

# A comparative study of the surface glaze characteristics of concrete treated with CO<sub>2</sub> and high power diode lasers Part II: mechanical, chemical and physical properties

J. Lawrence \*, L. Li

*Manufacturing Division, Department of Mechanical Engineering, University of Manchester Institute of Science and Technology (UMIST), Manchester, M60 1QD, UK*

Received 4 November 1999; received in revised form 25 February 2000

## Abstract

The hardened ordinary Portland cement (OPC) surface layer of concrete which was glazed using a CO<sub>2</sub> and a high power diode laser (see Part I of this paper) has been tested in order to determine the mechanical, chemical and physical characteristics of the glazes. The work showed that the generation of the surface glazes resulted in improved mechanical, chemical and physical properties over the untreated OPC surface of concrete. However, differences in the performance of the CO<sub>2</sub> and high power diode laser (HPDL) generated glazes were observed. These are believed to be due to the differences in the morphology and microstructure of the glazes generated as a result of the differing beam absorption characteristics of the two lasers. Life assessment testing revealed that the laser-glazed OPC surfaces effected an increase in actual wear life of 1.3–17.7 times over the untreated OPC surface of concrete depending upon the corrosive environment. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** CO<sub>2</sub> laser; High power diode laser; Concrete; Cement; Surface glazing; Properties

## 1. Introduction

Building and civil engineers alike employ concrete in a broad area of applications. Over time, however, and as a direct consequence of the operating environment the concrete becomes corroded and/or contaminated. This ultimately necessitates the arduous and costly undertaking of repairing or replacing the affected concrete either by physical or mechanical means. Clearly, any means by which the life of the concrete can be extended would be of great interest to engineers.

As has been demonstrated in Part I of this paper, both the CO<sub>2</sub> laser and the high power diode laser (HPDL) are feasible tools to produce a glaze on the hardened ordinary Portland cement (OPC) surface of concrete. However, marked differences in the characteristics of the glazes generated on the OPC surface of concrete when treated with CO<sub>2</sub> laser and HPDL radia-

tion were clearly apparent. This part of the paper reports on the comparative testing of the CO<sub>2</sub> and HPDL generated glazes in terms of their mechanical, chemical and physical properties, as well as a comparison with the untreated OPC surface properties. Mechanical tests were conducted to determine properties such as pull-off (bond) strength, rupture strength, wear resistance and absorptivity to water. Additionally, chemical tests were carried out to examine the corrosion resistance of the laser glazed and untreated OPC with regard to acid (nitric acid) alkali (sodium hydroxide) and common industrial detergents. Life assessment testing of the laser glazed and untreated OPC was also carried out.

## 2. Experimental procedures and results

Current British and international standards in relation to concrete and coated concrete are concerned only with water sorptivity and compressive strength. No British or international standards exist regarding the

\* Corresponding author. Tel.: +44-161-2363311, ext. 2383; fax: +44-161-2003803.

E-mail address: j.lawrence@umist.ac.uk (J. Lawrence)

testing of glazed concrete. It was therefore generally not possible to test the CO<sub>2</sub> and HPDL generated glazes in strict accordance with established tests. As such, wherever possible, tests based on current standards or the work of others were developed to investigate specific aspects of particular relevance to the laser-generated glazes. These aspects were the pull-off strength; the surface roughness; the rupture strength; the wear resistance and the corrosion resistance.

### 2.1. Pull-off strength

To determine the strength of the bond between the CO<sub>2</sub> and HPDL-generated glazes on the OPC surface and the concrete substrate itself, pull-off tests were conducted based on the work of Bungey et al. [1] and Carino [2]. For experimental convenience the concrete was prepared as relatively small area samples (25 × 25 mm). High tensile aluminium test dollies were then attached onto both the glazed surfaces, and to the axially opposite concrete substrate surface, using Araldite epoxy and left to cure for 24 h. The diameter of the test dollies was 12 mm. In order to ensure axial accuracy (essential for true results) the test dollies were set in position using identical V-blocks. The samples were placed into an Instron 4507 tensile/compressive test rig by mounting the test dollies into the jaws of the rig. A tensile force was then applied until sample failure, with the force being simultaneously recorded.

