The effect of burnt lime addition on hydration of Ultra-high performance cementitious composites

R Novotný1, E Bartoničková1 and J Kotrla1

1 Institute of Materials Chemistry, Brno University of Technology, Purkyňova 464/118, Brno 61200, Czech Republic

Email: xcnovotny2@fch.vut.cz

Abstract. The paper deals with the burnt lime utilization as a source of calcium ions participated during hydration process of ultra-high performance cementitious composites. These type of ultra-high performance cementitious composites are based on the high content of silica fume that together with calcium ions form the binder phase. In the case of ordinary Portland cement, the hydration during induction period supposed to be too slow for dissolution of required amount of calcium ions necessary for the pozzolanic reaction of presented silica fume. The low addition of the lime should be a sufficient calcium source that allow the starting of the pozzolanic reaction before the acceleration period occurs. The calcium ions content from the beginning of the reaction was controlled by an addition of soft-burnt and dead-burnt lime. Its influence was studied in terms of hydration process by isothermal calorimetry. Based on the experimental data, the hydration reaction mechanism was proposed.

1. Introduction

Commonly used types of concretes could be typically characterized by their low homogeneity closely related to low tensile flexural strengths. The possible solution to solve this problem is to substitute coarse aggregates with fine sand, to increase content of Portland cement (OPC), addition of extremely fine reactive components (i.e. silica fume, precipitated silica, metakaolin, ground blast furnace slag) and to reduce the water to cement ratio by superplasticizer application [1]. These types of concretes are generally named as ultra-high performance cementitious composites (UHPC). High content of cement, reactive components and low water to cement ratio, typical for this type of composite system, cause volume changes that result in formation of micro-cracks due to plastic and autogenous shrinkage and self-exsiccation [2]. Due to the shrinkage phenomena, it is necessary to apply water curing during hydration and further hardening of prepared composites [2, 3].

High silica fume content, which in dispersion may behave as an aggregate causing less friction between cement particles, is also typical for UHPC [4]. Silica fume and calcium cations, coming from OPC hydration as a secondary product, react together and form binder phases which are beneficiary to mechanical properties of binder species [5]. Nevertheless, the velocity of calcium ions formation for pozzolanic reaction is directly connected with the cement hydration rate [6]. During the first hours of hydration, the induction period occurs and the hydration process is slowed down. Induction period can be prolonged due to the higher content of superplasticizers [7]. High bulk density also reduces the ionic transport, therefore the binders with high content of silica fumes against OPC demonstrate slower strength development [8].
Paper deals with the possibility of calcium oxide usage as a source of calcium cations for silica fume (SF) hydration during the cement induction period. The advantages of calcium oxide is its high reactivity, no other ion contaminations and signs of exhibit the undesirable plastic behavior as it is in case of calcium hydroxide [9]. The utilization of soft-burnt (SBL) and dead-burnt lime (DBL) and curing conditions with respect to the reactivity and long term stability were studied. Srinivasan et al. studied the effect of lime water on OPC-SF binders [10].

2. Materials and methods
The white OPC CEM I 52.5 R (Aalborg Portland A/S, Denmark), white undensified silica fume RW-Füller Q1 (RW silicium GmbH, Germany), SBL CL 90-Q (Kotouč Štramberk, spol. s r. o., Czech Republic) sieved under the 63 µm, dead-burnt lime CL 90-Q (Vápenka Vitošov s r.o., Czech Republic) sieved under the 63 µm, superplasticizer Master Glenium ACE 446 (BASF Stavební hmoty Česká republika s.r.o., Czech Republic) and deionised water were used for UHPC preparation.

All the components were gradually mixed for 1 min, and then the ¾ of gauge water with the superplasticiser dosage was added and mixed for 5 min. The ½ of the missing gauge water was added and mixed for other 5 min. The homogenized mixture was moulded to moulds with the dimensions 4 × 4 × 16 cm intended for mechanical testing. After 24 h the experimental specimens were demoulded and the dry or water curing conditions were applied under the controlled temperature of 25°C. Hydration process of binder was analysed by using of isothermal calorimeter TAMair (TA Instruments) under the 25°C. All of the used components were storage before using under the same conditions for 24 hours, i.e. controlled 25°C. Analysed samples were prepared by hand mixing of bath contents of 40 g of binder, deionized water and additives for 2 min, and then 5 g of this mixture was placed into lockable plastic ampules. The measurements were performed against to reference sample (i.e. water) with similar heating capacity. The studied hydration process was precisely stopped by acetone washing [11]. Formed hydration products (50 mg) were observed by TG-DTA analysis (Q600, TA Instruments) up to 1000°C with heating rate 10°C/min under the dried air atmosphere. Table 1 summarizes the composition and designation of studied samples.

