REHEATING OF CERAMIC TILES FOR THE CRAZING RESISTANCE TEST

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ABSTRACT

According to standard ISO 10545 Part 11, all glazed ceramic tiles, with the exception of freshly fired tiles, must be reheated to 500°C ± 15°C, with a heating rate of less than 150°C/h, and remain at the maximum temperature of the firing cycle for at least two hours as part of the procedure for determining crazing resistance. In order to verify whether the reheating procedure in the standard fulfils the purpose for which it was included in the test method, five commercial products (BIIb tiles measuring 50x50 cm and 62x62 cm) were characterised with regard to crazing resistance after their manufacture with no reheating process and using the method in the standard (including heat treatment at 500°C as per ISO 10545-11). As all products were resistant to crazing, several autoclave hydration cycles were performed, and the number of cycles required for glaze crazing to eventually occur was recorded for each product. Surprisingly, the reheating procedure established by ISO 10545-11 reduces the crazing resistance of ceramic tiles. In order to explain the phenomenon, measurements of tile curvature before and after reheating at 500°C were carried out using a laser measuring system (three-dimensional arm). The results showed that, for the tiles tested, reheating causes alterations in the curvature of the original tiles, making them significantly less convex or more concave. In order to understand the reasons for such alteration in curvature, shrinkage tests were conducted on test specimens made with the bodies, engobes and glazes used in the products under evaluation. The shrinkage tests were carried out at 500°C (the same firing cycle as the reheating test in the standard) using test specimens that had previously been fired at the same temperature and firing cycle as the ceramic tiles. The results indicate that reheating at 500°C generates different movements between the layers making up the ceramic tiles, thus explaining the changes in curvature observed in the ceramic tiles during the reheating specified by ISO 10545-11. To conclude our work, the reheating temperature required to eliminate the moisture adsorbed by the ceramic tiles was studied. This stage of the work was carried out by means of dilatometric analyses with tiles pre-hydrated in an autoclave.

1. INTRODUCTION

Crazing of a ceramic tile occurs when the thin layer of glaze that coats the tile is subjected to a tensile stress great enough to overcome its mechanical strength [1, 2]. This phenomenon is directly related to the mechanical behaviour of the glaze which, like the other elements that make up the ceramic tile (body and engobe), is a brittle material [3]. In this sense, the glaze that covers the bodies undergoes little or almost no plastic deformation and ruptures quickly. As mentioned, brittleness is a typical property of ceramic materials, among which glass tends to be the most brittle. This characteristic, together with the typical thinness of the glaze layers, makes this a very delicate issue.

In practice, crazing is the result of a sum of forces acting on the glaze layer. These forces are governed by the various interactions that occur between the components of a ceramic tile. In an ideal scenario, where the product does not undergo immediate crazing (at the end of the manufacturing process), the glaze layer is concluded to be under compressive stress; however, this state can change as a result of the stresses and strains the product is subject to [2, 4].

The crazing resistance test described in ISO 10545 Part 11 seeks, through accelerated moisture expansion, to place the test product in an extreme situation capable of altering the stresses acting on the glaze layer and, in the worst case, causing crazing [5]. An important stage in this procedure is the reheating process, which simply aims to eliminate the natural expansion of the substrate and return it to its original state so that it can be used in the test under fair conditions [4, 5]. In theory, the glaze and engobe layers should not shrink due to reheating, which takes place at 500°C, so that only the substrate should move (shrink) during heat treatment. However, especially in the case of red-ware products made by the dry method, whose firing cycles are around 20 minutes, with maximum temperatures around 1100°C, a reheating temperature of 500°C may reasonably be considered to be high enough to generate movements in those layers [6].

If the energy supplied by reheating is high enough to generate structural transformations in any of the layers making up the product, the crazing resistance readings after the process will not evaluate the original product but rather the by-product created by reheating. Therefore, this study aims to better understand the possible transformations undergone by BIIb ceramic tiles made with red-firing clays during the reheating stage required by the crazing resistance test and its effect on the results of such analyses.

2. METHODOLOGY

Initially, the analysed products were tested for crazing resistance but, in contrast to what the standard specifies, the products were subjected to up to five cycles of hydration in an autoclave with and without reheating. To better evaluate movement in the tiles as a result of the reheating process, the curvatures of the selected ceramic tiles were measured using a laser arm before and after reheating.

