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Abstract. In the construction industry, aggregates, in the form of fine powder up to gravel, play a significant role as a stabilizing and filling materials for many applications. With increasing demands on quarrying of this valuable commodity, its natural resources have become to be depleted. This work outlines the potential application of waste carbon-based mineral admixture as a partial replacement of natural silica aggregate in the production of cement-based composites. In addition, the influence of used waste material on hydration products formation in cement pastes was investigated. On hardened concretes stored 28 days under water, material properties were characterized by measuring flexural and compressive strengths. Cement pastes were subjected to X-ray diffraction analysis and scanning electron microscopy observations. Obtained results revealed specific behaviour of an incorporated material allowing its addition in a limited amount. Increased content of ettringite was detected in composites with the highest amount of added carbon-based mineral.

1. Introduction

The high and fast development of, e.g. construction industry and infrastructure, would not be possible without the usage of fundamental versatile material - concrete. It is material with irreplaceable properties like formability, high compressive strength and resistance to weathering. In general, concrete is composed of cement, mineral aggregate and water. Portland cement is the most manufactured material world-wide with annual estimated production over 4.6 billion tons [1] which has a significant impact on the environment. One ton of produced cement releases up to 0.9 tons of CO_2 and thus the cement production contributes to 8 % of total CO_2 emissions [2]. Many studies, such as Liu et al. [3] and Záleská et al. [4] are preferably focused on the application of alternative materials in blended binders; therefore, the mitigation of carbon footprint is induced.

The most abundant component in concrete mixes is aggregate. A mix of sand, coarse aggregate and gravel occupies approximately ¾ of concrete's volume. In this sense, the aggregate blend is an important part of a hard skeleton and its material properties have a direct impact on the quality of fresh as well as hardened composites [5]. Mineral aggregates are sorted among low-energy intensive construction components, however, their world-wide production achieves up to 5 billion tons per year [6]. Based on the aforementioned facts, there is a justified need to search for alternative sources of raw materials that could at least partially substitute the declining amount of natural resources.

The utilization of carbon mineral admixture as a nature silica aggregate substation in concrete mixes was investigated in this paper. The raw materials and produced composites were characterized by a number of techniques. An additional effect of incorporated material on hydration product development was studied as well. The experimental analysis showed a possible application of carbon-based material for the substitution of natural aggregate in limited quantities.

2. Experimental

Portland cement 42.5 R (PC) provided by Cemex, Ltd., Czech Republic, was used. Given binder disposes the specific surface area of 344 $m^2 \cdot kg^{-1}$ on average and met the specifications according to the EN 197-1 [7]. Oxide composition and some material characteristics of used cement, provided by its producer, are summarized in Table 1. In produced concrete mixtures, the fine aggregate was partially replaced by coal dust (CD) having particle size distribution in the corresponding range to that of given aggregate. This waste material, originated as a rest of coal storage, was delivered from Uhlotherm, Ltd., Czech Republic. Its average powder density was 482 $kg \cdot m^{-3}$ and specific gravity 1 285 $kg \cdot m^{-3}$. Compared to silica sand with powder density of 1 619 $kg \cdot m^3$, applied coal dust was approx. 3.4-fold lighter.

Particle size distribution (PSD) of all input raw materials was measured with the usage of sieving analysis according to the standard EN 933-1 [8]. Before analysis, material samples were dried in a hot air dryer at 105 ± 5 °C until the constant mass was reached. After subsequent cooling, representative aggregate samples were sieved through the set of sieves having a mesh size of 2.0; 1.0; 0.5; 0.25; 0.125 and 0.063 mm and shaken by vibratory apparatus Retsch AS 200 (Germany). In the case of fine Portland cement, a set of sieves including sizes 0.125; 0.90; 0.063; 0.050; 0.038 and 0.020 mm respectively was employed. In order to determine the specific gravity of aggregates, the pycmometric method specified in EN 1097-7 [9] was used. Powder densities of sand and coal dust were measured accordingly to the standard EN 1097-3 [10].

