# HIGH-RECYCLING CONTENT PORCELAIN STONEWARE TILES: FROM INDUSTRIAL PRODUCTION TO PRODUCT CERTIFICATION

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## 1. ABSTRACT

The present work deals with the industrial production of porcelain stoneware tiles containing 85% of secondary raw materials, in particular scrap packaging glass from urban-separated collection (post-consumer waste) and industrial ceramic waste (pre-consumer waste).

This innovative ceramic product is sintered about 200°C lower than a traditional porcelain stoneware tile. It maintains high technical performances belonging to class BIa of the International Standard of ceramic tiles classification (EN ISO 14411). Moreover, this product fulfils the standard requirements for dry-pressed ceramic tiles with low water absorption (≤0.5%). This product obtained the certification UNI Keymark. The LCA study was also performed and results showed that the significantly lower environmental impact of this innovative product compared to a traditional porcelain stoneware tile.

## 2. INTRODUCTION

The European ceramic market of ceramic tiles is huge. In 2015, it reached a production size of 1,218 million m$^2$, of which 910 million m$^2$ were sold in Europe [1]. In this frame, Italian ceramic production returns to pre-crisis level, reaching 415.9 million m$^2$ in 2016 [2].

Recently, the European Commission published several communications focusing on energy recovery from waste [3] and greater recycling and reuse [4], able to bring benefits for both the environment and the economy. The revised legislative proposals on waste set clear targets for waste reduction and the establishment of ambitious and credible long-term paths for waste management and recycling. In this frame, Ceram-Unie stressed that resource efficiency requires an LCA approach, highlighting that social and economic aspects of sustainability should always be considered in the EU legislation.

With the target of demonstrating a reduction of environmental impact and a significant reuse of end-of-waste materials and by-products, a new concept of traditional ceramic was developed in the last years. In the European-founded project WINCER [5], porcelain tiles containing 85% of natural raw materials, which were replaced by different types of opportunely-balanced waste, were developed. This allowed for a “waste synergy” during firing process. The innovative ceramic mix is mainly constituted by secondary raw materials able to crystallize during firing, showing good stability and overcoming the technological risk linked to pyroplastic deformation [6-8].

The industrial technological transfer of high-recycling content ceramic tiles has been demonstrated thanks to the Marazzi company, which has carried out the first industrial production in two different formats (15x15 and 30x60 cm).

Beyond the social and environmental benefits for the sustainability of waste management, about 30% of industrial costs abatement can be reached due to the lower expenses for raw materials, lower energy and methane consumption, as these products can be fired about 200°C lower when compared to traditional tiles.

A complete characterisation of these highly-recycled porcelain tiles was carried out in terms of their compliance with EN 14411 for CE certification and UNI Keymark. Moreover, to assess their complete potential environmental impact, an LCA study was performed according to EN 15804 "Sustainability of construction works - Environmental product declarations - Core rules for the product category of construction products", following the "cradle to gate" criteria.

## 3. MATERIALS AND METHODS

To reach 85% of recycled materials in porcelain stoneware tiles, scrap packaging glass from urban-separated collection (SAVEL C, supplied by Minerali Industriali) and industrial ceramic waste (unfired scrap porcelain stoneware tiles, coming from MARAZZI's production) were used. A low amount of plastic clay (15%) was added to the mix, in order to obtain tiles with rather good mechanical properties before firing (flexural strength of dried specimens 2.5±0.3 MPa).

Milling, spray drying, shaping and glazing, drying, and firing cycle were carried out at industrial level in one of the MARAZZI plants. In Table I, the most relevant conditions are shown.

