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SUSTAINABLE CONCRETES CONTAINING SUPPLEMENTARY CEMENTITIOUS MATERIALS

This paper is devoted to the most important developments in the field of sustainable concrete production and evaluates various approaches. In the global context of cost reduction and CO_2 constraints, producers are striving to lower the cement content in concrete. Limits are set by regional and global availability of appropriate materials. The use of supplementary cementitious materials (SCMs), where no additional clinkering process is involved, leads to a significant reduction in CO_2 emissions per ton of cementitious materials (grinding, mixing and transport of concrete use less energy compared to the clinkering process) and also provides the utilization of by-products from industrial manufacturing processes. Such new materials might be able to play a significant role as main cement constituents in the future.

Keywords: **sustainable concrete production, supplementary cementitious materials**

INTRODUCTION

Concrete is a traditional construction material, which can solve a complex of the most difficult problems. The trend analysis of world concrete production shows that production and consumption of this universal composite material increases with each year, which is caused by social, economical and demographic factors. The average consumption of Portland cement in quantities of 300 kg/year per capita (1 m^3 of concrete) determines the minimum rate of civilization comfort (in European countries this rate is equal to 500 kg/year per capita). Increaseing in the world production of cement and concrete (more than 2 billion tons of cement and 6 billion m^3 of concrete correspondingly) accompanied by the consumption of natural raw materials (approximately 20 billion tons of aggregates, 800 billion m^3 of water) and energy (500 billion MJ), indicates the urgent need for a more rational use of material and energy resources. Taking into account both the energy consumed to produce concrete and its natural characteristics, it can be considered to be one of the most “sustainable” construction materials. The use of concrete in construction is very important when humanity strives to reduce the emissions of CO_2 causing to some extent the greenhouse effect. However, this emission can be lower, if the cement content in concrete is substituted with recycled materials or waste from other economic sectors, e.g. supplementary cementitious materials (SCMs) such as granulated blast furnace slag from the steel industry or fly ash from power plants [1, 2]. For each ton of supplementary cementitious materials used in place of Portland cement, approximately one ton of greenhouse gas emissions is avoided.

The production of concrete that consists of 10÷15% cement results in emissions of about 0.13 ton of CO_2 per ton of concrete, equal to 1/8 the emissions of cement [3]. Total energy consumption in the process of obtaining clinker is 6500 MJ/t, the grinding process also takes approximately 360 MJ/t and the total energy on the ton of cement is equal to 6860 MJ/t [4]. The substitution of 20% cement with fly ash leads to great ecological effect, as the CO_2 emissions are lowered to 17% (Fig. 1). This effect can be increased, while using highly efficient grinding systems [5]. Concrete manufacturing results in less CO_2 per unit than almost all other construction materials, making it the sustainable construction material of choice.

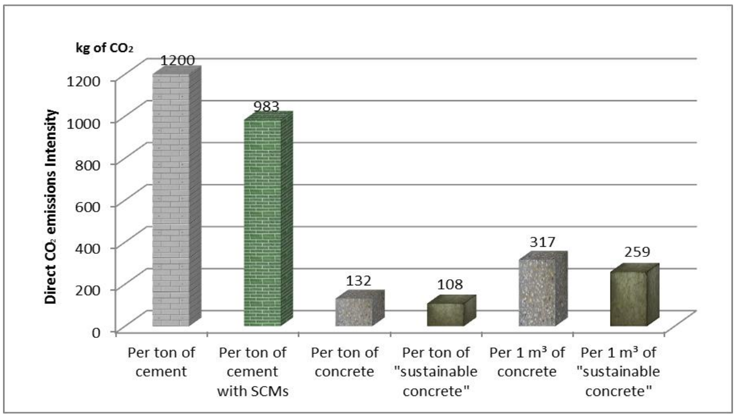

Fig. 1. Typical direct CO_2 intensity - cement and concrete

This practice also has the added environmental advantages of avoiding air pollutant emissions, reducing energy consumption, making use of materials destined otherwise for landfill, and increasing production capacity without installing new cement kilns. The reactivity of SCMs as well as the improvement of blended cements were studied by different authors [2-6]. One commonly used way is to optimise the grading of the SCMs in order to minimise the void content between the particles of cementitious systems and by that to lower the required cement content. SCMs can enhance long-term concrete properties as well.

