Val-LIBS: A novel attempt to decipher the transport processes in concrete – A case study

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ABSTRACT

In order to evaluate the status of concrete structures, the advance of several potentially damaging processes needs to be evaluated. In Europe, one of the most common damaging mechanisms is the chlorine-induced corrosion of the concrete-reinforcement or of pre-stressed concrete e.g. due to the usage of de-icing salt on the streets during the winter. In this context, multi-storey car parks are a highly vulnerable kind of building because a mixture of salt and snow is sticking to the car and after entering the warm car park, this mixture drops down resulting in a massive salt entry. Such salt entries can hardly be prevented. However, the concentration and depth of the chlorine entry into the concrete can be detected in order to assess the occurrence of possible chlorine-induced corrosion of the concrete-reinforcement. A promising method is the so called "laser-induced breakdown spectroscopy" (LIBS) which is characterized by a high spatial resolution (generating 2D data maps in the µm range), precision (down to 0.1 wt.-% Cl) and measuring velocity (ca. 30 minutes per measurement). The Valtest AG (Lalden in Switzerland) is the first industrial building material testing laboratory using the LIBS technique for quantitatively measuring the chlorine concentration in drill cores from concrete-made buildings. Here we present results obtained from measuring campaigns in multi-storey car parks in Switzerland. The results reveal that the Cl concentration are highly variable within each drill core underlining the need of using high spatial resolution methods to quantify the Cl entries. As LIBS enables the measurement of several elements simultaneously, we also investigated the carbonatization of the drill cores. First preliminary results indicate that the Cl concentration and the carbonatation front are running counter to each other. Such effects can only be resolved with high spatial resolution methods such as LIBS.

1. INTRODUCTION

Evaluating the condition of concrete structures is a very important instrument in order to extract information about the status of buildings during their planed life cycle. At the latest, since the collapse of the Morandi Bridge in Genoa, Italy, the urgency of this problem has been broad (back) to public attention. Several methods (Truffer 2018) can be applied (also in combination) to construct a clearer picture about the investigated building. In this context the so called "laser-induced breakdown spectroscopy" (LIBS) represents a very promising and innovative method (BAM 2018) that can help to reveal the puzzle.

The LIBS method is directly applied on the surface of divided drill cores extracted from the building of interest. Subsequently, the drill core is spectroscopically and, therefore, analysed by a laser beam (SECOPTA analytics GmbH 2018). Due to the capability of LIBS to detect all elements of the periodic table, LIBS serves a very broad operational framework. However, at the current state of research most of the studies (Millar, et al. 2015; Gottlieb, et al. 2017; Millar, et
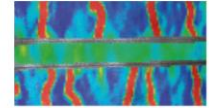
al. 2018) focus on the detailed 2D detection of chlorine considering its potential for harm in civil engineering and the construction of buildings. Due to several reasons, which will not be discussed further in this article (keyword "natural chlorine content"), construction materials are not completely free of chlorine. However, as long as the critical threshold values are not exceeded, corrosion is considered to be non-existent. However, if chlorine concentrations exceed the threshold, corrosion can be initiated which is one of the most feared damaging mechanisms in concrete-reinforcement or of pre-stressed concrete. Especially, in regions where de-icing salt is applied on the streets in winter, the passivity of concrete is destroyed and in combination with water and oxygen, chlorine-induced corrosion can easily attack the reinforcement leading to their weakening and finally to construction failure. In order to protect the building very costly measures are required such as removal of contaminated parts, electrochemical chlorine extraction from reinforced concrete or cathodic corrosion protection.
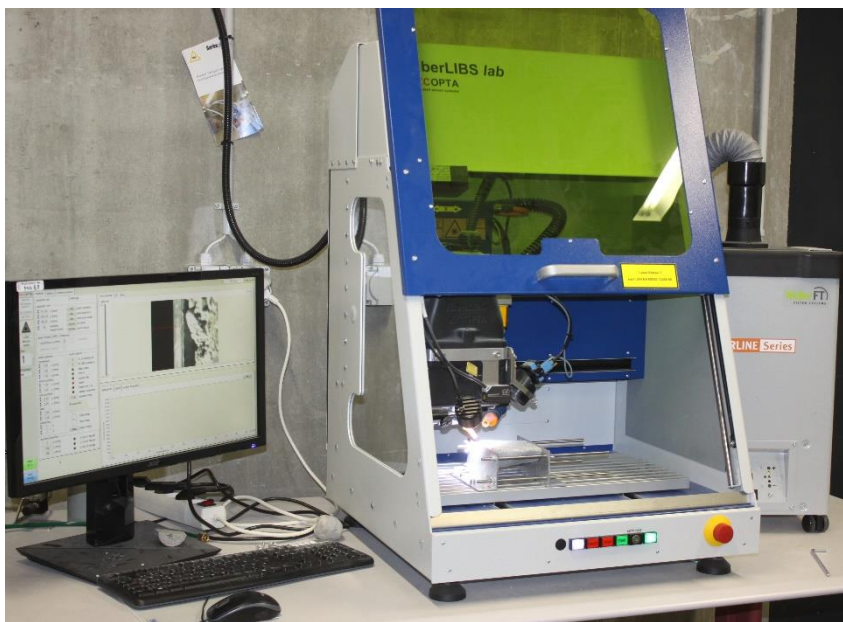

