MECHANISM OF ENHANCED SULFATE ATTACK BY LOW MAGNESIUM CONCENTRATIONS

K. Lipus[a], M. Böhm[b]

a.   VDZ gGmbH, klaus.lipus@vdz-online.de
b.   VDZ gGmbH, matthias.boehm@vdz-online.de

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Introduction

According to the German standard DIN 1045-2 Portland cement/fly ash and Portland limestone cement/fly ash blends can be used for making sulfate resistant concrete, if the sulfate attack is ≤ 1500 mg sulfate per liter. It is well known that additional magnesium in the attacking water can increase the sulfate attack, as long as the magnesium concentration is clearly above 300 mg/l. Recently it was observed that mortar and concrete test samples on the base of such cement/fly ash blends showed unexpected damages, although the magnesium concentration was well below 300 mg/l (Lipus, 2011; Müller, 2012; Nobst, 2009). To prove the observation and to investigate this phenomenon an extensive research program was realized over the last three years at the research institute of the German cement industry. So, the material requirements and boundary conditions under which this type of sulfate attack (with 1500 mg sulfate/l and ≤ 300 mg magnesium/l) can lead to damages in mortars and concretes, manufactured with cement and hard coal fly ash according to DIN 1045-2, have been investigated in more detail in this research program.

Investigations

The investigations have been carried out with five cements (CEM I, CEM II/A-LL, CEM II/B-S, CEM II/B-M (S-LL), CEM III/A) and two fly ashes from hard coal as well as a reference with a CEM III/B-SR and a CEM I-SR. The focus of the investigations was on the use of Portland and Portland limestone cement. The analyses of the cements and the fly used are listed in Table 1.

Table 1: Properties of the cements and fly ashes used; n.a. = not analysed

		CEM I	CEM II/A-LL	CEM II/B-S	CEM II/B-M (S-LL)	CEM III/A	CEM I-SR	CEM III/B-SR	SFA X	SFA Y
Spec. surface (Blaine)	cm²/g	2995	3580	3700	4030	3850	3625	4725	3010	4080
CO_2	%	1,75	3,27	1,73	5,59	0,91	1,20	0,61	0,46	0,44
Water	%	0,55	0,66	0,49	1,00	1,74	0,70	0,51	0,31	0,10
SiO_2	%	20,20	20,09	23,93	19,31	27,14	21,16	28,85	48,19	47,45
Al_2O_3	%	5,44	5,31	6,79	5,39	7,16	3,54	9,13	23,22	27,93
TiO_2	%	0,27	0,31	0,63	0,23	0,41	0,20	1,23	0,94	1,21
P_2O_5	%	0,11	0,10	0,08	0,36	0,04	0,32	0,05	0,03	0,70
Fe_2O_3	%	2,46	2,56	1,91	2,84	1,30	5,07	1,16	12,14	9,56
Mn_2O_3	%	0,06	0,06	0,12	0,11	0,09	0,06	0,23	0,13	0,05
MgO	%	1,58	1,53	2,61	2,68	5,40	0,79	4,47	2,02	1,02
CaO	%	63,66	61,72	56,73	57,94	51,77	63,44	48,80	5,14	1,45
SO_3	%	2,92	3,30	3,23	2,94	2,08	2,43	3,01	0,90	0,27
K_2O	%	0,76	0,90	0,63	1,28	1,08	0,73	0,58	2,30	2,86
Na_2O	%	0,19	0,18	0,16	0,29	0,28	0,20	0,22	0,96	1,08
C_3S	%	59,1	57,5	39,8	41,9	n.a.	57,9	19,3	-	-
C_2S	%	13,0	11,7	8,7	7,0	n.a.	20,0	4,8	-	-
C_3A, cubic	%	6,9	6,6	6,5	2,4	n.a.	1,2	2,7	-	-
C_3A, orthorh.	%	3,6	2,6	1,0	2,7	n.a.	0,5	0,7	-	-
C_4AF	%	5,6	5,6	3,7	7,1	n.a.	12,8	2,9	-	-
Calcite	%	3,5	7,4	3,7	11,8	n.a.	2,3	0,6	-	-
Blastfurnace slag	%	0	0	28,9	19,3	n.a.	0	64	-	-

In addition to the variation of the cement composition, the following parameters have been varied to evaluate the influence on the sulfate resistance:

