

Optical sensors for the durability assessment of cement-based infrastructure

Cyrill Grengg¹ | Bernhard Müller² | Iris Zögl¹ | Marlene Sakopanig³ | Florian Mittermayr³ | Torsten Mayr² | Karl Leonhard Sterz² | Joachim Juhart³ | Isabel Galan¹

Correspondence

Dr. Cyrill Grengg
Graz University of Technology
Institute of Applied Geosciences
Rechbauerstraße 12
8010 Graz, Austria
Email: cyrill.grengg@tugraz.at

¹ Graz University of Technology,
Institute of Applied Geosciences,
Graz, Austria

² Graz University of Technology,
Institute of Analytical Chemistry
and Food Chemistry, Graz, Austria

³ Graz University of Technology,
Institute of Technology and
Testing of Construction Materials,
Graz, Austria

Abstract

The corrosion-related damages on concrete infrastructure account globally for several billion US dollars annually. Up to 38 % of these costs could be saved by the application of optimized materials and/or more efficient monitoring technologies. In this contribution a novel sensor technology is presented, based on luminescent pH sensitive dyes, to quantitatively determine the pH distribution in cement-based construction materials. Different sensor platforms were explored resulting in high-resolution imaging techniques, as well as in miniaturized sensor probes for field application and in situ monitoring. To this point, pH sensors were successfully applied for cementitious materials to (i) quantitatively characterize the carbonation state in the lab, (ii) gain further understanding on phase assemblages and internal pH evolution related to carbonation, (iii) reveal that the actual pH at the inflection point of phenolphthalein may strongly vary depending on physicochemical material properties, (iv) monitor the pH evolution during the early hydration of different cementitious materials, and (v) measure carbonation depths using miniaturized sensor probes adopted for field applications.

Keywords

Durability assessment, optical sensors, carbonation, chloride ingress, monitoring

1 Introduction

A precise and effective corrosion and durability assessment of concrete structures is essential to guarantee their structural functionality and to minimize operational costs. In this context carbonation and chloride ingress are the most common corrosion mechanisms. State-of-the-art technologies to evaluate corrosion progress, such as phenolphthalein (PHPHT) spraying for carbonation assessment, or drilling dust extraction and subsequent chloride titration are associated with a high workload and corresponding high costs, while at the same time exhibiting limitations in precision and informative value [1]. Furthermore, to date, several open question in respect to the corrosion mechanisms are still in debate, such as the impact of physicochemical material properties on the inflection point of PHPHT.

Opto-chemical sensor technology has been used for more than 40 years in many areas of biotechnology, medical technology and life sciences [2]. In principle, opto-chemical sensors consist of a polymer layer in which an indicator dye is embedded that changes its optical properties in the presence of the substance (analyte) to be investigated. These changes comprise colour and/or colour intensity, luminescence properties (fluorescence or

phosphorescence) or other photo-physical properties. Opto-chemical sensors can be implemented in different sensor platforms potentially enabling (i) point and in situ measurements, (ii) imaging and (iii) particle-based measurements.

An overview of different sensor platforms envisioned for concrete applications is presented in Figure 1.

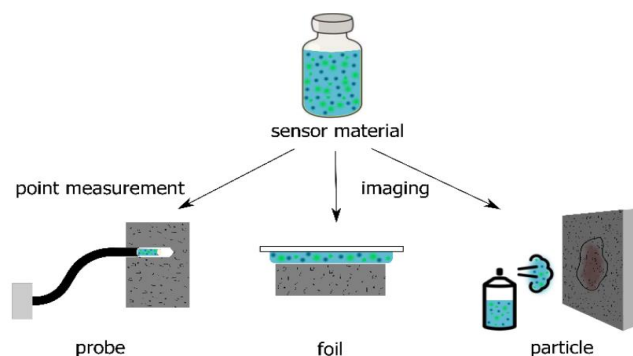


Figure 1 Envisioned platforms for opto-chemical sensor systems in building applications.

This contribution describes advances in the development and application of luminescent-based, optical dyes to

quantitatively measure pH in cement-based construction materials. Within recent years, several findings in this regard were already published by this group of authors in relevant journals. This includes a detailed description of the development of pH sensors for cement-based construction materials, including high-pH sensitive dye synthesis [3], calibration functions and different measurement platforms [4,5], as well as in situ experiments conducted to understand the pH evolution during early hydration in different cementitious materials [6,7]. For in depth information on those topics the reader is referred to the presented literature. In the following, focus will be laid on novel findings on the carbonation progress of concrete samples extracted from infrastructure facilities including road tunnels and bridges and the implications to material durability and in respect to the informative value and limitations of standard PHPHT analytics.

