Micro-Raman and Raman Imaging studies of glassy material produced by continuous wave (CW) CO_2 laser irradiation of lime/pozzolan mortar

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Abstract
This work describes the distribution of the portlandite over the surface of the lime/pozzolan mortar and the mineral composition of the glassy material formed when the mortar was irradiated with continuous-wave-CO_2 (CW-CO_2) laser. Both Micro-Raman and Raman mapping have been used for structural studies.

Lime/pozzolan/sand 1/1/2 mortars, 5 years at room temperature, were irradiated with CW-CO_2 laser (Synrad Firestar t80, Mukilteo, WA) operating at a wavelength of 10.591 μm, 10P(20) CO_2 laser line. Laser output: 8W, 18W and 38W (Synrad PW-250 (Mukilteo, WA)). The laser beam was focused by means of a NaCl lens of 10 cm focal length and the irradiation time was 5 seconds.
Raman spectra were collected with a Raman Spectrometer (*Renishaw Invia*) *equipped with a CCD camera, using 532 nm (Nd:YAG) excitation line. The laser on the sample was 5 mW and the integration time was 10 seconds. For mapping measurements, an area of 80 µm x 80 µm was chosen in the internal part of the glass. The step size was 5 µm with an individual grid size of 25 µm^2.*

Glazing, vaporization and spalling process can produce over an irradiated surface with a high power laser beam. When the power density of the irradiating laser beam is high enough to raise the temperature beyond the glass transition, a glassy surface layer is formed. However, if surface temperatures are below that melting point, the vaporization of water can be produce over the material surface. Due to the small diffusivity of water vapour, its transport is hindered and an overpressure is attained. Hydraulic building materials have about 4-10% bounded water, after irradiation with the CW-CO_2 laser, water vapour spread out in a vaporization front reacting with the CaO present in the sample and producing $Ca(OH)_2$, besides a glassy surface.

Originality
The surface temperature of the lime/pozzolan mortar after irradiation with the CW CO_2 laser is about 4800 K, however portlandite can be observed over the surface of the sample due to water vapour reacts with CaO. The CW-CO_2 laser irradiation over hydraulic materials can be considered as an accelerating test of fire exposure.

Keywords: *Raman, fire test, laser, lime/pozzolan mortar*

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1. Introduction

A CO_2 laser beam can be absorbed by many organic and inorganic materials such as natural stone, concrete, wood, rubber, plastics, etc., but is reflected on the most metal surfaces. Optical energy is absorbed by the interaction of the electric field of the electromagnetic radiation with electrons. If the energy is high enough, the structure of the material begins to vibrate which it is detected as thermal energy. With greater photon fluxes the vibration becomes sufficient to break the solid structure and it first melts, then evaporates; the vapour is then ionized forming a plasma plume and finally the solid is ionized introducing Coulomb forces to remove the material.

There are some papers that study the effect of different CO_2 laser in concrete samples with different proposes. In some studies (Gomez-Heras M., *et al*., 2008), laser radiation has been used in order to simulate fire conditions, since laser irradiation allows concentration at high energy in a small area. Another studies (Kawaka K. *et al.*, 2004) analysed the amount of carbon emitted for the sample after laser radiation over the concrete sample in order to determine the $CaCO_3$ content in the sample. However it is also possible to study the effect of the impact of the CO_2 laser over the mechanical and the structural change in the concrete sample. Thus it has been demonstrated that the impact of the CO_2 laser has a positive influence on the mechanical properties of cement paste, not due to the heat produced during irradiation, but due to the effect of electric field propagation on water molecules (Moreno-Virgen M.R. *et al*,. 2011). From the microstructural point of view it is possible to identify molecular structural changes in cement and concrete with a glassy compound formation after concrete laser radiation at 10.6 µm (Moreno-Virgen M.R. *et al*., 2006).

