# THERMAL PERFORMANCES OF CERAMIC GLAZES CONTAINING ZIRCON

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## 1. ABSTRACT

A widespread solution to mitigate the urban heat island effect is the use of materials for the building external envelope that have high radiative properties, so called cool materials. Materials used for cool roof construction include spray paints and sheaths, waterproof membranes and polymer bitumens. These materials are, however, affected by the deposition of dirt and degradation, and so require periodic washing, maintenance or restoration treatments. To reduce the level of maintenance it is advantageous to use materials with high durability physical-chemical characteristics, such as ceramic tiles.

The aim of this work was to study the effects of the addition of zircon ($ZrSiO_4$), as frit and as opacifier, in different percentages, to different ceramic coloured glazes (five coloured and one “no colour” glaze) on solar reflectance (□s) and on thermal performance of the coloured glazes prepared and applied at an industrial scale on ceramic tiles.

The results showed that zircon increases the cool effect in the composition of coloured glazes for ceramic tiles. Such tiles, if used as a building envelope material, will improve the thermal comfort in the home by reducing energy requirements and, compared to other commercial solutions already on the market (such as paints), are able to reduce maintenance costs due to their high resistance to wear, dirt and staining.

## 2. INTRODUCTION

In urban areas, buildings are known to absorb the heat of solar radiation during the day and re-emit it at night. The low solar reflectance generates the so called "heat island effect", causing discomfort, increasing energy consumption, decreasing the environmental quality and aggravating diseases related to thermal stress [1]. Nowadays, to mitigate this effect, so-called cool materials having a high solar reflectance are frequently considered in building applications. It has been widely demonstrated that these materials when used as roofing are able to reduce a building's energy needs for summer cooling and the consequent emissions of $CO_2$ to the atmosphere [2]. By way of example, in a medium latitude (temperate climate), the measured annual energy saving from roof whitening of previously dark roofs ranged from 20 to 22 kWh/$m^2$ of roof area, corresponding to a cooling energy use reduction of 14-26% [3]. As a consequence, the annual direct $CO_2$ reductions associated with the reduced cooling energy use were estimated to be 11-12 kg $CO_2/m^2$ of flat roof area [3].

In urban areas, the roof surfaces generally account for approximately 20-40% of the total area exposed to solar radiation and the paved area for 29-44% of the total area [3, 4]. Especially in densely populated cities the deployment of green areas is a challenge, making the use of reflective surfaces for buildings and pavements the most viable solution in the short term.

Widely used cool materials are organic based, such as spray paints and sheaths, waterproof membranes and polymer bitumens. However, these materials are affected by the deposition of dirt and degradation, and so require periodic washing, maintenance or restoration treatments. It is estimated that white paints with high solar reflectance and excellent thermal emissivity undergo a degradation throughout the useful life of these materials, almost halving their value of solar reflectance from $\rho s=0.8$ to $\rho s=0.46$ within two years [5].

On the other hand, ceramic tiles have significantly better performance in terms of durability, environment protection and aesthetic characteristics than organic-based materials.

The addition of zircon ($ZrSiO_4$) in ceramic glazes, to increase solar reflectance, can improve the potential of ceramic tiles as a cool material. An added value compared to the existing cool materials is the fact that ceramic glazes in general, and those containing zircon in particular, are characterized by greater durability in terms of resistance to chemical attack and wear [6]. Furthermore, with a view to reduce building maintenance costs, ceramic glazes can be designed with a surface finish to increase the tiles' cleaning performance.

Until now, few scientific studies are available in literature concerning the design and development of inorganic cool glazes for ceramic tiles [7, 8, 9]. Some of these glazes are not suitable for porcelain stoneware tile [7] and most of them [8, 9] deal with the application of a whitening substrate (engobe) before the glaze application.

This novel study was carried out to evaluate the effect of zircon additions to ceramic glazes of various colours and, importantly, without using any Zr-based engobe or Zr-based pigments, thus avoiding any other contribution. Zircon was added both as an opacifier directly to the glaze formulation and as frit component. The solar reflectance index (SRI) was calculated on all glaze samples and the CIELab L *, a *, b * colorimetric coordinates were also determined, to evaluate any colour variation due to the presence of zircon. The thermal performance of the samples was then studied whilst exposed in the outdoor environment during the hot summer period.

## 3. EXPERIMENTAL APPROACH

Industrial glaze formulations were prepared by a glazing company. Zircon was added in two ways, in different percentages, as indicated in Table I.

The compositions obtained (standard soft matt glazes) fired at 1180 ºC in an electric kiln (industrial cycle) were prepared and applied on a standard porcelain body.

Five different ceramic pigments were added at 3 wt% to all the glaze formulations to obtain five coloured glazes (black, blue, yellow, green and brown). The glazes were also prepared without pigment, obtaining the "no colour" samples. Overall, 36 different samples were prepared.

In the samples in which zircon was added as opacifier, it is possible to note a colour lighting effect at 5 wt% zircon and, more clearly, at 10 wt%, compared to 0 wt% zircon addition.

The lighting effect does not occur in the samples where the zircon was added as frit. Note that due to the addition of a refractory material (i.e. zircon), it was necessary to adjust the composition of the glaze by adding a higher amount of fluxing materials (such as nepheline or dolomite). Therefore, the composition of the glazes with frits containing 0 wt%, 3.3 wt% and 6.6 wt% zircon is different.

| Addition as OPACIFIER | Zircon, wt% |
|---|---|
| A-O | 0 |
| B-O | 5 |
| C-O | 10 |
| **Addition as FRIT** | **Zircon, wt%** |
| A-F | 0 |
| B-F | 3.3 |
| C-F | 6.6 * |

* maximum percentage to achieve a soft-matt glaze

***Table I:*** *Amount of zircon (wt%) added as opacifier (O) or as frit (F) to the glaze formulations.*

All samples were analysed in terms of Solar Reflectance spectra in the solar irradiance spectrum range (250-2500 nm) by using an UV/Vis/NIR spectrophotometer (Jasco V670, USA).