Figure 1: The FiberLIBS Lab unit in the Valtest AG laboratory.

To date, the concentration of chlorine in concrete is analysed by wet chemistry methods such as titration or photometry. Here, the samples are taken either in the form of homogenized borehole cuttings or as drill cores. Later are cut into 10 mm sized slices in the lab and are subsequently homogenized. This homogenization of the aggregates and the cement results in a limited depth resolution accompanied by the loss of important information such as the lateral distribution of elements or along cracks. The measured concentrations obtained from wet-chemistry are only averaged values referring to the homogenized volume of one slice or one single step of the borehole cuttings (Millar, et al. 2015). These methods do not account for heterogeneity in the sample material. Subsequently, highly precious measuring methods are used to calculate the element concentration in relation to the total mass of processed sample material which is then re-calculated to the (unknown) cement content based on an estimate of the ratio aggregates to cement content (in Switzerland 1:8). However, in contrast to these conventional and time-consuming methods, especially regarding the preparation of the sample, LIBS displays a faster alternative accompanied by a higher resolution (measurements are possible in the µm range). In combination with the application of certain filters and algorithms (based on particular element ratios such as Ca/O), the binding agent can be separated analytically from the aggregates after the measurement so that solely the chemical composition of the cement is determined (meaning that the measured chlorine concentration is that of the cement). Additionally, with LIBS mm-sized areas can be

scanned resulting in a 2D analysis of the sample surface allowing closer examination of transport processes from other damaging chemical species such as SO_4^{2-}, Na^+ und CO_2 along cracks in the concrete (Millar, et al. 2015; BAM 2018). Here, we present for the first time LIBS data from multi-storey car parks revealing the transport path of chlorine and carbon along cracks.

2. METHODS

2.1. Sampling

The samples were taken from various levels as well as various constructional elements of a multi-storey car park in Switzerland. The sampling was performed with a commercial driller and drill cores varied in diameter between 50 to 100 mm. After the sampling campaign, the drill cores were cut parallel to their longitudinal axis in half with a saw without the usage of water (dry) in order to prevent the washing out of chlorine. Subsequently, the samples were placed in the sample holder within the measuring chamber and were measured with the FiberLIBS Lab unit from the German company SECOPTA analytics GmbH.

Table 1: Technical data of FiberLIBS lab unit.

laser class	1
wavelength	1064 nm
puls duration	< 1.5 ns
puls energy	3 mJ
spot diameter	< 100 µm
energy density	> 6.5 GW/cm^2
scanning rate	up to 100 Hz
measurable spectral range	190 - 1000 nm

2.2. Measuring

As LIBS is not a commonly used measuring device, we give some general information about the system (Fig 2a). Generally, LIBS is based on the bombardment of the sample surface with a very short (ns), focused (spot size of ~ 100 µm) and energy-rich (~ 400 mJ) laser pulse from a Nd:YAG laser. This results in the ablation of a small amount of sample material from the surface (for cement: around 30 µm depth and around 20 µg of ablated mass (Gottlieb, et al. 2018)) which is converted into plasma (Fig. 2b) caused by the prevailing high temperatures (> 10000°K (Kearton, et al. 2008)). Within the plasma, the chemical bindings of the molecules are destroyed and the electrons of the atoms are excited partly leading to an ionization of the elements. After termination of the energy supply, the plasma cools rapidly and breaks down so that the electrons and ions recombine. During the breakdown, element-characteristic light is emitted which can be measured with a suitable spectrometer (detector). The detected spectrums are assigned to elements (Fig. 2c) and their particular intensity holds information about the distribution and the qualitative concentration of the elements in the sample. Self-made standards need to be utilized with a known concentration of the particular element, preferentially characterized by the same matrix as the sample, in order to establish a calibration curve and quantify the results (e.g. in the case of chlorine, 12 standards have been produced for the quantification).

