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Investigations on the influence of cement type on thaumasite formation

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Abstract

A high sulfate resistance is required if cements are to be used in sulfate bearing waters and soils especially under conditions favouring thaumasite formation. A long period program of laboratory investigations was carried out on CEN cements to assess thaumasite and ettringite formation. The experimental concept involved mixing ground cement pastes with stoichiometrical components of gypsum, calcite and water. The specimens were stored at 6 °C whereby chemical worst case conditions for thaumasite formation were simulated. At time intervals XRD analysis was conducted. Apart from pure cements mixtures containing additives, pure C_3S pastes with and without Al_2O_3 addition were investigated. The results confirm that thaumasite formation can be accelerated by Al_2O_3 bearing components in cements. However, thaumasite formation is also possible without active participation of Al^{3+}. The assessment of sulfate resistance of cements only from the chemical point of view apparently gives results which are contrary to the field experience.

Keywords: Cement; Sulfate resistance; Chemical attack; Thaumasite; Ettringite

1. Introduction

Concrete structures subjected to permanent sulfate bearing waters and soils can be deteriorated or damaged in diverse ways. Generally, the sulfate solutions penetrate the concrete and react with the hydration products of the cement paste leading to the formation of sulfate bearing phases like gypsum, ettringite or thaumasite causing profound changes in the microstructure and strength of the original cement paste [1].

Severe damage to concrete structures under sulfate attack has up to date been attributed to the formation of secondary ettringite as an expansive mineral phase in the cement paste [2]. However, the dependance of secondary ettringite formation upon metastable hydrate phases of C_3A has lead to the development of high sulfate resistant Portland cements (CEM I-HS) by limiting the C_3A and Al_2O_3 contents. According to the German standard DIN 1164 a maximum content of 3% C_3A or 5% Al_2O_3 is allowed for Portland cement with high sulfate resistance. Slag cements containing a minimum 66% of granulated slag and cement with pozzolan additions are also formulated to produce durable concretes with high sulfate resistance. This is achieved by casting concretes with low permeability and physical properties which hinder the penetration of water and sulfate solutions into the microstructure of the cement paste. Moreover, in the last few years remarkably high contents of the apparently chemically inert limestone fillers have been used in concrete technology to produce concrete mixtures. However, in case of sulfate attack at low temperatures which often occurs in foundations and maritime structures, the calcium carbonate of the fillers becomes a significant component for the formation of thaumasite $CaO \cdot SiO_2 \cdot CaCO_3 \cdot CaSO_4 \cdot 15H_2O$ which can damage the concrete by destroying the strength bearing C–S–H phases [3].

Currently, the conditions needed for thaumasite formation (TF) in concrete are generally believed to be the availability of calcium carbonate, wet conditions and low temperatures. On the contrary, the role of the cement, its hydration products as well as the additives used is not yet clarified.

Several hypotheses exist to describe the mechanism of thaumasite formation in Portland cement systems. They are generally based on the sequence of different

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chemical reactions taking place [4–6]. One part of the mechanism is the evolution of ettringite when it incorporates Si^{4+} (in octahedral coordination) in its structure, substituting Al^{3+} ions in the presence of CO_3^{2-}. In this mechanism the transformation of ettringite into thaumasite is believed to take place through the Woodfordite Route or a catalyst reaction. The other route to thaumasite formation is the direct C–S–H route. It is still not known why and how the exchange of the tetrahedral SiO_4-coordination into octahedral SiO_6-coordination of thaumasite takes place especially in the absence of Al_2O_3 or MgO. Currently, no thermodynamic data are available to facilitate the calculation of possible reactions of the hydrate phases of standard cements with calcium carbonate and calcium sulfate.

The objective of this laboratory investigation was to gain new knowledge on the chemical behaviour of cements and additive materials as well as on the reaction mechanisms prior to conditions needed for thaumasite formation. To avoid the influence of the geometry and permeability of compact specimen, hydrated cement pastes in grounded form were used. The powder was mixed in stoichiometric proportions with gypsum, calcium carbonate and a 20% excess of water to form a paste which was then stored at 6 °C and room temperature for 24 months. For the cement paste involved these investigations can be considered as “chemical worst case” for the thaumasite form of sulfate attack (TSA). At different time intervals XRD analysis was conducted to identify various SO_3 bearing phases and gain information on the reaction partners and mechanisms leading to thaumasite formation.