In order to consolidate the results, the input materials constituting the reference materials were evaluated in terms of their reheating shrinkage. To do that, test specimens were prepared using typical industrial pressure, temperature and firing cycle conditions, after which the test specimens were subjected to reheating, carried out according to the parameters used to determine crazing resistance in ISO 10545-11. The dimensional variation in length as a function of reheating, which was referred to as linear reheating shrinkage, was determined in mm/m with the use of a micrometric gauge with an accuracy of ± 0.001 mm.

Water release from the tiles was assessed and the reheating temperature specified by the standard was critically analysed by wet cutting the specimen using a diamond cutting disk. The test specimens were obtained with dimensions of about 50x5x5 mm, so that they would fit in the thermodilatometer before being hydrated under two harsh conditions: 2 hours in an autoclave at 5 bar, and 5 hours in an autoclave at 5 bar. From these results, the ideal reheating temperature was determined.

Finally, the references were again tested for crazing resistance in multiple cycles, this time with reheating at the empirically determined ideal temperature. The same samples were also tested for shrinkage movement before and after refiring by laser arm measurement. This gave a comparative evaluation of the results obtained with both the reheating temperature in the ISO standard and the empirically validated ideal reheating temperature.

3. RESULTS AND DISCUSSION

To verify the possible damage caused by reheating, five BIIb product references were subjected to various tests. Initially, the selected references were evaluated for crazing resistance with and without reheating at 500°C (ISO 10545-Part 11). The tiles were subjected to up to five successive autoclave hydration cycles. The results are presented in Tables I to V.

Reference 1	Cycle in which crazing occurred	
	No reheating	Reheated at 500ºC. (ISO 10545 – Part 11)
Test specimen 1	4th Cycle	2nd Cycle
Test specimen 2	4th Cycle	2nd Cycle
Test specimen 3	4th Cycle	2nd Cycle
Test specimen 4	4th Cycle	2nd Cycle
Test specimen 5	4th Cycle	2nd Cycle

Table I. *Evaluation of tile crazing resistance at 500°C.*

Reference 2	Cycle in which crazing occurred	
	No reheating	Con recalentamiento a 500ºC (ISO 10.545 – Parte 11)
Test specimen 1	4th Cycle	3rd Cycle
Test specimen 2	4th Cycle	3rd Cycle
Test specimen 3	4th Cycle	3rd Cycle
Test specimen 4	4th Cycle	3rd Cycle
Test specimen 5	4th Cycle	3rd Cycle

Table II. *Evaluation of tile crazing resistance at 500°C.*

Reference 3	Cycle in which crazing occurred	
	No reheating	Reheated at 500ºC. (ISO 10545 – Part 11)
Test specimen 1	Did not crack until 5th cycle	3rd Cycle
Test specimen 2	Did not crack until 5th cycle	3rd Cycle
Test specimen 3	Did not crack until 5th cycle	3rd Cycle
Test specimen 4	Did not crack until 5th cycle	4th Cycle
Test specimen 5	Did not crack until 5th cycle	4th Cycle

Table III. *Evaluation of tile crazing resistance at 500°C*

Reference 4	Cycle in which crazing occurred	
	No reheating	Reheated at 500ºC. (ISO 10545 – Part 11)
Test specimen 1	Did not crack until 5th cycle	3rd Cycle
Test specimen 2	Did not crack until 5th cycle	3rd Cycle
Test specimen 3	Did not crack until 5th cycle	4th Cycle
Test specimen 4	Did not crack until 5th cycle	4th Cycle
Test specimen 5	Did not crack until 5th cycle	4th Cycle

Table IV*. Evaluation of tile crazing resistance at 500°C*

Reference 5	Cycle in which crazing occurred	
	No reheating	Con recalentamiento a 500ºC (ISO 10.545 – Parte 11)
Test specimen 1	4th Cycle	3rd Cycle
Test specimen 2	4th Cycle	3rd Cycle
Test specimen 3	4th Cycle	3rd Cycle
Test specimen 4	4th Cycle	3rd Cycle
Test specimen 5	4th Cycle	3rd Cycle

Table V. *Evaluation of crazing resistance in tiles at 500°C*

The results show that the number of autoclave hydration cycles capable of causing crazing in tiles reheated at 500°C is always lower compared to that of non-reheated pieces. Therefore, these results prove that pieces reheated according to ISO 10545-11 become less resistant to crazing.