2.3.　　　Modelling

The software from SECOPTA analytics GmbH provides the raw data that are, in the case of chlorine, based on the calibration curve. However, in order to illustrate the results customer-friendly, the Valtest AG used self-developed MATLAB algorithms to process and analyse the raw data. Powerful statistical analysis tools such as nonlinear regression analysis and have been implemented to enable deeper investigations of the drilling cores. Different subroutines are able to bring into relation chlorine concentrations with some other non-destructive testing methods (e.g. cover meter and ground penetrating radar) to provide the engineer expanded tools to assess the state of the investigated construction.
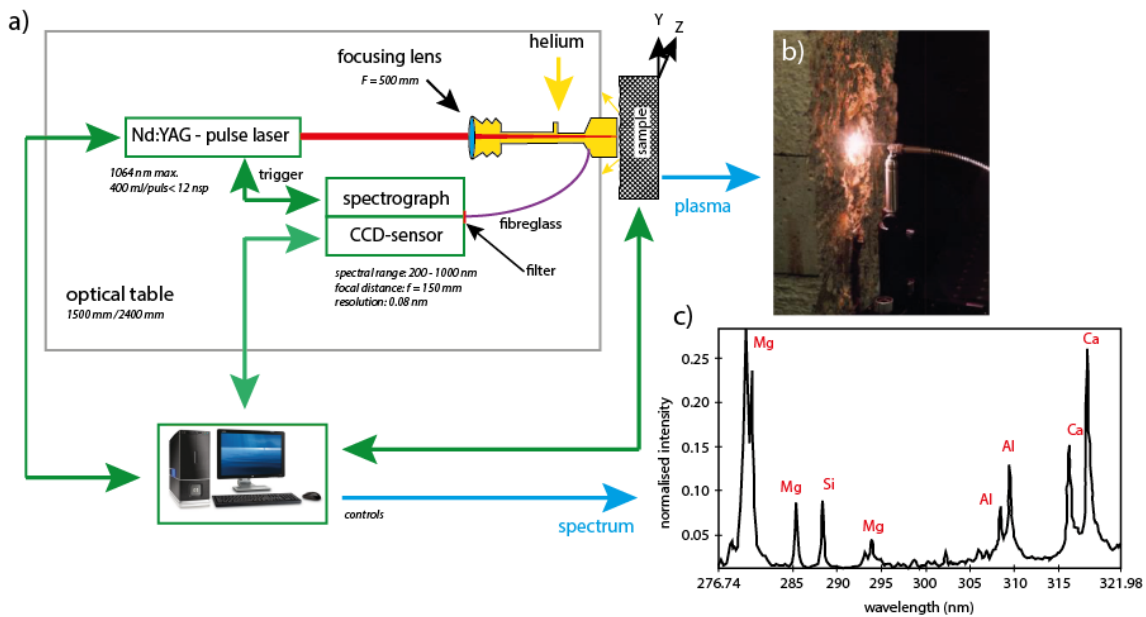

Figure 2: **a)** Schematic measuring setup of the LIBS system in the laboratory of the Valtest AG; **b)** Picture of the plasma hitting the concrete surface; **c)** Typical spectrum from concrete within the wavelength area of 276 nm to 322 nm (modified after BAM (2018).

3.　　RESULTS

As already pointed out in section 2.1, the samples were extracted from a multi-storey car park. Measurements are based on daily-calibrated operation settings (using the chlorine standards). In total 18 drill core were extracted. However, we will present only two originating from the ceiling of the same storey (Fig. 3). First, the analysis tools from SECOPTA allows for differentiation between cement and aggregates (here, based on the Ca/O ratio used as filter). Hence, the chlorine concentrations obtained from the processed raw data are that of the cement.

