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CO_2 Laser as a Sustainable Alternative for the Mitigation of Sanitary Ware Manufacturing Defects

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Abstract: The development of society through the centuries led to the improvement of healthcare and hygiene conditions throughout the world and, thus, the generalization of ceramic sanitary ware. Indeed, this industry possesses a huge financial impact on the global economy, employing thousands of people worldwide. In spite of their high production levels and increased efficiency, the sanitary ware manufacturing process is still characterized by some defects which make the commercialization of these products unfeasible. Currently, these flaws are rectified by a refiring in the kiln; however the defective parts occupy space intended for new ones to be produced and there is a high chance of new defects arising or the component to break due to the excessive heat of a second firing, hugely increasing the production costs. Accordingly, in this article a sustainable alternative is proposed, using a CO_2 laser to repair only the defect area, thus leaving the remaining part untouched. Several laser parameters were tested in experimental tests of two different kinds of defects, using quantitative and qualitative analysis methods, through colour difference reading (with an ANOVA approach), and the optical microscope, SEM-EDS and chemical analyses, respectively. The best results considering defects provoked on a white coloured part were obtained with the manual firing for a laser power between 50 and 70 W, and an interaction time of 1 to 3 firings of 10 s each. These values apply for both pinholes and fissures, with a 50 W power and an interaction of 30 s being the best.

Keywords: ceramics; pinholes; fissures; ANOVA; sustainability

1. Introduction

The art of pottery is one of the oldest in the world, not only due to the high abundance of clay, but also because of its easiness of extraction and processing. The first applications using this technique, in prehistoric times, were simple baskets made from clay, used mainly to store seeds. With the human being's evolution, the survival techniques of the species became increasingly more developed, as did their knowledge of the available materials and respective fabrication methods. Eventually, the plasticity of clays was discovered, when they realised that by adding water to it, this material was possible to be moulded and dried in the sun, with its rigidity increasing when subjected to high temperatures. This is how ceramic materials emerged [1].

By definition, a ceramic material consists of any non-metallic material of inorganic nature with a crystallized structure, resultant from a heat treatment at elevated temperatures. Although clay is the main raw material forming the ceramics, these are composed of a variety of constituents and possess a great range of structural arrangements.

Typically, traditional ceramic materials, produced from raw materials available in the nature, have silica (SiO_2) and alumina (Al_2O_3) in their constitution. The most common examples of these are tiles, porcelain or sanitary ware, such as toilets, washbasins or shower trays. On the other hand, the modern ceramics, also referred to as advanced or technical, have improved mechanical properties, since they use special chemical and thermal techniques with high purity intended to achieve the desired properties. In this case, they are usually composed of silicon nitride (Si_3N_4) and silicon carbide (SiC) [2]. Traditional white ceramics, besides having a high superficial hardness, also feature a glazed coating, whose low water absorption, which in sanitary ware is near zero, and low porosity, directly related to their firing process at high temperatures, is responsible for providing them a high resistance, preventing the adherence of impurities to the part's surface and improving its appearance [3]. In addition, these ceramics possess a high flexural resistance, equivalent to twice to three times that of granite stones, abrasion resistance, fire resistance, as well as a good chemical resistance. Comparing the fracture toughness between different families of materials, ceramics have the lowest fracture toughness values, being left behind metals, composites and polymers in general. For this reason, special precautions must be taken in their handling, since these materials are fragile and during their manufacture, storage and transport a small mistake may cause defects such as fissures or other types of fractures, which make it unfeasible to sell the workpiece [4].

The ceramic sanitary ware manufacturing process' first stage is performed resorting to moulds. Firstly, a mixture of the raw materials takes place, consisting mainly of clay and kaolin, to increase the part's plasticity and mechanical strength, feldspar and quartz, which keeps the workpiece's structure intact and prevents high deformation [5]. After this mixture has the required properties, namely the viscosity, pH, specific weight, temperature and thixotropy, it is poured into the mould [6,7]. Throughout this process, the product's initial shape deforms significantly owing to plastic domain stresses and volumetric shrinkage, which can be up to 20% of its original dimensions. Considering that tolerances are only accepted if they do not vary more than 0.5% of their dimensions, the predictability of moulds for sanitary ware represents an extremely challenging engineering problem, reason why techniques of mould predictability through numerical methods began to be developed [8]. Afterwards, the part is removed from the mould and undergoes a surface finishing stage, by removing burrs, cutting or retouching. Later, the parts are left for drying at ambient conditions, decreasing in water content from 1.5% to 0.5% and increasing in mechanical properties; however, an excessively quick drying phase may lead to the development and propagation of defects. At last, after a 0.8 to 1.6 mm thick glaze is applied on their surface, the products are placed in the kiln for a firing phase consisting of a cycle of temperatures up to 1200 °C, where a new volumetric shrinkage occurs, leading to some dimensional variations in the part and chemical composition variation in the glaze. At the sintering temperature, the voids are filled with the molten phase, causing the microscopic ceramic structure to fully reorganize [9].

This manufacturing process is characterized by harsh conditions, where several different defects usually emerge in the products, being the two most frequent the pinholes, originated in the migration of air from the workpiece [10], and the fissures, caused by a lack of concordance between the coefficient of thermal expansion of the base ceramic material and the one of the glaze [11]. Other common defects are the shivering/peeling, stains and delamination [12]. The occurrence of these defects takes place especially during the firing stage, due to the excessive temperature variations, since these directly affect the products' physical, chemical and structural properties, leading to residual stresses generation. Notwithstanding, the glaze application stage is also responsible for some failures detected in the parts, such as lack of adhesion, if there was a poor glaze placement [13]. Initially, their detection was manual, although this quality control was unreliable because of factors which could hinder it, for example the operator's level of attention, or the surrounding noise. Motivated by the difficulty to detect these defects without assistance, as sometimes they appear in hidden places around the products, several automatic detection methods have been developed in the literature to support the operators, proving to be quicker and more effective than the traditional way [14–18]. Nevertheless, these robotic methods also contain some challenges in precision and defect detection, reason why their implementation is still not widespread. These are mostly related to economic reasons, as many companies in this sector still use traditional methods, since although less efficient, these do not require a great investment in machines and training for the workers to learn to use these new technologies, but as the industry is quickly evolving, companies must adopt new techniques to stay competitive.

Currently, the more efficient method to eliminate these defects is through the hot recovery process, used generally in functional and visible areas of the products. Firstly, there's a surface preparation, where the defect in abraded and smooth for a better final finish. Then, a very liquid glaze is spread homogenously over the area to be treated and dried with an air compressor. Afterwards, a repair paste is applied over the previous region, and another layer of glaze is reapplied to the surface of the repaired defect. Finally, the product is placed once more in the kiln to be refired. This procedure is effective, managing to repair almost half of the defective workpieces; however, it has two major disadvantages. On the one hand, it makes the process too expensive, since refiring the workpieces involves additional costs, besides the time required for them to undergo a new total temperature cycle, equivalent to twice the initial firing time. On the other hand, there is a high probability of the parts to develop new defects, with exactly the same origin as the previous ones, which can be even more serious, sometimes culminating in a rupture of the product. This has the aggravating effect of increasing the environmental impact, material and human resources, added to the fact that the space occupied by the workpieces for repair decreases the total number of products manufactured [19]. For this reason, the laser technology stands as a viable and sustainable alternative to this method, firing just the defective area, so that the remaining part stands safe and untouched.

