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The role of calcium hydroxide in the formation of thaumasite

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ABSTRACT

It has recently been derived by thermodynamic calculation that the presence or absence of calcium hydroxide plays a vital role in the resistance of cement paste or concrete against the formation of thaumasite. To obtain experimental data on this matter, special binders have been mixed and used for the preparation of mortar bars. These specimens were exposed to moderate sulphate attack for a period of 18 months at a temperature of 8 °C. Mortar bars containing calcium hydroxide showed visual signs of attack a few months after exposure, leading to expansion, mass loss and complete failure. In contrast to this, no signs of attack were observed when no calcium hydroxide was present in the microstructure.

These results confirm the conclusions of earlier thermodynamic calculations that the presence of calcium hydroxide has an important impact on the formation of thaumasite. Calcium-rich C–S–H formed in the presence of calcium hydroxide is vulnerable against sulphate attack and the formation of thaumasite. In the absence of calcium hydroxide, C–S–H has a much lower calcium/silicon ratio and a higher resistance against the formation of thaumasite.

1. Introduction

Sulphate attack on concrete can lead to expansion, strength loss and ultimately to disintegration [1]. This behaviour is due to a reaction of the hardened cement paste with sulphate ions from the environment to ettringite ($C_3A\cdot 3CaSO_4\cdot 32H_2O$), gypsum ($CaSO_4\cdot 2H_2O$), and thaumasite ($CaSiO_3\cdot CaCO_3\cdot CaSO_4\cdot 15H_2O$) [2].

Several concepts have been introduced to avoid the formation of these minerals, thereby increasing the sulphate resistance of concrete. The formation of ettringite can be repressed by the use of sulphate-resisting Portland cement (SRPC) containing only a limited amount of the clinker mineral C_3A. In this way, the amount of ettringite formed during hydration and sulphate attack is significantly reduced [3]. The formation of gypsum can be prevented by converting calcium hydroxide (resulting from the reaction of Portland cement clinker with water) into C–S–H upon a pozzolanic reaction. Subsequently, there is no degradation of concrete due to the formation of gypsum in the absence of calcium hydroxide [4]. An additional concept has been introduced to avoid the formation of the third mineral, thaumasite. It has recently been suggested that silicon-rich C–S–H formed during the reaction of blast furnace slag and pulverised coal fly ash is more resistant against the formation of thaumasite than calcium-rich C–S–H formed during hydration of Portland cement clinker [5]. Silicon-rich C–S–H forms in the absence of calcium hydroxide ($Ca(OH)_2$), whereas calcium-rich C–S–H is precipitated in the presence of calcium hydroxide. Therefore, the availability of calcium hydroxide is indicated to determine the resistance of hardened cement paste and concrete against the formation of thaumasite during sulphate attack. Until now, only a limited amount of experimental data is available to support this concept.

There are a number of studies showing that concrete containing cement with a high amount of latently hydraulic or pozzolanic material has a superior resistance against the formation of thaumasite in sodium sulphate solution when compared to ordinary Portland cement or Portland limestone cement [6–10]. However, the results of these studies are hard to generalize and several assumptions can be put forward to explain the improved resistance of cements containing latently hydraulic or pozzolanic materials. It may, on one hand, be attributed to an improved physical resistance due to the slow reaction of the aforementioned materials. On the other hand, it is possible that the chemical resistance is increased by consumption of calcium hydroxide and lowering of the calcium/silicon ratio of C–S–H.

To gain further insight into this issue and to evaluate the thermodynamic concept used to improve the resistance against the formation of thaumasite, specific investigations were set up, their results being reported in this paper. Special binder types were mixed to obtain differing amounts of calcium hydroxide after hydration. The behaviour of mortar bars prepared from these binders during exposure to sulphate attack was monitored for a period of 18 months. The relative performance of the binders can be used to test the hypothesis that silicon-rich C–S–H possesses a higher resistance against the formation of thaumasite than calcium-rich C–S–H, which is formed in the presence of calcium hydroxide. Different methods of

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Table 1
Composition of the binders, estimated molar calcium/silicon ratio in C–S–H, porosity of water-stored mortar samples

Binder	SSC	SCC+CH	CEM III/B	CEM III/B +PFA	CEM III/B+CH
Composition	85% SSC +15% $CaCO_3$	55% SSC +30% $Ca(OH)_2$ +15% $CaCO_3$	85% CEM III/B +15% $CaCO_3$	55% CEM III/B +30% PFA +15% $CaCO_3$	55% CEM III/B +30% $Ca(OH)_2$ +15% $CaCO_3$
Estimated molar Ca/Si	0.6	2.1	0.9	0.1	2.4
Porosity [vol.%]	14.2	19.6	18.7	21.4	20.0

Fig. 1. Mortar bars after 12 months of exposure to Na_2SO_4 solution (SO_4^{2-} = 3000 mg/l) at 8 °C.

testing such as length change, mass loss, and visual rating of the appearance of the samples were used in order to find the most suitable way of detecting damages occurring due to the formation of thaumasite. Previous investigations have shown that it is difficult to assess the degree of deterioration in a quantitative manner.

2. Materials and methods

The investigations reported in this paper had a special focus on the role of calcium hydroxide in the formation of thaumasite during sulphate attack at low temperatures. Binders used in this study were prepared in a way that they differed with respect to the absence or presence of calcium hydroxide in the microstructure of the mortar samples produced from these binders. Thus it was possible to compare the relative performance of silicon-rich C–S–H with a calcium/silicon ratio of about 1.1 (formed in the absence of calcium hydroxide) to the behaviour of calcium-rich C–S–H with a calcium/silicon ratio of about 1.7 (formed in the presence of calcium hydroxide) [3].

