

Durability of cement-based materials in drinking water storage

M. Schwotzer

Karlsruhe Institute of Technology (KIT), Institute of Functional Interfaces (IFG), Eggenstein-Leopoldshafen, Germany

A. Gerdes

Karlsruhe Institute of Technology (KIT), Institute of Functional Interfaces (IFG), Germany and University of Applied Sciences Karlsruhe, Institute for Prevention in Construction, Karlsruhe, Germany

ABSTRACT

In order to provide a hygienic storage drinking water reservoirs have been coated with mineral mortar linings in all epochs of European history. However, modern cement-based materials often show in this special operational environment an inadequate durability. Even though drinking water is commonly not considered particularly harmful to cementitious systems, the chemical degradation of mortar linings in drinking water storage systems can occur very fast compared to other common deterioration reactions. This results in cost intensive repair measures and thus high life-cycle costs as well associated with an ecological burden. Furthermore, an insufficient understanding of degradation mechanisms and their underlying physical, chemical as well as biological processes currently impedes performance-oriented approaches to improve durability. In this regard a research project aims to unravel the potentially combined multiple deterioration mechanisms, integrating results of case studies and laboratory experiments. In this context a specific issue of this research activity is to evaluate the applicability of an accelerated degradation test that takes advantage of the impact of electrical fields on the stability of cement-based materials in permanent contact to aqueous environments. Laboratory experiments show, that such tests are suitable to compare the resilience against reactive transport processes of materials and to draw conclusions regarding their performance, illustrating material changes in terms of depth and time. Furthermore, the results indicate, that the transport properties of the rim zone of cement-based materials are regulating its sturdiness in aggressive aqueous environments. This approach appears therefore suitable for a performance assessment in material development and provides as well new impulses for quality control in practice paving the path for increased durability of materials applied in drinking water supply infrastructure.

Keywords: durability, cement-based coatings, drinking water storage, accelerated degradation

1.0 INTRODUCTION

The performance of infrastructure is of utmost importance for continued societal development. Nonetheless, the condition of the technical infrastructure is far from perfect. In this regard, major attention has to be paid to the durability of cement-based materials, as concrete is, the most widely and diversely used construction material. In their various application fields, cement-based materials are subject to a number of environmental and operational loads. Especially, the detrimental impact of aggressive aqueous environments on the stability of cementitious systems is among the most important factors that affect durability. Resulting damages lead to cost intensive repair measures as well as increased life-cycle costs and are further associated with an ecological burden. Apparent examples are concrete structures of the transport infrastructure exposed to the impact of de-icing agents or offshore buildings and wastewater treatment plants that are permanently exposed

obviously harsh aqueous environments. In such cases, chemical attacks can endanger the continued functionality by means of structural damages. However, in the case of the drinking water supply infrastructure, the distinguishing features of the functionality are more differentiated, as e.g. surface properties of the materials determine the performance regarding hygienic aspects in water storage. Thus, drinking water reservoirs have been coated with mineral mortar linings in all epochs of European history, in order to promote a hygienic water storage. Nowadays, due to their high alkaline characteristics, cement-based materials are commonly considered as most suitable for this purpose. They are frequently used because flat "easy-to-clean" surfaces showing a low bioreceptivity can be produced with them. Furthermore, they are used to provide an efficient sealing of the concrete structures, e.g. in repair measures. As tap water is commonly not considered particularly harmful for cement-based materials (DIN 4030-1, 2008) concerns regarding the durability of

these systems were not present in the past decades. Thus, only minor attention has been paid to the material performance of such mortar linings. As a result since the 1990ies, a noteworthy number of cases has been reported in which “modern” cement-based materials, subjected to the special operational environment of tap water storage, showed an inadequate durability (e.g. Gerdes & Wittmann, 1992 or Schwotzer & Gerdes, 2009). The material degradation showed up particularly unusual damage symptoms and was denoted as hydrolytic corrosion (Wittmann, 1997). The hydrolytic corrosion becomes visible by coloured spots (Fig. 1a). In these areas, the cementitious binder is completely disintegrated (Fig. 1b). This chemical degradation is featured by an extensive depletion of the $\text{Ca}(\text{OH})_2$ -inventory concomitant to a significant increase of the CaCO_3 -content (Fig. 1c) and an attack on the C-S-H phases. The velocity of this reaction is remarkably high. In some cases, the degradation reaches a depth of several mm after a service life of a few months.

