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Protective or damage promoting effect of calcium carbonate layers on the surface of cement based materials in aqueous environments

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ABSTRACT

Cement based materials permanently exposed to aggressive aqueous environments are subject to chemical changes affecting their durability. However, this holds also for tap water that is considered to be not aggressive to cementitious materials, although in that case a formation of covering layers of $CaCO_3$ on the alkaline surfaces is commonly supposed to provide protection against reactive transport processes.

Thus, investigations of the structural and chemical properties of the material/water interface were carried out in laboratory experiments and case studies to elucidate the consequences of surface reactions for the durability of cement based materials exposed to tap water. Focused Ion Beam investigations revealed that a protective effect of a $CaCO_3$ covering layer depends on its structural properties, which are in turn affected by the hydro-chemical conditions during crystallization. Surface precipitation of $CaCO_3$ can trigger further chemical degradation, if the required calcium is supplied by the pore solution of the material.

1. Introduction

In the past, numerous investigations were performed to predict the long term behavior of cement based materials exposed to various environmental factors in order to evaluate the aggressivity of a surrounding aqueous environment. The long term stability of cement based materials in permanent contact to aqueous solutions is determined by reactive transport processes. By means of diffusive transport the composition of the pore solution will be changed affecting in turn the chemical equilibrium between the pore solution and the solid phases of these materials. Dissolution as well as crystallization reactions are the consequences, leading to a change of the pore structure [1]. The chemical reactions influence the transport. Conversely, transport processes influence local equilibria which in turn impact the chemical reactions. This is referred to as reactive transport (e.g. [2]). This process is supposed to be determined by the properties of the pore structure of the material [3,4]. For the deduction of reaction mechanisms and predictive models commonly long term observations with a time scale ranging from weeks to years are the basis. However, chemical changes occur at the material/water interface starting immediately after coming in contact with the potentially aggressive aqueous environment. Sometimes a potential relevance of the properties of the material water interface for the chemical resistance against reactive transport is mentioned. For instance regarding sulphate attack by aqueous solutions containing Mg-sulphate it was suggested, that the precipitation of a $Mg(OH)_2$ surface layer significantly accounts the reactive transport processes [5]. In particular, in carbonate rich water a dense surface layer of $CaCO_3$ is deposited on the alkaline surface of cement based systems [6]. Especially in contact with hard, carbonate rich water it is concluded that the dense surface layer greatly constrains the transport which slows the leaching process [2,7]. In this regard it has often been mentioned that such carbonate covering layers are important factors for the long term stability of cementitious systems. However, structural as well as chemical changes in the material/water interface and their role for the progress of degradation reactions — e. g. in the context of the reliability of leaching test — are still debatable [8,9].

In this context observations made in the past years on cementitious mortar linings of tap water reservoirs are of a noticeable relevance. The water stored in these reservoirs at temperatures below 10 °C is saturated with respect to calcite and is relatively hard (>3.5 mmol/L CaO). This water is considered not to be aggressive to concrete [10] and should encourage the development of a transport inhibiting $CaCO_3$ layer on the surface of these cementitious mortar linings. Although $CaCO_3$ layers have accumulated on the whole surface of the mortar lining, circular and often brown shaded damage areas are to be found where the material has locally lost its mechanical strength (Fig. 1a, b). In some cases the damaged areas exhibit regular patterns on the material surface (Fig. 1c).

The damage becomes apparent through a local degradation of the $Ca(OH)_2$ and the CSH gel as well as an increase in the $CaCO_3$ content, which would not be the case exhibited by leaching under ideal conditions, and in the absence of carbon dioxide [11]. Of significant relevance is the high rate of degradation. In a slew of cases these patches with a degradation

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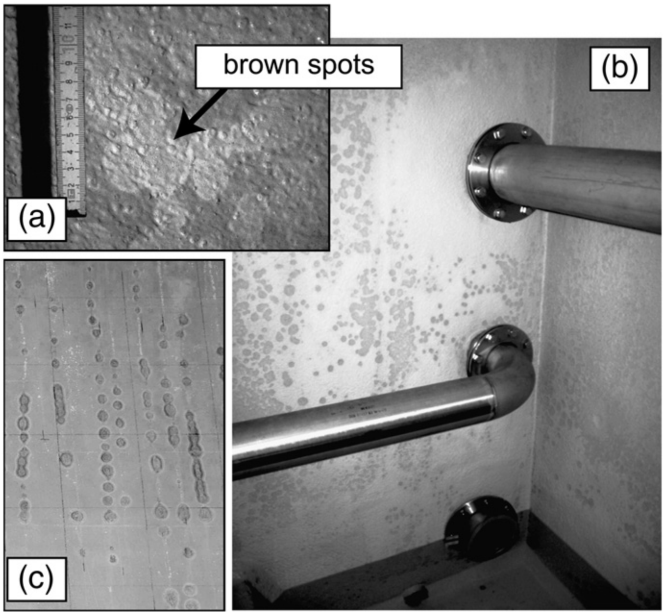


Fig. 1. Characteristic damage patterns on mortar linings in tap water reservoirs as a consequence of local hydrolytic corrosion.

depth of several millimetres were ascertained already six months after application.

In order to elucidate the damage mechanisms of this particular type damage — denoted as local hydrolytic corrosion [12] — on cementitious materials, several research projects were performed [12–14]. This research did not lead to a generally accepted understanding of hydrolytic corrosion [15]. Especially the reasons for the local formation of the patches have remained unclear. In spite of the area-wide carbonate covering of the material, reactive transport processes seem to proceed with locally differing reaction velocities, suggesting the existence of local differences of the transport properties of the materials. In order to characterize these local differences in the resistance against reactive transport processes an investigation program was set up with special focus on the interrelationship between the interactions at the cement paste/water boundary and the macroscopic appearance of the local hydrolytic corrosion. Therefore detailed investigations on samples from case studies were performed to correlate the surface properties of the material with the proceeding of the degradation reaction.

