Study on the Accuracy of Chloride Determination Methods and Their Predictions

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Abstract

At ASFiNAG, most structures are made of reinforced or prestressed concrete. In Austria strong winters are obligatory. Therefore, de-icing measures with salt are used for thawing. These substances contain chlorides, that ingress into the concrete and lead to degradation. Several elements are strongly exposed to chlorides, such as girders of overpasses and columns of bridges beside and between roadways.

For condition assessment and service life prediction of existing road structures the determination of a reliable chloride content is key. The article presents the results of the chloride content of reinforced concrete obtained by two methods. One is the conventional Cl-determination described in standards. The other is the LA-ICP-MS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry) method, which is a fast, reliable, accurate and high-resolution analysis method. This method allows the determination of the chloride content as a fraction of cement and additionally distinguishes between the aggregate and the cement phase. The profiles were determined densely at steps of 3 mm in depth.

Regressions with different boundary conditions were used to fit the obtained data according to Fick's second law. For comparison and prediction purposes, the corresponding convection depth as well as the chloride diffusion coefficients were determined. These parameters, as well as the fluctuations of chloride profiles for one year deliver important insights for assessment and prediction.

Significant differences were observed in the results obtained by the applied analysis methods. The study addresses the origins of these differences and shows the variances when it comes to prediction of remaining service life. The results are compared and discussed to show the complex nature and sensitivity of the derived input parameters. These results show on one hand the importance for an accurate chloride analysis (LA-ICP-MS) and gives hints for an improved assessment of structures.

1 MALICE OF STANDARD CHLORIDE DETERMINATION METHODS

Currently the standard method to determine the chloride content is the titrimetric Volhard method, which is described in the European standard EN14629:2007. Thereby, concrete samples are gathered by drilling concrete cores or borehole dust at different depth levels. Nowadays, the titration is a state-of-the-art analysis method. However, the problem is that the samples may not contain a representative chloride content, which results on one hand to high scatter and on the other to wrong results. The high scatter leads from a not representative sample, which may contain aggregates in a higher or lower content than the concrete bulk. In the titration analysis the chloride content is determined for the entire sample. If the amount of aggregates (assume that they do not contain chloride) in the sample is higher than in the representative concrete a lower chloride content is determined. The samples are usually very small so these deviations are likely to be high (1). A second reason for a high scatter is that the cement content is usually not known for these analyses and a conservative value must be chosen. Additionally, the result may be erroneous, in terms that the aggregates may contain chlorides (see Fig. 1b). The aggregates are usually very dense, and the chloride is not free in the aggregates and does not contribute to a corrosion susceptibility. Inside the aggregates accumulations of chloride can be observed and during specimen preparation this chloride content is mixed with the free chloride in the cement paste. The chloride from inside the aggregates would not contribute to corrosion susceptibility and leads to an erroneous chloride to cement content.

2 LA-ICP-MS FOR MORE ACCURATE CHLORIDE CONTENT IN CONCRETE

Since maintenance cost is high and premature renewal is even higher, accurate prediction models are necessary. The basis for an accurate prediction is an accurate measurement of the decisive parameters. For that propose the evaluation of depth profiles of precise chloride per cement content were developed (2). Based on these measurements an evaluation method was developed to determine the total chloride to cement content. For short LA-D (Laser Ablating Deicingsalt) Method.

In this novel approach, selective quantification of chloride in the cement phase is performed. Aggregates containing chloride are excluded from the data evaluation and thus, a very reliable determination of the free chloride content in the cement phase combined with high depth resolution can be obtained. Additionally, the chloride content is determined as a fraction of the cement content – the major parameter for the susceptibility to corrosion.

The method was developed to analyze drilled core samples taken from structures by wet drilling. The diameter of the core was about 50 mm and the length (the depth of the Chloride/cement-profile) was about 60 mm. The cores we cut into halves and the LA-ICP-MS analysis was performed along lines, which were parallel to the outer surface, having a length of about 25 mm and a distance of 10 mm from each other. Sample analysis was conducted with a laser beam dimeter of 250 µm, enabling the measurement of depth profiles with increased depth resolution. From each line the analysis was evaluated by excluding the regions with aggregates and determining the mean of the Chloride to cement content. This mean value results in one point of the chloride in cement profile (see Figure 1). A detailed description of the LA-ICP-MS method and its development as well as the calibration, analysis and the verification of obtained results can be found in (2). From the other halve of the sample a titrimetric Volhard analysis according to EN 14629:2007 was performed. Both methods were applied to a core, which contains high amounts of chloride in the aggregates (see Figure 1). One can see that the difference between the LA-ICP-MS and the titration for this specimen is enormously high, not even the trend is the