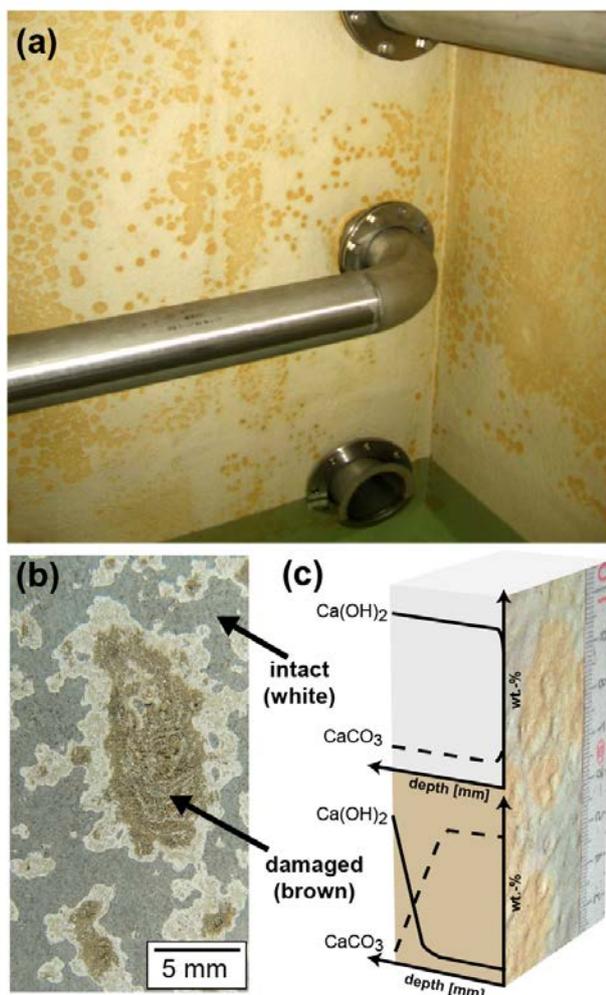


Fig. 1. Characteristic appearance of the hydrolytic corrosion on the wall of a tap water reservoir showing up as coloured areas (a), with a strictly local manifestation of a degradation of the binder (b), and resulting in significant chemical and mineralogical changes (c)

The fundamental reaction mechanism was recently elucidated, comprehending it as a two-step reaction (Schwotzer *et al.*, 2010). The process starts with an initial damage resulting from the impact of condensate on the materials surface at a young material age. It is followed by an extensive degradation due to an “underwater carbonation” resulting from a permanent exposure to tap water during the operational phase of the tap water reservoir. Generally, the fundamentals of the hydrolytic corrosion are transport processes of dissolved ionic species, resulting in changes of the chemical equilibria between the solid phases and the pore solution. This is commonly referred to as reactive transport (Moranville *et al.*, 2004). Particularly in this case, a wide range of characteristics of the use scenario has been investigated regarding their potential impact on the deterioration process. Among them topics such as the influence of electrical effects present on the reinforcement and stainless steel installations in the reservoirs (Wittmann, 1997) and the relevance of microbiological activities for the material degradation have been discussed (Herb, 1999). These manifold aspects are suspected to contribute to reactive transport processes and therefore promote deterioration processes. To cope with this issue in practice the design of more durable materials and application techniques is mandatory. For this, performance-oriented approaches are essential to improve durability. Indeed, a comprehensive understanding of the load scenario including the underlying physical, chemical as well as biological processes has to be targeted by fundamental research. However, just as important is applied research focusing on a reliable assessment of the material performance. In this context, it is the aim of this study to investigate and establish an adequate methodology to characterize the resilience of cement-based materials against reactive transport processes and therefore aggressive aqueous environments. This test takes advantage of the accelerating impact of electrical fields on material degradation due to reactive transport processes (e.g. Castellote *et al.*, 2002). This approach appears admissible, because the causes for the chemical stresses, which the cement-based materials in tap water storage have to withstand (e.g. the hydrolytic corrosion), are essentially reactive transport processes. Such accelerated degradation tests were investigated in the past decades in order to study the long-term behaviour of cement-based materials (e.g. Faucon *et al.*, 1998 and Saito & Deguchi, 2000). Thus, this study will provide proof of concept of a performance assessment by means of a comparative study adapting such an accelerated degradation test. In this regard, the impact of the electrical fields on the chemical composition and relevant material properties as porosity and pore size distribution was investigated. Furthermore, the material changes were monitored time-resolved as a function of depth. In order to investigate the applicability, mortar samples differing in the