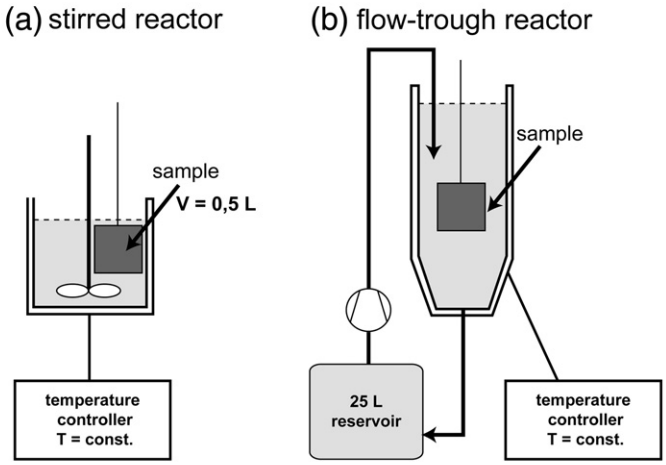


Fig. 2. Scheme of the laboratory experiments, performed both, with carbonate-rich tap water and demineralized water, respectively; a) exposition of the cement slices in a stirred reactor without water exchange and b) exposition of the cement slices in a continuous-flow reactor.

Table 1
Composition of the used water (n.s.: not specified).

Parameter	Demin. water	Tap water	Unit
pH value	6.0	7.5	–
Conductivity (20 °C)	0.52	530	µS/cm
Hardness	n. s.	2.2	mmol/L CaO
Saturation index ($CaCO_3$, 25 °C)	−7.5 [16]	0.32 [16]	–
Saturation index ($Ca(OH)_2$, 25 °C)	−17.5 [16]	−10.7 [16]	–
Calcium	<0.01	89.1	mg/L
Magnesium	<0.01	10.8	mg/L
Sodium	<0.01	17	mg/L
Potassium	<0.01	3.2	mg/L
Chloride	<0.01	30	mg/L
Nitrate	<0.01	1.8	mg/L
Sulfate	<0.03	56.7	mg/L

Additionally laboratory experiments were performed in order to elucidate the processes occurring at the material/water interface by means of exposure to water differing in composition, hard tap water and demineralized water, respectively. The results of this investigation and the resulting findings concerning the reaction mechanism will be introduced here along with their meaning for the long term stability of cementitious materials.

2. Materials and methods

2.1. Samples from case studies

To characterize the damage under real conditions, core samples of the affected mortar were taken from tap water reservoirs. For the

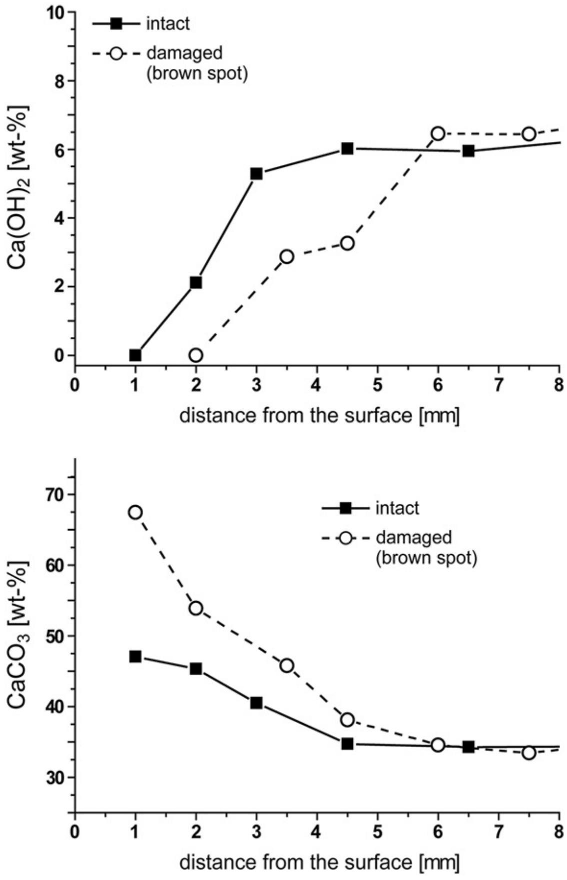
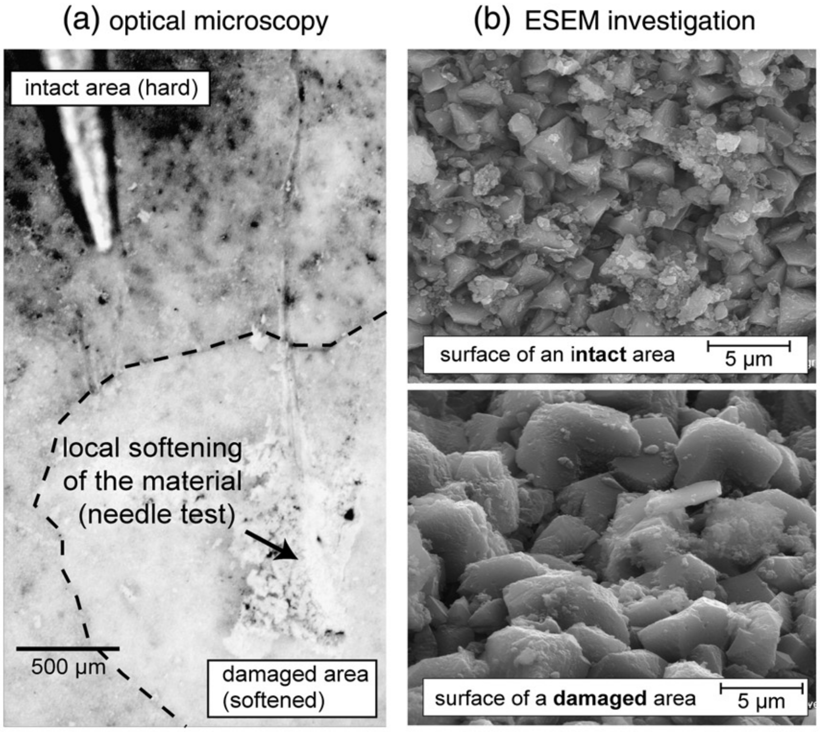


Fig. 3. $Ca(OH)_2$ and $CaCO_3$ content as a function of the distance to the surface for samples from tap water reservoirs.



