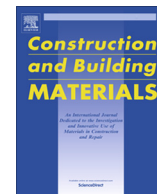




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Effect of calcined Czech claystone on the properties of high performance concrete: Microstructure, strength and durability

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HIGHLIGHTS

- Effect of calcined Czech claystone on the properties of HPC is analyzed.
- A fast course of pozzolanic reaction is observed.
- Synergetic effects of calcined Czech claystone and silica fume are identified.
- HPC mix with 30% of calcined Czech claystone is found the most successful solution.

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ABSTRACT

Most supplementary cementitious materials (SCM) have been only rarely used in high performance concrete (HPC) design to date, silica fume being one of the very few exceptions in that respect. The content of many SCMs in blended cements was also often low because at higher dosage they were not capable to replace Portland cement effectively. Their environmental and economical advantages could thus be utilized in a limited extent only. In this paper, the effect of calcined Czech claystone (CCC) on the properties of HPC based on a binary binder containing Portland cement and silica fume was analyzed over a 10–60% range of Portland cement replacement in the mix. The material characterization experiments carried out using mercury intrusion porosimetry and scanning electron microscopy showed that an up to 30% presence of CCC in the blend resulted in a formation of closer packed HPC microstructures than if only silica fume was used as SCM. The highest compressive and bending strengths were achieved for the 30% Portland cement replacement level over the whole one year testing period. The best durability properties expressed in terms of water and water vapor transport parameters were observed for the same mix with 30% of CCC used instead of Portland cement.

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1. Introduction

The possibility of using pozzolans as supplementary cementitious materials (SCM) has been known already in the beginning of the last century [1,2] but their application in the building practice was rather limited. The environmental and economic considerations of the past several decades affecting most industrial processes, not excepting the building sector, changed the attitude of cement and concrete producers to SCM completely. Nowadays, their role in blended cements is generally accepted and their application in the building industry is growing continuously.

Industrial byproducts present currently the highest volume of SCMs which are used as partial replacement of Portland cement. The applications of silica fume [3], fly ash [4], ground granulated blast furnace slag [5], or waste glass [6] became common in the concrete industry. In the countries producing large amounts of agricultural waste, the pozzolanic properties of bagasse ash [7], rice husk ash [8], or sugar cane straw ash [9] are utilized in the same way. Natural materials exhibiting pozzolanic activity, such as zeolite [10], volcanic dust [11], or diatomite [12], and artificial pozzolans produced by calcination of various clay types [13–15] can also be used for the preparation of blended cements.

In the Czech Republic the prospective sources for an increased use of SCMs in concrete are limited. Ground granulated blast furnace slag is nearly unavailable on the market since 2008 because cement producers make use of all its production countrywide. The high-quality

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fly ashes with suitable composition may soon meet a similar fate. Agricultural waste is produced in small amounts so that its potential for the use in cement industry is low. The Czech territory also always lacked natural pozzolans in significant quantities. Therefore, the artificial pozzolans can be considered a logical solution for increasing the production of blended cements in the country.

Metakaolin as a characteristic representative of artificial pozzolans has been produced in the Czech Republic for a long time. The country has considerable resources of kaolinitic clays which were in the past centuries widely used in the ceramic industry. Nevertheless, the utilization of metakaolin in the building sector is still far behind ground granulated blast furnace slag, fly ash, and even silica fume although it has been shown that it is well applicable also for the production of high performance concrete (HPC) [16]. The main reason may be the high price of metakaolin (three to four times higher than cement) which is supposedly due to its lower production amounts but perhaps also the specific market strategies of its producers.

Calcined clays from the illite group were in the Czech Republic widely used for the production of red ceramics for centuries. The residues produced by the ceramic industry present thus a potential source of active pozzolans for the cement industry; after milling to the corresponding granulometry they can be used as partial replacement of Portland cement. The results of preliminary analyses showed that for lower dosage (up to 10% of the binder) the ceramic powder from the Czech brick factories can be used as an equivalent alternative to metakaolin [17]. However, the practical applications are still rare. Ceramic powder is not yet widely available either as a part of blended cement or a ready-to-use product which is presumably the main reason; another one may lie in the conservative strategies of cement producers.

One of the ways how to change the current attitude of cement and concrete manufacturers in the country to the use of artificial pozzolans in blended cements is to provide them with additional options which can affect the market conditions. Sedimentary rocks containing clay minerals which are widely available in the Czech Republic may present a good opportunity for supplying new pozzolans. Although calcination of this kind of rock seems to be a prospective way for producing artificial pozzolans suitable for an application in blended cements, they were investigated rarely in the past; the studies on calcined shales reported by Taylor-Lange et al. [18] and Meddah [11] belonged to the very few exceptions in that respect.