The colour of the samples was determined according to the *Commission Internationale de l'Eclairage* (CIE), which is the regulatory body responsible for international recommendations for photometry and colorimetry. In this system, the values measured are L*, a* and b* and are called CIELAB. Each colour is represented by the coordinates in a three-dimensional system generating a set of three members. The vertical L* axis represents the differences between light (L*=100) at the top and dark (L*=0) at the bottom. The axis a* displays the difference between red (+a*) and green (–a*), while b* corresponds to the difference between yellow (+b*) and blue (–b*).

The thermal performance, in outdoor conditions, of the samples prepared with various percentages of zircon, added as frit and as opacifier, were evaluated by monitoring the surface temperature during the summer period (from June to September 2018).

The samples were exposed to sunlight, monitoring the thermal surface: six tiles with the same pigment and zircon added as opacifier (O) or as frit (F) in different percentages (A-O, B-O, C-O and A-F, B-F, C-F, respectively) were placed on a panel, mounted on the monitoring station in a horizontal position (0 °), in order to simulate a floor. The monitoring station was placed in a position that simulates the "real operating conditions" of a floor, so it was subject, in addition to atmospheric agents, to shading by vegetation or buildings.

A temperature and relative humidity sensor (Delta OHM, Italy) was used to measure the environmental conditions. A datalogger with six thermocouples (Delta OHM, Italy) was used to measure the surface temperature of the samples. Data collection was made every 30 minutes (from 9:00 to 17:00 approximately) for five days and for each colour. Figure 1 shows the set-up of the outdoor monitoring phase.

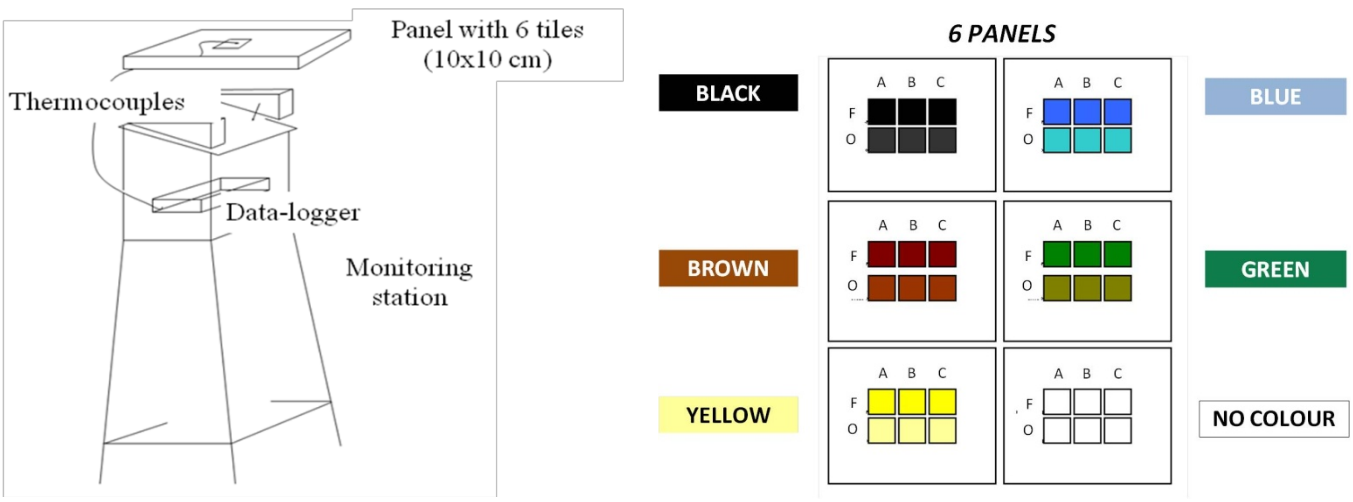
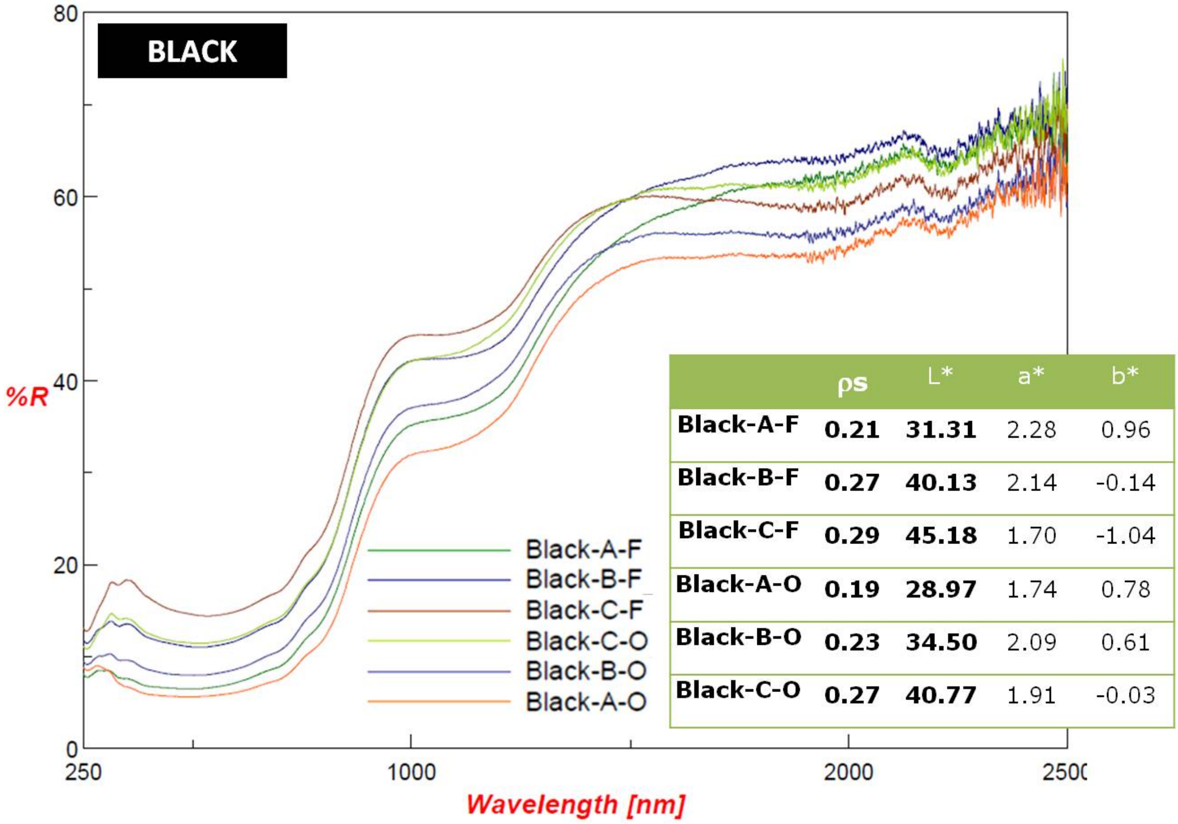