- Pre-storage period: first 2 d in mould and then 0, 12 or 88 d under water or 12 or 26 d in air, all at 20 °C
- Test solution (sodium sulfate solution): 1500 mg/l sulphate plus 0 or 160 or 300 mg Mg/l
- Temperature during storage in test solution: 8 °C or 20 °C
- Sample size: mortar flat prisms (1x4x16 cm³), standard prisms (4x4x16 cm³) and concrete cubes (10x10x10 cm³),
- Mortars: w/c ratio = 0,5; concretes: equivalent w/c ratio = 0,5, with k = 0,4 for fly ash

The sulfate soultion was exchanged on a regularly base. During 24 month the flat mortar prisms have been used for length change (expansion) measurements and the standard prisms for the determination of the dynamic E-Modulus and the compressive strength development. All mortar and concrete specimens have been used for a visual assessment and for microstructural examinations, using scanning electron microscopy (SEM) in combination with energy dispersive microanalysis (EDS).

Results

First, test specimens based on Portland limestone cement showed severe expansion and initial damages in form of structure softening thaumasite formation, when stored at 8 °C in sodium sulfate solution with 300 mg Mg/l or in sodium sulfate solution with 160 mg Mg/l, but with a short pre-storage period of 2 days. Correspondingly stored test specimens based on Portland cement showed similar expansions and deteriorations a few months later. The condition of some flat mortar prisms after 12 months storage in test solution is shown in Figure 1 and Figure 2.

Figure 1: Mortar flat prisms based on Portland limestone cement with 20 % fly ash, 14 days pre-storage, 12 month storage at 8 °C in test solution without Mg (top prism), with 160 mg Mg (central prism) and with 300 mg Mg (bottom prism) per liter

Figure 2: Mortar flat prisms based on Portland cement with 20 % fly ash, 12 month storage at 8 °C in test solution with 160 mg Mg/l after 2 days (top prism), after 14 days (central prism) and after 90 days pre-storage (bottom prism)

The differences in the sulfate resistance became also apparent in the expansion of the flat mortar prisms. The differences between the cements, even with and without fly ash addition (Figure 3) were not as pronounced as initially assumed. The impact of the magnesium concentration and the pre-storage and storage conditions were clearly higher (Figure 4). Test solution with 300 mg Mg/l or a short pre-storage period of 2 instead of 14 days led to serious expansions for specimens based on CEM I and CEM II/A-LL within one year.
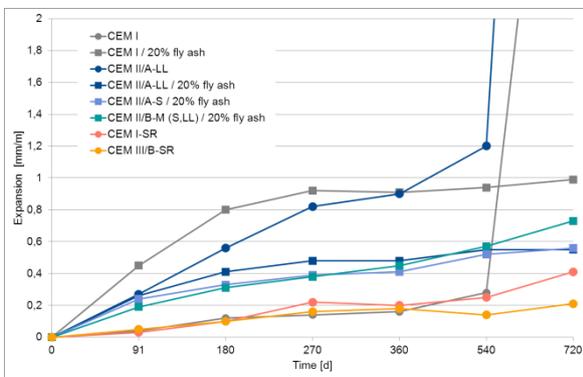

Figure 3: Relative length change of flat mortar prisms during storage at 8 °C in sodium sulfate solution with 160 mg Mg, cements with and without 20 % fly ash, storage temperature 8 °C, pre-storage period 14 d
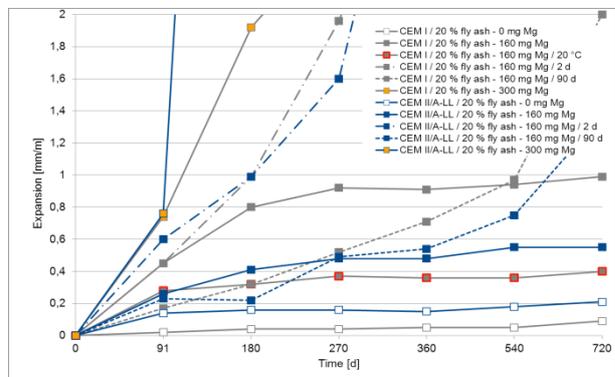

