



The rim zone of cement-based materials – Barrier or fast lane for chemical degradation?



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ABSTRACT

Sophisticated evaluation models for the long-term stability of cement-based systems demand a precise knowledge of the mechanisms of deterioration reactions, particularly respecting a permanent exposure to aqueous environments. Commonly, insights into these mechanisms are deduced from long-term investigations. However, these chemical reactions start immediately after exposure to aggressive environments causing rapid changes of composition and structure. Consequently, properties of its rim zone change, which affects transport processes in aqueous solutions. In laboratory experiments, the influence of these surface processes on the stability of cement-based materials exposed to different chloride solutions was studied as a function of time and temperature. Analysis of compositional and structural changes beneath the surface reveal the role of crystalline covering layers for chemical resistance. Such layers are often described as protective barriers. However, these processes in the rim zone can accelerate chemical degradation and subsequently reduce the resilience of the cement-based materials to aggressive aqueous environments.

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1. Introduction

Maximizing the service life of concrete structures as well as achieving an utmost long-term stability of cement bound waste forms, resulting from the solidification and stabilization of hazardous waste as potential final treatment prior to the disposal (e.g. Ref. [1]), are important challenges in the context of a sustainable development in construction and waste treatment. This holds true in particular for cement-based materials, which are permanently exposed to aggressive aqueous environments. With this in mind, rating material performance and precisely assessing the detrimental impact of aqueous environments is a major issue. In this regard, refined approaches in terms of an evaluation for the long-term behavior and durability are needed. A precondition for promising modeling approaches, in particular for service-life prediction, is a detailed and fundamental understanding of deterioration reactions. However, past research activities often showed no

clear and detailed picture of the reaction mechanism and the various factors determining the course of the damaging processes as denoted for sulfate attack [2] or in the context of the critical chloride content in steel reinforced concrete structures [3]. In order to characterize the material performance of cementitious systems, the behavior of these materials over time periods of weeks and months has mostly been studied [4]. Nevertheless, chemical reactions occur at the material/water interface and start immediately after exposure to aggressive environments. Transport processes are initiated due to concentration gradients between the alkaline pore solution of these highly porous materials and the surrounding aqueous media. Thus, chemical equilibrium between the pore solution and the solid phases will be disturbed and consequently dissolution and crystallization reactions are triggered. These reactive transport processes change the chemical and mineralogical composition of the material.

The first location where this reaction takes place is the near-surface region. This area also represents the first hurdle that must be overcome by an attacking aqueous solution. Thus, a crystalline covering layer on the surface of cement-based materials is said to act as a protective layer against reactive transport. This holds true in particular for carbonate precipitations on the surface of cement-

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based systems in contact with hard, carbonate-rich water, which hinders the transport and slows down e.g. the leaching process [5,6]. Also, the formation of $\text{Mg}(\text{OH})_2$ coatings as consequence of an attack by a MgSO_4 solution is assumed to restrict reactive transport processes [7].

However, the presence of carbonic acid species does not always lead to the formation of covering layers. In recent studies regarding the reliability of a specific leaching test for the evaluation of the stability of cement bound waste, the formation of a complex composed rim zone due to the presence of CO_2 was described. It was discussed whether this rim zone is potentially closely related to a non-satisfactory reproducibility of these tests [8–10]. It is announced that due to the development of complex chemical and mineralogical gradients, a modeling approach simply based on diffusion laws, in particular in an abundant presence of CO_2 , is not a promising way to extrapolate the long-term behavior based on the short-term experiment [9]. Similarly, the presumed protective effect of crystalline covering layers is closely related to the hydrochemistry of leachant and pore solutions, as well as to changes of the cement paste regarding permeability, cracking due to decalcification shrinkage [11], mineralogical and chemical composition [12]. In the case of calcium carbonate layers, it has been addressed that both the hydrochemical frame conditions during the growth of the covering layer and the mineralogical and structural evolution of the rim zone determine their effectiveness as a diffusion barrier [13]. Further, the reaction temperature is assumed to have an impact on the evolution of the properties of the rim zone due to reactive transport.

In order to illustrate the role of the rim zone for the chemical stability of cement paste samples, immersion experiments have been performed in salt solutions of different composition. This contribution focuses exemplarily on the chemical and mineralogical changes in the rim zone of cement paste samples exposed to different chloride solutions. A potential relation between temperature and the time dependant development of the material due to reactive transport processes will also be addressed.

2. Materials and methods

For the exposure tests with cement pastes, ordinary Portland cement (CEM I) was used to make prisms with a water to cement ratio of 0.5. For this, cement and water were mixed in a laboratory mixer and placed in $160 \times 40 \times 40$ mm molds and hydrated in the atmosphere of 20°C and 98% relative humidity for 24 h. The prisms were cured in tap water at 20°C for 32 days after demolding. The outer part of the prisms, where cement paste was in contact with water, was cut off and rectangular plates of $70 \times 30 \times 5$ mm were cut out. The plates were wrapped with polyvinylidene chloride foil to prevent shrinkage and kept for ten months at $\sim 15\text{--}20^\circ\text{C}$.

