



# Ceramic flaws: Laboratory tests and analysis using Scanning Electron Microscope to identify surface defects

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## Abstract

The pollution of raw materials and ceramic products is a problem that affects all ceramic companies operating in the fields of traditional ceramics and thus needs to be further investigated. The presence of impurities in ceramic glaze and bodies, or between their contact surface, causes aesthetic defects.

The aim of this work is to analyse ceramic flaws generated during the processing phases. Analysis of the morphological and compositional imperfections was carried out on different samples by the use of a Scanning Electron Microscope. An efficient model of the flaws in the final ceramic product was later developed, correlating imperfections and pollutants which caused them. In this way the phases of the process, where the pollution might occur, are successfully identified. In order to reach this goal, ceramic samples were created and contaminated in laboratory by the use of potential pollutants, previously and carefully selected in the planning phase of the study.

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## 1. Introduction

Pollution phenomena of bodies and glaze frequently affect sanitary-ware production during the ceramic process itself. Pollutants may derive from raw materials, such as organic compounds in clays, or may be introduced during the ceramic process (namely metals or alloys).<sup>1</sup> Moreover, since the production cycle involves different stages, attention has to be devoted to choosing appropriate raw materials for producing bodies and glaze. Thus, an extremely careful selection of clays, kaolins, feldspars, quartz, and other raw materials needs to be performed; this goal is successfully reached by chemical and mineralogical analysis which leads to minimize ceramic flaws.<sup>1</sup>

However, it has to be noted that pollution may be due to several phases of the cycle production.

For instance, the operation of slip casting – especially in plaster moulds – may cause residual impurities of gypsum on the final product. After drying and glazing the product, defects

may emerge if any impurity occurs during the painting phase or within the paint plant. Furthermore, if we consider the firing phase – which is extremely expensive and crucial – temperature curves may vary depending on the body slip and glaze formulations (Fig. 1). During this step, well known phenomena occur, e.g. the quartz transition at 573 °C, the decomposing of organic matter (400–600 °C), carbonates (700–1050 °C) and sulfates (950–1100 °C). Some of these transformations lead degassing and formation of defects, such as pinholes or detachment of glaze from support.<sup>2,3</sup>

The present project involves an extensive study of aesthetic defects in ceramic products due to the pollution of body slip or glaze. They consist of spots with different morphology and colouration, pinholes phenomena, air bubbles due to degassing of impurities.

The aim of the survey is to identify the relationship between polluting materials (such as gypsum, coal, asphalt, iron, copper, aluminium, steel, brass, polycarbonate, PVC, tin, glue, oil, etc.) and defects generated on the final product. A ceramic defects database has been created, describing the tests results, showing the images of the flaws deriving from the samples pollution, and providing their chemical and morphological analysis through the

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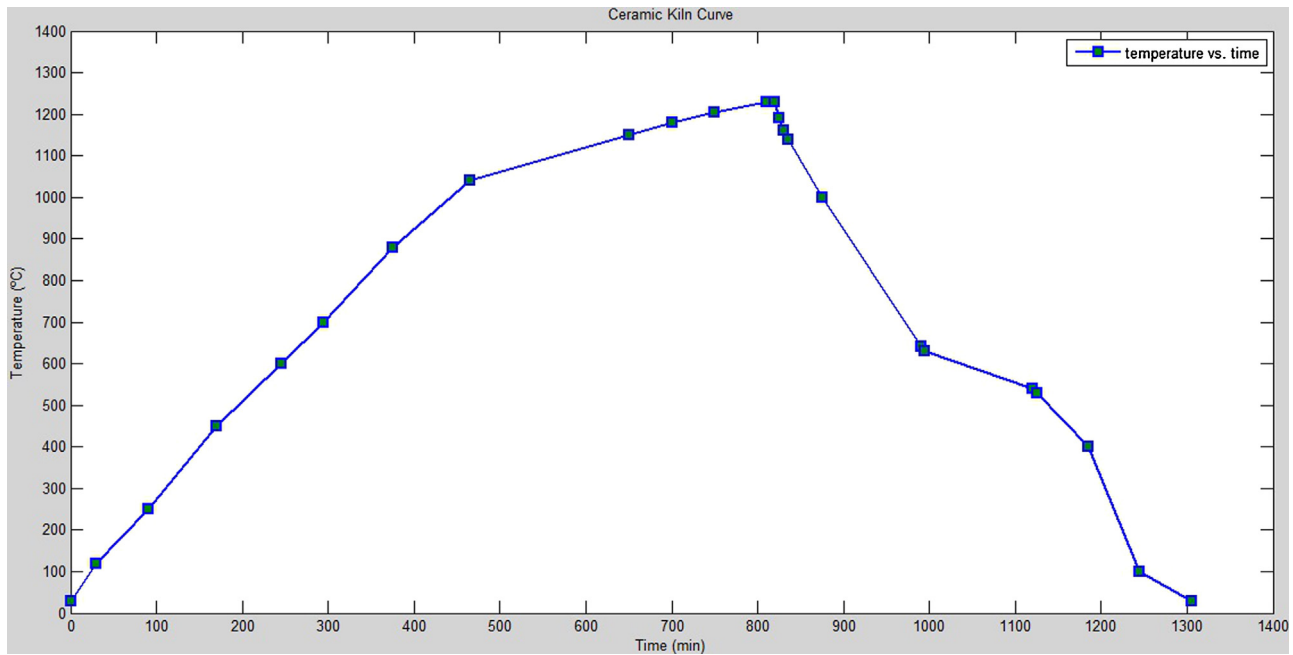


