Semi- and full quantitative EDS microanalysis of chlorine in reinforced mortars subjected to chloride ingress and carbonation

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Abstract

Energy dispersive X-ray spectrometry (EDS) is a powerful tool for research studies on building materials. Elemental quantification in cementitious phases contained in the concrete microstructure can be performed at an excellent spatial resolution. However, accurate compositional quantification requires a standard-based analysis, whereas currently the most common are standardless microanalysis. Reasons behind this approach lie on the difficulty of finding appropriate microanalysis standards in EDS studies. In standard-less analyses, elemental quantification from an EDS spectrum provides normalized quantification, i.e. an analytical total of 100%. Most EDS detectors cannot provide reliable data for elements with smaller atomic number than sodium, which results in the stoichiometric determination of oxygen. The aim of this paper is raise awareness about the importance of a controlled experimental parameters and the use of mineral standards when performing EDS analysis on cementitious materials. For this purpose, both types of investigation (with and without standards) are performed simultaneously in order to obtain chloride profiles in six reinforced mortar specimens subjected to chloride ingress and carbonation. Results illustrate that differences in element concentrations can be derived by the absence of mineral standards which could lead to inaccurate interpretations of element concentrations such as chlorine.

Keywords: EDS, chloride profiles, carbonation, reinforced mortar.

I. INTRODUCTION

Durability of concrete structures is a serious concern around the globe. Reinforcement corrosion is the predominant degradation mechanism affecting concrete infrastructure. In normal conditions, a stable oxide layer forms at the steel surface due to concrete alkalinity. This oxide layer, also known as the passive film, is capable of preventing deterioration due to reinforcement corrosion. Nonetheless, the change of local pH (carbonation) or the ingress of chloride ions result in the dissolution of this film (Hansson, 1988; Bertolini et al, 2013). Chlorides dissolved in sea water or de-icing solutions penetrate through the concrete pore network. As they accumulate at the steel surface, the amount of chloride ions needed for destroying the passive layer is known as the critical chloride content, which once reached, initiates localized reinforcement corrosion (Mehta and Monteiro, 2008; Grantham, 2011). Conversely, the ingress of carbon dioxide (CO_2) is responsible for consuming the available calcium ions (Ca^+) in the pore water and portlandite ($Ca(OH)_2$) in a reaction resulting in the precipitation of calcium carbonates ($CaCO_3$). This reaction, known as carbonation, causes a reduction in the pH of the paste (Bijen, 2003; Neville, 2011).

Chloride induced reinforcement corrosion is the most common cause of corrosion degradation. In order to estimate the remaining service life of concrete infrastructure, assessment of chloride concentrations is usually carried out by wet chemical analysis. This method is performed in layers throughout the concrete cover (chloride profiles). Then, chloride concentrations are fit to a transport model from which predictions on the time necessary for chloride concentrations to be equal to the critical chloride content is determined. As the critical content indicates the start of attack in steel, most standards use it as a guidance value for service life predictions, emphasizing the necessity of accurate measurements (EN 1992-1-1, 2004; fib, 2006; CUR, 2009). Further, chlorine can usually be found in the paste as a component of Friedel's salt due to precipitation or chemically bound to the C-S-H (Glass and Buenfeld, 2000; Reddy et al, 2002), and carbonation is known to change it between those two forms by releasing bound chlorides (Glass and Reddy, 2000).

Carbonation induced corrosion is common in

concrete infrastructure with high water/cement ratios and low cover thickness. The assessment of the depth of carbonation is performed by splitting concrete cores and spraying the fractured concrete surface with phenolphtalein, or more accurately by polarized light microscopy.. Visual inspections on the penetration of carbonation are possible because concrete in alkaline conditions, pH higher than 10, will be pigmented whereas carbonated concrete, pH lower than 9, will not. Usually, this carbonation induced corrosion proceeds at a slower rate compared to chloride induced corrosion. The rate at which the carbonation front proceeds has been studied in service life prediction models (DuraCrete, 2000; LIFECON, 2004). However, a combination of chloride ingress and carbonation presents a more severe environment for reinforcement corrosion. In fact, this combination has been considered as the most common case in practice (Basheer et al., 2001).

