The influence of ultrafine supplementary cementitious materials on the properties of Portland cements

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This paper describes the influence of ultrafine supplementary cementitious materials (SCM's) on the properties of Portland Cements. The combined using of ultrafine ground SCM's with polycarboxylate superplasticizer allows to obtain high flowability, physical and mechanical properties of Portland cements. Advanced interpretation of the ultrafine (SCM's) and their surface activity contributes the most complete realization of potential in binding properties of new types of Portland cements and producing High Performance Concretes on their base.

Keywords – ultrafine supplementary cementitious materials, Portland cements, flowability, cement paste, shrinkage.

I. Introduction

Approximately 0,85 t CO₂ are emitted during the production of a tonne cement clinker. Because of high specific CO₂ emissions during the production of clinker the cement industry accounts for around 5% of the global output of CO₂. Reduction of the clinker is now being driven to a great extend by the use of supplementary cementitious materials (SCM) [1]. In most SCM are represented by industry waste products, such as fly ash, slag, silica fume or other natural materials such as quartz sand, limestone and others. In some cases the process of mechanical activation can significantly influence on the properties of ultrafine supplementary cementitious and thus, on the building and technical properties of binders [2]. It is shown while the grinding of particles to nanoscale structure the superficial energy is similar to volume energy and then superficial atoms obtain more substantial influence on the synthesis of the cementitious systems strength. The nanotechnological manipulation and control of properties cementitious systems with fine ground mineral additives give the possibility of producing new kinds of sustainable concretes [3]. Considerable interest for the future investigations study is a byproduct of coal burning - fly ash [4]. The pozzolanic activity of fly ash measures the ability to react with calcium hydroxide and depends on the content of reactive silica or alumina, the grain size and state of the material (glass content, metastability) [5].

One of the most important characteristics of concrete is shrinkage. The main source of moisture-related deformations in concrete is the hydrated cement paste. Therefore, many attempts have been made to obtain expressions relating the drying shrinkage or creep strain to the volume fraction of the hydrated cement paste in concrete (as determined by the cement content and the degree of hydration) [6]. It is useful to consider the role played by the different ingridients (cement, aggregate, water, chemical admixtures, mineral additions, a.o.). Supplementary cementitious materials in form of pozzolanic materials (fly ash, silica fume, ect.) or ground granulated blast furnace slags, increase shrinkage only if used to increase the volume of cement paste. Addition of ground fillers could increase compressive strength, but they do not increase shrinkage since they are not cementitious materials [7].

The main idea of using ultrafine SCMs considered on the evaluating of the role of ultrafine 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 special properties.

II. Materials and methods

Ordinary Portland cement (OPC) CEM I - 42,5 R JSC "Ivano-Frankivskcement" with specific surface of 380 m^2/kg was used in the investigations. The samples of SCMs were ground in laboratory vibration mill to obtain the samples of high specific surface area. Fly ash (FA), ultrafine fly ash (UFA) were used as supplementary cementitious material and ultrafine quarz sand (UFS) was used as filler. Polycarboxylate type superplasticizer (PC) was included in cementitious systems as modifier.

The D_{10} , D_{50} , D_{90} of SCMs are given in Table I. The specific surface area (BET) of fly ash, fine ground fly ash and fine ground sand is 1,147; 3,949 and 4,271 m²/g.

TABLE 1

THE CHARACTERISTICS OF PARTICLE SIZE DISTRIBUTION OF PORTLAND CEMENT AND SCMS

Material	D ₁₀ , μm	D ₅₀ , µm	D ₉₀ , µm
OPC (CEM I-42.5)	5,75	19.42	56.29
FA	0.78	24.0	138.92
UFA	0.39	1.62	7.78
UFS	0.53	1.96	11.69

Physical and mechanical tests of cements were carried out according to usual and special procedures. The evaluation of the properties of cements modified with ultrafine supplementary materials and superplasticizer was carried out through a flowing and compressive strength tests.

III. Results and discussion

The investigations of Portland cement pastes with ultrafine fly ash, quarz sand and polycarboxylate superplasticizers showed that flowability of cement pastes is 2,81 higher compared to the paste without additives with the same water to cement ratio (W/C=0,3). This is caused by increasing of effectiveness of superplasticizer action by ultrafine SCMs (Fig. 1).

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Fig. 1. Flowability of cement pastes

It was observed that Portland cements with ultrafine supplementary cementitious materials such as fly ash and quarz sand together with PC admixture (W/C=0,3) are characterized by higher strength characteristics of paste after 28 days compared to OPC paste (Fig. 2). At the same time, the most significant compressive strength development was achieved by the using of ultrafine quartz sand and PC. It was equal to 67,1; 85,3; 93,8 and 98,4 MPa respectively after 2, 7 28 and 90 days of hardening.



Fig. 2. Compressive strength of cement pastes

The investigations of shrinkage of cement pastes (dry conditions) showed that cement pastes with UFS and PC is charecterised by the highest shrinkage, in the same time shrinkage of OPC is lower at the same water to cement ratio (W/C=0,3). It was observed that shringae of cement paste with UFS, UFA and PC is 1 mm/m after 28 days of hardening.



Fig. 3. Shrinkage of cement pastes with SCMs and PC

The using of ultrafine supplementary materials and polycarboxylate type admixtures provide the increasing of flowability of cement pastes up to 230 mm. It is caused by optimal distribution of particles in system. As the result the superplasticizer is located on the grains oa ultrafine material, what provides participle slipping and increasing the flowability with the same W/C ratio (W/C=0.3). Thus using the combination of mineral additives with different action (pozzolanic and filler) provides the increasing of compressive strength and decreasing of shrinkage of cement pastes.

Conclusion

The production and use of sustainable cements make a substantial contribution to climate protection. The combined use of fine ground supplementary cementitious materials with polycarboxylate superplasticizer allows to increase flowability of cement pastes (technological effect), to increase compressive strength through decreasing the W/C ratio (technical effect) and to lower the cement content in concrete (ecological and economical effects) and also low shrinkage wchich is very important while using such cements in concretes. The new challenges in construction materials mean that such sustainable, efficient cements will have even more benefits in the future.

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