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Influence of active alumina on the hydration process of Portland cement

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Abstract

The work is interested in the study of the hydration process by means of the isothermal calorimetry method. The Portland cement hydration process led to gradual consumption of contained calcium sulfate. This sulfate depletion is observed on the calorimetry curve as a shoulder of main silicate peak. The addition of hydratable alumina to Portland cement was studied in order to determine its influence on hydration process. Experimental results showed the shifted position of this shoulder according to alumina and calcium sulfate content. It was also observed that the overall hydration process was almost unaffected by alumina addition.

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1. Introduction

Hydration of Portland cement is complex process of the reactions which lead to setting and hardening of cement paste. The water addition to cement starts contemporary dissolution reaction of some cement components and formation of the insoluble hydrated products. The main part of Portland cement, alite (C_3S), reacts with water to form the C-S-H gel and portlandite. The same hydration products are also formed during the hydration of other cement component, belite (C_2S). Portland cement is produced by continuous milling of Portland clinker with gypsum. The final properties of cement are strongly influenced by this milling process [1].

Ettringite ($C_6A\bar{S}_3H_{32}, AFt$) as a hydration product, is a result of the reaction between tricalcium aluminate phase

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(C₃A) and gypsum in aqueous conditions. C₃A phase dissolves immediately after the first contact of cement with water and its dissolution is stopped when the minimal heat flow in the induction period is reached. During hydration reaction of alite, the dissolution of C₃A phase is retarded. The re-dissolution of C₃A phase occurs after the all present sulfates are consumed. This process causes the rapid AFt precipitation [2].

The required sulfates for rapid AFt precipitation are released to the solution from the C-S-H gel after sulfate depletion [3]. The source of C₃A necessary for AFt formation during the time between induction period and the sulfate consumption are amorphous hydroaluminates. These hydroaluminates are formed from C₃A phase in the beginning of the overall hydration reaction [4]. The retardation of C₃A phase should be caused by sorption of sulfate ions to its surface. The peak position assigned to sulfate depletion is dependent on the sulfate content in the cement [5]. The occurred retardation also influences the strength of hardened paste [6]. The cement particle size strongly affects the velocity of the sulfate depletion. The fine particles cause rapid sulfate consumption which can be seen on the calorimetry curve as a strong sharp peak. While, the coarse particles need more time for consumption reaction and can be seen as a weak broad peak. Nevertheless the hydration heat of both processes is identical [7]. Some cement admixtures can be considered as a source of reactive aluminates. For example, the high furnace slag (as a typical cement admixture) is not involved to the aluminate reaction but influences the reaction by filler effect [8].

2. Materials and methods

Portland cement was prepared by ball milling of Portland clinker (Českomoravský cement a.s., plant Mokrý, CZ) with resulted specific surface area 400 m²/kg (determined via Blaine method). Gypsum (commercially purchased; phase composition – 73.6 wt. % of gypsum and 26.4 wt. % of bassanite; Penta, CZ) was used as setting regulator. Alfabond 300 (commercially purchased; phase composition - boehmite and ρ -alumina; Almatix, factory Leetsdale, USA) was used as substitute of clinker and gypsum species. Samples for calorimetry measurements were mixed and homogenized in vibrational mill in stainless steel bowl for 10 s. Samples for mechanical properties determination were ball milled for 10 min. The clinker composition is summarized in Table 1. The composition of the measured samples is shown in Table 2. The particle size of the samples was assessed by laser diffractometry (Helos KR, Sympatec) and is shown on Fig. 1a.

Table 1. Chemical and phase composition of the clinker.

Chemical composition	(%)	Phase composition	(%)
CaO	70.6	C ₃ S	76.6
SiO ₂	19.2	C ₂ S	8.5
Al ₂ O ₃	3.9	C ₃ A	3.0
Fe ₂ O ₃	5.1	C ₄ AF	11.9

Table 2. Composition of measured samples.