<table>
<tr><th colspan="9">MILLING</th></tr>
<tr><td colspan="2">Slip density</td><td colspan="7">1660 g/l</td></tr>
<tr><td colspan="2">Slip dry content</td><td colspan="7">64%</td></tr>
<tr><td colspan="2">Slip residue (45 μm screen)</td><td colspan="7">2%</td></tr>
<tr><th colspan="9">SPRAY DRYING</th></tr>
<tr><td colspan="2">Carbonate content</td><td colspan="7"><0.5%</td></tr>
<tr><td rowspan="2">Powder size distribution</td><td>Size (mm)</td><td>0.630</td><td>0.500</td><td>0.400</td><td>0.315</td><td>0.250</td><td>0.125</td><td><0.125</td></tr>
<tr><td>Weight %</td><td>4.2</td><td>15.0</td><td>18.0</td><td>30.1</td><td>14.5</td><td>15.9</td><td>2.3</td></tr>
<tr><th colspan="9">SHAPING</th></tr>
<tr><td colspan="2">Reference fired size</td><td colspan="7">300X600 mm</td></tr>
<tr><td colspan="2">Specific pressure</td><td colspan="7">30 MPa</td></tr>
<tr><td colspan="2">Moisture content</td><td colspan="7">5.5%</td></tr>
<tr><td colspan="2">Dry modulus of rupture</td><td colspan="7">2.5 MPa</td></tr>
<tr><th colspan="9">DRYING</th></tr>
<tr><td colspan="2">Cycle duration</td><td colspan="7">24 min</td></tr>
<tr><td colspan="2">Maximum temperature</td><td colspan="7">230°C</td></tr>
<tr><td colspan="2">Tile temperature glazing line</td><td colspan="7">92-100°C</td></tr>
<tr><th colspan="9">FIRING</th></tr>
<tr><td colspan="2">Cycle duration</td><td colspan="7">39 min</td></tr>
<tr><td colspan="2">Maximum temperature</td><td colspan="7">1025°C</td></tr>
</table>

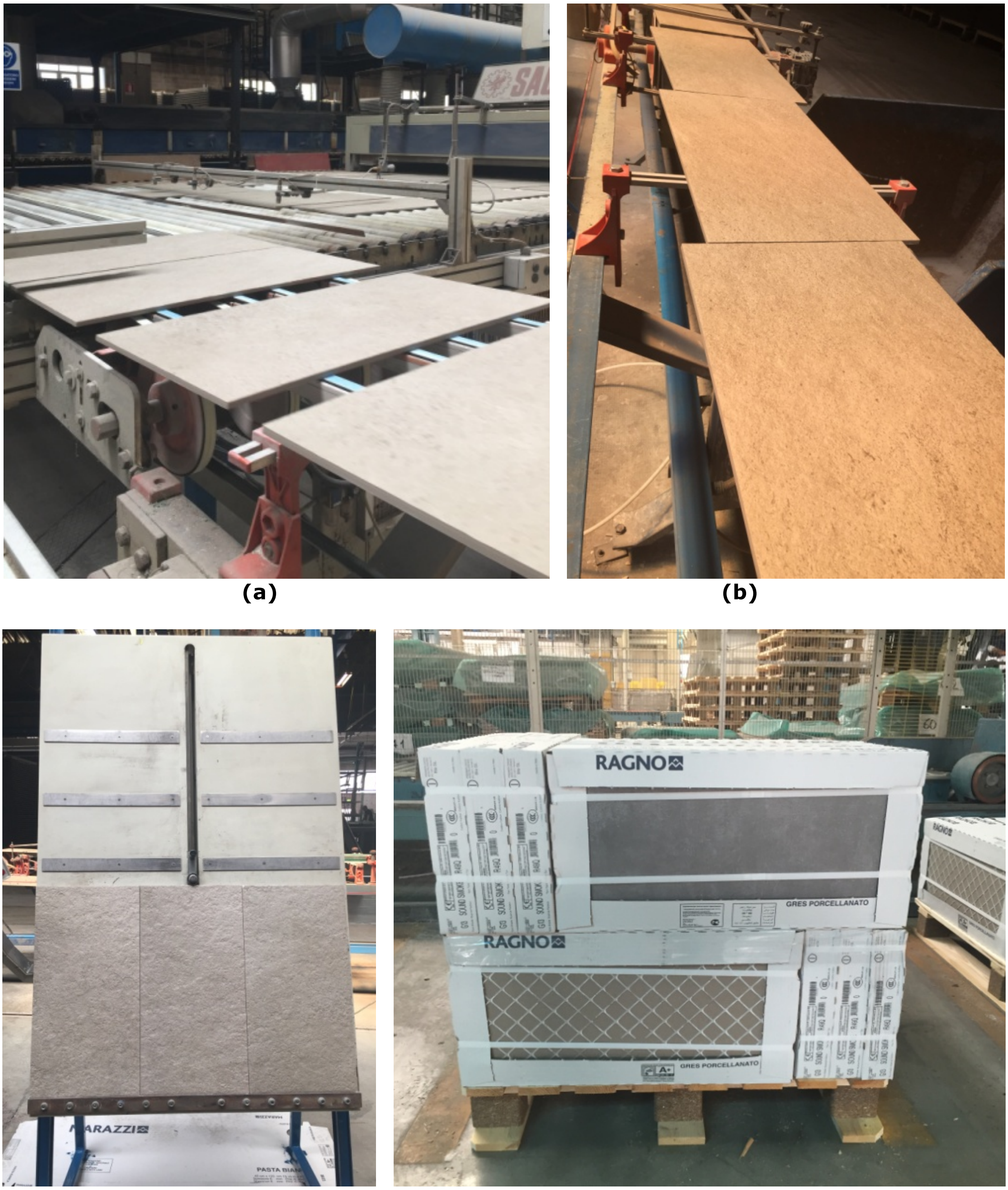
***Table I*** *- Most relevant conditions and parameters for the industrial production.*