Energy Dispersive X-ray Spectroscopy (EDS) is an increasingly available tool for element quantification at high spatial resolutions. Compared to WDS, EDS provides simultaneous quantification of elements present in the cement paste (Wilson et al, 2014; Krakowiak et al, 2015). The principle of microanalysis through EDS is the possibility to infer information about the concentration of elements through the ratio K between the intensity in the number of X-ray counts of a sample and a known standard. As the interaction of the beam with the substance changes for each material, corrections must be done to take into account differences in mean atomic number, differences in absorption of X-rays and differences in the production of secondary X-rays or X-ray fluorescence (Çopuroğlu and Einarsson, 2011). Also, the detection of elements with lower atomic number than sodium is not reliable due to their poor X-ray efficiency (Newbury, 2002). Therefore, phases with chemically bound water should have the amount of oxygen determined by stoichiometry. A fully quantitative analysis is defined by the consideration of matrix effect corrections (among others, the most commons are ZAF and $\Phi\rho Z$) using specific minerals for each element and accounting for test parameters such as beam current, accelerating voltage, type of detector, take off angle and working distance (Goldstein et al, 2003; Winter, 2012). The opposite, a semi-quantitative analysis is possible because most commercial software for microanalysis possess internal standards for the most common elemental peaks, allowing internal calculations to take place in disregard of beam current and the matrix corrections mentioned. This way of analyzing EDS spectra is considered to be 'point&shoot 'in this paper. This approach is very common among concrete researchers. The reason for this may lie in the complex composition and structure of hydrated cementitious materials, but it

Table 1: Cement composition CEM I 52.5R

Oxide	wt. %
CaO	63.98
SiO_2	19.76
Al_2O_3	4.93
Fe_2O_3	3.16
K_2O	0.54
Na_2O	0.27
SO_3	3.17
MgO	1.92
TiO_2	0.28
Mn_3O_4	0.11
P_2O_5	0.77
Cl	0.04
Total	98.93

is also possible that many researches are conducted without the awereness of the possibilities, since the software is typically marketed for qualitative analysis. Furthermore the greatest challenge to the cement-based materials microanalysis is the lack of proper microanalysisIdeal standards which are not widely available as e.g. rock-forming minerals or synthetic glasses.

In general, chloride quantification by means of microanalysis has been published elsewhere (Mori et al. 2006; Jensen et al. 1996; Jensen et al. 1999; Jakobsen 2013; Anzalone et al. 2013; Pacheco et al. 2012; Pacheco et al. 2013). Likewise, the investigation of carbonation through EDS and WDS has been reported elsewhere (Hidalgo et al, 2008; Groves et al, 1990; Groves et al, 1991; Lange et al, 1996; Chen et al, 2008; Liu et al, 2010; Pacheco and Copuroglu, 2015).

This paper examines the differences between using semi and fully quantitative microanalysis within the framework of corrosion of reinforcement on cementitious materials. For this purpose, microanalytical results obtained from 'point&shoot 'settings in the EDS spectra analyses (semi) and standarised (fully) X-ray spectra are presented. Carbonation is interesting in particular for this context, since the presence of precipitated carbonates (CO_3) could cause discrepancies in the stoichiometric calculations. Reinforced mortar specimens were fabricated and exposed to chloride penetration. Half of those specimens were later exposed to accelerated carbonation in order to study the possible influence of a combined degradation system, i.e. the release of bound chlorides. Attention is paid to the calculations of element concentrations made by the 'automatic 'and standard-based analyses and how it affects the measurements and its own variability.