The first binder type was supersulphated cement (SCC) containing 86% blast furnace slag and 14% anhydrite. The following mineral phases are formed during hydration of supersulphated cement: ettringite, silicon-rich C–S–H, and potentially hydrotalcite, AFm or $Al(OH)_3$ [11]. Calcium hydroxide is not present in the microstructure of hardened supersulphated cement. The performance of this binding material was compared to that of a second one in which 30% of the supersulphated cement was replaced by calcium hydroxide (denoted below as CH). Thus, calcium-rich C–S–H is expected to be present in the hardened cement paste produced from this binder. The relative performance of the two binders during sulphate attack can be used to test the hypothesis that silicon-rich C–S–H is more resistant against the formation of thaumasite than calcium-rich C–S–H.

Additional binder types were based on commercially available slag cement (CEM III/B 32.5 N–NW/HS) containing 66–80% blast furnace slag and 20–34% Portland cement clinker as main constituents (binder #3). The ratio of slag/clinker is relatively high in this cement. Most of the calcium hydroxide that is formed during hydration of the clinker is consumed during the hydration of the slag particles. Only traces of calcium hydroxide are present in the microstructure and mainly silicon-rich C–S–H is formed. The performance of mortar samples prepared from this cement is compared to the one made from binders in which 30% of the cement is replaced by pulverised coal fly ash (PFA) or calcium hydroxide (binder #4 and #5, respectively). The addition of coal fly ash further reduces the amount of calcium hydroxide in the microstructure thus making the mortar samples even more resistant. The replacement of cement by calcium hydroxide leads to the formation of calcium-rich C–S–H and it is expected that

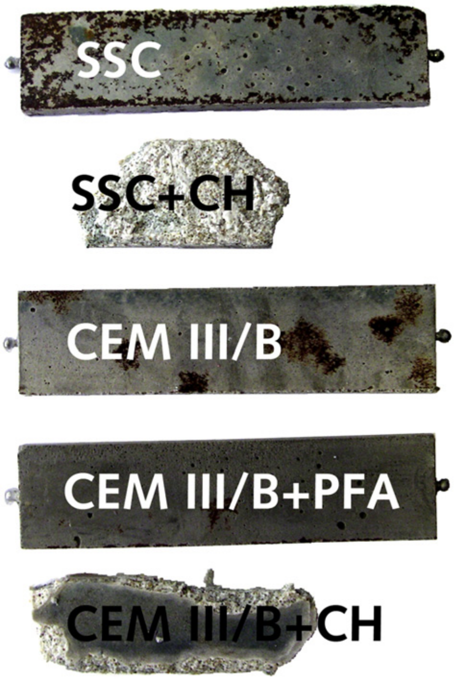

Fig. 2. Mortar bars after 18 months of exposure to Na_2SO_4 solution (SO_4^{2-} = 3000 mg/l) at 8 °C.

Table 2
Chemical and physical properties of the raw materials (w.s.—water soluble)

	SSC	CEM III/B	PFA
SiO_2 [mass%]	31.0	29.2	53.6
Al_2O_3 [mass%]	10.3	9.5	24.9
Fe_2O_3 [mass%]	0.5	1.4	7.6
CaO [mass%]	40.8	45.2	2.9
MgO [mass%]	5.6	7.0	1.8
MnO [mass%]	0.18	0.17	0.08
TiO_2 [mass%]	0.82	0.44	0.97
K_2O (w.s.) [mass%]	0.42 (0.07)	0.78 (0.39)	3.25 (0.12)
Na_2O (w.s.) [mass%]	0.41 (0.02)	0.29 (0.05)	0.74 (0.06)
SO_3 [mass%]	6.0	2.8	0.4
Loss of ignition [mass%]	3.0	1.7	2.8
Specific surface area (Blaine) [cm^2/g]	5870	3700	2820

Table 3
Final expansion and mass change after 18 months storage at 8 °C in different solution

	Expansion [mm/m]				Mass change [g] (The original mass of the specimen was approximately 147 g.)			
	water	$Na_2SO_4SO_4^{2-}=1{,}5$ g/l	$Na_2SO_4SO_4^{2-}=3{,}0$ g/l	saturated gypsum solution	water	$Na_2SO_4SO_4^{2-}=1{,}5$ g/l	$Na_2SO_4SO_4^{2-}=3{,}0$ g/l	saturated gypsum solution
SSC	−0,01	−0,04	−0,02	−0,03	0,6	1,8	1,6	0,7
SSC+CH	−0,08	1,59 (14 months)	5,87 (14 months)	0,30 (16 months)	0,2	−96,9	−107,9	−58,5
CEM III/B	−0,08	0,04	0,05	0,03	0,3	1,9	1,7	0,6
CEM III/B+PFA	−0,03	−0,10	−0,04	−0,06	0,1	0,5	1,0	0,3
CEM III/B+CH	−0,00	2,17 (16 months)	0,281(12 months)	0,39 (12 months)	0,6	−71,8	−89,3	−146,5 (16 months)

mortar made from this binder should exhibit a lower resistance against the formation of thaumasite at low temperatures. All five binders were prepared by mixing the raw materials. 15% calcium carbonate (reagent grade quality) was added to the binders to enable the formation of thaumasite. The composition of the binders and the chemical analysis of the raw materials are provided in Tables 1 and 2.