Fig. 1. Ceramic kiln curve.

use of a Scanning Electron Microscope (SEM). In order to reach this goal, a laboratory simulation procedure has been planned, addressed to reproduce the pollution phenomena of body and glaze inside the ceramic process for sanitary-ware production.

## 2. Materials and methods

An analysis of the surface defects of ceramic product has been carried out starting from samples made in laboratory. These samples have been polluted by substances that usually cause exterior defects, in order to assess their effect on the final product.<sup>4</sup>

Various tests have been carried out in order to define how the following parameters influence the final result:

- pollutant composition
- pollutant concentration
- method of application and positioning of the pollutant in the body slip or glaze.

According to these analyses the implementation procedures of the following tests have been planned. Initially the ceramic mixture has been characterized by internal procedures of laboratory in order to measure specific weight, viscosity and thixotropy. The studied ceramic mixture has been placed in a plaster mould to obtain small ceramic tiles. The tiles have been removed from the plaster mould and they have been dried, according to the following steps:

- drying at ambient temperature, 25–30 °C for about 15–20 h;
- drying in oven at 60 °C for about 24 h.

The residual moisture after the above mentioned phase has been around the 0.2–0.3% by weight.

After the drying, the samples have been glazed using an air-brush or a manual orifice, and fired in an electric oven. The firing curve reaches a maximum temperatures of about 1230 °C, with extremely low temperature gradients during pre-firing stage and near the transformation temperature of quartz (573 °C: Quartz  $\alpha \rightarrow$  Quartz  $\beta$ ).<sup>4</sup>

During this small-scale reproduction of the industrial production cycle, a pollutant has been added in the body slip or in the glaze, respectively in the slip casting phase or during the glazing phase, making sure that the impurities have been trapped in the ceramic materials. As above explained, the ultimate goal has been to identify the types of defects caused by each kind of pollutants and the limit quantity of pollutants exceeded which the defects begin to appear. This result could be useful in order to previously identify, by X-ray Fluorescence chemical analysis, abnormal quantities of impurities in raw materials that could cause imperfections on the final product.

In order to make the laboratory test results suitable to the real industrial production, it is important to highlight the following concepts: the concentrations measured in the laboratory tests are meant as percentage of pollutant in the fluid body slip or glaze, as they appear before casting and glazing phases. Conversely, the chemical analysis through the X-Ray Fluorescence is carried out on dried sample.<sup>5</sup> Hence, in order to establish a correlation between the pollutants concentrations in the laboratory tests (on liquid suspensions) and the pollutants concentrations in a dry powder analysed by X-Ray Fluorescence, it is necessary to take into account the loss in weight to which the body slip and glaze are undergone during the drying phase; this loss in weight is approximately equal to 27% for Vitreous China bodies, 21% for