II. Sample preparation

Materials

Mortar cylinders with water/cement ratio of 0.45 were cast with ordinary Portland cement (CEM I 52,5 R). The chemical composition of the used Portland cement is shown in Table 1. The specimens contained standard sand (CEN-NORMSAND DIN EN 196-1) with a maximum aggregate size of 4 mm and tap water.

Fabrication of mortar specimens

Six mortar cylinders of 24 mm of diameter per 35 mm of height, each containing a steel bar with 70 mm in length and 8 mm in width were fabricated. After casting, the cylinders were contained with plastic and kept in laboratory conditions for 24 hours, then de-moulded and stored in 20°C, >90% RH (fog) room for 28 days.

Chloride ingress and carbonation

After curing, the specimens were partially immersed in a 3.5wt.% sodium chloride (NaCl) solution for 60 days in laboratory conditions (22°C, 65% RH). During this period the solution was constantly renewed so the concentration would be kept constant. Then half of the specimens (Cl samples) were prepared for EDS analysis while the remaining specimens were subject to accelerated carbonation for 14 days (Cl + CO_2). The accelerated carbonation environment was set to 3% CO_2 and 75% relative humidity. Subsequently, the specimens were prepared for EDS analysis.

Specimen preparation for microanalysis

From each set of specimens two slices were sawn with an anhydrous cutting lubricant (transversal samples) and one was obtained by the Brazilian splitting test (longitudinal samples). The transversal samples had diameter of 24 mm with a depth of 6 mm and the longitudinal samples had a geometry of 24 x 24 x 6 mm. From these samples, polished sections were prepared. Surface polishing involved grinding with #320, #500, #800 and #1200 grinding papers; followed by 6 μm, 3 μm, 1 μm and 0.25 μm diamond paste polishing. The specimen surfaces were cleaned by immersing them in ultrasonic bath with laboratory graded ethanol for 10s between each grinding and polishing step.

EDS microanalysis

For the microanalysis and electron imaging a Philips XL30 environmental electron microscope equipped with EDAX energy dispersive spectrometer (EDS) was used under hi-vacuum chamber condition. EDS detector was a SUTW (sapphire) type with a calibrated resolution of 131.2eV at 15kV accelerating voltage. The take-off angle was 35.3° and a working distance of 10 mm. The polished specimens to be analyzed were carbon coated in a Leica EM CED030 carbon evaporator at a thickness of 10 nm.

A stable beam current of approximately 0.5 nA was regularly measured by means of a pico-ammeter and a Faraday cup. Under these conditions, a stable beam current aimed at a quartz crystal read around 2500 cps (counts per second) at 25% dead time. The X-ray collection time was set to 100 live-sec. per analysis. Before and after each spot analysis, the average beam current was measured and included into the ZAF quantification. The approximate size of the interaction volume was reproduced by a Monte Carlo simulation. A square of approximately 5 μm by size is the field in which the trajectory of electrons is estimated, covering approximately 2 x 3 x 3 μm^3, as simulated

Table 2: Mineral standards used in DTSA-ii® Software against oxides provided by automatic settings

	Semi quantitative	Fully quantitative	
Element	Default oxides	Mineral	Composition
Na	Na_2O	Albite	$NaAlSi_3O_8$
Mg	MgO	Diopside	$MgCaSi_2O_6$
Al	Al_2O_3	Sanidine	$KAlSi_3O_8$
Si	SiO_2	Quartz	SiO_2
P	Not detected nor quantified	Apatite	$Ca_5(PO_4)_3F$
S	SO_3	Anhydrite	$CaSO_4$
K	K_2O	Biotite	$K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$
Ca	CaO	Calcite	$CaCO_3$
Ti	Not detected nor quantified	Rutile	TiO_2
Mn	Not detected nor quantified	Willemite	$(Zn,Mn)_2SiO_4$
Fe	Fe_2O_3	Hæmatite	Fe_2O_3
Cl	Cl_2O^*	Scapolite	$(Na,Ca)_4[Al_3Si_9O_24]Cl$