water/cement ratio (w/c) and, therefore, in the porosity and pore size distribution, have been subjected to this testing procedure. This contribution presents selected results from this research activity.

2.0 MATERIALS AND METHODS

2.1 Experimental setup

The experimental setup for the accelerated degradation test is schematically shown in Fig. 2. The test chamber consisted of two polyvinyl chloride (PVC) tubes, capped with PVC disks. A PVC disk placed in the centre of the setup is dividing the two tubes in separate chambers. The mortar sample is placed in a hollow cylinder with a diameter of 9 cm in this middle disk, pasting it into the PVC frame using a silicone adhesive compound. Water of two different supply cycles flows through the two separated chambers in order to simulate the continuous exchange of water in a tap water reservoir. The outer capping disk is equipped with a feedthrough for electrodes. In each of the chambers, stainless steel electrodes are located equidistant (4 cm) to the surface of the mortar sample. The electrode setup is comparable to parallel-plate capacitor. A constant d.c. voltage is applied to the electrodes by an electronically controlled voltage supply system.

The mortar samples were prepared using a commercially available dry mix mortar based on white Portland cement with carbonate and quartz aggregates, containing as well a minor amount of silica fume. The samples were prepared applying w/c ratios of 0.43 and 0.52, respectively. After an initial curing for one day with a plastic foil, the samples were demolded and stored for further curing for 28 days in hard tap water (17°dH). Cores with a diameter of 90 mm were drilled from the slabs, adapted to be introduced in the middle PVC-frame of the test chambers.

The mortar samples were exposed to a continuous flow of hard tap water over a time period of 70 days. Samples were taken after 28 days and 70 days from the cathode side of the mortar disk.

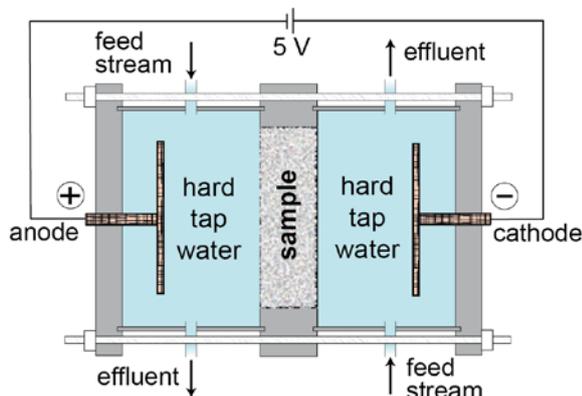


Fig. 2. Schematic representation of the experimental setup

The samples were cut in mm steps by means of a precision saw. The experiment was conducted in two different modes, one with an applied d.c. voltage of 5 V, another without a connection to the voltage supply (0 V).

2.2 Analytical methods

The thermogravimetric determination of the Ca(OH)_2 content was performed with a TGA/SDTA 851 system from Mettler-Toledo applying a heating rate of $10^\circ\text{C}/\text{min}$ under a N_2 atmosphere. The investigation of the total porosity and pore size distribution were done using Mercury intrusion porosimetry (MIP), by means of POROTEC Pascal 140 and 440 system. The samples were dried for 48 hours at 50°C and measured up to a maximum pressure of 200 MPa.