Mortar was prepared from the binders at a water:cement: aggregate ratio of 0.6:1:3. The maximum grain size of the quartz aggregate did not exceed 1 mm. After mixing, mortar bars having dimensions of 1 cm × 4 cm × 16 cm were cast and allowed to hydrate in water at 20 °C until the age of 6 weeks, when they were transferred to the storage solutions: water, saturated gypsum solution (sulphate ion concentration approximately 1500 mg/l), sodium sulphate solution with sulphate ion concentrations of 1500 and 3000 mg/l, respectively. Such moderate sulphate ion concentrations are typical field conditions when concrete is exposed to sulphate attack. The solutions were renewed every 4 weeks. The temperature of testing was fixed to 8 °C. Mass and length of the specimen were recorded every 2 months until the age of 18 months. The results given below are the average of three samples. The formation of thaumasite, ettringite, and gypsum was controlled on hardened cement paste specimens using XRD. These specimens were produced from the same binders without using aggregate and were stored in the same way as the mortar samples. XRD analysis was carried after one year and after 18 months. Pieces of the hardened cement paste were removed from the storage solution, crushed and afterwards dried at 40 °C. After grinding (63 µm), they were qualitatively analysed in Siemens D 5000 operating at 40 kV and 40 mA using Cu-radiation. The results obtained on hardened cement paste specimens were corroborated by analyzing pieces that had fallen from the damaged mortar bars.

Mercury intrusion porosity was used to measure total porosity and pore size distribution of water-stored reference samples at the age of approximately 20 months (Micromeritics Autopore IV 9500).

3. Results

3.1. Visual appearance

All samples stored in water were in good condition after 18 months at 8 °C. In contrast to this, serious signs of disintegration were detected on some of the samples stored in sulphate solutions. Mortar bars made from CEM III/B with calcium hydroxide started to deteriorate after a period of two months when exposed to sulphate solution. The surface of the samples became eroded and a soft, white material was found below the surface layer. This feature was recognised in all three aggressive solutions. After four months, the samples made from supersulphated cement with calcium hydroxide also showed signs of attack in all sulphate solutions. There was progressive damage with time, leading to the complete failure of the samples after about one year.

The samples made from the other binders did not show signs of deterioration during the entire time of exposure (18 months). These binders are: pure supersulphated cement, pure CEM III/B, CEM III/B with 20% coal fly ash.

Figs. 1 and 2 show examples for deteriorated and non-deteriorated samples.

3.2. Length change

The length change of the samples was recorded for a period of 18 months. Table 3 provides data on the final expansion for

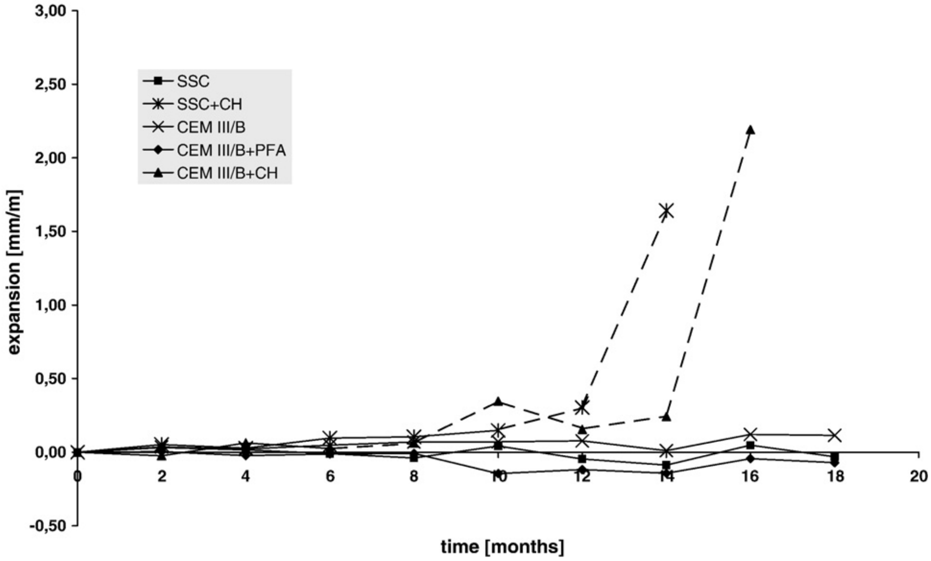

Fig. 3. Expansion of mortar bars exposed to Na_2SO_4 solution with a sulphate ion concentration of 1500 mg/l at 8 °C.

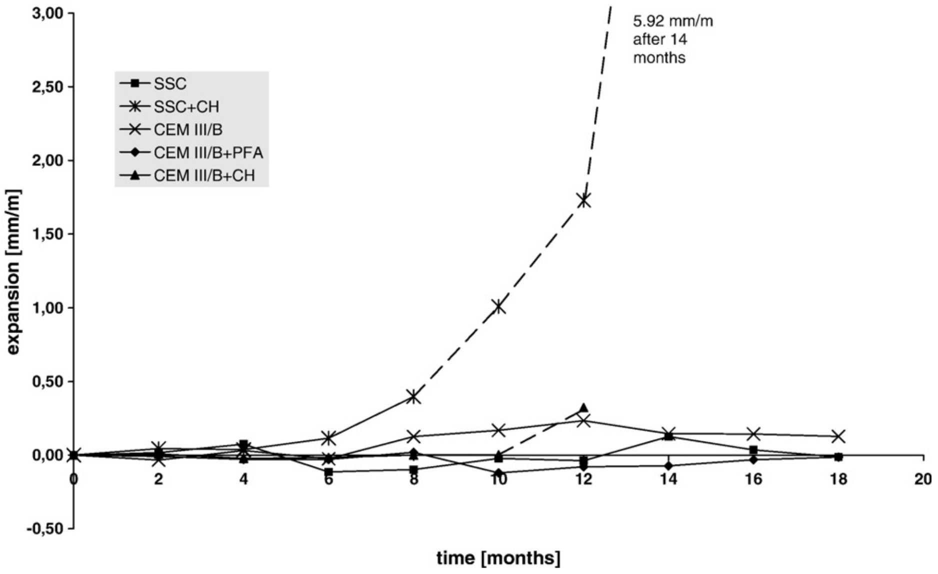

Fig. 4. Expansion of mortar bars exposed to Na_2SO_4 solution with a sulphate ion concentration of 3000 mg/l at 8 °C.