According to our knowledge, it is the first time that the process of chlorine transport along cracks could efficiently be detected. The samples were obtained from the ceiling meaning that the chlorine transport occurred downwards (capillary rise; sensu stricto). The most important outcome of this study are the increased chlorine concentrations around the crack and how they decay with further distance into the flanks of the crack. Most likely, chlorine was distributed within the drill core via further transport mechanisms e.g. diffusion which is underlined by the chlorine coronas that are formed around the cracks (Fig 3c/d). The chlorine concentrations reach values of ± 1.5 wt. % at depths up to 70 mm (Fig. 3c) indicating that chlorine was capillary
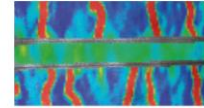
transported along the entire crack leading to relatively high chlorine concentrations at the underside of the ceiling.
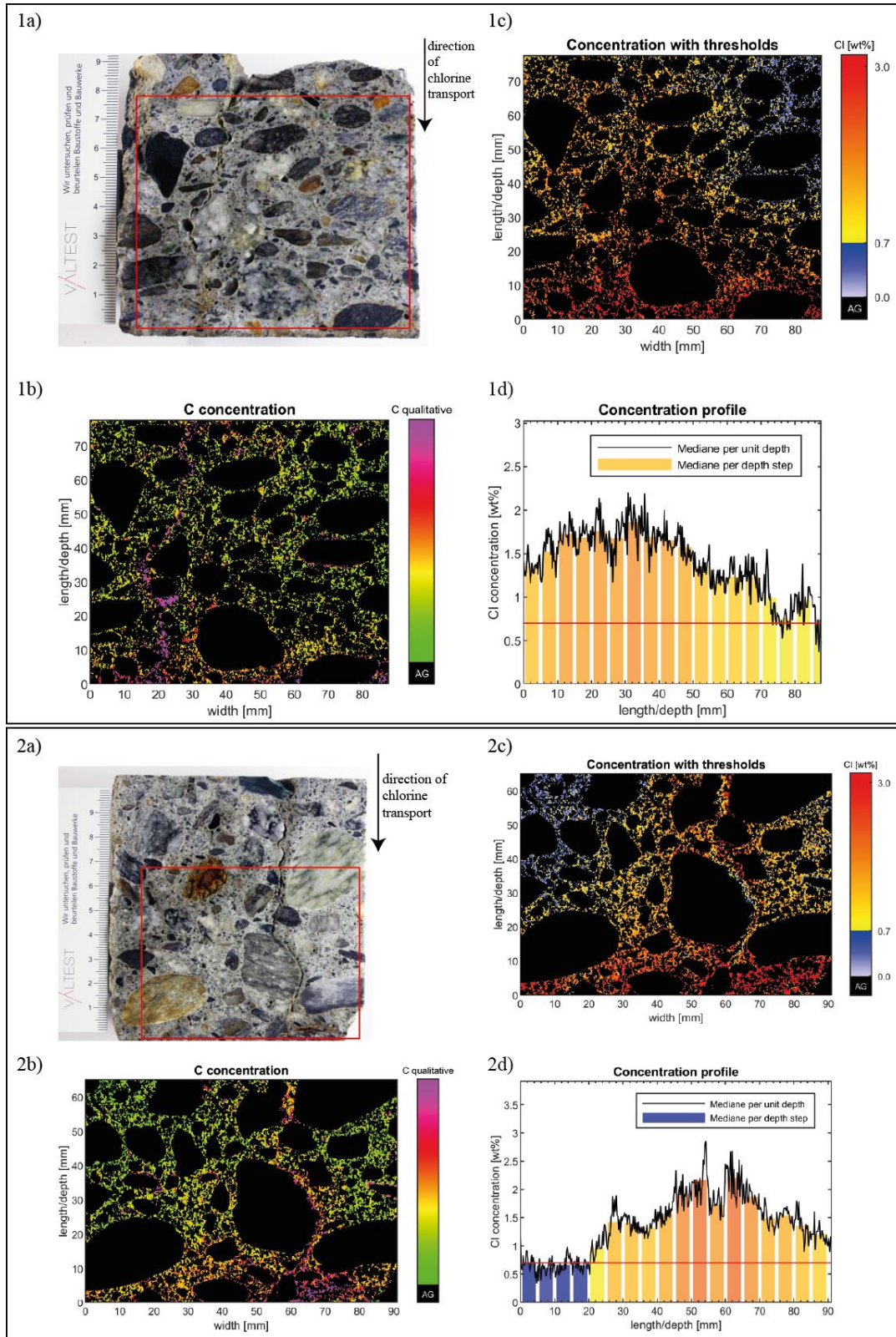

Figure 3: **a)** Photograph of the drill core with the LIBS measuring area in red. **b)** Map of the carbon distribution. **c)** Map of the chlorine distribution with different thresholds for better visualization. **d)** Chlorine concentration profile based on calculating the median value along the y-axis from the maps of c.