As Fig. 1 shows, the results obtained varied markedly with both changes in the laser operating parameters and, perhaps more importantly, with the laser used. A post-test analysis of both the CO<sub>2</sub> and HPDL-generated surface glazes on the OPC surface revealed that the material failed well below the laser treated surface, within the heat affected zone (HAZ). As is evident from Fig. 1, when using laser operating parameters that produced good quality glazes with both lasers (1.5 kW cm<sup>-2</sup> power density, 480 mm min<sup>-1</sup> traverse speed),

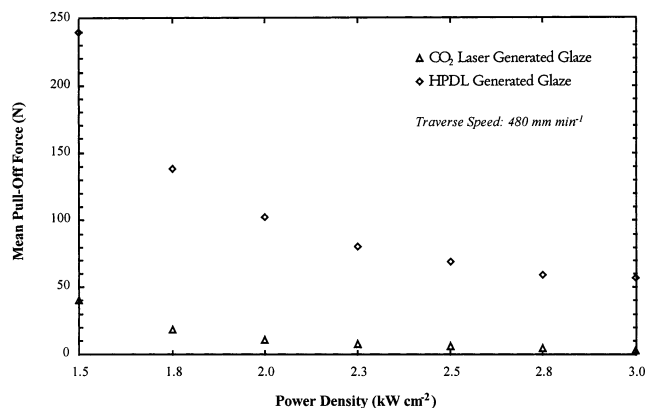


Fig. 1. Relationship between pull-off strength of laser glaze and laser operating parameters for the CO<sub>2</sub> and HPDL.

the average maximum pull-off force required for the CO<sub>2</sub> laser generated glaze was recorded as 40.3 N, whilst that for the HPDL generated glaze was 235.6 N. This compares with 636.8 N for the untreated OPC surface of concrete.

### 2.2. Rupture strength

In order to determine the rupture strength of the CO<sub>2</sub> and HPDL generated OPC glazes test samples were prepared as described above. The samples were placed onto the sample stage of the Instron 4507 tensile/compressive test rig and then subjected to a compressive rupture force until the OPC glazes failed (cracked), with the energy being recorded simultaneously. The rupture force was applied by means of a high tensile steel indenter with a 1-mm radius point. The results of the tests revealed that the average rupture strengths of the CO<sub>2</sub> and HPDL generated OPC glazes were almost similar, 0.82 and 0.8 J, respectively. In contrast, the rupture strength of the untreated OPC surface was 4.3 J. This is perhaps expected as the OPC surface has been partially (CO<sub>2</sub> laser) and fully (HPDL) vitrified, effectively generating a glass.

### 2.3. Water absorptivity testing

In order to test the absorptivity of the CO<sub>2</sub> and HPDL generated OPC glazes, a series of comparative experiments with the untreated OPC surface were conducted in terms of water absorptivity. The tests were conducted in accordance with the standard procedure employed by Hall et al. [3] and Wilson et al. [4]. For the experiments the laser treated and untreated OPC samples were cut into smaller pieces (25 × 25 mm). The samples were then dried to a constant weight in an air oven at 65°C to ensure that all the pores were free of water. The OPC laser glazes and the untreated OPC surfaces were then immersed in water and weighed at regular intervals. The side faces of the three samples were shielded from water by means of an Araldite coating. In order to determine the absorptivity of the OPC laser glazes and the untreated OPC surface,  $i$  was plotted against the square root of time so as to give a straight line, as shown in Fig. 2.  $i$  is defined as

$$i = \frac{1000\Delta m}{A} \quad (1)$$

where  $\Delta m$  is the cumulative change in mass with time and  $A$  is the immersed surface area. The sorptivity,  $s$ , of the laser generated OPC glazes and the untreated OPC surface is simply the gradient of this line.

As one can see from Fig. 2, the sorptivity of the untreated OPC surface was a typical 0.096 mm min<sup>-1/2</sup>, compared with 0.047 and 0.043 mm min<sup>-1/2</sup> for the CO<sub>2</sub> and the HPDL glazed OPC surfaces, respectively.

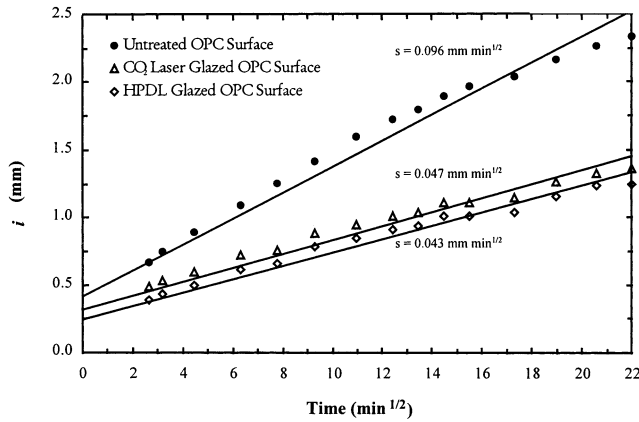


Fig. 2. Water absorption for the untreated and for the CO<sub>2</sub> and HPDL glazed OPC surfaces.