2. Experimental

For the investigations, standard cements with different mineral contents and chemical composition were chosen (Table 1). Cement pastes were cast with a water/cement ratio of 0.5, demoulded after 2 days and stored under water for 26 days of hydration. After drying the pastes at 105 °C they were ground to a fineness of <200 μm using a zirkonoxide vibration mill.

Some cements were also partially modified by adding fly ash, microsilica and nanosilica, i.e. a pure silica with nanoscale fineness. For comparison, pastes with pure C_2S and C_3S were prepared separately and also with additives from aluminate components (C_3A, kaolin, ettringite). Table 2 shows the experimental program and Table 3 presents the composition of the chosen fly ash.

Depending on the calculated SiO_2 content of the cement the paste powders were mixed with stoichiometric parts of high quality gypsum powder ($CaSO_4 \cdot 2H_2O$) and chemically produced calcite ($CaCO_3$) as well as with an excess of 20% of distilled water to investigate the thaumasite formation. The pastes were batchwise stored in tight closed polyethlene boxes with half of the specimen stored at 6 °C and the other half at 20 °C. At chosen time intervals the partially dried specimens in the boxes were crushed. The reaction was stopped using isopropanol and acetone followed by air drying.

The XRD analysis was conducted using the X-ray diffractometer D5000, Siemens AG using CuKα radiation. The recording and control parameters were held constant throughout the investigation period. The intensity of the X-ray tube was controlled regularly using quartz standards and corrections were made using a factor. Taking an interference of a pure ettringite specimen to be 250 cps (= 100%) as relative intensity, the peaks of chosen interferences of calcite ($2\theta = 29.4°$), gypsum ($2\theta = 11.6°$); portlandite ($2\theta = 18.0$; 34.0°), ettringite ($2\theta = 9.0$; 15.8; 18.9°), thaumasite ($2\theta = 9.2°$; 16.0; 19.4°) were used for the partial quantification of the primary and secondary products of sulfate attack. Therefore, the relative intensity of a phase represents the measure of its content in the specimen. A solid solution between ettringite and thaumasite as in woodfordite [4] was not detected.

The relative intensities of thaumasite and ettringite measured on separate mixtures were graphically presented depending on storage time. Both the formation of thaumasite and of ettringite was increasing with time. The typical curve is presented in Fig. 1 taking a slag cement as an example. The intensities of ettringite and thaumasite after 200 days were isolated from the graphical presentation and compared to assess the reactivity of different cements under sulfate attack.

3. Results and discussions

3.1. TF by CEN cements

The XRD analysis of the phases in the cement pastes at different time intervals show that all investigated cements are capable of forming thaumasite under “chemical worst conditions”, that means at low temperatures and in the presence of satisfactory amounts of $CaSO_4$ (as gypsum) and $CaCO_3$. Considering the Woodfordite-Route, thaumasite formation in ordinary Portland cements (OPC) can be strongly influenced by C_3A as a catalyst of the ettringite formation.

Fig. 2 shows the formation of ettringite and thaumasite in hardened OPC pastes after 200 days storage as a function of the C_3A content. It is observed that at 6 °C the increase of the thaumasite content is in direct proportion to the C_3A content. Even the sulfate resistant cements with very low contents of C_3A have shown a strong tendency to the thaumasite formation. In the linear function even the Portland limestone cements can be included considering the calculated C_3A content. At low temperatures the ettringite formation is