Table 1. Oxide composition and material characteristics of used Portland cement

Oxide composition (mass %)	
SiO_2	18.21
Al_2O_3	5.18
Fe_2O_3	2.98
CaO	62.89
MgO	2.40
K_2O	0.70
Na_2O	0.40
SO_3	3.27
Cl^-	0.08
Powder density ($kg \cdot m^{-3}$)	960
Specific surface ($m^{-2} \cdot kg$)	344
Loss on ignition (wt.%)	4.89

Table 2. Particle size distribution (PSD) of raw materials

Powder	d_{10}	d_{50}	d_{90}
		(μm)	
PC	6.0	22.8	36.4
CD (125 μm)	9.4	34.8	65.5
Aggregate	d_{10}	d_{50}	d_{90}
		(mm)	
Sand (0/2 mm)	0.14	0.75	1.70
CD (0/2 mm)	0.17	0.68	1.83

Silica sand (Filtrační písky Ltd., Czech Republic) in the fraction 0/2 mm confirming requirements listed in the EN 196-1 [11] was partially replaced by raw coal dust in the portion of 5 – 20% by aggregate volume. Four mixes with blended aggregate were manufactured and compared with reference cement composites with only natural silica sand-based batch. The water/binder ratio varied in order to keep constant value of spreading 160 × 160 ± 10 mm for all mixes was achieved. The mix proportion of concretes is presented in Table 2. The effect of coal dust addition on the mineralogy of hydration products formed in cement pastes with water/binder ratio 0.3 was examined only in samples with cement substitution 5 and 20 vol% by coal dust. It is essential to note, that coal dust with particles below 0.125 mm was incorporated into cement pastes.

Table 3. Mix proportions of prepared concretes

Material	Content ($kg \cdot m^{-3}$)			
	PC	CD	Sand	Water
REF	492.5	-	1 477.5	246.3
CD 5	492.5	22.0	1 403.6	256.1
CD 10	492.5	44.0	1 329.3	265.9
CD 15	492.5	66.0	1 255.9	275.8
CD 20	492.5	88.0	1 182.0	285.4

Cement pastes, as well as concretes, were mixed in laboratory mixer E095 (Matest S.p.A., Italy). In the first step, Portland cement or the blend of Portland cement and aggregate was added and homogenized for 1 minute at 1st speed regime (62 rpm). Then the batch water was poured into mixing vessel and the process continued another 1 minute. In the next step, the device was switched to the 2nd speed (125 rpm) regime for 30 seconds. After running out the time, mixing was interrupted for 90 seconds when the lees from the bottom of the mixing vessel were removed. The procedure was finished at 1st speed regime for 1 minute. The fresh mixture was cast into iron prism shaped moulds with dimensions of 40 × 40 × 160 mm, compacted by 60 hits, covered by polyethylene foil and left in laboratory conditions at 20 ± 1 °C for 24 hours. Subsequently, partially hardened specimens were cured under the water at conditions mentioned above for the other 27 days.

The consistency of fresh mixes was controlled with shook table (Matest, S.p.A., Italy) according to the EN 1015-3 [12]. Hardened concrete samples were subjected to bulk density and strength measurements whereas on cement pastes mineralogy of formed hydration products and their structural arrangement were studied. Bulk density values were determined according to the standard EN 1015-10 [13] with the relative expanded uncertainty of 3 %. Flexural and compressive strength tests were performed with the usage of hydraulic press Servo Plus Evolution (Matest, S.p.A., Italy) with a disposing loading capacity of 300/15 kN. At first, prismatic samples with dimensions of 40 × 40 × 160 mm in a three-point bending setting were tested. Maximum compressive forces were recorded on the broken halves of prisms. Mineralogical composition of hydrated cement pastes was analysed with X-ray powder diffraction (XRPD) employing a diffractometer D8 Advance (Bruker, Germany) with Bragg-Brantano geometry and equipped with LynxEye detector using CuK_{α} radiation and Ni filter. Data were recorded in the angular range from 15 to 90° (2θ) with a step of 0.01° and counting time 0.4 s. Rietveld refinement method was used for quantitative phase analysis in Topas 4.2 software (Bruker). Selected samples were observed under the scanning electron microscope (SEM) Quanta 450 FEG (FEI). The acceleration voltage was set to be 20 kV and prior to the analysis, samples were gold coated with a layer of 5 nm thickness.

3. Results and discussion

SEM image of coal dust, its particles with a size lower than 0.125 mm, is depicted in Figure 1.