specimen still available at this time. For mortar bars that were destroyed before that date, the last record is given with an indication of the age of measurement. The development of expansion over time is presented in Figs. 3–5. All values in these figures are relative to the performance of the control samples stored in water. After 8 months of exposure, disintegration led to the break down of the first sample, and more samples broke thereafter. This is indicated by the use of dashed lines when only one or two samples were available for reading instead of three.

It can be inferred from Figs. 3–5 that there was hardly any expansion measured for resistant samples. Non-resistant samples showed expansion only in the late stage of attack when deterioration was already visible. Some specimens had disintegrated without exhibiting expansion. Generally, some samples were already broken at the time expansion started and the data was read on only one or two samples instead of three. The maximum expansion was recorded for the sample made from supersulphated cement and calcium hydroxide, stored in Na_2SO_4 solution at $SO_4^{2-}=3000$ mg/l, the appropriate value being 5.9 mm/m. The data presented above refers to the longest axis of the samples (160 mm). Expansion was, however, optically visible at the shortest dimension (10 mm) of the deteriorating mortar bars. It was not quantitatively assessable.

3.3. Loss of mass

The gain and loss of mass of the samples is presented in Figs. 6–8; final values recorded after 18 months are provided in Table 3. Again, all values given in the figures are relative to the behaviour of specimens stored in water at the same temperature.

It is evident that there is virtually no change in mass for the samples that appeared optically sound (pure supersulphated cement, pure CEM III/B, CEM III/B with coal fly ash). A high loss of mass is encountered for samples which showed serious signs of damage (supersulphated cement with calcium hydroxide, CEM III/B with calcium hydroxide). In the case of the supersulphated cement with calcium hydroxide, a temporary gain in mass was measured before

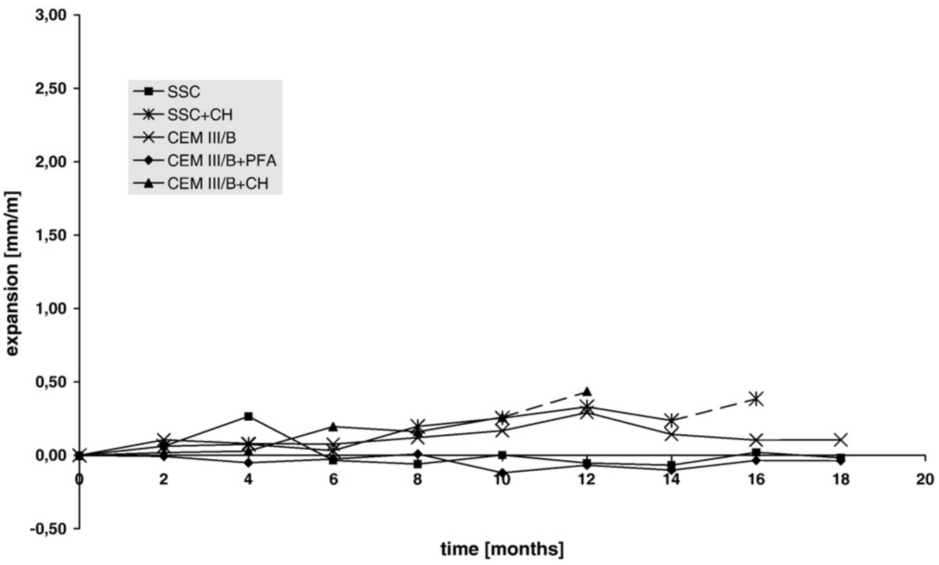

Fig. 5. Expansion of mortar bars exposed to saturated gypsum solution at 8 °C.

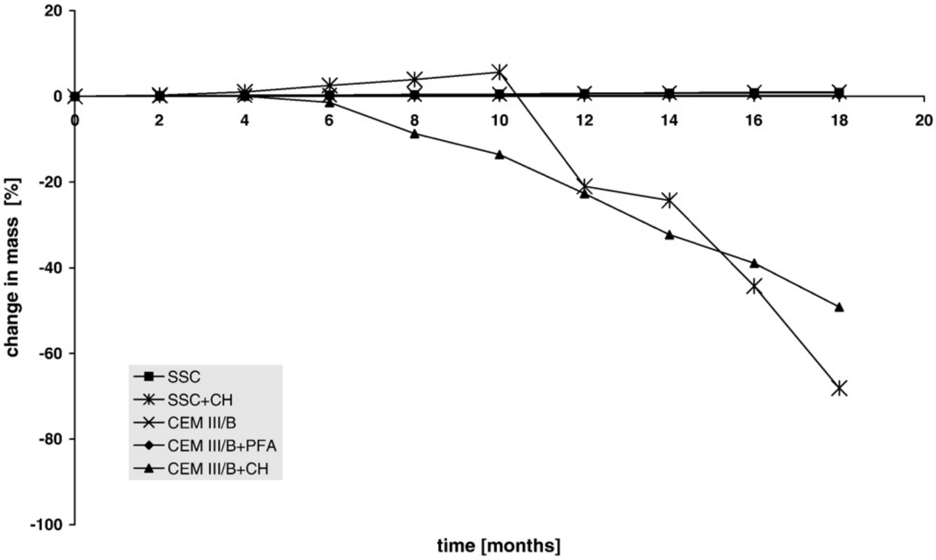

Fig. 6. Change in mass of mortar bars exposed to Na_2SO_4 solution with a sulphate ion concentration of 1500 mg/l at 8 °C.

losing weight. After 18 months, non-resistant samples lost between 40% and 100% of their original mass (approximately 147 g). The same behaviour was present in all three aggressive solutions.