***Figure 1:*** *Scheme of the monitoring station (left) and panels with the samples (right).*

## 4. RESULTS AND DISCUSSION

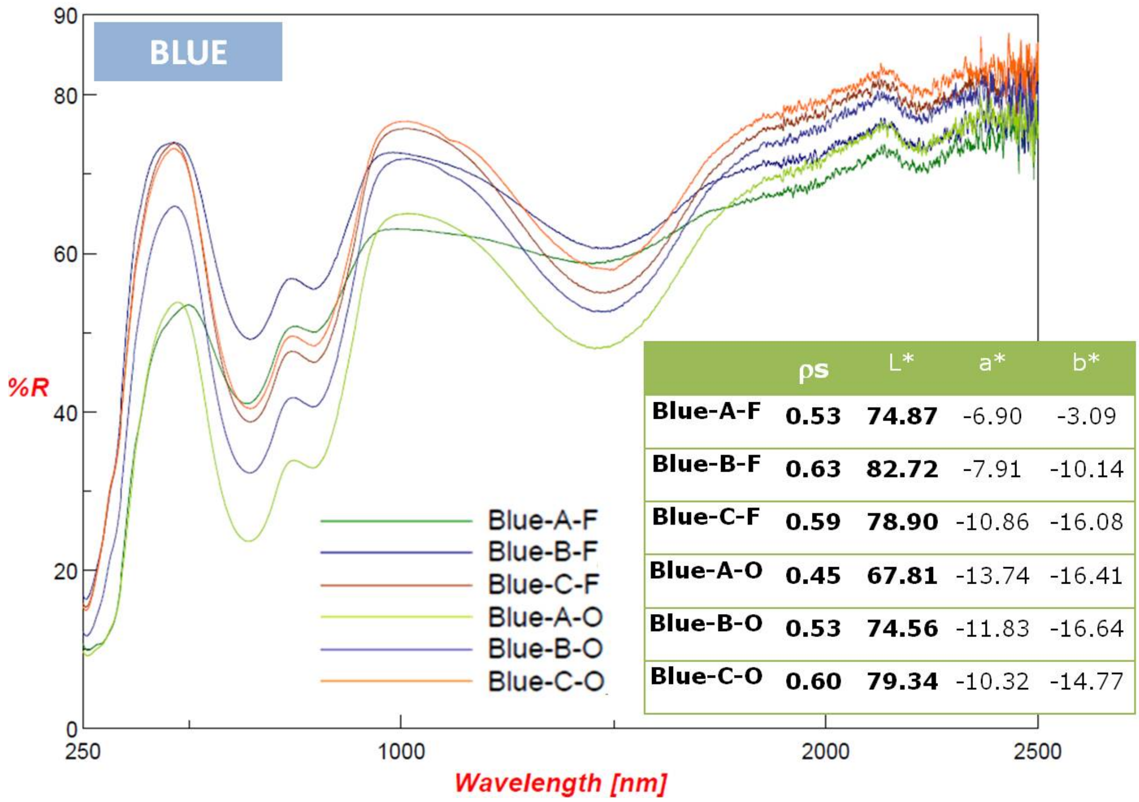
The reflectance spectra in the solar irradiation spectrum range, the solar reflectance values (ρs) and the colorimetric coordinates (L*, a*, b*) of the samples with zircon added as frit and as opacifier, in different percentages, are reported in Figs. 2-7 for each of the coloured glazes. From these figures it is possible to note that the addition of zircon produces, in general, an increasing solar reflectance values of the glazes.

The higher solar reflectance is linked to the increase in the colorimetric coordinate L*, related to the lightness of the colour, but also to an increase in spectral components in the NIR range (780-2500 nm). The effect is more pronounced when it is added as opacifier and less when it is added to frits. It is probably due to the glaze formulations because when a refractory material like zircon is added to frits, the glazes composition has to be changed by adding more melting agents (nepheline or dolomite) in order to maintain the same glaze characteristics, such as fluxing behaviour during firing and gloss of the finish surface after firing. Therefore, the solar reflectance values of the glazes are not directly proportional to the amount of zircon added, as occurs when zircon is added as opacifier. In light-coloured glazes, such as the yellow one, when zircon is added as frit, ρs increases by 23% and L* (lighting effect) by 11% from the A-F to the B-F composition, the best performing one. Always in yellow glaze, when zircon is added as opacifier, ρs increases by 19% and L* (lighting effect) by 9% from the A-F to the C-O composition. In dark-coloured glazes, such as the brown one, when zircon is added as frit, ρs increases by 10% and L* (lighting effect) by 12% from the A-F to the B-F composition. Always in brown glaze, when zircon is added as opacifier, ρs increases by 28% and L* (lighting effect) by 23% from the A-O to the C-O composition. In general, the results show that when zircon is added in frits, the best performing glazes are those containing 3.3 wt% zircon (B-F) for each colour. On the other hand, when zircon is added as opacifier, the best performing glazes are those with the highest amount of zircon, 10 wt% (C-O) for each colour.