Some images of MARAZZI's production of glazed WINCER tiles 30x60 cm are shown in Fig. 1.

Quantitative mineralogical composition of the fired tile was determined by X-rays diffraction analysis (PW3830, Philips, NL). Powdered tile specimens, diluted with 10 wt% of corundum NIST676 as internal standard, were side loaded to minimise preferred orientation. Data were collected in the angular range 10–80° 2θ with steps of 0.02° and 5s/step. Rietveld-RIR refinements were performed using GSAS–EXPGUI software [9].

These tiles were characterised in terms of their compliance with EN ISO 14411 [10]. First of all, water absorption was determined according to UNI EN ISO 10545-3, in order to classify the product on the basis of the international classification (Table 1 of EN ISO 14411) that considers both the water absorption value and the shaping technique(dry pressing method B).

Moreover, the following characteristics were determined: dimension and surface quality (UNI EN ISO 10545-2), modulus of rupture (UNI EN ISO 10545-4), abrasion resistance for glazed tiles UNI EN ISO 10545-7), moisture expansion (UNI EN ISO 10545-10), crazing resistance for glazed tiles (UNI EN ISO 10545-11), frost resistance (UNI EN ISO 10545-12), chemical resistance (UNI EN ISO 10545-13), stain resistance (UNI EN ISO 10545-14).



(a) (b)

(c) (d)

***Figure 1**. (a-d) Images of industrial production of WINCER tiles 30x60 cm.*

LCA study was performed according to ISO 14040 ("Environmental management - Life cycle assessment - Principles and framework") and ISO 14044 ("Environmental management - Life cycle assessment - Requirements and guidelines") in order to evaluate environmental performance. The modules of production life cycle in included the EPD are those related to production phases:

**A1.** Raw materials supply (extraction, processing, recycled material)
**A2.** Transport to manufacturer
**A3.** Manufacturing

The environmental impact assessment categories/indicators considered are those required by EN 15804:

- Pothochemical Ozone Creation Potential (POCP): ozone formation in the lower atmosphere causing summer smog
- Ozone Depletion Potential (ODP): ozone depletion in the higher atmosphere
- Global Warming Potential (GWP 100): greenhouse gases causing climate change
- Eutrophication Potential (EP): emissions causing over-fertilization of soil or water
- Acidification Potential (AP): emissions causing acidifying effects (acid rain, forest decline)
- Abiotic Depletion Potential fossil (ADPf): scarcity of resources (fossil energy carriers)
- Abiotic Depletion Potential elementary (ADPe): scarcity of resources (ores, silicates)