3.4. X-ray diffraction

After 12 and 18 months, the samples made of hardened cement pastes that had been stored under the same conditions as the mortars were examined by XRD. Pastes were selected because the analysis of mortars is complicated by the fact that these specimens consist mainly of aggregate which has a diluting effect. The detection of minor phases is enhanced by using samples of hardened cement paste. Peak intensities of ettringite (15.7° 2θ), thaumasite (16.1° 2θ), gypsum (20.7° 2θ) and portlandite (18.1° 2θ) after subtracting the background are given in Table 4. Fig. 9 shows a graphical presentation of XRD spectra of samples stored in sodium sulphate solution ($SO_4^{2-}=3000$ mg/l).

The results obtained by XRD at 12 months showed relics of clinker phases such as belite and ferrite that had not been consumed during cement hydration. These phases were not detected after 18 months. Calcite added during binder preparation to enable the formation of thaumasite was found in all samples. The mineral ettringite was detected in all binder types and at all storage conditions because it is formed during hydration of the binders as well as during sulphate attack.

Thaumasite was identified in some of the samples stored in sulphate solution. This mineral was detected after 12 and 18 months in binder types which had shown visual signs of destruction: supersulphated cement with calcium hydroxide and CEM III/B with calcium hydroxide. These binders contained serious amounts of calcium hydroxide.

In contrast to this, thaumasite was not detected in resistant binders: supersulphated cement, CEM III/B, CEM III/B with coal fly ash after 12 and 18 months. Only in the samples made from pure CEM III/B minor amounts of thaumasite may have been present after 18 months storage in sodium sulphate solution with $SO_4^{2-}=3000$ mg/l and saturated gypsum solution. Minor amounts of calcium hydroxide were noted in the specimen made from CEM III/B, whereas this mineral was completely absent in all samples made from supersulphated cement and CEM III/B with coal fly ash.

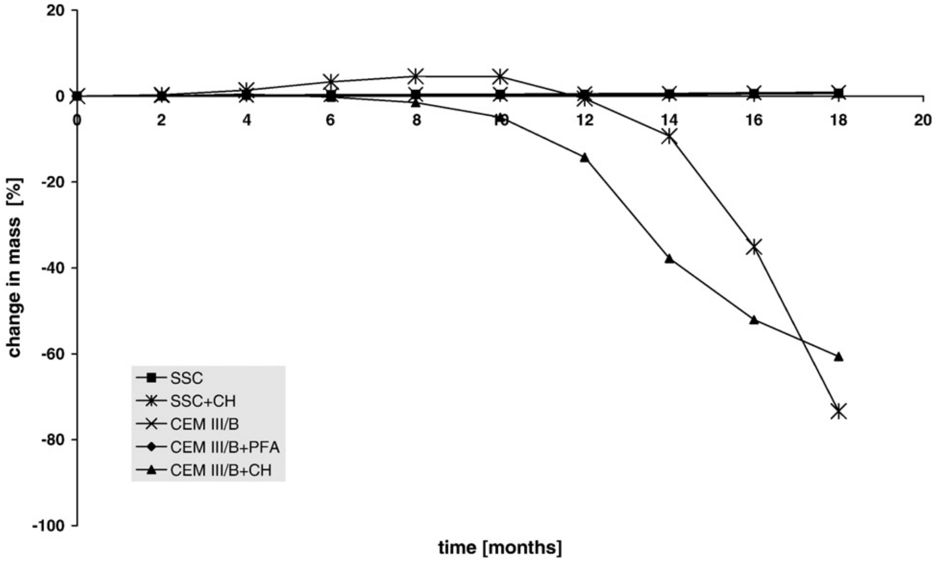

Fig. 7. Change in mass of mortar bars exposed to Na_2SO_4 solution with a sulphate ion concentration of 3000 mg/l at 8 °C.

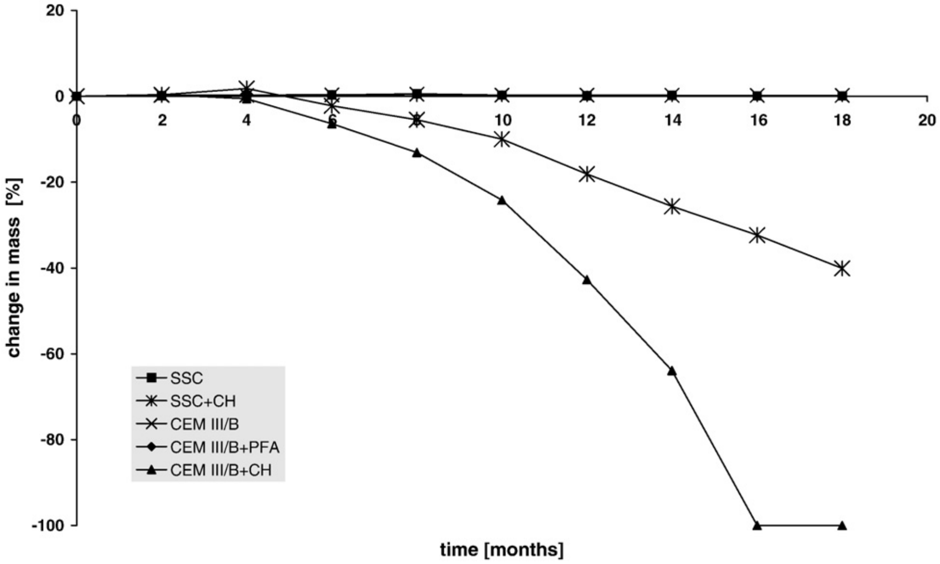

Fig. 8. Change in mass of mortar bars exposed to saturated gypsum solution at 8 °C.

