
TESTING SULFATE RESISTANCE OF CONCRETE – LIMITATIONS OF ACCELERATION

Duration

Project team

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INTRODUCTION

External sulfate attack on concrete is a common occurrence in Swiss tunnels. Therefore, testing the sulfate resistance of specific concrete mixtures for tunnel construction is essential. A test allowing to assess sulfate resistance of job site mixes is incorporated in the Swiss standards since 2003 [1]. Recently, some concrete produced with ordinary Portland cement (OPC) passed the test. As a consequence, its applicability has been questioned and alternative test protocols have been proposed.

EXPERIMENTAL PROGRAM

In this study, 17 concrete mixtures were produced using various cements with low and high sulfate resistance (3 different CEM I, 1 CEM I SR, 3 CEM II/B HS (HS = high sulfate resistance according to SN EN 197-1), 1 CEM II/A-LL, 1 CEM III/B) at w/c of 0.45 and 0.50. They were tested using three different test protocols: the Swiss standard method ("method 1") and two alternative methods ("methods 2A and 2B"). In method 1 [1,2] six concrete cores ($\varnothing = 28$ mm, length 148 mm) are subjected to four drying (five days at 50 °C)/wetting cycles (two days in 5% Na₂SO₄ solution at 20 °C) at the age of 28 days. After the cycles, the cores are immersed in 5% Na₂SO₄ solution at 20 °C for eight weeks. The length change during this immersion period is measured. The limit value is 1 ‰. In method 2A, six cores ($\varnothing = 50$ mm, length 148 mm) are dried at 80 °C for five days. Afterwards, three are pressure impregnated with water and three with 4.4% Na₂SO₄ solution and subsequently immersed in the corresponding liquid for 168 days. The difference in length change between the samples stored in water and sulfate solution, respectively, is the used parameter to assess sulfate resistance. The limit value is 0.5 ‰. Method 2B is identical to 2A, but the drying temperature is only 50 °C instead of 80 °C with a prolongation from five to 21 days. In addition to the length (and mass measurements), selected concrete mixtures were studied after the tests using scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS). The analyzed elements were O, Na, Mg, Al, Si, S, K, Ca and Fe. Sulfur profiles of selected cores after the sulfate tests were acquired performing EDS line scans with 40 points per depth. Additionally, mortar mixtures were produced using four different CEM I supplementing the investigation of the concrete. They were characterized with X-ray diffraction and thermogravimetry before drying, after drying at 50 and 80 °C for five days and after water immersion for 91 days following the drying at 80 °C.

RESULTS

XRD and TGA of the mortar showed that the amount of ettringite was slightly decreased by drying at 50 °C and completely disappeared by drying at 80 °C. Additionally, monocarbonate disappeared as well by drying at this temperature. After water immersion for 91 days of the cores dried at 80 °C, ettringite was present again in a similar amount compared to the undried state.

The length changes in method 1 are considerably lower than the length changes in method 2A. A few concrete mixtures showed a larger length change in method 2A immersed in water than the corresponding concrete tested according to method 1. However, the length changes in method 2B are smaller than in method 1. Figure 1 shows a comparison between the results obtained with the three methods. Four concrete mixtures are above the limit value in method 2A, but below it in method 1. Seven concrete mixtures are above the limit value and six below it in both methods. Only three concrete mixtures are slightly above the limit value in method 2B. It stands out in methods 2A that the concrete mixtures produced with CEM I reach very high length changes compared to the other concrete mixtures. This is not the case in method 1 and 2B.

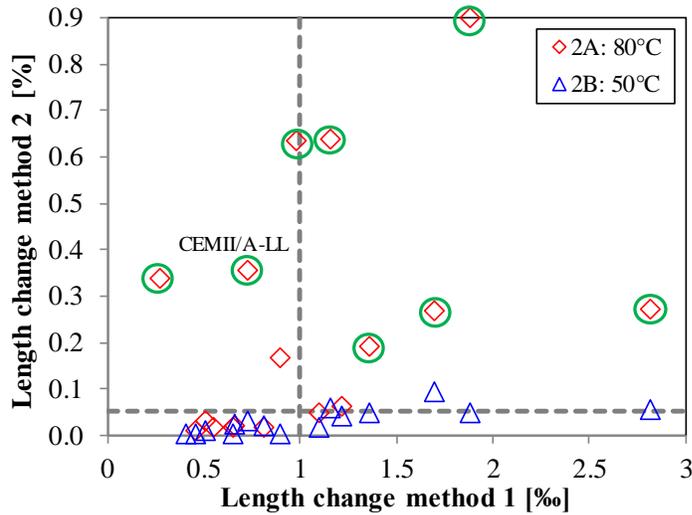


Figure 1: Length change in method 2 as a function of length change in method 1. The green circles indicate concrete mixtures produced with CEM I including one concrete produced with CEM II/A-LL.