1. MATERIALS AND METHODS

Ordinary Portland cement CEM I-42.5 was used in the investigations. Polycarboxylate type superplasticizer was included in cementitious systems as a modifier. Fly ash, blast granulated furnace slag (BGFS) were used as supplementary cemen-titious materials and finely ground sand and limestone were used as microfiller.

Physico-mechanical tests of cements and concretes were carried out according to usual procedures. The evaluation of the properties of plasticized cementitious systems was carried out through flowing and compressive strength tests. The physico--chemical analysis (methods of X-ray diffractometry, electron microscopy, differential calorimetry) was used for investigation of cementitious systems hydration processes. The particle size distribution of finely ground SCMs was determined with a laser granulometer Mastersizer 2000.

2. RESULTS AND DISCUSSION

The samples of SCMs were ground in electromagnetic mill to obtain the samples of high specific surface area. The particle size distributions of CEM I 42.5, finely ground sand, fly ash and finely ground fly ash are shown in Figure 2.

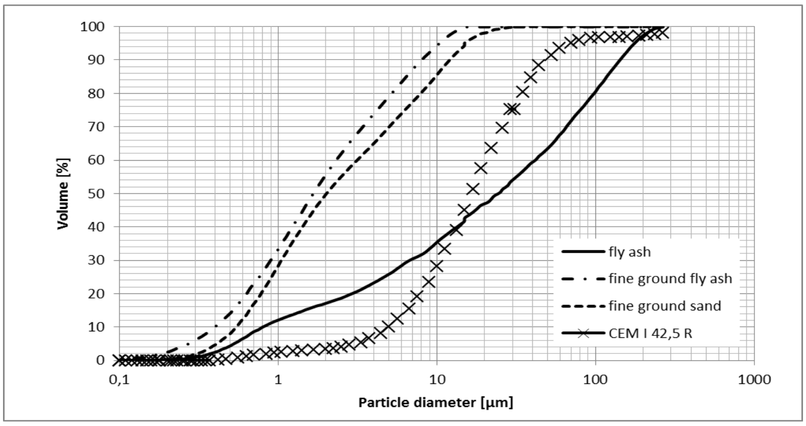

Fig. 2. Particle size distribution of cement and SCMs

The content 10.0; 50.0 and 90.0 vol. % of CEM I-42.5 particles is equal to 5.75; 19.42 and 56.29 µm correspondingly. The D_{10}, D_{50}, D_{90} of SCMs are given in Table 1. The specific surface area (BET) of fly ash, finely ground fly ash and finely ground sand is 1.147; 3.949 and 4.271 m^2/g.

Table 1. **The characteristics of particle size distribution of SCMs and Portland cement**

Material	D_{10}, µm	D_{50}, µm	D_{90}, µm
CEM I-42.5	5.75	19.42	56.29

Fly ash	0.78	24.0	138.92
Finely ground fly ash	0.39	1.62	7.78
Finely ground sand	0.53	1.96	11.69

The quartz sand after activation in electromagnetic mill is characterized by the presence of pores with size 10÷850 nm. The most significant in the total pore volume is the content of pores with diameter of 550 nm. The specific surface area of pores is 6.062 m^2/g and the total volume of pores is 0.3850 mL/g. Figure 4 shows the incremental volume percent of finely ground sand particles.

