



Immediate impact on the rim zone of cement based materials due to chemical attack

A focused ion beam study



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ABSTRACT

Cement based materials are in their widespread application fields exposed to various aqueous environments. This can lead to serious chemical changes affecting the durability of the materials. In particular in the context of service life prediction a detailed knowledge of the reaction mechanisms is a necessary base for the evaluation of the aggressivity of an aqueous medium and this is deduced commonly from long term investigations. However, these processes start immediately at the material/water-interface, when a cementitious system comes into contact with an aqueous solution, altering here the chemical composition and microstructure. This rim zone represents the first hurdle that has to be overcome by an attacking aqueous solution. Therefore, the properties of the surface near area should be closely associated with the further course of deterioration processes by reactive transport. In this context short term exposure experiments with hardened cement paste over 4 and 48 h have been carried out with demineralized water, hard tap water and different sulfate solutions. In order to investigate immediate changes in the near-surface region, depth profile cuts have been performed on the cement paste samples by means of focused ion beam preparation techniques. A scanning beam of Gallium ions is applied to cut a sharp edge in the cement paste surface, providing insights into the composition and microstructure of the upper ten to hundred microns. Electron microscopic investigations on such a section of the rim zone, together with surface sensitive X-ray diffraction accompanied by a detailed characterization of the bulk composition confirm that the properties of the material/water interface are of relevance for the durability of cement based systems in contact with aqueous solutions. In this manner, focused ion beam investigations constitute auspicious tools to contribute to a more sophisticated understanding of the reaction mechanisms.

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1. Introduction

Cement based materials are porous and characterized by a significant chemical reactivity, that is in practice often underestimated. In particular, when cement based materials come in contact with aqueous solutions, reactions occur, changing their chemical and mineralogical compositions affecting in turn their durability by means of resistance against chemical attack. Such processes arise at the material/water interface starting immediately after coming in contact with the aggressive environment. Due to concentration gradients between the alkaline pore solution of these highly porous materials and the surrounding aqueous media transport processes are initiated. Thus, chemical equilibria between the pore solution and the solid phases will be disturbed and consequently dissolution and crystallization reactions are triggered. This is commonly referred to as reactive transport [1]. In order to investigate the material performance of

cementitious systems usually the long term behavior (weeks and months) of these materials is studied (e.g. [2] and [3]). Up to now the relevance of the properties of the surface near tens or hundreds of μm on reactive transport processes has attracted only minor attention regarding the durability of cementitious systems. However, studies in the context of the long term stability of cement bound waste have pointed out, that due to reactive transport processes – in particular as a consequence of the presence of carbonic acid species – complex composed rim zones can develop and their influence on the stability in aggressive aqueous environments was discussed [4–6]. Such processes proceed with high velocity and are in certain cases considered as the initial stage of chemical deterioration of cement based materials in contact with aqueous solutions [7]. Furthermore, in their multifaceted application fields, cement based materials come in contact with waters of various compositions. Thus, a huge variety of processes can occur.

Generally in this context the formation of crystalline covering layers is supposed to play an important role. Also the presence of other ions besides carbonic acid species can constrain or even prevent the

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development of protective crystalline layers in the cement paste/water interface.

However, if or to what extent such layers provide a protective effect is actually not understood in detail. Thus, many aspects of the mechanisms of complex damaging reactions, as for instance occurring in the presence of sulfate ions [8], but also leaching reactions are still debatable, in particular regarding their impact on structural properties of the materials [9]. In this context all the properties and concomitant to this the behavior of the material/water interface are of relevance. They are supposed to be affected by short term reactions, which accordingly should be of importance for the performance and durability of cement based systems. Therefore, in this study detailed investigations of processes at the material/water interface have been performed in order to contribute to the fundamentals for an assessment of their relevance for the progress of damaging reactions. For this purpose short term exposure experiments with aqueous solutions of different composition were carried out, in order to trigger the formation of rim zones with different properties. Leaching scenarios should have been created by exposure to demineralized water and hard tap water, whereas the hard tap water is supposed to be much less aggressive due to an intensive formation of carbonate layers on the materials surface. A MgSO_4 and a Na_2SO_4 solution was applied to simulate two different types of sulfate attack on cement based materials. The impact on the chemical and structural properties in the areas nearest to the surface due to a 4 h exposure was investigated by means of focused ion beam techniques as well as surface sensitive X-ray diffraction. The investigation of the processes on the surfaces of the samples was accompanied by a detailed characterization of the bulk sample. In this way, the study is focusing on the interrelationship between the properties of the rim zone and the development of the cement based material subjected to a chemical attack.

2. Experimental

For exposure tests a white Portland cement (CEM I 42,5 R) was used to make prisms in $4 \times 4 \times 16$ cm molds with a water to cement ratio of 0.4. 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. For curing, the samples were stored for 100 days in tap water (~20–25 °C). For the tests 1 mm thick slices were taken from the middle of the prisms.

The freshly cut cement paste slices were immediately placed for a time period of 4 h and 48 h, respectively, in a reaction vessel filled with 100 ml of different aqueous solutions at a temperature of 20 °C (stationary exposure, open system). The exposure tests were carried out with hard tap water (~15°dH), demineralized water, and both, a 0.1 M MgSO_4 and a 0.1 M Na_2SO_4 solution. A freshly cut slice of the cement paste prism was used as the reference material.