Laser technology has a wide range of applications, for example in the marking, engraving or cutting functions, being used to process different kinds of materials for decades. Currently, this technology is divided into several types with diverse properties, making them suitable for any particular purpose which is required. The application of lasers in ceramics is not new, since this process has been adopted for several years to provide a great number of benefits in performing surface treatments on ceramics [20,21]. This choice is sustained by the heating, surface fusion and vaporization characteristics of the laser's action, as it allows a localized fusion, as well as high heating and cooling rates. In work of Basile et al. [22], a dense glazed layer with a controlled microstructure was achieved on the surface of ceramic materials through a powder glazed coating, which was only possible to accomplish due to the concentrated Nd:YVO_4 laser beam for surface treatment. Mahmod et al. [23] defends the use of the Ytterbium (Yb) fibre laser as one of the most fit lasers for surface treatment applications, not only due to its benefits of managing to obtain a high localised heating, which is vital for an improved precision of treatment, but also owing to its higher energy conversion efficiency (>30%), which is higher than that of CO_2 or Nd:YAG lasers. Regardless of these studies, there are authors in the literature which suggest otherwise. Rodríguez-López et al. [24] claimed that the CO_2 is one of the most viable options, since it showed better results when fusing the ceramic glaze, adding to the reason that it needs lower requirements regarding the work safety, it reaches higher laser powers and is less expensive than the Nd:YAG and the Diode lasers [25]. Considering the presented studies, the CO_2 laser system was chosen for the development of the current work.

After the laser application for the defective products' recovery, a set quality control procedures must be put into practice, to guarantee that the product will not show problems during its lifetime. A first visual analysis through the microscope assists in a detailed view of the recovered defect's area, to evaluate the effectiveness of this novel approach. Nevertheless, after this a set of more technical quality control tests specific of the ceramic sanitary ware industry is required to ensure the viability of the procedure in the products' daily applications after commercialization. In terms of the physical properties of the product, according to the USA patent on the manufacturing method for sanitary ware [26], it must fulfil at least one of three different conditions:

- A pore area ratio of 3% or less in relation to the total area of a surface obtained by cutting the upper layer of glaze in the direction of its thickness;
- An average pore size of 50 μm or less present in a surface obtained by cutting the upper layer of glaze in the direction of its thickness;
- A difference of 50 μm or less between the maximum and minimum values of the thickness of the upper layer of glaze.

Some examples of these tests consist in the following:

- Hanging basin load test, which according to the Portuguese standard NP EN 997:2012 + A1 2017 [27], aims to determine the robustness of suspended sanitary ware by applying a load of (4.00 ± 0.05) kN for one hour in the product, although in practical cases this application is extended to twenty four h to guarantee that it will always be capable of withstanding the load during its lifetime;
- Autoclave test, which according to the standard BS EN ISO 10545—11:1996 [28], assesses the existence of crazing, i.e., if there is a difference in thermal expansion between the product's ceramic body and the glaze, by subjecting it to a pressure between 3.0 and 4.0 kgf/cm^2 for fifteen hours to simulate the wear endured during its lifetime;
- Water absorption test, to guarantee the product will not retain any water resulting from its use. In this test, the product is placed in a bath with demineralized water, which is boiled for (120 ± 5) min, followed by an immersion of the samples for (20 ± 1) h. After the removal from the water and all of its cavities dried, the samples are weighed once more, and this value is compared to the original weight. For the product to be considered non-defective, its water absorption coefficient must not exceed 0.5%;
- Resistance to acids, bases and staining agents (ABS), whose objective is to submit the product to three different reagents of various natures, namely the acetic acid, the sodium hydroxide and the methylthionine chloride, also known as methylene blue, to evaluate if there is a chemical reaction. This will guarantee that

the product will not be dangerous to the user during its lifetime, independent of the cleaning products that will be in contact with it.

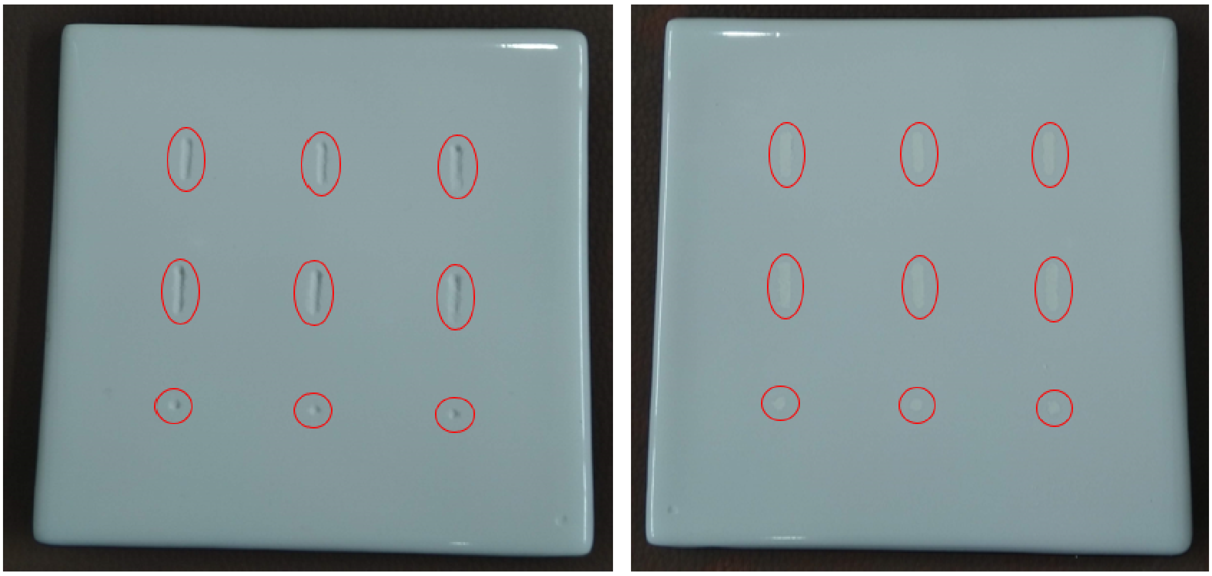
This work's main objective is to develop a novel alternative and sustainable technology for the recovery of damaged sanitary ware to solve a problem in a ceramic industry company in Portugal. For this to happen, the following sub-objectives have to be accomplished:

- To create a set of glazes (both white and coloured) which fuse at a temperature of 1200 °C and whose colour difference does not exceed 0.8 in the colourimeter reading, so as not to be distinguishable from the pattern (workpiece) in the user's perspective;
- To create a technique using a laser system that can reach the necessary temperature to achieve a tone identical to the one of the glass and that, through a combination of the most fit parameters, allows the fusion of the glaze only in the place where it is required to cover the defect;
- To perform a quantitative and qualitative analysis using a variety of equipment such as the colourimeter, the optical microscope, the scanning electron microscopy/electron discharge spectroscopy (SEM-EDS) and chemical tests, to evaluate the laser-repaired defects with the support of a statistical analysis.

2. Methodology

The experimental tests consisted in using a laser to repair defects on specimens which, in this case, were ceramic tiles measuring 150 × 150 × 10 mm^3. Their formulation was equal to a sanitary ware product, with a 1 mm thick glaze applied on the surface of a ceramic base. In the surface of the tiles, several defects were generated using a percussion pen with the support of a squared grid, to guarantee the same distance between them, as the geometrical pattern is helpful to program the laser. Furthermore, in some defects a tungsten bur (emery) was applied to round their edges. Two different kinds of defects with a depth of 0.5 mm were provoked in the tiles: 3 mm diameter circles, the pinholes, and 3 mm × 13 mm fissures, as shown in Figure 1a.

Subsequently, several different formulations were developed in the laboratory and tested to fill the provoked defects, circled in red (Figure 1b), with the requirement that when they were fused with the laser's heat, the previous defect was undistinguishable from the remaining tile. The first substance tested was the glaze already used in the original recovery method, which fused at 1200 °C, followed by an alternative substance, the frit, that had similar properties, but fused at 900 °C. Later in the experimental testing phase, a glaze was produced in the laboratory based on white ink, usually intended for logotype laser marking, mixed with different solutions: water, ethyl alcohol, and diluted or concentrated PL960, a carboxymethyl cellulose (CMC) viscous liquid diluted in water which acts as a fixative. Comparing the results obtained with each one of the developed formulations, the one with the best quality was the white marking ink mixed with ethyl alcohol, reason why it was the only one shown in the results section tests.

