

EFFECT OF THE GYPSUM STATE IN INDUSTRIAL CEMENTS ON THE ACTION OF
SUPERPLASTICIZERS

F. Basile, S. Biagini, G. Ferrari, MAC, R & D Laboratories, Treviso, Italy;
M. Collepari, Department of Materials and Earth Science, University of Ancona,
Ancona, Italy

(Refereed)
(Received March 31, 1987)

ABSTRACT:

The reduction in mixing water of the concrete, caused by the addition of a superplasticizer, depends also on the type of cement used. Superplasticizer based on naphthalene sulfonated polymer acts much more effectively on cement containing gypsum dihydrate than on that containing calcium sulfate hemihydrate. Moreover, an improvement of the superplasticizer quality caused by ultrafiltration of the polymer, is more effective on the cement containing gypsum than on that with hemihydrate.

Introduction

The reduction in mixing water of the concrete, caused by the addition of a superplasticizer based on a sulfonated polymer depends on many parameters such as chemical composition, molecular weight distribution and dosage of the polymer; chemical composition and fineness of cement; time of addition of the superplasticizer; mix proportion of the concrete; mixing time; etc (1).

In the present work only one parameter - composition of cement - was studied in detail. In particular two industrial Portland cements (A and B) which had shown significant differences in their performances when used for superplasticized concretes, were examined. Cement B has been chosen as a representative of the average behaviour of many Portland cements in the presence of superplasticizers, whereas cement A always performed much better than other cements in the presence of superplasticizers, for both the lower amount of mixing water and the reduced slump loss. Moreover, cement A seemed to be much sensitive even to small changes in the quantity of superplasticizers.

Experimental

Table 1 shows the chemical composition of the clinkers used for the two industrial Portland cements: A and B, both ground with 5% of gypsum at about the same Blaine fineness of $0.45 \text{ m}^2/\text{g}$. The main differences between the two clinkers are in the $\text{C}_3\text{A}/\text{C}_4\text{AF}$ and $\text{C}_3\text{S}/\text{C}_2\text{S}$ ratios which are lower in clinker for cement A than in that for cement B, and in the alkali content which is higher for the clinker of cement A.

TABLE 1

Chemical analysis of the clinkers used for cements A and B.

COMPOSITION	CLINKERS FOR CEMENT:	
	A	B
SiO_2	22.30	21.77
Al_2O_3	4.77	5.08
Fe_2O_3	3.54	2.59
CaO	64.86	66.69
MgO	1.75	1.63
SO_3	0.70	0.43
Na_2O	0.23	0.12
K_2O	0.87	0.12
C_3S	52.7	61.7
C_2S	24.0	15.7
C_3A	6.7	9.1
C_4AF	10.8	7.9

XRD and DTG analysis showed that the main difference between the two cements substantially consists in the state of gypsum probably because of the different conditions of grinding in the two industrial mills. Gypsum is present almost completely as CSH_2 in cement A and as $\text{CSH}_{0.5}$ with traces of CSH_2 in cement B.

In order to understand whether the different behaviours of A and B cements in superplasticized concretes were to be ascribed to the difference in the chemical composition of clinkers (Table 1) or to the difference in the state of gypsum, both the clinkers used for the A and B industrial cements were separately ground in a pilot mill at the Blaine fineness of about $0.45 \text{ m}^2/\text{g}$ and then they were blended in a laboratory mill with 5% of pure byhydrate or hynhydrate calcium sulfate. Therefore four different laboratory cements were obtained: A_b , A_h , B_b and B_h , where A (or B) and A (or B) indicate the laboratory cements containing byhydrate (b) and hynhydrate (h) respectively.

As a superplasticizer a 40 % aqueous solution of calcium salt of sulfonated naphthalene-formaldehyde condensate was used. Such a polymer was utilized as received from the chemical plant or after an ultrafiltration process by Amicon membrane mod. YM2 with a nominal cut-off of 1000 dalton. The

purpose of the ultrafiltration process was to remove the low molecular weight fractions (including the monomer) from the original polymer in order to improve its superplasticizing effect. Gel permeation Chromatography (GPC) was used in order to characterize a) the polymer as received, b) the polymer treated by ultrafiltration technique and having a higher molecular weight, and c) the removed low molecular weight polymer which was not used as a superplasticizer in the present work (Fig. 1): the number average molecular weights (\bar{M}_n) of the three polymer were 635, 735 and 260 respectively.

Measurements of minislump test, adsorption, zeta potential and heat hydration development rate were carried out on cement pastes (w/c ratio = 0.35) with and without superplasticizer according to the techniques described in previous papers (2, 3). Minislump, adsorption and zeta-potential tests were carried out at 20°C after 2 min of mixing cement with pure water or an aqueous solution containing 0.40% of dry polymer by weight of cement. In some cases concrete were manufactured in order to confirm the results obtained on cement pastes. The nominal mix proportion of the concrete was: 400 kg/m³ of cement; 750 kg/m³ of sand (with a fineness modulus of 2.80); 1100 kg/m³ of gravel (with a maximum size of 20 mm); 0.40% of dry sulfonated polymer by weight of cement; enough mixing water to produce flowing mixes with a slump of 220 ± 5 mm.

