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Sulfate attack - Reaction mechanisms revealed by a multi proxy approach

Florian Mittermayr[1,2], Andre Baldermann[2], Dietmar Klammer[2], Albrecht Leis[3], Josef Tritthart[1], Martin Dietzel[2]
[1]Institute of Technology and Testing of Building Materials, Graz University of Technology, Graz, Austria
[2]Institute of Applied Geosciences, Graz University of Technology, Graz, Austria
[3]RESOURCES – Institute for Water, Energy and Sustainability, Joanneum Research, Graz, Austria

Abstract. The destructive effects of sulfate attack on concrete structures are well known, but the reaction paths and mechanisms that cause the deterioration are still under debate. The aim of this study is to contribute to a deeper understanding on investigating concrete damage by introducing a novel and promising multi proxy approach method. The methodology comprises advanced mineralogical and hydro-geochemical methods as well as stable isotope signals. Investigations were performed on various field case studies in Austria, where the locally occurring ground water was classified as slightly aggressive to concrete, in accordance to DIN EN 206-1. Nevertheless intense concrete damage related to sulfate attack was found. Severely damaged mushy concrete consisted mainly of thaumasite, secondary calcite, gypsum and relicts of aggregate. The expressed interstitial solutions from such material were extremely enriched in SO_4 (up to >30000 mg L^{-1}). Stable hydrogen and oxygen isotope were applied successfully and demonstrated that the degree of evaporation provoked enrichments in SO_4 and other dissolved, potentially harmful ions such as Cl. Furthermore, the enormous accumulation of incompatible trace elements (e.g. Rb and Li) clearly indicated that numerous wetting and drying cycles had occurred. Such a highly dynamic system is known to induce severe destructive effects on concrete. In this study we demonstrate that the application of a multi proxy approach can provide a better understanding of the complexity of reaction mechanisms involving sulfate attack on concrete structures. More detailed knowledge on the individual reactions that promote concrete damage in field structures will help to find specific counter measures for already affected buildings and to develop tailored concrete recipes, applications and constructive measures for future projects.

1 Introduction

In recent decades, building sites are more and more limited in size, especially in densely populated areas, thus, e.g. traffic routes become more frequently built in the underground. An important requirement for such underground structures is that the applied concrete is highly durable under such (potentially aggressive) environmental conditions. Therefore, investigations on mechanisms and potential threats for concrete structures that may lead to enormous repair costs and significantly shorten the lifespan are of great economic interests.

It is well known that deterioration due to aggressive aqueous environments acts as one of the major threats for the durability of underground concrete structures. Multiple types of chemical attacks have been described, however, the reaction processes and alteration mechanisms are commonly still not fully understood [1, 2]. One good example of concrete alteration is sulfate attack and in particular the thaumasite form of sulfate attack (TSA). The destructive nature of TSA causes CSH-phases to disintegrate, which subsequently leads to a reduction of the material strength of the concrete and may result in its total destruction. TSA frequently occurs in wet, highly sulfate-loaded and cold (<15 °C) environments such as in underground structures [3-6].

A typical approach to investigate sulfate attack is testing concrete specimens in the laboratory, under well-defined boundary conditions. Commonly, samples are submersed in highly sulfate loaded solutions up to several years, whereby the solutions are replaced periodically. After defined time intervals the samples are investigated in terms of mechanical parameters (e.g. compressive strength) and mineralogical and microstructural aspects (e.g. X-ray diffraction and scanning electron microscopy) [7-9]. This testing procedure can provide important results with respect to the chemical resistance of concrete materials. However, this approach has also been criticized in the past, as the actually occurring reactions that cause the damage in the field are not mimicked properly [10, 11].

In the present study sulfate attack due to thaumasite formation in field case studies is highlighted in order to contribute to a deeper understanding of alteration mechanisms on concrete, by introducing a novel approach based on combined methodologies. This includes hydro-geochemical as well as mineralogical and microstructural methods. Additionally, we introduced trace elemental and isotopic methodologies, which are commonly used in climate studies to trace e.g. mineral formation conditions. This multi methodology approach has not yet been applied for understanding concrete damage [12-14].