Sample	Clinker (%)	Gypsum (%)	AB300 (%)	Sample	Clinker (%)	Gypsum (%)	AB300 (%)
1.a	95.25	4.75	0	2.c	94.00	6.00	0.50
1.b	95.00	5.00	0	2.d	94.00	6.00	0.75
1.c	94.75	5.25	0	2.e	94.00	6.00	1.00
1.d	94.50	5.50	0	3.a	92.50	7.50	1.00
1.e	94.25	5.75	0	3.b	90.50	9.50	2.00
1.f	94.00	6.00	0	3.c	93.25	6.75	1.50
2.a	94.00	6.00	0.10	3.d	92.50	7.50	2.00
2.b	94.00	6.00	0.25				

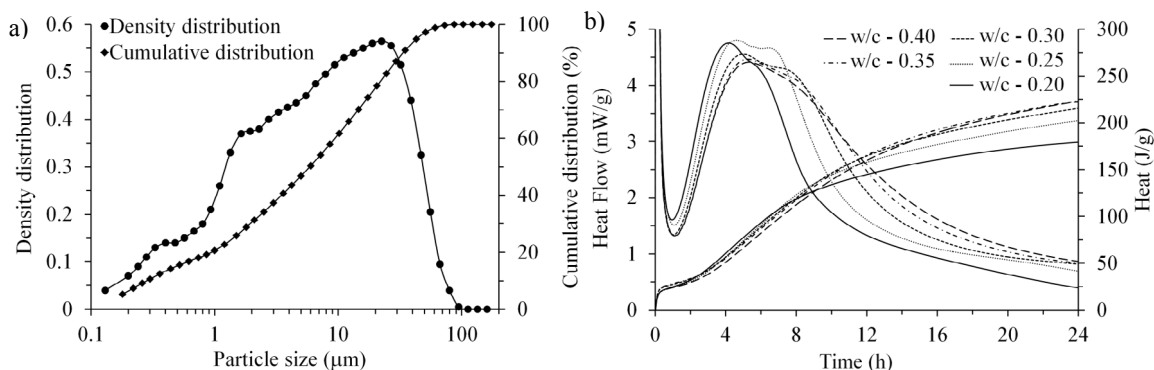


Fig. 1. (a) Particle size distribution of clinker (b) Adjustment of water to cement ratio (composition 1.f).

The hydration process was analyzed by isothermal calorimeter TAM air (TA Instruments) at the isothermal temperature of 25 °C. The temperature of the source material under the constant climatic condition took place for 24 h. The samples were prepared by mixing of 30 g of cement with 9 ml of deionized water (w/c ratio = 0.3) for 1 min. The 6.5 g of mixture was placed into closed glass ampoule for calorimetry analysis. The analysis was measured against to the reference sample (quartz) with the same heat capacity as the measured sample. The samples for DTA analysis (Q600; TA Instruments) were crashed and the hydration process was stopped by immersing them in acetone. Residual acetone was removed by evaporating at the 50 °C. The mechanical properties were assessed on the prisms with the dimensions 2 × 2 × 10 cm (4 pieces for each sample).

3. Results and discussion

The water to cement ratio was adjusted to 0.3 (see Fig. 1b). The influence of different w/c ratio can be clearly seen from the Fig. 1b. Insufficient homogenization of samples was observed at w/c ratios lower than 0.3 and on the other hand the third hydration peak is not distinguishable at higher values of w/c.

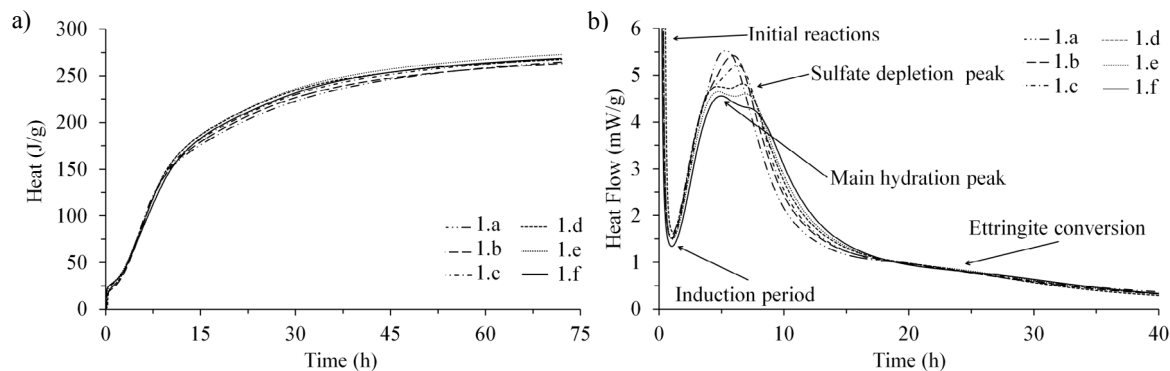


Fig. 2. Clinker with gypsum (a) Total heat of hydration (b) Heat flow.