If the only reaction to occur during such heat treatment is the elimination of the moisture adsorbed after tile manufacture, which consequently leads to shrinkage of the ceramic substrate as a result of eliminating the moisture-induced expansion, from a macroscopic point of view, what one could expect to observe *a priori* would be a slight tendency towards increased convexity in the reheated pieces. Such an alteration should not lead to negative changes from a technological point of view but should rather benefit the products. However, our visual observations in routine laboratory procedures have shown the opposite effect.

In order to visually materialise the alteration in curvature in the commercial tiles under evaluation, the topology of the reference pieces before and after reheating at 500°C was recorded using a laser measurement system (three-dimensional arm), which shows the relative position of each region in the ceramic tiles in the form of a topographic map.

The results obtained are presented in Figure 1. The warm colours (yellow, orange, red) on the topographical maps represent the highest points of the ceramic tiles and the cool colours (green, blue) represent the lowest points. Therefore, it may be concluded that the warmer the colours in the centre of the tiles and the cooler the colours towards the ends near the edges, the greater the convexity of the tiles. Conversely, the tiles with the greatest concavity are those with cooler colours in the centre and warmer colours at the edges.

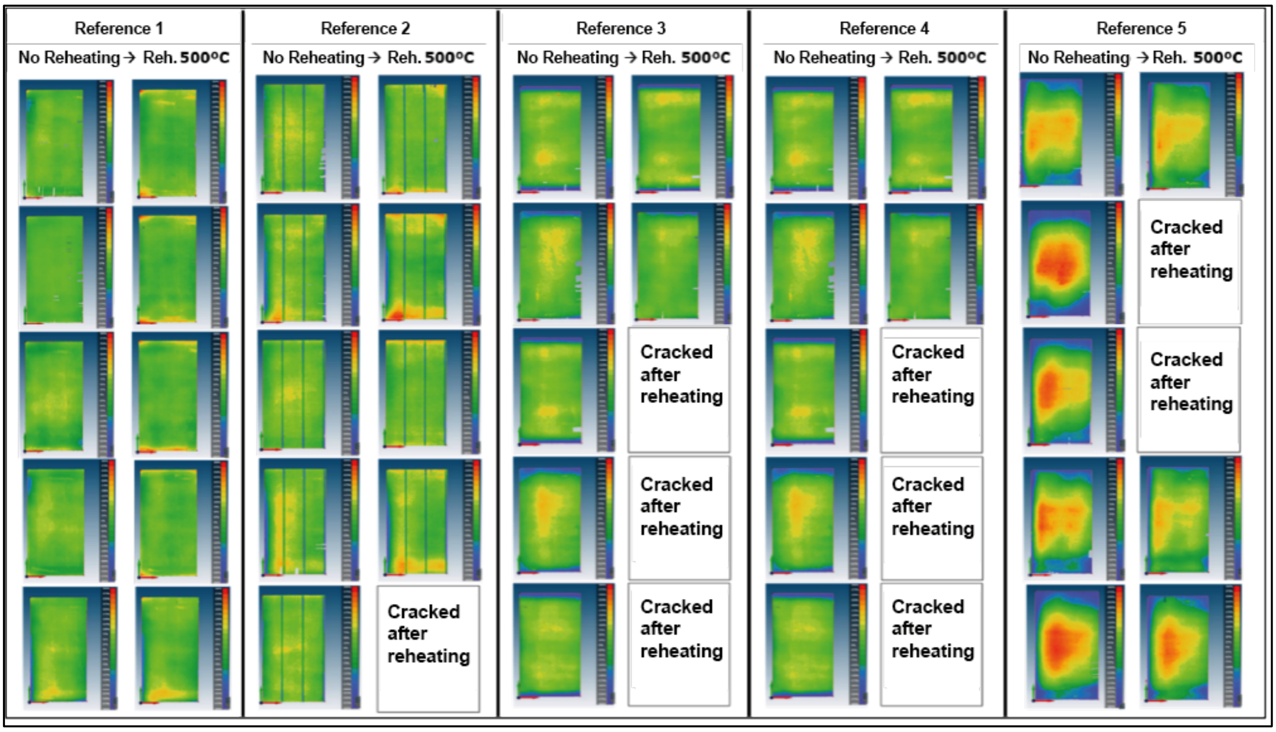

Figure 1. *Effects of reheating at 500ºC on tile curvature.*

As ceramic tiles are made up of superimposed materials of different natures and thicknesses (multilayers), a possible explanation for the increased concavity in ceramic tiles during reheating at 500°C is the possibility that these layers exhibit different movements. Therefore, to account for the increased concavity seen in the reheated tiles, the engobe and glaze layers would have to display greater shrinkage than that of the body during heat treatment. To investigate this assumption, reheating shrinkage was measured on separate test specimens of the body, engobe and glaze that make up the references under evaluation. The results are shown in Table VI.

