APPLICATION OF LIBS TECHNOLOGY FOR DETERMINATION OF CL CONCENTRATIONS IN MORTAR SAMPLES

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Abstract

In a society where the cement and concrete industry is of great importance, the diagnosis of the quality of these materials has become a matter of highest priority. One of the maximum exponents of the deterioration of a reinforced concrete structure is the chloride ion content. In this work it has been shown that its evaluation, traditionally carried out by chemical methods, can also be performed by laser-induced breakdown spectroscopy (LIBS), a much faster and advantageous technique. This work develops an optimal experimental set-up based on the generation of small discharges using a 532 nm Nd:YAG laser of 320 mJ, in a helium atmosphere. The experimental conditions have been optimized and a calibration curve, relating the ratio of intensities of Cl I 837.60 nm and Ca II 849.80 nm obtained from the LIBS and the actual chloride concentration, has been determined from a set of samples with different ion chloride concentrations. These samples have been simultaneously subjected to a traditional chemical analysis, as well as instrumental contrast analysis using energy-dispersive X-ray spectroscopy (EDX). Finally, LIBS technique has been applied to the study of mortar samples that had been submerged in

saturated sea salt water for 60 months, and in this way their average ion chloride concentration and their depth profiles have been obtained.

Keywords: Laser-induced breakdown spectroscopy, atomic emission, chloride content, mortar corrosion, building materials

1. Introduction

Mortar and concrete are the most important materials used in building and construction. Concrete industry involves millions of dollars, being one of the basis of the modern society development. It is well known that environmental conditions can affect these materials. The presence of aggressive elements in air and water produces continued degradation of the structures what eventually results in their spalling and final collapse. One of the most harmful elements is the chloride ion which particularly affects reinforced concrete structures. Chloride ions cause localized depassivation of the reinforcing steel and its later corrosion. These ions may be introduced in the concrete either during the manufacturing process or by its exposure to external agents including pollution, marine environments or de-icing salts.

The corrosion of reinforcing steel in concrete structures is an electrochemical process [1-2], due to the electron current between an anodic and a cathodic area in the bars, given by the following half-cell reactions:

$$Fe \rightarrow Fe^{2+} + 2e^{-} \quad (1)$$

which is the anodic oxidation of Fe from the steel bars, and

$$\frac{1}{2}O_2 + H_2O + 2e^{-} \rightarrow 2OH^{-} \quad (2)$$

which is the cathodic reduction with H_2O present in the inner hole and O_2 from the air diffusion through the concrete.

In the absence of chloride ions the pH of the concrete is about 12-13, due to the presence of calcium, potassium and sodium hydroxides. Under these alkaline conditions, a stable film of the Fe oxides Fe_2O_3 and $Fe_3O_4$is formed thus passivating the surface of the bars of reinforcing steel:

$$4Fe^{2+} \rightarrow 4e^- + 4Fe^{3+}$$

$$O_2 + 4e^- \rightarrow 2O^{2-} \quad (3)$$

$$2Fe^{3+} + 3O^{2-} \rightarrow Fe_2O_3$$

$$2Fe^{3+} + Fe^{2+} + 4O^{2-} \rightarrow Fe_3O_4$$

Corrosion reactions (1) and (2) are avoided as long as this passivation film exists.

In the presence of chloride ion, the passivation film is locally destroyed and then processes of localized corrosion are again initiated. If there is not enough oxygen, reactions (3) are not produced, giving instead ferric hydroxide through the following reactions:

$$Fe^{2+} + 2OH^- \rightarrow 2Fe(OH)_2$$

$$4Fe(OH)_2 + O_2 + H_2O \rightarrow 4Fe(OH)_3 \quad (4)$$

$$2Fe(OH)_3 \rightarrow Fe_2O_3H_2O + 2H_2O$$

The accumulation of these corrosion products taking a volume several times larger than that of the original iron (almost 600% higher) results in the cracking and spalling of the concrete cover.

67 The corrosion process has been studied by several authors. A parameter of special
68 interest is the so-called *chloride threshold level*, defined as the chloride concentration at
69 the steel/concrete interface resulting in a significant corrosion. Glass and other authors
70 report experimental values obtained under different conditions [3-4]. From those values it
71 was shown that the total chloride content, expressed in wt. % cement, is in the range of
72 0.17–2.5.

73 Thus, to know the chloride concentration and whether or not its values are over
74 threshold levels is important to know about the corrosion state of reinforced concrete, in
75 order to avoid the collapse of structures with an early prediction.

76 Among all the existing techniques to determine Cl concentration of mortar and
77 concrete, those based on chemical analysis are much extended. The Volhard´s method is
78 one of the most used for this kind of materials. It consists on an indirect argentometry, i.e.
79 an indirect titration to determine the chloride ion that precipitates with silver ion. It was
80 described for the first time by Jacob Volhard in 1874. However, despite giving reliable
81 quantitative results, chemical analysis has the drawback of being a destructive method, as
82 it requires to reduce the sample to dust in order to carry out the determination. Besides,
83 these methods are time-consuming as samples need to be transported to the laboratory,
84 and previous adaptation of the samples is also needed.

85 In this work LIBS technique has been used for the determination of Cl concentration
86 in mortar and concrete, as an alternative method to chemical analysis. LIBS technique is
87 based on the spectral analysis of the optical emission of the plasma generated by the
88 interaction of a laser pulse with the surface of the sample [5-6]. This interaction is mainly
89 ruled by the electronic properties of the solid, so that the light can be reflected,
90 transmitted or absorbed. During absorption, under the action of the laser, the free
91 electrons oscillate and interact with the crystalline lattice, producing a transfer of heat,
92 followed by a diffusion of that heat in the solid phase. The resulting effect is a balance

between the heat gain, produced by the laser, and the losses given by thermal diffusion. In this balance the duration of the pulse is a key parameter.