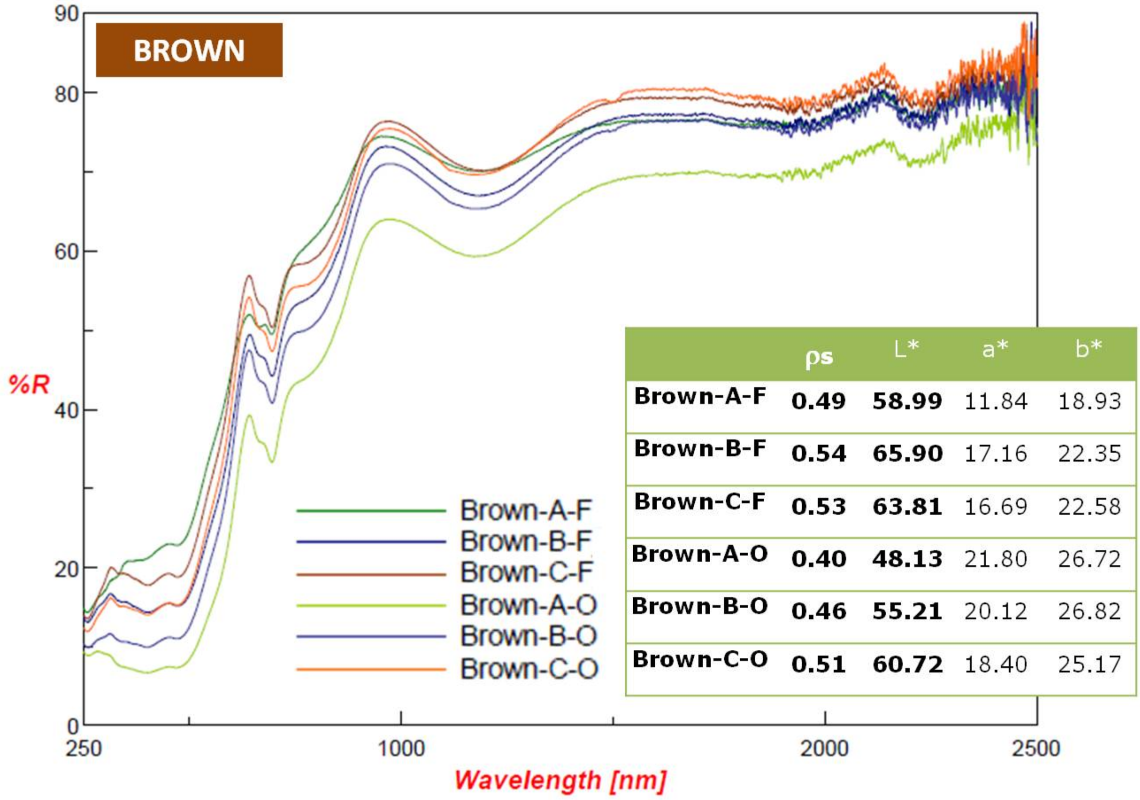

| | ρs | L* | a* | b* |
|---|---|---|---|---|
| **Black-A-F** | **0.21** | **31.31** | 2.28 | 0.96 |
| **Black-B-F** | **0.27** | **40.13** | 2.14 | -0.14 |
| **Black-C-F** | **0.29** | **45.18** | 1.70 | -1.04 |
| **Black-A-O** | **0.19** | **28.97** | 1.74 | 0.78 |
| **Black-B-O** | **0.23** | **34.50** | 2.09 | 0.61 |
| **Black-C-O** | **0.27** | **40.77** | 1.91 | -0.03 |

***Figure 2:*** *Solar reflectance curves (reflectance, R, versus spectral wavelength), solar reflectance values ($\rho$s) and colorimetric coordinates (L*, a*, b*) of the black samples.*



