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VPLYV DRUHU POPOLČEKA A CEMENTU NA REOLÓGIU CEMENTOVEJ KAŠE

EFFECT OF THE FLY ASH AND CEMENT TYPE UPON THE CEMENT PASTE RHEOLOGY

V článku je uvedená analýza vplyvu dvoch druhov popolčeka na reologické vlastnosti cementovo-popolčekových zmesí za použitia cementov s rozličným množstvom C_3A. Bol zistený významný vplyv druhu popolčeka a cementu na reologické vlastnosti cementovo-popolčekových zmesí.

In the paper an analysis of the the influence two types of fly ashes on rheological properties of cement pastes with cements containing different amount of C_3A is presented. It was stated that a type of fly ash and content of C_3A in cement have significant influence upon rhelogical behaviour of cement pastes.

1. Introduction

Fly ashes (pulverised fuel ashes – pfa) are waste materials produced as a result of coal combustion. In this process the pulverised coal is fed to the combustion chamber and burnt at high temperature. The incombustible mineral substances are then subjected to the phase and chemical transformations. Over 80 wt. % of this material is transported with the flue gas and collected in electrical or mechanical precipitators. The residue is deposited as a bottom ash in a furnace.

Fly ashes are composed mainly of glass with some amount of crystalline phases. An unburned coal residue can be also present. The type and properties of fly ash are affected by the following factors [1], [2]:
- type of coal (anthracitic, black, bituminous, subbituminous, brown),
- fineness of coal before combustion,
- type of furnace, temperature and other conditions of the process,
- method of flue gas de-dusting,
- transport and storage of fly ash.

There are many of fly ash classification systems. According to the ASTM C 618 89 [3] the high calcium class C fly ashes and low calcium class F ones can be distinguished. This classification is based on the total $SiO_2 + Al_2O_3 + Fe_2O_3$ as well as CaO content.

It is generally known that the fly ashes from the black coal combustion exhibit low CaO content while those originating from the brown coal are the high calcium materials, with CaO content attaining 40 wt. % [4].

The fly ash particles are composed of glass and crystalline phases. The glass content is usually about 80 % by mass, in some cases attains 90 %. In the high calcium fly ash it is low, about 60 % by mass. In the low calcium fly ash the following crystalline phases can be present: quartz (SiO_2), mullite ($3Al_2O_3 \cdot 2SiO_2$), magnetite Fe_3O_4) and haematite (Fe_2O_3). On the surface of low calcium fly ashes, a film of metallic iron is often observed on the magnetite or haematite crystals.

In the high-calcium fly ash, apart from the phases mentioned above, the following ones can be found: calcium silicates and aluminates ($2CaO \cdot SiO_2$, $CaO \cdot Al_2O_3$, $5CaO \cdot Al_2O_3$), calcium aluminosilicates ($2CaO \cdot Al_2O3 \cdot SiO_2$) and calcium sulphates ($CaSO_4$, $CaSO_4 \cdot 2H_2O$), calcium ferrites ($2CaO \cdot Fe_2O_3$), calcium oxide (CaO and periclase (MgO)).

The hydration of fly ash should be considered separately for the low and high-calcium materials, because of the substantial difference in chemical and mineral composition [5], [6], [7]. Reactions occurring between cement and fly ashes in an early stage of hydration influence the rheological properties of cement pastes. The hydration of cement with fly ashes is a complex process because of the mutual interactions between the hydrating cement and fly ash components. Introduction to cement higher amounts of the fly ashes (also high-calcium fly ashes) require investigation of their impacts on the rheological properties of cement pastes dependent on their type and type of cement [8], [9], [10].

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2. Experimental

2.1. Materials

The portland cements with differed content of C_3A (7,6 and 3,8 % wt.) and similar Blain's specific surface ~ 340 m^2/kg were used. The high-calcium fly ashes from the brown coal combustion and low-calcium fly ashes also with similar Blain's specific surface ~ 320 m^2/kg were taken. The chemical composition of the cements and fly ashes used in experiments is given in Table 1 phase composition of cement is presented in Table 2.

Chemical composition of cements and fly ashes. Table 1

Component composition	Cement I	Cement II	Fly ash I Low-calcium	Fly ash II High-calcium
	Content in % wt.			
Loss on ignition	0.8	0.6	1.0	1.9
SiO_2	22.7	20.1	50.4	30.0
Fe_2O_3	3.0	5.0	8.6	6.0
Al_2O_3	4.6	2.8	26.8	18.0
CaO	66.5	69.2	4.3	30.1
MgO	1.4	1.0	2.6	2.1
SO_3	0.6	0.5	1.2	10.8
Na_2O	0.2	0.1	1.6	0.2
K_2O	0.7	0.2	1.4	0.2
CaO free	0.8	0.5	0.2	3.0

Mineralogical composition of cements. Table 2

Phase composition	Cement I	Cement II
	Content in % wt.	
C_3S	64.7	73.2
C_2S	17.0	12.0
C_3A	7.6	3.8
C_4AF	7.8	11.0

The phase composition of fly ashes was characterized by XRD. The following crystalline phases have been detected: quartz, mulite in fly ash I and in fly ash II together also free CaO, anhydrite, calcium sulphate dihydrate – gypsum, hematite and gehlenite in fly ash II.

The cement - fly ash mixtures used in the rheological investigations were prepared and homogenised in a laboratory mill. The fly ash content in cement was 20%, 40%, 60% and 80% wt.

2.2. Rheological measurements

The rheological measurements were carried out using the rotative viscosimeter type Rheotest RV – 2.1, with the modified surfaces of both cylinders. The rheological properties of pastes with fly ashes were determined from the flow curves, at growing and reduced rates of shearing in the range from 0 to 146 s^{-1}. The yield value and plastic viscosity were determined from the descending part of the flow curve, according to the Bingham's model.