Table 1
Overview of the normal cements used in the investigations

Type of the cement			Chemical composition [%]						Clinker phases [%]			
Code	Acc. to EN 197-1	Acc. to DIN 1164[a]	Al_2O_3	SiO_2	Fe_2O_3	CaO	MgO	SO_3	C_3A	C_3S	C_2S	C_4AF
Ordinary Portland cements												
PC1	CEM I 42.5R	HS	3.9	20.2	4.6	63.5	1.3	2.5	2.6	61.4	11.6	14.0
PC2	CEM I 42.5R	HS/NA	4.2	20.8	5.9	62.9	0.7	2.2	1.1	53.0	19.7	18.0
PC3	CEM I 42.5R		4.5	20.3	2.5	63.9	1.3	3.3	7.7	54.5	17.1	7.6
PC4	CEM I 42.5R		5.3	21.7	2.6	63.4	1.9	3.2	9.6	39.0	32.8	7.9
PC5	CEM I 52.5R		5.5	19.9	2.5	63.4	1.3	3.9	10.3	50.7	18.8	7.6
PC6	CEM I 32.5R		5.7	20.0	2.7	62.7	1.8	3.1	10.5	49.4	20.1	8.2
PC7	CEM I 42.5R		6.2	20.8	2.5	63.1	1.1	3.2	12.2	39.9	29.5	7.6
PC8	CEM I 32.5R	NW	6.5	21.9	2.3	60.6	2.4	3.7	13.3	18.6	48.7	7.0
PC9	CEM I 42.5R		6.8	20.6	2.3	61.8	1.2	3.2	14.1	32.8	34.3	7.0
Granul. blast-furnace slag cements												
SC1	CEM III 32.5A	NW/NA	8.5	26.5	1.6	49.7	5.4	3.2				
SC2	CEM III 32.5B	NW	8.6	27.4	1.75	50.4	4.2	4.0				
SC3	CEM III 32.5B	NW/HS	9.1	29.5	1.5	47.4	6.0	3.6				
Portland-limestone cements									Calculated[b]			
PL1	CEM II 32.5A/L		5.2	17.7	2.3	60.4	1.2	3.3	9.5	43.9	17.9	7.3
PL2	CEM II 32.5A/L		5.3	17.9	2.5	60.6	2.1	2.7	9.6	44.5	17.0	7.6

[a] NW (= low hydration heat); HS (= high sulfate resistance); NA (= low alkali cement).

[b] Calculated acc. to BOGUE taking into account a limestone content of 15%.

Table 2
Composition of Al-doped C_3S mixtures prior to hydration

Matrix	Al_2O_3 additive		Chemical components [%]		
	Compound	Amount [%]	Al_2O_3	SiO_2	CaO
β-C_2S	–	–	1.6[a]	34.1[a]	64.0[a]
C_3S	–	–	0.8[a]	26.8[a]	72.4[a]
C_3S	C_3A	2.0	1.5	26.3	72.2
C_3S	C_3A	4.0	2.2	25.7	72.0
C_3S	C_3A	8.0	3.7	24.7	71.6
C_3S	C_3A	16.0	6.6	22.5	70.8
C_3S	Ettringite	20.0	2.2	21.4	63.3
C_3S	Ettringite	34.0	3.3	17.7	56.9
C_3S	C–A–H	5.0	2.1	25.5	71.0
C_3S	C–A–H	10.0	3.4	24.1	69.5
C_3S	Kaolin	8.0	4.0	28.4	66.6

[a] Determination by chemical analysis (the other values are calculated).

clearly evident by C_3A content above 8%. As expected at room temperature the high sulfate resistant cements exhibit only low tendency to the ettringite formation, whereas the thaumasite formation is negligible. An

Table 3
Composition of the fly ashes

Fly ash		Chemical composition [%]							
Code	Quality/Origin	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	fr. CaO	SO_3
FA1	Hard coal	49.2	27.2	8.1	4.0	2.0	3.9	0	0.8
FA2	Hard coal	50.4	26.5	7.2	4.1	2.2	4.1	0	0.6
FA3	Lignite coal	49.8	13.1	10.1	16.3	4.6	1.5	0.8	2.5