2 Materials and Methods

2.1 Field site and sampling

The samples presented in this study were extracted from various Austrian road tunnel and bridges and are part of a comprehensive field study conducted on several concrete infrastructure facilities. On site, drill cores with a diameter of 50 mm were extracted and carbonation depths were assessed by standard PHPHT spraying. In lab, drill cores were cut along the longitudinal site using a diamond saw. One half was used for additional PHPHT measurements, whereas the other one was used for optical pH imaging. This enabled a direct comparison of the PHPHT spraying and the optical imaging method within the same concrete specimens.

2.2 pH imaging and data processing

The same imaging setup as described in Grengg & Mueller et al. [4] was applied. Therefore, the sensor foil, consisting of two aza-BODIPY pH indicator dyes and a reference (chromium(iii)-activated gadolinium borate) immobilized in a hydrogel (HydroMed D4), was soaked in a 150 mM KCl solution and placed on the concrete specimen. Two consecutive pictures were taken through a RG9 long pass filter using a SensiCam from PCO in order to utilize dual lifetime referencing in the time domain (t-DLR) for the subsequent pH characterization [8]. The first picture was taken during illumination using high-power LEDs with an emission wavelength of 635 nm, recording the emission signal of the fluorescent indicator dyes and the phosphorescent reference, while the second image was taken right after illumination where only the phosphorescent reference contributed to the signal. Quantitative pH images were produced by plotting the intensity ratios of the two images (R) against the pH value. A schematic description of the setup and the principle of t-DLR are described in Figure 2A and B, respectively.

The calibration of the sensor foil was conducted using 10mM buffer solutions (CHES, TRIS, CHAPS) with 150mM KCl as background electrolyte with staggered pH values [5]. The calibration curve was calculated using the Boltzmann function, resulting in an apparent pKa value of 8.68 and a corresponding sensitivity range between pH 7.0 and 12.0 (Figure 3).

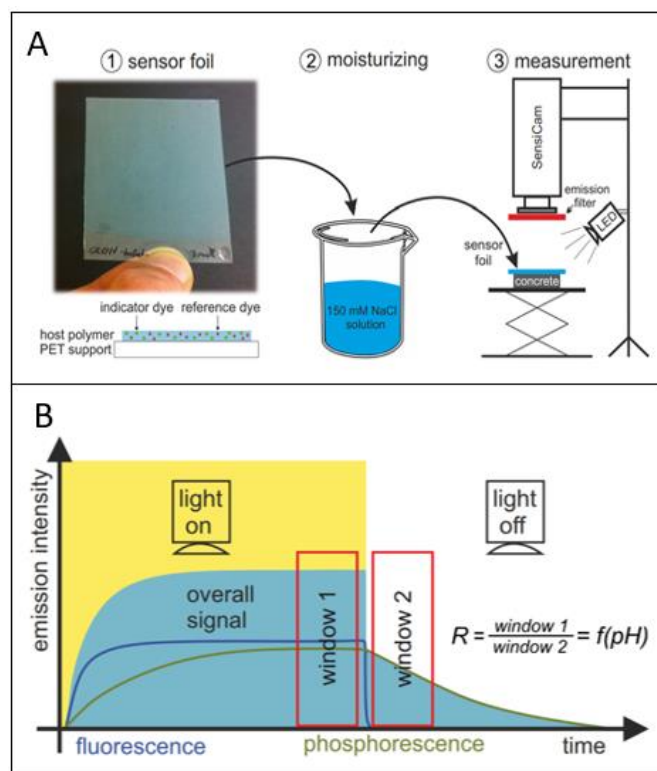


Figure 2 Schematic display of the imaging setup (A) and the t-DLR reference method (adopted from [5]).