When a high energy laser is used, the surface of the sample is melted and vaporized **(Fig. 1)**, resulting in the phenomenon of ablation. A number of atoms and electrons are removed from the surface, producing an acceleration of these electrons by the inverse bremsstrahlung effect as a result of their interaction with the laser. The atoms are ionized by the collision with these accelerated electrons, so that the number of electrons increases exponentially, producing the ignition of a plasma. The plasma produced in LIBS is a transient plasma, so that the excitation of the particles decreases with time after the laser pulse. As it is a highly ionized plasma, its emission spectrum shows a strong background radiation and highly broadened lines (due to Stark effect) during the first microseconds after the laser pulse. Because of this, in LIBS measurements, delay generators must be used for the signal to be detected in a certain period of time after laser pulse, in order to avoid this Stark effect, and to ensure that the laser energy has completely dissipated and cannot damage the measuring instruments. Thus, LIBS measurements are taken in the vapor of excited atoms formed right after the plasma phase.

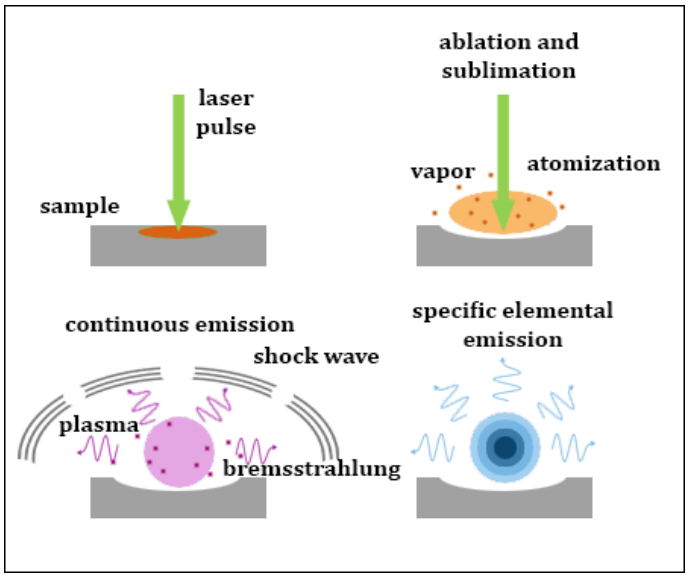


Fig. 1 –Fundamentals of LIBS technique.

111 This process is followed by a relaxation phase, where the excited atoms return to
112 their ground state, emitting energy in the form of photons that are characteristic of each
113 element. This energy is associated with a line at a given position in the spectrum, whose
114 intensity depends directly on the energy of the photon and the number of photons
115 emitted. Also, the number of photons emitted is directly proportional to the number of
116 atoms excited in that energy level and to the probability of that electronic transition. The
117 number of atoms excited at that energy level and the total number of atoms of the
118 considered element are directly related by the Boltzmann equation.

119 Unlike other spectroscopic techniques, LIBS technique has the advantage of being able
120 to analyze any substance regardless of its state of aggregation, whether solids, liquids,
121 gases, or even colloids such as aerosols, gels and other types of samples. Because all
122 elements of the periodic table emit light when they are properly excited, LIBS technique
123 can potentially solve the elemental composition of any sample, its capacity being mainly
124 limited by the power of the laser, the spectral resolution of the spectrometer and the
125 detector sensitivity.

126 LIBS systems, in their different modalities (simple pulse, multiple pulse, double laser,
127 etc.), have been integrated in the research laboratories as a response to the demand for
128 systems capable of performing fast, non-destructive elemental analysis, and that provide
129 accurate quantitative information on the analyte. Thus, thanks to the simplicity of the LIBS
130 set-up, it can be found in many fields, with industrial, environmental, biomedicine,
131 archeology, metallurgy or forensic science applications [7-13]. Data obtained from LIBS can
132 be analyzed by using several methods, including artificial neural networks as an
133 alternative to the traditional calibration methods [14-15].

134 Some authors have previously reported on the use of LIBS for the analysis of building
135 material using single and double lasers [16-24]. Wilsch et al. showed the linear relationship
136 between intensity of atomic lines of Cl and its concentration in mortar, showing that this

technique is suitable for analysis of samples [16]. They use the ratio of integral values of the chlorine spectral line to carbon spectral line for this purpose. As the concentration of chlorine could eventually change in deteriorated samples due to carbonation processes, in this work it is shown that it is advisable the normalization of the intensity of Cl atomic line by the emission of any other element present in cement (such as calcium).

Also, Gehlen et al. have investigated the influence of pressure and integrating time on the Cl line intensity [23]. They studied the range from 10 mbar to 320 mbar of He atmosphere, finding an optimum value at 60 mbar. In the present paper, the pressure range has been extended to 1000 bar; besides, different gas atmospheres (Air, He and Ar) have been tested in order to find the most suitable one. Labutin et al. used LIBS technique to determine chlorine in concrete in air, but they needed a double laser for this purpose [24].

As a main drawback of the use of LIBS technique in building materials analysis could be mentioned the low limit of detection necessary to study components at trace level, and whose corresponding emission lines are also masked in their majority by the ones of other major elements. It must be also considered the great dependence of this technique on the homogeneity of the sample, since the laser pulse impacts on the surface of the sample and create the plasma with only a few nanograms of the material, and this is going to be considered as representative of the whole. For heterogeneous samples, therefore, the technique presents major drawbacks, especially when working with a single pulse [12]. This makes it necessary to perform a previous calibration of the method, as well as a treatment of the obtained data and a statistical analysis of the results, as it will be shown later in this work.

2. Material and Method

The LIBS technique has many points in common with other laser-based analytical techniques, such as Raman or fluorescence, with most of the instruments being identical. The working set-up **(Fig. 2)** consisted of a *Litron Nd:YAG Nano series* laser operating at 532 nm wavelength, capable of generating pulses of up to 320 mJ energy with a duration of 10 ns and a frequency of 10 Hz, that were directed through a lens system towards a vacuum chamber where the sample was located. Light produced during the atomic emission was focused by another set of lenses on the detection system, consisting of an *Andor Shamrock 303* spectrograph with a grating of 1200 lines/mm and an intensified CCD (Andor iStar ICCD model DH734 18mm), operating in conjunction with a digital delay generator (DDG).