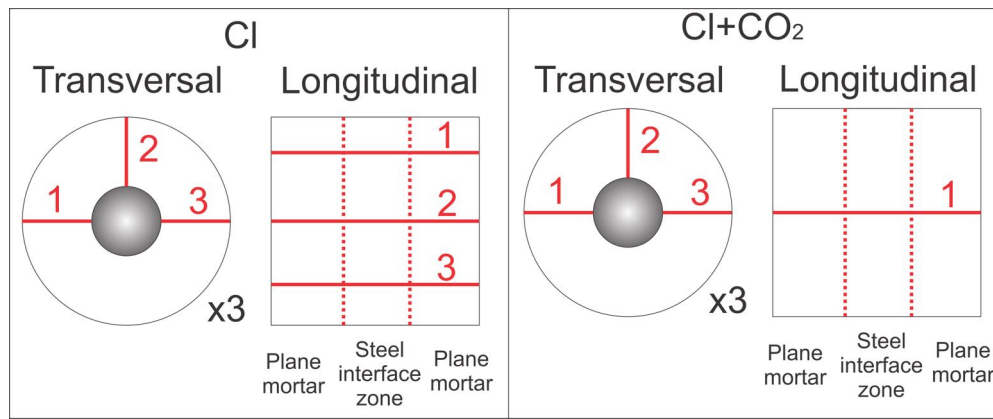* Note: Cl_2O is a gas at room temperature.

Figure 1: Schematic of EDS samples and analysis positions.

by CASINO® Software V. 2.48. It was chosen to perform the measurements in C-S-H points due to its binding capacity and abundance through the hydrated matrix with respect to chlorides.

The analyses were carried out in three manners as follows (shown in Figure 1):

(a) Three lines were taken in each transversal sample. Each line had EDS spectra collected at every 500 μm from the specimen surface towards the rebar;

(b) Three lines were taken in the Cl longitudinal sample. Each line had measurements at every 1000 μm from one extreme to the other (crossing the rebar previous position);

(c) One line was taken in the Cl+CO_2 longitudinal sample. The line had measurements at every 500 μm from one extreme to the other (crossing the rebar previous position).

For displaying puroses, averaging of chlorine concentrations of points collected at similar distances from the reinforcement was carried out. The same procedure was performed on the longitudinal analyses.

The procedure for element quantification was as follows: first, an EDS spectrum was collected from the mortar sample. Then, the raw spectrum was saved for full quantitative analysis. Full quantitative analyses were processed in DTSA-ii Software using both stoichiometry and oxygen by difference methods. Afterwards, semi quantitative analyses were performed by the native EDS software (EDAX Pheonix) from which normalised results were obtained under automatic settings. Table 2 presents the predetermined standards in the automatic settings of the EDS software. In parallel, minerals employed for fully quantitative analysis are presented. Apart for scapolite, the rest of minerals were present in a commercial mineral standard mount (ASTIMEX MINM25-53)