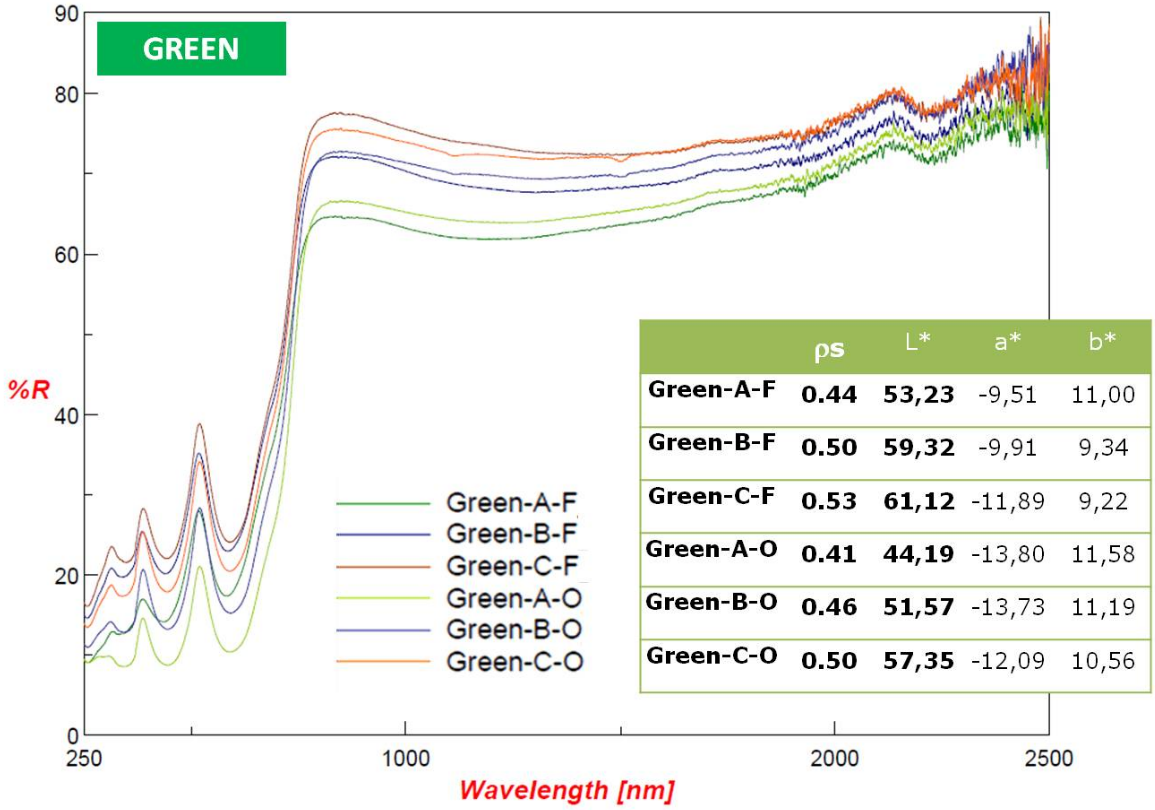

| | ρs | L* | a* | b* |
|---|---|---|---|---|
| **Blue-A-F** | **0.53** | **74.87** | -6.90 | -3.09 |
| **Blue-B-F** | **0.63** | **82.72** | -7.91 | -10.14 |
| **Blue-C-F** | **0.59** | **78.90** | -10.86 | -16.08 |
| **Blue-A-O** | **0.45** | **67.81** | -13.74 | -16.41 |
| **Blue-B-O** | **0.53** | **74.56** | -11.83 | -16.64 |
| **Blue-C-O** | **0.60** | **79.34** | -10.32 | -14.77 |

***Figure 3:*** *Solar reflectance curves (reflectance, R, versus spectral wavelength), solar reflectance values ($\rho$s) and colorimetric coordinates (L*, a*, b*) of the blue samples.*



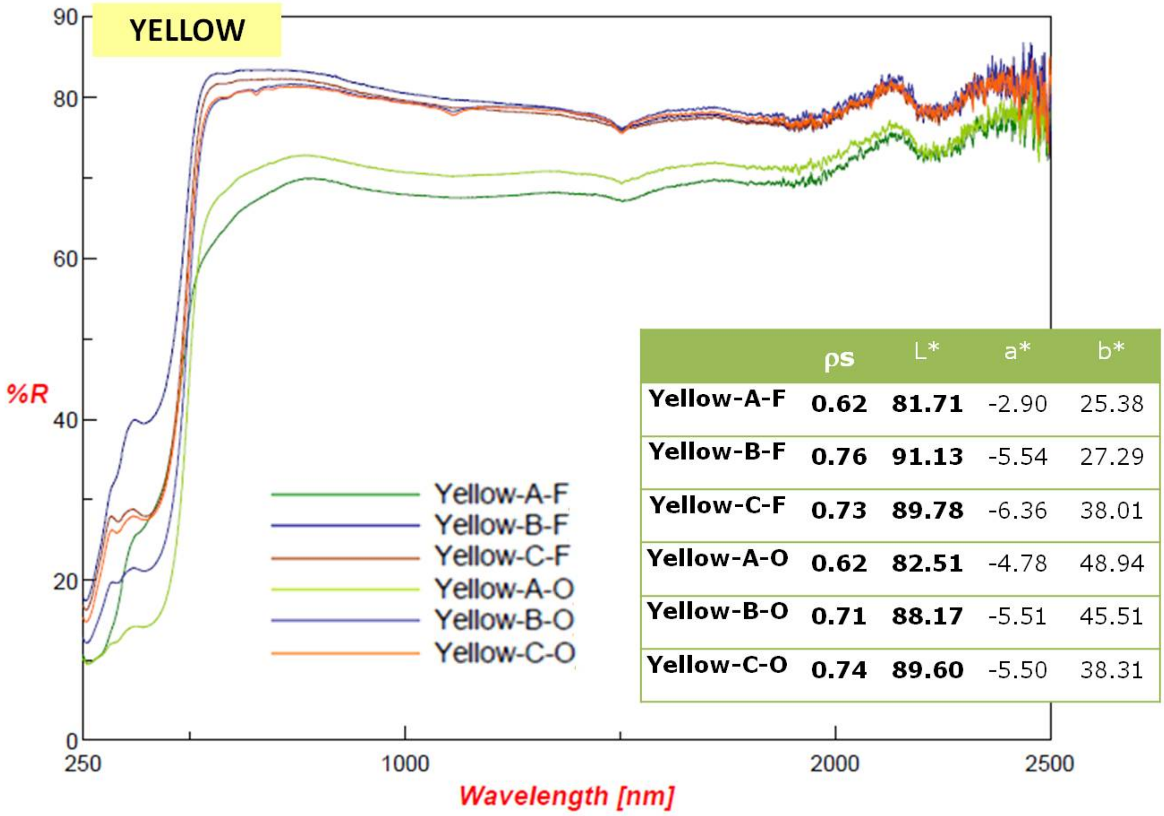

| | ρs | L* | a* | b* |
|---|---|---|---|---|
| **Brown-A-F** | **0.49** | **58.99** | 11.84 | 18.93 |
| **Brown-B-F** | **0.54** | **65.90** | 17.16 | 22.35 |
| **Brown-C-F** | **0.53** | **63.81** | 16.69 | 22.58 |
| **Brown-A-O** | **0.40** | **48.13** | 21.80 | 26.72 |
| **Brown-B-O** | **0.46** | **55.21** | 20.12 | 26.82 |
| **Brown-C-O** | **0.51** | **60.72** | 18.40 | 25.17 |

***Figure 4:*** *Solar reflectance curves (reflectance, R, versus spectral wavelength), solar reflectance values ($\rho s$) and colorimetric coordinates (L*, a*, b*) of the brown samples.*