same. Thus, based on the results received from titration it is not possible to develop an accurate prediction model. As known concrete samples do not only consist of cement, but also of aggregates. Usually the chloride content, as well as the amount of aggregates in the concrete is not exactly known. Further, some aggregates contain considerable amounts of chloride. A comparison of the determined chloride concentrations is given in Fig.1b. While LA-ICP-MS analysis and titration yielded consistent results in the case of granite (acid insoluble) as aggregate material, the values differed significantly for the aggregate type river gravel and limestone. Based on the results, the titration does not seem feasible for the exact determination of chloride in the cement phase.
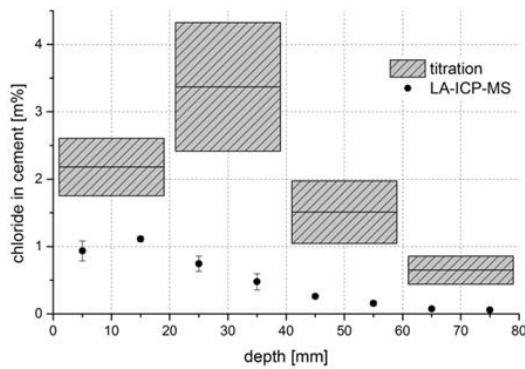

Figure 1a: Comparison of titrimetric chloride determination and LA-D analysis (3).
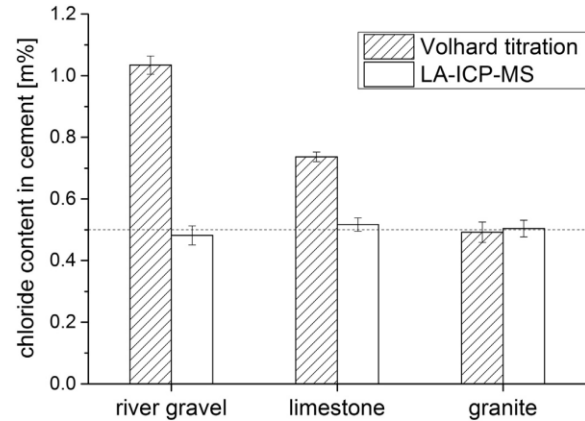
Figure 1b: Comparison of different aggregates in the concrete composition and their impact on the chloride content using titrimetric and LA-D (3).

3   PREDICTION OF CHLORIDE TRANSPORT IN CONCRETE

3.1 Mathematical formulation

In Crank (4) first times Fick's second law was introduced for modelling chloride ingress by diffusion in concrete structures using following one-dimensional partial differential equation:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \cdot D \cdot \frac{\partial C}{\partial x} = D \cdot \frac{\partial^2 C}{\partial x^2} \qquad (1)$$

where C and D are defined as the chloride content as a function of position x and time t, and the chloride diffusion coefficient, respectively. Also Crank (4) derived the closed-form of Eq.(1) as mass transport model to simplify chloride diffusion prediction in concrete. The first example for using the closed-form of Eq.(1) for constant surface chloride content C_s to predict the diffusion of chloride ions in concrete was found in (5).

The transport processes of chloride in concrete are complex and influenced by strewing intervals, material parameters and environmental conditions. Therefore, a constant surface chloride function is in many cases not enough. Hence, it is very common on aged concrete structures exposed to de-icing salt, to find the maximum chloride concentration in the concrete bulk. This indicates, that the exposed side of the concrete surface is not fully driven of a diffusion dominated process. Environmental actions induce a gradient of moisture along the cover depth, the so called convection zone Δx. Additionally, it is proposed in (6) that the chloride diffusion

coefficient as a characteristic material parameter is time dependent. This leads to the constituted mathematical model used in (7), which is based on the error function solution of Fick's 2nd law of diffusion.

$$C_{(x,t)} = C_{s,\Delta x} \cdot \left[1 - erf \left(\frac{x - \Delta x}{2 \cdot \sqrt{D_{app}(t) \cdot t}} \right) \right] \qquad (2)$$

where $C_{s,\Delta x}$ is the substitute chloride concentration resulting from the prevailing exposure environment at depth Δx [m-%/c], Δx is the depth of the convection zone [m], x is the depth with a corresponding chloride content [m], t is the time [s], $D_{app}(t)$ is the apparent chloride diffusion coefficient [m²/s] and erf is the Gaussian error function.