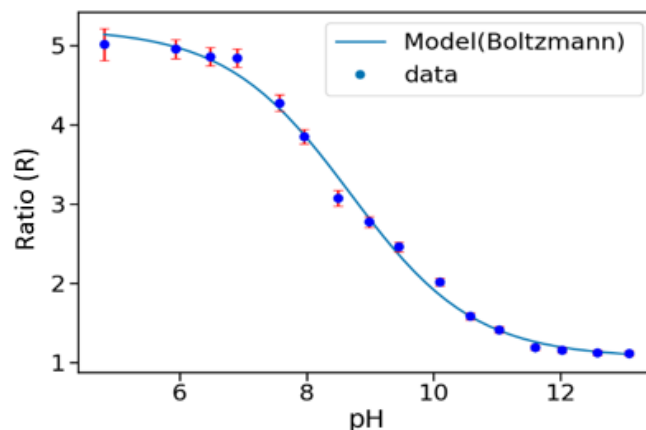


Figure 3 Calibration curve of the pH sensor foil using the Boltzmann function.

Data evaluation and analytics was performed using a python software (Jupyter Notebook 6.4.5). Quantitative pH profiles were calculated from the obtained pH distribution images representing a cross section through the carbonation front. Three pH depth profiles, each representing the average pH value of 20 pixels at each depth, were determined. The obtained pH evolution with depth was subsequently compared to the depth of PHPHT inflection, which represents the carbonation depth according to standard procedure.

3 Results and Discussion

The application of optical sensors using t-DLR referencing resulted in high-resolution pH distribution images of partially carbonated concretes, showing a good agreement between the carbonation depths measured via PHPHT spraying and the transition zone from low to high pH (>12) (Figure 4).

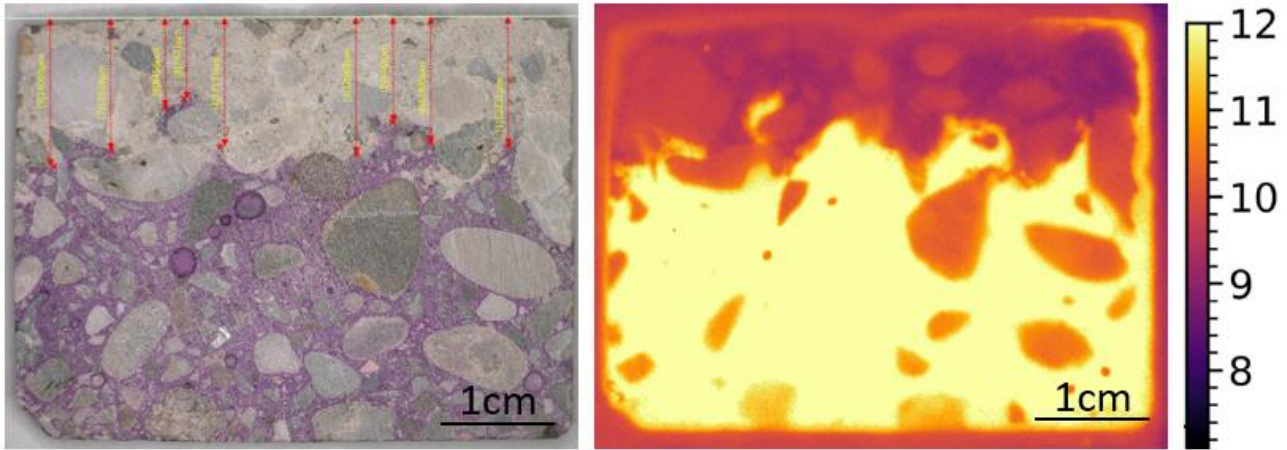


Figure 4 Carbonation depths quantified on a concrete cross section via PHPHT spraying (left) and optical pH imaging (right).

In addition, the novel sensor technology enabled an in-depth assessment of individual material response to carbonation progression and corresponding evolution of internal pH.

Within the carbonated areas high variations in pH were observed between samples showing a similar carbonation depth. Described variations comprise differences in the absolute pH of the carbonated zones and homogeneity of pH distribution in the latter. Figure 5 shows three examples of pH images obtained from different concretes, and the corresponding pH profiles, together with the carbonation depth measured via PHPHT (light purple zone, representing the measured depth \pm standard deviation). The absolute pH of the carbonated zones of the different samples shows high variation between pH 9 and 11. These changes are most likely related to differences in mineralogical compositions and porous microstructure and associated changed physicochemical material response to carbonation. This includes CO_2 diffusion kinetics, dissolution and decalcification of Ca-containing hydrates

(CH and C-S-H) and formation of Ca-carbonates [9].