Input material	Linear shrinkage with reheating (mm/m)	Input material	Linear shrinkage with reheating (mm/m)
Semi-sealing engobe	0.19 ± 0.02	Transparent glaze 1	0.11 ± 0.01
Sealing engobe 1	0.19 ± 0.01	PEI glaze – V	0.08 ± 0.01
Sealing engobe 2	0.19 ± 0.01	Transparent glaze 2	0.15 ± 0.01
Refractory engobe 1	0.11 ± 0.01	Matt glaze 2	0.17 ± 0.01
Refractory engobe 2	0.20 ± 0.02	Matt glaze 3	0.17 ± 0.01
Matt glaze 1	0.10 ± 0.01	Body by dry method	-0.01 ± 0.01

Table VI. *Shrinkage resulting from reheating of the test engobes, glazes and bodies.*

The reasons why glazes and especially engobes exhibit greater shrinkage movements than the body in a BIIb product under heat treatment at 500°C lie beyond the scope of this study. However, it seems reasonable to assume that this firing temperature is high enough to cause the glassy phases that developed in the glazes and engobes of these products to soften and, as a result of that transformation, for slight shrinkage to occur in those layers. This assumption is most evidently supported by BIIb products which, as we know, are generally made with highly fusible red clays that favour the use of fast firing cycles and low firing temperatures. Therefore, the engobes and glazes used in such products also need to exhibit high fusibility in order to develop their attributes in the cycles and temperatures required by these red-firing clays.

Our results suggest that the reheating temperature specified in ISO 10545-11 may be too high for these ceramic tiles, as unforeseen transformations may be occurring in their glazes and engobes and, consequently, causing changes in the stress state of the tiles prior to autoclave hydration. In that case, the need to use such high temperatures is worth questioning, since the aim of reheating is simply to return the ceramic tiles to their original stress state after manufacture. In order to monitor water release from the substrate and to critically verify the necessity or effectiveness of the current reheating temperature, the five references in this study were pre-hydrated in autoclave for 2 and 5 hours to simulate severe accelerated ageing of the products. The samples extracted from these references were then heated to 550°C in a thermodilatometer. This procedure enables the temperature at which the adsorbed moisture is removed from the specimens to be identified from the derivatives of the resulting dilatometric curves. The results are shown in Table VII and Figures 2 and 3.

