Sulphate Mineral Formation in Hydraulic-setting Cements

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Introduction

The formation of sulphate minerals in hydraulic-setting cements is well known. However, significant lack of knowledge exists with respect to the secondary transformation reactions, which may be accompanied with substantial micro structural changes and a decrease of stiffness e.g. of respective tunnel walls. A series of studies are proposed combining several analytical techniques (e.g. ICP-OES, ICP-MS, XRF, XRD, SEM, TEM, FT-IR, Raman spectroscopy, AFM), solidity test procedures, experiments (e.g. batch, column and flow through reactors) as well as field studies at selected tunnels to provide new insights into the reaction kinetics, controlling parameters and environmental conditions for the formation of sulphate minerals in hydraulic-setting cements in particular thaumasite. The studies are embedded in several research topics on water rock interaction and in the Waterpool Network Austria (WP 431).

Experiments will be focussed on transformation mechanisms within the hydraulic-setting cements and the stability of thaumasite with special regard to the fractionation of stable isotopes of carbon, sulphate, oxygen and hydrogen. In a first step field studies were carried out in tunnels with recent sulphate damage of cements or sulphate attack at gunite panelling (Bosruck and Arlberg railway tunnel) by combining respective material analyses with local geological settings and hydrogeochemical data.

Results

The damage in the Bosruck railway tunnel is macroscopically characterized by a dry, foliate or humid pastry like material with micro crystalline intercalations. The damaged zone destroys the mechanical binding between the lining and the gunite panelling and is therefore an enormous security problem. XRD, FT-IR, SEM and XRF investigations of decomposed materials from several places along the railway tunnel identified the formation of ettringite, thaumasite and isolated gypsum. Morphology of ettringite and thaumasite is quite similar but the needle like and prismatic thaumasite crystals are a little shorter. The current analyses were not able to answer if the thaumasite was the result of a direct formation from the cement minerals + Ca-sulphate + carbonate + water or from the transformation of the precedingly formed ettringite. However SEM-analyses proved the presence of ettringite-thaumasite compounded crystals. Further investigations should settle this question. ICP-OES analyses of pore waters which circulated through the gunite panelling revealed high amounts of SO_4^{2-} and Cl^-. As several sources (e.g. SO_4^{2-} containing rock water, SO_2 of the fumes) are discussed in the literature, the $\delta\ ^{34}S_{CD}$ isotopic signature of some damaged materials was analysed. The results are in a range of $\delta\ ^{34}S_{CD}$ +14,79 - +22,18 ‰, which agree with the results of evaporates ($\delta^{34}S_{CD}$ +10 - +27 ‰). The sulphate therefore originates form SO_4^{2-} bearing pore waters. It is to be expected that significant damaging will continue.

The damaged zones in the Arlberg railway tunnel appear quite similar. In the damaged gunite panelling materials both thaumasite and ettringite are frequent. Moreover in the damaged space mortar significant amounts of of secondary formed gypsum and some sodium-carbonate-hydrate and potassium-sodium-sulphate were found. Especially the intensive formation of gypsum requires a high influx of sulphate (> 1300 SO_4^{2-} mg/l). Standard analyses of the pore water however classified them as not aggressive against concrete. This indicates that in some places in the Arlberg railway tunnel high sulphate mobilisation must take place. Fumes and weathering of sulphide minerals could be responsible for the massive gypsum formation in the damaged space mortar. Isotopic investigations is a topic of a further research and should settle this question.

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