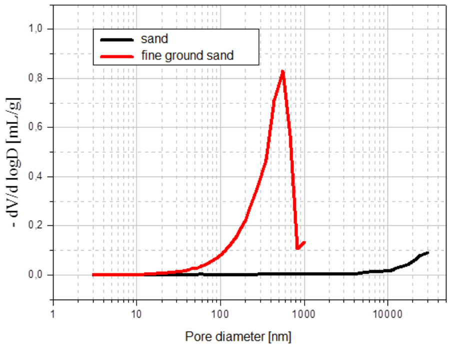

Fig. 3. Cumulative pore volume of sand and finely ground sand

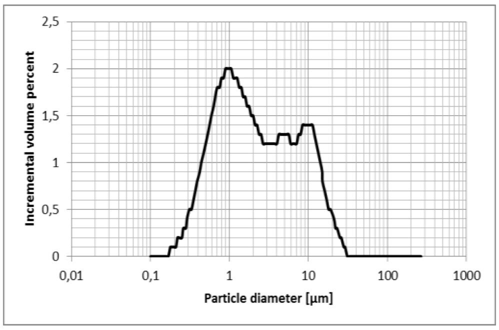

Fig. 4. The incremental volume percent of finely ground sand particles

The degree of additional interfacial active surface of SCMs could be obtained by determination of the ratio of specific surface particles to their volume (surface activity coefficient) [7]. For the spherical particles the surface activity coefficient increases from 6 to 30 μm^{-1} with a decrease in particle diameter from 1 to 0.2 µm. It should be mentioned that while the particle diameter decreases from 10 to 1 µm the surface activity coefficient increases from 0,6 to 6 μm^{-1}. That indicates the increase in the surface activity of finely ground particles.

The coefficient of incremental surface activity K_{isa}, which shows the influence of particle content in total volume was obtained by the product of surface activity coefficient and incremental volume of each fraction (Fig. 5). It is shown that K_{isa} of particles 0.2÷0.5 µm in finely ground fly ash is 2 times higher than in raw fly ash (Fig. 5b).

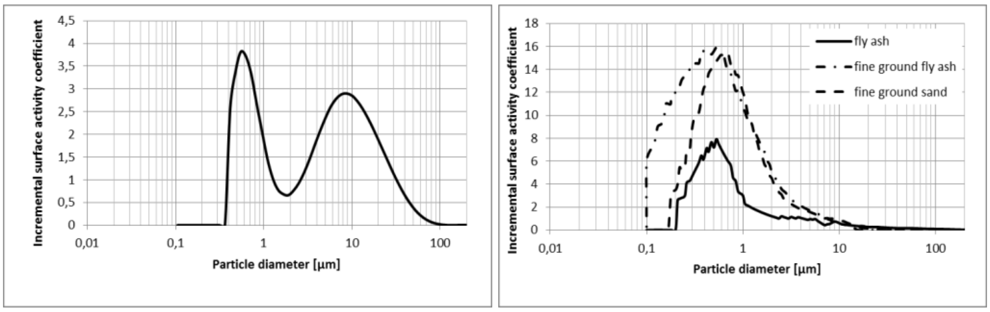

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Fig. 5. Coefficient of incremental surface activity K_{isa} of cement (a) and SCMs (b)

Nowadays, major findings show that dissolution of crystals preferentially occurs at specific surface sites that are characterized as having "excess surface energy". This suggests that dissolution is directly controlled by surface reactions at reactive sites that include defects, dislocations, twinning and grain boundaries [5]. While grinding particles to nanostructure scale, the superficial energy is similar to volume energy, what causes more substantial influence of superficial atoms on the synthesis of the cementitious systems strength [7, 8].

Finely ground SCMs and microfillers accelerate the increase in strength, compact of concrete matrix due to the effect of "fine powders" and play active structure formatting role due to creation of possibility of hydrate phase formation. These hydrate phases, in particular hydrosilicates of type CSH (B), structure active AF_m-phases - calcium hydrocarbonates and AF_t-phases - ettringite, are characterized by binder properties in mineral unclinker part of composition [9, 10].

