The Influence of Limestone Microfillers on the Rheology of Cement Pastes

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Abstract

The effect of limestone microfillers on the rheological properties of cement pastes was investigated. The results show that the limestone meal addition to cement brings about the increase of rheological parameters. They increase with the content of the filler and with the percentage of finest fractions. On the other side, in the presence of superplasticizer the reverse phenomenon is observed. The degree of fluidization of the pastes rises with the fineness of microfiller.

1. Introduction

The effect of fine grained fillers, including limestone ones, on the properties of fresh concrete mixtures and hardened HPC has been the subject of growing and growing interest [1, 2, 3]. Limestone is used, apart from fly ash, as an important component of self – compacting concrete mixtures, to rise the content of powder fraction. Limestone fillers supply generally the fine fraction in cement, that is the fraction below 10 μm. In traditional, normal concrete the application of limestone brings about the workability improvement and lowers the permeability of hardened material [4, 5].

Both in HPC and in SCC technology the simultaneous application of microfiller and superplasticizer at low w/c is recommended. There are many controversial opinions dealing with the influence of limestone fillers on the rheological properties of cement pastes and concrete mixtures at the presence of superplasticizer at low w/c ratio. Some authors find that in the presence of limestone powder the improvement of concrete mixture rheological properties takes place and this relates also to the SCC mixtures. The others observe the substantial loss of workability of fresh mixtures. It seems that the effect of finely ground limestone on the rheology of pastes, mortars and concrete mixture is controlled by the grain size composition [6]. In most cases limestone is ground together with cement clinker and therefore the fineness of cement is higher, because of the better grindability of limestone.

It has been found in some works [7, 8] that the microparticles of limestone could play the similar role as microsilica in the rheology of cement pastes and concrete mixtures. Then the percentage of superplasticizer is reduced and the workability of HPC is enhanced. In turn, in the works [9, 10] the loss of fluidity was reported for the mixtures with limestone filler. The authors [11] observed the shear stress decrease and plastic viscosity increase with growing limestone content. The relationship between the yield value and plastic viscosity is important particularly when the limestone is used as filler in self-compacting concrete mixtures.

One can presume that the loss of workability in the mixture with fine grained limestone additive is the consequence of accelerated C_3S hydration and the formation of calcium carboaluminates. However, the modification of rheological properties in the presence of limestone, as observed simultaneously, does not approve this. The results indicate that the degree of fluidization in the systems with microparticles of limestone depends not only on the grain size composition but also on the characteristics of grain surface – structure and morphology of outer layer and chemical composition. This has been found in the studies [10].
The development of self-compacting concrete technology, with limestone micro-filler used to raise the content of powder component, creates the need of thorough investigations aimed in the determination of limestone microparticles effect on the rheological properties of cement suspensions as well as on the properties of SCC, produced with new type superplasticizers, based on the poly-carboxylic ether [12]. The source of differences, observed as the rheological behavior of pastes and concrete mixtures with limestone microfiller is tested, should be pointed out.
In this work the studies of the effect of limestone filler addition to cement on the rheological properties of cement pastes were carried out.

2. Experimental

2.1. Materials

The rheological properties were tested on the pastes produced from „neat" cement type CEM I 32,5 (C) with 10 to 80 % (by mass) of limestone meal (M1, M2); M1 and M2 samples differ with fineness.
In table 1 the percentages of finest fractions, from 0,62 to 11,43 μm, in cement and in micro-fillers, as determined using laser granulometer, are given. One can see that the limestone meal M2 exhibits higher content of finest particles (Table 1).

Table 1. The content of fine particles in cement CEM I 32,5 and in limestone micro-fillers M1 and M2

Particle size [μm]	Percetage of fraction [% by mass]	
	M1	M2
0,62	0,67	1,11
1,15	4,43	7,46
1,96	8,45	14,61
2,47	10,73	18,61
3,62	16,15	29,38
5,31	24,09	43,66
7,79	34,37	58,76
11,43	46,01	71,88

Cement sample used in this study was produced by co-grinding of Portland cement clinker with 5% (by mass) of gypsum. The limestone powder was mixed with cement in a laboratory mill for 5 hours. The chemical composition of Portland cement clinker and limestone microfillers is given in table 2, together with their Blaine specific surface.

Table 2. Chemical composition of cement clinker and microfillers, in mass %

Component	Clinker	Microfiller	
		M1	M2
SiO_2	22,57	1,35	0,40
Fe_2O_3	2,13	0,50	0,0
Al_2O_3	4,97	0,46	0,20
CaO	68,11	51,60	52,77
MgO	0,82	2,24	1,68
SO_3	0,40	not determined	not determined
K_2O	0,20	not determined	not determined -
CaO free	0,68	-	
Blaine specific surface [m^2/kg]	Cement CEM I 32,5 318,8	390,4	608,7

The effect of superplasticizer on the rheological properties was studied on the samples of cement pastes with 40% (by mass) of limestone filler, differing with fineness. The superplasticizer based upon the poly-carboxylic ether (EP), with 40 % by mass of solid substance in the suspension, was added as 1; 1,5 and 2 %, (by mass of cementitious material) respectively.

