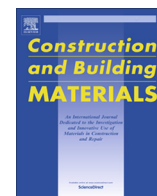




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High temperature durability of fiber reinforced high alumina cement composites

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HIGHLIGHTS

- High temperature durability of high alumina cement fiber reinforced composites was studied.
- Simultaneous presence of CAH_{10} , C_2AH_8 , C_3AH_6 , and AH_3 was found after 2–28 days hydration.
- Basalt aggregates and basalt fibers improved significantly high temperature durability.
- Residual compressive and bending strengths were up to 50% and 34% after 1000 °C exposure.
- Thermal strain was almost linear within the whole 20–1000 °C range.

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ABSTRACT

The effect of high temperature exposure on the durability of fiber-reinforced composite materials based on high alumina cement is studied. A combination of X-ray diffraction- and thermal analyses of hydrated phases shows a simultaneous presence of all principal hydrates (CAH_{10} , C_2AH_8 , C_3AH_6 , AH_3) in significant amounts during the whole 2–28 days hydration period. The application of basalt aggregates and basalt fibers is found to improve significantly the high-temperature durability, in a comparison with the cement paste. The residual values of compressive and bending strength of the most successful mix with the combination of longer and shorter basalt fibers in a 90:10 ratio are 50% and 34%, respectively, after 1000 °C exposure. The fiber reinforced composite material with the most favorable mechanical properties exhibits also the highest resistance to water and water vapor transport and the lowest water vapor adsorption after 1000 °C pre-heating, which correlates well with its lowest amount of pores bigger than 100 nm. The thermal conductivity and specific heat capacity of all analyzed composites show a significant increase with the increasing moisture content; the differences between the values in dry and water saturated state are up to 100% and 65%, respectively. The thermal strain of all studied materials is almost linear within the whole 20–1000 °C range, with the basalt fibers being able to decrease it by up to 7% at 1000 °C.

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1. Introduction

Durability of concrete is mainly governed by its permeation properties and the harshness of the environment [1,2]. Transport of water, soluble salts, and gases in concrete presents the basic prerequisite for concrete deterioration because of their possible interactions with concrete components, which can affect the integrity of the cement matrix, aggregates, interfacial transition zone, or the steel reinforcement [3]. Therefore, water transport in concrete became a subject of many research studies to date. For example,

Guimaraes et al. [4] tried to develop a numerical program for prediction of water absorption in porous media. Bao et al. [5] focused on the investigation of the influence of effects of short-term sustained uniaxial compressive or tensile loadings on water transport. Smyl et al. [6] studied isothermal unsaturated moisture transport and simulated moisture ingress in damaged mortar and concrete. Very frequent were also investigations of salt transport in cement composites.

Wang et al. [7] simulated water and chlorides transport in cracked unsaturated concrete. Chloride transport coupled with simulation of fracture mechanics in cracked concrete was described in the study of Tavares et al. [8], while Real et al. [9] investigated corrosion induced by the presence of chlorides in structural lightweight aggregate concrete. Similarly to the pres-

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ence of chlorides, also sulfates can induce degradation processes. For example Najjar et al. [10] investigated damage mechanisms caused by both chemical and physical sulfate attack. Modeling of this kind of attack was also the matter of the study performed by Cefis et al. [11]. Among other kind of chemicals, for example mineral and organic acid attack was studied by Beddoe [12] and Dyer [13].

The external conditions acting negatively on concrete elements in building structures can be represented mainly by the marine environment, ground water, gas environment, or the freeze/thaw cycles. Bo et al. [14] proposed probabilistic durability assessment of concrete structures in marine environments. Du et al. [15] analyzed inhibitory effects of chloride ions on concrete sulfate attack in the marine conditions. Ghobadi et al. [16] studied ground water effect on concrete lining of tunnels. In addition to ordinary environments, concrete can be used also in some specific application, which can harmfully affected its structure. Voefel et al. [17] investigated the mechanisms of concrete deterioration in biogas digester. Yu et al. [18] formulated an equation for determining freeze-thaw fatigue damage in concrete. Freeze-thaw loadings can though act together with some previously mentioned degradation processes. For example, Chen et al. [19] assessed the effects of simultaneous sulfate attack and freeze-thaw cycle damage of cement based material, while Wang et al. [20] studied concrete under chloride-salt freeze-thaw cycles.

