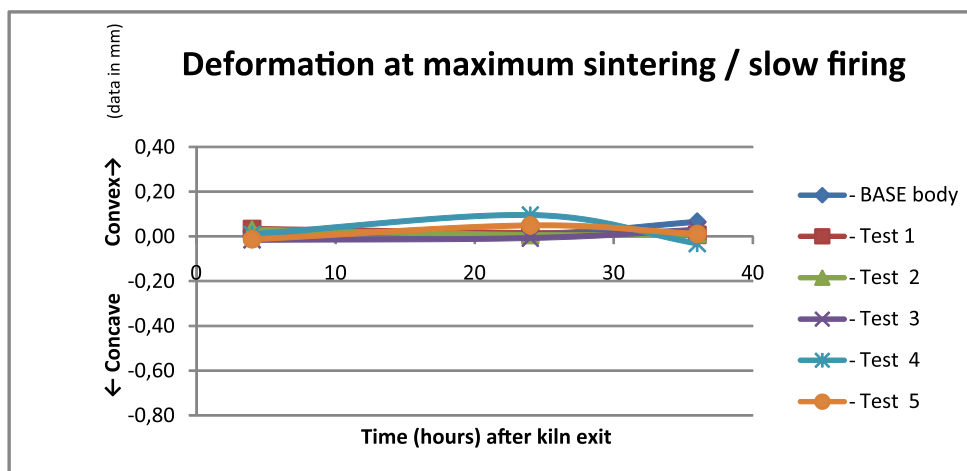


Figure 6. Deformation trend after firing: slow firing and complete degree of sintering

3.2. Pyroplastic deformation

The results of the comparative analysis of the samples subjected to a deformation cycle with the Flexa instrument, described above, are presented below (graph in Figure 7).

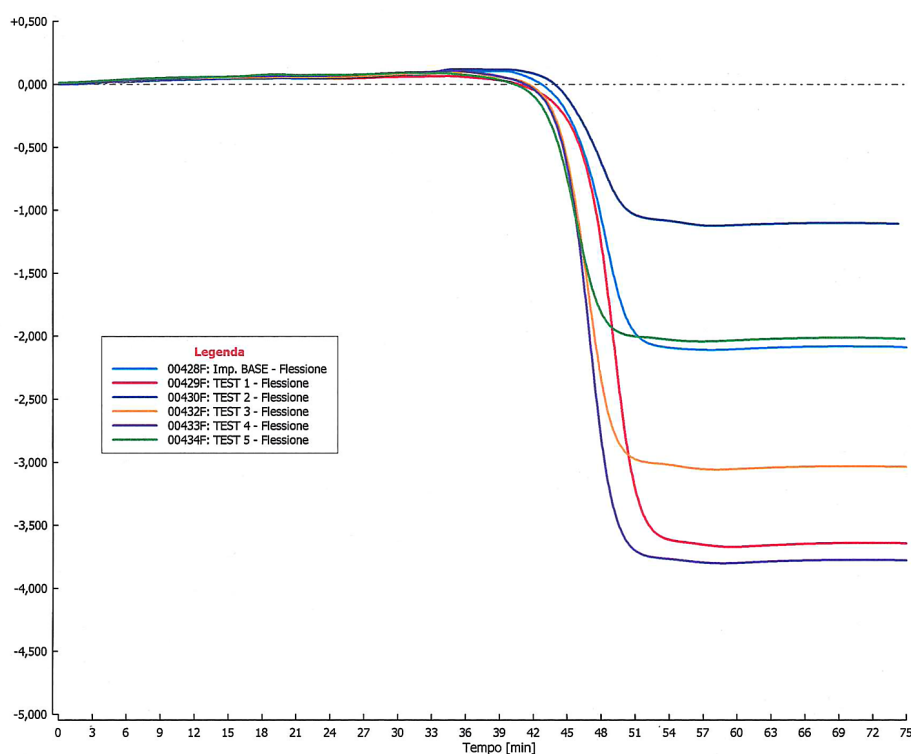


Figure 7. Deformation trend after firing: slow firing and complete degree of sintering

The best deformation result, in absolute value (absolute value of about 1%), was obtained with the body corresponding to test 2, in which a kaolinitic clay was introduced at the expense of the sodium flux and the quartz.

In addition, very good results were also obtained for the base body and the test 5 body; this last ceramic mass also exhibited very positive results in the tests on the variation of planarity as a function of kiln exit time, as already described in the foregoing paragraph.