Sulfur ingress reaches the central part of the cores tested according to method 1 with increasing concentration towards the surface of the cores (Figure 2A). In contrast, sulfur content in the cores tested with method 2A is only above the initial sulfur content of the cement paste in the outermost area representing a depth of 1 and sometimes up to 4 mm (Figure 2B). As the mass change from the dried to the immersed state is recorded, the amount of sulfur uptake can be calculated. As method 1 includes four drying immersion cycles the sulfur uptake is larger compared to method 2A that includes only one drying-immersion step (Figure 2).

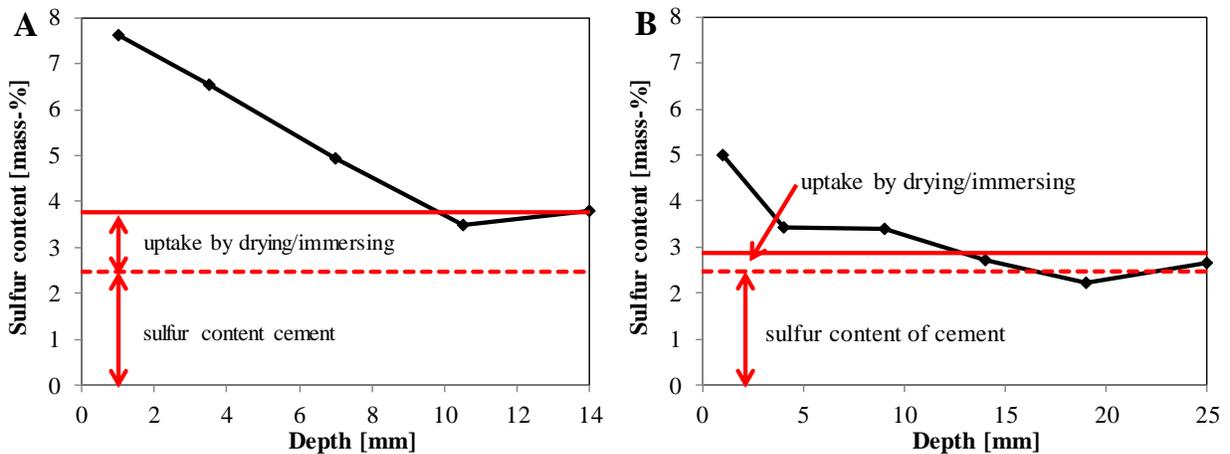


Figure 2: Sulfur content as a function of depth in the cores tested according to method 1 (2A) and 2A (2B). The initial sulfur content of the cement paste and the uptake by drying/immersing are indicated.

There are significant differences in the microstructure of the concrete mixtures tested according to method 1 and method 2A. In the former, ettringite is finely distributed in the cement paste as identified with atomic ratio plots with occasional pockets within the boundaries of former C₃A grains. Cracks are empty. In the later, ettringite fills larger capillary pores and partly fills air voids. In most of the concrete mixtures produced with CEM I ettringite veins run across the entire sample. This not only applies to the cores stored in the sulfate solution but as well to the cores stored in water (Figure 3).

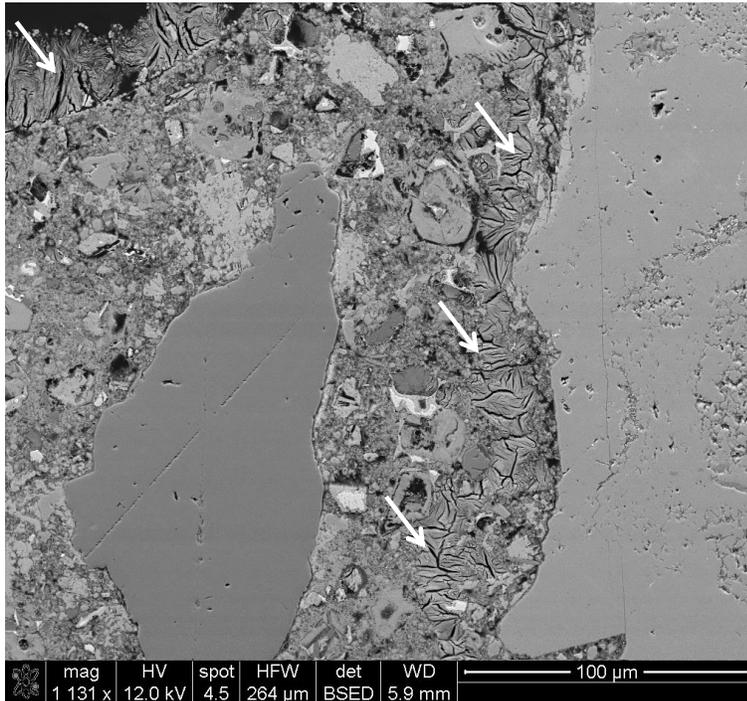


Figure 3: Ettringite vein (white arrows) along aggregate and air void partly filled with ettringite in a concrete produced with CEM I and stored in water according to method 2A.

