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RESIDUAL PROPERTIES OF FIBER-REINFORCED REFRACTORY COMPOSITES WITH A FIRECLAY FILLER

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Abstract. The aim of our study was to develop a composite material for industrial use that is resistant to the effect of high temperatures. The binder system based on aluminous cement was modified by adding finely-ground ceramic powder and metakaolin to reduce costs and also to reduce adverse effects on the environment due to high energy consumption for cement production. Additives were applied as a partial aluminous cement replacement in doses of 10, 20 and 30 % by weight. The composites were evaluated on the basis of their mechanical properties and their bulk density after gradual temperature loading. The influence of basalt fibers and modifications to the binder system were studied at the same time. Basalt fibers were applied in doses of 0.5 % and 2.0 % by volume. The results confirmed the potential of the mineral additives studied here for practical applications, taking into account the residual mechanical parameters after thermal loading. The addition of ceramic powder reduced the bulk density by 5 % for each 10 % of cement substitution, but the residual values were very similar. The bulk density and the compressive strength were reduced when basalt fibers were applied, and the flexural strength was significantly increased in proportion to the fiber dosages. Metakaolin seems to be a more suitable additive than the ceramic powder that was applied here, because there was a significant increase in the mechanical parameters and also in the residual values of all properties that were studied.

Keywords: temperature loading; fireclay filler; aluminous cement; metakaolin additive; ceramic powder; basalt fibres; mechanical properties.

1. Introduction

Refractories are composite materials developed for high temperature applications to protect industrial technologies, structures, and also people. The composites investigated here are made from high-utility, high-quality materials. This has a significant influence on their price and on the amount of energy consumption. Heat-resistant materials can be divided into several classes, based on: chemical composition (acid, basic and special), method of implementation (shaped and unshaped), method of manufacture (fused and sintered), and porosity content (porous and dense) [1, 2]. The major categories of traditional refractories are fireclays, high alumina, and silica. One of the best-known techniques for producing refractory composites is by mixing selected components and then casting them to obtain the required shape [3]. The choice of material for traditional refractory applications, and also for advanced material applications, has always been based on balancing costs and performance lifetime [1].

The residual properties of refractories are often ensured by applying a fiber reinforcement, which helps to resist predominantly tension stresses emerging from volume changes. Increasing tensile strength of the final composite reduces crack initiation [4–7]. The fibres can be made from natural materials such as asbestos, sisal, basalt and cellulose, or from manufactured products such as glass, steel, carbon and polymers [8]. However, a number of these fibres cannot be successfully applied in fire-resistant composites, due to their combustibility or low heat resistance. Basalt and carbon fibers are most widely used, due to their suitable mechanical and durability properties, and the absence of health risks [9].

Traditional Portland cement-based concrete undergoes sequences of structural changes according to the actual thermal load level. After evacuation of the physically bonded water at 200 °C and gradual decomposition of CSH, there is a crucial temperature level at about 400 °C when portlandite $Ca(OH)_2$, an important hydration product, decomposes to quicklime and water [10]. When a thermal load of 573 °C is reached, there is crystal lattice transformation of quartz, which is accompanied by extensive volume changes and crack formation. Increasing the thermal level causes loss of integrity. The origin of the ceramic bond was observed, but the weak binding ability of this system cannot withstand successive hydration of quick lime. For this reason, Portland cement-based composites and concretes are not suitable for high temperature applications. An indispensable component is aluminous cement, which exhibits excellent resistance to high temperature.

Luminous cement production uses a great deal of energy, because of the higher burning tempera-

	Al_2O_3	CaO	SiO_2	Fe_2O_3	MgO	TiO_2	LOI	**Blaine** [m^2/kg]
Cement	70.8	27.5	0.58	0.42	0.21	0.37	0.49	381
Metakaolin	41.9	0.13	52.9	1.08	0.18	1.8	3.81	306
Ceramic Powder	20.26	10.92	50.73	6.36	4.75	–	6.98	336

TABLE 1. Chemical composition of binder components [1, 15] (in %).

ture (about 1700 °C). For this reason, there have been many attempts to find materials with cementitious properties that could replace part of the cement. Much attention in the field of refractories is currently being paid to various clay-based materials, such as metakaolin and ceramic waste powder [1]. The lower energy consumption of these cement supplementation materials could also be more economical. Modern composites are often a complex system with a binder modified by mineral additives and a number of other chemical admixtures. Thanks to advanced technologies, it is possible to achieve desirable properties such as high strength and good durability, for which an extremely low water-cement ratio is required [11].