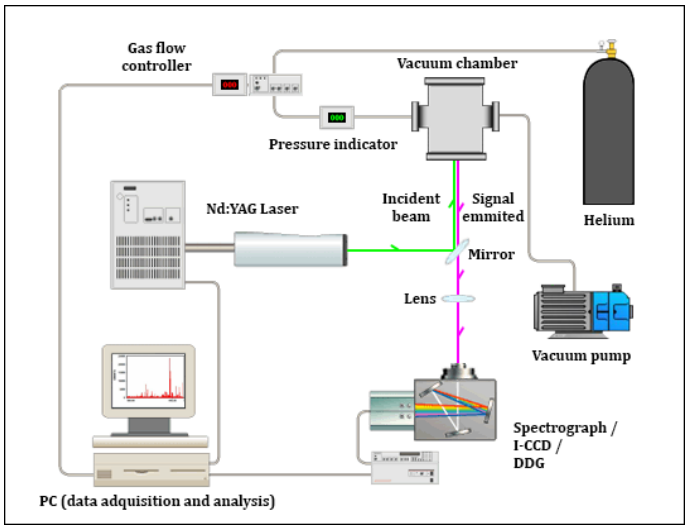
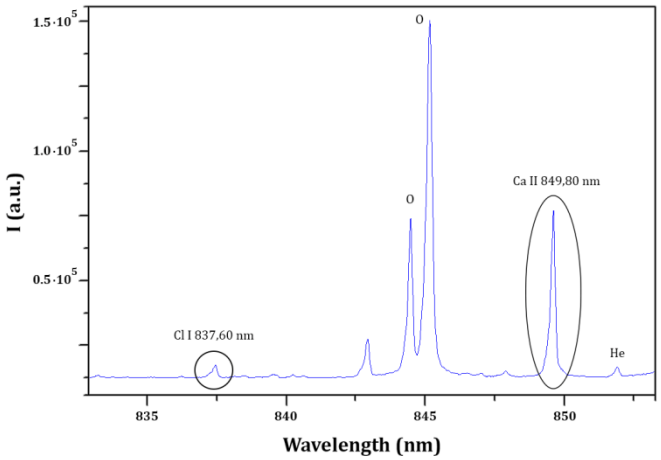


Fig. 2 –Experimental set-up of LIBS technique.

LIBS measurements were performed with a delay time of 700 ns (to avoid interference of laser light), a gate time of 10 μs and a number of accumulations of 20 per measurement.

For the analysis of Cl presence in mortars a vacuum system was incorporated to operate at low pressures, adding a pressure indicator inside the vacuum chamber and a digital controller for the gas flow. To carry out the optimization of system, a study of the detectable spectral lines of chlorine present in the halite (NaCl) and sylvite (KCl) minerals

180 **(Table1)** was made, taking as reference the atomic chlorine line located at 837.60 nm
181 **(Fig. 3)**, which had been previously established as optimal for detection in the cement
182 matrix [13-15].



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184 **Fig. 3** – Cl I line 837,60 nm and Ca II line 849,80 nm used in LIBS measurements.

185 **Table 1** – Detectable chlorine lines in NaCl and KCl minerals.

Line (nm)	*NaCl*	*KCl*	*Ion*	*Relative intensity*	*Lower level configuration*	*Upper level configuration*
391,387	✓	-	Cl II	1.500	$3s^2 3p^3(^2D^o)4p$	$3s^2 3p^3(^2D^o)4d$
391,663	✓	-	Cl II	1.100	$3s^2 3p^3(^2D^o)4p$	$3s^2 3p^3(^2D^o)4d$
422,734	-	✓	Cl II	-	$3s^2 3p^3(^2P^o)4p$	$3s^2 3p^3(^2P^o)5s$
486,186	✓	-	Cl II	-	$3s^2 3p^3(^2D^o)4p$	$3s^2 3p^3(^2D^o)5s$
725,662	✓	✓	Cl I	7.500	$3s^2 3p^4(^3P)4s$	$3s^2 3p^4(^3P)4p$
741,411	✓	✓	Cl I	5.000	$3s^2 3p^4(^3P)4s$	$3s^2 3p^4(^3P)4p$
754,707	✓	✓	Cl I	11.000	$3s^2 3p^4(^3P)4s$	$3s^2 3p^4(^3P)4p$
771,758	✓	-	Cl I	7.000	$3s^2 3p^4(^3P)4s$	$3s^2 3p^4(^3P)4p$
774,497	✓	✓	Cl I	10.000	$3s^2 3p^4(^3P)4p$	$3s^2 3p^4(^3P)4p$
777,109	✓	✓	Cl I	650	$3s^2 3p^4(^3P)4p$	$3s^2 3p^4(^3P_2)4d$
808,667	✓	✓	Cl I	3.000	$3s^2 3p^4(^1D)4s$	$3s^2 3p^4(^1D)4p$
822,045	✓	✓	Cl I	3.000	-	-
833,331	✓	✓	Cl I	18.000	$3s^2 3p^4(^3P)4s$	$3s^2 3p^4(^3P)4p$
837,594	✓	✓	Cl I	99.900	$3s^2 3p^4(^3P)4s$	$3s^2 3p^4(^3P)4p$
842,825	✓	✓	Cl I	15.000	$3s^2 3p^4(^3P)4s$	$3s^2 3p^4(^3P)4p$
858,597	✓	✓	Cl I	75.000	$3s^2 3p^4(^3P)4s$	$3s^2 3p^4(^3P)4p$

186

187 Preparation of samples

For the determination of chloride ion in mortars, a set of prismatic specimens of dimensions 40x40x160 mm were prepared following the EN 196-1:2005[16] standard. The composition of the mass was one part of Portland CEM I42.5R/SR cement **(Table2)**, three parts of standardized CEN sand, and half part of water, resulting in a water/cement ratio of 1/2.