(a) optical microscopy

(b) ESEM investigation

(c) ESEM and EDX investigation of a FIB cut

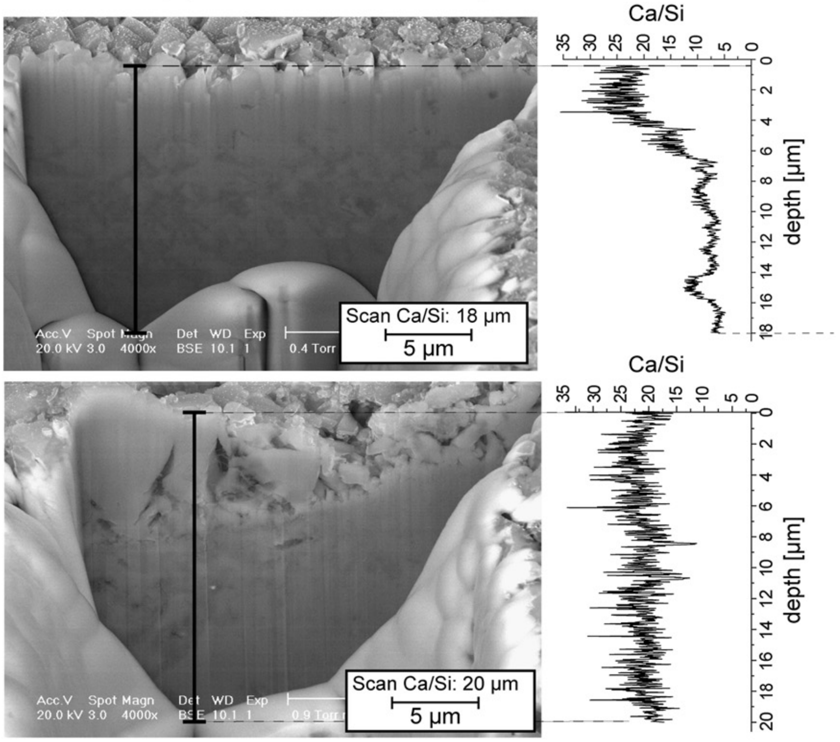


Fig. 4. Results of the microscopic investigation in the material/water interface of mortar samples with features of local hydrolytic corrosion and spatial Ca/Si ratios by means of EDX line scans in intact and damaged area of the surface; (a) overview by means of optical microscopy, (b) ESEM images of the sample surface, and (c) ESEM images and EDX measurements on FIB profile cuts.

investigation of the chemical characteristics of the hydrolytic corrosion, samples from an approximately one year old mortar lining have been taken from a tap water reservoir.

Detailed investigations of the properties at the material/water interface were performed on samples of another mortar lining some weeks after application showing already initial signs of hydrolytic corrosion. Intact and damaged areas have been identified and chosen by means of optical microscopy for further chemical analysis and electron microscopic investigations.

2.2. Preparation of samples for laboratory studies

For the exposure tests with cement pastes a commercially available white Portland cement (WPC) (CEM I 42.5 R) — a common binder for mortars for linings in tap water supply systems — was used to make prisms with a water to cement ratio of 0.4. For this, cement and water were mixed in a laboratory mixer and placed in 40 × 40 × 160 mm molds. The cement paste was compacted using a vibrating table. The prism molds were covered with a plastic foil and allowed to set over 24 h in a climate controlled chamber held at 20 °C and 65% relative humidity. After demolding they were stored for curing for 100 days in tap water under laboratory conditions (~20–25 °C). For the exposure tests 1 mm thick slices were taken from the middle of the prisms.

2.3. Experimental setup

The freshly cut cement paste slices were immediately placed in a reaction vessel permanently exposed to water with varying compositions. The samples were treated to different types of exposure (schematically shown in Fig. 2). The experiments were performed as an open system allowing the potential equilibration between the laboratory atmosphere and the aqueous solution, regarding the CO_2 uptake. In order to examine the effect of differences regarding the availability of carbonic acid species at the alkaline surface of the cement paste samples two types of exposure experiments were designed.

In one part of the experiment 0.5 L of solution was stirred intensively, in order to provide a major availability of carbonic acid species to the reactive surfaces of the cement paste samples (Fig. 2a). In another part of the experiment the samples in the reaction vessel were continuously rinsed using a solution from a 25 L tank that was continually re-circulated by 25 L of solution (Fig. 2b).

The tests were performed both with hard tap water and demineralized water, respectively, at a constant temperature of 11 °C. The chemical composition of the used water is shown in Table 1.

2.4. Analytical techniques

The quantification of the $Ca(OH)_2$ and $CaCO_3$ content was performed by means of thermogravimetry (TGA/SDTA 851, Mettler-Toledo) applying a heating rate of 10 °C/min under an N_2 atmosphere.

The investigation of the total porosity and properties of the pore system with respect to pore sizes were done using Mercury Intrusion Porosimetry (MIP), using a combination of POROTEC Pascal 140 and Pascal 440 machines. The samples were dried for 48 h at 50 °C and measured up to a maximum pressure of 200 MPa.

The Focused Ion Beam (FIB) preparation technique enables detailed investigations of surface reactions by means of electron microscopic methods. A scanning beam of Gallium ions is applied in order to remove material from the sample surface with a spatial precision in nanometer scale. In this way, depth profile cuts are performed in order to investigate depth dependant chemical and structural properties of the surface near areas. With Focused Ion Beam machines of the type Nova Nanolab 200 (FEI) and XBeam 1540-EsB (Zeiss) samples were prepared and analyzed. Further electron-microscopic analysis was performed with an ESEM type ESEM XL 30 FEG (Philips) equipped with an EDX system (EDAX).