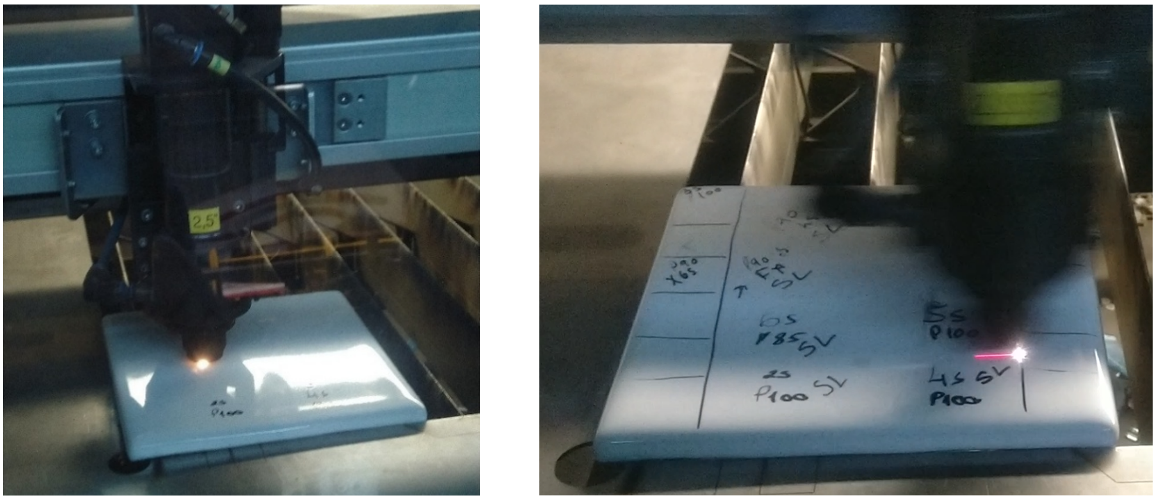


(**a**) (**b**)

Figure 1. Specimens used in the tests: (**a**) tile with provoked defects, and (**b**) tile with glaze filling the defects.

The laser used for the tests was the Trotec SP1500, a CO_2 laser with a 1500 × 1250 × 53 mm^3 working area. Its maximum laser power is 200 W, beam speed of 1.65 m/s and a 10,600 nm wavelength beam (infrared radiation). The laser's focal distance used in the tests and respective spot size were 2.5″ and a 3 mm circle, and the ambient conditions during the experimental phase corresponded to a temperature of 20 °C.

Two different methods were used in the laser interaction to understand which one led to the most fit outcomes: single firing (pulsed wave) and continuous firing (continuous wave), represented in Figure 2a,b, respectively. The continuous firing option required the JobControl software to be automatically programmed to work. The parameters under study, used in the CO_2 laser system, were the laser power (W), which is the main factor in this process, the incidence time (s) in case of the single firing, and the beam speed (m/s) in case of the continuous firing. The laser power and beam speed values were defined in the machine as percentages of the maximum respective values. Throughout the tests, the laser power had values tested from 20 W (10%) to 120 W (60%), the beam speed between 0.0195 m/s (1%) and 0.33 m/s (20%), and the incidence times between 2 and 30 s, being the cases of 20 and 30 s equivalent to two or three firings of 10 s each, respectively. Although the incidence time is more used for pinholes and the beam speed for fissures, both parameters can be used for the two types of defects.



(**a**) (**b**)

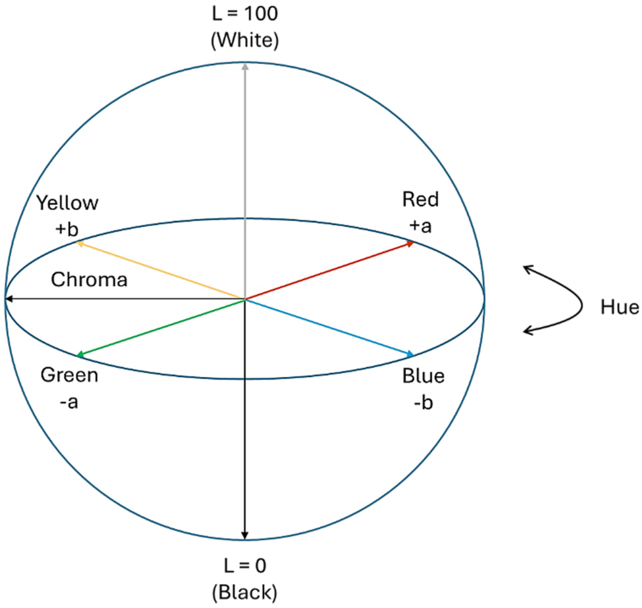
Figure 2. (**a**) Single firing; (**b**) continuous firing.

In the first case, a single firing is performed by the laser beam, which focuses on a specific place for a certain period of time, whereas in the second, the laser beam starts in one point and sweeps a pre-defined line repeatedly in order to fire the entire region in stages. Both these methods intended to replace the refiring process in the kiln, recreating the same heating conditions through a combination of the laser parameters with the aim of successfully recovering the defects.

After the tests, some equipment was used for the analysis, more precisely the Konica Minolta CR-10 Plus colourimeter, which quantifies the colour difference from the glaze on the newly recovered the defect in relation to the original ceramic product. Then, the Olympus SZ-PT optical microscope and the Zeiss Sigma VP FE scanning electron microscope (SEM) and the energy dispersive spectroscopy (EDS) technologies were also used to perform a superficial and an atomic/chemical analysis of the specimens.

Figure 3a shows the colourimeter used and Figure 3b depicts the CIELAB colour space diagram, for it to be easier to understand its functioning. Also referred to as L*a*b colour space, defined by the International Commission on Illumination (CIE), this represents a quantitative relationship of colours on three axes: $L*$ value indicates lightness, and $a*$ and $b*$ are area chromaticity coordinates. The vertical axis corresponds to the $L*$ value, which varies from 0 (black) to 100 (white). The $a*$ value is the red-green component of a colour and the $b*$ axis expresses the yellow-blue component. The centre of the plane is neutral or achromatic, and the distance from the central axis is called the chroma (C*), i.e., the saturation of the colour. The angle on the chromaticity axes represents the hue [29]. The colourimeter can also measure the exact difference in a colour scale between two different parts.

(a)



(b)

Figure 3. (**a**) Colourimeter; (**b**) CIELAB colour space diagram (adapted from [29]).

Apart from the already mentioned measurements, the colourimeter also directly provides the colour deviation (ΔE^*) value, which calculated through the square root of the three squared components deviation (ΔL^*, Δa^* and Δb^*) sum, using Equation (1).

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

The quantitative results obtained from the colourimeter readings were later used for a statistical analysis, to assess the impact of each parameter in the results. Firstly, the design of experiments (DOE) adopted was firstly supposed to be a complete factorial design, where every possible combination of parameters would be tested; however when the experimental phase began, it was soon understood that some values were not worth keep testing, because of the repaired holes' visual analysis, so a fractional factorial design was used instead. In this case, only a portion of the parameter combinations was chosen, maintaining just the values which led to a better result, thus reducing the total number of experiments, which saved time and resources. After the conclusion of the tests, an analysis of variance (ANOVA) was conducted with the colourimeter results, with the aim of understanding the effect each parameter had on the colour difference reading between the recovered defect and the remaining tile.

Besides the initial microscopic analyses, of high importance for a first visual understanding of whether the recovery was effective or not, two technical quality tests were performed in the specimens according to the manufacturer company's advice, in order to evaluate if the parts repaired with the new method, laser, would be able to withstand the conditions of the ceramic sanitary ware daily-based functions. These were the autoclave test and the resistance to acids, bases and stains test.

3. Results

For the beginning of the tests, the different parameters were changed in several possible combinations to evaluate their impact on the results. Before the laser was used in the defects aiming for their recovery, it was pointed to a region in the tile without defects, to understand with which power and incidence time values the ceramic itself was not negatively affected, as if the defect is repaired, but the surrounding area is damaged, the product will still be unfit for commercialization. For this reason, the beginning of the experiments was with lower, but increasing laser powers for it to be possible to identify which was the minimum laser power the material could withstand without changing its appearance.

Then, 130 defects were experimented using a trial-and-error approach, where the parameter combination used for each test were established taking into consideration the previous defect's result, so that the best parameters for this application could be found. Among these, some good results were achieved, mostly in the pinholes' recovery. Figure 4, containing 6 pinholes and 3 fissures numbered for identification, shows the tile with the best recovered defects, circled in green, and also two worse recovered defects, circled in red.

