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Review

Effect of the superplasticizer type on the properties of the fly ash blended cement

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HIGHLIGHTS

- Superplasticizer improves consistency of cement paste at lower water/cement ratio.
- The most water reduction is observed for polycarboxylate and polycarboxylate ether.
- Cement prepared using PC and PCE has higher hydration heat and initial setting time.
- Addition of PCE to cement mortar gives cement fly ash Portland cement of class 52.5N.

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ABSTRACT

In the paper the effect of the superplasticizer type on the properties of fly ash blended cement – in terms of hydration heat, setting time and compressive strength – was studied. The used admixtures were sulfonated melamine-formaldehyde condensate (SMF), sulfonated naphthalene-formaldehyde condensate (SNF), polycarboxylate (PC) and polycarboxylate ether (PCE). Control sample was Portland fly ash cement CEM II/A-V 42.5R. Superplasticized Portland fly ash cement mortars were prepared taking the values of standard water of consistency with different addition of each type of superplasticizers used. Results revealed that the decrease in water content required was 15% for SMF, 31% for SNF, 42% for PC and 47% for PCE. Polycarboxylates were found to have to higher efficiency in improving the hydration heat evolution, setting time and mechanical properties of cement than that of traditional superplasticizers SMF and SNF. Addition to control fly ash blended cement polycarboxylate ether-based superplasticizer gives cement CEM II/A-V 52.5N.

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1. Introduction

Fly ash is a waste residue that is released from coal combustion process in electric power stations. ASTM C618 [1] defines two classes of fly ashes for their use in concrete, class F and class C. Class F is a pozzolanic fly ash normally produced from burning anthracite and bituminous coals and will have minimum $SiO_2 + Al_2O_3 + Fe_2O_3$ of 70 wt%. Class C is a pozzolanic and cementitious fly ash derived from burning lignite or subbituminous coal and will have minimum $SiO_2 + Al_2O_3 + Fe_2O_3$ of 50 wt%.

It is generally recognized that the incorporation of fly ashes as the partial replacement for Portland clinker in cement is effective means for improving the properties of cement. Due to its pozzolanic properties ashes react with $Ca(OH)_2$ during hydration reaction and form calcium silicate hydrate. This can reduce the size of pores of crystalline hydration products, make the microstructure of cement paste more compact and consequently improve compressive strength and durability of cement [2–11]. Because pozzolanic reaction is slow in early stage of curing, at the beginning the strength of fly ash cement is lower than that of Portland cement. Over time, after about 90 days and later, the fly ashes start to react with $Ca(OH)_2$ and increase strength of producing additional, densifying C–S–H. Use of fly ashes improves durability of cement through the pore refinement and reduction in content of portlandite in cement. One of the most important aspects of durability of fly ash cement is resistance to sulphate attack. Incorporation to cement fine fractions of ashes, <32 μm or even <16 μm, gives fast rate of cement strength gain at early ages [11–17] and increases durability of cement more than original fly ashes [18,19].

Literature reports that fly ashes improve cement workability and lower water demand. Mostly spherical and smoother surface particles of ashes can readily roll over cement particles, reducing inter-particulate friction and raising paste fluidity [20–22]. Fly ashes of fineness category S according to PN-EN 450-1 [23] improve consistency of mix at lower water-cement ratio [24–27]. Category S fly ashes provides the effective reduction of water demand, by at least 5 wt%. Reduction in water required together with pozzolanic reactivity of ashes leads to better mechanical properties of fly ash cement.

Authors [28–33] study the effect of superplasticizer admixtures on fly ash cement paste rheology. Results show that introduction of fly ashes to cement requires using of water reducers in order to obtain cement paste with constant workability without having to increase in water requirement. Amount of superplasticizer depends highly on replacement proportion of Portland cement with ashes and to much less extent on nature of addition.

In this paper, the influence of superplasticizer type on rheological properties and hydration process of Portland fly ash cement CEM II/A-V 42.5R is investigated. Superplasticizer is used to reduce water in cement mortar while maintaining a constant workability. Water to cement (w/c) ratio is held constant at 0.5 for all mixes. The following parameters are tested: heat hydration, setting time, compressive strength and microstructure. Results show that polycarboxylate-based superplasticizers give the greater water reduction at the same consistency of mortar, which leads to shorten setting time and increase of early and 28 d strength. In the opposite to the previous research, with relative low dosage water reducers PC and PCE allow to obtain Portland fly ash cement CEM II/A-V 42.5R or 52.5N according to PN-EN 197-1 [34].