3. Results

3.1. Characterization of localized hydrolytic corrosion in case studies

In the following chapter, the results of chemical properties and investigations of the material/water interface performed on mortar linings from tap water reservoirs that exhibit the macroscopic characteristics of local hydrolytic corrosion are presented. In order to investigate the extent and the development of the damaged areas, $Ca(OH)_2$ and $CaCO_3$ content was determined as a function of depth in 1 mm gradations on samples taken from a approximately one year old mortar lining. Afterwards a progressive degradation of $Ca(OH)_2$ as well as a significant rise in $CaCO_3$ was found in the water contacted surface zone up to a depth of 5 mm. In intact areas these changes in the chemical composition could only be shown in a depth of 2–3 mm (Fig. 3).

Detailed investigations of chemical and structural properties at the material/water interface have been performed on samples of a few weeks old mortar lining (Fig. 4). The sample showed initial signs of local hydrolytic corrosion. A slight local discoloration on the surface of the materials was noticeable and the optical microscopy investigations revealed a sharp boundary between the affected and the intact area (indicated by a dashed line) (Fig. 4a). In both cases — on the damaged areas as well as on the intact areas — electron microscopic investigations revealed the presence of a crystalline covering of $CaCO_3$ crystals on the surface of the cement mortars applied from tap water reservoirs (Fig. 4b).

In the intact areas the surface was covered with a dense and regularly developed layer of $CaCO_3$ crystals (Fig. 4c top). The surface of a damaged area only a few hundred microns away showed an irregular $CaCO_3$ crystal growth (Fig. 4c below). In both areas a Ca/Si ratio as a function of depth was calculated on EDX results. In the intact areas the investigations showed a Ca/Si ratio of approximately 20 only in the upper 5 µm. In this area the material consists mainly of $CaCO_3$, whereas the underlying material, with a Ca/Si ratio of approximately 10 implies the composition of an unaffected base mortar. This value is relatively high due the presence of $CaCO_3$ as filler in the investigated mortar samples. In the damaged area a molar Ca/Si ratio of

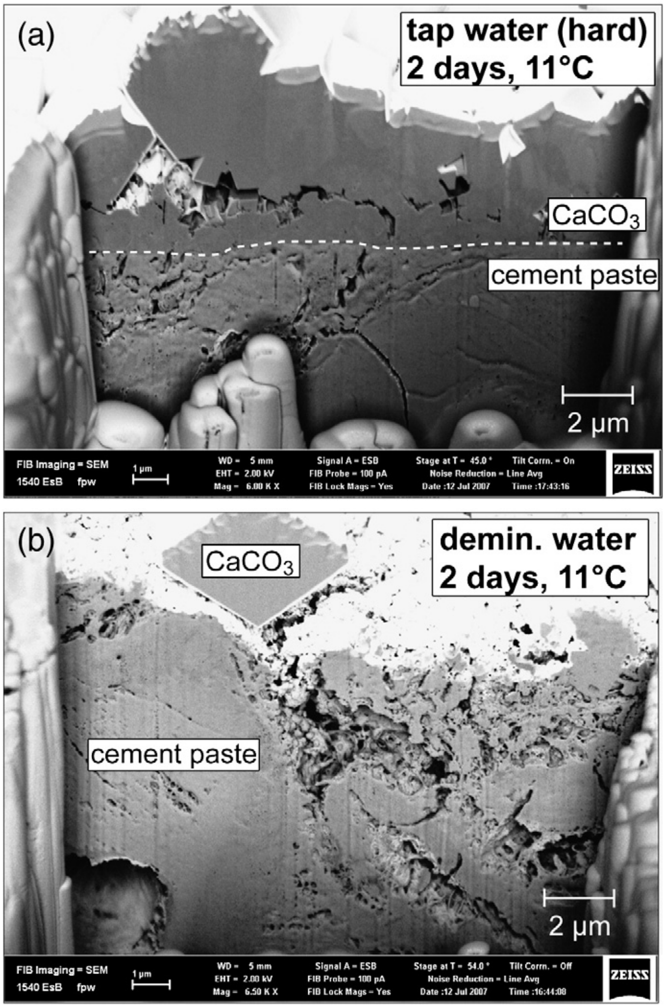


Fig. 5. Electron microscope photographs of FIB cuts in the cement paste/water interface of a sample immersed for two days at 11 °C in (a) hard tap water and (b) demineralized water.