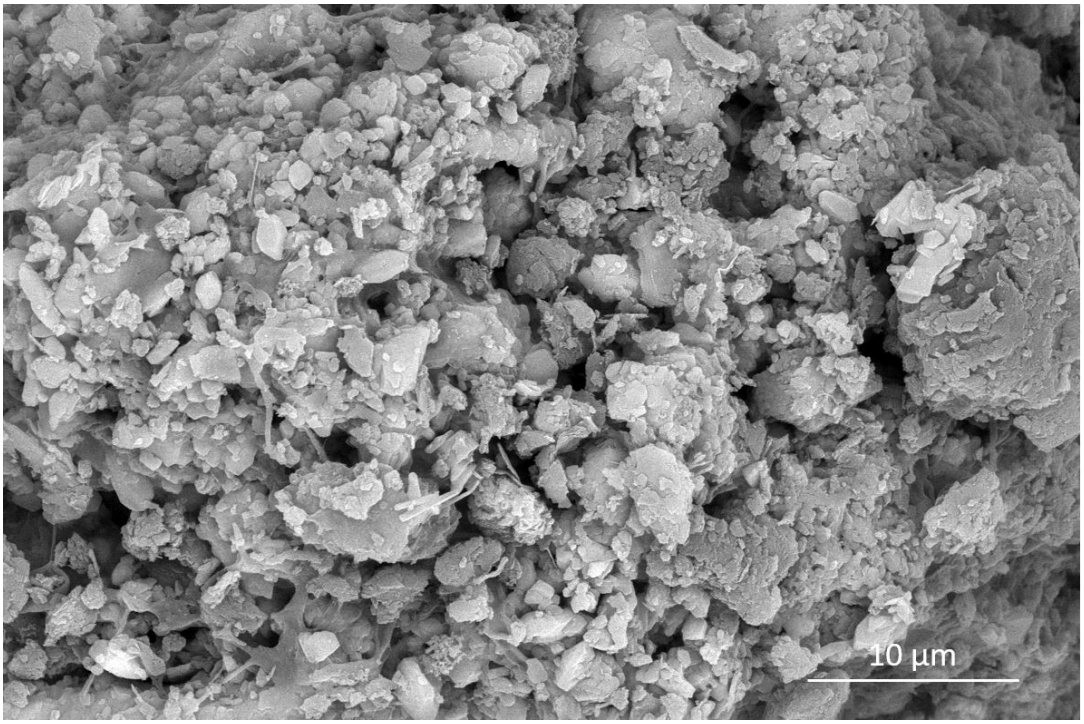

Figure 1. SEM image of raw coal dust

The selected image gives evidence about the morphology, distribution and overall mutual grains position. Very fine particles of coal dust with diameter approx. 1 – 6 µm adsorb on the surface of larger conglomerates with size up to 15 µm are clearly visible. The adsorption of fine particles is supported by the presence of rugged surface of bigger conglomerates and thus such surfaces can easily catch fine powders. The coal grains' shape is rather irregular in comparison to the often used coal fly ash that exhibits spherical particles as reported, e.g. in the work of Mirza et al. [14]. These findings explain the increasing water demands in mixes with increasing amounts of raw coal dust material.

The material and strength properties of produced concretes are listed in Table 4. Obtained data shows the reduction in bulk density of hardened materials with blended aggregate in comparison to reference samples. Accordingly, the most noticeable bulk density, drop about 10 %, was detected for concrete CD 20. The substitution of silica sand by artificial aggregate led to a decrease in strengths. The compressive strengths were decreased, with regard to REF, for 8.2; 15.6; 23.7 and 30.2 % for composites with the 5, 10, 15 and 20 vol. % replacement of natural silica sand, respectively. The values of detected flexural strengths showed the same trend as in the case of data obtained from the compressive strengths measurements. A decrease in strength may be, on the one hand, assigned to increase demands of batch water in fresh concrete mixtures influencing total open porosity of hardened concretes and, on the other hand, to the quality of transition zone between aggregate and cement binding paste. Such behaviour may lead to the formation of a matrix with higher porosity in samples with partial replacement of natural silica grains with rugged coal dust grains.

Table 4. Material and strength properties of concretes cured under water for 27 days

Composite	Bulk density ($kg \cdot m^{-3}$)	Flexural strength (MPa)	St. deviation (MPa)	Compressive strength (MPa)	St. deviation (MPa)
REF	2 036	8.7	0.60	48.6	1.8
CD 5	1 984	7.7	0.25	44.6	1.1
CD 10	1 935	7.0	0.20	41.0	0.3
CD 15	1 882	6.2	0.23	37.1	1.0
CD 20	1 833	5.5	0.25	33.9	0.6