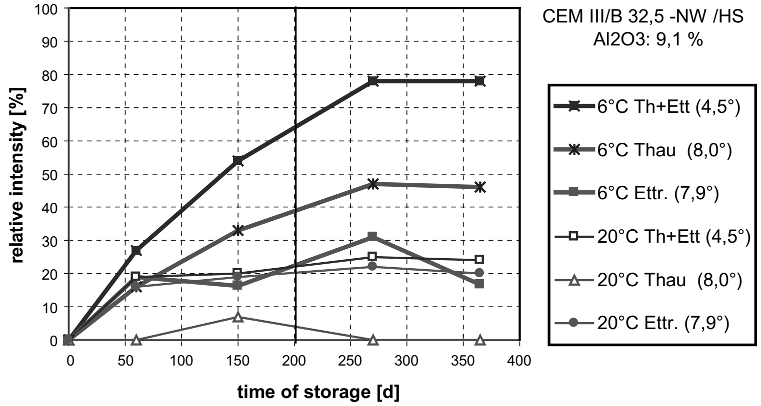

Fig. 1. Relative XRD intensity of thaumasite and ettringite (θ scale) vs. the time of storage.

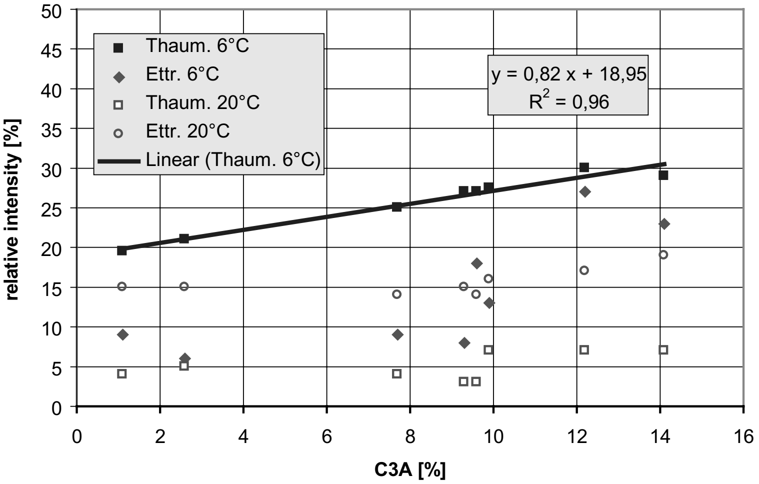

Fig. 2. Thaumasite and ettringite in hydrated OPC pastes after 200 days vs. C_3A content of the cements.

analogous relation can also be found between the thaumasite formation at 6 °C and the Al_2O_3 content of the OPC. The Al_2O_3 contents are derived from the components of the clinker phases C_3A and C_4AF amounting to 3.9–6.8% Al_2O_3.

As shown in Fig. 3, a linear relationship of the thaumasite formation at 6 °C with the Al_2O_3 content is not only observed by Portland cements but also by all cements including slag cements (CEM III/B and C). This is a surprising result because the slag cements are generally classified as high sulfate resistant cements according to the German standard DIN 1164, despite their high Al_2O_3 contents. However, it should be mentioned that the sulfate resistance of cements with high slag contents is mainly based upon its ability to hinder the penetration of sulfate solutions due to its low permeability. Our investigations are on the contrary only based on assessing the reactivity of the cements under conditions that can promote thaumasite formation.

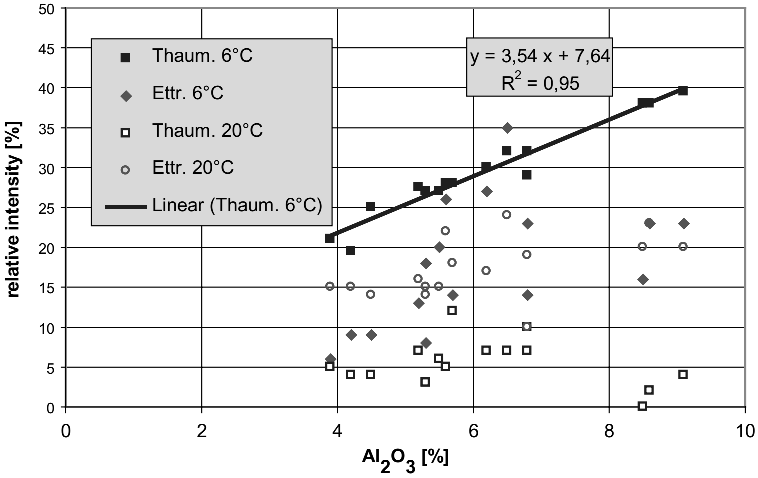

Fig. 3. Thaumasite and ettringite in hydrated cement pastes after 200 days vs. Al_2O_3 content of the cements.