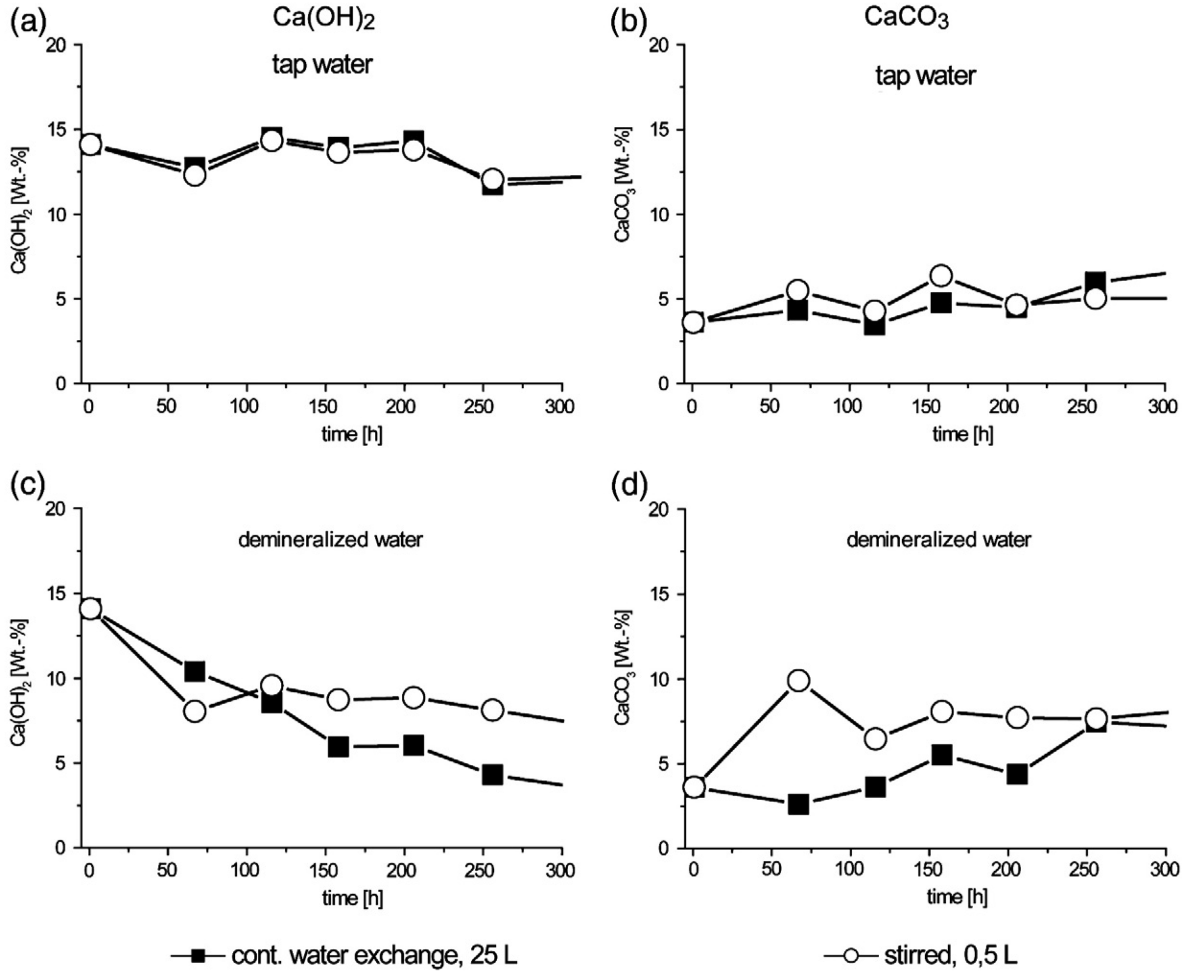


Fig. 6. $Ca(OH)_2$ (a, c) and $CaCO_3$ (b, d) content as a function of time for samples from the laboratory tests using tap water (a, b) and demineralized water (c, d), performed at 11 °C.

approximately 20 was found also beneath the rough crystalline cover layer (~0–20 µm), indicating a crystallization of $CaCO_3$ proceeding into deeper zones of the material.

3.2. Exposure tests with WPC paste in the laboratory

Fig. 5 shows the electron microscope photographs from FIB cuts in the water contacted surface zones of the exposed WPC slices. After two days of being exposed to hard tap water a dense covering layer of $CaCO_3$ crystals was observed (Fig. 5a). Under this sharp delineated covering layer (dashed line), no significant changes in the structure of the underlying cement paste could be observed. In contrast to the samples immersed in tap water, the samples exposed to demineralized water showed an irregular $CaCO_3$ crystallization. After two days of exposure in demineralized water the existence of a pore network with maximum pore sizes of several microns was observed directly under isolated $CaCO_3$ crystals (Fig. 5b).

In Fig. 6, the development of the $Ca(OH)_2$ and $CaCO_3$ content of the exposed specimens in the 0.5 L reactor vessel is shown over time. No significant changes in the $Ca(OH)_2$ and $CaCO_3$ content could be shown for the samples exposed with either method to hard tap water (Fig. 6a, b).

Using demineralized water a reduction of the $Ca(OH)_2$ content from 15 wt.% to 4 wt.% was observed (Fig. 6c). The experiment in the continually stirred 0.5 L reaction vessel showed a slower loss of $Ca(OH)_2$ than by continuous rinsing, and in the 300 h test duration a value of approximately 8 wt.% was measured. In this test the $CaCO_3$ content significantly increased within already 2–3 days (Fig. 6d).

After 10 days of exposure to tap water no significant change was found in the total porosity and in the deduced pore size estimation (Fig. 7a). After an exposure in demineralized water the total porosity rose from 10 vol.% to 25 vol.% in the stirred system and in the rinsed system to 35 vol.%. Both testing methods showed a development of a maximum in the deduced pore size estimation between 0.10 and 0.15 µm as well as a rise in the estimated relative pore volume for estimated pore sizes <0.03 µm (Fig. 7b).

Fig. 8 shows results of electron microscopic investigations of the surfaces of WPC samples after exposure to demineralized water after the two different exposure procedures. The electron microscope investigation of the surface of the WPC paste could not show a significant growth of $CaCO_3$ crystals on the samples that were exposed to rinsing with continuous water exchange using demineralized water (Fig. 8a–c). At the surface a development of micro cracks was visible (Fig. 8a) which continually broadened with time (Fig. 8b). The cross section shows a significant change in the cement paste structure up to a depth of approximately 100 µm (Fig. 8c).

The surface of the cement paste samples that were exposed to constant stirring in the 0.5 L reactor vessel featured a fine but not wholly covering growth of $CaCO_3$ crystals after three days (Fig. 8d). After ten days the surface was covered with an approximately 20 µm thick layer of $CaCO_3$ crystals (Fig. 8e, f). The crystal growth was fragmentary and showed no strong mechanical bond to the underlying cement paste substrate, but the thickness of the $CaCO_3$ layer was up to five times higher, than in the experiments with hard tap water.

Results of EDX examinations of the WPC paste samples after 10 days exposure to demineralized water and hard tap water using

