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# Characterization of microstructural evolution and mechanical properties of refractory composite

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ABSTRACT

The possibility to increase the stability of the heating unites combustion zone refractory structures, made of the aluminate cement composite concrete, using for this aim polypropylene and carbon fiber additives, was investigated in this work. The peculiarities of microstructure evolutions in the fiber and binder contact zone, the channels formation, the changes of porosity and compressive strength of fiber additives having refractory binder under temperature treatment was investigated; the investigation results allowed to predict the hybrid fiber more effective action than using them individually. The influence of fiber additives on porosity, mechanical characteristics and resistance to explosive spalling of the refractory concrete with fiber additives was tested. The concrete testing results showed that, when the hybrid fiber additive is used, the synergetic effect, that appeared in this case, is higher than effect, observed in fiber individual application. In particular, in the case of using the hybrid fiber additive in refractory concrete, a risk of explosive spalling of concrete is eliminated and the drop of its compressive strength is prevented, when refractory concrete is fired approaching the limiting temperature.


## 1. Introduction

One of the most important elements of furnaces, boilers and other heating units is the structure (lining) of the fuel combustion zone, usually made of refractory concrete with calcium aluminate cement as a binding material. The production of refractory concrete used for fuel combustion zone structures differs from the production of concrete employed for building constructions in civil engineering. Unlike concrete used for building structures which is made of ordinary cement, refractory concrete should be dried after hardening for humidity removing. It is achieved by gradually rising its temperature from 20 to 110 °C. Dried concrete should be fired at high temperature. In the process of heating, the temperature is gradually raised until the limiting temperature (1320 °C) is achieved. In dried concrete firing, chemical and physical processes, causing the remove of chemically bound water and the formation of new crystalline phases, take place. All these processes also cause great changes in the microstructure of concrete and pose a threat of its explosive spalling [1]. In Fig. 1, the part of the structure of the heating unit used in oil refineries, which was damaged by explosive spalling, is shown.

Explosive spalling is usually caused by the pressure of water vapors, which are developed, when chemically bound water is turned to free water. The threat of explosion of the structure is greatly increased, if the currently used types of concrete are employed: medium-cement content concrete (MCC, with cement content, reaching 8–15%), low-cement content concrete (LCC, with 2–7% of cement) and ultra-low-cement content concrete (ULCC, with 0.5–2% of cement). To avoid the explosion of refractory concrete due to the pressure of water vapors developed at the initial stage of heating, new concrete structures of heating units have been dried and fired for the first time in a very careful way [2]. In practice, it is hardly technically possible to perform the procedure of concrete drying very accurately. Therefore, to reduce a risk of explosive spalling, when concrete drying and the initial heating modes are not rigorously controlled, various concrete additives (e.g. aluminium powder, polymer fiber, etc.), increasing concrete permeability by forming a capillary system for removing water vapors without damaging concrete, are used [3,4]. Aluminium powder reacts with water in the alkaline medium, releasing hydrogen, which causes the formation of open porosity in concrete and makes it more easily permeable to water vapors. However, though the addition of aluminium powder increases concrete permeability to water vapors, its mechanical strength is decreased [5].

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**Fig. 1.** The part of the combustion zone structure in the heating unit used in oil refineries damaged by explosive spalling (metal anchors can be seen on the photograph).

It has been found that the additive of polypropylene fibers (PPF) is well suited for decreasing the risk of explosive spalling both of concretes used in building structures and the refractory concretes used at high temperatures [6–9]. A positive effect of this additive, with regard to its ability to decrease the risk of explosive spalling, is explained by the fact that it undergoes disintegration at the temperature of 150–160 °C, which causes the formation of microchannels, allowing water vapors to pass through, and helping to avoid a dangerous rise of pressure.

It has been noted [10–13] that concrete permeability and resistance to explosive spalling are determined by the geometrical parameters of the fibers used and the conditions of concrete production. Therefore, from the perspective of decreasing the risk of explosive spalling, PPF is a very promising additive. However, the effective solutions of problems, associated with the production of refractory concretes with this additive in real conditions, the most important of which is associated with increasing concrete strength by firing, requires more investigations than those that have been performed before. More thorough knowledge of the effect produced by this additive is required, which can be acquired by investigating the PPF impact on the process formation of channels in the concrete binding material. It is appropriate to search for other fibers, which are destroyed in the process of concrete production and thereby make the conditions for channels' (a capillary structure) formation, but whose action in the hardening binding material medium and the nature of destruction differ from those of PPF. Carbon fiber (CF), which is burnt at the temperature of about 500 °C, and whose burning is likely to cause the channels' formation, could be an interesting material, when considered from this perspective. The temperature of CF destruction is higher than PPF destruction temperature. Besides, CF does not melt before being destroyed, and its geometric parameters (particularly, the thickness of fibers) differ from those of PPF.