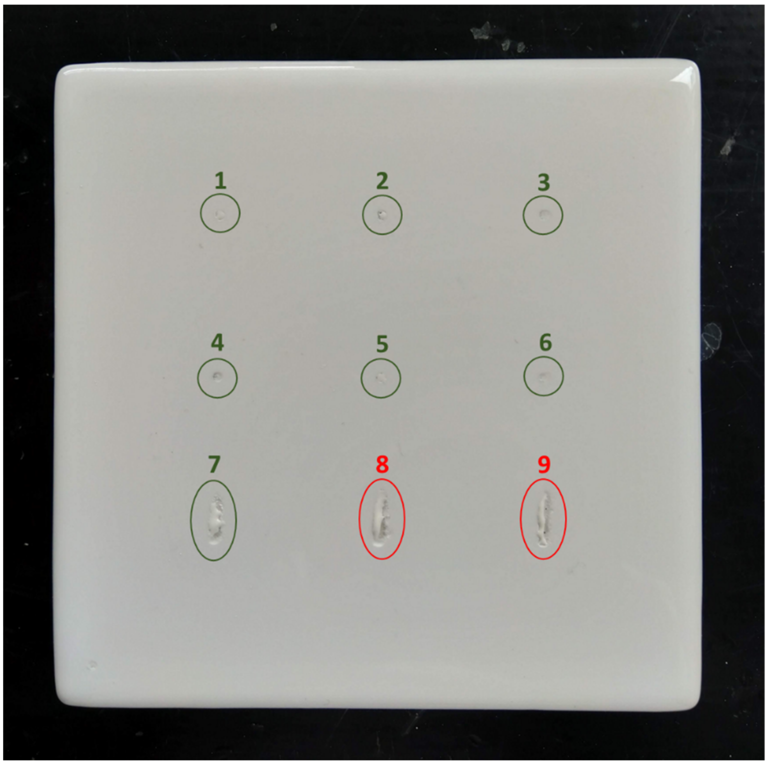


Figure 4. Tile 1's repaired defects.

The defects in the tile were divided in better and worse recovered, being the green ones the positive results. In general, the pinholes had all a good recuperation, being difficult to distinguish the defect zone from the remaining tile in some cases. As for the fissures, the first one had a better result, although its glaze did not fill the defect completely. The remaining two defects are circled in red, because the result is far from conform. When compared to the pinholes, the fissures had a worse laser recovery, since the laser's focal point is equivalent to the size of a pinhole, whereas the fissures have a more complex geometry, being longer and requiring a more precise laser interaction to be correctly repaired. For this reason, the fissures resist effective glaze fusion. Table 1 shows the parameters with which each defect was recovered, following the nomenclature: "No." is the defect's number, "P" is the laser power, in Watt, and "T" is the incidence time, in seconds. In this tile, the single firing option was used for every defect, which is why the time in the fissures is stated as "3 × 30", meaning that a manual firing of 30 s was used in three different points of the same defect, one in each extremity and one in the middle. Some consecutive defects shared the same parameter combinations not only to ensure repeatability of the results, but also to assess if the next defects would have the same visual level of repairing, since the first one of each group seemed to be visually a good result. From a visual analysis of Figure 4's defects, especially in the pinholes it is difficult to distinguish them from the remaining tile, with highlight to defects 1 and 5, result reflected in Table 2's colourimeter values. The colourimeter reading had an uncertainty of 0.1. Defect number 3 also had a good result, although there was a collapse of the recovered glaze due to the laser heat.

Table 1. Parameters used to repair tile 1's defects.

No.	1	2	3	4	5	6	7	8	9
Defect	Pinhole	Pinhole	Pinhole	Pinhole	Pinhole	Pinhole	Fissure	Fissure	Fissure
P (W)	50	70	70	60	60	70	50	50	50
T (s)	30	30	30	20	30	30	3 × 30	3 × 30	3 × 30

Table 2. Colourimeter values for the tile 1's defects.

No.	Standard	1	2	3	4	5	6	7	8	9
$L*$	91.8	91.2	91.4	91.3	91.0	91.4	91.7	91.3	91.4	91.3
$a*$	0.4	0.3	0.2	0.3	0.3	0.2	0.3	0.2	0.3	0.3
$b*$	1.3	1.1	1.5	1.5	1.1	1.7	1.2	1.6	1.5	1.6
$\Delta E*$	-	0.5	0.5	0.6	0.5	0.7	0.4	0.7	0.8	0.8

Firstly, the standard colour components were registered in the tile's glaze, away from the provoked defects, so that a comparison could be made. Afterwards, all the defects had their colour components taken, as well as the ΔE^*, the most important one, which is the colour deviation from the standards. The colourimeter reading of every defect from tile 1 was below than 0.8. This means that, in terms of colour deviation, they achieved good results, as the colour of the fused glaze is similar to that of the remaining tile. Defects 8 and 9 had the highest deviation value, as expected, since these were the most poorly corrected defects of this specimen. In spite of this, and although the glaze in the fissures did not spread correctly, in the zones where it fused and correctly filled the defect, the difference value of 0.8 in the colourimeter reading was not exceeded, indicator of a good result, nonetheless.

As a method of comparison, another set of defects was analysed through the colourimeter, but this time with some fissures which had bad results, as seen in tile 2, with only six fissures circled in red to prove it and identified with numbers. This specimen is shown in Figure 5 and the respective parameters used are in Table 3.

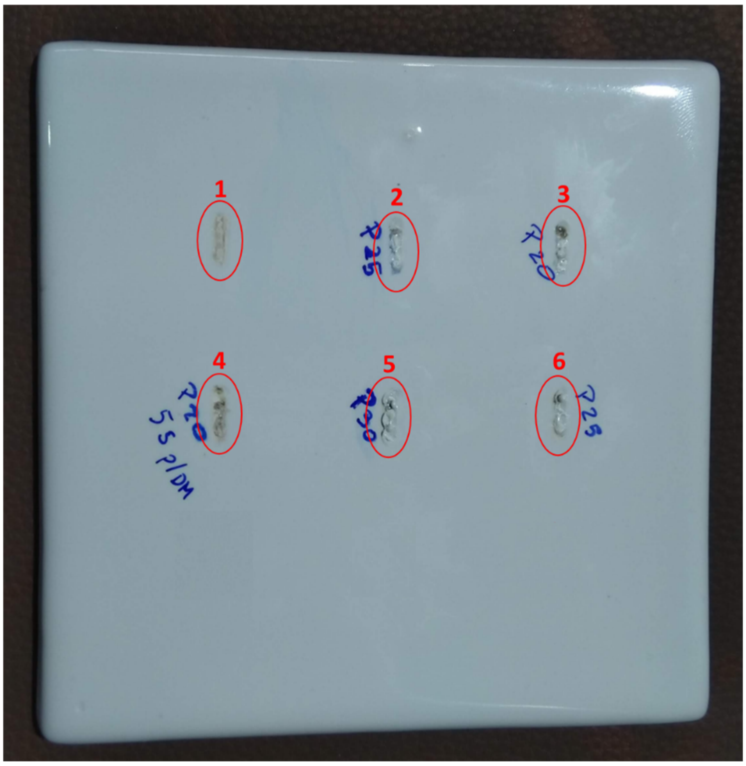


Figure 5. Tile 2's repaired defects.

Table 3. Parameters used to repair tile 2's defects.

No.	1	2	3	4	5	6
Defect	Fissure	Fissure	Fissure	Fissure	Fissure	Fissure
P (W)	40	50	40	40	60	50
T (s)	-	30	30	15	30	30
V (m/s)	0.0495	-	-	-	-	-

Regarding tile 2, present in Figure 5, there is a clear difference to tile 1's repaired defects. In this case, the fissures burned with the laser interaction, leaving dark zones in most of the defects. Fissure number 2 had a similar colour to the remaining tile in the region where the glaze was correctly fused with the laser, but it did not fill completely the defect hole, which proved to be a bad result. On the other hand, the glaze filled the defect number 1 completely, but the laser was unsuccessful in fusing it correctly.