2 Materials and Methods

For this study solid materials and aqueous solutions were sampled in Austrian highway and railroad tunnels. Some samples were also taken from corresponding structures such as from the drainages as well as from a separate ventilation tunnel.

In Figure 1 a sampling site in a railroad tunnel is displayed, showing heavily deteriorated concrete. Intense alteration at the border of the old brick wall lining (early 1900) and on the surrounding shotcrete that was installed in the 1960ies had caused large areas of the shotcrete to fall off, resulting in endangering the traffic that passes through the tunnel.

Fig. 1. Sample taking at a damaged tunnel shotcrete lining. The drill core is taken above an area, where the shotcrete lining has been fallen off. White needle-like efflorescence is present at the transition between the damage area and superficial sound shotcrete.

2.1 Solids

In general, the collected solid samples are comprised of shotcrete and concrete, either unaltered or deteriorated. Completely disintegrated mushy material was shoveled into plastic bags, while concrete samples with a more stable appearance were excavated by taking 20 cm drilling cores (Figure 2). Furthermore, samples that show intense alterations such as efflorescence were carefully brushed from the tunnel walls and stored in air-tight containers.

The efflorescence was analyzed without any previous treatment by a PANalytical X'Pert PRO X-ray powder diffractometer (XRD). All other solid samples were dried at 40°C, ground and subsequently measured by XRD. Mineralogical phase identification was carried out with the PANalytical X’Pert HighScore Plus software. Secondary electron images (SEI) were acquired using a Zeiss DSM 982 Gemini scanning electron microscope (SEM), on gold-palladium sputtered samples using an accelerating voltage of 10kV. Backscattered images (BSE) and semi-quantitative spot analyses (EDX) were obtained from carbon coated samples using a JEOL JXA-8200 Superprobe electron probe micro analyzer (EPMA).

Fig. 2. Alteration products at the border between the old brick wall lining and the shotcrete.

2.2 Aqueous solutions

2.2.1 Chemical composition

Liquid samples include drainage solutions, local ground water and interstitial solutions. The latter solutions were separated from the damaged concrete with a specific hydraulic press, using the setup described by Tritthart [15]. Subsequently, the alkalinity and the pH value were measured. Along the lines of the expressed solutions, ground and drainage water samples were filtered and the temperature, alkalinity and the pH value were analyzed directly in the field. The concentrations of the major and trace elements were determined by a Dionex ICS-3000 ion chromatograph (IC) and an Agilent 7500ce inductively coupled plasma mass spectrometer (ICP-MS).

2.2.2 Stable isotope measurements

The stable isotope ratios of hydrogen ($^2H/H$) and oxygen ($^{18}O/^{16}O$) of the liquid samples were analyzed using a Picarro L1102-I wavelength-scanned cavity ring-down spectrometer (WS-CRDS). The isotope values are given in the δ–notation and are expressed as δ^2H and $\delta^{18}O$ in ‰, relative to the Vienna Standard Mean Ocean Water (VSMOW). Replicate measurements agreed within ±0.8 and ±0.1 ‰ for δ^2H and $\delta^{18}O$, respectively.

3 Results and Discussion

The XRD pattern of unaltered concrete and shotcrete revealed CSH-phases (expressed as amorphous content), portlandite as well as silicate and carbonate aggregates like quartz, feldspar, dolomite and calcite. Mineralogical investigations (XRD, EPMA, and SEM) of the severely damaged concrete clearly showed that the deterioration was caused by sulfate attack, because the completely disintegrated materials consisted mainly of thaumasite, calcite and silicate aggregates (Figure 3) [14]. Gypsum was detected in small quantities, whereas ettringite was not found. Furthermore, a significant reduction or even a total lacking of dolomite aggregates was detected by comparison of unaltered and deteriorated material.