Table 2 – Composition of Portland CEM I42.5R/SR cement

	Cement characteristics	**Standard**	**Usual**
Components	Clinker (%)	95-100	95
	Limestone (L) (%)	-	5
	Pozzolana (P) (%)	-	-
	Volatile ashes (V) (%)	-	-
	Steel slag (S) (%)	-	-
	Setting regulator, "plaster" (%)	-	6
Chemical	Sulfur trioxide (SO_3) (%)	4 max.	3,4
	Chlorides (Cl) (%)	0,10 max.	0,01
	Loss by calcination (%)	5 max.	3,1
	Insoluble residue (%)	5 max.	0,8
Physical	Blaine specific surface area (cm^2/g)	-	3.800
	Le Chatelier expansion (mm)	10 max.	1
	Setting start time (minutes)	60 min.	130
	End time of setting	-	170
Mechanical	1 day compression (MPa)	-	18
	2 days compression (MPa)	20 min.	31
	7 days compression (MPa)	-	41
	28 days compression (MPa)	42-62	57
Additional	C3A	5 max.	3
	C3A + C4AF	22 max.	17
	Heat of hydration (J/g)		300

The chloride was added by dissolving several amounts of anhydrous sodium chloride in the mixing water. The quantities were calculated on the total mass in each mix, trying to approximate the final concentration of chlorides to certain percentages. Five mortar samples were prepared following this procedure, with different Cl concentrations: **MS-1**, **MS-2**, **MS-3**, **MS-4** and **MS-5** (see **Table 3**). Also, a sample with no added chlorides was prepared to be used as blank, **MS-B**, and other sample with chloride saturated mortar for calibration measurements, **MS-S.**

Table 3 – NaCl contents and Cl percentages in cement and mortar samples.

Sample	MS-1	MS-2	MS-3	MS-4	MS-5
Total weight (gr) of NaCl anhydride	83,40	66,72	50,04	33,36	16,68
Cl content (% weight) with respect to the cement	11,37	9,10	6,82	4,55	2,27
Cl content (% weight) with respect to the mortar	2,53	2,02	1,52	1,01	0,51

Each specimen was cut transversely into eight equal portions **(Fig. 4)**. Of all of them, portions #3 and #5 were ground down for chemical analysis, which will determine the actual concentration of chloride ion. On the other hand, portion #4 was subdivided into four fragments, and one of them was selected to carry out LIBS analysis.

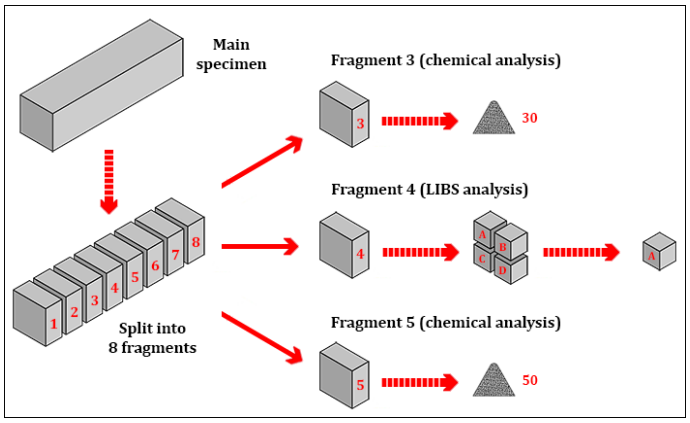

Fig. 4 – Preparation of mortar samples.

2.1 Optimization of measurement parameters

Previous to LIBS analysis of the mortar specimens, a series of tests were carried out to optimize the variables that affect the measurements, in order to perform the analysis under the best possible conditions. These tests address the parameters corresponding to the gas pressure at which the measurements were made, and the composition of the gas used for the plasma creation.

To carry out these calibration tests, the sample of chloride-saturated mortar **MS-S** was used, as it provides intense and well-defined spectral lines in which it is easier to observe variations in intensity.

2.1.1 Gas atmosphere composition

Measurements were made in air, argon and helium atmospheres, respectively, in order to find the best condition for chlorine detection **(Fig. 5)**.

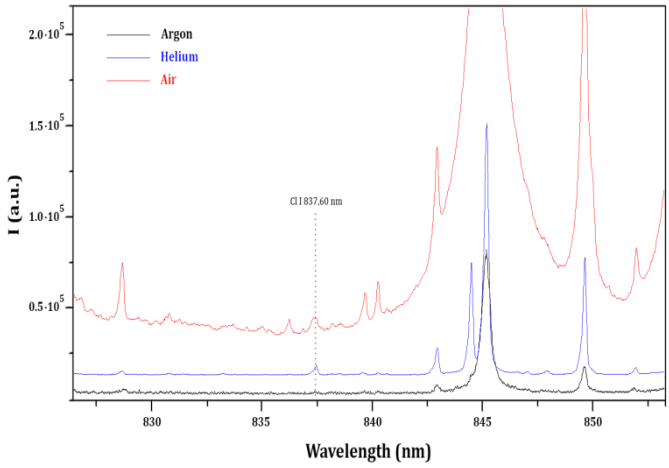

Fig. 5 –Comparison of LIBS measurements in Argon, Helium and Air atmospheres.

Air provides the highest LIBS signal, but it is composed by a set of atoms and molecules (such as O_2) whose emission signals interfere with those of Cl line. To avoid this overlapping becomes particularly important when the element to be analyzed is at trace level, as it is the case of the chloride ion in mortars.

Argon and helium are simpler gases, whose emission lines barely interfere with the signal of the sample. But, as it is shown in figure 5, in argon atmosphere the emission of Cl I 837.60 nm line has a lower signal compared to that detected in a helium one. This fact is due to the higher ionization energy of helium ($E_{i,Ar}$ = 15.75 eV, $E_{i,He}$ =24.59 eV), and so the greater excitation capacity of the helium plasma. For this reason, a helium atmosphere was chosen in the LIBS set-up proposed in this work.

2.1.2 Pressure optimization

Atmospheric gas pressure is a factor that directly affects the quality of the measurement. High pressure leads to a greater gas abundance in the environment and therefore to more intense emissions corresponding to this gas. This can be inconvenient when trying to analyze trace elements, with a dimmed emission that could be masked. On the other hand, at low pressure the population of emitting species is low, and so is the signal detected.

To figure out the optimum pressure value for the Cl determination in mortars, a set of measurements varying this parameter were made for the sample **MS-S**, using a helium atmosphere. The line used as reference was Cl I 837.60 nm, corresponding to radiative transitions between atomic chlorine levels.

Measurements were performed increasing the pressure gradually by steps of 50 mbar covering the range of values between 50 and 1000 mbar.

Fig. 6 represents the normalized intensity versus pressure, where normalization was carried out from peak (I) and background (B) signals, and $\frac{I-B}{B}$. The fitting to a Boltzmann sigmoidal function is also shown in this figure. There, it is shown how the line intensity undergoes an increase with the pressure until stabilizing from 400 mbar. This stabilization corresponds to the dependence of discharge parameters (such as the electron density) on the pressure-[14]. It is well-known that electrons have a high influence on the excitation capacity of the discharge.