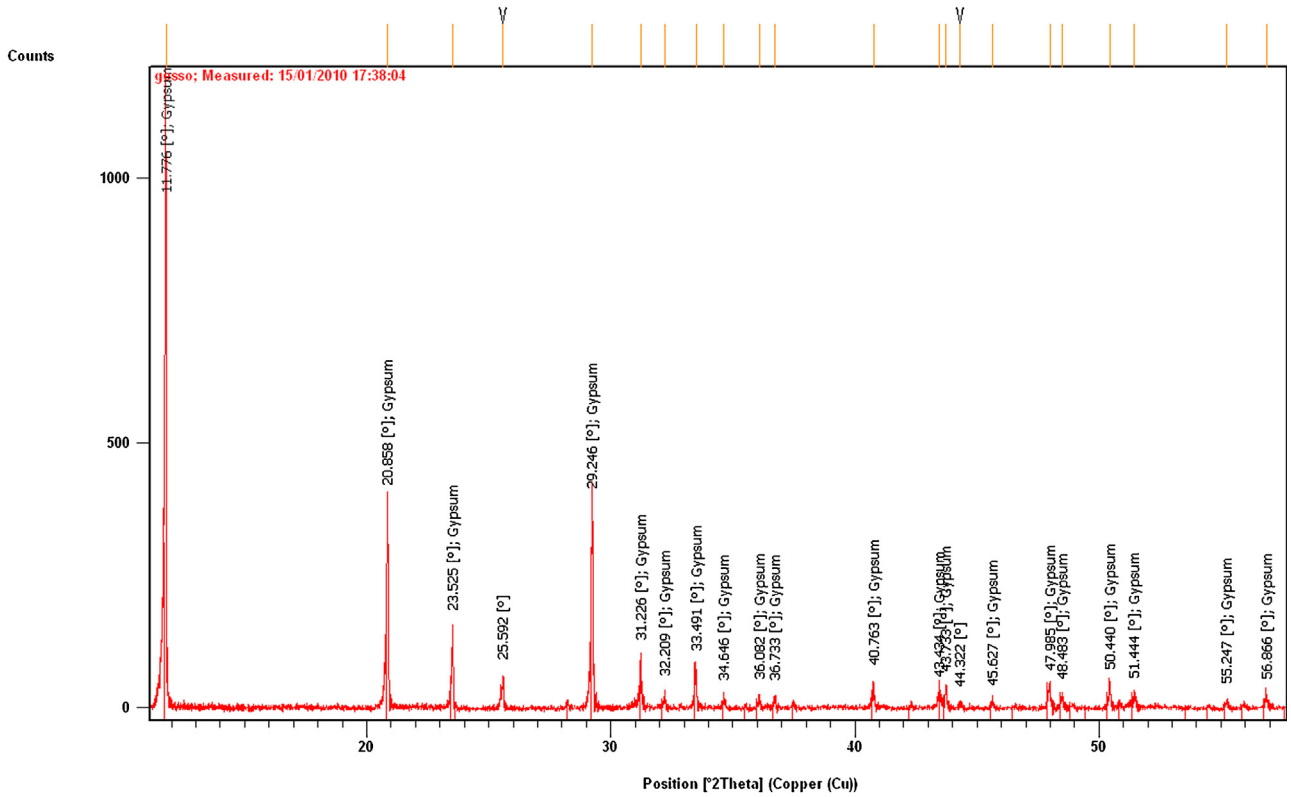


Fig. 2. Analysis of the gypsum with an X-ray diffractometer.

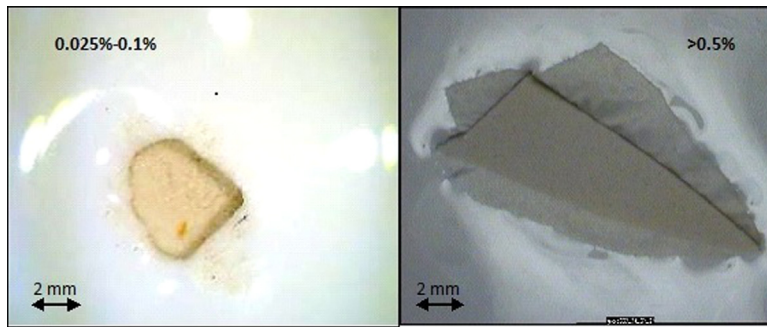


Fig. 3. Defects generated by percentages of gypsum between 0.025% and 0.1% (left) or greater than 0.5% (right).

Fire Clay bodies and 31% for glaze. Among the multiple pollutants used, gypsum and iron tests have been selected in order to demonstrate how the results obtained can be used to facilitate the interpretation of the possible causes of flaws, and minimize their

occurrence. The iron and the gypsum are some of the most common pollutants in the manufacture of ceramics. The iron can pollute the raw materials needed for the ceramics production, mixture and glaze. The presence of the gypsum can result from

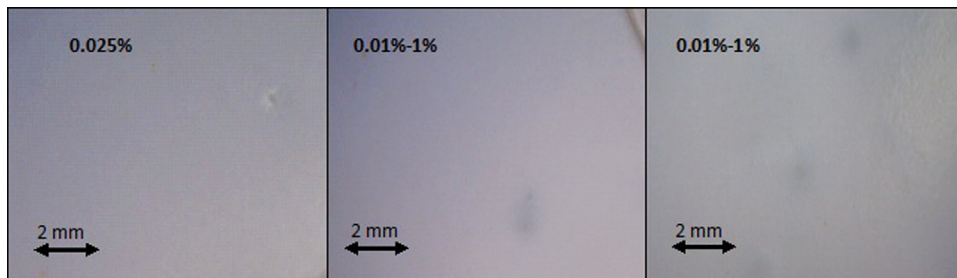


Fig. 4. Defects generated by percentages of iron in the body slip equal to 0.025% (left: pinholes), and between 0.01% and 1% (centre and right: black stains).