The thermogravimetric investigations of the bulk materials were performed with a TGA/SDTA 851 system from Mettler-Toledo applying a heating rate of 10 °C/min under an N_2 atmosphere. X-ray diffraction (XRD) measurements have been performed directly on the surfaces of the cement paste slices using a Bruker D8 machine (Cu-K α radiation). Prior to the investigation, the sample surfaces were shortly rinsed with demineralized water in order to prevent contamination of sulfate salts due to evaporation. The focused ion beam (FIB) cuts and the electron microscopic investigations have been performed with a FEI Strata 400 STEM dual beam system equipped with an Oxford Instruments INCA PentaFET x3 energy-dispersive X-ray spectroscopy system (EDX). Prior to the investigations the specimen was vacuum dried and a gold coating was sputtered on the surfaces.

3. Results

In contact with the different solutions, the chemical composition of the materials is changing with exposure time. Fig. 1 shows the

differential thermogravimetry plots (DTGs) of the cement paste slices after a reaction time of 4 h and 48 h, respectively. These results are almost comparable, indicating only minor changes in the bulk composition of the specimen resulting from the exposure to the different aqueous solutions. The dehydration of portlandite ($\text{Ca}(\text{OH})_2$) is denoted by a peak between 440 °C and 540 °C. The signal in the temperature range from 700 °C to 800 °C shows a slight increase, indicating the growth of carbonate minerals. Only the DTG plot of the sample exposed to the MgSO_4 solution reveals the appearance of a new phase indicated by a peak between 360 °C and 420 °C (arrow in Fig. 1c) increasing in intensity with time. This peak can be ascribed to the presence of brucite ($\text{Mg}(\text{OH})_2$).

In Fig. 2 calculated values for the $\text{Ca}(\text{OH})_2$ and CaCO_3 content from thermogravimetric data after 4 h and 48 h are given. All the samples showed a slightly lower $\text{Ca}(\text{OH})_2$ content compared to the reference (0 h). For the material exposed to the MgSO_4 solution, the most significant loss of $\text{Ca}(\text{OH})_2$ was measured. Regarding the determination of CaCO_3 due to a considerable scattering of results no clear tendency can be reported during the first 48 h of the experiment. Furthermore, an estimation of the $\text{Mg}(\text{OH})_2$ content of the sample after 4 h and 48 h exposure to the MgSO_4 solution was performed by an integration of the peak in the DTG plot. After 4 h the $\text{Mg}(\text{OH})_2$ content is significantly below 0.5 wt.% and after 48 h between 1.0 and 1.5 wt.% (not shown).

The results of the surface investigation by means of XRD are shown in Fig. 3. Only on the surface of the freshly cut cement paste slice, the mineral portlandite was detected. Also distinct peaks which can be attributed to residual clinker minerals ($\text{C}_3\text{S}/\text{C}_2\text{S}$) and CSH are mainly found in the investigation of the reference sample. During immersion in hard tap water the crystallization of calcium carbonate on the sample surface was observed (Fig. 3a). The formation of such a covering layer restricts the investigation of the phase composition of the material below, protecting it from the penetration of the X-ray beam. After an exposure of 48 h the development of aragonite was detected. As a consequence to the exposure in demineralized water, the most significant difference to the reference sample regarding the mineralogical composition was the disappearance of portlandite (Fig. 3b). An increase of the signal of calcite was observed within the first 4 h. However, after 48 h it was only of minor intensity. Immediately after immersion in the 0.1 M MgSO_4 solution a significant formation of brucite was observed concomitant to an increase of the intensity of the gypsum peaks (Fig. 3c). In the progressive course of the experiment (48 h), a continuous formation of brucite and a decrease of the intensity of the gypsum peaks were noticed. Distinct peaks attributed to the formation of aragonite were detected. After the exposure to the 0.1 M Na_2SO_4 solution, no Na-sulfate-phases were observed (Fig. 3d). In this case the gypsum signal disappeared after a reaction time of 4 h. Furthermore a significant increase of the intensities with respect to ettringite was observed. After a time period of 48 h a further growth of calcite could be noticed, affecting the measured intensities of mineral components below. Due to the overlapping main diffraction peak of gypsum und hydrotalcite, the presence of hydrotalcite, a compound mentioned in literature in the context of cement paste/water interaction [10] and sulfate attack on cement based materials [3], cannot be fully excluded.

The comparison between XRD measurements performed directly on the sample surface and a powder diffractogram of the corresponding bulk sample (1 mm thick slice) is shown in Fig. 4. Both samples have been exposed for 48 h to the 0.1 M MgSO_4 solution. The XRD results of the direct investigation of the surface display a distinct signal for the mineral brucite (see also Fig. 3c), whereas the diffractogram collected by the analysis of the bulk sample shows only an extremely weak signal (indicated by an arrow in Fig. 4). In the bulk sample strong signal intensities with respect to portlandite were detected.

As the XRD measurements reveal only information concerning the mineralogical composition of the surface (top layer) or of bulk samples (powder diffractogram), further analytical techniques are required in order to characterize the surface near area as a function of depth in

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