Table 1
Chemical composition of sample CEM II.

Chemical component	Content (wt%)
Loss on ignition	3.3
SiO_2	26.5
Al_2O_3	5.0
Fe_2O_3	2.5
CaO	56.5
MgO	1.4
Na_2O	0.41
K_2O	1.09
Na_2O_e	1.13
SO_3	3.2
TiO_2	0.1
CaO_{free}	1.6
Blaine's surface (m^2/kg)	460

2. Experimental

2.1. Materials

Portland fly ash cement CEM II/A-V 42.5R (namely as CEM II) is used as control sample. Its chemical composition is shown in Table 1. Its phase composition by XRD-Rietveld is: C_3S-61.3 wt%, C_2S-15.7 wt%, C_3A-8.6 wt% and C_4AF-7.3 wt%.

The used superplasticizers are: sulfonated melamine-formaldehyde condensate (SMF), sulfonated naphthalene-formaldehyde condensate (SNF), polycarboxylate (PC) and polycarboxylate ether (PCE).

Superplasticizers are used to reduce water in cement mortar CEM II-A/V 42.5R while maintaining a constant workability as compared with Portland cement CEM I 42.5R (CEM I). Consistency of mortars CEM I and CEM II is examined using flow test according to PN-EN 1015-3 [35]. Flow diameter of CEM I is 185 mm, whereas that of CEM II – reaches 153 mm. In order to increase flow of CEM II, without increasing of w/c ratio, superplasticizer is added to mix. Dosage of each admixture is given in Table 2.

Results of superplasticizer effectiveness in plasticizing cement paste are presented in Table 3. Effectiveness of each superplasticizer is assessed using the w/c ratio of standard water of cement paste consistency with optimum addition of superplasticizer. Test confirms that polycarboxylate-based superplasticizers are the most effective water reducers. With relative low dosage (1.5–1.8 wt%), these admixtures give the highest water reduction. Decrease in water demand of CEM II-PC and CEM II-PCE is respectively 42% and 47% as compared to CEM II. Due to much smaller numbers of ionic groups (weaker polyelectrolytes) and spatial structure related to presence of side chains, PC and PCE prevent cement grains closer to each other [36–38]. Improvement of mortar fluidity in presence of polycarboxylate admixtures is resulted from the electrostatic repulsion of electric charges, which appear on the surfaces of cement particles due to the superplasticizer adsorption, as well as from the steric hindrance effect following from the presence of long side chains in plasticizer's structure [39,40]. Effectiveness of other superplasticizers is less. Using 2.0 wt% of SMF or SNF to prepare cement paste of normal consistency, the amount of water decreases by 15% for CEM II-SMF and 31% for CEM II-SNF.

2.2. Experimental methods

Cement pastes for microcalorimetric measurements are prepared by mixing water and cement for several minutes. The w/c ratio in all samples is constant, 0.5. Superplasticizers are added to reaction system together with water. Addition of superplasticizer is as follows: SMF-0.57 wt%, SNF-0.33 wt%, PC-0.22 wt% and PCE-0.22 wt%. Hydration of cement pastes takes place in differential microcalorimeter at 25 °C for 72 h.

Measurements of initial setting time is made on cement mortars using Vicat needle apparatus in accordance with PN-EN 480–2 [41]. Mortars are prepared with constant w/c ratio, 0.5. Superplasticizers are added to reaction system with water, and their dosage is the same as in sample for microcalorimetric measurements. After mixing the mortar is placed in Vicat mould and then Vicat needle is brought into contact with top surface of sample and released. Initial setting time is determined when distance of Vicat needle penetrated into sample is less than 5 mm to mould's base.

Compressive strengths are determined on standard mortars (450 g cement, 1350 g standard sand, w/c = 0.5) according to PN-EN 196-1 [42]. Superplasticizers are added together with water, and their content is the same as in microcalorimetric measurements. For each mortar, 3 prism specimens having 40 × 40 × 160 mm dimensions are prepared. Specimens are stored for 24 h in closed box, which is filled with water to obtain high humidity. After 24 h the samples are dismantled from the form and stored under water. At the required age of 2, 7, 28, 90 and 180 days, the specimens are taken from their wet storage, broken in flexure into two halves and then each half is tested for compressive strength.

3. Results and discussion

3.1. Microcalorimetric measurements

Cement hydration is a strongly exothermal reaction, which takes place in a number of stages [43]: (I) rapid initial processes