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Environmental controls and reaction pathways of coupled de-dolomitization and thaumasite formation

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ABSTRACT

Deteriorated concrete and interstitial solutions (IS) were collected from Austrian tunnels to elucidate potential connections between de-dolomitization caused by coupled alkali carbonate reactions (ACR) and thaumasite form of sulfate attack (TSA). A conceptual reaction model for the portlandite–CSH phases–dolomite–calcium sulfate–calcite–brucite–thaumasite system was developed based on experimental data, hydrochemical modelling, IS chemistry and apparent concrete compositions. During the initial stage of sulfate attack, ettringite and gypsum formation weakened the concrete's microstructure and initiated ACR. Leaching of hydrated cement phases resulted in IS with a pH ~ 12-13, which promoted incongruent dolomite dissolution. Infiltration of Ca–SO_4–type ground water into the de-dolomitization zone facilitated calcite and brucite neo-formations at $13 > pH > 10.5$ during advanced states of concrete deterioration and subsequently resulted in thaumasite precipitation at pH ~ 8.7. In this contribution, the reaction mechanisms and environmental controls of de-dolomitization are discussed in relation to the durability of concrete under sulfate attack.

1. Introduction

Down to the present day, deterioration of concrete and cement-based materials used in various underground structures is frequently related to chemical alteration. Although external sulfate attack has been considered to be a major threat, significant gaps in knowledge persist regarding the environmental controls and reaction mechanisms linked to external sulfate attack on concrete. Sulfate attack and alkali aggregate reactions (AAR) are strongly reducing the durability of cementitious materials and typically result in of ettringite (Ett) formation, precipitation of sodium sulfate efflorescence and gypsum (Gp), thaumasite form of sulfate attack (TSA), delayed Ett formation (DEF), bacteriogenically-induced sulfuric acid attack, alkali silica reactions (ASR) or alkali carbonate reactions (ACR). The above processes result in severe (micro)structural and mechanical damage and, probably most importantly, chemical alteration of the concrete through multiple and partly overlapping mineral dissolution and replacement reactions [1–9].

TSA is one of the most hazardous processes causing concrete corrosion and typically occurs at temperatures < 10 °C, a pH around 9 and during multiple wetting-drying cycles, in particular at high concentrations of aqueous SO_4^{2-} (up to 30 g L^{-1}), silicic acid, Ca^{2+} and CO_3^{2-} ions (total dissolved solids, TDS from 15 to 60 g L^{-1}) in the interstitial solutions [10–12]. TSA is a rather slow concrete damaging process and it is commonly initiated by cracking and softening of the concrete due to previous Gp and Ett formation. Other possibilities for thaumasite formation are via direct precipitation or the reaction of calcium carbonate with severely Ca-leached CSH phases [11,13–27]. TSA is known to cause (micro)structural damage to the cement paste by generating expansive forces in particular in the small pores of the microstructure [18,28,29]. While the influence of limestone fillers on TSA have been extensively studied in lab experiments, the effects of dolomite (Dol) fillers in this context have not been clearly identified [7,13,18,19,30–33].

In acidic environments, the apparent dissolution rate of Dol [$CaMg(CO_3)_2$] positively depends on H^+ concentration, but is notably slower than that of calcite [34]. Under strongly alkaline pH found in pore solutions of most cementitious materials, it is currently believed that magnesium carbonate aggregates such as Dol are on the long term transformed into brucite [$Mg(OH)_2$] and calcite [$CaCO_3$] through liberation of alkali and calcium hydroxide ions from the cement paste

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[35–43]. This incongruent Dol dissolution (de-dolomitization) increases the concrete's microporosity and helps SO_4^{2-} ions to infiltrate the altered concrete, resulting in the precipitation of volume expansive minerals such as Ett $[Ca_6Al_2(OH)_{12}(SO_4)_3\cdot 26H_2O]$ and thaumasite $[(Ca_3SiO_3)(SO_4,CO_3)\cdot 15H_2O]$. Due to the low solubility product of ordered Dol ($K_{Dolomite} = 10^{-17.09}$ at 25 °C), the rate of de-dolomitization in strongly alkaline solutions is considered to be slow [44,45] and hence the role of coupled ACR and TSA during de-dolomitization remains questionable.

Advanced knowledge about highly dynamic water-rock-cement-aggregate-interstitial solution interaction, involving ACR and TSA, is therefore required to better predict the performance and durability of concrete in alkaline, sulfate-loaded environments. In this study, we report results from heavily deteriorated shotcrete and concrete sampled from Austrian tunnels that have suffered from coupled ACR and TSA. Using mineralogical and chemical analytical methods as well as experimental and modelling approaches, we decipher the spatiotemporal connections of the reaction paths, mechanisms and the environmental controls of de-dolomitization linked to ACR and TSA in alkaline cementitious media.

2. Study sites

Damaged concrete that has suffered from intense sulfate attack was sampled from an Austrian railroad tunnel (RR) as well as from a ventilation tube for an adjacent highway tunnel (HW). Both tunnels are ~5400 and ~4800 m in length and are passing nearly parallel, in a distance of ~100 m, through the same mountain ridge. The mountain ridge exposes massive lime- and dolostone units in the center of the transverse section and low-grade metamorphic rocks with embedded evaporitic, Gp $[CaSO_4\cdot 2H_2O]$ and anhydrite $[CaSO_4]$, lenses in the northern and southern areas of both tunnels. Intensive concrete damage occurred especially in these sections that are exposed to evaporite-hosting horizons. In these restricted areas, ground water discharge is generally lower compared to the regions adjoining to the lime- and dolostone units, where runoffs up to 100 $L\ s^{-1}$ are reached. More information about the local geological units, hydrogeology, hydrogeochemistry and the spatial distribution of different damage zones in the concrete linings from both tunnels is given in [11,16].