The substitution of 4.75 – 6 wt. % of clinker with gypsum did not influence the overall hydration process, what was confirmed by analysis of the total hydration heat after 72 h with the values 257 – 274 J·g⁻¹ (see Fig. 2a). The values of total hydration heat were increased with the increasing amount of the gypsum content. Sample 1.f reached the minimal heat flow value in induction period. In the Fig. 2b there can be seen the influence of the gypsum content on the main hydration peak. The gypsum content slightly delayed the silicate phase hydration. The main dynamic

response on the calorimetric curve connected with the clinker substitution is characterized by the shift of the peak position related to sulfate depletion. The gypsum content of 6 wt. % in the reference sample 1.f was adjusted to be able to observe this peak at 2.5 h after the main hydration peak. This position (optimal) was defined by Lerch [6]. The decreasing content of the gypsum in the system was resulted in the shift of the depletion peak towards earlier times, i.e. closer to maximum of the main hydration peak. This shift is coupled with an increase heat flow of this process. When the gypsum content is lower than 5 wt. % the peak of sulfate depletion was monitored before the main hydration one and found to be merged with him. The increasing of the sulfate depletion peak mentioned above is probably negatively influenced by the diffusion process as a main driving force of the overall hydration process [1,6].

Sample 1.a with the 4.75 wt. % of the gypsum achieved 21.5 % higher maximum heat flow during main silicate phase hydration compared to reference sample. This finding (i.e. lack of the gypsum content in cement) can explain the technological problems with concreting of massive constructions. Weak peak observed at around 22.5 h was assigned to the decomposition of AFt to monosulfate (AFm). The varying of the gypsum content in the cement-gypsum mixture did not have the influence on the AFt to AFm decomposition process (see Fig. 2b).

From the current knowledge, Alphabond 300 (further AB300) is the source of AlO_4^- ions and should be involved in AFt hydration. AB300 addition should not influence the main silicate hydration process. The obtained experimental data (see Fig. 3a) showed the total hydration heat released during 72 h in the range from 259 to 269 $\text{J}\cdot\text{g}^{-1}$. Nevertheless the first distinction occurred in the place of induction period (see Fig. 4a), where the minimal content of AB300 caused appearance of the peak which should be assigned to portlandite formation in accordance with [9]. The presence of this peak was not confirmed in the analyses of the samples without AB300. The cement admixtures, with low content of Ca^{2+} ions and taking place in hydration process, have decreasing tendency of portlandite formation [1]. AB300 consumes Ca^{2+} ions from other hydraulic phases present in the hydration process and accelerate their dissolution. The consumption of all aluminates coming from AB300 can cause saturation of the solution with Ca^{2+} ions and consequently lead to portlandite precipitation. The peak assigned to portlandite formation was varied from 0.7 h to 1.3 h in the range of AB300 0.1 – 1 wt. %, resp. With the increasing content of AB300 in the mixture the heat flow values during dormant period were increased. The increase should be explained with the presence of aluminates from AB300, which also play a role in quantification of hydration process. AB300 did not influence the main silicate peak, but strongly influenced the peak of sulfate depletion. With the increasing amount of AB300 up to the 1 wt. %; the sulfate depletion process in the cement is accelerated. In comparison of analyses, the behaviour of samples with gypsum or AB300 addition by means of the peak position shift is similar.

From obtained data (comparison Fig. 2b with Fig. 3b), it can be assumed that 1 wt. % of AB300 was compensated by addition of 1.25 to 1.5 wt. % of gypsum (factor of gypsum / AB300 compensation). Position and intensity of the 4th peak of the conversion AFt to AFm was stable until the sample 2.d, but the AFt to AFm decomposition is strongly accelerated for sample 2.e.