According to the manufacturing technology for monolithic refractories based on hydraulic bonding, cement composites should reach maturity, after which a drying procedure and the first firing are carried out. A high heating rate may cause mechanical breakage of the refractory. This is most likely to occur if the concrete is held at a low temperature (< 21 °C) [12].

In particular, the components of refractory composites are usually contaminated with small amounts of impurity oxides, including TiO_2, Fe_2O_3, CaO, MgO and alkali oxides, which act as fluxing agents at high temperatures. These fluxing agents reduce the eutectic temperature of alumina-silicate refractories. However, the number of fluxes is kept to a minimum, in order to minimize their effect on the development of the liquid phase at higher temperatures [13, 14].

The aim of the research work presented here is to develop high temperature resistant composites, based on aluminous cement, that offer significant environmental benefits. Two different mineral additives were used as a partial replacement for aluminous cement. Further application of alternative binding systems could reduce the negative impact of the building industry on the environment. The additives investigated here are interesting locally-available alternative raw materials.

2. Materials and methods

Aluminous cement. The refractory composites were based on aluminous cement in order to achieve the required high temperature resistance, which is determined by the content of Al_2O_3. Secar71 aluminous cement containing ≥ 71 % of Al_2O_3) was used in our experimental program. The chemical composition and the specific surface area measured by Blaine apparatus are shown in Table 1. This composition enables the cement to be applied at up to 1700 °C.

Finely ground ceramic powder. To increase the energy efficiency of the composites, we used finely-ground ceramic powder that originated from grinding advanced hollow brick blocks produced by Heluz cihlářský průmysl, v.o.s., Czech Republic. Finely-ground ceramic powder is a waste material of major scientific interest in the Czech Republic. Its potential for practical use in the building industry has been confirmed by several research studies [14–19]. However, its use for substituting aluminous cement is a quite novel approach. Its chemical composition is shown in Table 1.

Metakaolin. Another part of the experiment focused on the impact of adding Mefisto L05 metakaolin from České lupkové závody, a.s., Czech Republic, on the final and residual mechanical properties of refractory composites. Metakaolin is produced by controlled clay calcination. The calcination temperature is dependent on the actual composition of the raw materials, but is generally about 800 °C [20]. The composition of the raw clay, predominantly its kaolinite content, defines the final designation of the product [21].

Ceramic aggregate. Ceramic aggregate in the form of chamotte fireclay was used as a filler. Fireclay aggregates are commercially-produced artificial materials used for producing temperature-resistant elements. The amount of aluminous oxides (a minimum of 40 has an essential influence on the aggregates that are used. The amount of Fe_2O_3, which has a negative effect on the temperature resistance, is limited to 4 % [22]. The fireclay is crushed and is distributed in the required grading. A suitable composition of ceramic aggregates ensures that it can be applied at over 1700 °C, which is of great interest in the metallurgical and chemical industries. The refractory quality of high-alumina materials is usually higher than that of fireclay-bearing refractories. Nevertheless, fireclay refractories are still the most widely used type, due to their ease of fabrication, their resistance to chemical attack and their relatively low cost [14].

Basalt fibers. Natural basalt is a material of volcanic origin that is found all over the world. It is primarily resistant to corrosion in an acid environment, and also in an alkaline environment, and is characterized by excellent resistance to high and low temperatures, from -260 °C to $+750$ °C. Igneous basalt rocks have a sufficient melting temperature, between