High temperature durability of concrete is mostly understood in terms of its fire resistance. Current research can be divided into two groups. The first is focused on the behavior of structural elements, such as concrete-filled steel plate composite walls (Wei et al. [21]), or concrete-filled steel tubular columns (Shekaste-hband et al. [22], Song et al. [23]), under fire. The second group deals with residual properties of cement composites. Concrete based on Portland cement (PC) was probably the most often analyzed material in that respect. Tan et al. [24], in a characteristic example of such studies, analyzed the influence of high temperatures up to 600 °C on residual properties of PC based foamed concrete and reported a decrease of compressive strength at maximal temperature exposure by about 50–70%. Cementitious composites based on blended cement (PC with fly ash) with hybrid PVA and steel fibers were examined by Liu et al. [25]. They presented a decrease of compressive strength after exposure to 800 °C by about 50%, despite the use of silica sand and Portland cement, which was probably due to the positive effect of pozzolanic fly ash and PVA fibers. Bodnárová et al. [26] investigated behavior of blended cement (PC with pozzolan) based composites with polypropylene or steel fibers and basalt or lightweight aggregate and reported a decrease of compressive strength in the range of 42%–65% due to the loading by 800 °C. In general, it can be concluded that PC does not resist to high temperatures very well. Thermal behavior of PC depends on temperature decomposition range of particular cement phases, specifically of calcium silicate hydrates (CSH), portlandite, and calcium carbonate, and of the content of bound water [27]. Dehydration of CSH begins at about 100 °C [27–29], which is accompanied by decomposition of ettringite and other sulfoaluminates at 100 °C–200 °C [29]. Another important reactions are portlandite decomposition occurring in the temperature range of 400 °C–600 °C [27–29] and decomposition of calcite from 500 °C to 920 °C [27,29]. All mentioned processes are accompanied by big mass losses. The material transformation is often manifested in explosive spalling (up to about 300 °C) and crack formation.

Calcium aluminate cement (CAC) rich in Al_2O_3 may present an alternative to PC in high temperature applications. Its utilization may seem controversial, in general. Because of the loss of long-term strength, which led to collapse and defects of buildings in the second half of 20th century, CAC was forbidden in 1970s for construction of load-bearing structures. However, on the other

hand, its overall suitability for a production of concrete elements and composites exposed to temperatures even above 1000 °C was never infirmed. In a comparison with PC, CAC fundamentally differs in phase composition; calcium silicates are not present. The main phase of calcium aluminate cement is monocalcium aluminate (CA), which in the case of higher alumina cement is accompanied by dicalcium aluminates (CA_2) and dodecacalcium heptaaluminate ($C_{12}A_7$) [30]. Minor phases which calcium aluminate cement can contain are gehlenite (C_2AS), brownmillerite (C_4AF) and dicalcium silicate (C_2S) [30]. The hydration process is widely influenced by phase composition. However, in contrast to the hydration of calcium silicate compounds (the formed hydrates are similar for temperatures up to 100 °C), the process of CAC hydration is strongly dependent on temperature. The main products are calcium aluminate decahydrate (CAH_{10}), occurring mainly at temperatures under 22 °C, followed by dicalcium aluminate octahydrate (C_2AH_8), arising primarily from 20 °C to 30 °C [31]. Both mentioned phases are hexagonal and metastable. The last most common product is cubic and stable tricalcium aluminate hexahydrate (C_3AH_6), which is usually present in paste when hydration temperature is above 30 °C or due to the conversion process [32]. In addition to the mentioned calcium aluminate hydrates (CAH), also aluminum hydroxide (AH_3), either in the form of amorphous phase or as crystalline gibbsite, is present in hydrated CAC pastes. Similarly to PC, also CAC thermal decomposition begins at about 100 °C, with the amorphous AH_3 in this case [33]. The dehydration of CAH phases takes place in a wider temperature range, from 100 °C to 370 °C [29,33,34], or actually up to 750 °C taking into the account the final dehydration of $C_{12}AH_7$ [34]. At higher temperatures, 900 °C–1000 °C, the recrystallization process of $C_{12}A_7$ to CA and CA_2 occurs [33,34]. In a comparison with PC, the mass changes are generally lower and CAC is able to withstand even temperatures above 1400 °C [35].

Current practical applications of CAC are mainly connected with designing refractory castables. Wang et al. [35] investigated a material composed of tabular alumina, reactive alumina, CAC and dispersant agent and reported mechanical strengths growth at temperatures above 1000 °C, which was caused by the sintering process and densifying effect of recrystallization of calcium aluminate phases. Klaus et al. [36] studied a similar refractory castable but they focused on the influence of specific surface area of alumina filler on the hydration kinetics of CAC. Regarding the high temperature under 1000 °C, Khaliq et al. [37] studied the difference between the behavior of concretes based on CAC and PC. They confirmed higher compressive strength of concrete based on CAC in the temperature range of 20 °C–800 °C, as well as higher elastic modulus and compressive toughness. Zhang et al. [38] compared the temperature dependence of thermal diffusivity of cement pastes based on these two kinds of cement. Alonso et al. [39] proved in their study the applicability of CAC blended with blast furnace slag in the conditions of long term repeated thermal loading up to 550 °C.

One of the most common possibilities how to improve the performance of cement composites is reinforcing them by fibers. Specifically, the fibers application can lead to increasing the toughness of concrete, tensile, flexural, and shear strength, impact resistance, frost resistance, or restraining the shrinkage. The choice of fibers (steel, glass, synthetic, organic fibers) depends on the required properties, and where the improvement is desired. For fire resistant concrete, an important characteristic is the ability of fibers to lessen the spalling of the surface layer and also to increase the fracture energy after heating. Basalt fibers can be considered as a very suitable choice in that respect, which is due to their high-temperature resistance up to 1255 °C [40]. In a comparison with glass fibers, they exhibit lower mass changes due to the high-temperature exposure [41]. Basalt fibers also have one of the

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