

## **New Analysis Method for the Accurate Determination of Chloride Content in the Cement Phase of Concrete**

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### **ABSTRACT**

Corrosion of reinforcing steel in concrete is on one hand a major security problem and on the other a cost driver, which is very often not appropriately considered. Corrosion induced by chloride leads to localized corrosion phenomena, which reduces the cross section rapidly. Already corroded steels have to be replaced. When the initiation of the corrosion can be predicted accurately, the reinforcing steels can be prevented from corrosion and a comparatively small rehabilitation measure is sufficient. The cost for rehabilitation, which is necessary approximately every 20 years, can be reduced to half the costs. For an approximate structure lifetime of 100 years this leads to enormous cost savings. Accurate measurements are the basis for understanding and defining the process of Cl-ingress into concrete structures. In this paper, the deficiencies of the standard methods are demonstrated and a new evaluation method is applied. The calibration process as well as real life applications on retaining walls are presented and discussed.

### **INTRODUCTION**

The longevity of reinforced concrete itself is in most cases determined by the protection against corrosion of the steel reinforcements. Together with oxygen and an electrolyte (wet concrete), the steel reinforcements may corrode. While oxygen and an electrolyte are in most cases available, the protection against corrosion is accomplished by the natural alkalinity of the concrete, which is generally provided by the alkalinity of the surrounding cement paste. This alkalinity is mainly determined by the amount of cement in the concrete and can be reduced by a number of factors, one of them being the chloride content due to uptake from the environment.

Completely chloride-free concrete constituents cannot be gained economically; therefore, a low “natural chloride content” is present, which should not lead to corrosion and is accepted by the standards. On motor highways, de-icing salts are used during the winter season. Those de-icing salts contain chlorides which are mobilized by water and carried into the concrete and towards the reinforcements. As a

result, the chloride content increases during the lifetime of the structure. The chloride-induced corrosion is defined in standards (e.g., ÖNORM B 4706), to start above a chloride to cement ratio of about 1.0 m%.

After the exposure of concrete to chloride, it is only a question of time until the critical chloride to cement ratio is reached. Chloride-triggered corrosion leads to a pitting corrosion phenomenon which reduces the cross section of the steel reinforcements in relatively short time. This leads to a structural safety problem. A retrofitting action where only the alkalinity has to be re-established (e.g., new concrete cover) is approximately half of the cost of replacing the reinforcements. Thus, there is an ideal point in time for the retrofit measure, which is shortly before the reinforcements start to corrode. For the determination of this optimal point, appropriate evaluation techniques are essential.

Currently, the standards suggest determination of the chloride content from borehole cuttings by titration. The problem with this method is that the chloride content of the entire borehole cuttings are analyzed and calculated with an assumed cement content of the sample. The fraction of aggregates in the borehole cutting sample is usually not representative for the concrete, as the sampled volume of concrete may contain a higher or lower content of aggregates. These variations lead to a result that is subject to high scatter. Due to the low number of samples, the result has to be considered as not accurate enough to assess or predict any danger of corrosion.

Additionally, the aggregates may contain chlorides which will not be mobilized under natural (non-acidic) conditions and therefore will not contribute to corrosion effects. However, these chlorides falsify the evaluation suggested by the standards.

Because of these shortcomings a new method (LA-ICP-MS, Laser ablation inductively coupled plasma mass spectroscopy) was applied for that purpose. The advantages of the method presented in this paper are:

- The chloride content can be determined selectively in the cement phase.
- Aggregates and cement phase can be distinguished.
- Depth-profiles of the chloride content in the cement phase can be determined at a very high resolution, which makes a reliable assessment easier.
- The specimen preparation is strongly simplified and less prone to errors.

A forecast model can be derived and calibrated from the data (future work). The profile determined from borehole cuttings is too coarse for such purposes.

## EXPERIMENTAL

### Collection and preparation of the samples

Drilled cores were sampled from a highway bridge in Vienna. The samples were taken at four different heights with 6 cores sampled at each height. The drilled cores had a diameter of 45 mm, and were 100 mm in length. Before analysis, the samples were cut in two halves to enable LA-ICP-MS analysis in the center of the cores. Dry cutting was performed, to prevent mobilization of chloride.