	Basalt fibres		Aluminous Cement		Fireclay			Plasticizer	Water
	6.35 mm	12.7 mm			0/1 mm	1/2 mm	2/4 mm		
Ref-0	0	0	900		520	140	320	16.2	200
Ref-0.5	1.45	13.05	900		520	140	320	16.2	200
Ref-2.0	5.8	52.2	900		520	140	320	16.2	200
	Basalt fibres		**Aluminous Cement**	**Ceramic Powder**	**Fireclay**			**Plasticizer**	**Water**
	6.35 mm	12.7 mm			0/1 mm	1/2 mm	2/4 mm		
CP10-0	0	0	810	90	520	140	320	16.2	200
CP10-0.5	1.45	13.05	810	90	520	140	320	16.2	200
CP10-2.0	5.8	52.2	810	90	520	140	320	16.2	200
CP20-0	0	0	720	180	520	140	320	16.2	200
CP20-0.5	1.45	13.05	720	180	520	140	320	16.2	200
CP20-2.0	5.8	52.2	720	180	520	140	320	16.2	200
CP30-0	0	0	630	270	520	140	320	16.2	200
CP30-0.5	1.45	13.05	630	270	520	140	320	16.2	200
CP30-2.0	5.8	52.2	630	270	520	140	320	16.2	200
	Basalt fibres		**Aluminous Cement**	**Meta-kaolin**	**Fireclay**			**Plasticizer**	**Water**
	6.35 mm	12.7 mm			0/1 mm	1/2 mm	2/4 mm		
MK10-0	0	0	810	90	520	140	320	16.2	200
MK10-0.5	1.45	13.05	810	90	520	140	320	16.2	200
MK10-2.0	5.8	52.2	810	90	520	140	320	16.2	200
MK20-0	0	0	720	180	520	140	320	16.2	200
MK20-0.5	1.45	13.05	720	180	520	140	320	16.2	200
MK20-2.0	5.8	52.2	720	180	520	140	320	16.2	200
MK30-0	0	0	630	270	520	140	320	16.2	200
MK30-0.5	1.45	13.05	630	270	520	140	320	16.2	200
MK30-2.0	5.8	52.2	630	270	520	140	320	16.2	200

TABLE 2. Composition of the mixtures (all data in kg/m^3).

1500 °C and 1700 °C, which enables them to be used in the form of fibers in a wide range of industrial applications [23, 24]. Basalt fibers are predominantly produced in the form of a continuous fiber, which is cut to the required length. There has been intensive development of basalt fibers in the form of textiles, bars, rovings, etc., because, unlike toxic asbestos fibers, they pose no health risks [9]. For our study, we used fibers produced by the Basaltex, a.s., Czech Republic. The density of the basalt fibres corresponds with the density of the raw material (2900 kg/m^3). The tensile strength of basalt fibres is more than 2000 MPa.

The experimental program investigated the composition of refractory fiber-reinforced composites and their response to gradual thermal loading. The evaluation was based on determining the basic physical and mechanical properties. The binder system was modified by adding ceramic powder and metakaolin. The mineral additives were gradually dosed up to 30 % of cement substitution. The mixtures were reinforced by two different dosages of basalt fibers (0.5 % and 2.0 % by volume). It is necessary to apply an efficient plasticizer in order to preserve good workability and a low water-cement ratio. On the basis of previous research, we decided to use polycarboxylate plasticizer in a dosage of 2.5 % of the binder mass. No negative impact of this organic compound on the residual properties was confirmed [25].

The composite was composed with three fractions of finely-crushed fireclay aggregates: 0–1 mm, 1–2 mm and 2–4 mm. These fractionswere used, because their absence could reduce the final mechanical properties.

Previous research had confirmed a positive impact of dosing fibres of different lengths [26]. To achieve better fracture properties and to limit crack initiation, it is more effective to use longer fibres. For this reason, fibres 6.35 mm and 12.7 mm in length and 13 µm in diameter were added in doses of 0.5 % and 2.0 % by volume. The greater amount of fine components in the mixture was designed to ensure good spatial distribution of the basalt fibers. This reinforcement was applied for each modification of the binder with finely-ground ceramic powder (CP) and metakaolin (MK). Details of the composition of all studied composites are shown in Table 2. Sets of prismatic specimens with dimensions of $40 \times 40 \times 160\,\mathrm{mm}^3$ were produced

