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Assessing the potential of ToF-SIMS as a complementary approach to investigate cement-based materials — Applications related to alkali–silica reaction

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ABSTRACT

In this study, the potential of time-of-flight secondary ion mass spectrometry (ToF-SIMS) for the application in cement-based materials is assessed in combination and comparison with scanning electron microscopy (SEM) and energy dispersive X-ray (EDX). Mortar, concrete and samples from model systems providing products formed by the alkali–silica reaction (ASR) were studied. ToF-SIMS provides qualitative data on alkalis in cases where EDX reaches its limits in regard to detectable concentration, lateral resolution and atomic number of the elements. Due to its high in-depth resolution of a few atomic monolayers, thin layers of reaction products can be detected on the surfaces and chemically analyzed with ToF-SIMS. Additionally, it delivers information on the molecular conformation within the ASR product, its hydrogen content and its isotope ratios, information not provided by EDX. Provided the samples are carefully prepared, ToF-SIMS opens up new possibilities in the analysis of cement-based materials.

1. Introduction

Several techniques are used today allowing a characterization of both microstructure and composition of cementitious materials with high spatial resolution. Scanning electron microscopy (SEM) in combination with energy dispersive X-ray spectroscopy (EDX) has been established for about 30 years as a main tool for this purpose [e.g. 1–4]. Preferably, SEM is used in the backscattered mode (BSE) on polished surfaces, as this approach permits reliable EDX analysis and imaging suitable for representative image analysis [5]. However, EDX has intrinsic limitations, such as elemental-only chemical detection, no detection of low-mass elements (such as lithium or hydrogen) and limited lateral resolution (~1 μm). There are various other techniques complementing and expanding the possibilities of SEM and EDX in the microstructural analysis of cement-based materials. To name a few, transmission electron microscopy (TEM) improves the spatial resolution of SEM and permits a more detailed imaging of the morphology of cement hydrates [6–9]. High resolution (15–20 nm) 3D-imaging of the pore structure is possible with focused ion beam nanotomography (FIB-nt) [10–12]. As it permits their detection on specific particle surfaces and at very low concentrations, X-ray photoelectron spectroscopy (XPS) is used to analyze heavy metals in cementitious materials [e.g. 13–15]. Additionally, XPS enables conclusions on the structure of calcium-silicate–hydrate (C-S–H) based on the binding energy of silicon and oxygen [16].

A technique rarely used on cement-based materials so far is time-of-flight secondary ion mass spectrometry (ToF-SIMS). Elements and molecules ionized by a primary ion beam are analyzed in a mass spectrometer based on their time-of-flight from the sample surface to the detector. ToF-SIMS can access the elemental and molecular information from mass 1 to 10,000 mu, but also delivers qualitative chemical information with high lateral (~100 nm) and in-depth (~2 nm) resolution. As ToF-SIMS is a scanning technique, maps of elements or molecules can be made. In the few existing studies on cementitious materials, ToF-SIMS was applied for studying widely different problems.

In Tremblay et al. [17] a secondary ion mass spectrometer equipped with a microbeam was used to look for hydrates with increased lithium concentrations in two concrete mixtures where $LiNO_3$ was added to prevent alkali–silica reaction (ASR). However, no hydrates with increased concentration were detectable. In contrast to this study, increase lithium concentrations were observable in microsilica agglomerates within a cement paste and in the ASR product within aggregates of mortar doped with $LiNO_3$ [18]. A combination of ToF-SIMS with EDX enabled localizing superplasticizer on a polished cement clinker surface and correlating it with clinker mineralogy [19]. Barnes-Davin et al. [20] attempted to trace boron distribution on polished surfaces of cement clinker.

The aim of this study is to further assess the potential of ToF-SIMS for the application in cement-based materials when used in combination

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with SEM and EDX. For this purpose, three examples dealing with specific issues related to ASR are chosen.

ASR is a reaction between the alkalis in the highly alkaline pore solution of the concrete (pH ~13) and SiO_2 in the concrete aggregates. Due to moisture uptake and subsequent swelling of the reaction product, stress is generated [21, 22]. As a result, concrete structures can be severely damaged by crack formation.

In the first example, ToF-SIMS is used for the detection of alkalis in a reacting aggregate of a mortar with ASR. In the second example, the ability of ToF-SIMS to analyze thin layers is used to get information about the role of aluminum in the mitigation of ASR by studying glass plates after immersion in alkaline solutions containing aluminum. The third example focuses on the ratios of secondary ions of different ASR products in a model system and in concrete from structures damaged by ASR.

2. Materials and methods

2.1. Materials

In the first example, a mortar with ASR is studied. In the production of the mortar (cement content = 493 kg/m^3, microsilica content = 97 kg/m^3, water content 290 kg/m^3, aggregate content = 1340 kg/m^3), $LiNO_3$ was added to the mixing water (6.9 kg/m^3). The used dosage of $LiNO_3$ is able to reduce the expansion caused by ASR, but still some ASR products were able to form [18]. A slice of the cross section of a mortar bar ($40 \times 40 \times 160$ mm^3) was cut, dried at 50 °C for three days, impregnated with epoxy resin, polished and carbon coated. After the analysis with the SEM, the carbon coating was removed by re-polishing to allow ToF-SIMS analysis.