Table 4 shows the colourimeter reading difference values for the defects in tile 2.

Table 4. Colourimeter values for the tile 2's defects.

No.	Standard	1	2	3	4	5	6
L^*	91.6	90.6	87.3	83.8	88.2	90.1	87.7
a^*	−0.1	0.1	−0.4	0.3	1.1	−0.3	0.4
b^*	0.8	0.6	1.0	2.7	4.2	0.6	0.6
ΔE^*	-	1.6	5.3	7.1	5.2	1.9	3.6

As expected, the values are not only above 0.8, but in some cases are even multiple times higher. Besides the glaze not spreading as it should through the whole provoked defect area, in the parts where it fused, the parameters were not correctly established, or the used formulation (mainly the medium) was not the most appropriate for the application.

After the first colourimeter reading, a deeper analysis using the collected data was conducted, namely by performing ANOVA tests for significance, using the SPSS software. This statistical analysis compared the means of the parameters Laser power, Incidence time and Beam speed in order to verify if there is a significant difference between its means and if the factors have any influence on the colourimeter reading difference. The ANOVA tests use the F-test for statistical significance, with a 95% confidence level for the p-value, meaning that a variable is significant if the p-value is under 0.05. Figure 6 shows the difference in colourimeter reading comparing both types of defects and ranges of laser powers used.

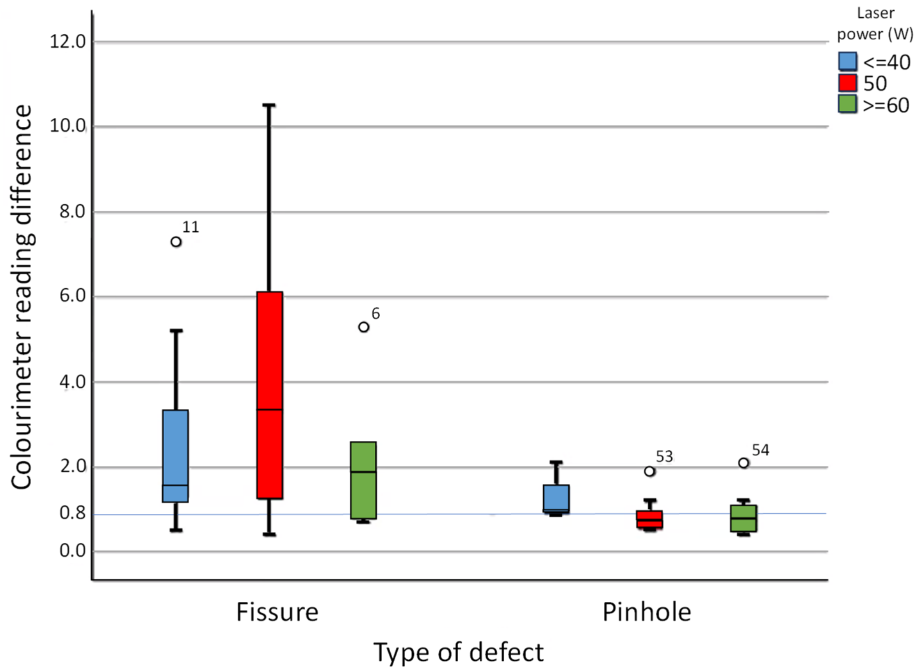


Figure 6. Influence of the laser power in the colourimeter reading differences by type of defect.

The graphs clearly shows what was already understood by visualizing the tiles after the tests, that the pinholes had much lower colourimeter reading difference values than the fissures. Furthermore, most of the pinholes which managed to have a value under 0.8, as required by the quality standards, had laser powers of 50 W or above, being these the best results.

Considering all the data available and the combined influence of the factors involved in the experiments (laser power, incidence time and beam speed), the results in the colourimeter reading difference value for the two types of defects experimented are present in Table 5.

Table 5. Mean and Variance for the colourimeter reading difference by defect.

Fissure	Mean		2.8517
	95% Confidence Interval for Mean	Lower bound	1.9322
		Upper bound	3.7712
	Variance		5.8430
Pinhole	Mean		0.9120
	95% Confidence Interval for Mean	Lower bound	0.7129
		Upper bound	1.1111
	Variance		0.2330

These results show that both the mean and the variance of the pinholes' delta values are much lower than the ones of the fissures, confirming once more that the first type of defects had a better recovery ratio with the laser incidence than the second group. Additionally, the mean for the pinholes is just slightly above the 0.8 limit, which shows that a great number of pinholes had a good recovery in terms of colourimeter reading.

Afterwards, the ANOVA test was performed for two different groups. The first one compared laser power with the incidence time (Table 6), with a total of 35 samples in study, and the second one did a comparison between the laser power and the beam speed (Table 7), contemplating just 13 samples. The number of samples is reduced, since these were the ones which had a good laser fusion in the respective glazes. In future works, a higher number of samples can be tested, so that the ANOVA test is more effective.

Table 6. Two-way ANOVA test for Laser Power vs Incidence Time.

Parameter	F	*p*-Value
Laser Power	0.030	0.971
Incidence Time	3.145	0.043
Interaction	0.904	0.476

The ANOVA intended to evaluate if the tested parameters had a significant effect on the ΔE^* values, i.e., if the *p*-value is lower than 5%. Table 6 showed that only the incidence time has a statistically significant impact on the ΔE^*, whereas the laser power and the interaction between these two factors have a high *p*-value, therefore their variance contributes little to the variance of the ΔE^*. In spite of this, the combination of the two said parameters has more influence on the final outcome than just the laser power, because of the incidence time.

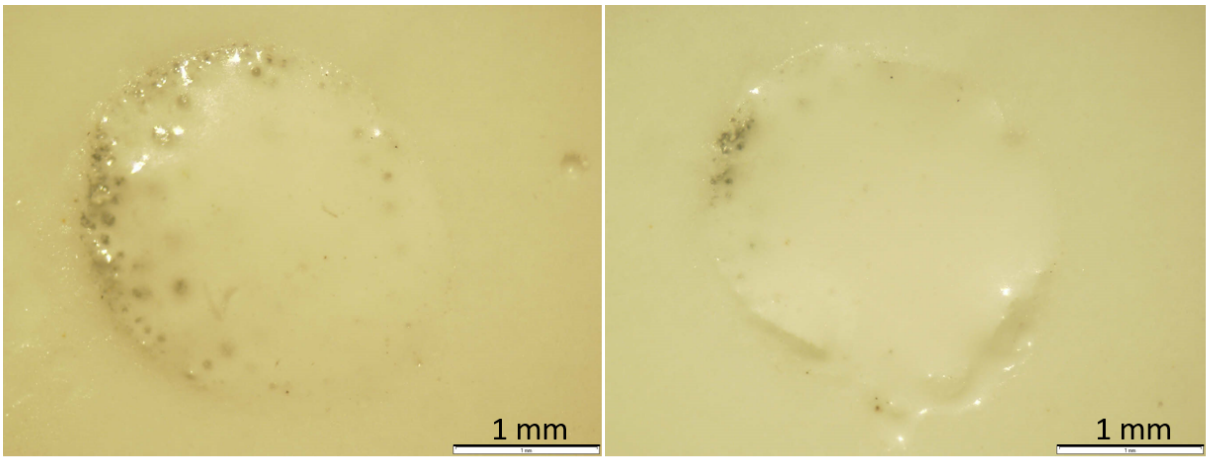
Table 7. Two-way ANOVA test for Laser Power vs. Beam Speed.

Parameter	F	*p*-Value
Laser Power	0.652	0.560
Beam Speed	1.087	0.435
Interaction	0.769	0.511

As for the case of Table 7, neither of the two parameters has an impact on the ΔE^*, and not even the interaction between them stands with a significant influence on the colour of the repaired glaze-filled defects through the laser recovery process. This last result is not as reliable as the first one, since it had a small number of samples for analysis.

