



Improved volume stability of mortar bars exposed to magnesium sulfate in the presence of bicarbonate ions



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ARTICLE INFO

Keywords:

Sulfate attack (C)
Carbonation (C)
Corrosion (C)
Expansion (C)
Blended cement (D)

ABSTRACT

The effect of the simultaneous occurrence of sulfate and bicarbonate ions in magnesium containing solutions was investigated for a CEM I and CEM III/B mortar under laboratory conditions. The presence of bicarbonate ions, which is common in natural waters, prevents the typical expansion and surface erosion of CEM I mortars and the surface deterioration of CEM III/B mortars. The chemical effect of the bicarbonate ions is twofold. The precipitation of CaCO₃ lowers the availability of CaO for the formation of additional sulfate bearing phases like ettringite and gypsum. The second effect is the reduction of supersaturation of the pore solution with respect to ettringite. The absence of deterioration is linked to the formation of only small amounts of ettringite and to the absence of gypsum in the affected zones. Thermodynamic modeling suggests that relatively small bicarbonate concentrations suffice to prevent damage, contribute to the scarcity of damage under natural exposure conditions and to the diversity of results under laboratory exposure conditions.

1. Introduction

The chemical reactivity of cementitious binders makes them susceptible to interaction with sulfate, carbonate or chloride ions in their service environment. These ions are often termed “aggressive” and the term “sulfate attack” is commonly used to describe the interaction with sulfate bearing waters [1–4]. The sulfate concentrations on the outside of the specimen as well as the transport and binding in the mortar or concrete play an important role for the deterioration process and lead to varying sulfate distributions within a specimen. Direct analysis of the compositional variation of the pore solution in a specimen with spatial resolution is not (yet) possible and transport models suffer from the ill-defined changes in porosity during sulfate interaction and their effects on the transport properties [5]. Our knowledge of the observable ingress is thus based on the analysis of the solid phases, e.g. from electron microscopy combined with energy dispersive X-ray spectroscopy, as the sulfate content in the solids is dominating in comparison to the small quantities contained in the pore solution.

The varying sulfate distributions within specimen exposed to external sulfate makes it difficult to distinguish the effects of transport, additional volume generated and crystallization pressure. In cases of internal sulfate attack, as e.g. calcium sulfoaluminate cements with

high calcium sulfate additions, transport of sulfate is not a significant factor and the pore solution composition of the specimen can be studied and considered representative. In such cements it has been documented that the supersaturation of the pore solution with respect to ettringite and the resulting crystallization pressure explains the observed expansion for calcium sulfoaluminate cements (e.g. [6–8]).

The composition of cement plays an important role as it determines how much ettringite forms initially and the level of supersaturation with respect to ettringite that can be reached under sulfate exposure. The expansion of mortars containing conventional cement blended with supplementary cementitious materials (SCMs) such as blast furnace slag, fly ash or silica fume is considerably lower than the expansion of plain Portland cements. The pozzolanic reaction of SCMs lowers the availability of CaO, which leads to less ettringite and gypsum formation, as well as to lower crystallization pressures [9]. In addition, more aluminum is bound in the low Ca/Si C-S-H phases present in these binders and thereby reduces the availability of aluminum for additional ettringite formation [10].

In a previous publication, it has been shown that the presence of bicarbonate ions in sodium sulfate solutions was beneficial for the volume stability of CEM I and CEM III/B mortar bars [11]. These investigations focused on laboratory tests with high sulfate

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concentrations typical for standard tests (50 g Na₂SO₄/l or 350 mmol/l [12,13]). After an extended period of at least 1 year, in which no expansion was observed in the presence of bicarbonate ions, individual samples showed cracks and volume instability exclusively at corners/ends, most likely due to the very high sulfate concentration used and singular flaws in the mortars where the ingress occurred from more than one direction [11]. It can be expected that the presence of carbonate ions might also play an important role for sulfate related changes in cementitious materials in real service environments, but unfortunately bicarbonate concentrations are often not reported in groundwater analysis.

In this article, the effect of bicarbonate ions (HCO₃⁻) in magnesium sulfate solutions (MgSO₄) was investigated for long exposure times and a sulfate concentration of 35 mmol/l or 2.8 g/l SO₃ (=1/10 of the sulfate content of standard tests), which are the main deviations from engineering tests [12,13]. The chosen sulfate concentration corresponds to sulfate concentrations in natural waters [14–16]. In contrast to sodium sulfate which leads to strong expansion, magnesium sulfate solutions cause predominantly deterioration on mortar surfaces in particular for blended cements [17,18]. Bicarbonate ions are the most common carbon ion species in natural waters with near neutral pH values and present in service environments of concrete structures. Typical bicarbonate concentrations in surface and ground waters are in the range of 0.1 to 10 mmol/l [16,19–21] and thus lower than the 35 mmol/l HCO₃⁻ utilized here, where the same molar quantity of sodium bicarbonate (NaHCO₃) and magnesium sulfate was tested. The impact of changes in the molar ratio between sulfate and bicarbonate ions was therefore calculated by thermodynamic modeling.