Concrete tested according to method 2A and immersed in sulfate solution showed two peculiarities. Firstly, aluminum gel occasionally formed in aggregates containing mica and feldspar. Its formation was accompanied by the formation of ettringite (Figure 4). Secondly, some aggregates were cracked and ASR gel was present (Figure 5). Its composition that is usually dominated by K (representing cement composition) showed very high levels of Na.

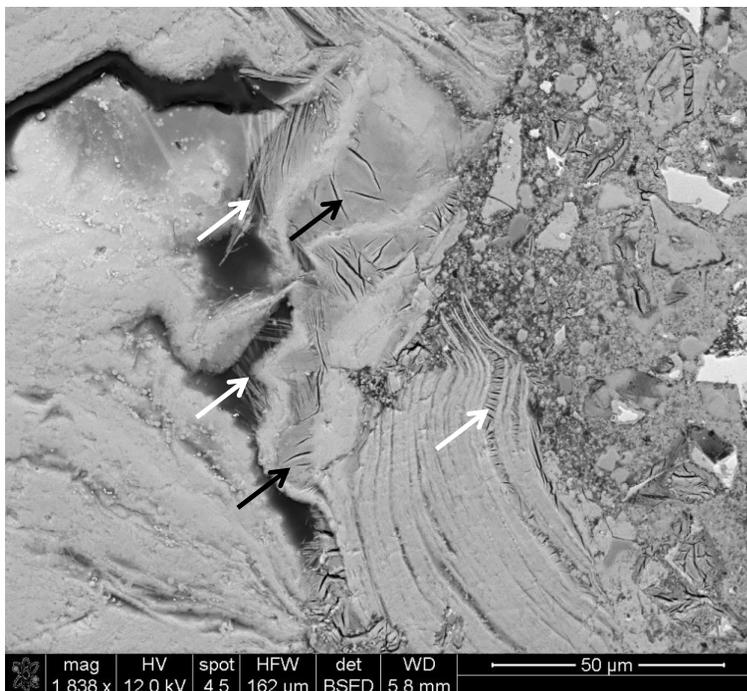


Figure 4: Occurrence of aluminum gel (black arrows) and ettringite (white arrows) in an aggregate with mica and feldspar of a concrete produced with CEM I and stored in sulfate solution according to method 2A.

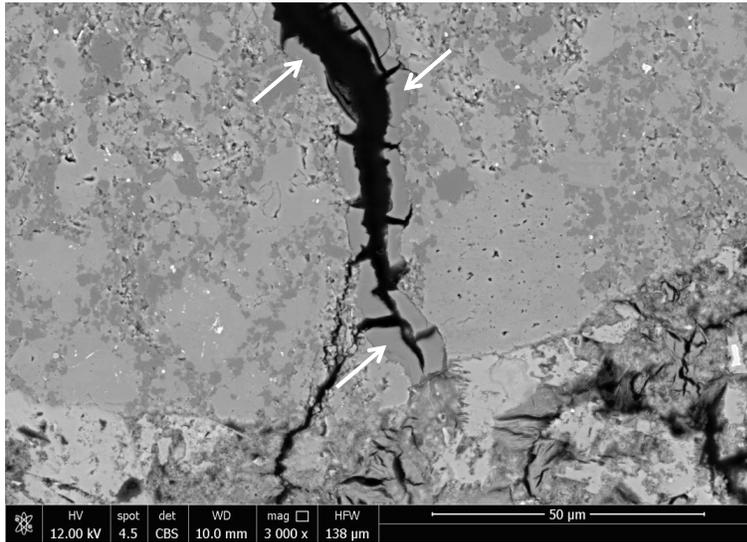


Figure 5: ASR gel (white arrows) with Na/K-ratio of 10 in siliceous limestone of concrete stored in sulfate solution according to method 2A.

CONCLUSION

Drying at 50 °C preserves the ettringite formed during cement hydration, while it is destroyed by drying at 80 °C.

Method 1 assesses the potential of concrete expansion due to ettringite formation and as such, is a reliable method for sulfate resistance.

The expansion in method 2A is caused by several mechanisms. Substantial damage going along with expansion is caused by secondary ettringite ("delayed ettringite") formation in the samples stored in water and sulfate solution as a result of the drying temperature of 80 °C. Ettringite formation due to external sulfate attack contributes to the observed length changes. Partial dissolution of mica and feldspar provides additional aluminum for ettringite formation. Moreover, the high drying temperature additionally leads to SiO₂ dissolution causing expansion due to ASR. Additionally, the Na₂SO₄ solution provides Na that is incorporated in the ASR product. Consequently, the method is inapt for testing the resistance of concrete to external sulfate attack.

Due to the low amount of sulfate uptake in method 2B the resulting length changes are small and do not allow to reliably identify concrete mixtures with high or low sulfate resistance.

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