Gypsum formed in the late stage of attack. After 12 months, ettringite and thaumasite were detected in all samples showing signs of destruction. In contrast to this, only some of them contained gypsum at this date. From the data in Table 4, it can be derived that gypsum was present after 18 months in all samples made from supersulphated cement with calcium hydroxide and from CEM III/B with calcium hydroxide. This indicates that ettringite and thaumasite form prior to gypsum. Gypsum was not contained in samples with no or a low amount of calcium hydroxide. However, the gypsum peak at 11.6° 2θ coincides with that of monocarbonate ($C_3A \cdot CaCO_3 \cdot 11H_2O$), identified in samples containing CEM III/B. Mullite and quartz were found in specimens with coal fly ash (CEM III/B+PFA). The presence of the quartz peak at 20.8° 2θ complicates analysis of peak height intensity of the gypsum peak located at 20.7° 2θ.

3.5. Mercury intrusion porosimetry

Water-stored reference samples were tested by mercury intrusion porosimetry at the age of 20 months. The data obtained is shown in Table 1 and Fig. 10. Apart from the mortar made from supersulphated cement, which proved to be very dense, all samples had a similar pore size distribution and a porosity of approximately 20%.

4. Discussion

Mortar bars prepared for this study were different in their relative contents of calcium hydroxide. Some binders contained amounts of blast furnace slag or coal fly ash high enough to consume all calcium hydroxide during hydration. According to XRD analysis, no calcium hydroxide was detected in the following binders: supersulphated cement, CEM III/B with coal fly ash. Traces of this mineral were found in specimens made from pure CEM III/B. In contrast to this, serious amounts of calcium hydroxide were detected when 30% of this phase was added during binder production (supersulphated cement with calcium hydroxide, CEM III/B with calcium hydroxide). Both binders with a high amount of calcium hydroxide showed a poor resistance against moderate sulphate attack at low temperatures (8 °C). They were prone to deterioration even at a sulphate ion concentration of 1500 mg/l, exhibiting first signs of erosion after only two months of exposure. Only fragments of the samples had remained after a testing period of 18 months. The damage was first detected by visual inspection of the specimen. They were already badly corroded before expansion was recorded. Ettringite, thaumasite and in the late stage also gypsum were detected by XRD and deterioration can be attributed to the formation of these minerals. It has been shown before, that high pH values in the pore solution are able to prevent the formation of gypsum at moderate sulphate ion concentrations [12]. Subsequently, almost a complete loss of alkalis is required before portlandite can react with sulphate ions to gypsum at low sulphate ion concentrations. This process may thus occur after disintegration of the hardened cement paste due to the formation of ettringite and thaumasite enabling leaching of alkalis. Also, the presence of portlandite is an essential precondition for the formation of gypsum [4].

Considering that the samples had a thickness of only 10 mm and a serious amount of material had disintegrated into a white pulpy mass before expansion took place (SSC+CH, CEM III/B+CH), it can be deduced that the presence of an intact core may potentially prevent the expansion of the specimen [13]. Also the transformation of C–S–H into thaumasite reduces strength and thus allows for the reduction of inner tensions without expansion.

Serious loss of mass was recorded for all non-resistant samples in the late stage of attack. However, in some conditions the loss of mass was superposed by a temporary gain in mass in the early stage, and

Table 4
Peak intensity of ettringte (E), thaumasite (T), gypsum (G), and portlandite (P) in hardened cement paste specimen after 18 months sulphate attack at 8 °C (Tr. = traces)

	Water				Na_2SO_4, SO_4^{2-} = 1,5 g/l				Na_2SO_4, SO_4^{2-} = 3,0 g/l				Sat. gypsum solution			
	E	T	G	P	E	T	G	P	E	T	G	P	E	T	G	P
SSC	360	0	0	0	340	0	0	0	400	0	0	0	350	0	0	0
SSC+CH	290	0	0	440	430	130	120	460	380	170	370	400	360	50	130	590
CEM III/B	130	0	0	340	160	0	0	320	170	Tr.?	0	170	150	Tr.?	0	360
CEM III/B+PFA	120	0	0	0	90	0	0	0	90	0	0	0	140	0	0	0
CEM III/B+CH	110	0	0	780	150	50	320	530	130	80	150	650	not available			