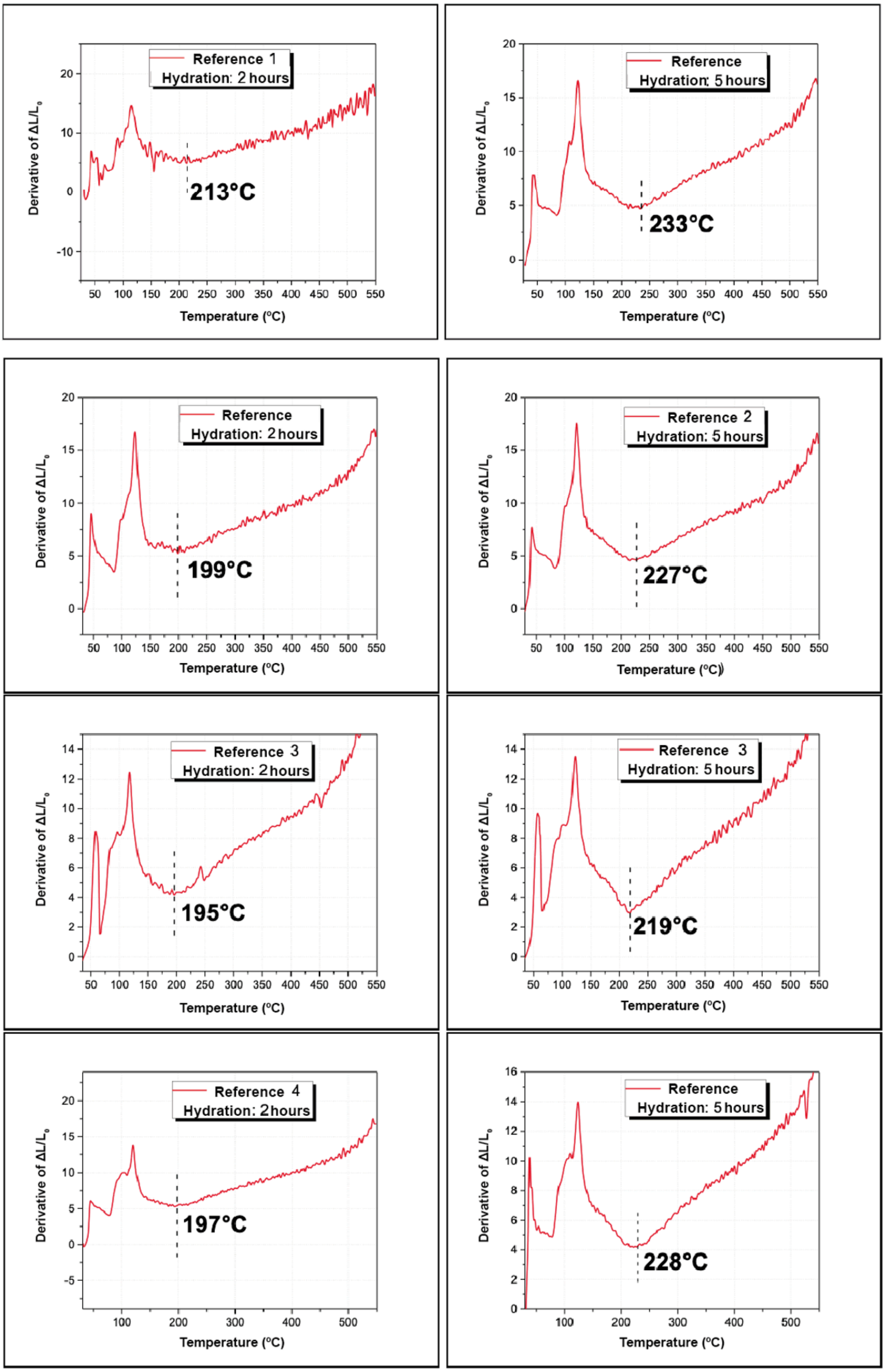

***Figure 2**. Water release temperature obtained from the dilatometric derivatives.*

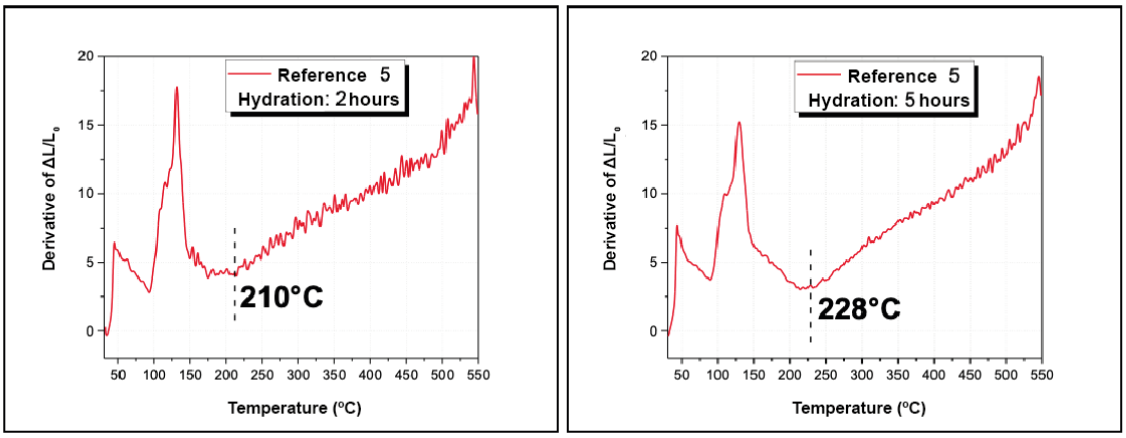

Figure 3. *Water release temperature obtained from the dilatometric derivatives.*

Product	Temperature of adsorbed water release (°C)	
	2-hour hydration	5-hour hydration
Reference 1	213	233
Reference 2	199	227
Reference 3	195	219
Reference 4	197	228
Reference 5	210	228

Table VII. *Summary of the water release temperatures in the two test conditions.*

The curves obtained from the dilatometric derivatives exhibit the same characteristics, regardless of the degree of hydration or the reference under analysis. They are formed by two peaks located between 50ºC and 150°C, which correspond, respectively, to the release of (not chemically bound) absorbed water and the release of (chemically bound) adsorbed water, followed shortly after by a trough region that represents total water release. From this result, it is suggested that the ideal re-firing temperature (with a certain safety margin) would be 300°C, exposing the tiles to this temperature for 2 hours.