| Sample | OPC | SF | SBL | DBL | SP | Sand | H₂O |
|--------|-----|----|-----|-----|----|------|-----|
| R      | 188 | 62.0| 0   | 0   | 7.5| 750  | 67  |
| 1.a    | 186 | 61.5| 2.5 | 0   | 7.5| 750  | 67  |
| 1.b    | 184 | 61.0| 5   | 0   | 7.5| 750  | 67  |
| 1.c    | 180 | 60.0| 10  | 0   | 7.5| 750  | 67  |
| 1.d    | 176 | 59.0| 15  | 0   | 7.5| 750  | 67  |
| 1.e    | 169 | 56.0| 25  | 0   | 7.5| 750  | 67  |
| 1.f    | 0   | 0   | 250 | 0   | 7.5| 0    | 67  |
| 2.a    | 186 | 61.5| 0   | 2.5 | 7.5| 750  | 67  |
| 2.b    | 184 | 61.0| 0   | 5   | 7.5| 750  | 67  |
| 2.c    | 180 | 60.0| 0   | 10  | 7.5| 750  | 67  |
| 2.d    | 176 | 59.0| 0   | 15  | 7.5| 750  | 67  |
| 2.e    | 169 | 56.0| 0   | 25  | 7.5| 750  | 67  |
| 2.f    | 0   | 0   | 0   | 250 | 7.5| 0    | 67  |
3. Results and discussion

3.1. Setting of UHPC
With the increasing content of the SBL (see figure 1.a), the heat flow in pre-induction period was gradually increased, the difference between R and 1.e sample was 12.2 mW/g. If the un-influenced hydration process of SBL in UHPC occurs the difference in heat values supposed to be 35.7 mW/g. In case of DBL addition (see figure 1.b), the increase of the heat flow between R and 2.e samples was determined to 2.1 mW/g. From the obtained results is obvious that in the UHPC system the retardation of the CaO hydration occurred which was more substantial when the DBL was applied.

![Figure 1. Heat flow in the pre-induction period a) SBL, b) DBL.](image)

Figure 2 shows the retardation of main hydration peak when the SBL was applied. The retardation of the peak in the case of the sample 1.c is almost 1 hour against the R one. The hydration of samples with SBL addition was not significantly retarded too. Sample 1.e reached the maximum of main hydration peak in the same time as the reference R one. Without the dependence on the weight of the addition of SBL, the heat flow value of the main peak maximum was increased of 0.4 mW/g.

The significant influence of soft-burned lime to hydration process was observed in part of induction period. The lowest heat flow 0.4 mW/g was determined in the case f R sample, with the increasing amount of lime addition the heat flow gradually increased to 2.3 mW/g in the case of 1.e sample. Samples 1.d and 1.e showed local minimum of heat flow after 1 hour of hydration. From this point the hydration rate was accelerated to the end of induction period. This phenomenon is clearly visible on the figure 2.b, where during first hour of hydration process the difference in total hydration heat, as well as the amount of formed hydrates, was between particular samples minimal. The total hydration heat increased proportionally with increasing lime content and proved the reaction of silica fume during the induction period and cement hydration process. Sample R reached for 60 mW/g heat more than the sample 1.e after 30 hours of hydration.

![Figure 2. Calorimetric measurement of the UHPC with SBL a) heat flow, b) heat.](image)
Samples with DBL addition showed similar hydration coarse as the one with SBL (see figure 3.a). However, during the first hour of the induction period the almost depletion of the previously observed local minimum occurred and the hydration rate after this minimum to the end of induction period was approximately constant. The retardation of the main hydration peak was similar in case of both types of the limes. Nevertheless, the maximum of the main hydration peak was with the DBL addition slightly decreased. Also the course of the main hydration heat was for the both types of the lime similar (see figure 3). The total hydration heat produced by sample R after 30 hours was or 57 mW/g less than the sample 2.e.

3.2. Testing of mechanical parameters

Tensile and compressive strengths for samples stored under the dry and water curing condition for hydration after 1 day were almost similar due to demoulding after 24 hours and subsequently set up of the different curing conditions for 24 hours. After 1 day of hydration (figure 1.a) the increase of tensile strengths values for 1 MPa was observed for the samples with low content of SBL. On the contrary the higher content of SBL caused the decrease of tensile strength values for 1 MPa against reference sample R. After 7 days of dry curing conditions the gradual increase of tensile strengths with increasing soft-lime content was observed from 9.5 MPa for sample R to 13.2 MPa for sample 1.d. Higher soft-lime content again caused the decrease of the tensile strength values. After 28 days of dry curing conditions the tendency in mechanical behaviour was identical as was observed after 7 days. The tensile strength value of sample R under the water curing conditions was 19 MPa, but the any addition of SBL caused the decrease in tensile strength values. Also the similar tendency after 28 days of water curing was observed, the value for reference sample R was even decreased to 17.5 MPa.