2.2. Methods

The rheological measurements were carried out with help of rotation viscometer with co-axial cylinders type Rheotest RV2 (Germany). The properties of pastes were determined basing on the flow curves for growing and decreasing shear rates in the range from 0 to 150 s^{-1}. The measurement took place 10 minutes after the cement had come into contact with water. The establishment of flow curve took 6 minets. The yield value and plastic viscosity were determined from declining part of the flow curve basing on the Bingham model. The measurements for cement pastes only were done at constant water to solid ratio (w/s) 0,35; for pastes with superplasticizer – at w/s=0,25 respectively. The temperature was 21^{o}C.

The grain size composition was determined using the laser granulometer type Mastersizer (UK).

3. Results and disscussion

In tables 3 and 4 the yield value values and plastic viscosities for cement pastes, as determined basing upon the Bingham model, are presented.

Table 3. Yield value τ_0 [Pa] and plastic viscosity η_p [Pa·s] of cement pastes produced from cement CEM I 32,5, with different limestone microfillers M1 and M2, added as 10 to 80 % by mass of cement; w/c =0,35

Percentage of microfiller in cement [%]	Paste components				Cement CEM I 32,5 (C)	
	C + M1		C + M2			
	τ [Pa]	η [Pa·s]	τ [Pa]	η [Pa·s]	τ [Pa]	η [Pa·s]
10	4,2	0,30	13,4	0,40	4,5	0,29
20	13,6	0,32	14,7	0,42		
30	14,6	0,35	21,5	0,45		
40	15,6	0,37	24,5	0,48		
50	16,2	0,40	29,2	0,57		
60	19,1	0,55	30,5	0,71		
70	19,5	0,62	32,1	0,74		
80	20,2	0,65	60,8	0,76		

Table 4. Plastic viscosity η_p [Pa·s] of cement pastes with 40 % (by mass) of limestone different limestone fillers with superplasticizer; w/c=0,25

Percentage of superplasticizer	Paste components		Cement CEM I 32,5 (C)
	C + 40 % M1	C + 40 % M2	
	η [Pa·s]	η [Pa·s]	η [Pa·s]
1 % EP	0,24	0,14	0,65
1,5 % EP	0,19	0,08	0,57
2 % EP	0,14	0,05	0,51
2 % EP, w/c=0,35	0,06	0,01	0,08

Basing upon the rheological measurements on cement pastes with limestone fillers of different fineness it has been found that cement replacement by the microfiller would result in the improvement of rheological parameters, that is both the yield value and plastic viscosity increase with filler content. The rheological parameters become higher with filler content (table 3). Moreover, it has been found that the rheological parameters grow with the fineness of microfiller added to cement.

In case of microfiller M2, with higher content of fine particles (table 1), the highest rise of the yield value and plastic viscosity is observed, as compared to the pastes with microfiller M1, with lower content of the finest fraction (see table 1 and 3).

In the presence of superplasticizer the cement pastes with limestone filler exhibit the properties of Newtonian liquid. In this case the pastes show the inverse effect that the pastes without this admixture. The most significant effect of fluidization has been found for the paste with microfiller M2, having the higher content of the finest fraction, while for the microfiller M1 this effect was substantially lower. The rise of superplasticizer (from 1 to 2 % by mass) brings about the fluidity increase, more evident with higher admixture content and fineness of microfiller. The paste with M2 microfiller and 2% EP superplasticizer exhibits the highest fluidity (see table 4).

Application of superplasticizer based upon the poly-carboxylic ether (EP) leads to the reduction of water to cement ratio in the paste from w/c 0,35 to w/c 0,25 (see table 3 and 4).

From the data thus presented one can find that the limestone microfillers can play the role of water reducing agents when used together with superplasticizer; in such a way they improve the efficiency of superplasticizer. In case of cement paste produced from neat cement CEM I 32,5 with 2 % (by mass) of superplasticizer the plastic viscosity is 0,51 Pa·s, while for the paste with 40 % by mass of microfiller M2 and at the same content of superplasticizer the plastic viscosity falls substantially to the value of 0,05 Pa·s respectively (see table 4).

3. Conclusions

The following conclusions can be drawn from the experiments and analysis of the data presented in this work:

- Limestone powder addition as microfiller to cement brings about the increase of yield value and plastic viscosity of cement paste; this effect becomes more evident with growing filler content in cement and with the percentage of fine fraction in the filler.
- In the presence of superplasticizer the inverse effect is observed: the fluidity of cement paste with limestone microfiller becomes higher with growing fineness of the filler.

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