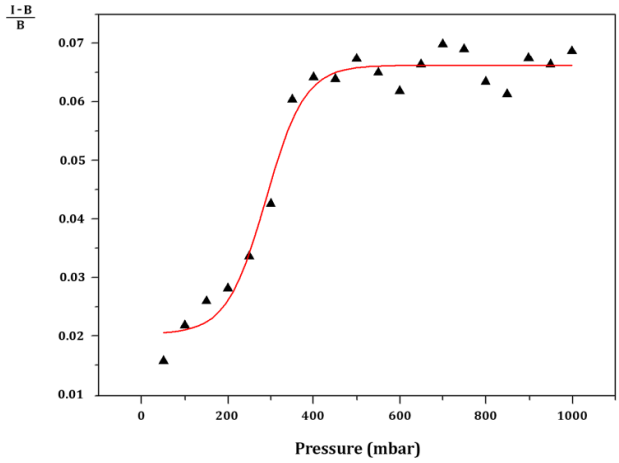

Fig. 6 – Dependence of normalize intensity of Cl I line 837,60 nm on He atmosphere pressure.

Thus, for the determination of chloride in mortars by the proposed LIBS technique, a working pressure of 1000 mbar will be established as the optimum measurement value, as it is easier to keep the pressure stabilized at this value rather than at lower ones.

2.2 Chemical analysis and EDX

While portion #4 of each mortar specimen was used in LIBS analysis, the immediately preceding and subsequent portions #3 and #5were ground to particles less than 250 μmin size. From them, samples labeled as #30 and #50 were taken to perform chemical analysis in order to determine the exact concentration of chloride ion.

The Volhard's method was used for this purpose, following the procedure described in EN 196-2:2013 [17] standard. However, since this standard is designed for samples with a much lower chloride concentration, when applied to the mortar samples in this work results were out of range. For this reason, the quantities of reagents indicated in the standard were modified and adapted to the high concentrations of chloride ion in the samples. Thus, to an amount of 0.5 ± 0.05 g of sample, 50 ml of distilled water and 50 ml of HNO_3 diluted to 1:2 were added, boiling for 2 minutes. After this, 20 ml of 0.1M $AgNO_3$ solution was added, boiling again for another 2 minutes. The solution was then filtered,

washing with HNO_3 diluted to 1:100 until the filtrated volume and wash water were around 200 ml. The solution was subsequently cooled below 25°C in the absence of light, and 5 ml of $NH_4Fe(SO_4)_2$ indicator solution were added, carrying out the titration with a 0.05M NH_4SCN solution.

The chloride content of each sample was calculated according to the following equation:

$$[Cl^-] = 7.092\, x\, \frac{(V_B - V_S)}{V_B x m_S} \qquad (5)$$

Where m_S is mass (in grams) of sample used in the analysis; V_S and V_B are volumes of thiocyanate solution consumed by the sample and by the blank, respectively, in millimeters.

Chemical analysis was carried out in triplicate for all mortar samples, as well as the analysis of one blank for each sample. Finally, averaged values of the chlorine ion concentration for the pairs of samples #30 and #50 belonging to the same specimen were obtained.

As an instrumental contrast analysis, an EDX analysis was performed in the same area of the samples where the LIBS analysis was performed **(Fig.7-8).** The electron microprobe technique was implemented on a JEOL JSM-7800F scanning electron microscope using an acceleration voltage of 15 kV and a working distance of 10 mm. The X-ray detector was an X-MaxN150 from Oxford Instruments.

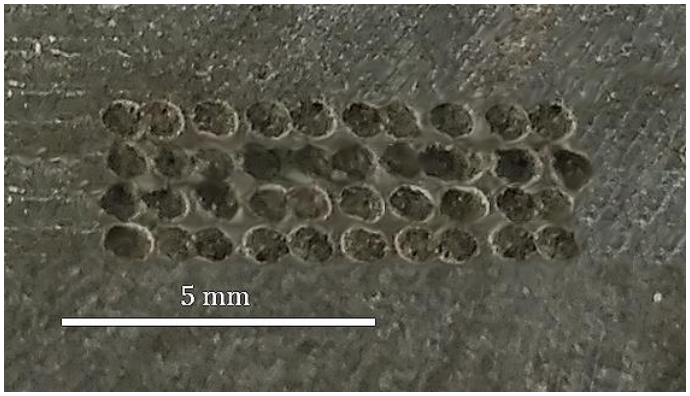

Fig. 7 – Image of laser impact distribution on sample surface obtained with the electron microscope used in EDX analysis.

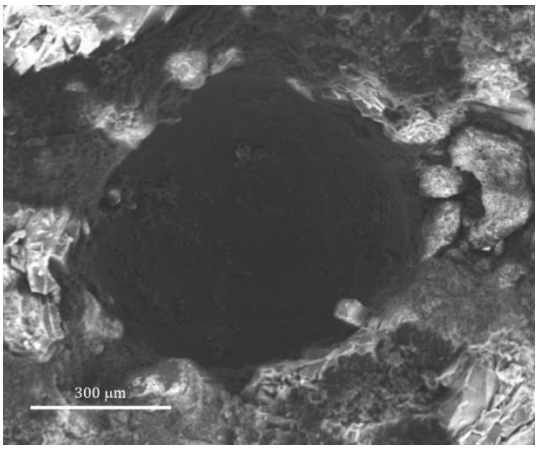

Fig. 8 – In-detail image of laser impact on sample surface obtained with the electron microscope used in EDX analysis.

3. Results

3.1 Chemical analysis and EDX

The average concentration of chloride obtained by the chemical analysis in all the samples is shown in **Table 4**. Comparison between the theoretical concentration predicted in the preparation of the test specimens and the actual concentration obtained in the chemical analysis can be found in **Fig. 9**. A gradual decrease of half point of percentage in the concentration of chloride ion between samples is observed.

Table 4 – Results of Cl concentration obtained from chemical analysis.