The compressive strength behaviour (figure 4.a) of the samples with the addition of SBL (R-1.d) and cured under the dry conditions was not significantly influenced and for 1.e the value even decreased. After 7 days of the water curing conditions (see figure 1.b) the compressive strength values decreased...
with the increasing lime content. The maximum was reached for sample 1.e. After 28 days of water curing, the values of compressive strength slightly increased for samples 1.a and 1.b with SBL addition. Sample 1.b reached the total maximum compressive strength’s value of 131.3 MPa. On the contrary sample 1.e reached the maximum decrease against the reference R one.

![Figure 5. Compressive strength of the specimens with soft b. lime a) dry curing, b) water curing.](image)

After 1 day of dry curing, the tensile strengths of the samples with dead-lime content reached the similar or higher values than the reference R one. In the case of the sample 2.a and 2.b (dead-burnt) the tensile strength increase was substantial then in the case of 1.a and 1.b (soft-burnt) after 1 day of the dry curing. The increasing tendency in tensile strength values with the increasing content of the lime was observed after 7 and 28 days of dry curing (see figure 6.a). The behaviour of the samples under the water curing conditions and dead-lime addition is given on the figure 6.b. The samples showed the minimal decreasing tendency after 7 and 28 days. Sample 2.d under the 28 day of the water curing conditions reached maximum value of tensile strength 19.3 MPa. The significant defects were observed for samples 2.e after the 7 and 28 day of water curing and the values were not able to determine. The compressive strength behaviour of the samples with DBL addition under dry and water curing conditions (figure 7) showed the identical tendency as the samples with soft-burnt one.

![Figure 6. Flexural strength of the specimens with dead b. lime a) dry curing, b) water curing.](image)

3.3. **DTA analysis of hydration products in time**

The thermal study of the hydration products formed after 1, 5 and 24 hours is given on figure 8. The mass loss visible on the TG curve in the region of 100°C can be assigned to free water content, decomposition of amorphous hydration products and ettringite. In the case of reference sample R the mass loss after 1 and 5 hours of hydration was minimal, however in the case of 1.d sample with the lime content was substantial. This finding proved the formation of hydration products in the presence of the lime even in induction period of cement hydration what was also proposed from the calorimetric data. Mass loss around 120°C can be assigned to gypsum decomposition, which was gradually depleted to the 5 hours of hydration and explain the absence of sulphate depletion peak in calorimetric curves.
with high intensity of heat flow within the main hydration peak [12]. Strong exothermic effect with low mass loss in the region from 250 to 300°C can be assigned to superplasticisers decomposition.

Figure 7. Compressive strength of the specimens with DBL a) dry curing, b) water curing.

This effect was not visible in the samples R and 1.d 0 h where the SP was not added. In the region around 450°C the decomposition of Ca(OH)$_2$ took place, which belonged to early stage hydration products.[13] In the case of reference sample R the portlandite peak was firstly depleted due to the portlandite consumption in reaction with silica fume species and afterwards formed due to the ongoing hydration process. In the case of sample 1.d the portlandite seemed to be slightly consumed within the first hour of hydration, further its content was increased due to the higher formation from the lime addition than the reaction rate with the silica fume. Decomposition of calcium carbonates took place above 650°C [14]. The addition of the lime to the system increased also the carbonate content even before the hydration process due to the not precise its firing and also carbonation process. During the hydration of the sample R the carbonate content was constant up to 5 hours of hydration, the significant increase was observed after the 24 hours of hydration. In the case of 1.d sample the content of carbonates during the whole hydration process was only slightly increased. Reaction of calcium ions with silica fume was observed by gradual depletion of portlandite in the end of cement induction period. In the case of the sample 1.d the significantly higher formation of hydration products during and also after induction period was observed.

Figure 8. TG-DTA analysis of hydration products by means of time a) sample R, b) sample 1.d.

4. Conclusion
The presented data proved that the lime content can improve the silica fume hydration in binder systems even during the induction period of OPC hydration regardless the lime burning conditions. In the case of the content of dead-burnt lime followed by water curing conditions, mechanical strengths were not significantly affected, but there is high risk of product destruction with the high content of this lime.
The dry curing conditions applied to samples with both types of the lime remarkably enhanced the flexural strengths with minimal influence to compressive ones.

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