Physico-mechanical and microstructural properties of rehydrated blended cement pastes

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HIGHLIGHTS

- Properties of blended cement pastes exposed to temperature up to 1200 °C and after their rehydration were studied.
- The addition of slag or fly ash improved the compressive strength of cement paste after heating.
- The strengths of rehydrated cement pastes were lower than of dehydrated pastes.
- The direct conjunction between the strength of rehydrated cement pastes and their brownmillerite (C_4AF) content was observed.

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ABSTRACT

This study aims to investigate the effect of high temperatures of up to 1200 °C and rehydration on the mechanical properties, microstructure and phase composition of blended cement pastes prepared from Portland cement (PC), granulated blast furnace slag (GBFS), high-temperature fly ash (FA) and ground limestone (GL). It has been found that the heating process induces a reduction in bulk density, flexural and compressive strength. The proportion of pores with a diameter higher than 0.1 μm increases with increasing temperature. The addition of GBFS or FA improves the strength properties of dehydrated cement paste (DCP), but this effect was not observed after rehydration. Cement paste with added GBFS has the best resistivity to high temperatures, but after rehydration, GL cement paste shows better mechanical properties.

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1. Introduction

Fire remains one of the greatest potential risks for concrete structures. The extensive use of concrete as a structural material has led to the need to fully understand the effects of fire on concrete structures. The behavior of concrete subjected to high temperatures is the result of many factors, particularly achieved temperature, exposure time and heating and cooling rates [1]. The strength of concrete structures is reduced during heating due to the decomposition of hydrated clinker minerals and changes in the pore structure of cement paste in concrete [2,3]. In the gradual heating of hydrated cement pastes the components of cement are transformed.

Elevated temperatures of up to 105 °C support the evaporation of free water present in pores, and the hydration of unhydrated components can occur (an increasing content of CSH gel and portlandite). At temperatures higher than 105 °C, free water has been completely desorbed and dehydration of tobermorite gel,

ettringite and CSH gel proceeds. In the temperature region from 105 °C up to 450 °C, portlandite coexists with calcite (formed by the carbonation of portlandite during heating), anhydrous cement phases, C_2S (larnite), C4AF (brownmillerite), dehydrated ettringite and CSH. Above 450 °C, portlandite decomposes to CaO and temperatures over 650 °C lead to the decomposition of calcite. At temperatures above 750 °C, dehydrated CSH phase is transformed to near C_2S nesosilicate structure and decomposition of dehydrated CSH occurs at temperatures above 800 °C. Free CaO, C_2S, wollastonite, C4AF and C_2AS (gehlenite) are the main components of cement paste exposed to temperatures over 800 °C [4–6].

The mechanical properties such as strength, modulus of elasticity and volume stability of cement paste and concrete are significantly reduced during exposure to high temperatures. It is possible to observe some crumbling and cracking of concrete subjected to temperatures of 600 °C and higher [7]. It is caused by the expansion of water and CO_2 during the decomposition of $Ca(OH)_2$ and $CaCO_3$, respectively. The water vapor from the air enables rehydration of CaO to $Ca(OH)_2$, which occupies a considerably greater volume than CaO. It causes the concrete to crack and disintegrate. Partial replacement (50%) of Portland cement with

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fly ash (FA) or granulated blast furnace slag (GBFS) reduces the number of cracks and also increases the residual compressive strength of cement paste submitted to high temperatures [8,9]. The presence of slag or fly ash reduces $Ca(OH)_2$ concentration in the binder as they react with the $Ca(OH)_2$, forming calcium silicate hydrate. In contrast, the addition of ground limestone (GL) negatively affects the residual strengths after exposure to high temperatures. The decrease in strengths is proportional to the amount of limestone and it is more evident than in the case of basalt [10].

Dehydrated cement paste (DCP) is not stable in humid environments, where it exhibits rehydration behavior. Dehydrated phases can react with water to form initial hydration products such as ettringite, CSH and portlandite. Larnite remains unchanged [4]. It is obvious that the rehydration capacities of DCPs subjected to various dehydration temperatures are different. The rehydration process of DCP results in the reduction of its post-cooling strength (15–40%). The dehydration temperature seems to be a major factor in resulting residual strength, but this also depends on the method of rehydration. If pastes are soaked in water for 7 days, they reach lower compressive strengths than specimens exposed to 100% relative humidity for the same period. This holds true for cement pastes subjected to temperatures up to 300 °C. The reverse is true for dehydration temperatures from 500 °C to 600 °C [11]. After resaturation by water absorption, cement pastes heated at temperatures up to 300 °C recover their original total porosity [12].

In spite of the common utilization of blended cement and concrete, very few studies have been conducted regarding the repair and rehabilitation of fire-damaged FA or GBFS concrete. It is known that the addition of FA or GBFS contributes to the better strength and durability recovery of rehydrated concrete (up to 80% of initial strength). The reason consists in the rehydration reaction between the newly formed CH and the unhydrated pozzolanic particles that fill the capillaries and decrease the total porosity of the concrete [13]. A detailed study of the composition of burned and rehydrated cement pastes with admixtures of GBFS, FA or GL has yet to be carried out.

There is a need to conduct a comprehensive investigation to understand the nature of the rehydration process and its effect on the strength, microstructure properties and composition of thermally treated cement pastes. For this reason, this experimental study was organized to investigate the rehydration process using different types of cement paste and exposure temperatures. The presented research is intended to be suitable for utilization in the assessment of the possibility of recycling cement construction materials which have been affected by fire.