III. Results

Figure 2 shows Si/Ca atomic ratios plotted against Al/Ca for all obtained spectra in order to confirm the phases studied. Winter (2012) states that a perfectly pure paste of clinker and water would have values of Si/Ca ratio for C-S-H between 0.45 and 0.55 and Al/Ca ratio of 0.04 and 0.08. As the research was conducted with CEM I, it is accepted that a small amount of fine limestone was added, which broadens the range of results. The transversal samples presented results within the expected boundaries, represented by the red lines in Figure 3. In contrast, longitudinal samples displayed a lower Si/Ca ratio in a number of points, most of them from the Cl+CO_2 sample.
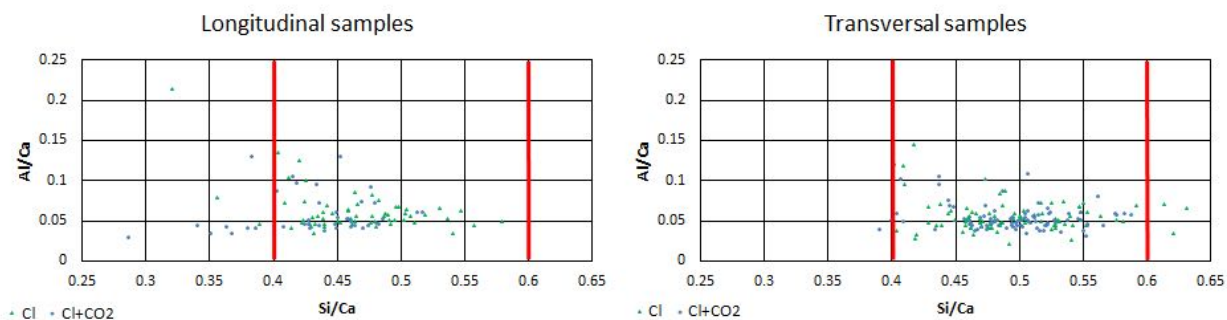

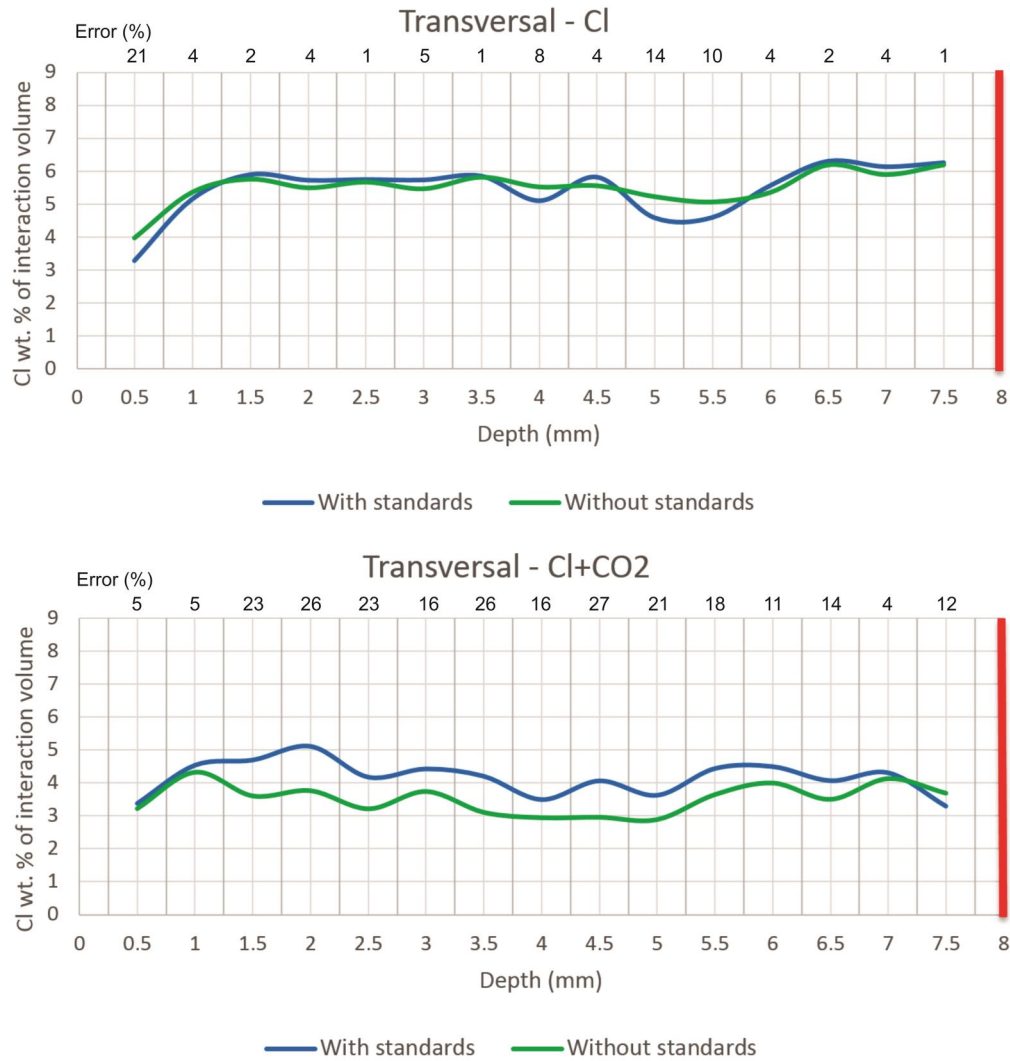*Figure 2: Atomic ratios of spectra taken for analysis.*