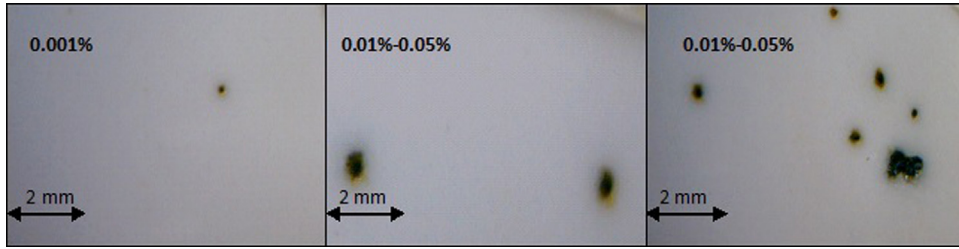


Fig. 5. Defects generated by percentages of iron in the glaze equal to 0.001% (left) and between 0.01% and 0.05% (centre and right).

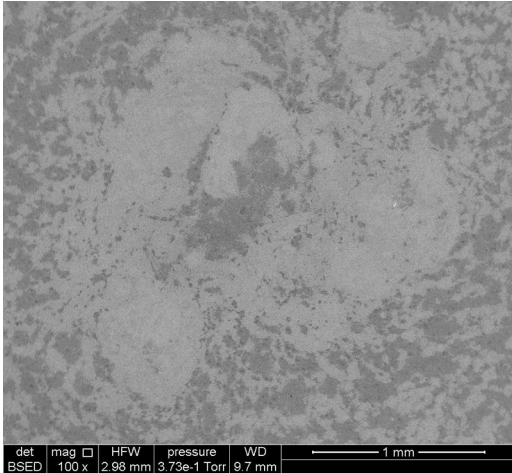


Fig. 6. Halos around the gypsum stain.

the deterioration of the gypsum casting moulds, and the latter determines percentages of gypsum on the ceramics surface.<sup>6</sup>

### 3. Results

#### 3.1. Gypsum

During the tests, the sample made in laboratory have been polluted by known percentages of gypsum, in order to check the surface defects depending on the amount of pollutants.

In order to ensure that the gypsum powder did not contain other impurities, it has been analysed using an X-ray diffractometer before being inserted into the body slip (Fig. 2).

The samples have been contaminated with different percentages of gypsum, specifically with hydrated calcium sulfate,  $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ .

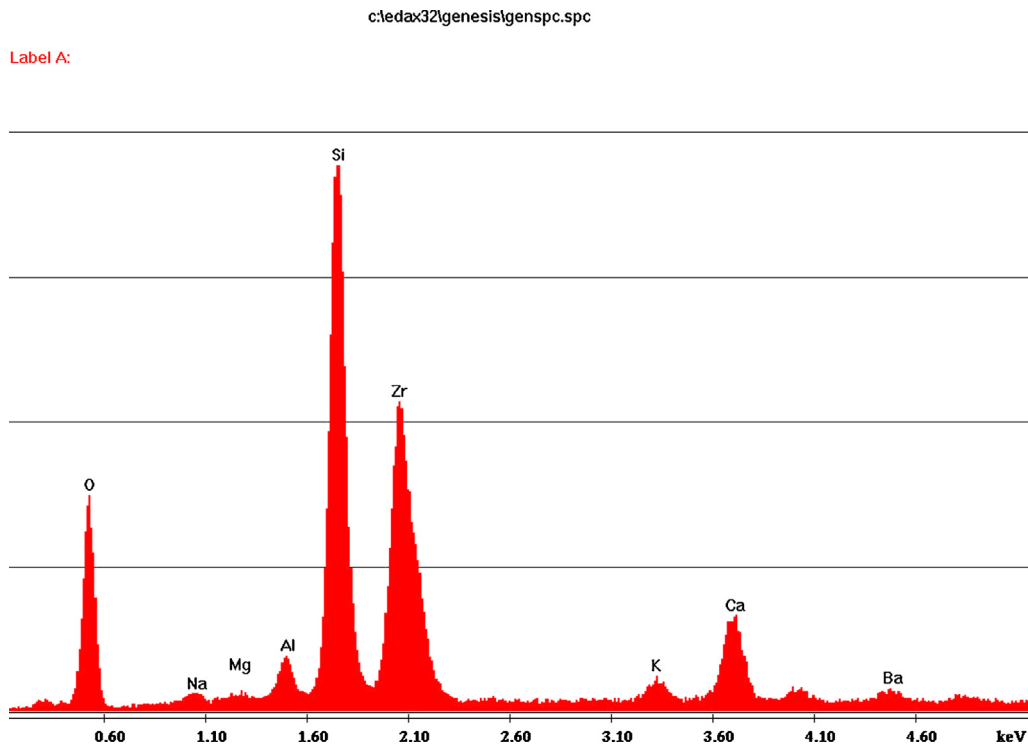


Fig. 7. Concentrations of zirconia in the halos around the stain.