3.2. TF of cements with different additive materials

To modify the chemical behaviour of the cement pastes towards thaumasite formation, selected cements were hydrated with different additive materials.

3.2.1. Addition of fly ashes

With the addition of fly ash in cement positive effects on the sulfate resistance are expected. The pozzolanic reaction consumes the $Ca(OH)_2$ leading to the formation of extra C–S–H. This hinders the formation of gypsum during sulfate attack and improves the physical properties of the cement paste such as the strength and permeability against the penetration of sulfate bearing waters. On the other hand, as shown above the increase of Al_2O_3 in the mixture could promote both the formation of thaumasite and of ettringite. The formation of thaumasite and ettringite in Portland limestone cement (PLC) with 20 M% of hard coal ashes (FA1 and FA2) as well as a lignite coal ash (FA3) after 200 days storage is presented in Table 4.

The results show that the addition of fly ash has very little influence on thaumasite formation, despite the accompanying increase of total Al_2O_3 content. However, at low temperatures, the addition of lignite coal fly ashes seems to increase the amount of thaumasite formed corresponding to the increase in Al_2O_3 content. At the same time the pozzolanic reaction of the lignite coal fly ash is more effective at low temperatures as compared to that of the hard coal fly ashes, whose reactions are better at room temperature and promote ettringite formation. Concerning the sulfate attack the high contents of SiO_2 in the fly ash has probably no significant effect.

3.2.2. Effect of active silica

Other additives like amorphous SiO_2 in form of microsilica (ELKEM product; BET surface area: 18–22 m^2/g) and nanosilica (test product; BET surface area: 50–60 m^2/g) were added to Portland cement before hydration. The results for specimen stored at 6 and 20 °C are presented in Table 5.

The results are contradictory. The addition of microsilica strongly increases the thaumasite formation at 6 °C while the pozzolanic reaction is retarded. On the contrary, by the addition of nanosilica, the total amount of $Ca(OH)_2$ was bound during the pozzolanic reaction and no thaumasite was found. The retardation of the pozzolanic reaction of microsilica at low temperature can probably cause the SiO_2 to be primarily used for

Table 4
Thaumasite and ettringite in hydrated PLC (PL1) containing 20% of fly ash

Fly ash	Total content in the binder [%]		Rel. intensity of phases [%] after 200 days					
	Al_2O_3	SiO_2	Storage at 6 °C			Storage at 20 °C		
			Thaum.	Ettr.	Portl.	Thaum.	Ettr.	Portl.
–	5.2	17.7	27	13	52	7	14	38
FA1	9.6	24.0	29	20	31	11	20	14
FA2	9.5	24.2	26	11	27	4	24	15
FA3	6.8	24.1	32	17	23	10	12	25

Ettringite ($\theta = 7.95°$), thaumasite ($\theta = 8.05°$) and portlandite ($\theta = 17.0°$).

Table 5
Thaumasite and ettringite in hydrated OPC (PC3) containing amorphous silica

Pozzolanic component		Total content in the binder [%]		Rel. intensity of phases [%] after 200 days					
Type	Amount [%]	Al_2O_3	SiO_2	Storage at 6 °C			Storage at 20 °C		
				Thaum.	Ettr.	Portl.	Thaum.	Ettr.	Portl.
–		4.5	20.3	25	10	53	5	15	47
Microsilica	5	4.3	24.3	32	14	43	0	20	33
Microsilica	10	4.0	28.3	39	19	33	20	8	20
Nanosilica	10	4.0	28.3	0	13	9	0	10	8

thaumasite formation. Nanosilica is even active enough at 6 °C to completely bind $Ca(OH)_2$ through its pozzolanic reaction.