### Instrumentation

The presented experiments were performed using an iCAP Q quadrupole ICP-MS (ThermoFisher Scientific, Bremen, Germany). For direct solid sampling experiments, an NWR213 laser ablation unit (ESI, Fremont, CA) was connected to the ICP-MS

device using PTFE tubing. For sample ablation, the ablation chamber was purged with helium, which was also used as carrier gas to transport the generated aerosol particles to the ICP-MS. Before introduction of the ablation stream into the plasma, argon was admixed (make-up gas) to create more stable plasma conditions. The instrumental conditions were optimized on a daily basis using a reference material (NIST 612, trace elements in glass, National Institute of Standards and Technology, Gaithersburg, MD). Instrument tuning was performed for highest signal intensity for  $^{115}\text{In}^+$ , while keeping the ratio of formed oxides (monitored by  $^{140}\text{Ce}^{16}\text{O}^+ / ^{140}\text{Ce}^+$ ) below 1.9%. Typical instrumental parameters are listed in Table 1. Using test samples, the optimal laser parameters for sample investigation were determined. Wherever possible, less abundant isotopes were used for analysis in the case of bulk constituents.

**Table 1. Typical instrumental parameters for the LA-ICP-MS measurements.**

<i>laser ablation</i>		<i>ICP-MS</i>	
wavelength	213 nm	plasma power	1550 W
pulse duration	4 ns	cool gas flow	14.0 Lmin <sup>-1</sup>
laser repetition rate	10 Hz	auxiliary flow	0.8 Lmin <sup>-1</sup>
laser beam diameter	250 μm	cones	Ni
laser energy	1.38 mJ	scanning mode	peak hopping
laser scan speed	40 μm s <sup>-1</sup>	dwelt time per isotope	10 ms
laser beam geometry	circular	monitored isotopes	$^{25}\text{Mg}^+$ , $^{27}\text{Al}^+$ , $^{29}\text{Si}^+$ , $^{35}\text{Cl}^+$ , $^{42}\text{Ca}^+$ , $^{49}\text{Ti}^+$ , $^{57}\text{Fe}^+$
He gas flow	0.4 L min <sup>-1</sup>	mass resolution	300 m/Δm
Ar make-up flow	0.8 L min <sup>-1</sup>		

### Quantification of LA-ICP-MS signals and LA-ICP-MS measurements

The sample surfaces were cleaned using pressurized air prior to analysis. Before LA-ICP-MS measurement of the samples, the ablation chamber was purged with helium gas for 20 minutes to reduce background signals to a minimum. Qtegra software, as provided by the manufacturer of the instrument, was used for recording of the time resolved intensity data for the selected isotopes. Each sample was analyzed using 24 scanned lines with a distance of 3.3 mm between the lines. Scanning direction was perpendicular to the drilling axis to obtain depth profiles from the chloride distribution.

Quantification of the chloride content in the concrete samples was performed using external calibration. Pressed pellets were prepared from cement with known chloride concentrations (certified reference materials). Homogenization of the material was performed using an ultrasonic swing mill; 300 mg sample material were pressed using a pneumatic press for 30 s at 10 bar. The chloride contents of the reference materials were 0.022, 0.040, 0.057, and 0.077 m%, respectively. To manufacture matrix-matched standards with higher chloride concentrations, pure sodium chloride was mixed with the previously described reference materials. Homogeneity of those standards was tested using LA-ICP-MS; standards with 0.23, 0.49, and 1.01 m% chloride were obtained.

## RESULTS

### Signal quantification using LA-ICP-MS

Analyte signals obtained from the pressed pellet standards were used for signal quantification of the samples with unknown chloride content. Two calibration functions (for low and high concentration) were calculated. Both calibrations yielded correlation coefficients above 0.9990. As calcium is main constituent of the cement, the  $^{42}\text{Ca}^+$  signal was used as internal standard to compensate for instrumental drifts as well as possible matrix variations. For the calibration functions, a limit of detection (LOD) of 0.008m% and a limit of quantification (LOQ) of 0.021m% chloride were obtained. The pressed pellet from the reference material containing 0.077 m% chloride was used for validation of the calibration and is therefore not included in the linear regression. The external validation resulted in a calculated chloride content of  $0.072 \pm 0.006\text{m}\%$  ( $\alpha=0.95$ ,  $n=4$ ), underlining the reliability of the calibration model.

### Quantification of chloride in the cement phase

Using LA-ICP-MS, reliable and fast analysis of the chloride concentration in the analyzed samples is possible. In comparison to titrimetric or other wet chemical methods, LA-ICP-MS allows for much more detailed resolution in the resulting depth profiles.