The time dependent diffusion coefficient is described as following:

$$D_{app}(t) = k_e \cdot D_{app}(t_0) \cdot \left(\frac{t_0}{t} \right)^{\alpha} \qquad (3)$$

where $D_{app}(t_0)$ is the apparent chloride diffusion coefficient determined at a reference to t_0 [m²/s] and α is the aging exponent indicating the decrease over time of the apparent chloride diffusion coefficient [-]. It should to be mentioned that the parameter $D_{app}(t_0)$ always represents the diffusion coefficient of the concrete over the entire considered time period t as an averaged constant. Temperature affects the mobility of ions and, hence, the diffusion rate of chlorides. The transfer parameter k_e has been introduced in order to account for the impact of the external temperature on the chloride diffusion in concrete.

$$k_e = exp \left(b_e \cdot \left(\frac{1}{T_{ref}} - \frac{1}{T_{real}} \right) \right) \qquad (4)$$

where b_e is the temperature coefficient proportional to the activation energy [K], T_{ref} is the reference temperature [K] and T_{real} is the temperature of the structural element or the ambient air [K]. In the following all fluctuating parameters will be described as mean values and corresponding distribution characteristics will be given.

3.2 Fitting procedure

To predict the transport of chloride ions, both C_s and D can be determined by curve fitting with real data taken from samples extracted from the structures. The usual procedure is to fit the error function into the chloride concentration gradient and to obtain, by regression analysis, the concentration, C_s, and the Diffusion coefficient D.

The procedure for calculating the chloride diffusion coefficient and surface concentration $C_{s,\Delta x}$ from a chloride profile when the maximum concentration is inside the concrete surface is described in (8).

From the chloride profiles diffusion coefficients were obtained. Initially the diffusion coefficient were the same in all three levels, but due to different exposure of chlorides and other phenomena the diffusion coefficient may change and differ in the three horizons (9).

The aim is to determine D_{app} from specimen taken from cores. As a result, the obtained model parameters can be used to characterize the ingress rate at the age of the sample or to predict the evolution of the profile over time.

To consider the time variant nature of D_{app}, the aging exponent α in Eq.(2) has to be quantified by fitting data from chloride profiles from at least two different points in time to a regression function as shown in (10).
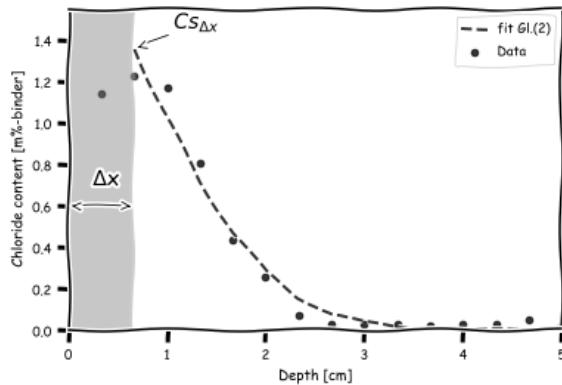
Figure 2a. Sketch of a typical shape of a chloride profile (dots) and its regression to MC Equation (2) (dashed line).
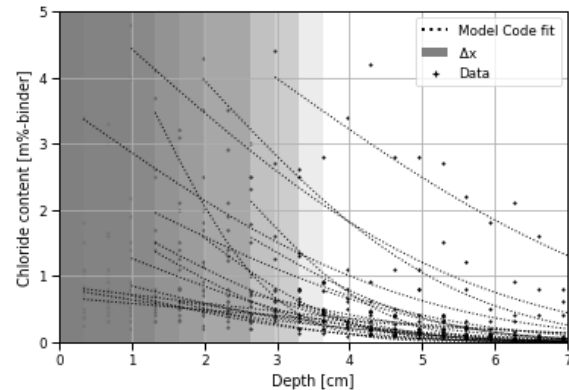

Figure 2b. Chloride profiles (cross), their fit (dotted) and derived convection zone (gray area) from field data.
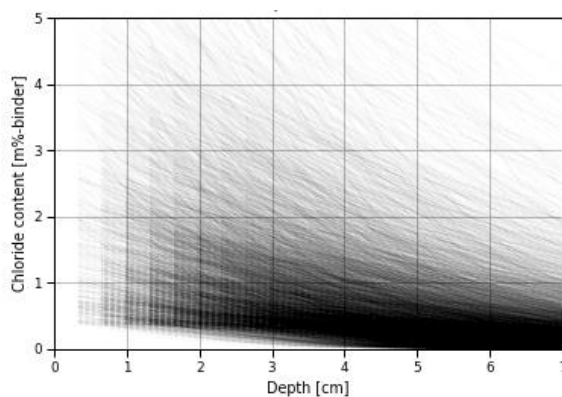