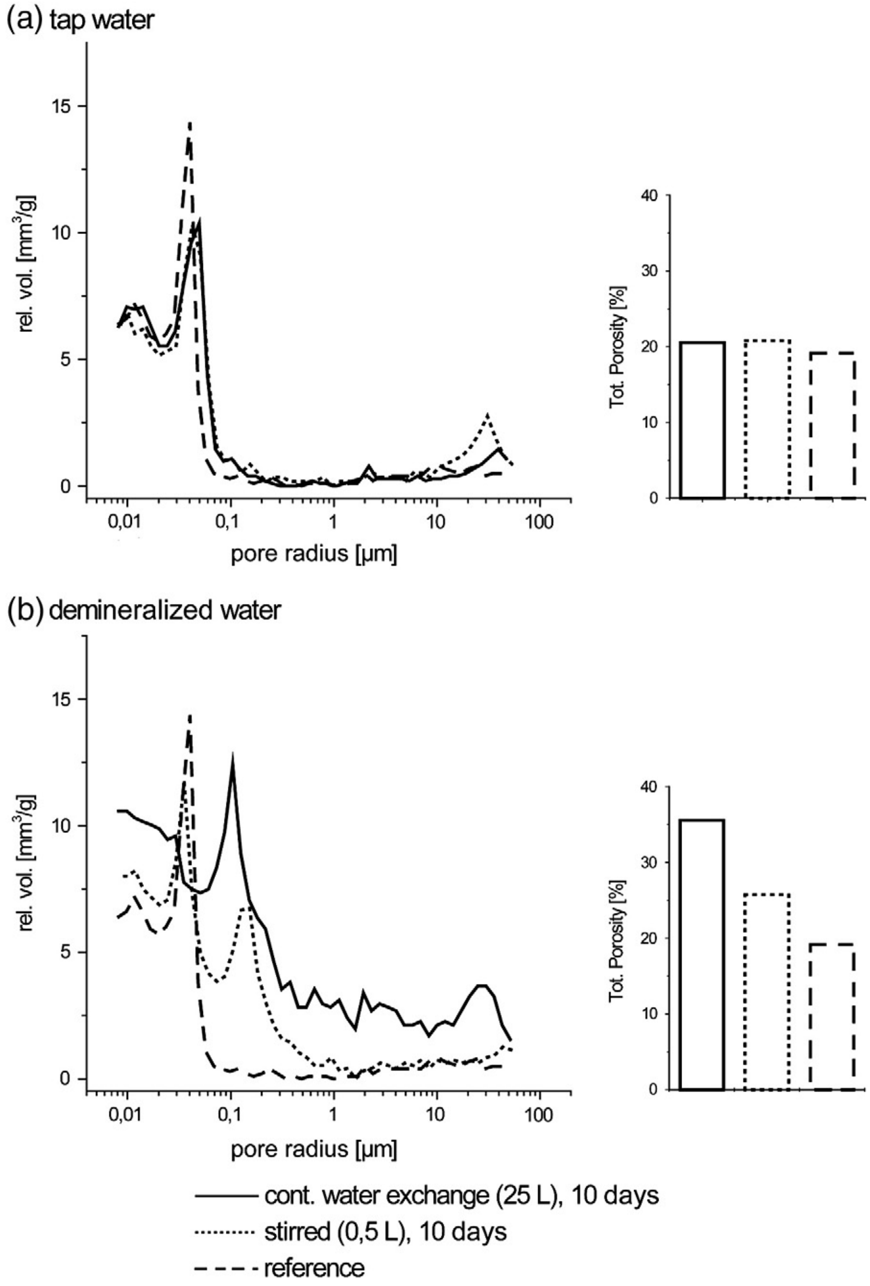


Fig. 7. Results of the MIP investigations for the examined laboratory specimens, exposed to (a) tap water and (b) demineralized water for 10 days at 11 °C.

the two different experimental setups are given in Fig. 9. The EDX mappings on cross sections of the cement paste slices exposed to tap water revealed that no significant loss of Ca occurred, even after ten days the 100 µm nearest to the surface showed no significant loss (Fig. 9, right). In contrast to that the samples exposed to rinsing with continuous water exchange in demineralized water showed a significant loss of Ca in a depth up to 100 µm. In the samples exposed to constant stirring in a 0.5 L reactor vessel with demineralized water a slight loss of the Ca content could be observed under the $CaCO_3$ surface deposits (Fig. 9, left, bottom).

4. Discussion

The results of the investigations on damaged and intact samples from tap water reservoirs (Fig. 1) show that reactive transport processes occur at varying velocity in the mortar linings. Despite the fact that the whole surface of the structure had contact with hard tap water over a period of several months during the use phase of the reservoir, the measured decrease of $Ca(OH)_2$ in the damaged areas (Fig. 2) reached a significantly greater depth than in the directly neighbouring intact area. At the same time a transport of HCO_3^-, leading to a progressive crystallization of $CaCO_3$ in deeper areas was observed in the damaged areas (Fig. 2).

On the other hand the laboratory experiments showed the expected transport inhibiting layer of $CaCO_3$ on the surface of the sample exposed to hard tap water (Fig. 5a). The transport inhibiting effect became evident within the 10 days of the experiment, as no significant change occurred in the chemical composition (Fig. 6a, b) or in the pore structure (Fig. 7a).

In contrast the rinsing with continuous water exchange with demineralized water from a 25 L reservoir, the leaching processes were dominant causing chemical changes (Fig. 6c, d) as well as significant damage to the micro structure (Fig. 7b). Besides the widening of the pore structure as a consequence of the leaching of $Ca(OH)_2$ from