3. Experimental

Stoichiometric Dol crystals from Eugui (Spain) in gemstone quality were taken from the mineral collection of the Institute of Applied Geosciences (Graz University of Technology) for the Dol dissolution experiments. The Dol crystals were crushed in an agate mortar for 10 min. About 250 mg of the <63 μm sized Dol powder was then placed in 300 mL gas-tight glass reactors. In order to investigate the effect of different alkalis and alkali earths on the dissolution behavior of Dol at pH 11.8 ± 0.3 and 12.2 ± 0.2 (starting solutions were modelled with PHREEQC), 2 mM and 20 mM NaOH and $Ca(OH)_2$ solutions were prepared by dissolution of adequate volumes of Merck-Titrisol and pro analysis chemicals in Milli-Q water (18.2 MΩ at 25 °C). The $Ca(OH)_2$ solutions were prepared under an argon atmosphere and filtered through 0.45 μm cellulose acetate filters to prohibit CO_2 absorption from the atmosphere into the solution and to remove any $CaCO_3$ impurities, if present. Immediately after adding the respective experimental solutions to the reaction vessels containing Dol, the reactors were sealed and kept gas-tight at a constant temperature of 8 ± 2 °C and 20 ± 2 °C for 4 months. In a second experimental series, Dol was reacted at pH 12.5 ± 0.1 for ~4.5 years at 8 ± 2 °C in 10 mM NaOH or 5.5 mM $Ca(OH)_2$ solutions containing 31 and 312 mM Na_2SO_4 (~3 and ~30 $g\ L^{-1}$ SO_4^{2-}), respectively, in order to study the de-dolomitization progress under conditions similar to those observed in the Austrian tunnels [11,16]. At the end of the experimental runs, the reactive fluid pH was immediately measured. The solids were filtered through 0.45 μm cellulose acetate filters, rinsed with ethanol and dried at 40 °C.

4. Materials, analytical methods and hydrochemical modelling

4.1. Solid sampling and analyses

Heavily deteriorated concrete and shotcrete as well as non-altered concrete and shotcrete were sampled from several delicate locations from the RR and HW tunnels and stored in a cooling box at 8 °C. Representative sample fragments were either cut out from drillcores or taken from concrete mush and embedded in epoxy resin under vacuum. Thin sections were prepared for petrological and (micro)structural analyses comprising of electron microprobe analysis (EMPA) and focused-ion beam and scanning electron microscopy (FIB-SEM). Back-scattered electron (BSE) images were first collected on polished, C-coated thin sections using a JEOL JXA-8200 Superprobe (JEOL, Tokyo, Japan) electron probe microanalyzer. Mineral identification was carried out by single spot analysis using the implemented energy-dispersive (EDX) systems operated at 15 kV and 10 nA. Elemental distribution images of Ca and Mg were recorded by the WDX analytical mode at the respective Kα line peak positions with a beam current of 30 nA. 1000 × 1000 point analyses and a step size of 1 μm yielded elemental distribution mappings of 1.0 × 1.0 mm. The quantification (in wt%) of the individual mappings was performed against certified Cal and Dol mineral standards from SPI. In order to trace variations at the microscale range the mineral phases Brc and secondary calcium carbonate (Cal_{sec}) were detected and quantified by setting elemental thresholds to 42 ± 7 and 40 ± 3 wt% of Mg and Ca, respectively. Small area spot analyses (4 × 3 μm) of Ett/Tha rich zones, Cal and Dol aggregates and Cal_{sec} were carried out with a probe current of 0.5 nA using SPI mineral standards for the quantification (for Ett/Tha analyses: pyrope for Al, Si and Fe, anhydrite for Ca and S and tugtupite for Cl; for carbonates analyses: dolomite for Mg, calcite for Ca and celestine for Sr).

The microfabric of heavily deteriorated concrete (taken at position 4156 m away from the north portal of the railroad tunnel) was studied using a Zeiss Auriga CrossBeam FIB-SEM. A Pt-coated surface area, about 25 × 20 μm in size, was tilted normal to the ion beam. Subsequently, ion milling was applied to create a cross-sectional surface of 15 × 15 μm that was imaged by the electron beam at an accelerating voltage of 5 kV. 3-D information of the investigated area was obtained using a serial sectioning procedure with alternating milling and imaging intervals to acquire a 2-D secondary electron image (SEI) sequence across the selected volume [46]. In total, 136 SEI were acquired with a 25 nm slice thickness. 3-D visualization of pore space and mineral phases present in the damaged concrete was realized based on grey-level contrasts of the SEI using the ImageJ© software and the threshold method of Baldermann et al. [47]. In addition, alteration features related to the Dol dissolution experiments were identified based on SEI acquired at 10 kV accelerating voltage on Au/Pd-sputtered samples with a Zeiss DSM 982 Gemini SEM.

For mineralogical investigations, the concrete samples were dried at 40 °C, following grinding in a McCrone micronizing mill for 8 min, together with 10 wt% of a ZnO standard. X-ray diffraction (XRD) was carried out on randomly oriented preparations using a PANalytical X'Pert PRO diffractometer outfitted with a Co-tube (40 kV and 40 mA), 0.5° antiscattering and divergence slits and a Scientific X'Celerator detector. The samples were examined over the 5–85° 2 Θ range with a step size of 0.004° 2 Θ and a count time of 40 s per step. Mineral quantification was carried out by Rietveld refinement of the powder XRD patterns using the PANalytical X'Pert HighScore software (version 2.2e) and pdf-2 database. Experimental precipitates were investigated in analogy to the concrete except for the determination of the amorphous content.