Additionally, two major trends could be observed in respect to the pH evolution with depth. One group of samples is characterized by a stable pH distribution at a given level throughout the entire carbonated zone (Figure 5, left and middle). Within this group the transition to the non-carbonated interior is marked by a very steep incline in pH above 12. Within the second group of samples the carbonated zone is divided in two subzones (Figure 5, right): The first one, close to the surface of the sample, showing a plateau-like pH distribution, which is followed by an inner zone of gradual pH increase. In this group of samples, the transition to the intact cementitious microstructure is marked by a slight incline in pH rise, however not as steep as within the first group. In order to understand the described differences in pH evolution in detail, additional systematic mineralogical analytics are required, which were not part of this field study since no compositional data of the concrete samples was provided by the corresponding authorities.

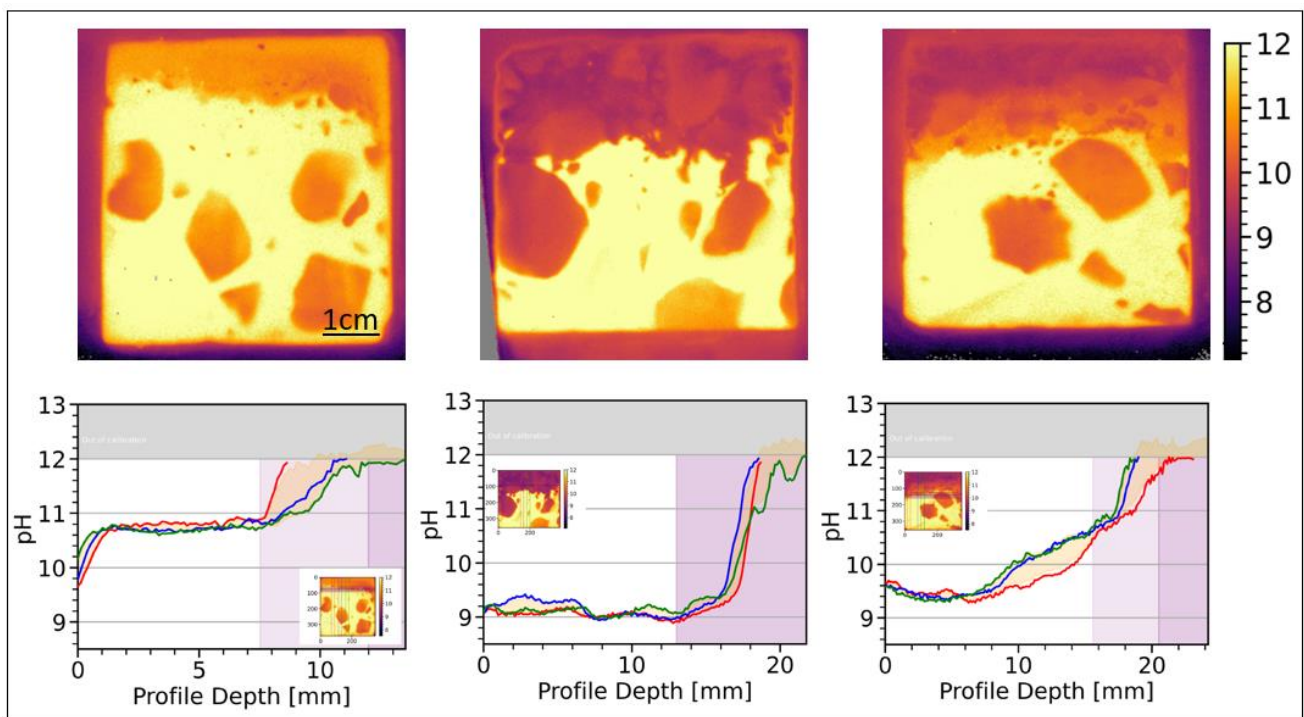


Figure 5 Examples of pH distributions within different concrete samples, together with corresponding pH profiles and the carbonation depth measured using PHPHT (light purple, showing the measured depth \pm standard deviation).

Further measurements showed high differences in absolute pH at which the colour transition of PHPHT took place. Considering the measured depth including the standard deviation of PHPHT, absolute pH values ranging from 9.2 to 11.8 at the inflection point within different concrete samples can be reported. Examples are presented in Figure 6 and can also be extrapolated from Figure 5 in which the pH of the PHPHT inflection point varies from 11.5, 9.2 and 11.2 for the samples left, middle and right, respectively.