Figure 3: Averaged weight percentage of chlorine in the interaction volume found with respect to transversal specimen depth. The red vertical line represents the position of the steel bar.

Figure 3 and Figure 4 presents the concentration of chlorine by weight percentage in the interaction volume. A lower amount of chlorides can be observed at the outer edges of the specimens, normally associated with loss by drying process. Considering the longitudinal samples, it is observed an increasing trend from the surface to the vicinity of steel, this is in opposition with the common belief that concentrations are maximum near the surface and decrease with increasing depth. This could be an indication that once chloride ions reach the reinforcement, a cumulative process start and local concentrations surpass the ones in materials surface. While maintaining the general behavior, the Cl+CO_2 samples seems to increase the error between standard and standardless analysis.

For transversal samples, the trend of increasing concentration from surface to steel is only present in Cl samples, while the Cl+CO_2 samples present drops in both extremes. It is also noticeable that

profile values for analysis with standards do not change much between Cl and Cl+CO_2 results, on the other hand, values without standard show considerable difference, which can be an indication of error in the detection. The influence of carbonation will be further discussed on the discussion section.

It is possible to perceive an underestimation of chloride content from standardless measurements with respect to the ones using standard minerals. This difference is not constant and even presents few exceptions where higher concentration values are found. However, it also shows an tendency against safety, since smaller values lead to inaccurate assumptions of remaining time for service life predictions.
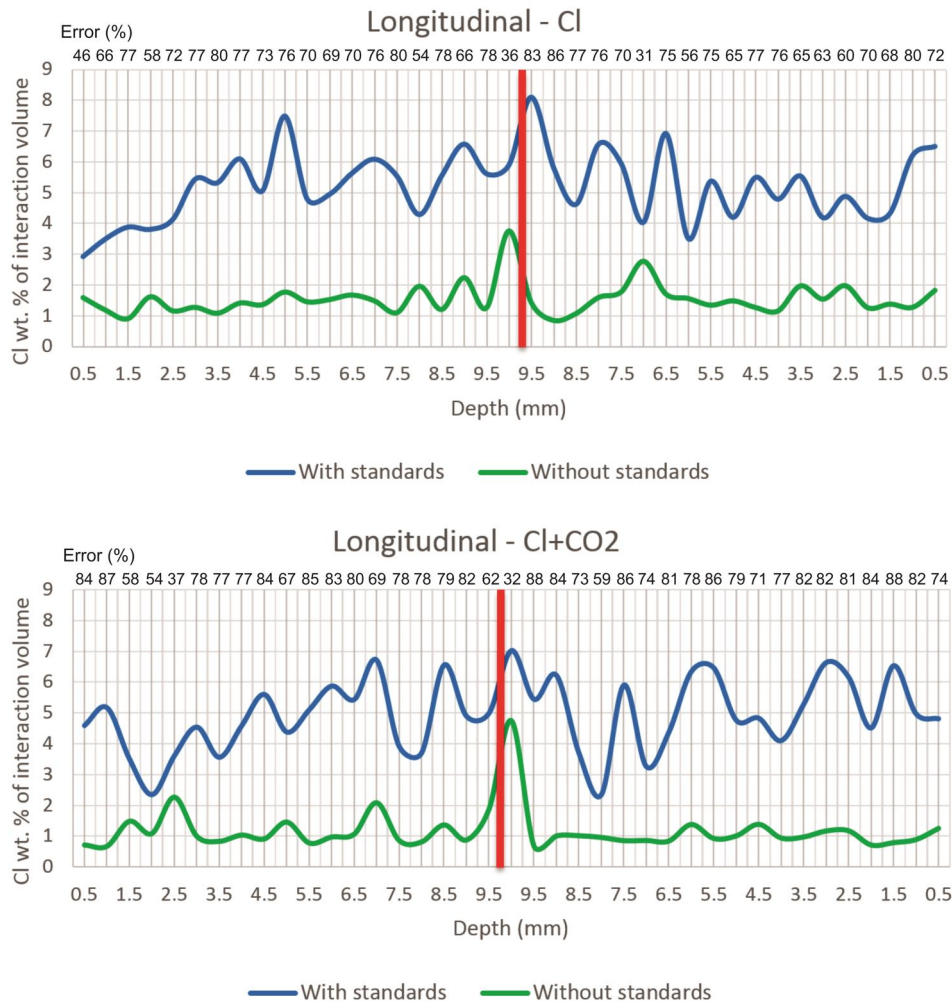
Figure 4: *Averaged weight percentage of chlorine in the interaction volume found with respect to longitudinal specimen depth. The red vertical line represents the position of the steel bar.*