Sample	Cl content (% weight) with respect to the mortar
MS-1	2,50% ± 0,17%
MS-2	1,91% ± 0,06%
MS-3	1,57% ± 0,12%
MS-4	0,99% ± 0,05%
MS-5	0,55% ± 0,07%
BLANK	0,02% ± 0,00%

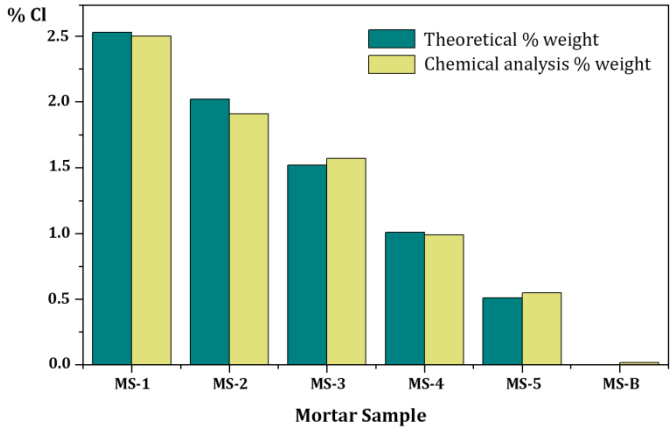

Fig. 9 – Comparison between theoretical Cl concentration and chemical analysis in the different samples.

On the other hand, the results obtained of EDX measurements are shown in **Table 5**. A good agreement between the Cl concentration values obtained by EDX for each sample and those provided by the chemical analysis is obtained, confirming the accuracy of results obtained through the chemical analysis.

Table 5 – Results of Cl concentration obtained from EDX analysis

Sample	Cl content (% weight) with respect to the mortar
MS-1	2,56% ± 0,04%
MS-2	1,95% ± 0,03%
MS-3	1,49% ± 0,03%

MS-4	1,02% ± 0,03%
MS-5	0,44% ± 0,02%

3.2 LIBS analysis of the mortar samples

LIBS study of the mortar samples was performed on one of the inner faces of fragment A of portion #4 of each one of the specimens corresponding to the different concentrations prepared for the tests. For each sample, 40 determinations were made at different points, with 20 accumulations for each determination. **Fig. 7** shows image of the different spots of typical LIBS measurement. The area of the region affected when taking forty measurements was under 1 cm^2. In-detail spot obtained with electron microscope used in EDX analysis is shown in **Fig. 8**. Spots under 1 mm of diameter and deep were observed, which means damages in the mortar lower than 3 mg by shot and, for typical measurement of 40 determinations, a total damage lower than 0.12 g. Thus, the degree of damage is significantly lower than that produced by other techniques. The minimum amount of mortar required for chemical analysis was 5 g per point according to EN 196-2:2013 [26]. In this sense, LIBS has been considered as a non-destructive technique and used in analysis of valuables, such as archeological remains and art treasures.

The determinations with a low or zero intensity in Ca ion lines have been discriminated, since they represent zones of the sample where the siliceous phase (free from the presence of chlorides) of the sample predominates.

Measured spectral zone included the reference line Cl I 837.60 nm, and a line representative of present cement, the Ca II849.80 nm line **(Fig. 3)**. In each determination,

the ratio of the areas of both chlorine and the calcium ion lines (*Cl/Ca ratio*) was obtained by calculating of their peak area fitting to a Voigt function **(Fig. 10)**. Absolute intensities of these lines depend on detection conditions and can vary for every measurement, but their ratio *Cl/Ca,* only depends on the chloride ion concentration of the sample. This is based on the fact that the area of the chlorine line accounts for–the concentration of chloride in the sample, whereas the area of the calcium ion peak is a function of the amount of cement used in the preparation of the test pieces, the same in all of them, and therefore constant.

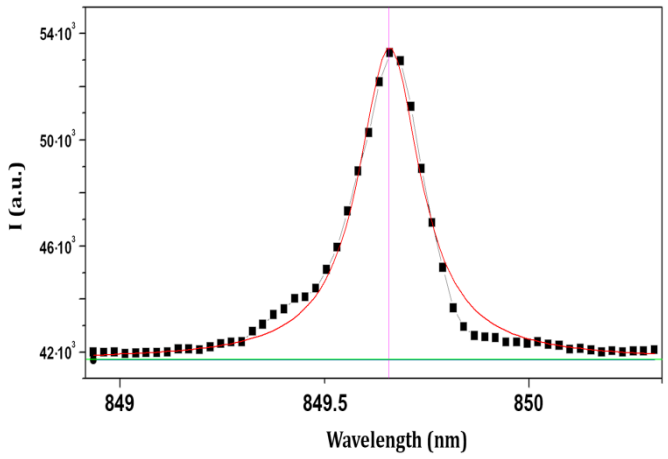

Fig. 10 – Voigt profile fitting to Ca II line 849,80 nm for area calculation.

Consistent with the fact that samples are not homogeneous, Cl concentrations and results vary from point to point. LIBS measurements give information of a reduced extent of about 300 μm (see **Fig. 8**). In order to obtain representative results for total sample, a statistical study of several data (40 measurements by sample), was done (see **Fig. 7**).

This number of data is too low to be enough to directly prove that its frequency follows a normal distribution. For this reason, the cumulative percentage was used in the statistical study. **Fig. 11** shows cumulative percentage of data obtained from, MS-1 to MS-5 samples. This percentage fits well with the Gauss error function corresponding to the normal distribution:

$$errf(x) = \frac{1}{\sigma\sqrt{2}} \int_{-\infty}^{x} e^{-(x'-\mu)^2/2\sigma^2} dx' \quad (6)$$

All R^2 coefficients of these fittings are higher than 0.994, showing that data distributions correspond to a normal type distribution with mean values and standard deviations included in figure 11. **Table 6** gathers mean values and error of *Cl/Ca* ratio from LIBS analysis.