Once again, the crazing resistance of the reference ceramic tiles was evaluated. This time, the tiles were tested (a) with no reheating, (b) with reheating at 500°C (ISO 10545-Part 11), and (c) with reheating at 300°C (recommended ideal temperature). The results are detailed in Tables VIII to XII.

Reference 1	Cycle in which crazing occurred		
	No reheating	With reheating at 500ºC (ISO 10545 – Part 11)	With reheating at 300ºC
Test specimen 1	4th cycle	2nd cycle	4th cycle
Test specimen 2	4th cycle	2nd cycle	4th cycle
Test specimen 3	4th cycle	2nd cycle	4th cycle
Test specimen 4	4th cycle	2nd cycle	4th cycle
Test specimen 5	4th cycle	2nd cycle	4th cycle

Table VIII. *Evaluation of tile crazing resistance at 500ºC and 300ºC.*

Reference 2	Cycle in which crazing occurred		
	No reheating	With reheating at 500ºC (ISO 10545 – Part 11)	With reheating at 300ºC
Test specimen 1	5th cycle	3rd cycle	5th cycle
Test specimen 2	5th cycle	3rd cycle	5th cycle
Test specimen 3	5th cycle	3rd cycle	5th cycle
Test specimen 4	5th cycle	3rd cycle	5th cycle
Test specimen 5	5th cycle	3rd cycle	5th cycle

Table IX. *Evaluation of tile crazing resistance at 500ºC and 300ºC.*

Reference 3	Cycle in which crazing occurred		
	No reheating	With reheating at 500ºC (ISO 10545 – Part 11)	With reheating at 300ºC
Test specimen 1	Did not crack till 5th cycle	3rd cycle	4th cycle
Test specimen 2	Did not crack till 5th cycle	3rd cycle	5th cycle
Test specimen 3	Did not crack till 5th cycle	3rd cycle	5th cycle
Test specimen 4	Did not crack till 5th cycle	4th cycle	5th cycle
Test specimen 5	Did not crack till 5th cycle	4th cycle	5th cycle

Table X. *Evaluation of tile crazing resistance at 500ºC and 300ºC.*

Reference 4	Cycle in which crazing occurred		
	No reheating	With reheating at 500ºC (ISO 10545 – Part 11)	With reheating at 300ºC
Test specimen 1	Did not crack till 5th cycle	3rd cycle	5th cycle
Test specimen 2	Did not crack till 5th cycle	3rd cycle	5th cycle
Test specimen 3	Did not crack till 5th cycle	4th cycle	Did not crack till 5th cycle
Test specimen 4	Did not crack till 5th cycle	4th cycle	Did not crack till 5th cycle
Test specimen 5	Did not crack till 5th cycle	4th cycle	Did not crack till 5th cycle

Table XI. *Evaluation of tile crazing resistance at 500ºC and 300ºC.*

Reference 5	Cycle in which crazing occurred		
	No reheating	With reheating at 500ºC (ISO 10545 – Part 11)	With reheating at 300ºC
Test specimen 1	4th cycle	3rd cycle	4th cycle
Test specimen 2	4th cycle	3rd cycle	4th cycle
Test specimen 3	4th cycle	3rd cycle	5th cycle
Test specimen 4	4th cycle	3rd cycle	5th cycle
Test specimen 5	4th cycle	3rd cycle	5th cycle

Table XII. *Evaluation of tile crazing resistance at 500ºC and 300ºC.*

Tables 8 to 12 reveal that the number of autoclave hydration cycles capable of causing crazing in tiles reheated at 500°C is always lower compared to non-reheated pieces and those reheated at a lower temperature (300°C). Therefore, the results prove that tiles reheated in accordance with ISO 10545-11 become less resistant to crazing.

This variation in results is explained on evaluating the movement of these tiles before and after reheating at the ideal temperature. In contrast to what was seen in Figure 2, the tiles reheated at 300°C move much less. This result, as shown in Figure 4, indicates that reducing temperature by 200ºC generates less movement in the layers that make up the tile and does not lead to the formation or increase of tensile stresses in the glaze layer.