IV. Discussion

Atomic ratios

Most of the spectra taken displayed a similar range of atomic ratios, nonetheless it is noticeable that the transversal samples possessed a higher Si/Ca ratio. Longitudinal samples had a decreasing Si/Ca ratio in the points collected on the interface zone. It might seem counter intuitive that similar specimens present diferent atomic ratios for the same experiment, but the data collected from transversal samples never reached the interface with the reinforcement, while for longitudinal samples, the focus was on that specifically. Initially the discrepancies were atributed to the possible wall effect near the steel, which causes a higher w/c ratio that leads to increased formation of CH. In Hu et al (2014), a higher amount of CH was one of the main reasons to the presence of inclusions in C-S-H gel, which diminished the Si/Ca ratio. However, the research observed a stronger relation of this phenomenum for smaller w/c ratios (e. g. 0.32), thus not as likely

to this study.

Rather, it was reported in Koleva et al (2007) that the presence of chloride ions, and in particular corrosion, could change chemical composition of hydration products, causing a shift in Si/Ca ratios of C-S-H into values similar to the ones reported hereby. Although the ratios on both researches are very similar, there is no straight forward explanation of how the microstructure of the gel is influenced by the presence of chlorides to increase the amount of calcium. Yet, this is evident in the longitudinal samples near the interface with the steel. Possibly, the presence of Cl- ions can attract enough Ca+ to reproduce the conditions observed in Hu et al (2007), creating a more propitious environment for a calcium rich C-S-H intermixture. An explanation for the higher number of points in Cl+ CO2 group is provided below.

Effect of carbonation

As most of the analysis presenting lower Si/Ca ratio were from Cl+ CO2 group, this can be used as

an indication that carbonation attacked portlandite throught the specimen, providing additional free Ca for the intermixture phases in C-S-H, the reason for it to be evident only in the steel interface zone probably is that just one of these effects is not sufficient to change the microstructure of calcium silicate hydrate. Nonetheless, the combination of the effect of carbonation with the presence of chloride ions should be enough. It is interesting to point out that this is an opposite behaviour to the observed in Sevelsted and Skibsted (2015), where the C-S-H studied did not contained chloride ions, reinfocement or the overall cement products, which allowed carbonation to be a more straight forward process. It is also pointed out the lack in literature concerning simultaneous effect of different degradation processes in Si/Ca ratios of concrete.