The ANOVA made it possible to conclude that the incidence time is much more important to the defect correction than the laser power used. This means that a small variation of the time can prevent a defect from being well recovered, whereas a larger range of laser powers can be used to correctly recover one pinhole or fissure. Nevertheless, the laser power is also very important, as it is one of the main parameters to define the input energy which will solidify the glaze with the remaining material.

On a more qualitative analysis, regarding the defect repairing in terms of surface quality (presence of impurities), glaze spread through the whole defect, or even glaze fusion with the remaining tile, Figure 7 shows an optical microscope view from defects 3 and 5 of tile 1, respectively, with a 4× amplification.

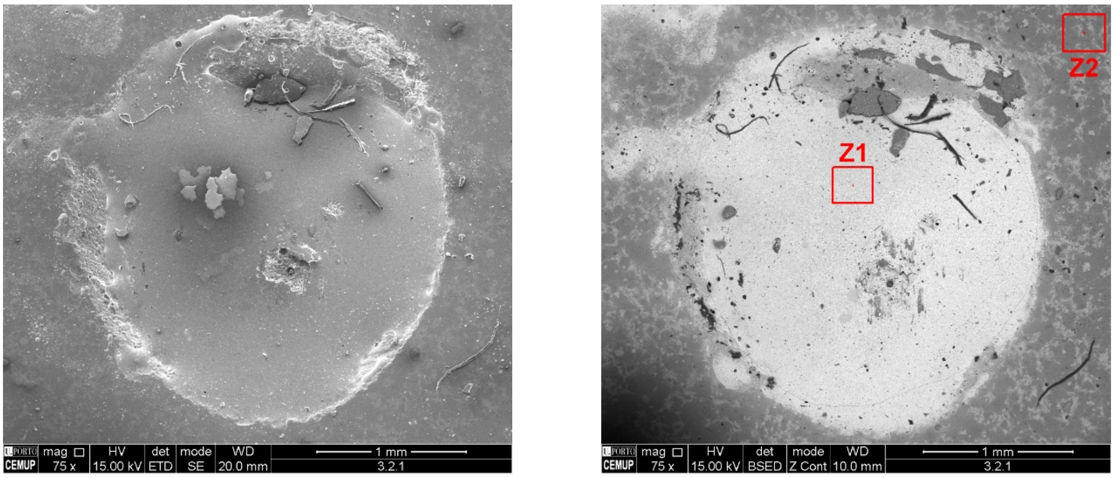


(**a**) (**b**)

Figure 7. Optical microscopic view of pinholes number (**a**) 3 and (**b**) 5 of tile 1.

In the first pinhole, Figure 7a, the right side is almost perfect, and it is difficult to see the interface zone between the defect and the remaining tile. Nevertheless, on its left side some trapped air bubbles formed during the fast fusion of the glaze, since the laser power was too high. On the other hand, Figure 7b shows a second hole which has this problem reduced, with only a small part in its top left side, but the remaining hole had an almost successful recovery.

Afterwards, a deeper analysis was performed to the defect number 3 of tile 1 using SEM to produce two different kinds of images with a 75× amplification: the topography and the backscattered electron image. In the first one (Figure 8a), the brightness is associated to the surface edges and inclination. It is also capable of identifying the surface's micro constitution. On the other hand, in the second case (Figure 8b), the brightness is related to the atomic number of the elements, reason why it offers a more heterogeneous picture. The shinier areas translate into a denser compound and two different zones (Z1 and Z2) were identified for posterior EDS analysis



(**a**) (**b**)

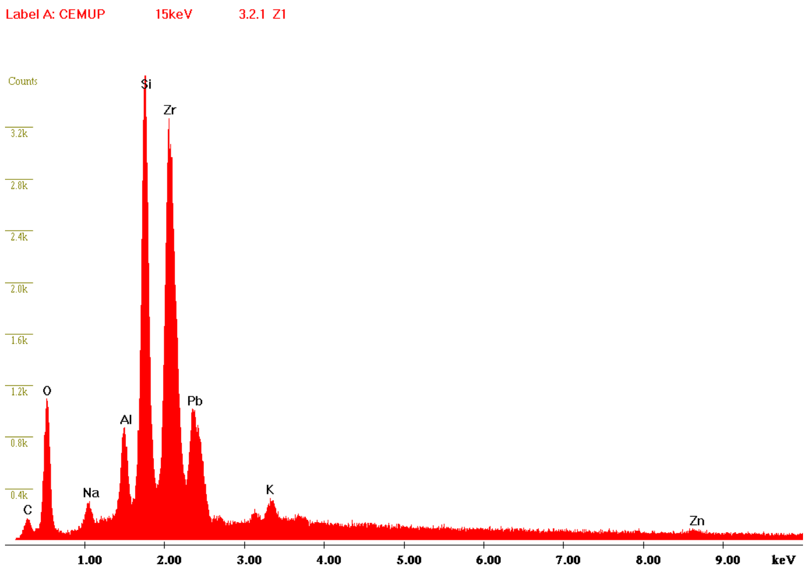
Figure 8. SEM (**a**) topography and (**b**) backscattered electron images of tile 1's defect number 3.

In the topographic image, the difference between the fused glaze and the surrounding tile is reduced; however, a bright line is visible around the defect, as well as some contamination and trapped air in the middle. On the other hand, in the backscattered electron image, some dark zones can be seen, representing small contaminations in the sample. Some grey zones are also present in the defect area, mainly at the upper area of the pinhole, where the glaze did not spread completely, although it had a satisfactory result. Besides the SEM analysis, the EDS function was also used, which represents the chemical analysis of the sample's surface, specifically in zone Z1 (Figure 9a) and Z2 (Figure 9b). The EDS makes it possible to observe the presence of key elements in the glaze deposited in the defect and fused through the laser. No further composition of the developed glazed can be shared due to confidentiality requirements.

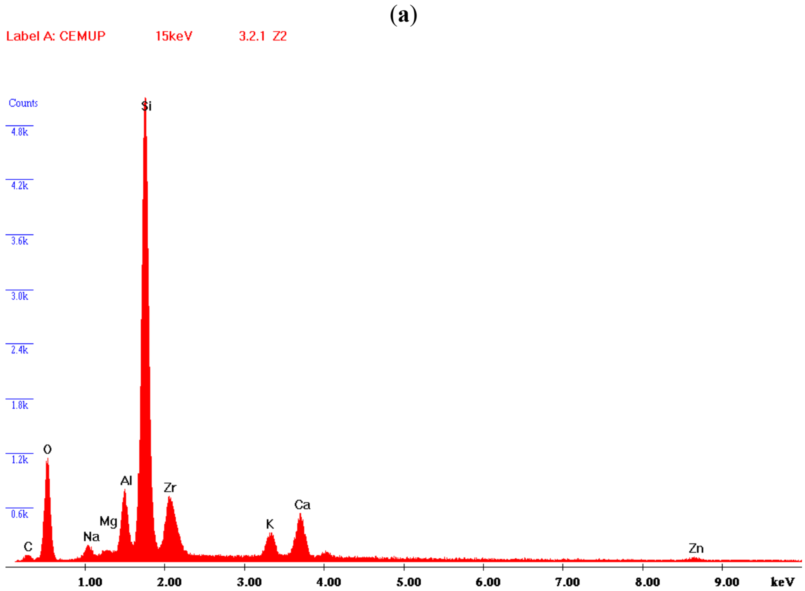
The most abundant elements in the graphs are the Silicium (Si) and Zirconium (Zr), although there are also smaller traces of Oxygen (O), Lead (Pb) and Aluminium (Al), and a few of Calcium (Ca), Potassium (K), Magnesium (Mg), Sodium (Na), Carbon (C) and Zinc (Zn). The ceramic sanitary ware is typically composed of materials rich in silica (SiO_2) and alumina (Al_2O_3). The Silicium is the main component of the vitreous phase and the ceramic matrix, derived from quartz and silicates, and the Aluminium is present in kaolinite or feldspathic materials, which typically compose a ceramic material. The Sodium and Potassium are common in ceramic bodies, typically from feldspars, and the Oxygen is inherent to all the oxide compounds. In the case of the Zirconium, Lead and Zinc, these are prevenient from the white paint used to cover the defects, as these elements are usually used as white pigment. The Carbon likely was originated from the decomposition of ethanol.