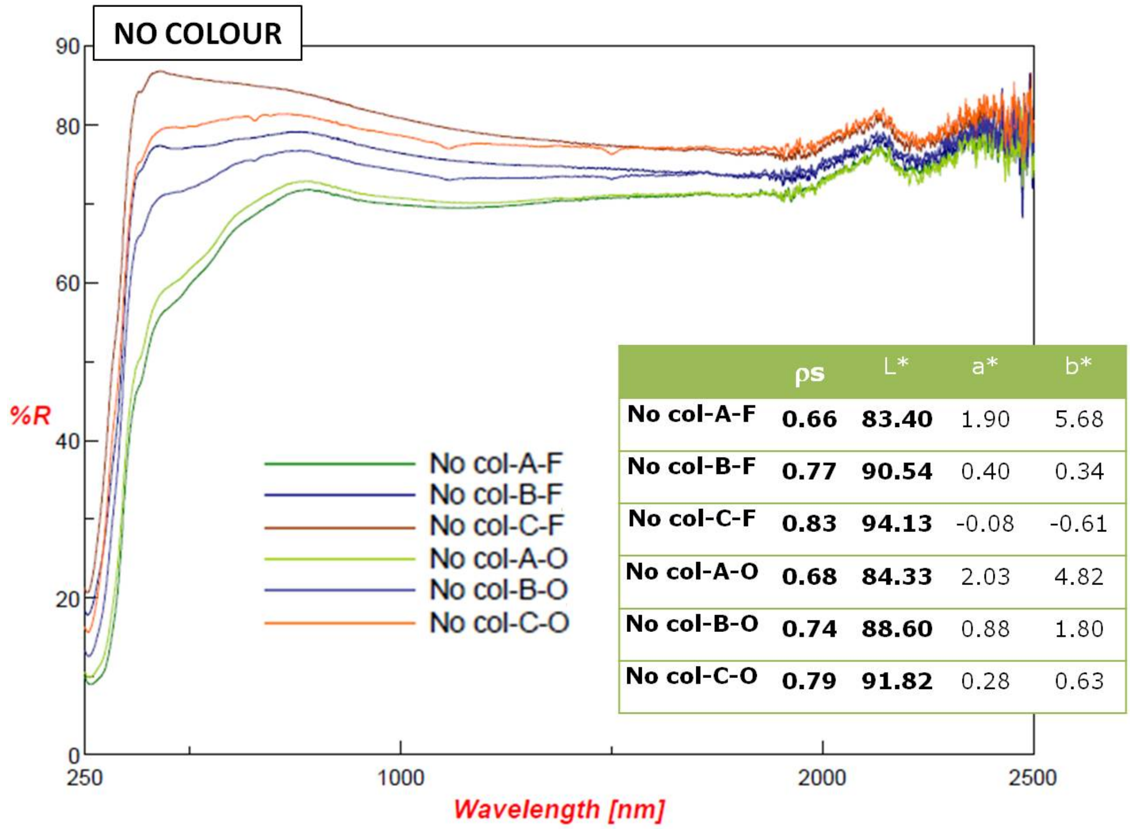

| | ρs | L* | a* | b* |
|---|---|---|---|---|
| **Green-A-F** | **0.44** | **53,23** | -9,51 | 11,00 |
| **Green-B-F** | **0.50** | **59,32** | -9,91 | 9,34 |
| **Green-C-F** | **0.53** | **61,12** | -11,89 | 9,22 |
| **Green-A-O** | **0.41** | **44,19** | -13,80 | 11,58 |
| **Green-B-O** | **0.46** | **51,57** | -13,73 | 11,19 |
| **Green-C-O** | **0.50** | **57,35** | -12,09 | 10,56 |

***Figure 5**: Solar reflectance curves (reflectance, R, versus spectral wavelength), solar reflectance values ($\rho s$) and colorimetric coordinates (L*, a*, b*) of the green samples.*




| | ρs | L* | a* | b* |
|---|---|---|---|---|
| **Yellow-A-F** | **0.62** | **81.71** | -2.90 | 25.38 |
| **Yellow-B-F** | **0.76** | **91.13** | -5.54 | 27.29 |
| **Yellow-C-F** | **0.73** | **89.78** | -6.36 | 38.01 |
| **Yellow-A-O** | **0.62** | **82.51** | -4.78 | 48.94 |
| **Yellow-B-O** | **0.71** | **88.17** | -5.51 | 45.51 |
| **Yellow-C-O** | **0.74** | **89.60** | -5.50 | 38.31 |

***Figure 6:*** *Solar reflectance curves (reflectance, R, versus spectral wavelength), solar reflectance values (ρs) and colorimetric coordinates (L*, a*, b*) of the yellow samples.*




| | ρs | L* | a* | b* |
|---|---|---|---|---|
| **No col-A-F** | **0.66** | **83.40** | 1.90 | 5.68 |
| **No col-B-F** | **0.77** | **90.54** | 0.40 | 0.34 |
| **No col-C-F** | **0.83** | **94.13** | -0.08 | -0.61 |
| **No col-A-O** | **0.68** | **84.33** | 2.03 | 4.82 |
| **No col-B-O** | **0.74** | **88.60** | 0.88 | 1.80 |
| **No col-C-O** | **0.79** | **91.82** | 0.28 | 0.63 |

***Figure 7:*** *Solar reflectance curves (reflectance, R, versus spectral wavelength), solar reflectance values (ρs) and colorimetric coordinates (L*, a*, b*) of the no colour samples.*

In general, during outdoor monitoring, a reduction of the surface temperature is observed in lighter-coloured glazes (such as yellow and no colour), due to their higher values of solar reflectance, and their ability to reflect solar radiation. Also, dark-coloured glazes (such as brown or blue), due to the addition of zircon, are able to act as cool materials.

The surface temperature curves of the yellow samples during the five days of outdoor monitoring are reported in Fig. 8, with indication of weather conditions (sunny or cloudy day).

In has to be considered that the outdoor monitoring phase was performed in "real operating conditions", so that samples were subjected to atmospheric changes (wind, shade, humidity, etc.). Therefore, the surface temperatures during the day are characterised by variations which, probably, do not reflect the contribution of the solar radiation alone. For example, the surface temperature curves of a sunny day are reported in Figs. 9 and 10 for the yellow and brown glazes, respectively.