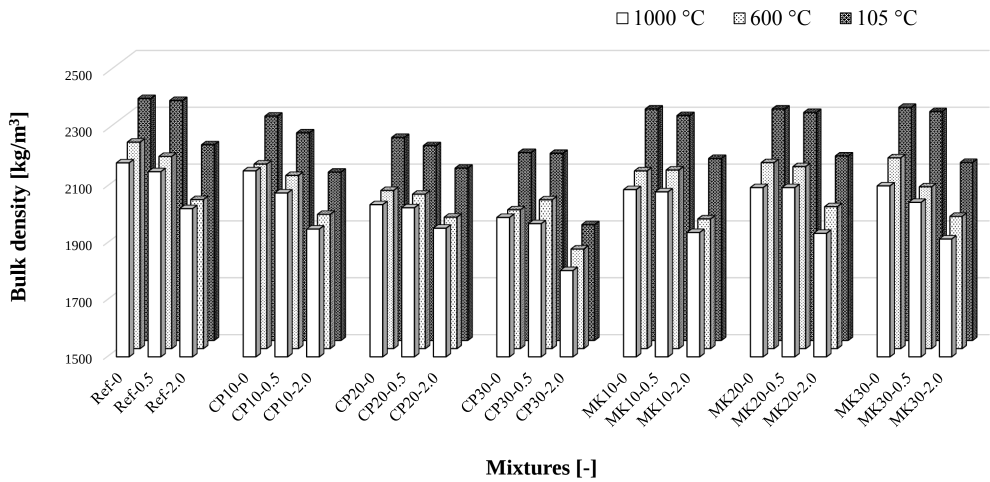

Figure 1. Bulk density of the tested composites.

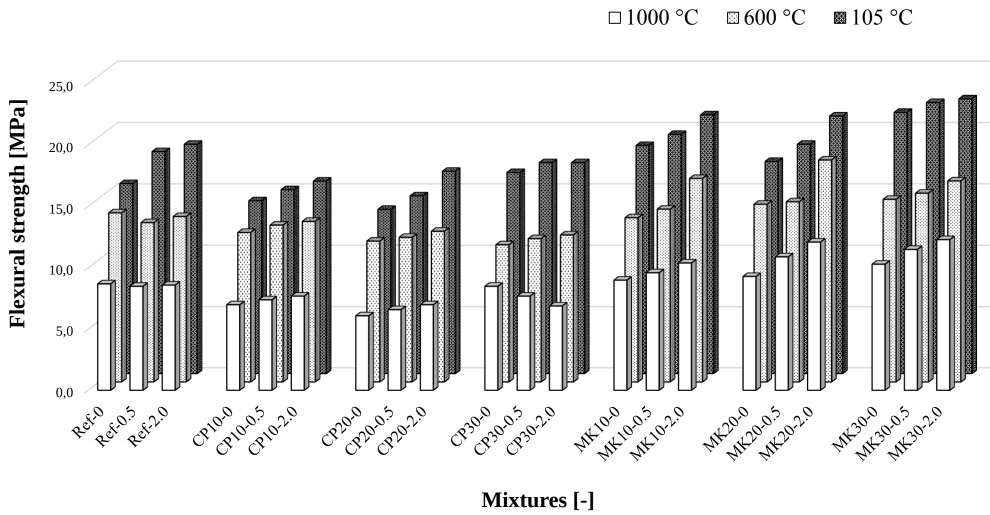

Figure 2. Flexural strength of the tested composites.

for the tests that followed.

We can observe a gradual decline in bulk density due to the effect of high temperature, when the moisture and the physically-bound water have evaporated. The increase in the temperature load leads to a further decrease in bulk density, which is caused by partial chemical decomposition of the hydration products and the siliceous components contained in the additives. For this reason, the highest bulk density values can be observed for the reference specimens without cement replacement, see Fig. 1. The bulk density values are also affected by the increasing application of basalt fibers. Doses of 2.0 % of fibers by volume had an air-entraining effect.

Flexural strength is predominantly affected by the fiber dosage, but the parameters that are reached indicate that increasing the fiber dose extensively seems not to lead to very high parameters. Ceramic powder provided no fundamental improvement in flexural strength, but the residual values, which are crucial for refractories, are slightly lower than the reference. In addition, metakaolin had an altogether positive effect on the flexural strength values in all cement substitutes studied here. Metakaolin replacement has a significant positive effect on the residual values. Detailed results are shown in Fig. 2, which also shows the potential of the cement supplementation materials for refractory composite production.