Figure 10 represents in the optical (Figure 10a) and electronic (Figure 10b) microscope views of a fissure repaired with laser, but it can be seen that it had a much worse result, as the glaze did not spread correctly along the entire defect, in spite of the parts of the glaze which fused having a smooth surface, as intended.

Firstly in the optical microscopic view of the fissure (Figure 10a), with a 4× amplification, and afterwards in a closer view of the SEM (Figure 10b), with a 70× amplification, there is a clear distinction between the bubble formed glaze and the remaining defect. In the second image, some parts even show several small spreading fractures, revealing that the glaze broke due a contraction in the cooling phase. Figure 11 shows two SEM images with a 500× magnification to highlight two different glaze-ceramic interface cases where the glaze was poorly spread (Figure 11a) and where it is almost undistinguishable from the remaining tile (Figure 11b). On the first case, the defect area can be clearly seen, whereas on the second one, only a thin line dividing two similar regions is present. This is also a proof that, after fusion, the glaze had a similar aspect to the remaining tile.

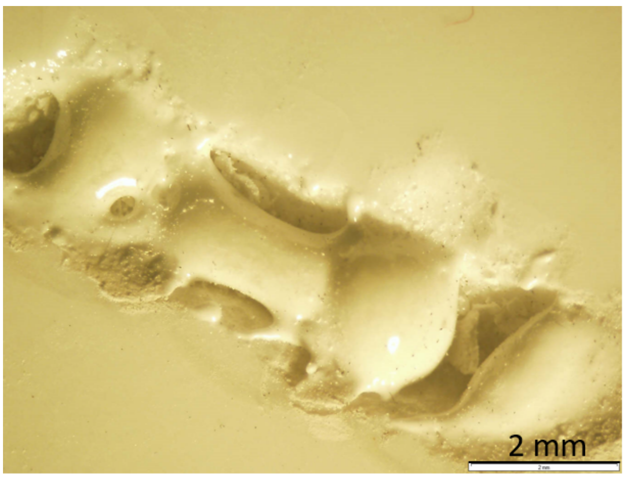


(**a**)

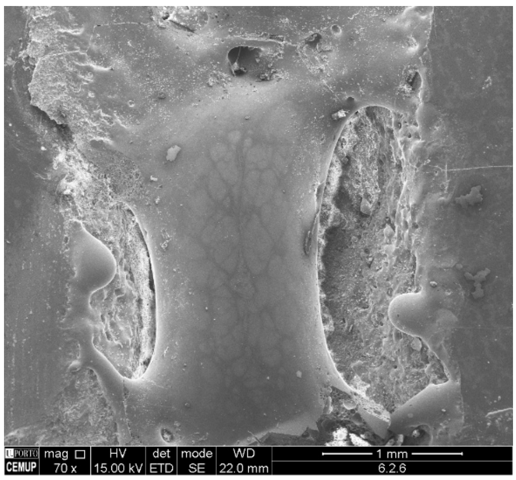


(**b**)

Figure 9. EDS analysis of defect number 1 from tile 1's (**a**) zone Z1 and (**b**) zone Z2.

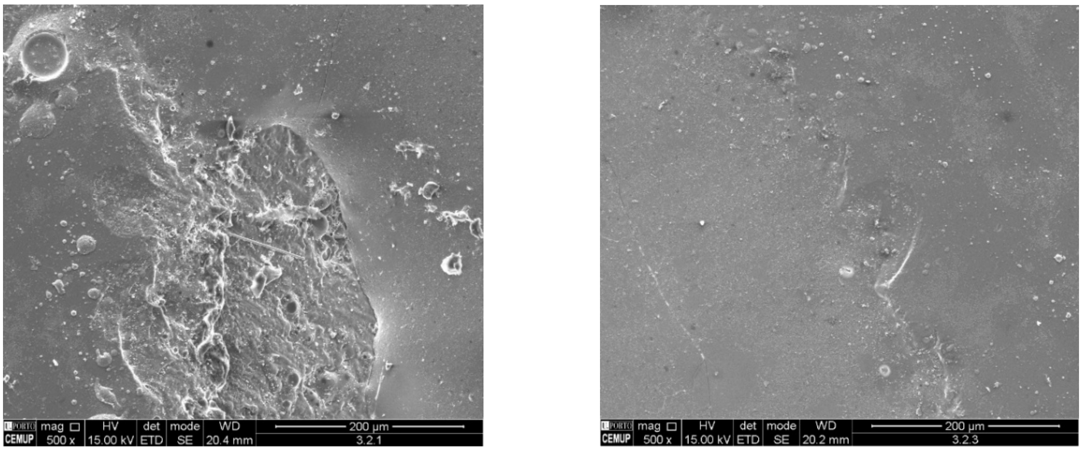


(**a**)



(**b**)

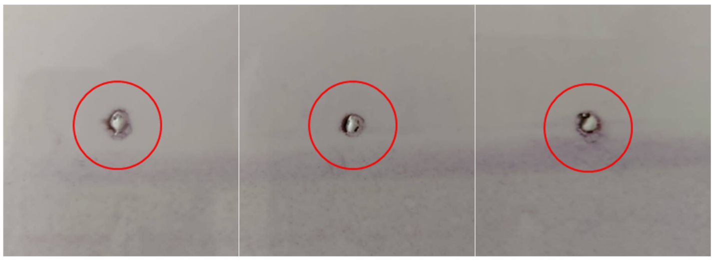
Figure 10. (**a**) Optical and (**b**) SEM view of an example of a laser-repaired fissure.



(**a**) (**b**)

Figure 11. SEM view of two glaze-ceramic interfaces: (**a**) poor glaze spread and (**b**) good glaze spread.

Regarding the quality control tests, at first the autoclave was used to assess if there was a formation of crazing in the glaze fused with the laser when subject to extreme levels of pressure for long periods of time. After putting the tiles inside the autoclave, the specimens were dived in an aniline solution, an organic compound, for twenty-four hours, in order to reveal possible fractures present in the corrected white ink, should they exist. Figure 12 shows the autoclave results for three pinholes.



(**a**) (**b**) (**c**)

Figure 12. Autoclave test results: (a-c) pinholes after the test.

After the test, it can be seen that although there is a dark halo around the defects, due to the incomplete spreading of the white ink in the pinholes, the glazed surface was not affected whatsoever by the aniline. The results were good, as none of the recovered defects showed signs of fissure appearance in their recent fused glaze.

On the other hand, the ABS test assessed the existence of a chemical reaction of the glaze fused with laser and different solutions which simulate real working conditions of sanitary ware, namely with 10% acetic acid, 5% sodium hydroxide and 1% methylene blue in the first three defects of the tile 1, respectively. Figure 13a–c show the pouring of the solutions in the respective defects, whereas Figure 13d–f show the exact same defects after removing the solutions.

After using a pipette to pour the solutions in the defects, these were left in reactive contact for one hour, after what they were removed by water to verify the results. This procedure also possessed a good outcome, as all the experimented defects were non-reactive after being contact with the reagents and did not change colour from their white tone. In the last pinhole, the blue dye only penetrated the non-glazed area, leaving the white ink untouched.

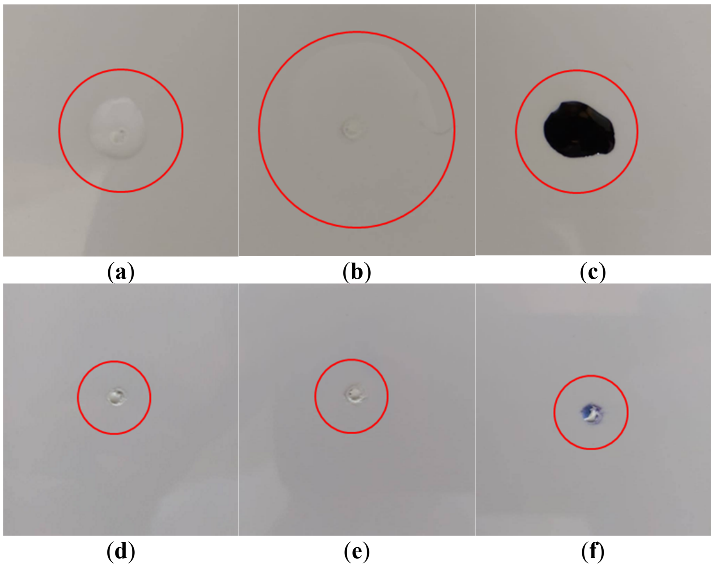


Figure 13. Acids, bases and staining agents' test: (**a**–**c**) solutions poured in the defects, and (**d**–**f**) respective results.