When the power density of the irradiating laser beam is high enough to raise the temperature beyond the glass transition, a glassy surface layer is formed. However, if surface temperatures are below that melting point, the vaporization of water can be produce over the material surface. Due to the small diffusivity of water vapour, its transport is hindered and an overpressure is attained. Hydraulic building materials have about 4-10% bounded water, after irradiation with the CW-CO_2 laser, water vapour spread out in a vaporization front reacting with the CaO present in the sample and producing $Ca(OH)_2$, besides a glassy surface.

The laser treatment produced novel surfaces, and the resultant structural and chemical characteristics of the post-process materials need to be studied. Hydraulic building materials used as modern Cultural Heritage, i.e. mortar, concrete, etc., has about 4-10% bounded water. After irradiation with the CW CO_2 laser, water vapour spread out in a vaporization front reacting with the CaO formed after calcium carbonate decarbonation producing $Ca(OH)_2$, besides a glassy surface (Lawrence J. and Li L., 2000).

The present work describes the distribution of the portlandite over the surface of the sample and the mineralogical composition of the glassy material. Both Micro-Raman and Raman mapping have been used for structural studies.

2. Experimental

2.1. Raw Materials

Lime pozzolan mortar with siliceous sand was prepared with the following composition: lime/pozzolan/sand 1/1/2. The chemical composition of the lime, pozzolan and sand used in the mortar preparation is showed in Table 1.

Tab. 1 Chemical compositions of lime, pozzolan and sand

	Compositions	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	Na_2O	K_2O	LOSS
Lime	Content	0.39	0.24	0.16	72.13				26.46
Pozzolan	Content	45.93	10.12	17.84	8.06	5.10	1.23	4.76	5.50
Sand	Content	98.92	0.06	0.18		0.28			0.05

2.2. Experimental Process

Lime/pozzolan mortar specimens with lime/pozzolan/sand ratio 1/1/2 and water/blended ratio 0.5 were placed in prisms of 5×5×10 mm. The mortar specimens were firstly cured in standard environment with RH 95% ± 5% and 20℃±2℃ for 24 hours. After demolding, the specimens were cured at 40ºC ± 5ºC and RH 95% ± 5% for 7 days (for puzzolanic reaction) and then were submitted to a carbonation process in a chamber at 21ºC ± 5ºC and 60% R.H.

until full carbonation (CaO < 0.2%). Samples were at room temperature for 5 years before submitted to the CW CO_2 laser irradiation. The irradiation was carried out with a CW (Firestar t80) CO_2 laser operating at a wavelength of 10.591 µm, 10P (20) CO_2 laser line. This laser has a maximum power output of 80 W, but in our experiments, laser output was kept at 8, 18 and 38 W as measured with a Synrad PW-250 power meter. The laser beam was focused by mean of a NaCl lens of 10 cm focal length. Irradiation time was varied between 5 and 30 s. In this way, the energy delivered to the surface sample surface range between 40 and 1200 J. Irradiation of the mortar samples with the CW CO_2 was made in air and in a vacuum of 3 Pa of background pressure.

Raman spectra were collected with a Renishaw Raman Invia Spectrometer, equipped with a CCD camera, using 532 nm (Nd:YAG) excitation line. The laser on the sample was 5 mW and the integration time was 10 seconds. The software employed for data acquisition and analysis was WIRE for Windows and Galactic Industries GRAMS/32TM. Five scans were recorded to improve the signal-to-noise ratio. Daily calibration of the wavenumber axis was achieved by recording the Raman peak of silicon at 520 cm^{-1}. For mapping measurements, an area of 80 µm x 80 µm was chosen in the internal part of the glass. The step size was 5 µm with an individual grid size of 25 $µm^2$.

3. Results and Discussion

The Raman spectra of the unexposed mortar, shows the typically feature of calcium carbonate, the narrow and strong peak at 1084 cm^{-1} that corresponds to υ_1 symmetric stretching from C-O bonds and the lattice mode Ca-O at 282 cm^{-1}.

The surface morphology of the irradiated lime/pozzolan sample, with the CW CO_2 laser is showed in Figure 1. Plasma produced in the air atmosphere, increases the surface temperature until it becomes incandescence, then some incandescent particles are ejected from the surface that reaches the melting temperature of the compounds, produces the loss of the retained water and an amorphous material is formed in the spot place. Depending on the irradiation time and laser power, different microstructure can be observed.