Table 6 – Results of mean Cl/Ca ratio and error obtained from LIBS analysis

Sample	Cl/Ca peak area ratio
MS-1	0,038288 ± 0,004262
MS-2	0,035909 ± 0,002883
MS-3	0,029625 ± 0,004837
MS-4	0,021689 ± 0,007199
MS-5	0,017360 ± 0,004374
BLANK	0,004214 ± 0,004289

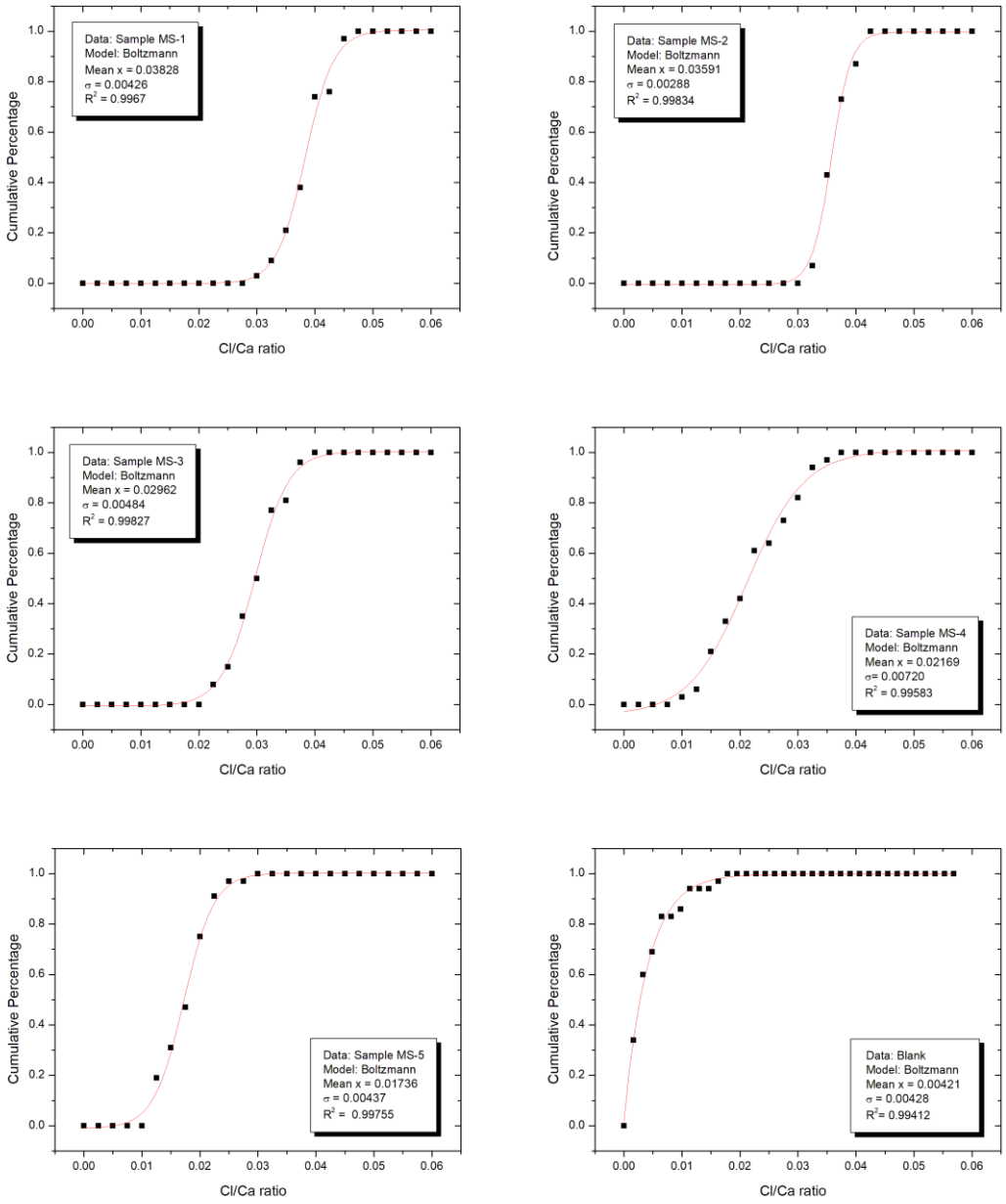

Fig. 11 – Cumulative percentage of LIBS measurement data for the different samples together its fitting to a Gauss error function.

Figure 12 depicts the mean Cl/Ca ratio obtained from the LIBS versus the actual chloride concentration provided by the chemical analysis. A linear relationship was found, which shows that despite the variation in the peak intensity for different measurements of the same sample, the mean Cl/Ca ratio retains a direct proportionality with respect to the chloride content of the sample.

Fig. 12 shows the calibration curve obtained from linear fitting of experimental data together with its residuals. This is an essential stage for determination of Cl concentration by LIBS technique. A regression factor of 0.977 and a standard deviation of the residuals of 21.6% are obtained, which ensures the goodness of the calibration process. This curve will be used in next section for the determination of Cl concentrations in unknown samples.

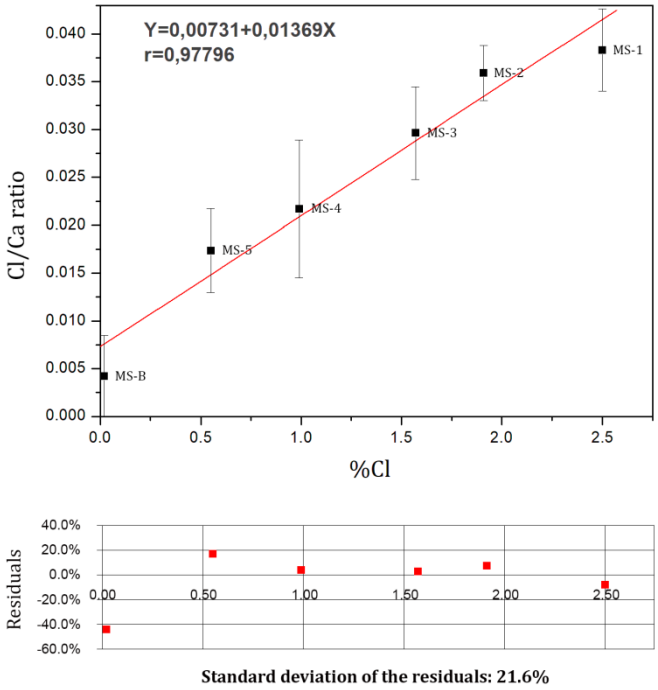

Fig. 12 – Calibration curve and residual plots for LIBS technique obtained from the linear least squares regression of mean Cl/Ca ratio vs Cl concentration.

3.3 Analysis of specimens submerged in saturated sea salt water

In order to compare the applicability of LIBS analysis in the study of chloride ion penetration in real mortar samples, a sample subjected to the continuous action of the chloride ion was analyzed. For this purpose, a chloride-blank mortar specimen was used. This specimen had been submerged in water saturated with sea salt for a period of sixty months.