3.0 RESULTS AND DISCUSSION

The recent increase of problems regarding the durability of cement-based mortar linings in tap water storage and distribution systems generates a need for action. In this context, performance oriented material developments as well as tools for quality control can contribute to a sustainable development. For this purpose, a reliable assessment of the performance of cement-based materials is essential. As the hydrolytic corrosion is caused by reactive transport processes, an accelerated degradation triggered by the impact of electrical fields represents a plausible approach for the evaluation of the resilience of cement-based systems (Castellote, 2003). In particular the presence of electrical fields is supposedly associated with the evolution of the damage in practice (Wittmann & Gerdes, 1995 and Wittmann, 1997). However, this concept was mainly applied to characterize leaching processes in demineralized water as reported in (Castellote, 2013). Thus, in view of a performance testing, the impact of the operational environment has to be addressed by a customized experimental setup. Therefore, the exposure tests have been performed with hard tap water, creating a chemical scenario in which the hydrolytic corrosion was mostly observed in practice.

The results of the determination of the Ca(OH)_2 content as a function of depth after 28 and 70 days exposure to hard tap water in the electrical-field-test-cells are shown in Fig. 3. In the test setup without the impact of an electrical field (0 V), almost all measurements show no significant difference compared to the reference (Fig. 3a and 3c). Only the mortar with the high w/c ratio showed after 70 days a slight decrease of the Ca(OH)_2 content (Fig. 3c). In contrast to this, the exposure to 5 V leads to an extensive decrease of the Ca(OH)_2 content for both mortar samples. This illustrates clearly, that the impact of the reactive transport triggered by the electrical field is advancing over

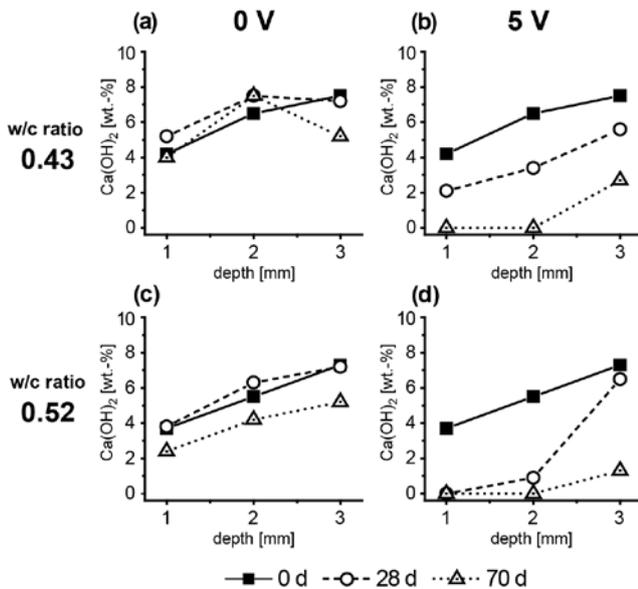


Fig. 3. Ca(OH)₂ content after 28 and 70 days as a function of depth for the mortar samples prepared with a w/c ratio of 0.43 and 0.52, respectively; without the impact of an electrical field (left) and with 5 V (right)

time from the material surface into deeper areas. The test reveals clearly, that the mortar with the lower w/c ratio appears definitely more robust against reactive transport processes due to a less extensive depletion of Ca(OH)₂ over time.

The investigation of the pore structure over time underpins these observations. Table 1 compiles the results of the determination of the total porosity of both mortar samples. As expected, the values for the total porosity of the mortar with a w/c ratio of 0.43 is significantly lower than the porosity of the mortar with w/c ratio of 0.52. The exposure in the testing cells without an applied tension (0 V) shows only a slight increase of the total porosity. In contrast to this, the exposure to hard tap water under the influence of 5 V causes a distinct increase of porosity, concomitant to the extensive depletion of Ca(OH)₂. This process proceeds significantly faster in the less dense material prepared with a w/c ratio of 0.52.