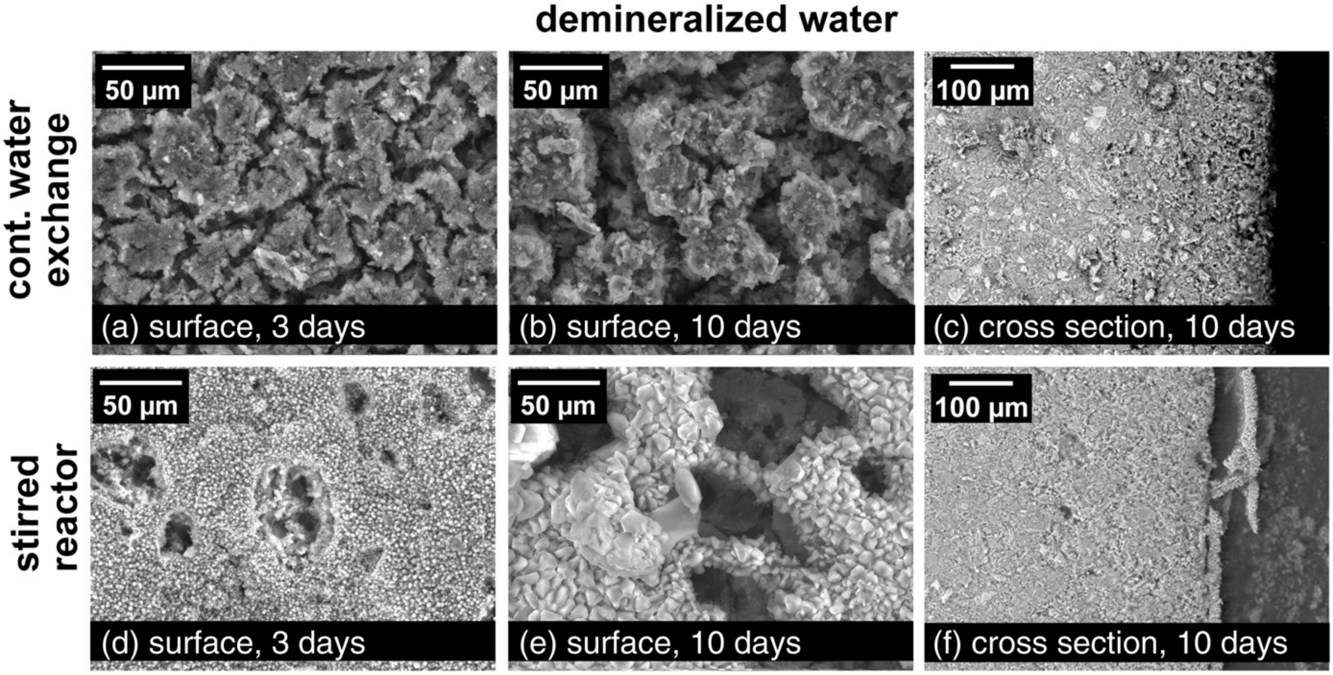


Fig. 8. Electron microscope photographs from the surface and cross sections of samples exposed to demineralized water. (a), (b), and (c) under continuous water exchange from a 25 L reservoir; (d), (e), and (f) under constant stirring in a 0.5 L reactor vessel.

the cement paste [1], micro cracks on the sample surfaces developed (Fig. 8a, b). Their appearance can be explained by the mechanism proposed by Chen et al. in [17] called "decalcification shrinkage". After the dissolution of $Ca(OH)_2$ in the surface zone a further attack on the CSH gel can occur [18] which leads to a decrease in volume [17,19]. The surface zone is affected by this mechanism greater than the deeper areas which leads to mechanical tensions which cause the formation of the observed micro cracks (Fig. 8a, b).

In the presence of carbonic acid species on the reactive surface area of the cement paste, as in the case of the laboratory experiment in the stirred 0.5 L reaction vessel with demineralized water, due to uptake of atmospheric CO_2, crystallization of $CaCO_3$ takes place (Fig. 8d–f). For the crystallization Ca^{2+} has to be drawn from the pore solution. Thereby the crystal growth on the material/water interface forces further reactive transport processes. Under continuous supply of HCO_3^- the growing layer of $CaCO_3$ promotes decalcification of the solid phases which induces further chemical and micro-structural changes affecting the interior of the material as well (Fig. 7b). As Ca^{2+} and HCO_3^- reach the growing crystal through diffusion, the fast development of a transport inhibiting surface layer of $CaCO_3$ is not unreservedly possible. Due to this mechanism the "front" in which the $CaCO_3$ crystallization is preferred shifts towards the interior of the material. In this case, the presence of $CaCO_3$ covering layers on cement based materials do not provide a protective effect against reactive transport processes, even if the thickness of the $CaCO_3$ covering layers built up by Ca supply from the pore water of the material can be much higher than the thickness of layers grown in hard tap water (Fig. 9). Under these conditions, a decrease in the diffusivity of the material as consequence of a decrease in porosity by surface precipitation of calcium carbonates [20] is not assumed to be plausible.

Considering practical applications this mechanism, schematically shown in Fig. 10, plays a special role when the boundary conditions are given in which the development of a condensed water film on the material surface is likely. Already during the application of mortar linings in tap water reservoirs condensate can easily form due to the low temperature and high relative humidity.

According to the mechanism described above local irreversible initial damage can be caused by the interaction between condensate and the mortar lining, especially when the applied mortar is fresh or young.

This process is additionally supported by the good solubility of CO_2 at low temperatures as well as the short diffusion path of the dissolved CO_2 in the condense water film.

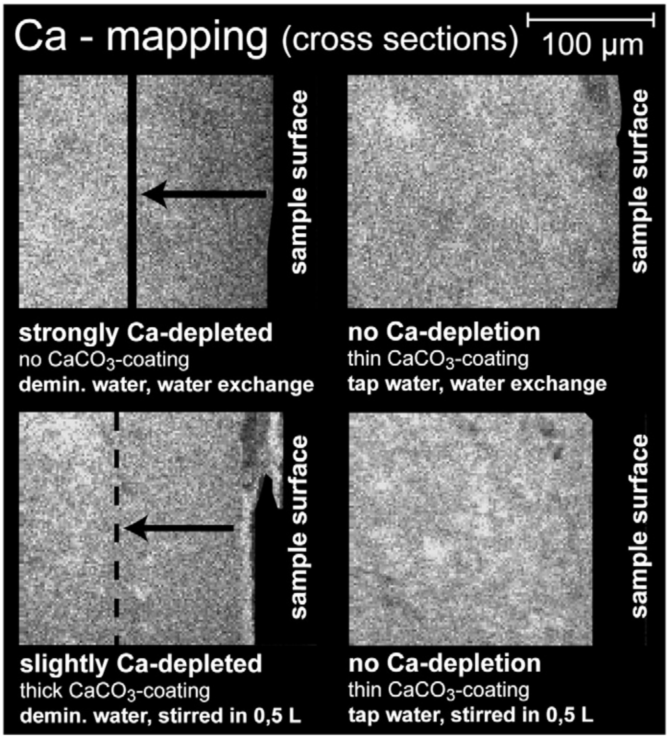


Fig. 9. EDX-mappings for the element Ca performed on cross sections of the cement paste slices exposed to both demineralized water (left) and tap water (right) under different exposure conditions, continuous water exchange (top) and stirred in a 0.5 L reaction vessel (bottom).