Positive results have been obtained, when CF was used in civil engineering for reinforcing both heavy-weight and cellular concrete [14–16]. It has been stated that a small amount of CF additive (0.5%) increases the strength of the hardening material of Portland cement [14] and aluminate cement [15]. When CF additive is used in the production of autoclaved concrete [16], the increase in concrete strength can be observed, which is caused by the changes in CF microstructure. Thus, crystallinity of the binding material at the joint with the CF surface is higher than that not adjoining it. This means that there are some crystallization centers on the surface of fibers. The research results presented in [17] have shown that the CF fibers can be used for hybrid reinforcement of Portland cement composite. The best results (as regards the enhancing of the mechanical properties of composite) were obtained, when material was reinforced with CF and steel fiber for achieving a synergetic effect by combining these two fibers.

The provided data have shown that, for solving the problem associated with explosive spalling of refractory concrete, the research into the mechanisms of PPF and CF action, as well as feasibility studies of the CF application to the solution of the problem of refractory concrete explosive spalling, are required. A promising approach to solving this problem can be also based on the synergetic effect associated with the simultaneous use of PPF and CF, which can reduce the risk of explosive concrete spalling and help to avoid the destruction of the structure, which are basic element of the heating unit structures.

The aim of this work is to investigate the possibility to increase the stability of the heating unites combustion zone refractory structures, made of the aluminate cement composite concrete, using for this aim PPF and CF additives.

The main tasks are as follows: to investigate the peculiarities of microstructure evolutions in the fiber and binder contact zone, the channels formation, the changes of porosity and mechanical strength of PPF and CF additives having refractory binder under temperature treatment; to estimate the influence of fiber additives on the porosity, mechanical characteristics and resistance to explosive spalling of the refractory concrete.

## 2. Experimental

### 2.1. Materials and specimen preparation

The materials used in the work included calcium aluminate cement (CAC) Gorkal 70 (with $Al_2O_3$ content making at least 70%); filler (F) made of calcium aluminate cement clinker Gorkal 50 (with $Al_2O_3$ content making at least 50%) produced by the enterprise "Górka" in Trzebinia (Poland); microsilica (MS) RW-Fuller produced by the company "RW Silicium GmbH" ($SiO_2$ – 96,1%); calcinated alumina (CA) CTC-20 produced by the company "Almatis" ($Al_2O_3$ – 99,7%); dispersive aggregate (DA) obtained by grinding BOS145 aggregate produced by the company "Tabex Ozmo" in the ring mill and screened through a 0.14 mm sieve; hybride deflocculant (HD): mix of polycarboxylate ether Castament FS20 supplied by the company "BASF" and sodium tripolyphosphate (NT). The ratio of NT to FS20 1:1.

In the refractory compositions, carbon fiber (CF) BMH-4 (the amount of carbon in CF 99–99.9%) and polypropylene fiber (PPF), as the additive were used. The morphology of the fibers is demonstrated in Fig. 2, their technical characteristics are given in Table 1.

Three kinds of refractory concrete binder, whose compositions are given in Table 2, were investigated.

Dry mixes for making the control specimens and specimens with fiber additive (M1 and M2) were obtained by mixing microsilica, calcinated alumina, dispersed aggregate and a hybrid deflocculant. Dry mixes for producing the control specimen (M0) and specimens with the respective amount of fiber additive (M1 and M2) had been mixed in the Eirich mixer for 2 min. Then, each specimen, after adding the required amount of water, had been mixed for 5 min in the Hobart mixer. In this way, masses for forming the specimens of the binder had been obtained. In all the formation masses, the ratio of water to dry materials was 0.16. The masses for the binder formation masses of two various compositions obtained in the described manner were poured into $10 \times 10 \times 10$ mm forms (Table 4), which were placed in the climatic chamber, and left for hardening for 72 h at the temperature of 20 °C.