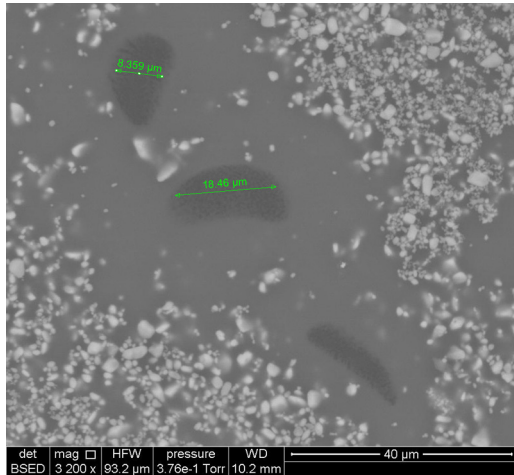


Fig. 8. Increasing the image of the flaw.

The following known percentage by weight of the gypsum have been added in the ceramic suspension of the mixture:

- 0.005%
- 0.01%
- 0.025%
- 0.1%
- 0.5%

The samples, after drying phase, have been glazed and fired. The glaze has been applied using an airbrush with a thickness

equal to 1 mm. In a real industrial production cycle of ceramic, the applied glaze has usually a thickness of 1 mm or less.

The hydrated calcium sulfate, during the firing cycle is inclined to lose water becoming anhydrous calcium sulphate after a few hundred degrees, undergoing a decomposition process in the temperature range of 950–1100 °C, emitting SO<sub>3</sub> as described below:<sup>7</sup>

$T = 0\text{--}190\text{ }^{\circ}\text{C}$  approximately: gypsum is stable in the form of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

$T = 190\text{--}225\text{ }^{\circ}\text{C}$  approx: gypsum loses  $3/2\text{ H}_2\text{O}$  and is stable as  $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$

$T = 225\text{--}1000\text{ }^{\circ}\text{C}$  about: gypsum loses  $1/2\text{ H}_2\text{O}$  and is stable as:  $\text{CaSO}_4$

$T = 950\text{--}1100\text{ }^{\circ}\text{C}$ : anhydrous calcium sulfate decomposes according to the reaction:

$\text{CaSO}_4 \rightarrow \text{CaO} + \text{SO}_3$  (sulfur trioxide gas tends to escape causing the detaching of the overlying glaze).

The gas developed within the paint layer tries to leak out, generating glaze lifting and, in some cases, the detachment from the ceramic support.

The analysis of the samples has shown that there are not defects in the samples polluted with percentage of gypsum lower than 0.01%.

In the samples with percentage of gypsum between 0.025% and 0.1% (Fig. 3, left) the defects are clear: there are some pinhole and detachment of glaze around the ceramic surface.

As for percentage greater than 0.5% the defects become even more evident and accentuated; indeed the detachment of glaze can reach dimensions of 1 cm (Fig. 3, right).