In the second example, the effect of aluminum on SiO_2 surfaces in an alkaline environment is studied. Rectangular plates ($25 \times 75 \times 1$ mm^3) of highly pure quartz glass were broken into pieces with an area of about 2 cm^2 and immersed in 0.6 M NaOH solutions saturated with Ca(OH) (portlandite) for six days. Portlandite saturation in the solutions was ensured by adding a surplus amount of it. One solution contained no aluminum, while $NaAlO_2$ was added to the other two solutions to reach an aluminum concentration of 10 and 20 mmol, respectively. The samples are labeled “Al-0”, “Al-10” and “Al-20” in the following text. After the immersion, the samples were shortly rinsed with pure water and placed in a desiccator until analysis. The samples were first examined with an optical microscope to identify areas of interest for the ToF-SIMS analysis. Locations with and without reactions products on the surface were chosen in the samples Al-10 and Al-20. In sample Al-0, only areas with reaction products were analyzed, as the entire surface was covered by them. After the ToF-SIMS analysis, the samples were carbon coated and studied with the SEM.

In the third example, the SiO_3/SiO_2-ratio was studied on a model system for ASR [18, 23]. The sample was produced using a solid to liquid-ratio of 1:2. The solid consisted of 90% by mass of microsilica and 10% by mass of portlandite. The liquid was 1 M NaOH with 0.74 M $LiNO_3$. After four weeks the reaction of microsilica with portlandite and the alkaline solution was stopped by drying the samples. The concrete samples used to study the ratios of different secondary ions of the ASR products were taken from a bridge built in 1969 (sample G5a) and a supporting wall built in 1980 (sample MU-01). Both structures show cracking due to ASR [24] and the selected samples show veins with reaction products cutting through aggregates. The names of the samples come from the previous study. Before the investigation, the sample of the model system and the concrete samples were dried in an oven at 50 °C for three days, impregnated with epoxy resin, polished and carbon coated. After the SEM analysis, the carbon coating was removed by re-polishing. After rinsing the samples with acetone, they were stored in a desiccator in N_2-atmosphere until analyzed with ToF-SIMS (the time from polishing to sample analysis did not exceed two days).

2.2. Methods

The samples were studied with an environmental scanning electron microscope (ESEM-FEG XL30) in high-vacuum mode ($3.0–5.0 \times 10^{-6}$ Torr) with an accelerating voltage of 10–15 kV and a beam current of 130–180 μA. The chemical composition of the reaction product was determined with energy dispersive X-ray spectroscopy (EDX). An EDAX 194 UTW detector, a Philips digital controller, and Genesis Spectrum Software (Version 4.6.1) with corrections for atomic number, adsorption and fluorescence (ZAF) were used. To study the glass samples, a Zeiss Axiophot with 5× and 10× lenses was used.

The further compositional analysis by ToF-SIMS was performed with a TOF.SIMS^5 instrument from ION-TOF GmbH, using a 50 keV Bi_3^{++} (25 keV Bi_1^+ for the second example) primary ion beam in combination with an electron flood gun for charge compensation. The detection was performed within a mass range from 1 to 200 mu.

In the first example, the instrument was set up in imaging mode, i.e. with high lateral resolution (typically 200 nm) but with nominal mass resolution only. However, whereas lithium is very specific at masses 6 and 7 mu, calcium and the other alkalis are strongly dominating at their respective masses. Images of 30×30 μm^2 were acquired for secondary ions of positive and negative polarities. For the second example, the analysis was performed in spectral mode, i.e. with high mass resolution (~7000), allowing for a precise determination of the intensities of elements and molecules at the surface. Areas of 20×20 μm^2 were considered to allow averaging. Note that, due to different ionization potentials and extraction probabilities of the different molecular species, the recorded intensities are not directly proportional to the species concentration. Hence, a quantitative analysis is only possible through comparison and/or the consideration of ratios. In the third example, we combined both imaging and spectral analyses as both high lateral resolution and high mass resolution were needed. Images allowed a precise determination of the respective areas of interest, in particular the spatial distribution of amorphous and crystalline reaction products within the vein. Because the respective reaction products are spread, and with size of tens of square micrometers only, larger areas around the vein were mapped. Sub-data sets for the two different products were subsequently extracted by post-processing at the specific areas only. The spectra were used to provide a precise determination of the chemical composition at each reaction product location, allowing a semi-quantitative comparison of the different constituents within amorphous and crystalline reaction products, in particular the respective SiO_3/SiO_2 ratios. Note that for the quantitative analyses led in the two last examples, the intensity peaks have been normalized to the total counts, so that a direct comparison between the different samples or positions is possible.

3. Results and discussion

3.1. Detection and 2D spatial mapping of alkalis in ASR product

The understanding of formation, expansion or mitigation of ASR within cement-based materials demands a precise knowledge of the chemical composition of the ASR products. Here, the chemical analysis of such a system is performed by a combination of SEM/EDX and ToF-SIMS techniques. The area selected for analysis shows a vein and side branches filled with ASR product in a gneiss aggregate (Fig. 1B). The vein composition as analyzed with EDX point measurements is shown in Table 1. However, as the interaction volume of the electron beam (diameter of 1–2 μm at the chosen acceleration voltage of 15 kV) is possibly enclosing some of the surrounding minerals (quartz), the composition can only be regarded as indicative.

The EDX maps are presented in Fig. 1A and the corresponding ToF-SIMS secondary ion images in Fig. 1C. The EDX map of sodium shows a signal in the main vein that is just slightly above the noise