Table 1. Results of the determination of the total porosity based on MIP measurements

w/c ratio	depth (mm)	reference 0 days porosity (vol.-%)	0 V 70 days porosity (vol.-%)	5V 70 days porosity (vol.-%)
0.43	1	10.7	13.9	24.9
	2	12	9.4	16.4
	3	10.4	13.2	11.6
0.52	1	8.1	12.3	27.4
	2	14.5	15.8	20.4
	3	16.3	14.1	15.2

This is confirmed by the examination of the related pore size distributions (Fig. 4). Confronting the results of the reference (Fig. 4a and b) with the 70-day-results without an applied voltage (Figs. 4b and e), it appears that pore size distribution remains comparable for both mortars. However, the results for pore size distributions of the experiment with an applied voltage of 5 V (70 days) reveal a significant increase of capillary pores, that must be attributed to the disappearance of Ca(OH)₂ as stated in literature (Haga *et al.*, 2005). Furthermore, a significant impact on the gel pore system (pores < 0.03 μm) became apparent (Figs. 4c and f). This is supposed to be the result of an attack on the C-S-H gel decreasing the Ca/Si ratio, as suggested in literature (Thomas *et al.*, 2004). Again, it can be seen that the process for the material prepared with a w/c ratio of 0.52 has advanced much further compared to the other material (w/c ratio 0.43) after a test duration of 0 days. The impact on the μ-structure in the experiment performed with the denser mortar (w/c ratio 0.43) after 70 days only the first mm was affected (Fig. 4c), whereas the mortar with the w/c ratio of 0.52 shows already significant changes in the second mm (Fig. 4f).

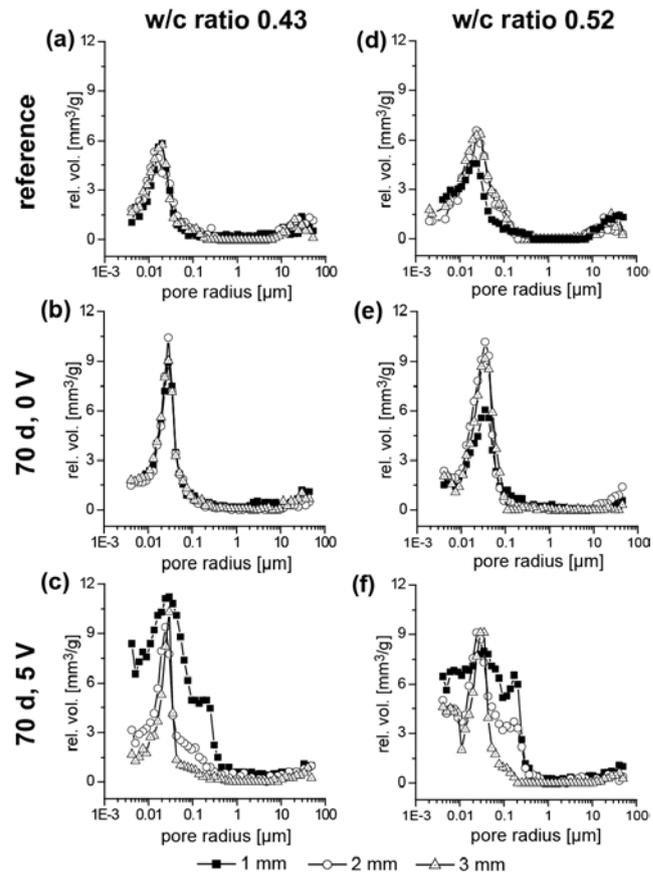


Fig. 4. Depth profile of the pore size distributions for the mortar samples with a w/c ratio of 0.43 and 0.52 of the reference sample (a) and (d), exposed for 70 days without the impact of an electrical field (b) and (e), and exposed to a potential difference of 5 V (c) and (f)

Thus, the results of this study show, that an accelerated degradation of cement-based materials by the application of electrical fields allows a comparison between different cement-based materials, subjected to the impact of tap water, regarding their resilience against reactive transport processes. Therefore, an accelerated degradation test, as described in this study, appears as a promising tool for the performance assessment in particular for operational load scenarios, as present in the water supply infrastructure.