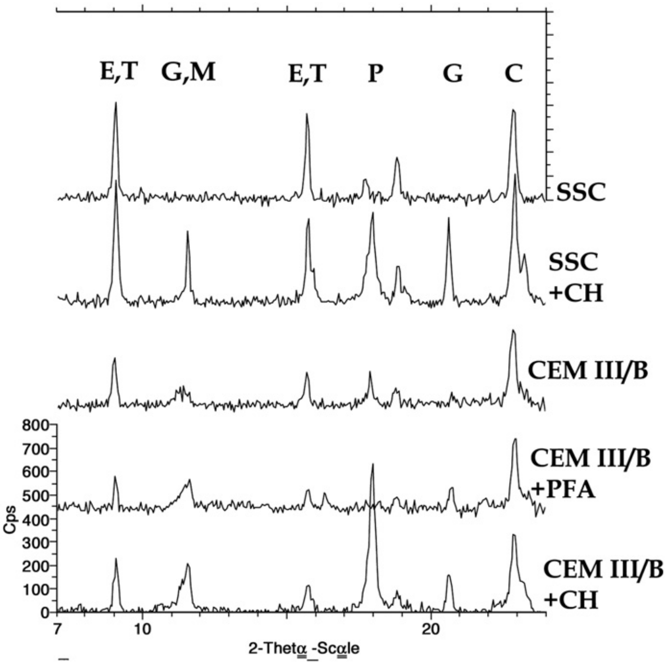

Fig. 9. XRD pattern of hardened cement paste specimen stored for 18 months in Na_2SO_4 solution (SO_4^{2-}=3000 mg/l) at 8 °C (E—ettringite, T—thaumasite, P—portlandite, G—gypsum, M—monocarbonate).

therefore a long test period (>12 months) is required to achieve definitive results. A comparison of the three methods used in this study indicates that deterioration is first detected by visual inspection and much later by mass loss and expansion.

The ionic concentrations in the aggressive solutions only had a minor influence on the performance of the mortar bars. The same binder types always showed signs of corrosion (supersulphated cement with calcium hydroxide, CEM III/B with calcium hydroxide) whereas the mortar bars made from the other binders were unaffected by the aggressive solutions. The extent of damage of non-resistant samples was higher at high sulphate concentration (SO_4^{2-}=3000 mg/l). The influence of the cation (Na^+ vs. Ca^{2+}) on the performance was variable and no clear information can be derived on this subject.

In contradiction to the poor resistance of the aforementioned samples, there was a high performance of other mortars bars. These were made from the following binders: pure supersulphated cement, CEM III/B, CEM III/B with coal fly ash. All three binders had in common that they contained no calcium hydroxide, or only traces of it, after hydration. No signs of attack were observed during the whole period of testing, regardless of exposure and testing method. With respect to thaumasite, the improved performance of these samples can be explained by the results of thermodynamic calculations regarding the resistance of C–S–H against sulphate attack [5]. In that study, it was derived that silicon-rich C–S–H is able to withstand sulphate solutions with a moderate concentration, whereas calcium-rich C–S–H undergoes destruction. The calcium/silicon ratio of C–S–H was estimated in that study using bulk chemical analysis of the raw materials and estimated degrees of hydration. This assessment is repeated here for the binders used in this study. The same relative degrees of hydration were used: 100% for cement and 75% for coal fly ash. This results in values between 0.1 and 0.9 for binders resistant against sulphate attack and values between 2.1 and 2.4 for non-resistant binders (Table 1). Despite the fact that such estimation is highly dependent on the exact relative degrees of hydration, it can nonetheless be used for an approximation. In the present study, molar calcium/silicon ratios significantly higher than 1.7 have been computed for non-resistant binders, which can be read as an indication that calcium hydroxide is present in the microstructure and C–S–H can be transformed into thaumasite. On the other hand, the calcium/silicon ratio for resistant binders was estimated to be lower than 1.1. It can be deduced that no calcium hydroxide, or only traces of it, may be present, and C–S–H is much more resistant against sulphate solutions.

Beside the prevention of thaumasite formation, also no damage due to the formation of ettringite was detected in specimen without calcium hydroxide. Earlier studies have shown that the presence of this mineral has an obvious influence on the formation of ettringite. It has been discussed that the solubility of aluminium is higher in the absence of calcium hydroxide. Thus these ions are able to migrate into pores and voids making the formation of ettringite innocuous [14]. Also from a thermodynamic point of view, the presence of calcium hydroxide is essential for the formation of ettringite [15]. In agreement with the aforementioned references, there was no significant increase in ettringite peak intensity observed in samples containing no portlandite.

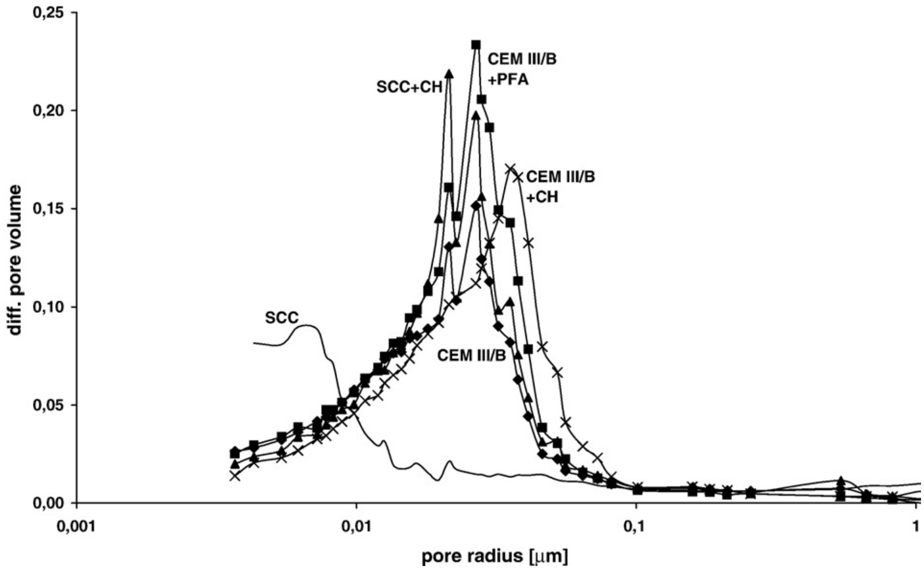

Fig. 10. Pore size distribution of water-stored mortar samples.