3.2.3. Addition of aluminate components

Different effects of additives on thaumasite and ettringite formation were also observed after introducing aluminate phases in a Portland cement paste. As shown in Table 6, there is no remarkable change in the amount of thaumasite in cement paste despite the addition of profound amounts of ettringite to the sulfate resistant cement. The amounts of ettringite increased respectively. This result contrasts with the hypothesis that thaumasite can be formed through the transformation of ettringite. A clear increase of the rate of thaumasite and ettringite formation was observed as a result of the addition of hydrated C–A–H. It is presumable that ettringite being thermodynamic more stable is less active to bind Si^{4+} and CO_3^{2-} in comparison to the metastable hydration products of C_3A.

3.3. Investigations on modified C_3S pastes

In the previous investigations on the synthetic hydration of C_3S with stoichiometric amounts of gypsum

Table 6
Thaumasite and ettringite in hydrated SRPC (PC1) containing aluminate additives

Aluminate addition		Total content in the binder [%]		Rel. intensity of phases [%] after 200 days			
Type	Amount [%]	Al_2O_3	SiO_2	Storage at 6 °C		Storage at 20 °C	
				Thaum.	Ettr.	Thaum.	Ettr.
–	–	3.9	20.2	21	0	8	13
Ettringite	5	4.1	19.2	20	20	0	20
Ettringite	15	4.5	17.2	22	20	0	22
Ettringite	30	5.1	14.1	22	27	12	30
C–A–H	5	5.1	19.2	28	26	5	22

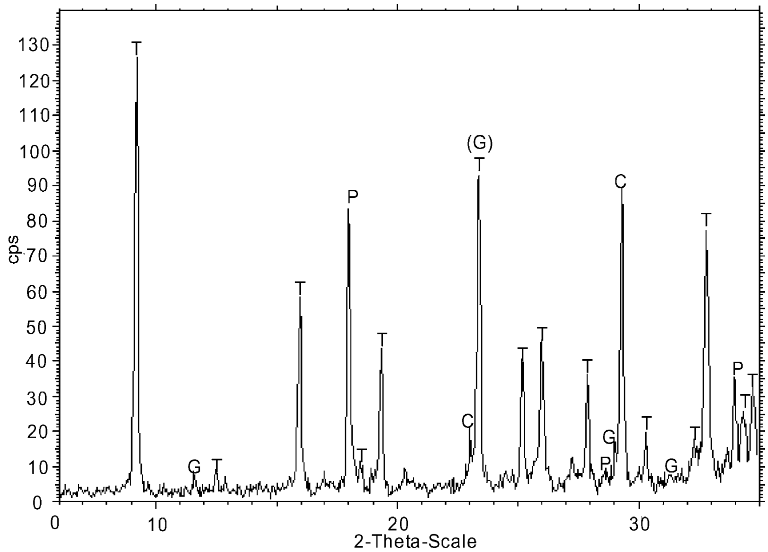

Fig. 4. X-ray diffraction pattern of thaumasite formed from a hydrated C_3S paste at 6 °C (T—thaumasite; P—portlandite; G—gypsum; C—calcite).