4.0 CONCLUSIONS

In order to contribute to a sustainable development in construction, a reduction of the total life cycle cost by means of an increased durability is mandatory. Indeed, a sophisticated requirement analysis for construction materials, addressing all the relevant load scenarios in detail, defines the destination route for performance-oriented innovations. However, the counterpart in this context is a reliable test procedure to confirm the performance of a material, e.g. in terms of resilience against chemical attacks by reactive transport processes. The results of this study show that an accelerated degradation test by means of electrical fields provides a valuable tool to perform a comparative assessment of the resilience of cement-based materials against reactive transport processes, in particular regarding the specific load scenarios that cement-based materials have to withstand during their use in tap water supply infrastructure. For an evaluation of the performance of materials with different properties, it is essential to investigate the impact of aggressive environments as a function of depth over time. Moreover, as the properties of the cement-based materials, and thus their resilience against chemical attacks, mostly develop after the application on the construction site, appropriate quality control concepts are needed in practice. Also in this context, concepts based on such accelerated degradation tests may represent promising approaches.

References

- Castellote, M. *et al.*, 2002. Synchrotron Radiation Diffraction Study of the Microstructure Changes in Cement Paste due to Accelerated Leaching by Application of Electrical Fields. *Journal of the American Ceramic Society*, 85(3):631-635.
- Castellote, M. *et al.*, 2003. Accelerated leaching of ultra high performance concretes by application of electrical fields to simulate their natural degradation. *Materials and Structures*, 36(2):81-90.
- Castellote, M., 2013. Tests for Leaching and Degradation in Soft or Carbonated Waters. *Performance of Cement-Based Materials in Aggressive Aqueous Environments*, Alexander, M., Bertron, A. and Belie, N. D., (Eds.), RILEM State-of-the-Art Reports; Springer Netherlands, pp. 235-250, (2013)
- DIN, 2008. Assessment of water, soil and gases for their aggressiveness to concrete - Part 1: Principles and limiting values, in German. DIN 4030-1:2008-06
- Faucon, P. *et al.*, 1998. Water attack of a cement paste: towards an improved accelerated test?. *Advances in Cement Research*, 10(2):67-73.
- Gerdes, A., Wittmann, F. H., 1992. Electrochemical Degradation of Cementitious Materials. *Proceedings of the 9th International Congress on the Chemistry of Cement*, New Delhi.
- Haga, K. *et al.*, 2005. Change in pore structure and composition of hardened cement paste during the process of dissolution. *Cement and Concrete Research*, 35(5):943-950.
- Herb, S., 1999. Biofilmbildung auf mineralischen Oberflächen in Trinkwasserbehältern. *Berichte aus Wassergüte- und Abfallwirtschaft*, Vol. 149, Technical University Munich, Germany, PhD thesis, in German.
- Moranville, M. *et al.*, 2004. Physicochemical equilibria of cement-based materials in aggressive environments -experiment and modeling. *Cement and Concrete Research*, 34(9):1569-1578.
- Saito, H., Deguchi, A., 2000. Leaching tests on different mortars using accelerated electrochemical method. *Cement and Concrete Research*, 30(11):1815-1825.
- Schwotzer, M. *et al.*, 2010. Protective or damage promoting effect of calcium carbonate layers on the surface of cement based materials in aqueous environments. *Cement and Concrete Research*, 40(9):1410-1418.
- Schwotzer, M., Gerdes, A., 2009. Durability of cement based materials in contact with drinking water. *RILEM Proceedings PRO 63, Concrete in Aggressive Aqueous Environments - Performance, Testing, and Modeling*, Alexander, M. G. & Bertron, A. (Eds.), Toulouse, France, pp. 125-132.
- Thomas, J.J. *et al.*, 2004. Effects of decalcification on the microstructure and surface area of cement and tricalcium silicate pastes. *Cement and Concrete Research*, 34(12):2297-2307.
- Wittmann, F.H., 1997. Corrosion of Cement-Based Materials under the Influence of an Electric Field. *Materials Science Forum*, 247:107-126.
- Wittmann, F.H., Gerdes, A., 1995. Beständigkeit zementgebundener Beschichtungen unter dem Einfluss elektrischer Felder. *Internationale Zeitschrift für Bauinstandsetzen*, 1:73-86.