3. Results and discussion

Figures 1 and 2 show examples of the obtained flow curves for cement-fly ashpastes with low content of C_3A in cement, Table 3 presents calculated yield values τ_0 and plastic viscosities η_{pl} cement-fly ash pastes.

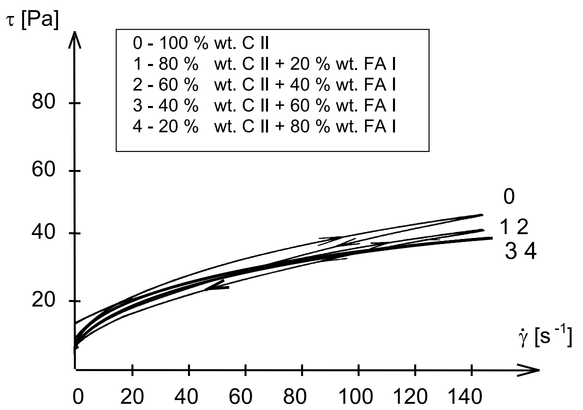

Fig. 1. Flow curves of cement pastes with cement (C II) containing 3.8 % wt. C_3A and addition of low-calcium fly ashes (FA I).

The results obtained shown that the addition of low-calcium fly ashes (FA I) to high content C_3A cement (C I), demonstrated by big yield values and plastic viscosity, resulted in significant

Rheological parameters τ_0 [Pa] and μ_{pl} [Pa · s]. Table 3

No.	Sample composition in % wt.	C I FA I		C II FA I		C I FA II		C II FA II	
		τ_0	η_{pl}	τ_0	η_{pl}	τ_0	η_{pl}	τ_0	η_{pl}
0	100%C+0%FA	69.1	0.83	9.9	0.28	69.1	0.83	9.9	0.28
1	80%C+20%FA	30.0	0.45	8.9	0.28	65.5	0.92	9.9	0.34
2	60%C+40%FA	25.1	0.43	9.7	0.29	68.4	0.99	14.5	0.52
3	40%C+60%FA	16.3	0.39	8.6	0.29	–	–	20.8	0.96
4	20%C+80%FA	13.1	0.33	9.1	0.27	–	–	–	–

improvement of rheological properties of cement pastes. A decrease of yield values and plastic viscosities with increasing fly ash content in cement is illustrated in Tab 3. The biggest improvement occurred (two times slope in plastic viscosity and yield value) with addition of 20 % of fly ashes in cement. A further growth of percentage of fly ashes in cement doesn't result in fluidity of cement pastes.

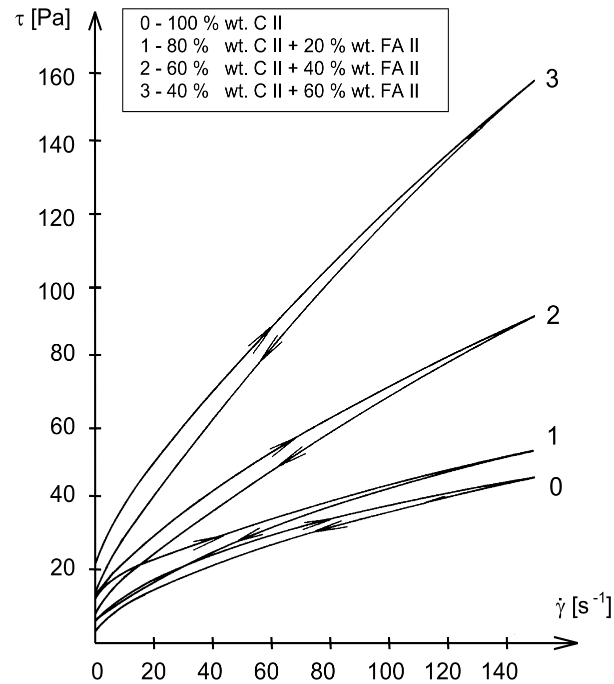

Fig. 2. Flow curves of cement pastes with cement (C II) containing 3.8 % wt. C_3A and addition of high-calcium fly ashes (FA II).

The addition of low-calcium fly ashes (FA I) in the mixtures with low amount of C_3A phase (C II), good fluidizated by calcium sulphur, results in insignificant changes of rheological properties Fig 1. Cement II paste with low amount C_3A phase (3,8 % wt.) is better fluidited than cement I pastes (C I) 7.6 % wt. of C_3A. The yield value of pure cement paste with cement (C II) is a few times lower compared to the pure cement paste with cement (C I), this is also observed for plastic viscosity.

In case of high-calcium fly ashe from lignite coal combustion its unfavourable influence on rheological properties is significantly lower for cement (C II) with lower content of C_3A phase (Fig. 2). It was stated that rheological measurement is impossible to carry out when the addition of fly ashes exceeds 40 % wt. in cement (C II), but for cement (C I) measurements were possible with 60 % wt. fly ashes content in cement.

4. Conclusions

- Generally, content of low-calcium fly ash in cement-fly ash mixture results in an increase of the cement paste fluidity, on the contrary to the high-calcium ash when the addition results in decrease of the fluidity for both type of cement.
- An increase fluidity cement paste effect developed by the addition of low-calcium fly ash depends on C_3A phase content in cement. In case of cement paste with low C_3A amount good fluidizated by calcium sulphur, influence of fly ashes on rheological properties is insignificant. A considerable increase of fluidity is observed in cement pastes reaches in C_3A which are characterized in low fluidity comparing to cement pastes poor in C_3A.
- Unfavourable impact of high-calcium fly ash in cement pastes on rheological properties of cement pastes occurs in a lower degree for cement pastes with low content of C_3A.

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