2. Materials and methods

Laboratory specimens ($20 \times 20 \times 100$ mm) made of fine-grained CEM I 42.5 R (PC) Portland cement; granulated blast furnace slag (GBFS); high-temperature fly ash (FA) and ground limestone (GL) were used in the experiments. The chemical compositions and physical properties of initial materials are given in Table 1.

Portland cement and mineral admixtures are taken as binders and all cement pastes were mixed with the water to binder (w/b) ratio of 0.5. In the mixtures, 20 wt% of cement was replaced by admixture. The mixtures with the additives corresponded to Portland blended cements with designations according to CSN EN 197-1 [14]. The test specimens were demoulded after 24 h and placed in a water bath for another 27 days. Then, the prisms were dried in an oven at 60 °C to a constant weight [15], and were subsequently heated in a furnace at temperatures of 200, 400, 600, 800, 1000 and 1200 °C with a heating rate of 5 °C/min and a duration at maximum temperature of 120 min. Heat treated specimens were tested for their residual mechanical properties, which were then compared with those obtained for unheated cement pastes. Flexural strengths were determined using a standard three-point-bending test and compressive strengths were measured on the far edge of both residual pieces obtained from the flexural test according to CSN EN 196-1 [16]. Flexural and compressive strengths were obtained for eight samples of each mixture and temperature. The specimens destroyed during strength determination were ground in a laboratory vibration mill. Only 0.125 mm undersize was used for the subsequent preparation of rehydrated cement paste samples (PC-R, GBFS-R, FA-R, GL-R). The amount of mixing water was variable with the aim of achieving cement pastes of a standard consistency [17]. The water to binder ratios and the

initial and final setting times of the rehydrated cement pastes (RCPs), which were determined using a Vicat Apparatus, are listed in Table 2. The treatment of the fabricated specimens was identical to the treatment of beams before heating. The pore structures of the samples were studied by high pressure mercury intrusion porosimetry (MIP) using a Micromeritics PoreSizer 9310 porosimeter that can generate a maximum pressure of 207 MPa and can evaluate a theoretical pore diameter of 0.006 μm. The MIP test is performed in two steps: first, the low pressure step evacuates gases, fills the sample holder with mercury and performs porosimetry from about 7–179 kPa; the high pressure step then reaches pressures between 414 kPa and 207 MPa. The contact angle and surface tension assumed for all tests were 130° and 485 mN m^{-1}, respectively. X-ray diffraction (XRD) analyses were carried out using a Bruker D8 Advance system equipped with a Cu tube ($\lambda K_\alpha = 1.54184$ Å).

3. Results and discussion

3.1. Mass properties

With increasing dehydration temperature up to 800 °C, the setting time of RCPs gradually became shorter, which is in agreement with the literature [18]. The rising amount of free CaO in DCPs is the main reason for it. The DCPs obtained at higher temperatures exhibited increasing setting time during their rehydration. These DCPs are more insusceptible to rehydration and the loss of free CaO via reactions with other components of DCP can occur at such high temperatures.

The relative mass loss (see Fig. 1), $m_0 - m_{dry}/m_0$ (with m_0 as the initial mass of the samples), was found to be proportional to the treatment temperature up to 1000 °C. At 1200 °C the mass loss slightly decreased, but this may be due to a statistical variation. FA cement pastes lost mass even at 1200 °C. The temperature range 200–400 °C is in fact the most favorable for the dehydration of general components of cement paste (tobermorite gel, ettringite and CSH gel). This could explain the mass loss in this temperature region. Above 450 °C, portlandite decomposes to CaO and escaping water vapor causes another mass loss. Temperatures over 650 °C lead to decomposition of calcite and originating CO_2 escapes from cement paste, thus decreasing its mass. Significant mass loss caused by the decomposition of calcite is evident for GL samples. Decomposition of anhydrite may be one of the causes of mass loss at temperatures above 800 °C.

Fig. 2 shows the bulk density of cement pastes before and after rehydration. The bulk density of dehydrated samples of PC slightly decreased with increasing temperature up to 600 °C. After exposure to temperature at 1200 °C, bulk density significantly increased. Samples of PC heated at 1200 °C also lost 47% of their volume, becoming considerably darkened and cracked. Thin cracking was observed also on samples burned at 600 °C and 800 °C. The same trend was observed for specimens with the addition of GL. The bulk density of pastes prepared from the mixture of PC with GBFS or FA did not change after burning at up to 800 °C. At 1000 °C an increase in bulk density occurred. A 35% reduction in volume and a slight darkening was observed, but no cracks appeared in GBFS samples after heating at 1200 °C. A different trend from the other studied pastes was observed for FA specimens heated at 1200 °C. A decrease in bulk density by 5% occurred in this case, as did a reduction in volume (19%); a slight darkening of the samples was also observed. GBFS and FA samples heated at 600 °C and 800 °C showed no cracking. This is in good agreement with Mendes's conclusions [8,9].

The bulk densities of cement pastes heated up to a temperature of 600 °C were nearly identical after rehydration (1000 kg m^{-3}), despite the variable quantity of mixing water. Pastes treated before rehydration at 800 °C had a bulk density of approx. 7% lower due to the high water-to-binder ratio ($w/b = 0.9$) necessary for achieving cement pastes of a standard consistency. The bulk density increased (1650 kg m^{-3}) after the rehydration of samples treated at temperatures higher than 800 °C mainly due to only half the