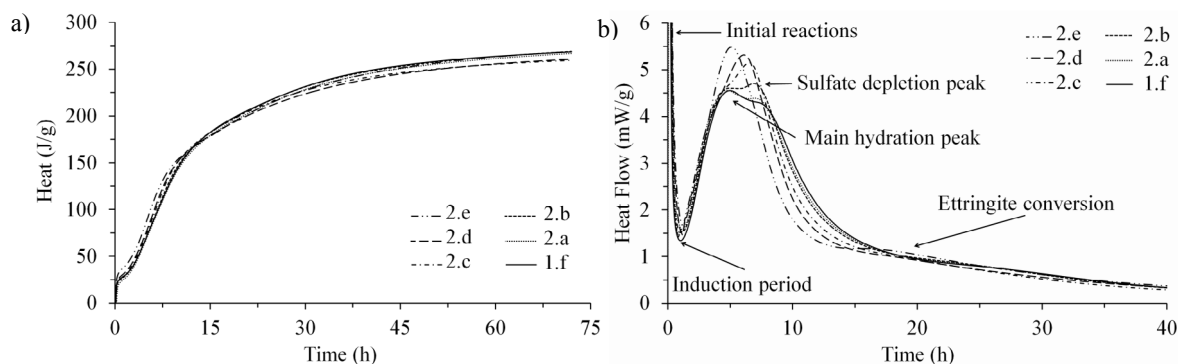


Fig. 3. PC with AB300 (a) Total heat of hydration (b) Heat flow.

From the experimentally determined factor of gypsum / AB300 compensation, the series of samples with designed position of sulfate depletion peak were prepared. Two series of samples with adjusted position of the sulfate depletion

peak were prepared. In first samples series (2.e, 3.c, 3.d) the sulfate depletion peak was adjusted before, the second series (1.f, 3.a, 3.b) approximately 2.5 h after the main silicate peak. The calorimetry analyses showed in the Fig. 4b confirmed the apparent behaviour of these samples. The minimal heat flow during induction period was increased with the increasing gypsum / AB300 compensation factor. The sample prepared with the various gypsum / AB300 compensation factor influenced the portlandite precipitation. In the case of sample 3.c the peak assigned to portlandite formation was observed around 1 h after the beginning of hydration process. Position of this peak for the other ones was observed around 90 min. The position of the main silicate peak was almost not influenced by the various amounts of AB300 and gypsum.

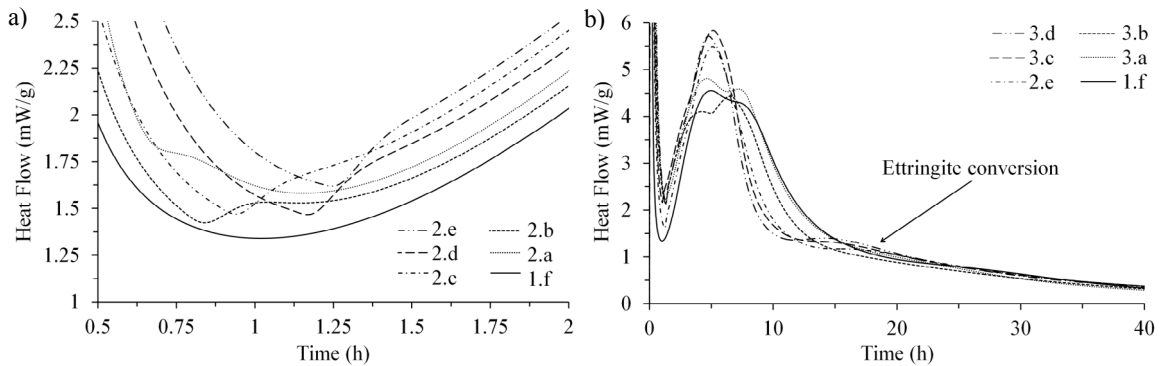


Fig. 4. (a) Induction period with peak of portlandite precipitation (b) Alphasond 300 compensation by gypsum.