Mechanical activation of quartz sand can significantly improve its structure-forming properties by increasing the active surface by 2-3 times. The dislocations on the surface of the crystals of quartz sand are the consolidation places for cement hydration products. Fine-grained concrete testing showed that 10 mass.% of finely ground sand and polycarboxylate type admixture provides the increase in flowability of fresh concrete from 115 mm up to 205 mm (technological effect) and early strength concrete on 27% (Table 2).

Table 2. The properties of fine-grained concretes (cement : sand = 1:2)

Binder	W/C	Flowability mm	Compressive strength, MPa at age, days		
			2	7	28
CEM I 42.5	0.40	114	16.1	25.1	38.5
CEM I 42.5 (90%) + finely ground sand (10%)	0.40	115	21.1	30.6	39.5
CEM I 42.5 (90%) + finely ground sand (10%) + PC*	0.40	205	26.8	37.5	40.1

* PC - polycarboxylate type admixture 0.75 mass % of cement

The substitution of 25 mass.% cement by BGFS (S = 540 m^2/kg) causes the increase in compressive strength on 10; 18.7 and 12.1% after 2, 7 and 28 days of hardening respectively compared with concrete containing BGFS (S = 360 m^2/kg) (Fig. 6). The results of testing fine grained concrete with 25 mass. - % finely ground BGFS (S = 540 m^2/kg) and 1.5 mass.% of polycarboxylate admixture provides the increase in flowability (F = 245 mm). It is shown that compressive strength of this concrete is higher than in concrete with 25 mass.% BGFS (S = 360 m^2/kg) and 1.5 mass.% of PC in all terms of hardening.

Differencial calorimetry was used to record the heat development as the cement hydration is an exothermal process. Cement pastes with superplasticizer and activated fly ash were prepared and compared to a reference sample of cement paste (Fig. 7). In comparison to cement solely with PC, cement with PC and activated fly ash is characterized by decrease in size of the first exoeffect by 20.1%. The curves show that the second exoeffect is also decreasing by 19.5%. Finely ground fly ash together with polycarboxylate admixture have a retarding effect on the cement hydration. The induction period is prolonged and the accelerating period appears later.