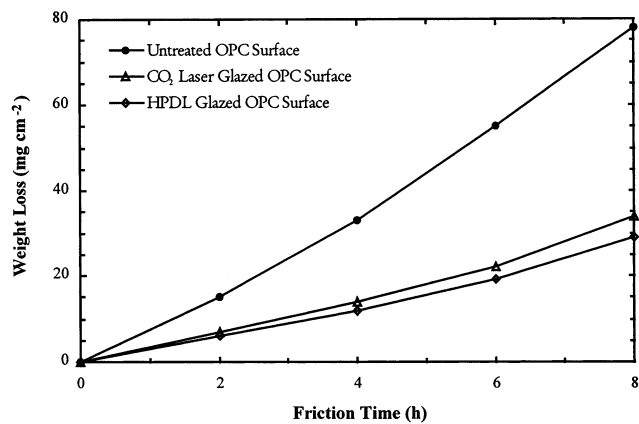


Fig. 3. Relationship between weight loss and friction time for the laser CO<sub>2</sub> and HPDL generated glazes and the untreated OPC.

It is therefore reasonable to conclude from this that both the laser-generated glazes provided approximately twice as much resistance to water absorption than the untreated OPC surface. In addition, it is a distinct possibility that the HAZ, which was identified as being composed of CaO resulting from the dehydration of the Ca(OH)<sub>2</sub>, may, once re-hydrated, act as a barrier towards liquids such as water. In this way the HAZ may therefore augment the resistance of the laser-glazed OPC surface to water absorption.

#### 2.4. Wear life characteristics

Generally, the wear resistance of a material is primarily determined by the hardness of the material in comparison to that of other materials with which it subsequently comes into contact [5]. However, wear resistance does not always increase with hardness [6]. Tests were therefore conducted in accordance with the procedure detailed by Petitbon et al. [7] and Lawrence et al. [8] to determine the exact difference in the wear resistance characteristics between the CO<sub>2</sub> and HPDL

generated OPC glazes, as well as those of the untreated OPC surface. For experimental purposes the OPC was cut into smaller pieces (25 × 25 mm), with half of the samples then being laser treated. All the samples were then weighed and subjected to a friction force for 8 h, being removed from the machine and weighed at 2-h intervals.

Fig. 3 shows the relationship between weight loss and the friction time for the laser generated OPC glazes and the untreated OPC. As one can see, the wear resistance of the HPDL generated OPC glaze is fractionally greater than that of the CO<sub>2</sub> laser generated OPC glaze. However, both the OPC laser glazes displayed a significant increase in wear resistance over the untreated OPC surface, with the weight loss being approximately two times lower after 4 h, and 3 times lower after 8 h.

#### 2.5. Corrosion resistance

Concrete surfaces are often subjected to corrosive substances, either as part of the normal service environment and/or as a result of routine cleaning. Therefore, corrosion resistance tests based upon BS 6431 [9] were conducted using nitric acid, sodium hydroxide and Premier Products MP9 detergent cleaner. The experiments were carried out by dropping small amounts of the corrosive agents on to the surface of the CO<sub>2</sub> and HPDL-glazed OPC surfaces, as well as the untreated OPC surface of the concrete, at hourly intervals for 4 h. The reagents were applied in the concentration ratios of 80, 60, 40, 20 and 10%. The samples were then examined optically, as well as mechanically tested in terms of compressive strength and wear. High concentrations of various corrosive agents were used principally to accelerate the tests. However, in practice 60% nitric acid is used within the nuclear processing industry as a solvent for nuclear fuels [10].

All three substances in the concentrations of 80, 60 and 40% were seen to immediately attack the untreated OPC surface, with nitric acid and sodium hydroxide attacking with greater severity than the detergent. On the other hand, both CO<sub>2</sub> and HPDL glazed surfaces displayed no discernible microstructural changes or signs of devitrification due to corrosion.

Tests conducted according to ASTM C579-91 [11] revealed that exposure of the untreated OPC surface to the reagents had a significant effect on the compressive strength and the wear resistance of the OPC. Exposure of the OPC to nitric acid and sodium hydroxide in the concentrations of 40–80% resulted in an average loss of compressive strength of approximately 19–37%. In the case of the detergent a discernible loss in compressive strength occurred only with concentrations above 40%. Here the average loss in compressive strength for concentrations in the range 60–80% was approximately 17%. This compares with no discernible difference in

either the wear resistance or the compressive strength of the laser-glazed OPC surfaces. Similarly, the wear resistance of the untreated OPC surface when exposed to the reagents with an 80% concentration was significantly affected, particularly through interaction with nitric acid and sodium hydroxide. Here the weight loss was approximately 5 times higher than for the unexposed OPC after 4 h, and approximately 11 times higher after 8 h for nitric acid. In the case of the detergent, the weight loss was marginal after both 4 and 8 h.