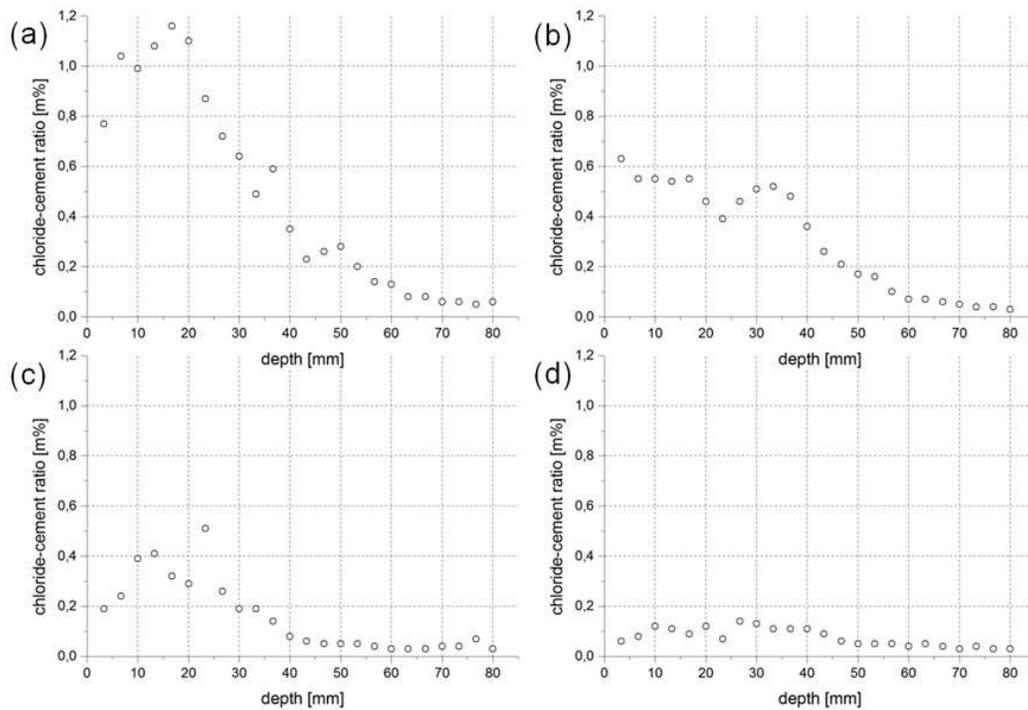
## DISCUSSION

The depth profiles obtained by LA-ICP-MS measurement are based on the mean value calculated from single measurements across a line perpendicular to the drilling direction. The line measured is approximately 30 mm long; measurements on the aggregates are neglected and therefore not taken into consideration for the chloride determination. In contrast to the strongly varying values obtained by titration of the borehole cuttings, using LA-ICP-MS much more reliable results can be obtained by sampling a large number of measurement points

Figure 1 shows depth profiles of drilled cores taken from four different height levels. It shows that the maximum chloride content at lower heights (Fig. 1a, and 1b) is higher, and becomes lower for higher sample heights. At depths higher than 60 or 70mm the chloride content appear to approach the “natural chloride content” which is in this case slightly lower than 0.1m%.

It is interesting to see that the maximum chloride content is not on the surface, but in most cases at depths of 10 to 20mm. We assume that this is a consequence of chloride being washed away from the surface during the drying process. Thus, under completely wet conditions the chloride content should be even higher in this depth range.

As we can see here, the depth profile needs to be fine to identify the maximum of the chloride content as well as to determine the shape of the chloride distribution. By application of titration of the borehole samples, often only depth resolutions of 20mm are achieved. Especially by the depth profile shown in Fig. 1a, this averaging process would strongly lower the maximum value and the information about the real chloride distribution is lost.



**Figure 1. Depth profiles from drilled core samples taken at different heights as ratio of chloride in cement [m%]: 0.8 m above street level (a), 1.8 m above street level (b), 2.6 m above street level (c), and 4.6 m above street level (d).**

## CONCLUSION

The standard method for the determination of the critical chloride value is the titration of borehole cuttings. This method suffers on one hand from high scatter in combination with a low number of replicates (in fact one for each borehole depth). The scatter is mostly a result of the strongly varying amount of aggregates in the sample, on the other hand by falsification of the results by taking the chloride content of the aggregates into account. In contrast, LA-ICP-MS represents a fast and reliable method for the analysis of chloride in concrete samples. Besides omitting tedious wet chemical analysis, depth profiles with very high resolution can be generated. This allows deeper insight into diffusion processes of chloride in the cement phase, accurate measurements, and the basis for a forecast model.