The apparent dependence between decomposition of AFt to AFm and position of sulfate depletion peak can be clearly distinguished in Fig. 4b. When the sulfate depletion occurred before appearance of the main silicate peak, then the 4th peak was intensive. In some cases the plot regression reached the positive values. On the other hand when the sulfate depletion occurred after the main silicate peak the 4th peak was observed only as a weak shoulder of the main silicate peak. The intensity of the 4th peak is strongly dependent of the AB300 content and on occurred sulfate depletion before maximum of the main silicate peak. The sulfate depletion before maximum of the main silicate peak also influenced the C-S-H gel structure (higher porosity). This finding was also confirmed in work of Lerch et al [6]. In the model system of C₃A-gypsum the velocity of AFt to AFm decomposition is forced by remaining C₃A surface, where the nucleation takes place [7]. The presence of AB300 in the system caused more amount of remaining C₃A and therefore more amount of C₃A that can react with AFt to AFm.

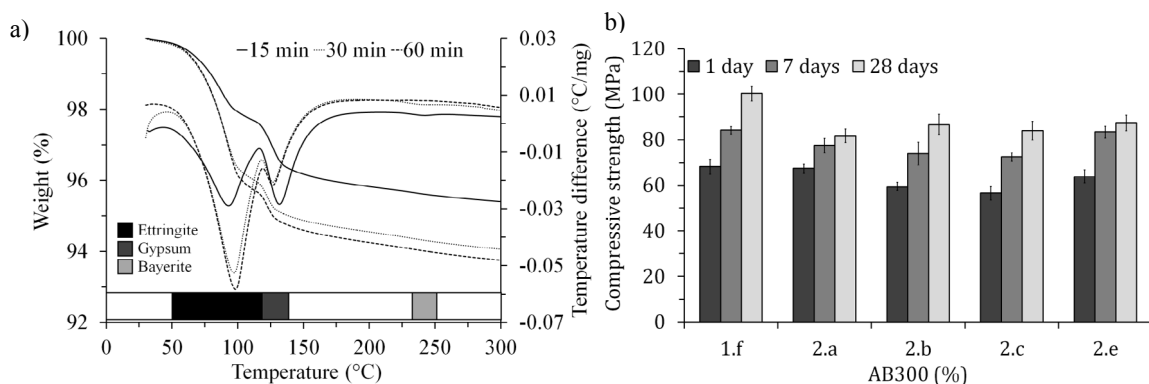


Fig. 5. (a) DTA curve of the hydration product 3.c in time (b) Mechanical testing of binder with AB 300.

The provided DTA analyses (see Fig. 5) of the samples clarified the mechanism of AB300 in the presence of Portland cement. AB300 hydrated through formation of amorphous products to crystalline bayerite was published elsewhere [10,11]. On the DTA curve, peak around 90 – 96 °C can be observed which can be assigned to Aft formation. The peak area corresponding to amount of formed Aft was enlarged with the increasing time of hydration. The size of formed crystallites influenced the peak position; peak is shifted towards higher temperatures with increasing crystallite size. Peak observed around 124 – 126 °C can be assigned to gypsum dehydration [1] and it is also influenced by the time of hydration and gypsum crystallite size (i.e. decreasing size connected with its dissolution). Third weak peak observed on the DTA curve (238 – 234 °C) is related to dehydration of bayerite, this process was observed [12]. Peak was observed after 15 and 30 min of the hydration. The peak disappeared after 60 min. of the hydration. This effect can be explained as a consumption of all present bayerite crystals to Aft formation. This finding should be closely connected with the observation from experimental calorimetry data. The relationship between bayerite consumption and portlandite precipitation is the subject of further investigation.

4. Conclusion

The partial substitution of cement by hydratable alumina showed acceleration of sulfate depletion during hydration process. This reaction should be predicated as a gypsum deficiency in the binder specie. This lack can be solved by another gypsum addition which can influence overall hydration process. It was found that the hydration process of modified samples was unchanged.

The addition of hydratable alumina is shown on the calorimetric curve as clearly detected peak of precipitated portlandite. The portlandite peak is shifted to higher reaction time with increasing content of hydratable alumina.

If the sulfates were depleted before the main silicate peak occurred (in samples with hydratable alumina content), the conversion of Aft to AFm was rapidly accelerated.

It was found that the minimal addition of hydratable alumina without gypsum compensation led to decrease of mechanical properties with no influence of the aging time.

Acknowledgements

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