### 3. Discussion

As the results of the mechanical and chemical tests show, the CO<sub>2</sub> and HPDL generated OPC glazes outperformed the untreated OPC surface in many of the test areas. This was especially true in the case of chemical resistance, where both the OPC laser glazes proved to be resistant during the time of the experiments. This marked variation in corrosion resistance can be ascribed to the difference in structure of the laser generated OPC glazes and the untreated OPC. Whereas the HPDL generated OPC glaze is of a fully amorphous nature, and the CO<sub>2</sub> laser OPC glaze is of a semi-amorphous nature, the untreated OPC is comprised of a porous polycrystalline structure. Thus, the untreated OPC is readily attacked by acids, whilst the amorphous structure of both OPC laser glazes ensures an increase in acid resistance [12].

The superior mechanical and chemical performance of the laser generated OPC glazes over the untreated OPC suggests that the life characteristics of the glazes may also be superior to those of untreated OPC. Yet in any practical analysis of the wear life of materials, the in situ relative thicknesses of the materials must be considered. Consequently, the laser generated OPC glazes and the untreated OPC layer on concrete must be taken into consideration in any calculation in order to give a true interpretation of the actual life characteristics. Thus, the increase in wear life can be given by

$$\text{Increase in wear life} = \frac{\text{Laser glaze wear life}}{\text{Untreated OPC wear life}} \quad (2)$$

$$\text{Wear life} = \frac{\text{Density thickness (mg cm}^{-3} \text{ cm)}}{\text{Wear rate (mg cm}^{-2} \text{ h}^{-1})} \quad (2a)$$

Table 1 summarises the wear rate details and the nominal life increase of both the CO<sub>2</sub> and HPDL generated OPC glazes over the untreated OPC surface. As Table 1 shows, the laser generated OPC glazes gave an increase in actual life over the untreated OPC surface regardless of the environment. Nonetheless, as one can see from Table 1 the increase in actual life of the laser generated OPC glazes over the untreated OPC surface varies considerably, depending upon the working environment. However, arguably the most common working environment for an OPC surface would involve some contact with at least detergent acids, therefore significant economic savings may be yielded since a OPC surface glazed with either laser lasts around 2.5-times longer than one which is unglazed. Furthermore, as Fig. 3 and Table 1 both show clearly, the wear rate and the wear life of the HPDL generated glaze was, although similar in value, consistently higher than that of the CO<sub>2</sub> laser generated glaze. This is believed to be due to the effects of the greater occurrence of porosities, in particular the 'knife edge' porosities discussed in Part I of this paper, which are prone to excessive wear. Consequently, the wear rate of the CO<sub>2</sub> laser glaze will therefore be somewhat higher than that of the HPDL glaze.

Of great importance is the resistance to water absorption offered by the concrete as a result of laser glazing with both CO<sub>2</sub> and HPDL. As Fig. 2 suggests, the CO<sub>2</sub> laser glaze offered slightly less resistance to water absorption than the HPDL glaze. Again, this is likely to be due to the greater prevalence of not only porosities, but also cracks, in the CO<sub>2</sub> laser glaze which will inherently allow more water to permeate through the glaze and be absorbed by the concrete.

As is evident from Fig. 1, surface glazing of the OPC with either laser effected a considerable decrease in the pull-off strength in comparison to the untreated OPC surface of the concrete. However, a significant differ-

Table 1  
Wear rate details and the nominal life increase of the OPC laser glaze over untreated OPC in various corrosive environments

|  | Density (kg m <sup>-3</sup> ) | Thickness (μm) | Wear rate (mg cm <sup>-2</sup> h <sup>-1</sup> ) |           |      |                  |
|--|-------------------------------|----------------|--|-----------|------|------------------|
|  |                               |                | Unexposed  | Detergent | NaOH | HNO <sub>3</sub> |
| Untreated OPC                            | 2220                          | 1500           | 9.8  | 18.5      | 73.8 | 114.8            |
| CO <sub>2</sub> laser OPC glaze          | 2000                          | 1000           | 3.9  | 3.9       | 3.9  | 3.9              |
| HPDL OPC glaze                           | 2000                          | 750            | 3.5  | 3.5       | 3.5  | 3.5              |
| Increase in wear life (CO <sub>2</sub> ) | —                             | —              | 1.5  | 2.8       | 11.4 | 17.7             |
| Increase in wear life (HPDL)             | —                             | —              | 1.3  | 2.4       | 9.5  | 14.8             |

ence between the required pull-off force of the CO<sub>2</sub> and the HPDL glazed surfaces was apparent, 40.3 compared with 235.6 N, respectively. This marked difference can perhaps be attributed to the fact that the HAZ generated on the OPC after CO<sub>2</sub> laser glazing was much larger than that generated as a result of HPDL glazing (see Part I of this paper). Thus, a larger dehydrated and CaO rich area is generated which is therefore inherently weaker.