0.8 mm thick slices were taken from the rectangular plates with a precision saw and stored under nitrogen atmosphere until the beginning of the experiment. Each sample was hung with a nylon string and placed into a plastic bottle filled with 70 mL of a solution. For the immersion test, four different chloride solutions were prepared: NaCl, KCl, MgCl_2 , and CaCl_2 , with a concentration of 1 mol/L of Cl^- , which is a common value for experimental work in the context of chloride attack on cement-based materials (e.g. Ref. [14]). Two additional experiments were carried out with hard tap water (saturation index for calcite of 0.32 (25°C) and for $\text{Ca}(\text{OH})_2$ of -10.7 (25°C), hardness of 2.66 mmol/L, calculated with PHREEQC [15]) and demineralized water, respectively. The immersion tests were carried out at a constant temperature of 20°C or 5°C in a closed system to inhibit a potential uptake of CO_2 .

The determination of the $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ content of the solid phases was performed with thermogravimetric analysis of

pulverized samples (TGA/SDTA 851, Mettler-Toledo). For electron microscopic investigations, an ESEM XL 30 FEG (Philips) equipped with an energy-dispersive X-ray spectroscopy system (EDX) (EDAX) was used. Surface sensitive X-ray diffraction (XRD) measurements were carried out with cement paste slices (D8 advance with $\text{Cu}_{K\alpha}$ radiation, Bruker). The composition of the reaction solutions was analyzed with Inductively Coupled Plasma- Atomic Emission Spectroscopy (ICP-AES) (Optima 8300, Perkin Elmer). The water soluble Cl^- content was determined by an aqueous extraction (1 g of a pulverized cement paste sample in 50 mL demineralized water) followed by a quantification of the anion content with ion chromatography (761 Compact IC, Metrohm).

3. Results

Fig. 1 shows the time dependant evolution of the composition of the solid phases regarding the $\text{Ca}(\text{OH})_2$ content (Fig. 1a) and the water soluble chloride content (Fig. 1d), as well as the leached quantity of Ca^{2+} (Fig. 1b) in the reaction solutions and their pH value (Fig. 1c), respectively.

The exposure to hard tap water did not lead to a significant leaching of the $\text{Ca}(\text{OH})_2$ and only a slight decrease of the Ca^{2+} concentration and the pH value was noted. The $\text{Ca}(\text{OH})_2$ content decreased significantly for all the other solutions. The loss of $\text{Ca}(\text{OH})_2$ in NaCl, KCl, and CaCl_2 solutions was more intense than in demineralized water and showed a similar behavior, whereas the most excessive loss of $\text{Ca}(\text{OH})_2$ was detected for the MgCl_2 solution (Fig. 1a). The reverse trend was observed for the calcium release (Fig. 1b). For most of the experiments, the pH values achieved a constant level of pH 11–12 during the first 24 h of the experiment. The immersion in the MgCl_2 solution did not lead to a high pH level and almost no change has been noticed in the pH value of the experiment performed with tap water (Fig. 1c). The uptake of Cl^- from the MgCl_2 and CaCl_2 solutions was more intense than from the NaCl and KCl solutions (Fig. 1d), generally resulting in the formation of Friedel's salt (identified in the bulk sample by means of XRD, not shown in this contribution).

Fig. 2 shows electron microscopic images of the cement paste surfaces after a 24 h exposure to different aqueous solutions. The pictures attached on the right hand side show the distribution of the element Ca analyzed in a cross section of the cement paste slices. Areas showing a significant decrease of Ca (attributed to a loss of $\text{Ca}(\text{OH})_2$) are surrounded with a white dotted line. A loss of $\text{Ca}(\text{OH})_2$ in the rim zones that have been in contact with the aqueous solutions was observed in the experiments with KCl, NaCl, CaCl_2 , and demineralized water (Fig. 2b, d-f).

After exposure to tap water, no significant leaching was noticed (Fig. 2a). The exposure to the MgCl_2 solution led to a complete loss of $\text{Ca}(\text{OH})_2$ (Fig. 2c). The microscopic view reveals a homogeneous deposition of crystalline reaction products only after the exposure to hard tap water and to the MgCl_2 solution.

In order to characterize potential crystalline reaction products on the surface of the cement paste samples, XRD investigations have been performed directly on the test specimen. The specimens have been mounted in the sample holders of the diffractometer without further preparation (such as grinding or drying). The results of the measurements after the immersion in the different aqueous solutions at 20°C for 24 h are shown in Fig. 3. The exposure to hard tap water led to a significant formation of calcite (Fig. 3a). The crystalline covering layer after exposure to the MgCl_2 solution was identified as $\text{Mg}(\text{OH})_2$ (brucite) (Fig. 3c). The investigation of the samples immersed in the NaCl, KCl, and CaCl_2 solutions showed only weak signals of calcite (Fig. 3d–f). After immersion in the KCl and CaCl_2 solutions, traces of Friedel's salt – and brucite in the case of CaCl_2 (Fig. 3f) potentially due to

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