It is possible to note that the lightest glazes (with higher L* value and higher $\rho s$) remain cooler. In particular, the glaze B-F, with 3.3% zircon, exposed to solar radiation, maintain lower temperatures compared to the other glazed samples, with differences up to 5°C.

Some studies on outdoor monitoring of cool roofs confirm these results [[i],[ii]], even if these studies concern roof membranes and/or coating paints located in Perugia (central Italy) [i] or in Mexico [ii]. The cooling capability of these "cool roofs" was estimated at about 3-10°C depending on the colour (light or dark), compared to a traditional roof.

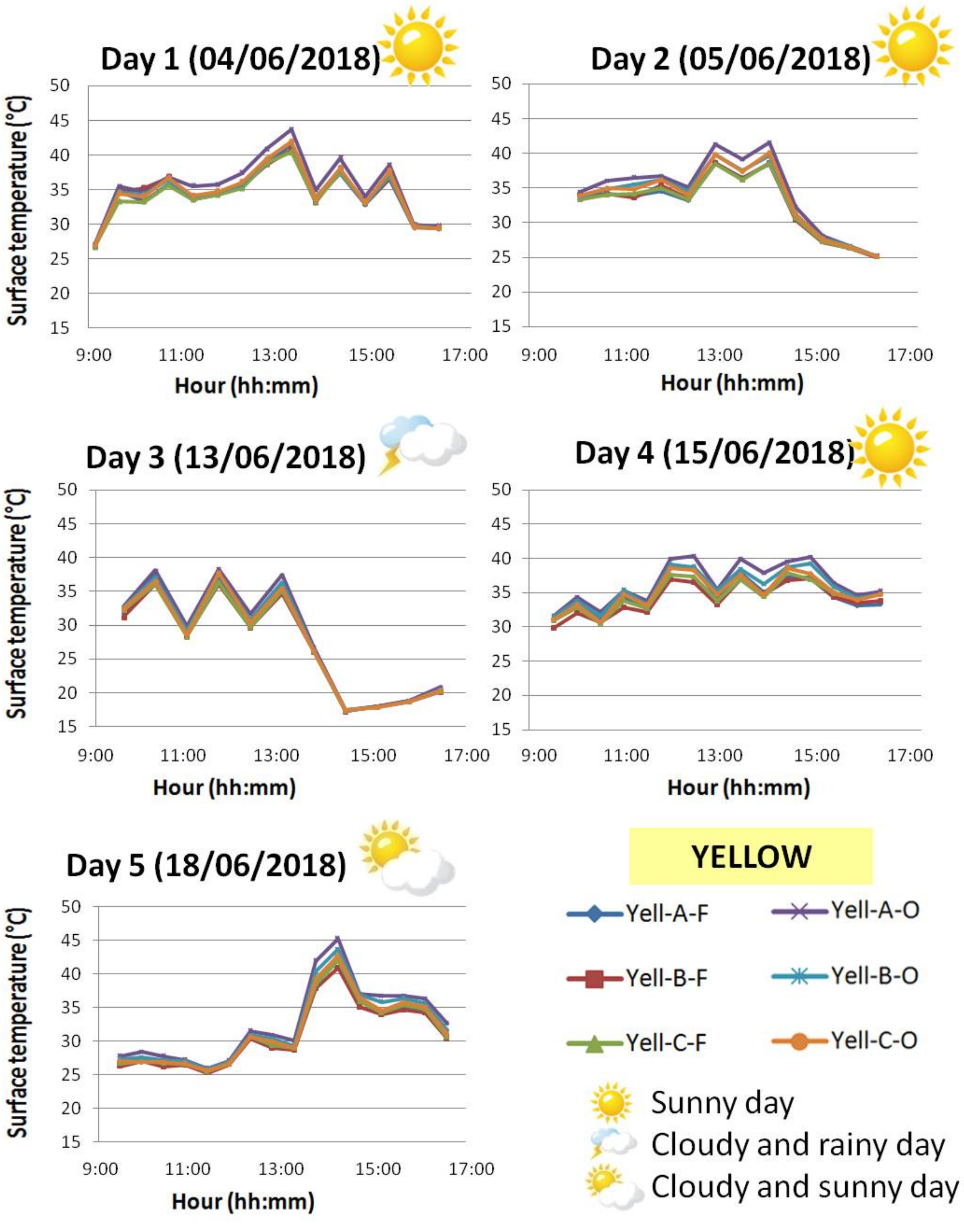



***Figure 8:*** *Surface temperature curves of the yellow samples during 5 days of monitoring.*

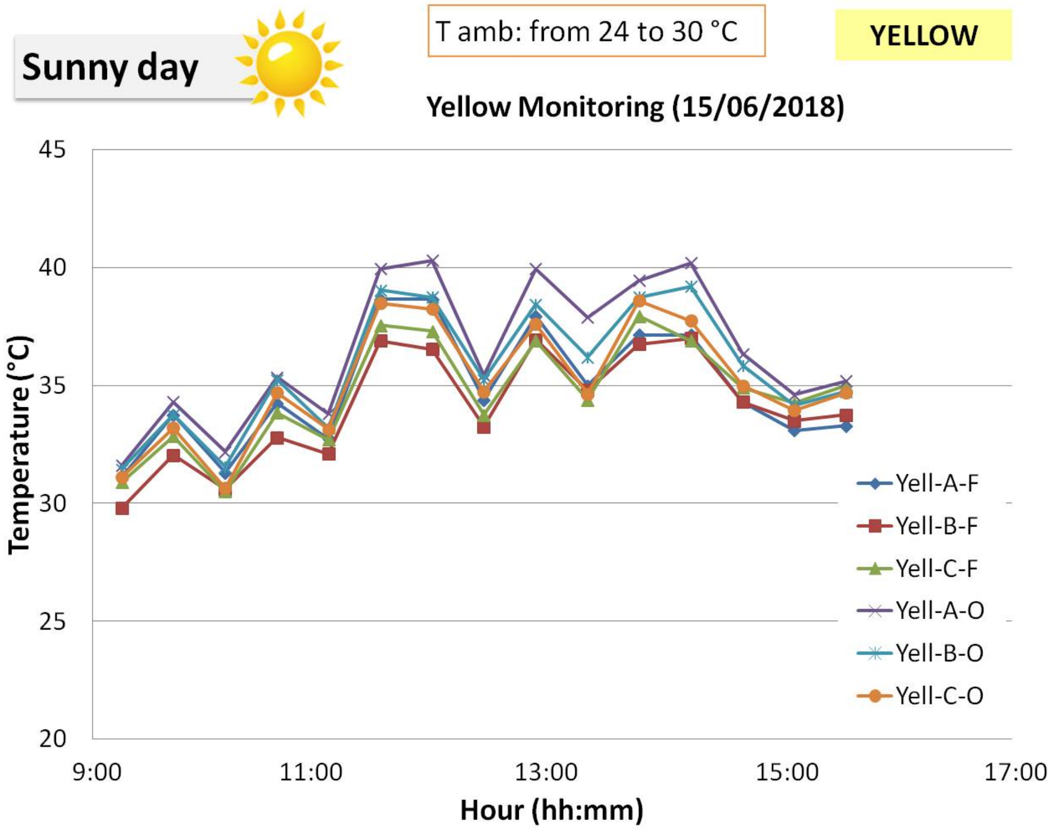



***Figure 9:*** *Surface temperature curves of the yellow samples, on a sunny day during monitoring.*

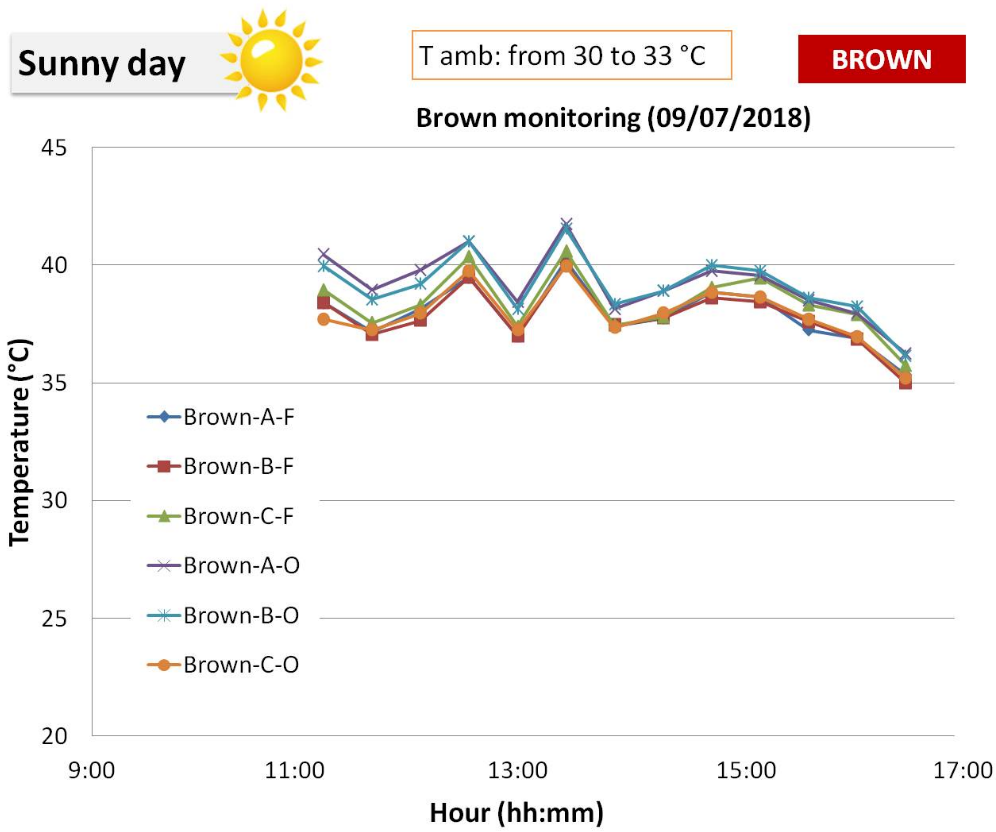



***Figure 10:*** *Surface temperature curves of the brown samples, on a sunny day during monitoring.*

## 5. CONCLUSIONS

Tests performed on glazed ceramic tile samples show that, in general, the addition of zircon ($ZrSiO_4$) increases the solar reflectance property of coloured glazes. This effect is more evident when zircon is added as opacifier. In this case, as the percentage of added zircon increases, the value of solar reflectance increases for all the colours analysed. Further, the whitening effect of the zircon is also highlighted by the linear increase in the colorimetric coordinate L*, linked to the lightness of the colour.