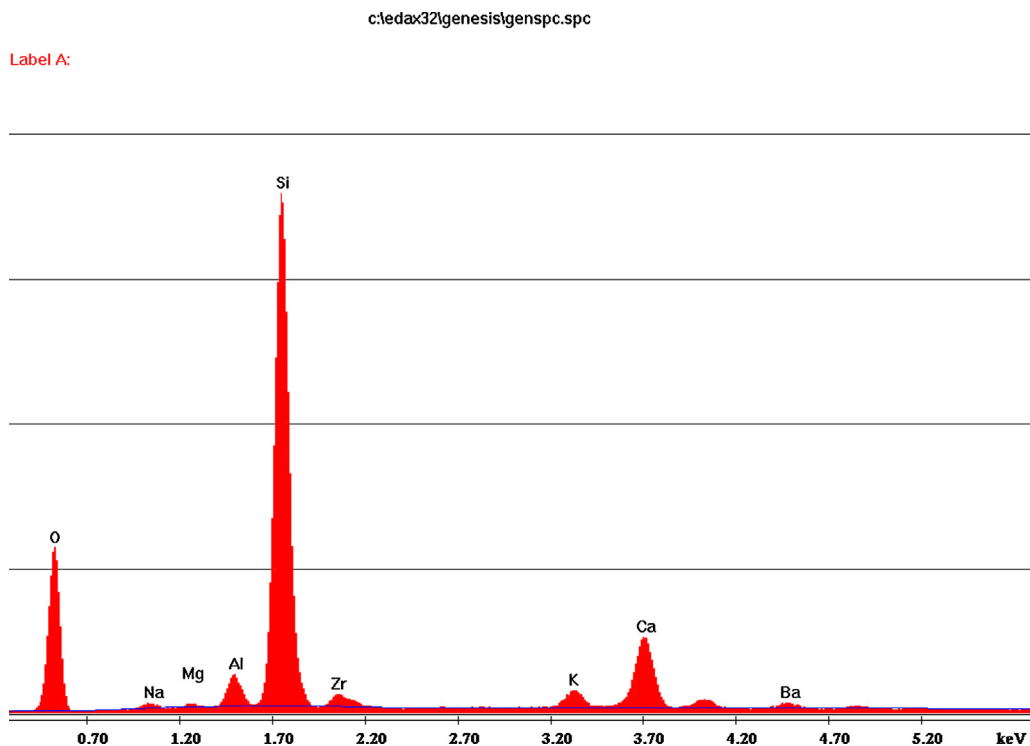


Fig. 9. Chemical analysis outside the stain.

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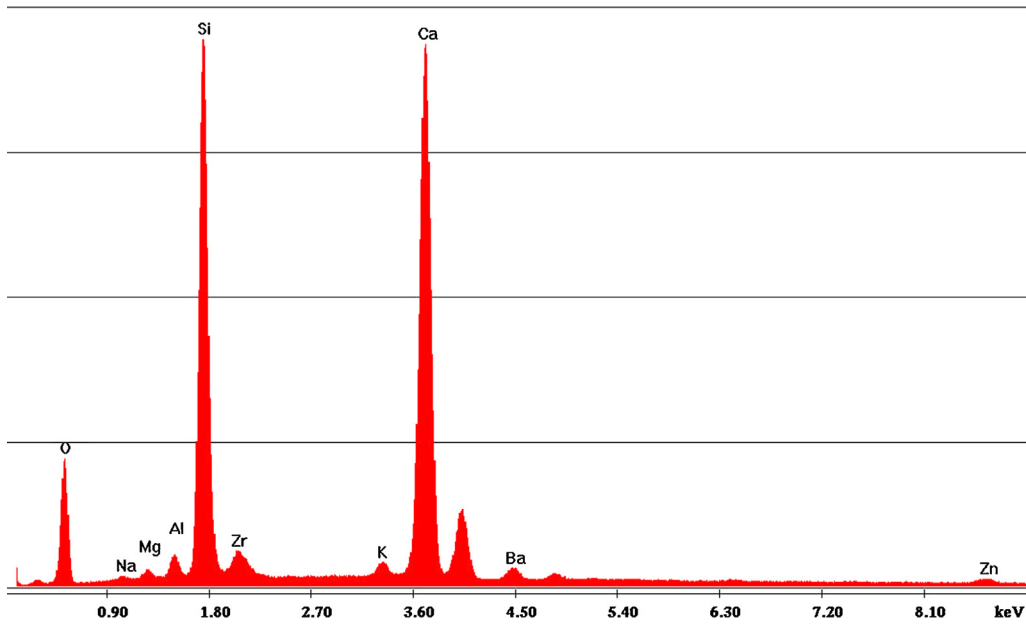


Fig. 10. Chemical analysis inside the stain.

3.2. Iron pollution

The same procedure has been performed with iron. A known concentration of iron has been added in the ceramic suspension of the mixture and in the glaze. In detail the following percentages by weight of iron have been added in the body slip:

- 0.001%
- 0.01%
- 0.025%
- 0.1%
- 0.5%
- 1%

Label A: INSIDE STAIN

Label B: OUTSIDE STAIN

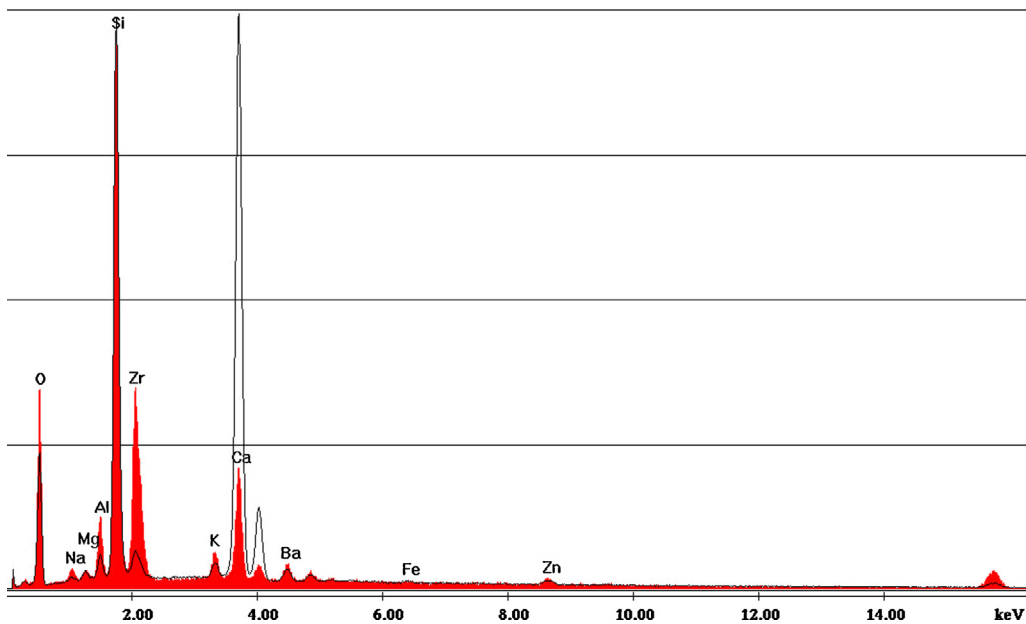


Fig. 11. Comparison of chemical analysis inside and outside the stain.

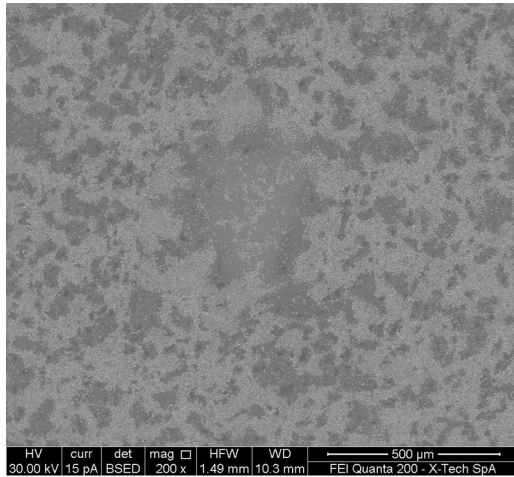


Fig. 12. Halos around the iron stain.

The analysis of the samples showed that the defects are not visible with iron percentages lower than 0.01%. Little pinholes are visible starting from 0.025% (Fig. 4, left), black stains appear increasingly evident with the growth of the iron concentration in the body slip (Fig. 4, centre/right).

The glaze has been polluted with the following iron percentage:

- 0.001%
- 0.01%
- 0.05%

Defects become evident for iron concentrations equal to 0.001%; on the surface of the samples some black points are

evident (Fig. 5, left). Surface defects are increasingly visible with the growth of iron percentage in the glaze surface (Fig. 5, centre and right).

#### 4. Discussion

The laboratory results have allowed to define the pollutants concentration that determine defects on the ceramic products surface.

The polluted samples have been analysed by the use of a Scanning Electron Microscope.

The Scanning Electron Microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals to the solid samples surface. The signals derived from electron-sample interactions reveal information relating to the external morphology, chemical composition, and crystalline structure of the sample.

These analyses have been used to confirm the laboratory results. The chemical composition of the samples polluted with gypsum and iron has been verified through tests of the defects on the inside and outside surfaces.

For the concentration, according to the laboratory tests, up to 0.01%, the gypsum quantity in the body is not such as to produce surface defects visible to the naked eye.

The following figures show the results of the analysis carried out with SEM.

Fig. 6 shows the presence of halos around the stain caused by pollution of gypsum. The chemical analysis for this zone has shown the presence of high concentrations of zirconia (Fig. 7). Increasing the image of the flaw (Fig. 8), we can see the presence of areas with a high silicon content if compared to the glaze average composition (Fig. 9). The calcium content increases