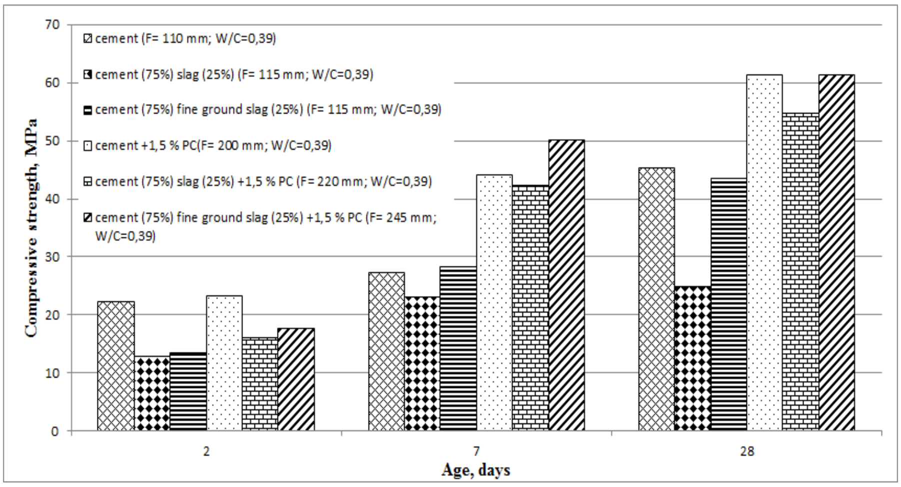


Fig. 6. Compressive strength of fine grained concrete with BGFS

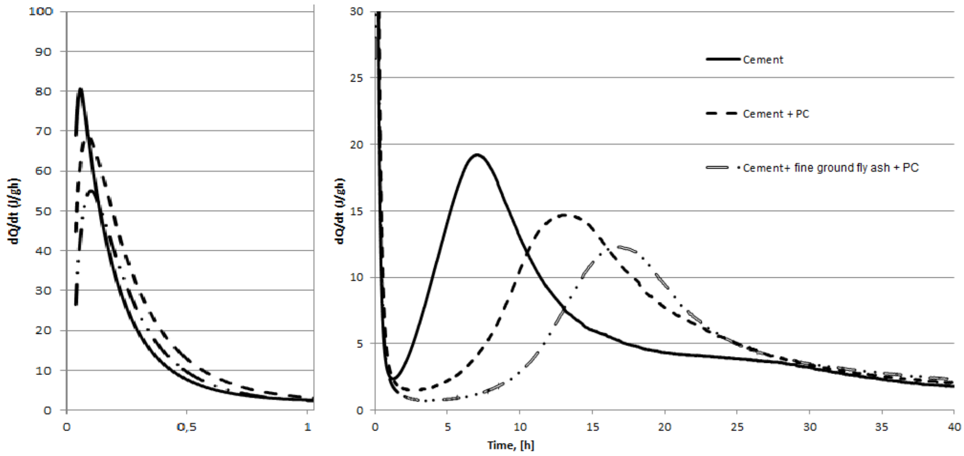
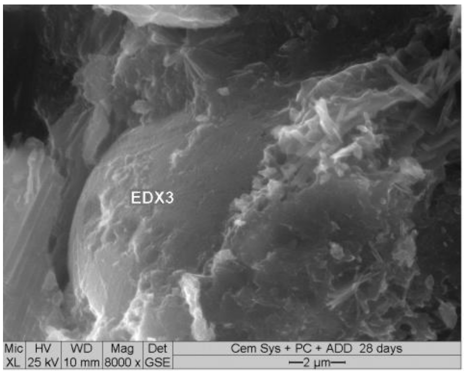


Fig. 7. Heat evolution during the hydration of Portland cement with SCMs

The investigations of phase composition and microstructure analysis of cementitious systems shows that SCMs influence the amount and kind of formed hydrates and thus the volume, the porosity and finally the durability of the materials (Fig. 8).



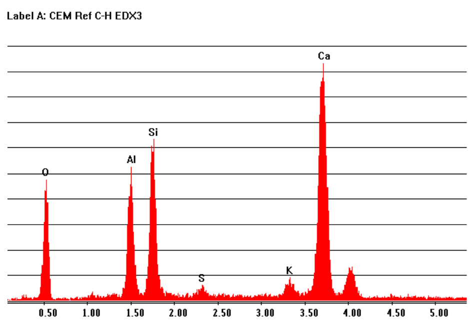


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Fig. 8. Microstructure (a) and EDAX spectrum in spot EDX3 (b) of cementitious system with finely ground fly ash after 28 days of hardening

The samples of fly ash and finely ground fly ash were investigated by the methods of IR-spectroscopy. It is shown in Figure 9 that the main absorption band due to valence vibrations of Si-O-Si bonds is shifted to higher frequency region, i.e. from 1057 to 1065 cm^{-1} and from 452 to 463 cm^{-1}. This indicates the polymerization degree of Si-O-Si bonds. There are observed bands with frequencies 3445 and 1623 cm^{-1} due to valence and deformation vibrations of water. The activation of the fly ash in electromagnetic mill influences its surface activity.