Figure 4: Relative length change of flat mortar prisms during storage in test solution, variation of the magnesium content: 0, 160 and 300 mg, storage temperature 8 °C, pre-storage period 14 d (if not designated otherwise)
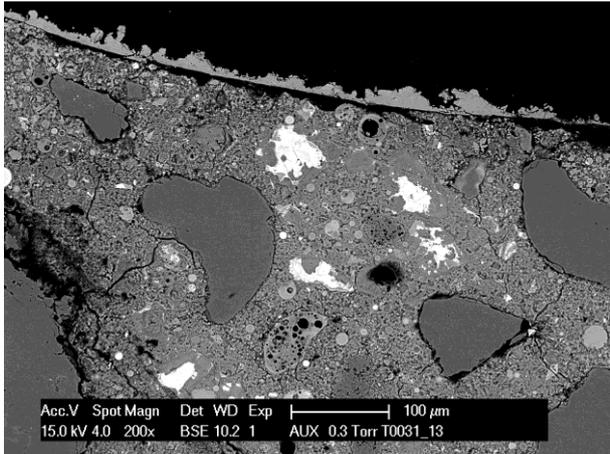
Figure 5: SEM micrograph of a polished section of a flat mortar prism based on CEM II/A-LL with 20 % fly ash, 14 days pre-storage, 12 month storage at 8 °C in test solution without Mg
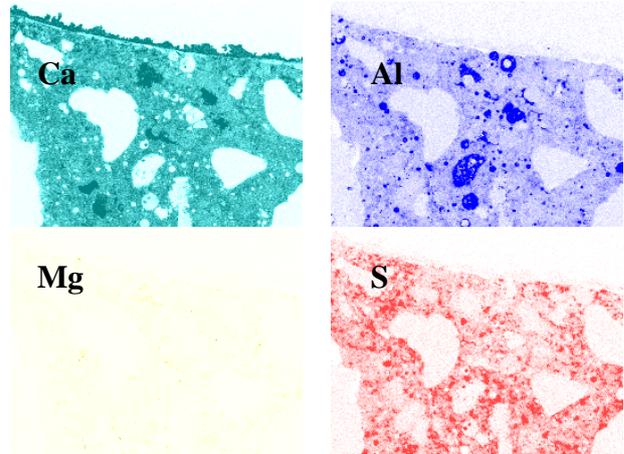

Figure 6: Elemental mappings of the sample shown in Figure 5, Ca (top left), Al (top right), Mg (bottom left), S (bottom right)
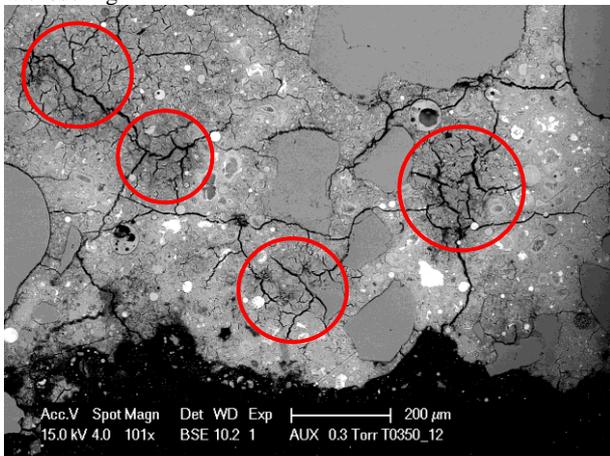

Figure 7: SEM micrograph of a polished section of a flat mortar prism based on CEM II/A-LL with 20 % fly ash, 14 days pre-storage, 12 month at 8 °C in test solution with 160 mg Mg/l; thaumasite formation is highlighted with red circles
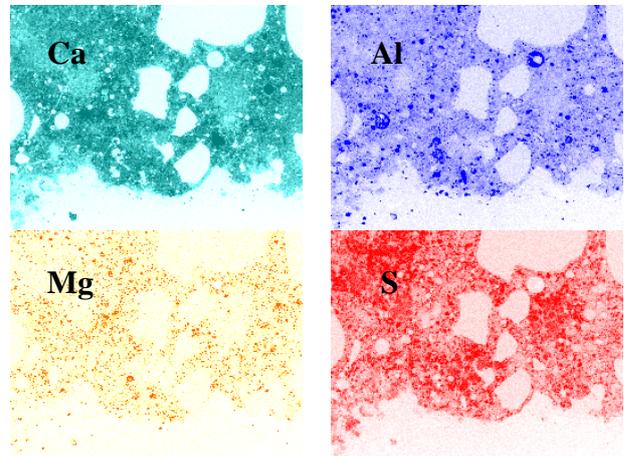