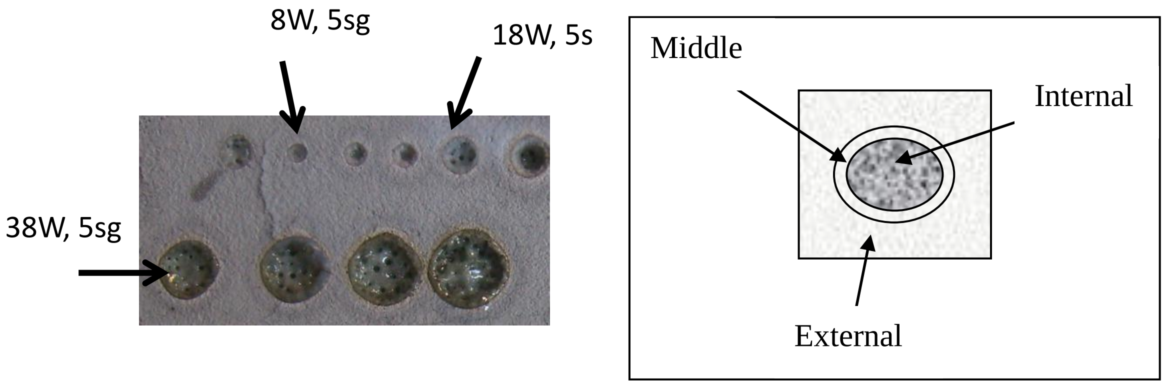

Figure 1.- Spost over the surface of the lime/pozzolan mortar after irradiation with different CW CO_2 laser power. Diagram of the analysed parts of the sample

The spot has an internal part with some holes from sample evaporation and/or particles ejection, that we can call external part. Around this cavity it can be observed a brown circle, middle part, and the external one corresponde with the unexposed part (see diagram in Figure 1). A Raman spectra of the three parts have been obtained (Figures 2 and 3). Internal deformations of the silicate tetrahedra of type υ_2 and υ_4 generate bands in the regions 300-500 and 400-600 cm^{-1}, respectively, that can be identified in the samples exposed to different laser power.

Quartz and cristobalite are the main polymorphs of SiO_2 with different structures and therefore different Raman spectra due to distortion in the SiO_2 structure (Shoval *et al.*1997). Then, cristobalite present two main bands at 411 and 219 cm^{-1} whereas, quartz predominant peaks appear at 463 and 199

cm^{-1}. High density SiO_2 glass can be formed after sample shocked at high pressure. On densification, this peak narrows and moves to higher wavenumbers, indicating a narrower of Si-O-Si average angles and a smaller distribution of angles (McMillan *et al.*, 1992). This can explain that the internal part of the sample irradiated for 5 seconds with 8W laser powers shows a broad band (440-470 cm-1) in the interval of the Si-O bending, but in the middle part this band rise to a narrow one with the maximum at 467 cm^{-1}, disappearing in the external part and giving rise to at small signal at 830-850 cm^{-1} from Si-O stretching. This can be an indication that a less density SiO_2 glass has been formed.
Additionally it is interested to remark that portlandite is formed in the external part of the irradiated mortar as can be be observed a small band at 358 cm^{-1} (Ca-O) and a strong narrow peak at 3617 cm^{-1} which arises from the stretching of the O-H groups bonding to a cation, Ca-OH, from $Ca(OH)_2$ (Figure 3). This is a very important fact since $Ca(OH)_2$ dehydrated at temperatures around 450ºC. At the irradiation conditions, evaporated H_2O, from C-S-H gel, can react with CaO coming from $CaCO_3$ decarbonation, and forming portlandite. In order to confirm that portlandite is formed from C-S-H gel water evaporation, the sample was irradiated under vacuum conditions and portlandite formation was also observed.