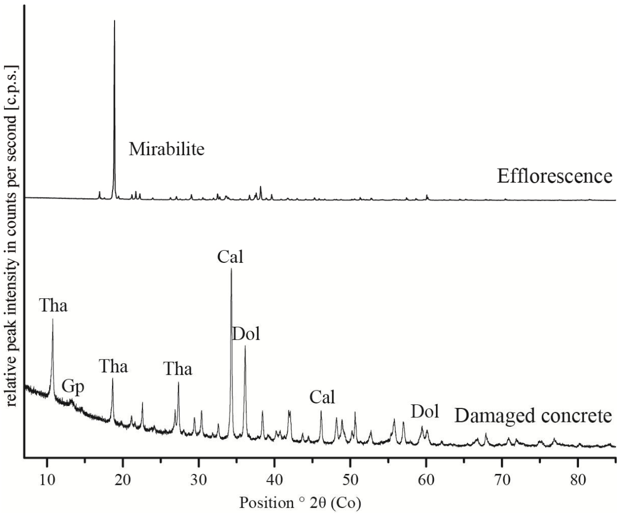

Fig. 3. XRD pattern. The needle-like efflorescence identified as mirabilite, a sodium sulfate hydrate mineral. In contrast, the damaged mushy concrete consisted mainly of thaumasite (Tha), calcite (Cal) and dolomite (Dol), among small amounts of gypsum (Gp). Modified after Mittermayr et al. [14].

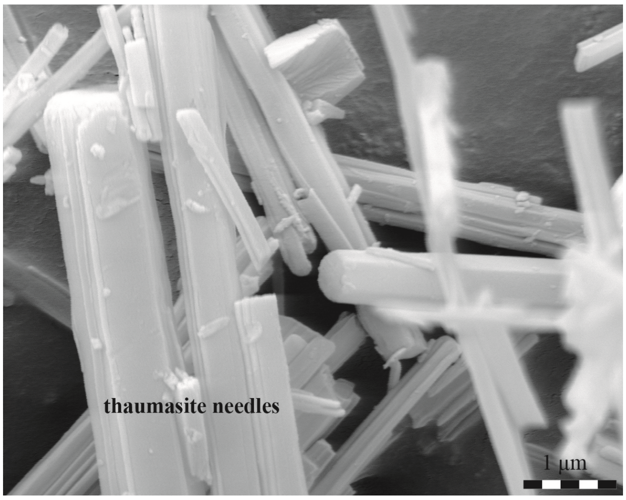

Fig. 4. The SEI of intensely damaged concrete displays plenty of thaumasite needles.

Consequently, the intense concrete damage is considered to be attributed to TSA. As TSA is known to occur preferentially in highly sulfate loaded environments, high amounts of dissolved sulfate were expected in the local ground water [16, 17]. Surprisingly, the ground water and the drainage water analyses generally revealed low to moderate SO_4 contents, with maximum values of about 500 mg L^{-1}. Hence, sulfate attack had mainly appeared in environments with generally low SO_4 concentrations and the underlying reactions were yet to be understood. Former studies have reported on similar observations [18, 19]. Evaporation was suspected to have caused the critical level of sulfate concentration, which have finally led to the TSA-induced concrete damage.

However, the effect of evaporation on TSA has not yet been proven and was by far not quantified in such a scenario. Therefore we analyzed the chemical and isotopic composition of ground and drainage water as well as of the interstitial solutions that were extracted from heavily damaged concrete samples. In these samples the extracted solutions accounted for about 5 up to 20 wt.% of the solids. In these aqueous solutions extreme accumulations of sodium and sulfate were observed. While the Na content ranged between 0.2 – 4.0 mg L^{-1} in the ground water, it reached >17000 mg L^{-1} in some of the expressed interstitial solutions [14]. SO_4 concentrations therein rose up to >30000 mg L^{-1}. An extreme and linear enrichment of univalent cations (e.g. K and Rb) with a conservative behavior in the expressed solutions suggested evaporation of water to have caused the extreme contents in the interstitial solutions. A further indication for highly concentrated sodium sulfate interstitial solutions is the existence of mirabilite ($Na_2SO_4{\cdot}10H_2O$) in the efflorescence, as identified by XRD (Figure 3).