2. Materials and methods

2.1. Materials and sample preparation

2.1.1. Cements

The oxide and mineralogical composition of the cements used are provided in Table 1. The Portland cement, CEM I (32.5 R), was from Germany. The cement CEM III/B (32.5 N HS LH), was composed of 30 wt% of the CEM I cement, 70 wt% of a blast furnace slag.

2.1.2. Test solutions

All test solutions contained 35 mmol/l magnesium sulfate, obtained by dissolving 4.2 g MgSO₄/l in de-ionized water. For the bicarbonate containing solutions, 35 mmol/l sodium bicarbonate were added (2.9 g NaHCO₃/l). The solution that contains magnesium sulfate and sodium bicarbonates is identified in this article as *bicarbonate solution* (in figures: +NaHCO₃). The solution volume to mortar volume ratio was 20.

Table 1

Chemical and mineralogical composition (wt%) of the Portland cement and slag blended cement [22].

	CEM I (32.5 R)	CEM III/B (32.5 N HS) LH
SiO ₂	20.3	29.9
Al ₂ O ₃	5.2	9.4
Fe ₂ O ₃	3.2	1.6
CaO	63.4	47.6
MgO	2.5	4.3
SO ₃	2.4	4.5
K ₂ O	0.9	0.7
Na ₂ O	0.2	0.1
TiO ₂	0.3	0.7
CO ₂	0.4	1.1
Loss on ignition	1.0	0.7
Alite	55.7	17.7
Belite	12.1	3.1
Aluminate	7.5	1.4
Ferrite	7.4	1.2

The solutions were exchanged after every length measurement (details given in Section 2.2.1). Additionally, some data was provided for samples stored in de-ionized water only.

2.1.3. Mortar bars

The volumes of the cement, sand, and water were kept constant for all mortars. The mortars were produced with water/binder ratios of 0.55 (CEM I), and 0.59 (CEM III/B): The higher w/b for CEM III/B reflects the lower bulk density of the slag compared to the cement clinker. The sand to binder volume ratio was 3.8, using Normsand (Normensand GmbH, Germany) which consists of silicate aggregates according to the standard DIN EN 196, part 1. Linear expansions were measured on mortar bars (25 × 25 × 150 mm³). The bars were cut from mortar slabs to remove the surface layer of dense paste and any carbonated surface layer. Prior to cutting, the specimens were cured for 28 days. The samples were cured during the first day in a humidity chamber and for additional 27 days as slabs in saturated lime solution. Gauge alignments were glued to the ends of the cut mortar bars by a two-component epoxy adhesive (Araldite 2014-1, Huntsman Advanced Materials, USA) to improve the repeatability of the measurements. Thereafter, the mortar bars were stored for 12 h at a relative humidity of 95% in a humidity chamber to harden the epoxy adhesive before being placed into the solutions in air tight buckets. This storage method was chosen to reduce the interaction of the test solution with ambient air. This procedure, however, will establish also a partial pressure of CO₂ in the bucket and thereby may alter the equilibrium condition of the solution in the bucket.

2.1.4. Cement pastes

The hydrate assemblages were studied by X-ray diffraction (XRD) and thermogravimetric analysis (TGA) on paste samples. To verify the characteristic phase assemblages predicted by thermodynamic modeling, paste samples were prepared to avoid the diluting effect of aggregates in mortars. Homogeneous samples were obtained by mixing 1.5 g of anhydrous cement directly with 100 ml of sulfate solution. The mixtures were stored in 100 ml PVC bottles. The sulfate solutions were not exchanged to avoid the loss of fine particles. The samples were investigated after 5 month of sulfate exposure after being vacuum filtered through a Whatman 40 filter. The remaining solids were rinsed with isopropyl alcohol and diethyl ether, shortly dried at 40 °C and ground by hand after which they were examined by XRD and TGA on the same day to minimize additional carbonation.

2.2. Methods

2.2.1. Investigations on mortar bars

Length changes of the mortar bars were determined in comparison to an Invar steel rod before sulfate exposure, after 7, 14, 28, 56, 91 days of exposure and every 91 days thereafter up to 910 days. A final measurement was performed after a total of 2300 days (6.3 years) of exposure. Lengths and masses were measured on four specimens and averaged.

For selected exposure times, sulfate profiles have been obtained by energy dispersive X-ray spectroscopy (EDX) in order to monitor the sulfate uptake in the different binders as described in more detail in a previous article [18]. The microstructural changes were studied on epoxy impregnated, polished, and carbon coated cross sections (following the steps described in [23], with the exception that the hydration was stopped with isopropanol) of the mortar bars imaged with backscattered electrons in a scanning electron microscope (Philips XL 30 ESEM FEG operated with an acceleration voltage of 15 keV). As the use of averaged numbers measured on phase mixtures dominated by C-S-H makes the identification of gypsum or ettringite difficult, the highest values of calcium and sulfate within a number of EDX points at the same depth (minimum 5, typically 10 ± 2 data points) were plotted. This explains also why the sum of SO₃ and CaO may add up

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