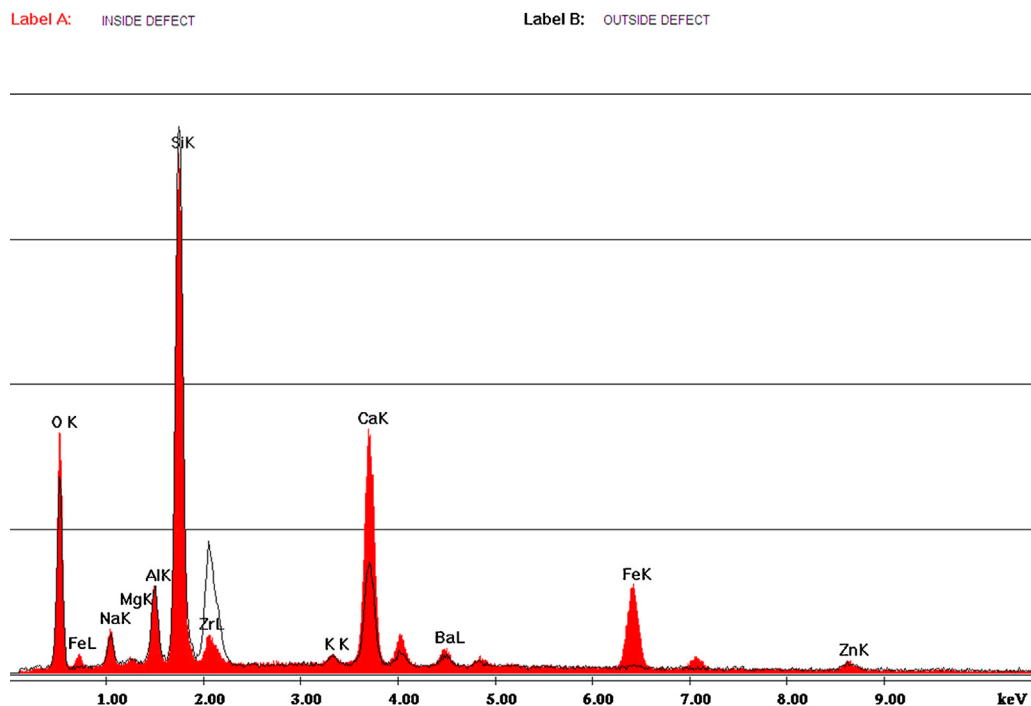


Fig. 13. Comparison of chemical analysis inside and outside the defect.

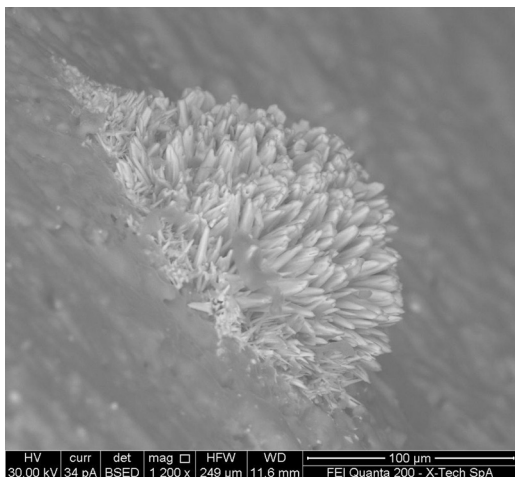
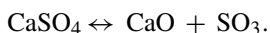


Fig. 14. Structure of iron particles.

moving the analysis to the centre of the spot, and its concentration reaches about 25%, as expected considering the type of pollutant used (Fig. 10). The concentration of calcium, measured by the SEM at the centre of the spot, is a value related to the exact point in which the analysis has been carried out. The analysis has been repeated in the surrounding areas, however the results did not diverge from those reported in Fig. 10.

The presence of calcium and the absence of sulfur are due to the calcium sulphate reaction during the firing phases, indeed it is transformed in sulfur trioxide and calcium oxide according to the following reaction:



After the firing phase we only find a high concentration of calcium, but no trace of sulphur, which is released in the oven at a temperature of approximately 1000 °C.

In Fig. 11 the comparison between micro analysis performed on the inside and outside surface of the stain is showed. The areas polluted by gypsum show higher concentration of calcium if compared to the surrounding areas, which instead have higher percentage of other elements such as zirconium and aluminium.

Analyzing the SEM image (Fig. 8), the accumulation of zirconium in the immediately surrounding areas of the spot is evident. The leakage of the gas  $\text{SO}_3$ , resulting from the firing stage, causes the removal of the zirconium particles from the point affected by pollution.

SEM analysis has been carried on the samples polluted with iron too (Fig. 12). SEM analysis has showed that iron

and calcium concentrations are very high near the defect (Fig. 13). Conversely, zirconium quantity decreases since has been removed from the defect area during the firing stage (Fig. 13). The variation in the concentrations of calcium and zirconium inside and outside the defect is due to redistribution of the two elements during the firing phase.

A morphological study has been carried out on some ferrous impurities trapped in the body slip and perfectly visible in the sample section. According to the acquired images, a very fascinating structure of iron particles can be observed (Fig. 14).

## 5. Conclusions

In addition to gypsum and iron, many other pollutants have been studied in order to define how they could affect the occurrence of defects on the ceramic products. All these pollutants have been itemized and inserted in a *ceramic defects catalogue*, where a correlation between pollution, surface defect and SEM analysis has been reported. The catalogue has been created with the aim of being helpful for the interpretation of the defects occurring in ceramic production, through their comparison with the laboratory tests results. Although the tests showed that the same type of defect can be caused by different pollutants, SEM analysis proved to be of considerable importance to generate hypothesis concerning the real cause of surface problems such as blemishes, dots, pinholes and glaze detaching.

## Conflict of interest

The authors certify that there is no conflict of interest with any financial organization regarding the material discussed in the paper.

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