4. Discussion

In this study, the first stage was to develop a glaze which could fuse in the region of the defects, filling them, through the laser's action. Since the laser provides localized heating, instead of a temperature cycle surrounding the entire product in the case of the kiln, the original method, the glaze also had to be created accordingly, with its properties adjusted to the new technique. Several studies have been conducted in the literature through the years to evaluate the morphological and structural characteristics of glazes as a function of their properties. For example, Topates et al. [30] studied the chemical durability and corrosion resistance of glazes containing zirconium, concluding this element contributes to a lower ceramic durability, and Li et al. [31] studied the production of better opaque glazes for tiles using safirine instead of zirconium silicate as an opacifier, i.e., to give them colour, achieving better opacity whiteness and gloss with this new solution. Cai et al. [32] investigated the feasibility of developing fast-firing opaque glazes without resorting to zirconium. They studied the structural and morphological characteristics of glazes using several characterization techniques and successfully developed a frit with better properties that can be an alternative to commercial zircon based glass-ceramic lasers. Pekkan et al. [33] developed temmoku glazes (created from ferruginous or feldspathic clay with iron oxides) and their respective application in different tiles under the industrial conditions of rapid firing at 1180 °C. Tezza et al. [34] analysed the effect of the firing temperature on the photocatalytic activity of anatase ceramic glazes with titanium dioxide, concluding that at lower temperatures the glazes have higher porosity, showing an hydrophilic behaviour.

Regarding the proposed approach for a new recovery method for sanitary ware resorting to laser technology, there are some ceramic repair methods with the laser technology contemplated in the literature, although not many studies have been produced in the sanitary ware field until this moment. Osvay et al. [35], for example, successfully studied the repairing of small defects (pinholes) in Chinese porcelain with a CO_2 laser. In this case, where the material was different but from the same family, the used laser powers were much lower, varying between 1 and 10 W, and the incidence time was much higher, from 1 to 8 min, an alternative and more time-consuming method. In addition, laser techniques to the marking of ceramic materials exist, namely in the American patents Laser marking of ceramic materials, glazes, glass ceramics and glasses [36] and Methods for vitrescent marking [37], where the latter uses a beam expander for the Nd:YAG in order to achieve better results, a substrate more resistant to low temperatures and abrasion. Another study, by Wang et al. [20], uses the same laser in the production of pure molybdenum by selective fusion (SLM) with the intent to reduce the fissures in the substrate. After studying the crack growth behaviours under different scanning strategies by electron backscattered diffraction, they concluded that crack growth resistance is formed under layer-wise rotated laser scanning. Laser treatment in ceramics has also been a topic studied in the literature, as proven by the work of Xiong et al. [38], where a RFL-QCW150 fibre laser with a 1080 nm wavelength was used to reduce the surface hardness of an AlN ceramic, a material known for its high hardness and brittleness, which makes it difficult to machine. This procedure using laser opens the possibilities for an easier posterior machining process and optimization of post-machining quality.

In spite of not many studies addressing the subject of repairing sanitary ware or the use of laser in ceramic materials, the environmental impact of this industry is still very concerning, and the authors are designing strategies in order to minimize it as far as possible and increase the sustainability of this sector. In their work, Cuviella-

Suárez et al. [39] addressed the water scarcity problem and provided a practical tool to increase the efficiency of sanitary ware facilities. Using computational modelling, a thermodynamical analysis was performed to save heat through the kiln's exhaustion, which was used in other operations of the factory. In addition, a 16% water usage was spared by the utilisation of the condensed water from combustion. More recently, Mingione et al. [40] aimed to lower energy used in this industry through the optimization of raw material formulations, altering the existing formula ratios and adding fluxing agents to enable lower firing temperatures and higher product performance. These studies show that every act counts to improve this industry's sustainability practices and reduce costs.

5. Conclusions

In this paper, a novel and more sustainable alternative for the recovery of sanitary ware products was proposed. Some defects of two different kinds, pinholes and fissures, were introduced in ceramic tiles, simulating sanitary ware products, and a glaze was developed to fill them, before resorting to a CO_2 laser to fuse the glaze, leaving no difference between the area where previously there was a defect and the remaining tile. Several different glazes and inks were tested with different laser parameters in order to understand under what conditions was the best outcome achieved. A quantitative analysis using a colourimeter reading difference between the repaired defects and the remaining part was performed with statistical analysis through an ANOVA, and a qualitative analysis using the optical microscope, the SEM/EDS and quality control tests was also carried out.

Comparing to the original refiring technique, the laser was able to overcome the obstacles during the sanitary ware recovery process. Firstly, it is a non-evasive method which focused its power and heat just in the defect zone, leaving the remaining part unharmed. Furthermore, several resources were spared with this method. By using laser, the entire available space in the kiln can be used to produce the new parts, instead of also correcting the defective ones, and the excessive energy and time are also saved.

The ANOVA showed that the incidence time is the parameter with the highest impact in the final outcome, as it contributes the most to reduce the colourimeter reading difference between the laser-recovered defects and the remaining tile with a 95% confidence level. On the other hand, both the laser power and beam speed have little effect on the results, showing that a great variation in their values is needed for a significative colourimeter reading difference to be noticed. The most effective recovered defects were using a glaze based on white marking ink mixed with ethyl alcohol and the following parameters: a laser power between 50 to 70 W, although lower values produce a better result, and a 30 s incidence time, in the case of pinholes, and 0.0495 m/s beam speed for the fissures.

The results achieved through the experimental campaign, using the previously mentioned formulation and laser parameters, demonstrated a good recovery of defects on the damaged tiles, validating the laser technology approach as a good alternative approach to solve the defective sanitary ware products problem. Although the pinholes have shown good outcomes, with an almost perfect defect recovery in some case, the fissures still need further tests for this novel technique to be proven effective. This novel solution increased the effectiveness of the process, reduced the waste generation and is more sustainable since with this new method, it is estimated that 9€ will be saved per product, on 5% of an annual production rate of 200,00 pieces. This way, it will be possible to consume less energy and save both money and resources.

6. Future Considerations

In spite of valuable advances having been made in this work, this subject needs to be studied even further, since the fissures still have a long path to follow in order to achieve a correct repairing, the same way as it happened with the pinholes, although these can be improved as well. In a chronological order, the future works consist in:

- Continue testing these defects, in special the fissures, changing the variables in more levels and evaluating different conditions. In future tests, the quality assessment should be performed not only qualitatively to confirm short-term durability, but also quantitively for long-term performance, by evaluating the hardness, wear resistance and thermal cycling of the repaired defect area and to quantify the interfacial bonding strength between the repaired area and the base ceramic;
- Apply this concept in more complex shapes, such as round surfaces, since these represent a more accurate approximation of real conditions;
- Test this technology in actual sanitary ware parts, so that this method can be implemented in the shopfloor operations on a daily basis;
- Automate this novel method by using a robotic arm with a high level of degrees of freedom, so that it may be able to reach even the defects located in the most difficult-to-access areas and to carry out a path planning for complex geometries.

Author Contributions

J.R.F.: conceptualization; R.D.F.S.C. and J.R.F.: methodology; R.D.F.S.C.: data curation, visualization; R.D.F.S.C.: writing—original draft preparation; R.D.F.S.C. and J.R.F.: investigation; L.M.P.D. and A.M.G.P.: supervision; J.R.F.: validation; A.A.G., I.F. and N.P.V.S.: writing—reviewing and editing. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement

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Conflicts of Interest

The authors declare no conflict of interest.

Use of AI and AI-Assisted Technologies

No AI tools were utilized for this paper.

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