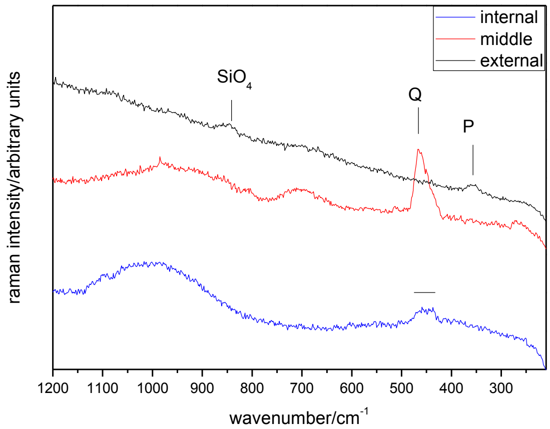

Figure 2.- Micro-Raman spectra of the lime/pozzolan mortar exposed to CW CO_2 laser 5 seconds at 8W.

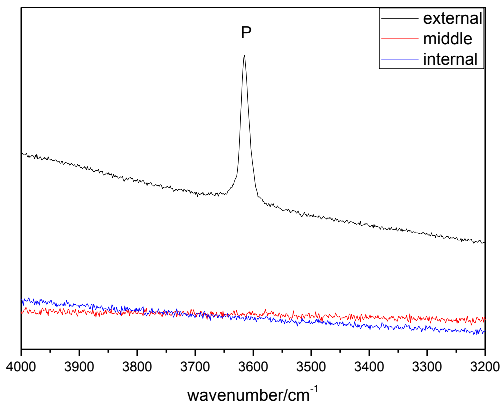

Figure 3.- Micro-Raman spectra of the lime/pozzolan mortar exposed to CW CO_2 laser 5 seconds at 18W.

For the lime/pozzolan mortar exposed 5 seconds at 38W, quartz it is observed in the internal part of the sample. Portlandite formation it is very scarcely as can be seen in the mapping (Figure 4) and the Raman intensity of the signal at 3616 cm^{-1} it is small.

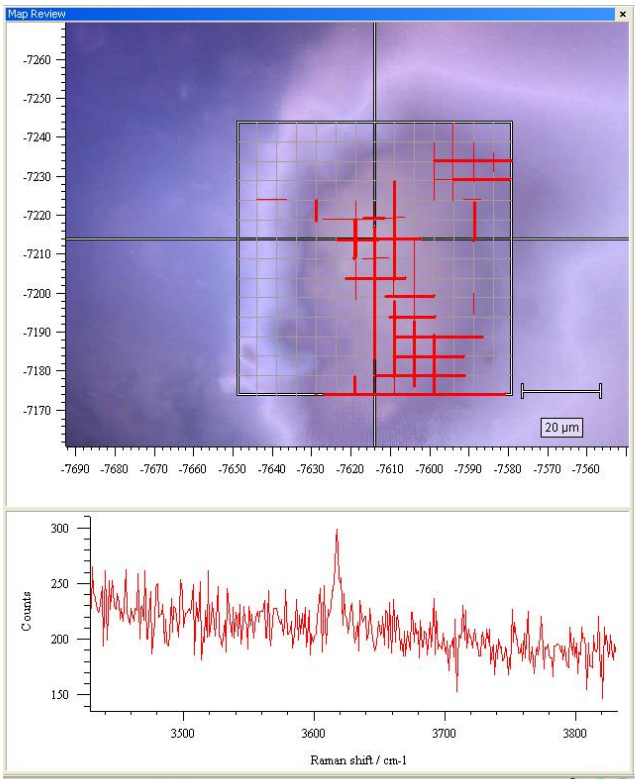

Figure 4.- Mapping of the lime/pozzolan mortar exposed to CW CO_2 laser 5 seconds at 38W

4. Conclusions

A glazing surface was formed in the lime/pozzolan mortar exposed to CW CO_2 laser. Micro-Raman spectra of irradiated surfaces show Si-O stretching and Si-O bending bands. From the internal to the external part of the laser exposure silicate bands modified and less density SiO_2 glass has been formed. Decarbonation of $CaCO_3$ under CO_2 laser produce CaO that react with water from C-S-H gel dehydration forming $Ca(OH)_2$.

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