## 4. RESULTS

The mineralogical composition of the fired tile is reported in Table II. Waste synergy during the industrial firing process gives rise to an incipient crystallization. In particular, trydimite and cristobalite crystallise directly from scrap glass, while plagioclase and wollastonite come from the reaction among clay, unfired scrap tiles and scrap glass [11].

| Mineralogical phases | Wt% |
|---|---|
| Quartz | 6.8±0.3 |
| Plagioclase | 13.8±0.5 |
| Trydimite | 1.5±0.5 |
| Cristobalite | 3.8±0.3 |
| Wollastonite | 7.5±0.6 |
| Amorphous phase | 66.6±1.8 |

***Table II*** *- Quantitative mineralogical composition of fired tile.*

Water absorption is 0.1%, and thus, below 0.5%, which is the limit of BIa group (Table 1 of EN ISO 14411). Therefore, this product belongs to the group commercially defined as porcelain stoneware tiles.

In Table III, the dimensions and surface quality characteristics are reported together with the requirements for dry-pressed ceramic tiles with low water absorption (Annex G of the of EN ISO 14411).

Physical properties are reported in Table IV and chemical ones in Table V.

All the results fulfil the requirements reported in Annex G of EN ISO 14411.

| | Dimensions, mm | Deviation from work size | Permissible deviation |
|---|---|---|---|
| Work size | 306.5 x 611.5 x 9.5 | - | - |
| Length and width | 306.2 x 612.0 | 0.1-0.3% | 0.6% |
| Thickness | 9.3 | 2.6-3.7% | 5% |
| Straightness | - | 0.1% | 0.5% |
| Rectangularity | - | 0.2% | 0.5% |
| Surface quality | No visible defects | | |

***Table III*** *- Dimensions and surface quality characteristics of fired tile and standard requirements (EN ISO 14411, Annex G).*

| | Results | Requirements |
|---|---|---|
| Water absorption | 0.1% | ≤0.5% |
| Breaking strength | 1599 N | > 1300 N |
| Flexural tensile strength on modulus of rupture | 42,3 N/mm$^2$ | > 35 N/mm$^2$ |
| Impact resistance, restitution coefficient | 0.73 | Declared value |
| Abrasion resistance | Class 4; 6000 cycles | Declared value |
| Coefficient of linear thermal expansion | 7.9-8.2 (10$^{-6}$ °C$^{-1}$) | Declared value |
| Moisture expansion | 0.1 mm/m | Declared value |
| Crazing resistance | No crazing effect | Pass |
| Frost resistance | No defects | Pass |

***Table IV*** *- Physical properties of fired tile and standard requirements (EN ISO 14411, Annex G).*

| | Results | Requirements |
|---|---|---|
| **Resistance to chemicals*** | | |
| Resistance to low concentrations of acids and alkalis | Class A | Declared value |
| Resistance to high concentrations of acids and alkalis | Class A | Declared value |
| Resistance to household chemicals and swimming pool salts | Class A | Minimum class B |
| **Resistance to staining**** | | |
| Glazed tiles | Class 5 | Minimum class 3 |

*** Classification:**

Class A: no visible effect

Class B: definitive change in appearance

Class C: partial or complete loss of the surface

**** Stain resistance class:**

Class 1: stain not removed

Class 2: Stain removed by dipping in a suitable solvent for 24 hours

Class 3: Stain removed by mechanical cleaning and strong cleansing agent

Class 4: Stain removed by manual cleaning with weak cleansing agent

Class 5: Stain removed by means of hot current water for 5 min

***Table V*** *- Chemical properties of fired tile and standard requirements (EN ISO 14411, Annex G).*

For the LCA study, the main outcomes are reported in Fig. 1 and Fig. 2.