One other important mechanism of carbonation is the diminishing of the capacity of the paste in binding the chlorides ions, since it represents a difference in corrosion resistance to any given structure (Lin et al, 2010; Li and Shao, 2014). Since EDS analysis take into account any chlorine in the interaction volume (bound or free), this process should take place mainly in the surface of the specimens, as drops in chloride contents caused by loss during drying. Conversely, the drop in chlorine due carbonation is only observed in standardless analysis, which will be discussed next.

Use of standards vs standardless analysis

As C-S-H is both, hydrated and porous, it presents a challenge for elemental quantification, and the high presence of hydrogen and oxygen intensify the miscalculations in a standardless analysis because the provided analytical total of 100%. Such mistake can be avoided by the adoption of a standard based protocol that takes into account the factors mentioned previously and allows stoichiometric determination of elements with smaller atomic number than sodium. Figures 3 and 4 show a concentration around 5% in weitgh of interaction volume for all measures taken using standard based analysis, but varying chloride contents from 1% to 5% in the standardless analysis. It is very unlikely that the values near 1% are correct since the solution used presented a much higher concentration and enough time was provided to penetration. Further, since all other analysis have a convergent result, it points to inaccuracy of standardless analysis. The underesimation of chlorine is most probable due to the choice of default peaks considering oxides that do not properly represent C-S-H phases composition and bulk structure.

For longitudinal samples (Figure 4), a high error between standard-based and standradless analysis is seen, and it also show a slight increase in

errors from chloride treated samples to chloride and carbonation treated samples. The clear underestimation in standardless analysis (up to 90%) is of utmost importance, since service life prediction is greatly dependent of accurate chloride concentration determination (Frederiksen, 2009; Markeset, 2009), which can lead to vast underrating of a structure true state. The increase in error for the samples subjected to carbonation is most likely due to the inclusion of carbon and oxygen atoms, since these elements can not be reliably measured by the probe, therefore, appearing to present lower concentrations. Which is another point of concern, as real structures are often subjected to carbonation and chloride rich environments simultaneously and forensic examination are usually carried regardless of it.

For transversal samples (Figure 3), the diference in accuracy between the use of standards or not isn't as evident as the one mentioned above. This only reinforces the random nature of standardless analysis in the sense that non controled factors (e.g. ZAF corrections) can or not be a big influence in the results. Comparing the data regarding carbonation, one can notice that for analysis with standard minerals the values of concentration keep somewhat constant, which is is agreement with what as previously discussed. For analysis with default software peaks, the concentrations show a decrease throughout the entire depth of the specimen when carbonated, pointing again to a increase in error generated by the presence of additional oxygen carbon atoms. Although also present in the longitudinal specimen, this phenomenum is harder to observe in them because of the already big diference between standard based and standardless analysis.

V. CONCLUSION

Results were used to illustrate differences in element concentrations that can be derived by the absence of microanalysis standards, which could lead to inaccurate interpretations of concentration peaks for different elements such as chlorine. By the end of the work, it is was considered evident the importance of using standardds for microanalysis. It was further discussed the influence of positionning of analysis within samples. Although it seemed to not be a major parameter regarding the acquisition of chloride profiles, the results using default software peaks showed major differences in concentrations for different orientation of analysis, reinforcing the conclusion above. It is expected that this will be a step forward for the use of standard-based microanalysis in the future of cementitious phases research.

Additionaly, the influence of carbonation was observed. While it seemed to not be a key parameter

for determination of chloride content, it played a useful role in pointing out a weakness of standard-less analysis. Concerning the atomic ratio, it was concluded that in opposition to what was reported before, it appears that might not be the presence of chlorides, but rather the presence of chlorides near the reinforcement that changes chemical composition of C-S-H decreasing the Si/Ca ratio. The effects of carbonation seem to assist this effect, but it is still not clear. As this work is part of an on-going research, further investigation will be carried out.

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