When the zircon is added to glazes as a frit component, its effect may be concealed by the other components of the frit itself. In fact, due to the addition of a refractory material (zircon), it was necessary, to change the composition of the glaze by adding a higher amount of fluxing materials (such as nepheline or dolomite). Therefore, the composition of the glazes with frits containing 0%, 3.3% and 6.6% zircon, are different.

In general, the results showed that for all the colours, the glaze with frit containing 3.3% zircon shows a higher value of L* (highest lightness) and a higher value of solar reflectance, compared to the glaze with frit containing 6.6% zircon. At room temperature, a comparison of the coloured glazed tile samples shows that the darker colours (i.e. brown) are less cool than the light ones. Comparing the same colour, the lightest glaze, with higher L* value and higher solar reflectance, remain cooler. In particular, the glazes with frit containing 3.3% zircon, exposed to solar radiation, maintain lower temperatures compared to the other glazed samples with measured temperature differences of up to 5°C. Excluding the colour appearance, the improvement of solar reflectance property, in terms of lower surface temperatures, is observed in those glazes with higher spectral curves in the NIR range, in particular after 1500 nm. The increase in spectral values in the NIR range is an effect that can be directly correlated to the addition of zircon in the glazes. Thus, zircon additions to glazes can result in ceramic tiles that can act as a cool material for building roofs.

## 6. ACKNOWLEDGEMENTS

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