Figure 2a. 5000 stochastic realizations of a chloride profile derived from fitting parameters according to Figure 2b.
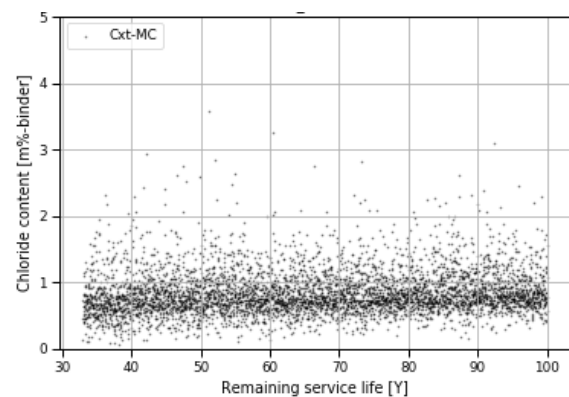

Figure 2b. Simulation of the chloride content on rebar level over time.

3.3 Model parameter

3.3.1 Convection zone Δx

As already mentioned, concrete in structures exposed to de-icing salt build a convection zone with alternating wetting and drying cycles. This depth of chloride convection zone is considered as a key variable, in the model based on Fick's second law (see Eq.(2)). So within the convection zone the chloride profile deviates from the proposed Eq.(2). Actually, the chloride convection zone depths are not constant but depend on the external environment, drying and wetting time ratio and concrete properties (11). Own studies on real structures exposed to 38 years lasting de-icing salt exposure used the novel chloride determination method LA-D discovered a wide range of the convection zone (aprox. 1-4 cm) (12). In (13) similar results are presented.

Hence, it is appropriate to determine the chloride convection zone depth on the basis of traditional approaches, i.e. fitted by the measured data, rather than recommended constant values. The depth of the maximum chloride concentration in concrete is defined as the chloride convection zone depth which can be determined by the fitting profiles of Eq.(3) based on measured data. After stochastic analysis a beta distribution of the convection zone is taken in the present paper. The mean and coefficient of variation are 16.93 and 10.30 mm, respectively.

3.3.2 Substitute chloride concentration Cs,Δx

In fib MC2010 is defining $C_{s,\Delta x}$ as the chloride content at the end of the depth of the convection zone in % by mass of cement.

The maximum surface chloride concentration on the concrete surface is typically considered as the demarcation point between the convection zone and diffusion area (14), which is a function of internal and external factors, e.g. solution concentration, environmental loads and concrete composition. According to existing studies, the surface chloride concentration in concrete follows a lognormal or normal function. (15-17). It is assumed that also the substitute chloride concentration follows this kind of statistical characteristic. After stochastic analysis a lognormal distribution of the substitute surface chloride content is taken in the present paper. The mean and coefficient of variation are 1.659 m%-binder and 1.278, respectively.

3.3.3 Diffusion coefficient $D_{app}(t)$

The determined chloride diffusion coefficient following the procedure described in section 3.2 obtain $D_{app}(t)$ at the time where the specimen was tested and is usually given in years and strongly depends on the season (date) when the extraction in-situ where executed (18). To derive $D_{app}(t_0)$ by using Eq. (3) $D_{app}(t)$ is an input variable. The reference point of time t0 was chosen to be t_0=0,0767 years (t_0=28 d). The statistical variation of chloride diffusion coefficients is adequately described by a Normal distribution (19). The mean and coefficient of variation are 10.195 m²/s and 9.022, respectively.

3.3.4 Environmental Transfer Parameter ke, T_{real}

For a given concrete structure in a given environment, the rate of chloride ingress highly depends on the temperature, as shown in Eq. (4). Based on local information on prevailing temperature conditions, data on average annual temperatures is used as a basis for the selection of this input parameter. All collected diffusion coefficients were converted to those based on T_{ref} = 293 K (20°C). The variable T_{real} describes the temperature of the structural element or the ambient air and is obtained by data grabbed from a moisture and temperature monitoring applicated on the structure itself. The variable is normal distributed with a mean value of μ=290.63 K and a deviation of σ=9.19. The values of the regression variable vary between 3500 K and 5500 K and can be statistically described by a normal distribution (μ=4800, σ= 700) (20).