Furthermore, the data obtained directly in the crack reveal lower chlorine concentrations compared to the surrounding concrete mantle. At the same time, the carbon data (measured only qualitatively) in the crack are higher in comparison to the concrete mantle data indicating that a possible carbonatation of the cracks occurred into relatively deep levels of the drill cores (Fig 3b).

4.   DISCUSSION

The innovative LIBS system can be used to explore a very broad range of questions in civil engineering. However, we will only tackle one in this article, which is, from our point of view, the most interesting phenom we could observe, i.e. the transport behaviour of chlorine in regions of cracks.

The high chlorine concentrations within deeper parts of the drill cores seem to be linked to transport along the crack with some subsequently occurring diffusion into the flank areas of the crack. This is accompanied by some washing out processes deeper into the drill core as measurements directly within the crack reveal relatively low chlorine concentrations (Fig 3c). This can be due to two different hypotheses:

a)   When measuring directly in the crack, the detector does not have the right focus position so that the number of counts reaching the detector is reduced diminishing the measured chlorine concentration.

b)   Transport processes deeper into the drill core along the crack itself cause the lower chlorine concentrations (here: transport from bottom to top). Drill cores from the ceiling side of the storey containing the continuous crack reveal very high chlorine concentration supporting the previous assumption that the chlorine was transported directly along the crack. The bottom parts of both drill cores reveal similar chlorine concentrations around and in the crack itself. Furthermore, at the area where the crack crops out at the ceiling underside, chlorine concentrations of > 3.0 wt. % (Fig. 3c) were detected (even salt precipitation at the ceiling was visible). This demonstrates that the chlorine transport took place along the whole crack.

The second hypothesis is supported by the higher carbon data measured directly within the crack. Furthermore, we also measured drill cores from the floor and here, the chlorine concentration decreases with further depth in the direction of chlorine transport. As expected, the concentrations (around 1.5 wt. %) of the inner parts of these drill cores match exactly with the values from the bottom parts of the ceiling drill cores. Therefore, we conclude that the lower chlorine concentrations present in the crack is not due to inaccuracy in the measurement procedure (e.g. wrong focusing) but rather to chlorine transport along the crack in combination with diffusion from the flank of the crack.

5.   CONCLUSION

First, such close investigations of possible transport mechanisms along cracks are only possible thanks to the higher spatial resolution and 2D visualisation analysis qualities of LIBS. In comparison, the classical wet-chemistry analysis is not appropriated for such a study and could not have revealed the high risk of chlorine-induced corrosion for the reinforcement emanating from cracks. In Switzerland, the normative values of Table 2 are used to assess the risk for corrosion. Therefore, such cracks represent large threats for concrete structures increasing substantially the probability of local failure. Furthermore, the reinforcement might not only be
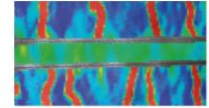
attacked where the cracks are in direct contact with the reinforcement itself but also on a wider front caused by diffusion.

6. OUTLOOK

Table 2: The risk of corrosion is directly linked to the chlorine concentration at the depth of the armatures.(SIA 269/2 2011).

concentration in chlorine < 0.4 wt. %/cement fraction	corrosion does not occur
concentration in chlorine from 0.4 up to 1.0 wt. %/cement fraction	corrosion may happen
concentration in chlorine > 1.0 wt. %/cement fraction	high risk of corrosion

One very important attribute that engineers are interested in when performing an evaluation of the status of concrete structures is its remaining useful life. It has been shown that based on semi-probabilistic methods in combination with wet-chemistry data, the total lifespan of concrete structures can be calculated (Rahimi 2016). The deterministic equation is described as follows:

$$C(x,t) = C_0 + (C_{s,\Delta x} - C_0) \cdot erfc \frac{(x-\Delta x)}{2\sqrt{(D_{app} \cdot t}} \tag{1}$$

where $C(x,t)$ is the concentration along the diffusion profile at depth x and time t. Δx is the depth range, where the behavior of the measured data deviates from the second Fick's law of diffusion (transition zone). C_0 is the initial chlorine concentration of the concrete and $C_{s,\Delta x}$ is the concentration at the transition zone. D_{app} is the apparent diffusion coefficient.