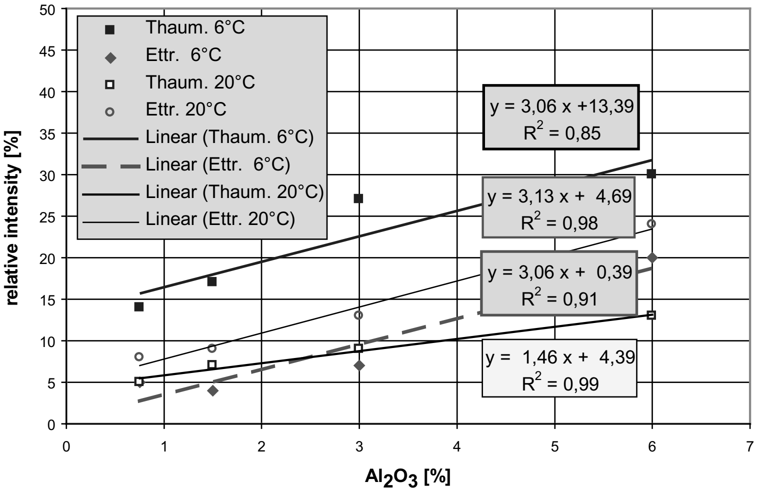

Fig. 5. Thaumasite and ettringite formed in hydrated C_3A doped C_3S pastes after 200 days vs. the Al_2O_3 content of the mixtures.

Table 7
Thaumasite and ettringite in C_3S pastes doped with hydrated Al_2O_3

Al_2O_3 component in C_3S		Total Al_2O_3 content [%]	Rel. intensity of new phases [%] after a 200 days			
Type	Amount [%]		Storage at 6 °C		Storage at 20 °C	
			Thaum.	Ettr.	Thaum.	Ettr.
Ettringite	20	2.2	26	23	4	8
Ettringite	34	3.3	27	7	9	12
Kaolin	8	4.0	27	0	8	4
C–A–H	5	2.1	40	4	18	11
C–A–H	10	3.4	44	8	28	20

and calcite, thaumasite was evident at 6 °C. The amount of thaumasite remained constant even after dry storage for several months. The reintroduction of water to the dried paste activated further thaumasite formation, so that after about 2 years gypsum was almost totally consumed (Fig. 4). The calcite required for the continuation of thaumasite formation was partly compensated by the carbonation of portlandite. Moreover, the transformation into the thaumasite was proved by ESEM images and EDX analysis at 15 kV under atmospheric conditions. The Al_2O_3 content of C_3S was recorded at 0.8%. On the contrary, the investigations on thaumasite formation in β-C_2S pastes always yielded negative results.

3.3.1. Effect of aluminate phases in C_3S pastes

The formation of thaumasite and ettringite in hydrated mixtures of C_3S and C_3A after 200 days of storage is presented in Fig. 5. The linear regression confirms a clear relation of the formation of the two complex sulfate bearing mineral phases to the Al_2O_3 content in the given areas of concentration and proves the promotion of thaumasite formation by low temperatures.

Table 7 shows that the tendency to the formation of sulfate bearing phases in the C–S–H matrix can also be influenced by the chemical structure of the Al compounds. In contrast to the stable compounds like ettringite and kaolin, additives from hydrated C_3A (C–A–H) accelerate the formation of secondary phases in C_3S pastes.

4. Conclusions

Fine ground cement pastes mixed with gypsum, calcite and water were used in the experimental concept. The specimens in form of pastes were stored at 6 °C for a long period of time and chemical worst case conditions for thaumasite formation were simulated. The investigations confirm that the tendency of cements to thaumasite formation is proportional to their C_3A and Al_2O_3 contents. Even small Al_2O_3 contents are capable of accelerating the thaumasite formation. This is also the case with the so-called sulfate resistant Portland cement with low C_3A contents.

The investigations were carried out without considering the physical properties which could hinder the penetration of sulfate solutions in cement due to low permeability of the microstructure. This has partially lead to such surprising results that the slag cements which are generally classified as high sulfate resistant cements were accompanied by the most intensive thaumasite formation. However, the addition of synthetic ettringite did not cause any remarkable effects on thaumasite formation contrasting the modal concept on thaumasite formation. The influence of fly ash was also very low despite their high Al_2O_3 contents. Unexpectedly, the use of microsilica strongly accelerated the thaumasite formation at low temperatures while the pozzolanic reaction was retarded. On the contrary, a complete pozzolanic reaction took place when nanosilica was added. The total amount of $Ca(OH)_2$ was bound at 6 °C and as a result no thaumasite formation took place.

Under the given conditions even the C_3S pastes were totally transformed into thaumasite in the absence of Al^{3+} or Mg^{2+} except for impurities as long as wet conditions were maintained.

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