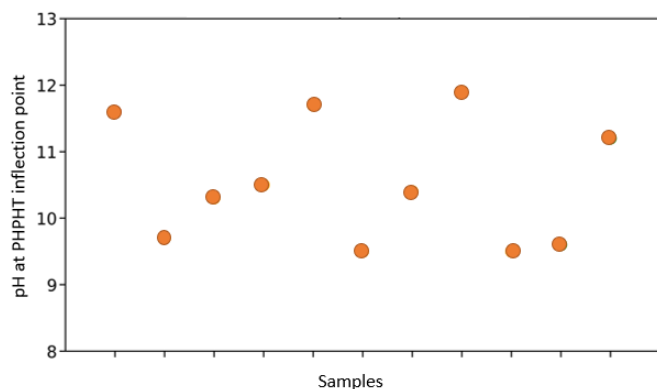


Figure 6 pH at which PHPHT colour transition took place within different concrete samples.

In order to understand in detail, the role of individual physicochemical material properties and exposure conditions on the pH at which PHPHT colour transition occurs, a systematic laboratory study is currently in progress. Relevant outcomes will be presented at the conference.

4 Conclusions and Outlook

Described findings are highly relevant in respect to the overall assessment of corrosion potential due to carbonation of concrete structures and to increase the fundamental understanding of carbonation-related alteration mechanisms. Major findings of the presented field study can be summarized as follows:

- The carbonation depth assessment via PHPHT spraying and the optical imaging technique show an overall good agreement.
- High differences in absolute pH within the carbonated zones, ranging from 9 to 11, were observed. Reasons therefore are differences in physicochemical material properties and corresponding individual material response to carbonation progress.
- High variations in pH (between 9.2 and 11.8) at which PHPHT colour transition proceeds were observed.

Results strongly argue for a general reconsideration of the definition of an absolute carbonation depth and moving towards a classification based on carbonation degrees of individual concrete materials.

References

- [1] A. Behnood, K. Van Tittelboom, N. De Belie, Methods for measuring pH in concrete: A review, *Constr. Build. Mater.* 105 (2016) 176–188. <https://doi.org/10.1016/j.conbuildmat.2015.12.032>.
- [2] I. Bergman, Rapid-Response Atmospheric Oxygen Monitor Based on Fluorescence Quenching, *Nature*. 218 (1968) 396–396.
- [3] C. Staudinger, J. Breininger, S. Borisov, I. Klimant, Aza-BODIPY based pH indicators with purely PET based quenching mechanism, *Analyst*. submitted (2018).
- [4] C. Grengg, B. Mueller, C. Staudinger, F. Mittermayr, J. Breininger, B. Ungerböck, S. Borisov, T. Mayr, M. Dietzel, Optical pH imaging of concrete exposed to chemically corrosive environments, *Cem. Concr. Res.* 116 (2019) 231–237. <https://doi.org/10.1051/mateconf/201819902007>.
- [5] B. Müller, C. Grengg, V. Schallert, M. Sakoparnig, C. Staudinger, J. Breininger, F. Mittermayr, B. Ungerböck, S. Borisov, M. Dietzel, T. Mayr, Wide - range optical pH imaging of cementitious materials exposed to chemically corrosive environments, *RILEM Tech. Lett.* 3 (2018) 39–45. <https://doi.org/10.21809/rilemtechlett.2018.72>.
- [6] I. Galan, B. Müller, L.G. Briendl, F. Mittermayr, T. Mayr, M. Dietzel, C. Grengg, Continuous optical in-situ pH monitoring during early hydration of cementitious materials, *Cem. Concr. Res.* 150 (2021) 106584. <https://doi.org/10.1016/j.cemconres.2021.106584>.
- [7] L.G. Briendl, C. Grengg, B. Müller, G. Koraimann, F. Mittermayr, P. Steiner, I. Galan, In situ pH monitoring in accelerated cement pastes, *Cem. Concr. Res.* 157 (2022) 106808. <https://doi.org/10.1016/j.cemconres.2022.106808>.
- [8] C.R. Schröder, B.M. Weidgans, I. Klimant, pH Fluorosensors for use in marine systems, *Analyst*. 130 (2005) 907. <https://doi.org/10.1039/b501306b>.
- [9] Z. Shi, B. Lothenbach, M.R. Geiker, J. Kaufmann, A. Leemann, S. Ferreira, J. Skibsted, Experimental studies and thermodynamic modeling of the carbonation of Portland cement, metakaolin and limestone mortars, *Cem. Concr. Res.* 88 (2016) 60–72. <https://doi.org/10.1016/j.cemconres.2016.06.006>.