Substitution of cement offers major environmental benefits and energy savings. The basalt fibers probably have good cohesion with the binder system, because the reduction in bulk density due to high doses of fibers did not have a negative effect on the final flexural strength values.

The compressive strength results are very interesting in relation to the additives studied here. The compressive strength values correspond well with the bulk density result, see Fig. 3. The residual properties of the high temperature resistant composites with the addition of metakaolin reached a similar level or a higher level for all mixtures. This is important, because it limits the negative impact of an additive with a relatively high amount of quartz, which passes through several phase changes during thermal loading. Our data corresponds with that presented in Keppert [10].

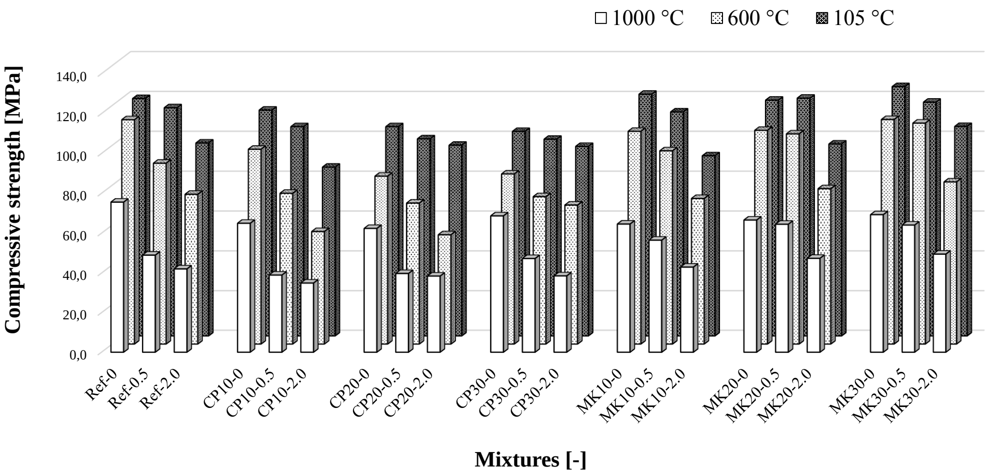

Figure 3. Compressive strength of the tested composites.

3. Conclusion

The experimental program that has been carried out dealt with the development of a new refractory fiber-reinforced composite using alternative binding materials. The program focused on the application of a finely-ground ceramic powder and metakaolin as a replacement for aluminous cement. Our aim was to develop a high temperature resistant fiber-reinforced composite with reduced environmental impacts. The basic physical and mechanical properties before and after temperature loading were measured in order to evaluate the behaviour of the system.

On the basis of the experiments that we performed, we can conclude that, in terms of flexural and compressive strength and residual strength after temperature loading, the most suitable properties are achieved when 270 kg/m^3 of aluminous cement (30 % of the aluminous cement weight) are replaced by metakaolin. The residual mechanical properties of all mixtures with added ceramic powder exhibited slightly lower values than those of the reference mixtures with full doses of aluminous cement. The reduction was by about 15 %.

Substitution of aluminous cement contributed to the stability, and also to the mean ratio of the original and residual properties, of the fiber-refractory composites that were developed. After 600 °C, the flexural strength decreases to 71.0 % of the original value, while the compressive strength decreases to 87.8 % of the original value. A similar trend, 51.9 % of the original values for flexural strength and 61.0 % for compressive strength, can be observed after 1000 °Cloading. This is probably caused not only the suitable composition of the additives, but also by the improved grading curve of the fine components. This corresponds with the research findings presented by Fujiwara et al [30]. A secondary consequence this effect is that there is improved efficiency of the basalt fibers, due to better cohesion.

Our experimental program has confirmed the great potential of ceramic powder, and especially metakaolin, as a supplementation material for aluminous cement in high alumina cement based composites. Further application of materials based on burnt clay and brick dust can help to reduce energy consumption and total costs.

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