The positive proof for evaporation has been delivered by the δ^2H and δ^{18}O analyses of the expressed water. Compared to the ground water the interstitial solutions displayed a strong enrichment of the heavy stable isotopes. Thus, this isotopic signature clearly indicates evaporation of the local ground water [20]. Using the multi-proxy approach we were able to calculate the evaporation degree to be 5 – 38 % (percent of evaporated water). This range is much lower than modeled evaporation degrees, based on trace elemental contents, e.g. K and Rb, which resulted in evaporation degrees of up to ~99.7 % [14]. These variations clearly relate that numerous wetting and drying cycles had been occurring. Physical and chemical alteration processes are enhanced in such a highly dynamic system, resulting in more destructive effects on concrete [21].

A further curiosity with a high need to be investigated was the incongruent dissolution of dolomite aggregates (Figure 5). In spite of being a well-known reaction for deteriorating concrete, it has not gained much attention in scientific research. The so-called alkali carbonate reaction (ACR) comprises the dissolution of dolomite at alkaline conditions in concrete [22]. Previously we have suggested that dolomite aggregates were preferentially dissolving incongruently governed by high Ca/Mg ratios in the interacting aqueous solution or interstitial solutions [23]. For the investigated cases, calcite was surprisingly more stable than dolomite, because as long as the pH remained above 10.5 the continuous leaching of Mg from the dolomite in the presence of interstitial solutions has led to the formation of brucite ($Mg(OH)_2$), which speeded up the breakdown of the dolomite. One typical example of sulfate attack in combination with the progressing alteration of dolomite aggregates is illustrated in Figure 5, where incongruent dissolution of dolomite takes place simultaneously with the formation of secondary calcite and brucite.

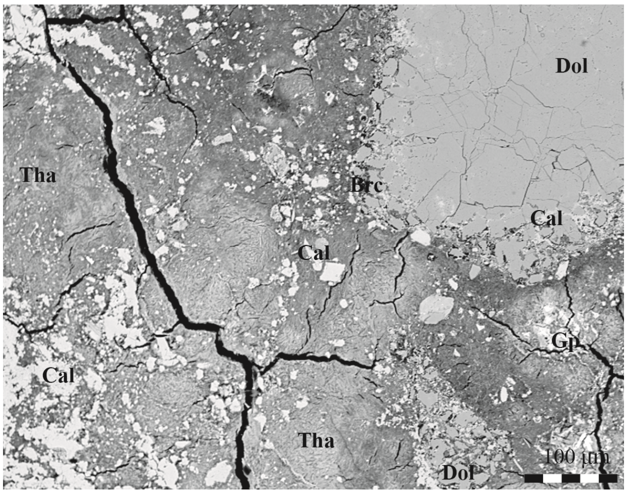

Fig. 5. BSE image of a polished damaged concrete sample. The cementitious matrix has been completely replaced by thaumasite (Tha), secondary calcite (Cal) and small amounts of gypsum (Gp). The dolomite (Dol) aggregates show incongruent dissolution features, as evident by the occurrence of marginal calcite and brucite (Brc) as alteration products.

4 Conclusions

The application of our novel multi proxy approach, which includes mineralogical and microstructural analyses as well as interpretations of stable isotope distributions and trace element signals, has shown to be a powerful tool to get a deeper and more sophisticated understanding of concrete deteriorating processes. Complex reaction paths and individual causes for the damage can be derived and reconstructed. Thus, repair and remediation measures can be conducted more efficiently and potential threats to the concrete structure can be assessed in the forefront of future projects.

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