Data obtained by mercury intrusion porosimetry showed that all binders (with the exception of pure supersulphated cement) had similar porosity and pore size distribution. Thus, they had a similar physical resistance against the ingress of sulphate ions from the aggressive solutions. The better performance of some of the mortar bars is therefore not due to an improved physical resistance but rather inherent chemical properties.

5. Conclusions

The reaction of C–S–H with calcium carbonate and sulphate ions to thaumasite may potentially lead to disintegration of cement paste, mortar or concrete. The resistance of C–S–H against this reaction depends on its properties. The bulk calcium/silicon ratio of C–S–H plays a vital role for the prevention of this deleterious reaction which itself depends on the presence or absence of calcium hydroxide. In the presence of calcium hydroxide, the calcium/silicon ratio of C–S–H is in the range of 1.6 to 1.8 and calcium-rich C–S–H can easily be converted into thaumasite. However, in the absence of calcium hydroxide, the calcium/silicon ratio of C–S–H can be estimated to be between 0.8 and 1.2. Silicon-rich C–S–H shows a much higher resistance against the formation of thaumasite at moderate sulphate ion concentrations.

This concept has been tested experimentally by exposing mortar bars to moderate sulphate attack. It can be concluded that:

- Binders with a high content of calcium hydroxide were susceptible to the formation of thaumasite and ettringite when exposed to moderate sulphate attack (sulphate ion concentrations of 1500 and 3000 mg/l) at low temperature (8 °C). Also gypsum has formed in the late stage of attack.
- Binders containing no or minor amounts of calcium hydroxide after hydration showed no sign of corrosion after 18 months of testing under identical conditions.
- Damage was first detected by visual inspection (2–4 months) and much later by expansion and mass loss (>12 months required).
- Thaumasite was identified by XRD analysis in samples containing high amounts of calcium hydroxide.
- Water-stored reference samples had an (with one exception) approximately similar porosity. This indicates that the high resistance can not be attributed to differences in physical properties of the mortar samples. The improved resistance is therefore due to different chemical properties: the availability of calcium hydroxide and the calcium/silicon ratio in C–S–H.
- Depletion of calcium hydroxide via a pozzolanic reaction increases the sulphate resistance of concrete. In the absence of this mineral, the formation of thaumasite, ettringite, and gypsum may be restricted.
- Testing was carried out employing sodium sulphate solution and calcium sulphate solution. The results are likely to be modified if additional reactions take place such as the formation of brucite ($Mg(OH)_2$) due to exposure to magnesium sulphate solution.

References

[1] P.K. Mehta, P.J.M. Monteiro, Concrete-Microstructure, Properties and Materials, McGraw-Hill, New York, 1993.

[2] Department of Environment, Transport and Regions, The thaumasite form of sulfate attack: Risks, diagnosis, remedial works and guidance on new construction, Report of the Thaumasite Expert Group, DETR, London, 1999.

[3] H.F.W. Taylor, Cement Chemistry, Thomas-Telford, London, 1997.

[4] B. Tian, M.D. Cohen, Does gypsum formation during sulfate attack on concrete lead to expansion? Cem. Concr. Res. 30 (1) (2000) 117–123.

[5] F. Bellmann, J. Stark, Prevention of thaumasite formation in concrete exposed to sulphate attack, Cem. Concr. Res. 37 (8) (2007) 1215–1222.

[6] S. Köhler, D. Heinz, L. Urbonas, Effect of ettringite on thaumasite formation, Cem. Concr. Res. 36 (2) (2006) 697–706.

[7] N.J. Crammond, The thaumasite form of sulphate attack in the UK, First International Conference on Thaumasite in Cementitious Materials, Garston, UK, 2002, 19.–21.6., paper 17.

[8] K. Lipus, H.M. Sylla, Investigations in Germany of the thaumasite form of sulphate attack, First International Conference on Thaumasite in Cementitious Materials, Garston, UK, 2002, 19.–21.6, paper 50.

[9] D.D. Higgins, Increased sulfate resistance of ggbs concrete in the presence of carbonate, First International Conference on Thaumasite in Cementitious Materials, Garston, UK, 2002, 19.–21.6., paper 52.

[10] D.D. Higgins, N.J. Crammond, Resistance of concrete containing ggbs to the thaumasite form of sulphate attack, First International Conference on Thaumasite in Cementitious Materials, Garston, UK, 2002, 19.–21.6., paper 53.

[11] T. Matschei, F. Bellmann, J. Stark, Hydration behaviour of sulphate-activated slag cements, Adv. Cem. Res. 17 (4) (2005) 167–178.

[12] F. Bellmann, B. Möser, J. Stark, Influence of sulfate solution concentration on the formation of gypsum in sulphate resistance test specimen, Cem. Concr. Res. 36 (2) (2006) 358–363.

[13] M. Santhanam, M.D. Cohen, J. Olek, Mechanism of sulfate attack: a fresh look. Part 2: proposed mechanisms, Cem. Concr. Res. 33 (3) (2003) 341–346.

[14] P.W. Brown, H.F.W. Taylor, The role of ettringite in external sulfate attack, in: J. Marchand, J. Skalny (Eds.), Materials Science of Concrete—Special Volume: Sulfate Attack Mechanisms, American Ceramic Society, Westerville (Ohio), 1999, pp. 73–97.

[15] D. Damidot, F.P. Glasser, Thermodynamic investigation of the $CaO–Al_2O_3–CaSO_4–H_2O$ system at 25 °C and the influence of Na_2O, Cem. Concr. Res. 23 (1) (1993) 221–238.