After that period, the specimen was divided into eight fragments following the procedure previously described, and three of the inner fragments were analyzed by LIBS (**MSW-1, MSW-2 and MSW-3**). The averaged values of chlorine concentration for each of the fragments are gathered in **Table 7** which also includes the values obtained through chemical analysis. It can be observed that, due to the heterogeneity of the samples, the results obtained by LIBS present a higher standard deviation. However, results from LIBS analysis present a great similarity with those measured by chemical analysis.

Table 7 – Comparison of LIBS results and chemical analysis in submerged samples

Sample	Average %Cl LIBS	Average %Cl Chemical
MSW-1	1,90 ± 0,27	1,91 ± 0,08
MSW-2	2,43 ± 0,32	2,05 ± 0,08
MSW-3	2,33 ± 0,31	2,03 ± 0,08

In order to study the penetration of chlorine into the cement matrix, another fragment of the mortar sample submerged in saturated chloride solution was analyzed by LIBS. This time the analysis was restricted to the innermost part of the fragment, the analysis zone being limited to a strip of 10 mm width by the 40 mm height of the fragment **(Fig. 13)**.

Fig. 13 shows the distribution of the chlorine concentration in the sample measured from LIBS analysis. It can be seen "channels" through which chlorine penetrates in the mortar sample. Cl concentrations are highest at top and bottom zones, due to both faces were in direct contact with the saturated solution, especially the top zone since the bottom one was resting on the treatment container.

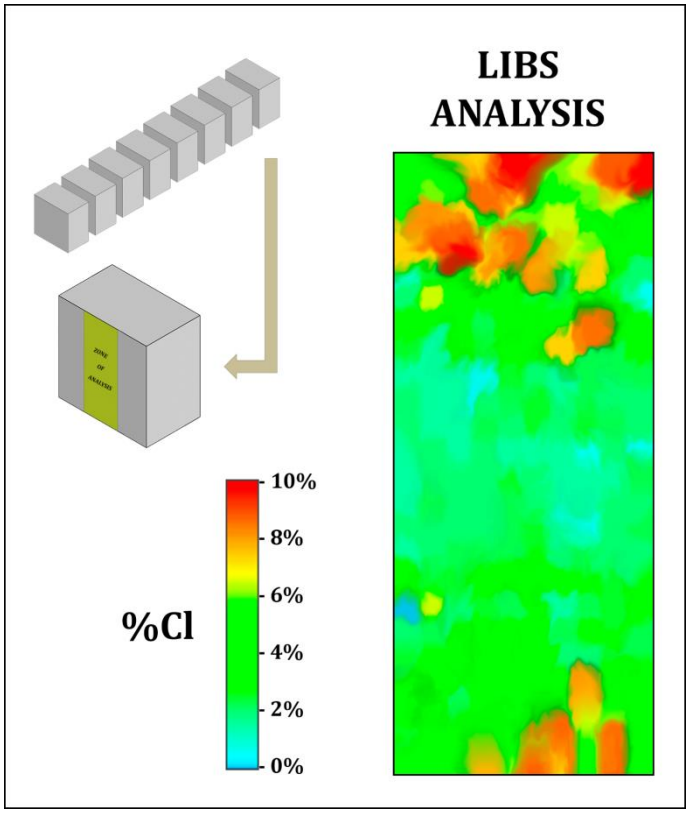

Fig. 13 – Chlorine distribution inside a mortar sample submerged in water saturated with sea salt for 60 months obtained from LIBS analysis.

Thus, this study shows LIBS analysis provides much detailed information about the sample due to its high resolution, being able to perform a mapping of the concentration of chloride ion on the analyzed surface. It has the added advantages of being a non-destructive technique and allowing to work on-site Definitely, this technique can help to diagnose the deterioration state of construction materials through the determination of Cl concentration in these materials.

4. Conclusions

This works aims to contribute to the development of an optimum LIBS technique, allowing for detection and measurement of chlorine in mortars and so, estimate of the deterioration state of this material.

The set-up and the optimum conditions for LIBS analysis of mortar samples have been described. Unlike previous studies of other authors, pressures above 400 mbar have been found as optimum for obtaining highest intensities of Cl atomic lines. Different gas atmospheres have been tested, and the use of helium gas has been shown to be best to give clearest spectra without line overlapping.

In this work, the ratio between area of chlorine atomic line 837.60 and line, calcium (one of the cement components) ion line 849.80 nm, is used. This parameter gives more accurate results, as concentration of calcium is considered constant in every kind of mortar. Different measurements in a small area of about 25 mm^2 of mortar have shown that ratio values follow a normal distribution whose mean and standard deviation give the representative value of the measure and its error. A linear correlation has been found between the average results obtained from LIBS and the concentration of chloride, obtained by chemical analysis, which allows to get a calibration curve for analytical use of this technique. This calibration curve depends on mortar composition, in particular, the Ca concentration in the material, which depends on type of cement used. The curve obtained in this work is valid for a mortar prepared with Portland CEM I42.5R/SR cement following procedure in EN 196-1:2005 standard. For a practical implementation of this technique to actual cases, different calibration curves would be needed for each kind of standard mortar.

To the best of the authors' knowledge, this work reports for the first time on the comparison of LIBS technique results and those obtained with other spatially resolved technique, EDX. A very good agreement has been found between results from LIBS, EDX and chemical analysis.

It has also been demonstrated that the LIBS technique developed in this paper is suitable for the qualitative and quantitative analysis of chlorine concentration in deteriorated building materials such as mortars and concretes. LIBS technique has been

validated from the study of chloride penetration in a sample of mortar subjected to the action of water saturated with sea salt.

Compared to classical chemical methods, the LIBS technique provides more information and has the advantage of being a non-destructive technique with the ability to perform on-site analysis.

In further work, the possibility of developing a mobile device based on LIBS technique will be studied. This device will allow *in-situ* evaluation of building and construction structures. The possibility to integrate laser, spectrometer and CCD in a single device will allow to reduce set-up costs. A first estimation of its cost is about 50.000 $. On the other hand, having a collection of calibration curves for the different types of standard mortar, all process (measurements, peak integration and determination of Cl concentration) could be automated, and no highly specialized personnel will be necessary for its use.

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