The mineralogical composition of cement pastes with adjusted coal dust and control material is summarized in Table 5. XRPD analysis revealed the presence of vaterite, calcite, ettringate, portlandite and clinker minerals, such as alite, belite and brownmillerite. Another mineral phase, quartz, was detected in the negligible amount. In addition, their content changes in all examined pastes only sporadically. Portland cement substitution with coal dust brought the decrease of clinker minerals content as well as the lower formation rate of portlandite and calcite. These observations are attributed to the nonreactive character of a coal dust in which the predominant carbon content, ranging from 40 up to 78 % in dependence on the coal type [15], is expected. Nevertheless, increased formation of ettingite was revealed for the sample with 20 vol% of replacing the material. The difference of ettringite amount in the comparison with reference paste (RP) may be connected to the sulphur content in coal. From the overall point of view, coals commonly have 2 – 8 % content of sulphur that is present mainly in the form of organic sulphur (up to 90 %) and the rest is ascribed to inorganic sulphur from different sulphates or pyritic minerals [16]. The high variability of sulphur content is due to dramatic differences in the geological profiles and conditions of given areas [15].

Table 5. Mineralogical composition of coal dust enriched cement pastes

Mineral substance (wt. %)	RP	CDP 5	CDP 20
Quartz	0.4	0.1	0.2
Vaterite	4.4	3.0	3.8
Brownmillerite	3.1	1.5	1.7
Calcite	11.8	7.1	8.3
Alite	8.8	5.2	4.0
Belite	4.7	4.6	3.1
Portlandite	8.9	5.9	4.3
Ettringite	3.6	3.6	6.2
Amourphous content	53.9	68.6	68.7

SEM images of hydration products of reference paste and paste with 20 % of coal dust after 28 days of water curing are showed in Figure 2. The structure of hydrated cement paste (RP) is consisted of hydrated calciumsilicate and calciumaluminate phases and calcium hydroxide crystals. Further, small crystals of vaterite in the left image were observed. In contrast, the sample enriched with coal dust comprised, except the aforementioned gel phases, higher occurrence of ettringite with its characteristic needle shaped crystals structures. Comparing both micrograph images, it is clearly visible RP cement paste has a more compact porous structure to that observed for the CDP 20. Lower Portland cement content, worse redistribution of batch water and carbon-based coal particles resulted in gaps and spaces in the inner structure of modified pastes.

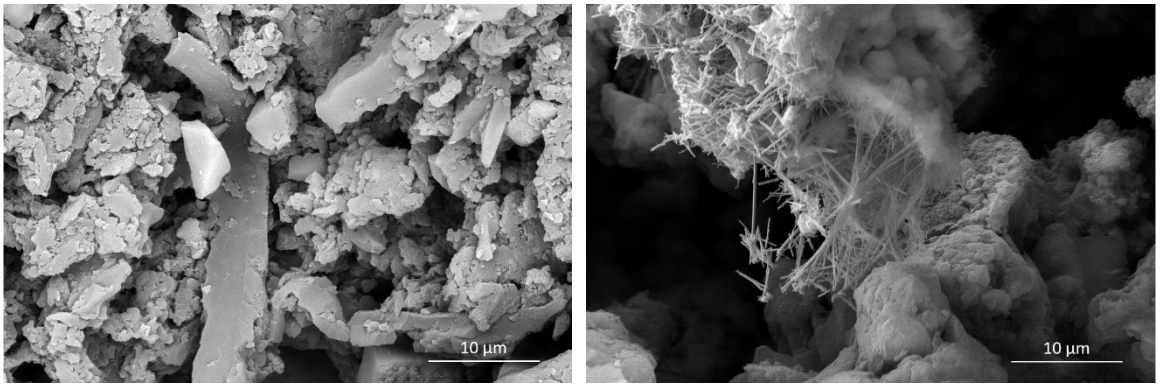

Figure 2. SEM image of reference paste (RP) after 28 days (left) and paste containing 20 vol.% of coal dust (CDP 20) (right)

4. Conclusion

Partial silica fine aggregate substitution with a coal dust on mechanic-physical properties of developed concretes was studied in the first part of this paper. The experimental investigation was further extended to the structural and mineralogical specification of neat and blended cement pastes. Although the used coal dust disposed of similar PSD as silica aggregate, the rugged surface of grains caused higher water demands of mixtures with blended aggregate content. Accordingly, the strength properties of hardened composites were reduced in regard to the reference material. Compressive strength losses were found not to be so significant (about maximum 16 %) for hardened samples with coal dust content up to 10 %. Lower unit weight of waste dust helped effectively to decrease bulk densities of produced concretes. Mineralogical analysis and SEM micrographs revealed a higher range of ettringite formation in cement pastes with 20 % of coal dust and the development of the less compact and more porous structure. In summary, the coal dust application in cement-based composites as an alternative aggregate is possible in a small amount due to a specific structure of carbon grains.

Acknowledgments

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