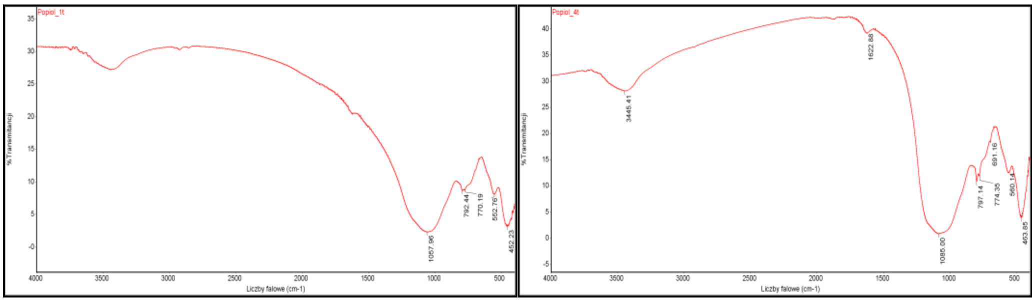

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Fig. 9. Transmission spectrum of fly ash (a) and finely ground fly ash (b)

The main idea of grinding SCMs considered evaluation of the role of finely ground particles in multicomponent cementitious materials, which can fundamentally change the processes of structure formation and synthesis of strength by the interaction between alumosilicate components of SCMs with hydrolysis product of alite phase OPC - calcium hydroxide - with formation of calcium hydrosilicates and hydroaluminates, regulating topochemical ettringite and accelerating of pozzolan reaction in unclinker part of a system for the obtaining new sustainable concretes with specified properties. The manipulation and control of properties of cementitious systems with finely ground SCMs offer the possibility of producing new types of High Performance Eco-Concretes.

CONCLUSIONS

The production and use of sustainable concretes make a substantial contribution to climate protection. With further increase in quantities of supplementary cementitious materials new types of sustainable concretes will also become increasingly important in building construction and civil engineering. The combined use of finely ground supplementary cementitious materials with polycarboxylate superplasticizer allows to increase fresh concrete flowability (technological effect) and compressive strength of concrete while decreasing the W/C ratio (technical effect) and lowering the cement content in concrete (ecological and economical effects). The new challenges in construction materials mean that such sustainable, efficient, highly specialized Eco-Concretes will have even more benefits in the future.

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ZRÓWNOWAŻONE BETONY ZAWIERAJĄCE DODATKOWE SKŁADNIKI WIĄŻĄCE

Artykuł dotyczy oceny produkcji zrównoważonych betonów zawierających dodatkowe składniki wiążące. Obecnie na całym świecie dąży się do zmniejszeniu kosztów i ograniczenia emisji CO_2, dlatego też celem producentów jest obniżenie zawartości cementu w betonach. Działania te wynikają z konieczności dostosowania się do narzuconych limitów emisji CO_2 oraz z faktu kurczenia się zasobów odpowiednich materiałów do produkcji cementu. Zastosowanie dodatkowych składników wiążących, które można pozyskać bez kosztownego procesu wypalania klinkieru, prowadzi do znaczącej redukcji emisji CO_2, przypadającej na tonę wyprodukowanego spoiwa cementowego. Obniża to także koszty związane z mieleniem, oraz umożliwia wykorzystanie ubocznych produktów procesów przemysłowych do wytworzenia materiałów wiążących. Nowe materiały mają szansę stać się głównymi składnikami cementów przyszłości.

Słowa kluczowe: **zrównoważona produkcja betonu, dodatkowe składniki wiążące do betonu**

ZRÓWNOWAŻONE BETONY ZAWIERAJĄCE MATERIAŁY SUPLEMENTUJĄCE CEMENT

Niniejszy artykuł poświęcony jest osiągnięciom w dziedzinie zrównoważonej produkcji betonu. W globalnym kontekście redukcji kosztów i ograniczania emisji CO_2 producenci dążą do obniżenia zawartości cementu w betonie. Zastosowanie materiałów cementopodobnych (SCMs) prowadzi do znacznego zmniejszenia emisji CO_2 oraz zapewnia wykorzystanie produktów ubocznych z procesów przemysłowych.

Słowa kluczowe: **zrównoważona produkcja betonu, materiały suplementujące cement**