4   DATA (SENSITIVITY) ANALYSIS

For the analysis the data was treated for every horizon separately, except Temperature and therefore the environmental transfer parameter ke respectively. The derived regression parameter from the chloride profiles are used to calculate the complete range of the chloride content over the remaining lifetime. The output was used to undertake a sensitivity analysis.

A sensitivity analysis (SA) can identify the most influential parameters and their interactions and how these parameters affect the output. In other words, sensitivity analysis quantifies the degree to which a model input effects an output. The sensitivity analysis was conducted using the programming language Python, in particular, the Sensitivity Analysis Library (SALib) (21)
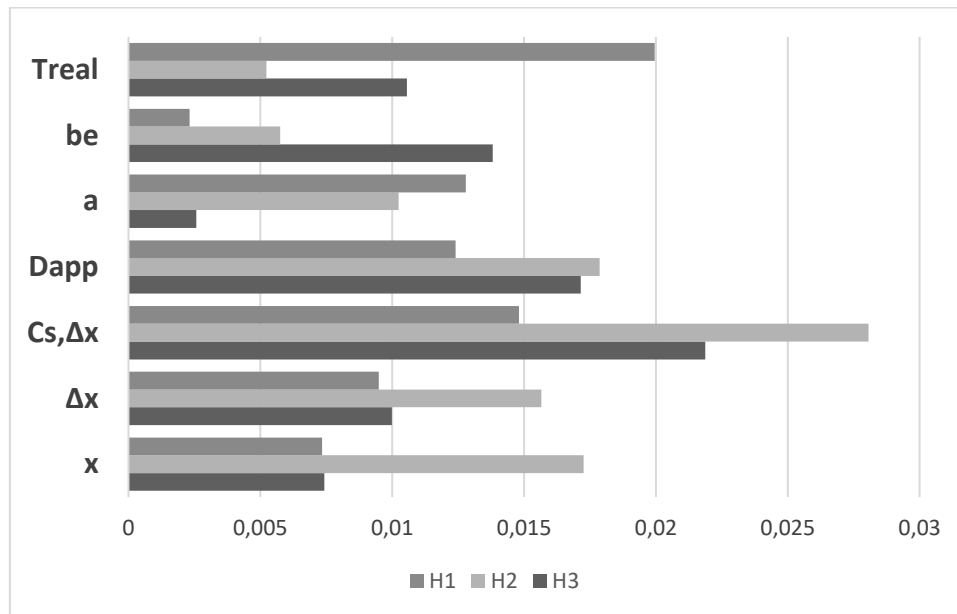
Figure 3. Global sensitivity indices derived from stochastic field data distinguished in 3 exposure zones
(H1 = 0 - 0.8 m, H2 = 0.8 - 1.8 m, H3 ≥ 1.8 m)

5   CONCLUSIONS

The LA-ICP-MS method presented in this paper shall contribute to improve forecast models. The analysis method is fast and reliable for determination of the chloride content in existing concrete structures. It was shown, that the traditional titrimetric method leads to high deviations and to systematic errors in the results. Therefore, the proposed LA-ICP-MS approach helps to increase the reliability of the obtained results. The high depth resolution of the chloride profiles enables a more exact data assessment for forecast models and supports the prediction of critical developments even further.

Since the convection process is much faster than the diffusion, the time variance inside the concrete is dominated by this process and the existing state-of-the-art models should consider that. The obtained data with the LA-ICP-MS method is an excellent basis for assessment and development of models and their predictions.

In general, a sufficiently large dataset must be available to make a valid prediction of the chloride content over time. Although the available data were very accurate in their quality regarding true chloride content, several uncertainties in the data quality, such as moisture, carbonation and chloride binding capacity of the concrete still exist. The data were not sufficiently accurate for this purpose. A continuing high fluctuation range can be observed, which is nevertheless still smaller in comparison to the conventional method.

The sensitivity analysis of the presented case study shows the important influence of the diffusion parameters D_{app} and of the exposure conditions during service life $C_{S,\Delta x}$. Other parameters have similar sensitivity. Uncertainty should be further reduced by exact determination of the convection zone Δx and exact chloride content $C_{s,\Delta x}$ on this interface.

Using fixed values of chloride convection depths lead to considerable uncertainties in the model outputs (e.g. the time to corrosion initiation), theoretical analyses of chloride concentration profiles may result in serious consequences (e.g. the real service life, the optimal time for inspection and maintenance), and thus analytical results fail to reflect the real deterioration of RC under deicing salt conditions.

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