Figure 8: Elemental mappings of the sample shown in Figure 7, Ca (top left), Al (top right), Mg (bottom left), S (bottom right)
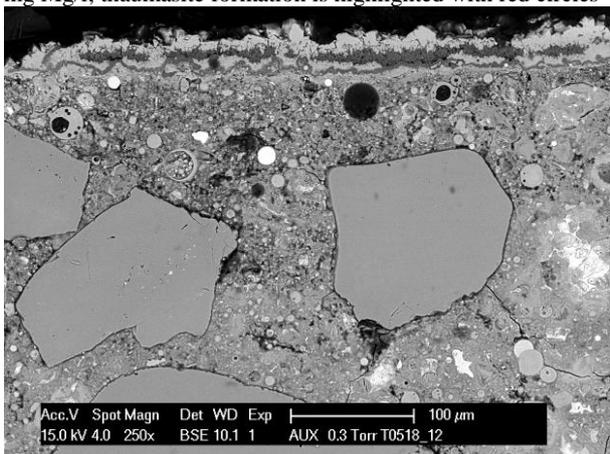

Figure 9: SEM micrograph of a polished section of a flat mortar prism based on CEM II/A-LL with 20 % fly ash, 90 days pre-storage, 12 month at 8 °C in test solution with 160 mg Mg/l
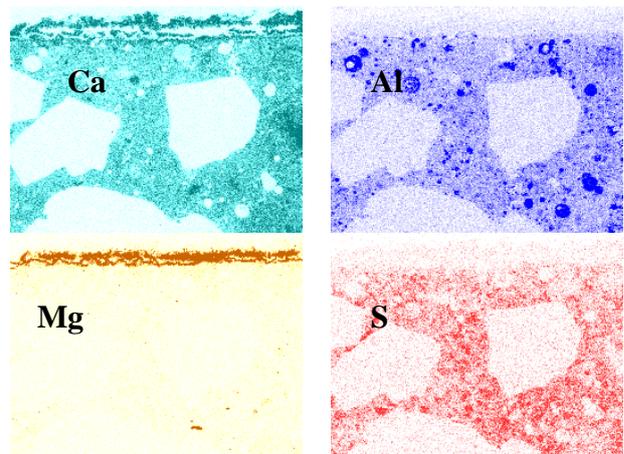

Figure 10: Elemental mappings of the sample shown in Figure 9, Ca (top left), Al (top right), Mg (bottom left), S (bottom right)

In the case of magnesium free test solution all tested samples remained non-deteriorated. An example is provided in Figure 5. It shows the microstructure of a mortar sample near the surface in a polished section.

Corresponding elemental mappings are given in Figure 6. Figure 7 shows the microstructure of a slightly deteriorated sample after storage in magnesium containing test solution. The outer calcium carbonate layer has been crumbled away and magnesium and sulfate are widely present in the microstructure. Moreover, thaumasite has formed in larger areas. The corresponding elemental mappings are shown in Figure 8. In comparison, Figure 9 shows a non-deteriorated sample after storage in magnesium containing test solution. In difference, the mortar prism was pre-stored over 90 days instead of 14 days. A brucite layer has been formed at the surface below the carbonate layer. The ingress of magnesium was low. Although sulfate is widely present, no relevant amounts of thaumasite or secondary ettringite have been formed.

Conclusions

The occurrence of high expansions and resulting damages was expected in mortars made with ordinary Portland cement or Portland limestone cement without fly ash. In contrast, high expansions and resulting damages were not expected for fly ash containing mortar samples. However, some of these samples have been affected. Most likely the process was caused by an insufficiently dense microstructure of the mortars, influenced by several aspects. Key parameters are the slow pozzolanic reaction of the fly ash in combination with a short pre-storage period (< 14 days), so that the fly ash was not able to contribute significant amounts of hydration products for the structure density. Although the test specimens were only stored in test solution with practical, i.e. low, sulfate and magnesium solutions after the pre-storage period, this still resulted in expansions and structure changes at 8 °C storage. However, at 20 °C storage no structural damages were observed.

This behavior can be explained with the following reaction sequence: The presence of magnesium in the test solution resulted in the formation of a dense brucite layer. This withdrew calcium hydroxide from the microstructure, which as a result lacked for the pozzolanic stimulation of the fly ash. However, in some cases the brucite layer was not sufficient in order to prevent sulfate ions from penetrating into the microstructure underneath. The 20 °C storage therefore resulted in the formation of common hydration products as well as additional ettringite from both the reaction with cement constituents as well as with fly ash. Overall, this resulted in the structure increasing in density more rapidly. The common hydration products developed more slowly at 8 °C storage. The penetrating sulfate was able to form ettringite as well as thaumasite. This resulted in more severe expansions and in loosening of the surface structure.

The differences in sulfate resistance due to the cement types were not as pronounced as expected from former research results. However, the performance of the reference cements CEM I-SR and CEM III/B-SR in the experiments shows that for SR-cements the presence of low magnesium concentrations presents no additional sulfate attack potential that could reduce the sulfate resistance.

References

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