In this paper, we present an application of calcined Czech claystone (CCC) as supplementary cementitious material (SCM). The claystone is currently extracted from several mines in Bohemia, and in the natural form it is used in the production of refractory ceramics. After calcination at temperatures similar to the kaolinite dehydroxylation temperature it exhibits pozzolanic properties; thus it has a potential for the use in blended cements. The motivation of the presented research is, however, not only to demonstrate that CCC is an active pozzolan but also show that it is applicable for the preparation of HPC with the compressive strength of ~120 MPa in higher volumes. Therefore, several concrete mixes containing different amounts of CCC are designed, aimed at the achievement of high strength and durability. The hardened concrete mixes are subjected to a set of experiments, covering the basic physical properties, mechanical properties, and durability indicators. The obtained results are linked to the microstructural analyses and phase composition and the differences between the designed mixes and two reference concretes are discussed.

2. Materials and mix composition

Claystone is hardened clay composed primarily of clay-sized particles less than 0.002 mm in diameter, which is not laminated or easily split into thin layers. Similarly to kaolin, also claystone

can be calcined to obtain a pozzolan active material. The raw Czech claystone used in this paper originated from a mine in Central Bohemia. Its thermal analysis, which was carried out using differential scanning calorimetry (DSC) and thermogravimetry (TG), is presented in Fig. 1. The first endothermic peak is the loss of physically bound water, the second endothermic peak reflects the dehydroxylation of kaolinite, the last exothermic peak can be attributed to spinel formation. Apparently, the appropriate calcination temperatures are within the range of 700–900 °C. For the preparation of HPC mixes, an industrial form of CCC produced by České lupkové závody Nové Strašecí, a.s., was utilized. In the manufacturing process, raw claystone was subjected to thermal treatment at 700 °C in an industrial furnace and then milled to a granulometry close to Portland cement. The pozzolanic activity of CCC according to the modified Chapelle test [19] was 911 mg(Ca(OH)₂) g⁻¹.

The HPC mix design was based on a combination of Portland cement and silica fume as main binders. Portland cement CEM I 52.5.R originated from the Lafarge, a. s., Čížkovice plant and its specific surface area (Blaine) was 393 m²kg⁻¹. The commercially produced silica fume Stachesil S (Stachema CZ s. r. o.) had the pozzolanic activity of 1615 mg(Ca(OH)₂) g⁻¹ according to the modified Chapelle test [19]. Two HPC mixes were used as reference materials. The first one denoted as BPR (Table 1) contained only Portland cement as one-component binder. The second reference concrete, BP0, was based on a binary binder composed of Portland cement and silica fume (Table 1). The silica fume (SF) dosage in BP0 was chosen according to the experience gained by other investigators before [20,21]; it replaced 18.5% of Portland cement in BPR. The amount of CCC in the ternary binders was within the range of 10–60% of mass of Portland cement in the BP0 mix; the corresponding mixes were denoted as BP10, BP20, BP30, BP40, BP50, and BP60, respectively (Table 1). The ratio water/(OPC + CCC + SF) was kept constant in all mixtures (0.213). Four different gradings of silica sand (Sklopísek Střeleč, a. s.) were combined to obtain a continuous grain-size distribution curve of coarser aggregates (Fig. 2). Silica flour (ST2, Sklopísek Střeleč a.s.) with the grain size in the range of 10–100 μm (Fig. 3) was used for refining the aggregate granulometry. Polycarboxylate-ether based superplasticizer Sika ViscoCrete 1035CZ was utilized for improving the workability of HPC mixes. The specimens were cured in water for 28-day testing and then stored in laboratory conditions.

The binders and fine filler components were characterized also by the determination of particle size distribution (PSD, a laser diffraction analyzer Analysette 22 MicroTec plus, Fritsch), chemical composition (X-ray fluorescence spectroscopy (XRF), a Thermo ARL 9400 XP device), and mineralogical composition (X-ray diffraction analysis (XRD), a PANalytical X'Pert PRO system), in addition to the basic information given above. The PSD of CCC was suitable for its

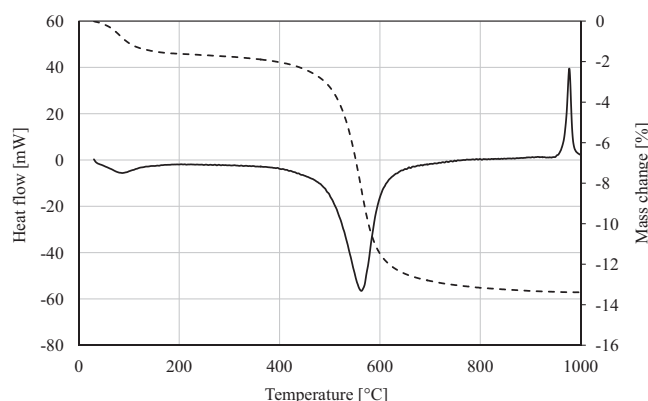


Fig. 1. DSC and TG of Czech claystone.

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