Rahimi (2016) has been limited by the resolution of chloride concentrations in depth arising directly from the framework of wet chemistry. LIBS has a much better spatial resolution so that many more datapoints along the depth axis are measured enabling in turn a better data curve fitting (less vulnerable to outliers). Moreover, the depth of the transition zone can be calculated more accurately (Fig. 4) guaranteeing that the whole set of appropriated data is used to get the useful life by solving equation 1 for t. Finally, the remaining lifespan is calculated by subtracting the calculated lifespan from the age of the structure.

As discussed in section 3, the data curves (Fig. 4) are based on element distribution maps. Due to the higher number of datapoints as well as the more precise determination of Δx (10.00 mm vs. 12.00 in Fig. 4a and b), the fitting procedure is characterized by a higher accuracy. Differences between both methods (LIBS and simulated wet-chemistry) often reveal deviations of up to20% in the determination of the lifespan. Moreover, the chlorine concentrations obtained from standard wet-chemistry methods does not refer directly to the cement. Inaccuracy arising from such an approximation is not taken into account in the calculations shown in figure 4a. Therefore, basing this calculation on conventional wet-chemistry methods may lead to inaccuracy in the determination of the remaining useful life of the evaluated structure.
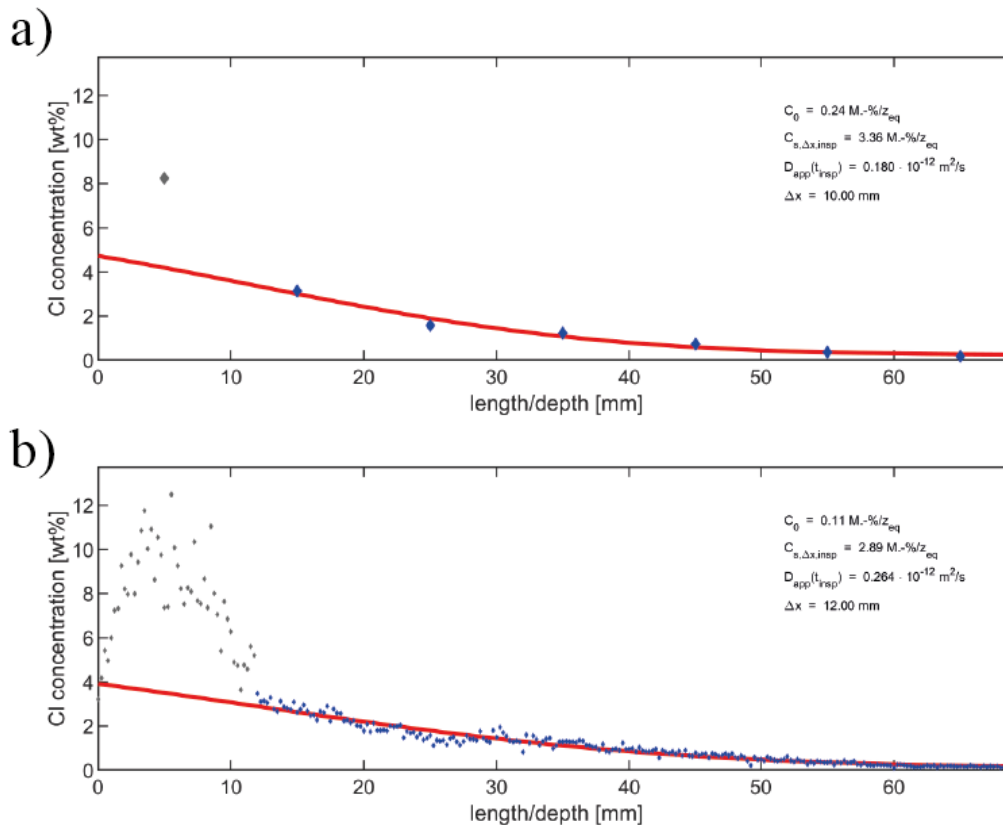
a)

b)

Figure 4: Determination of the crucial parameter by fitting that are used to determine the remaining life (t) of equation 1. The blue diamonds datapoints were used for the fitting and the grey diamonds were discarded. In order to simulate wet-chemistry conditions the datapoints of (**b**) were averaged at 10 mm step sizes in (**a**).

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