The remaining body tests exhibited excessively high results for pyroplastic deformation. In order to visualise the results more clearly, a histogram (Figure 8) follows with the pyroplastic deformation data independently of the variable 'test thickness', evaluated with reference to Table 2.

Pyroplastic deformation

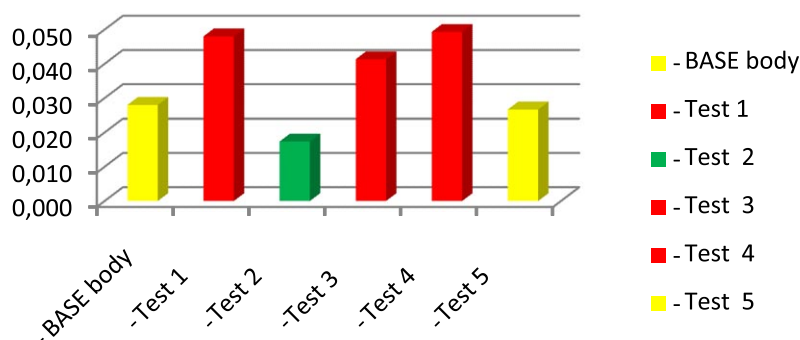


Figure 8. Deformation trend after firing: slow firing and complete degree of sintering

4. CONCLUSIONS

The study conducted has shown the possibility of identifying certain possible raw materials that, introduced in porcelain tile formulations, allow an appropriate reduction of pyroplastic deformation to be obtained and, at the same time, better control of planarity in the first 36 hours after kiln exit.

The results obtained are set out in the following graph (Figure 9), which evidences that the test bodies 1, 3, and 4 exhibited no satisfactory results with relation to pyroplastic deformation or to the absolute movement of finished product planarity in the first 36 hours after firing.

The best results with relation to those of the initial base body were obtained with test bodies 2 and 5.

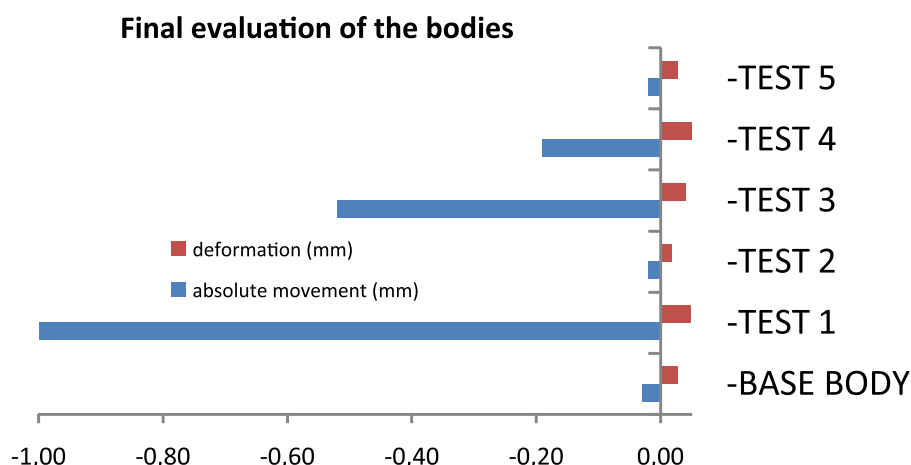


Figure 9. Final evaluation of test body performance

The conclusions drawn from these experiments with regard to the composition and the process may, therefore, be summed up as follows:

1. Increase the proportion of clays/complementary materials

This increases the presence of alumina in the body and, hence, the formation of structural mineralogical phases of the mullite type in the finished product.

2. Introduce potassium feldspar while reducing sodium feldspar

This favours the formation of a more viscous and, hence, more stable glassy phase in particular with relation to stress release.

3. Maintain a small quantity of quartz

This contributes to keeping the necessary 'skeleton' during firing to contain the pyroplastic deformation of the finished product. An excessive quantity of quartz should not be added in order to avoid problems in the cooling phase owing to the allotropic transformation of the β quartz – α quartz phase at 573°C, the problems becoming more pronounced as tile size increases.

4. Use an appropriate firing cycle with relation to the size/thickness ratio of the tile to be made

This is rarely taken into account by tile manufacturers in general, and by porcelain tile manufacturers in particular. It is also necessary to consider that with the race towards ever faster cycles, many of the qualities that made the porcelain tile superior to other ceramic materials are lost.

5. REFERENCES

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