In particular, in Fig. 1, the relative contribution of each life cycle stage is reported compared to different environmental indicators. The main contribution to total production impact from the cradle to gate processes is due to the A1 module, any impact indicator. This module takes into account both the energy and the raw materials production (such as clay, chemical compounds, pigments, etc.). Transports module, A2, has noticeable contributions to two indicators (EP and AP) and is due to both production of fuel and emissions related to its combustion.

Global production module, A3, contributes to EP, POCP and ODP because of paper/cardboard production for packaging. In Chapter 4.2, more detailed results are explained. ADPe is mainly influenced by inks, and ADPf by energy production processes, both belonging to the A1 module.

Fig. 2 shows in detail the contribution of the main processes, such as energy, emissions or raw materials production.

Finally, a comparison between the high-recycled content porcelain stoneware product and a traditional porcelain stoneware tile was performed. In particular, in Table VI, the relative contribution of the atomized powdered production is shown as percentages of the overall A1, A2 and A3 contribution (A1-A2-A3 is 100%). The relative contribution of the atomized powder production, compared to the overall tile production impact in the case of a high-recycled porcelain tile, is much lower than an average traditional porcelain tile.

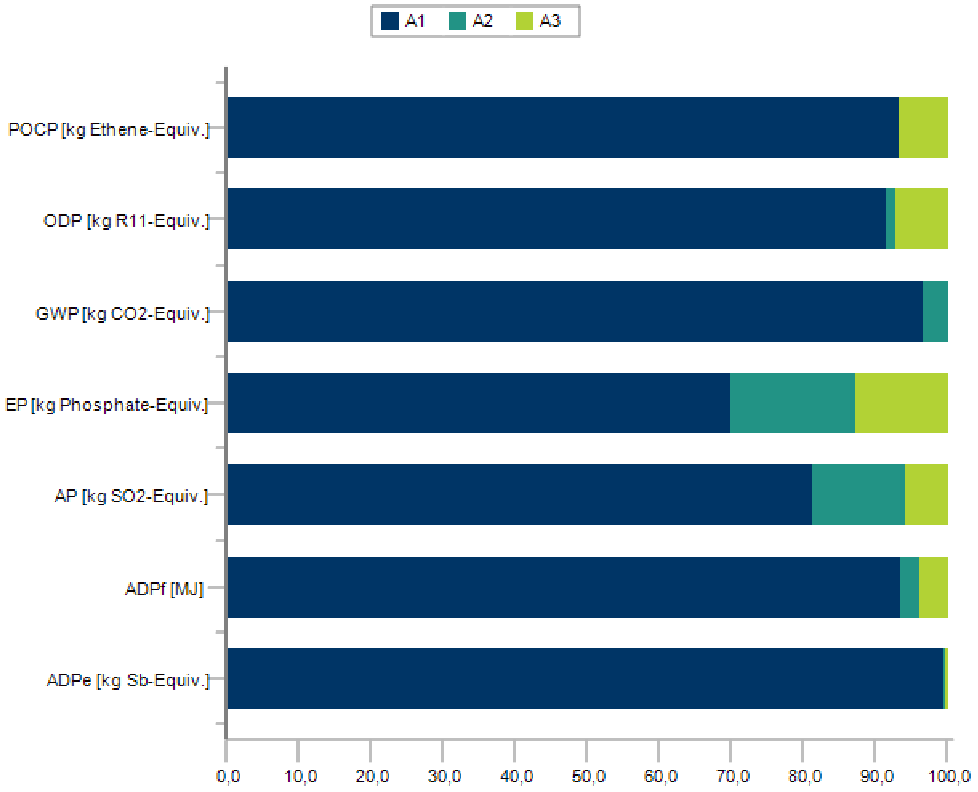