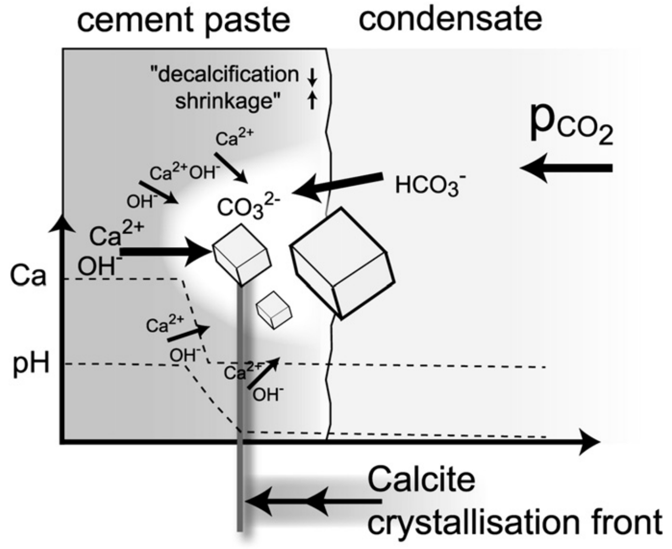


Fig. 10. Initial damage scheme on freshly applied cement based materials caused by reactive transport due to condensed water at low temperatures in the presence of CO_2.

During the operational phase of a tap water reservoir the cement based coating materials are exposed to contact with hard tap water. In areas initially damaged by reactive transport the transport processes can continue due to the increased porosity caused by leaching and the lack of a dense transport inhibiting protective $CaCO_3$ layer.

As a consequence of the initial damage, coming along with the shift of the $CaCO_3$ crystallization zone deeper into the interior, the development of the protective layer is hardly possible. The maintenance of this progressive $CaCO_3$ crystallization is determined by diffusion of components from the water (e. g. HCO_3^-). Thereby complex crystallization and dissolution processes permanently affect the chemical equilibria between pore solution and the different solid phases of the system. Therefore, after the attack on the $Ca(OH)_2$ the CSH gel will also be affected. In the intact areas directly adjoining the damaged areas, "decalcification shrinkage" causes the transport inhibiting $CaCO_3$ layers to detach. Therefore the damaged area can expand not only in depth but also laterally. This interrelationship is schematically shown in Fig. 11.

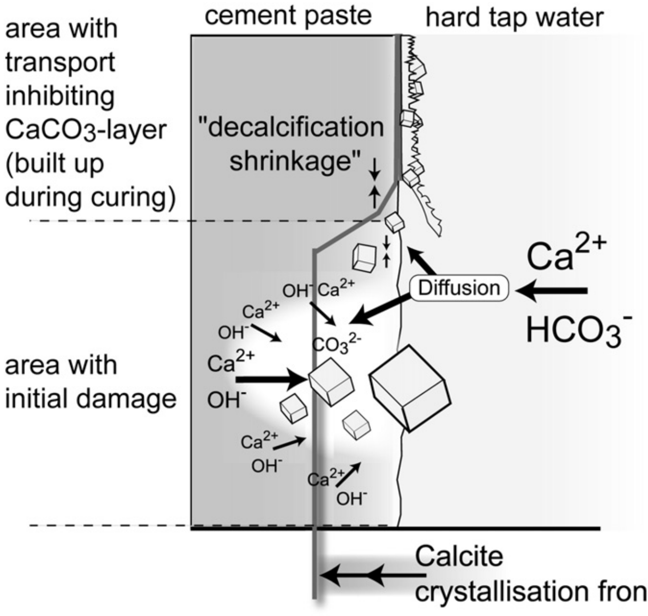


Fig. 11. Further development scheme of local hydrolytic corrosion during the operational phase of tap water reservoirs filled with hard water.

This reaction mechanism is substantiated through investigations of the contact zone material/water on practical case studies, showing that below the irregular covering layer of $CaCO_3$ in damaged areas extensive chemical changes occur, whereas under a dense $CaCO_3$ layer the base mortar remains unaffected by reactive transport (Fig. 4).

The structural properties of the upper microns in the near surface zone determine the reaction behavior of a monolithic material. These findings shows the relevance of the surface processes for the durability and long term stability of cementitious systems with regard to performance of building materials but also to hazardous waste stabilization. Especially in the context of the leaching tests performed in order to predict the long term behavior of cement based materials these inferred reaction mechanisms can play a crucial role with regard to the recent discussions on this topic [8,9,21].

Minor changes in the physical and chemical conditions can seriously affect the formation of $CaCO_3$ layers and determine whether their development plays a protective or a damage promoting role for cementitious systems.

5. Conclusions

The formation of a $CaCO_3$ layer in the interface cement paste/water can on the one hand play a protective role against reactive transport processes, depending on the structural properties of the $CaCO_3$ layer. Is Ca^{2+} and HCO_3^- supplied from the water, a dense protective layer can be built up. On the other hand, if Ca^{2+} is supplied by the pore solution, $CaCO_3$ formation affects the pore water chemistry and triggers thereby a further chemical degradation in the solid phases of the cement paste. In this way besides leaching, also $CaCO_3$ formation can cause micro structural changes in the CSH gel by decalcification shrinkage [17].

According to these results a two step reaction mechanism for the local hydrolytic corrosion of cement based materials is suggested. (1) An irreversible initial damage can occur due to leaching or an "aggressive" crystallization of $CaCO_3$ on the material surface under condensate water films in the presence of CO_2. This prevents any efficient protection against reactive transport during subsequent exposure to hard tap water, (2) leading to progressive deterioration laterally and in depth.

The structural properties of a $CaCO_3$ layer are determined by physico-chemical conditions, e.g. water composition, affecting its efficiency as a diffusion barrier. This can be crucial for the long term behavior of cement based materials in permanent contact with water.

In particular, the transport properties of the material in the surface near area are of relevance for the durability of the system. This emphasizes the importance of the curing phase of cement based materials for durability aspects.

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