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ABSTRACT: In this paper we present an overview about our findings concerning the damage of underground concrete structures. Case studies were performed in Austrian highway and railroad tunnels and associated structures for drainage and ventilation. In several cases severe damage of the concrete was found owing to sulphate attack, alkali aggregate reactions, leaching and drainage clogging. The focus of this study is to demonstrate by some selected examples how to decipher the causes and reaction mechanisms of damaging reactions. Thus besides conventional mineralogical and hydro-geochemical methods we apply stable isotope and trace element signals within multi proxy approaches. For instance stable isotope results indicate that SO_4^{2-} and CO_3^{2-} from local ground water are mostly responsible for thaumasite formation. More detailed knowledge on individual reactions responsible for concrete damage in underground structures will help to find specific counter measures for already affected buildings and to develop proper concrete recipes, applications and constructive measures for future projects.

1 INTRODUCTION

Remediation and reconstruction of damaged concrete structures in the underground caused by the interaction with the local environment is highly cost intensive and has to be reduced at all means. However, due to the environmental conditions, like geology, temperature and ground water chemistry, underground structures are frequently affected by serious damage (Leemann and Loser, 2011). Glasser et al. (2008) have pointed numerous reactions that may take place in the concrete—water—atmosphere system and may lead to concrete damage. In the present study sulphate attack and subsequent thaumasite formation is highlighted. In spite of enormous research effort there still persist many uncertainties in regard to causes and reaction mechanisms. Thus, the understanding has to be brought to the next level. A powerful tool to approach such matter is the application of stable isotopes (Iden and Hagelia, 2003). With this study we demonstrate that multi proxy approaches including isotopic signatures and trace element contents will lead to a deeper understanding of concrete damage.

2 MATERIALS AND METHODS

We have sampled solids and liquids from Austrian highway and railroad tunnels. Solid samples comprise shotcretes and concretes (unaltered and deteriorated) and secondary formations such as mushy concrete, efflorescences and sinter. Completely disintegrated mushy material was shoveled in plastic bags and consolidated concrete was excavated taking drilling cores. Furthermore natural host rock and soot relicts found in one railroad tunnel were investigated. Samples were analyzed by XRD, SEM and EPMA. Liquid samples comprise drainage solutions, local ground water and interstitial solutions that were expressed from damaged concrete material. In the field temperature and pH of ground and drainage water were measured. The alkalinity was determined by potentiometric titration with HCl in the lab. Concentrations of dissolved ions were analyzed by IC and ICP-MS. Furthermore stable isotope ratios of $^{34}\text{S}/^{32}\text{S}$, $^{13}\text{C}/^{12}\text{C}$, $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/\text{H}$ of were measured of solid and liquid samples.

3 RESULTS AND DISCUSSION

XRD pattern of sound concretes and shotcretes display poorly crystalline CSH-phases, portlandite ($\text{Ca}(\text{OH})_2$) as well as silicate and carbonate aggregates. Mineralogical investigations (XRD, EPMA, SEM) clearly show that severe concrete deterioration is caused by sulphate attack. Complete disintegrated materials consist mainly of thaumasite, calcite and silicate aggregates. Gypsum was found in small quantities and ettringite could not be identified unambiguously due to the structural similarity and the overwhelming presents of thaumasite. Furthermore significantly reduction and even total lacking of dolomite aggregates were detected by comparing sound and deteriorated material. Surprisingly ground water and drainage water analyses generally showed only low to moderately elevated SO_4^{2-} content with values ranging from about 3 to 500 mg/l. Consequently arising the question: Is dissolved SO_4^{2-} of ground water the only source or are we facing other S sources coming from e.g. internal from concrete/shotcrete, oxidation of pyrite, atmospheric contribution, or organic matter such as soot. The latter source was the most likely candidate for a more than 100 years old railroad tunnel which was not properly cleaned before shotcrete was applied about 50 years ago. In spite of rather low SO_4^{2-} content in the ground water S-isotope measurements clearly indicate that SO_4 in thaumasite is stemming from infiltrating ground water implicating the dissolution of local occurring gypsum and anhydrite rocks. $\delta^{34}\text{S}$ values of thaumasite, ground water SO_4^{2-} and host rock are mostly within the range of +14 to +27‰ (Mittermayr et al., 2012a). In a few locations significantly lower $\delta^{34}\text{S}$ signals were detected in thaumasite resulting from pyrite oxidation. Interestingly internal sulphate attack or contributions from soot or the Earth's atmosphere can be ruled out by the given $\delta^{34}\text{S}$ ranges which opens up a new subject: How does ground water with about 500 mg/l of sulphate or even less may cause intensive sulphate attack? Therefore we analyzed the chemical and isotopic composition of interstitial solutions extracted from heavily damaged concrete samples by using a hydraulic press. Proportions of extracted solutions correspond to about 5 up to 20 wt.% of the solid material and extreme accumulation of Na^+ and SO_4^{2-} is observed compared to the locally occurring ground water. Considering the dramatic increase of univalent cations compared to the local ground water and the rather conservative behavior of e.g. K^+ and Rb^+ suggests evaporation of water to be responsible for extreme SO_4^{2-} concentrations of up to 30000 mg/l (Mittermayr et al., 2011). Proof is gained from analyses of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of H_2O molecules which display a strong enrichment

of the heavy stable isotopes. The respective kind of isotopic evolution clearly indicates evaporation of H_2O from the local ground water. A further curiosity with a high need to be verified was the incongruent dissolution of dolomite aggregates. Previously we have suggested that dolomite aggregates are preferentially dissolving incongruently governed by high $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio in the interacting aqueous solution. Calcite becomes more stable versus dolomite. As long as the pH remains above 10.5 the continuous removal of dissolved Mg^{2+} from the solution is leading to brucite ($\text{Mg}(\text{OH})_2$) formation. Surprisingly in all cases where sulphate attack in combination with dolomite aggregates was found, a partial dissolution of the latter and precipitation of secondary calcite and brucite was observed. Thus we assumed carbonate released by dolomite dissolution to have contributed to thaumasite formation. Various studies suggest that the carbonate can be stemming from the absorption of atmospheric CO_2 , carbonate aggregates or DIC of ground water. To investigate the carbon source in thaumasite we applied stable carbon isotopes. In contrary to our assumption that carbonate is originating from dolomite aggregates, we found the carbon in thaumasite to be related to the uptake of ground water DIC. $\delta^{13}\text{C}$ values from thaumasite and DIC are mostly in the same range from -11 to -5‰ (Mittermayr et al., 2012b). Most carbonates used as aggregates are usually much heavier in isotopic values and are plotting at $0 \pm 2\%$. In contrary Dietzel (1995) has pointed out that the formation of calcium carbonate related to the absorption of atmospheric CO_2 is leading to a strong depletion of ^{13}C versus ^{12}C . The latter reaction occurs at high pH and is governed by a kinetic isotope fractionation leading to $\delta^{13}\text{C}$ values of $-25 \pm 3\%$.

4 CONCLUSION

Applications of multiproxy approaches including stable isotope distributions and trace element contents have shown to be very powerful tools for a deeper and sophisticated understanding of concrete deteriorating processes. Complex reaction paths can be reconstructed and individual causes for the damage can be revealed. Thus repair and remediation measures can be focused and potential threats to the concrete structure should be assessed in the forefront of future projects.

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