***Figure 2.*** *Relative contribution of each life cycle stage to different environmental indicators.*

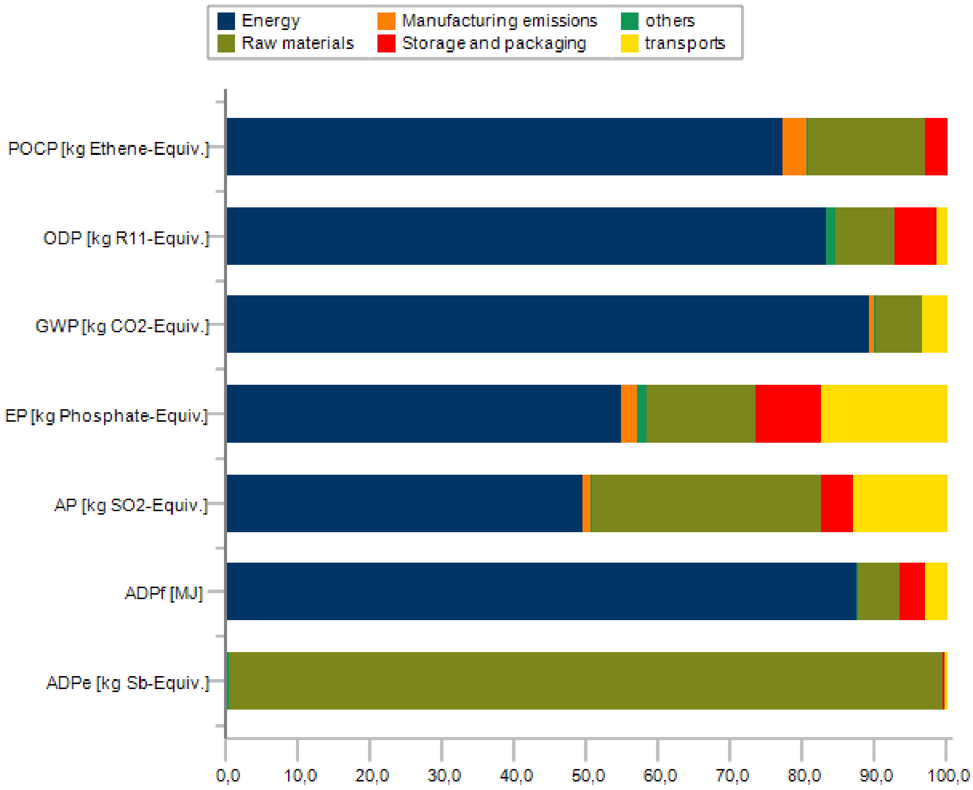


***Figure 3.*** *Relative contribution of main process phases to different environmental indicators.*

| | | Traditional porcelain tile | 85% recycled porcelain tile |
|---|---|---|---|
| **GWP** | [kg $CO_2$-eq.] | 24-25% | 1.09% |
| **ODP** | [kg CFC11-eq.] | 69-75% | 0.43% |
| **AP** | [kg $SO_2$-eq.] | 54-56% | 2.80% |
| **EP** | [kg $(PO_4)^3$-eq.] | 26-27% | 3.35% |
| **POCP** | [kg Ethen eq.] | 37-39% | 2.08% |

***Table VI*** *- Relative contribution of atomized powder production on A1-A2-A3, considering only the raw materials.*

## 5. CONCLUSION

The present work showed that it is possible to produce, at industrial level, high quality ceramic tiles containing 85% recycled materials.

The waste synergy during firing favours an incipient crystallisation, and the fired product maintains good technical performances, similar to those of traditional porcelain stoneware.

This new product obtained the UNI Key Mark certification. Moreover, it demonstrated a significantly lower environmental impact, according to an LCA study.

## 6. ACKNOLEDGEMENT

This publication has been produced with the assistance of the European Union in the frame of the WINCER project (http://www-wincerproject.eu/). The contents of this publication are the sole responsibility of Centro Ceramico and can in no way be taken to reflect the views of the European Union.

Co-funded by the Eco-innovation
Initiative of the European Union

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