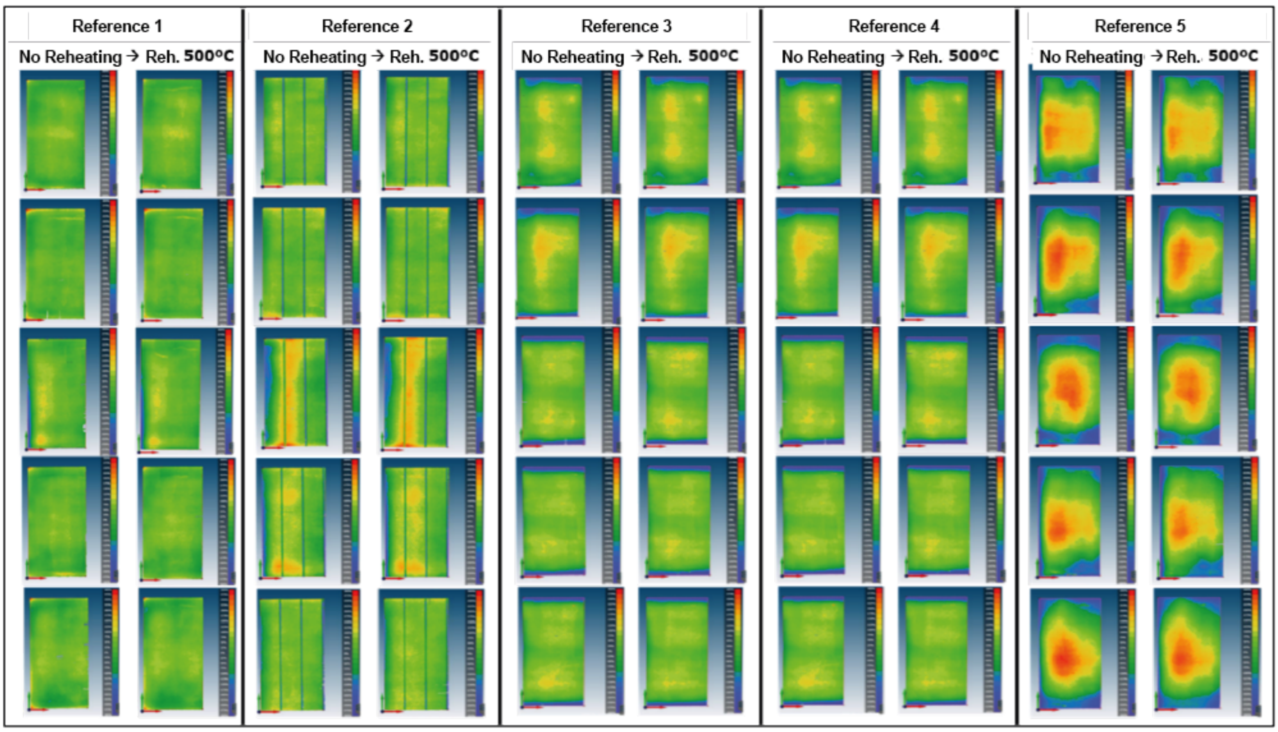

Figure 4. *Effects of reheating at 300ºC on tile curvature.*

4. CONCLUSION

The results obtained in this study clearly indicate that reheating at 500ºC as specified by ISO 10545-11 in the preliminary stages of the crazing resistance test does not fulfil its purpose of recovering the original stress state of ceramic tiles after tile manufacture. Contrary to expectations, the procedure performed as specified led to unexpected movements in the engobe and glaze layers of the commercial BIIb products evaluated in this paper, creating concave curvatures and tensile stresses on the surface of these products, directly resulting in lower tile crazing resistance.

It may be noted that removal of the water absorbed and adsorbed after ceramic tile manufacture can be fully completed by heat treatment at 300ºC. Reheating at that temperature (lower than the 500ºC specified in the standard test) is more effective in recovering the original state of the ceramic tiles, as it does not promote the same changes in the stress state of the glazes as those that develop with reheating at 500ºC. In view of these results, it is highly recommended that, in future revisions of the existing standards for testing the crazing resistance of glazed ceramic products, a firing temperature of 300ºC should be considered, replacing the current 500ºC firing temperature.

5. REFERENCES

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