#### 4. Conclusion

A comparative study of the mechanical, chemical and physical properties of the surface glaze generated on hardened OPC paste by means of CO<sub>2</sub> and a HPDL radiation has been conducted. Furthermore, the performance of both the laser-generated glazes has been compared with that of the untreated OPC surface. It was found that, (i) the required pull-off force after laser glazing was reduced from 636.8 to 235.6 N after HPDL glazing and 40.3 N after CO<sub>2</sub> laser glazing. The general reduction in required pull-off force after laser glazing is believed to be due to the inherent generation of a HAZ comprising mainly weaker CaO. Similarly, the marked difference between the pull-off strength of the CO<sub>2</sub> and HPDL glaze can be attributed to the fact that the HAZ after HPDL glazing was much smaller than that of the CO<sub>2</sub> laser glaze; (ii) the average rupture strength of the CO<sub>2</sub> and HPDL generated OPC glazes were very similar, 0.82 and 0.8 J, respectively, whilst the rupture strength of the untreated OPC surface was some 4.3 J. This is because laser glazing of the OPC surface has resulted in partial (CO<sub>2</sub> laser) and full (HPDL) vitrification, effectively generating a glass; (iii) laser glazing of the OPC surface afforded the concrete approximately twice as much resistance to water absorptivity than the untreated surface, 0.096 compared with 0.047 mm min<sup>-1/2</sup> and 0.043 mm min<sup>-1/2</sup> for the CO<sub>2</sub> and the HPDL glazes, respectively. The slightly higher water absorptivity of the CO<sub>2</sub> laser glaze is likely to be due to the greater

prevalence of porosities and cracks in the CO<sub>2</sub> laser glaze; which will inherently allow more water to permeate through the glaze and be absorbed by the concrete; (iv) life assessment testing revealed that surface glazing of the OPC with both the CO<sub>2</sub> and the HPDL effected an increase in wear life of 1.3–17.7 times over an untreated OPC surface, depending upon the corrosive environment. The wear life and the wear rate of the HPDL glaze were consistently higher than that of the CO<sub>2</sub> laser glaze; (v) Both the CO<sub>2</sub> and HPDL glazed OPC surfaces displayed no discernible microstructural changes or signs of devitrification resulting from exposure to corrosive agents. In contrast, the corrosive agents were seen to immediately attack the untreated OPC surface. Clearly, the economic and material benefits to be gained from the deployment of such an effective and efficient coating on OPC could be significant.

#### References

- [1] H.J. Bungey, R. Madandoust, *Mag. Concr. Res.* 44 (1992) 21–30.
- [2] N.J. Carino, Non-destructive testing of concrete, in: V.M. Malhotra (Ed.), *Concrete Technology: Past, Present and Future*, ACI, Detroit, MI, 1992, pp. 144–159.
- [3] C. Hall, K.M. Tse, *Building Environ.* 21 (1986) 113–118.
- [4] M.A. Wilson, W.D. Hoff, *Eur. J. Soil Sci.* 48 (1997) 79–86.
- [5] J.H. Dickson, *Glass: A Handbook for Students and Technicians*, Hutchinsons Scientific and Technical Publications, London, 1951, p. 148.
- [6] A. Petitbon, L. Boquet, D. Delsart, *Surf. Coat. Tech.* 49 (1991) 57–61.
- [7] A. Petitbon, L. Boquet, D. Delsart, *Surf. Coat. Tech.* 49 (1991) 57–61.
- [8] J. Lawrence, L. Li, J.T. Spencer, *Opt. Laser Tech.* 30 (1998) 215–223.
- [9] BS 6431: Part 19: 1984, *Ceramic Wall and Floor Tiles: Method for Determination of Chemical Resistance. Glazed Tiles*.
- [10] J. Verran, Letter to Author, October 1997.
- [11] ASTM C597-91, *Standards Test Method for Compressive Strength of Chemical-Resistant Mortars, Grouts, Monolithic Surfacing and Polymer Concretes*.
- [12] V.V. Vargin, *Technology of Enamels*, MacLaren, London, 1965, pp. 125–128.