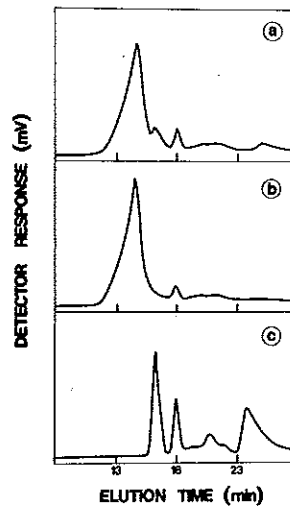


FIG. 1

Gel permeation chromatogram of: a) polymer as received; b) polymer subjected to ultrafiltration process; c) low molecular weight fraction removed by ultrafiltration process.

Discussion and Results

a) Industrial cements

Table 2 shows the effect of the superplasticizer (based on the sulfonated polymer as received from the chemical plant) on the rheological properties of cement pastes. Moreover the zeta-potential with or without superplasticizer, and the amount of polymer adsorbed on A e B cements are shown.

In the absence of superplasticizer the minislump of the two cement pastes was the same. The increase in fluidity of the cement paste caused by the superplasticizer addition was much greater for cement A than for cement B; however, no substantial difference has been found in the change in zeta potential or in the amount of adsorbed polymer for the two cement pastes (Table 2).

TABLE 2

Influence of cement brand on mini-slump, zeta potential and adsorption of sulfonated polymer (as received)

CEMENT BRAND	MINISLUMP (cm ²)		ZETA POTENTIAL (mV)		ADSORPTION ON CEMENT (%of original polymer)	
	WITHOUT POLYMER	WITH 0.4% POLYMER	WITHOUT POLYMER	WITH 0.4% POLYMER	WITHOUT POLYMER	WITH 0.4% POLYMER
A	24	188	- 3.1	- 23.5	--	80
B	23	87	- 2.0	- 20.4	--	83

This does not mean that the change in zeta potential or the polymer adsorption on cement particles are not in some relationship with the superplasticizer effect, as it has been found in other works (2, 3). This only means that some other parameter exists which must depend on the type of cement, as the superplasticizer used was the same but the superplasticizing effect was different for the two industrial cements.

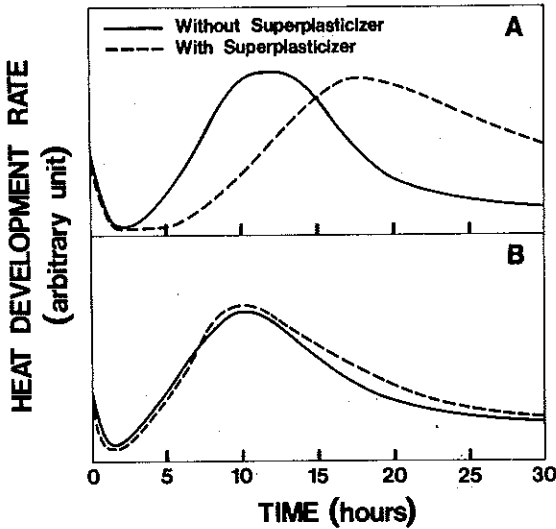


FIG. 2

Effect of superplasticizer based on calcium salt of sulphonated naphthalene polymer with A and B cements.

The early hydration process of the cement, for instance, could be related with the superplasticizer effect. The heat hydration development rate for the two industrial cements with and without superplasticizer, shown in Fig. 2, indicates that the admixture significantly retards the hydration process of the cement A, whereas it does not substantially affect the hydration process of cement B. This could be related with the difference either in the state of gypsum or in the chemical composition (Table 1) of the clinkers. In order to clarify this point, the same experiments as those carried out on the industrial cements A and B were made again by using the laboratory cements A_b , A_h , B_b and B_h .

b) Laboratory cements

Table 3 shows the effect of the sulfonated polymer (as received from the chemical plant) on minislump, zeta potential and amount of polymer adsorbed on the four laboratory cements.

Independently on the clinker used, in the presence of CSH_2 the superplasticizer effect of the admixture is much stronger than in the presence of $\text{CSH}_{0.5}$. The difference in the superplasticizing effect between cements containing bihydrate (A_b , B_b) and those containing hemihydrate (A_h , B_h) does not seem to be related with a change in zeta-potential or polymer adsorption, thus confirming the results found for the industrial cements (Table 2).

Test on concrete mixes manufactured from the four laboratory cements confirmed the results obtained on cement pastes. The reduction in mixing water caused by the superplasticizer addition was much higher with A_b and B_b than with A_h and B_h cements.

TABLE 3

Influence of the gypsum state on minislump, zeta potential and adsorption of sulfonated polymer (as received)

CEMENT TYPE	GYPSUM STATE	MINISLUMP (cm^2)		ZETA POTENTIAL (mV)		ADSORPTION ON CEMENT (% of original polymer)	
		WITHOUT POLYMER	WITH 0.4% POLYMER	WITHOUT POLYMER	WITH 0.4% POLYMER	WITHOUT POLYMER	WITH 0.4% POLYMER
A_b	CSH_2	23	175	- 2.7	- 24.1	--	82
A_h	$\text{CSH}_{0.5}$	22	79	- 2.1	- 23.7	--	84
B_b	CSH_2	24	189	- 3.1	- 23.2	--	83
B_h	$\text{CSH}_{0.3}$	23	83	- 2.9	- 22.4	--	82

Consequently, the increase in compressive strength, due to the superplasticizer addition was significantly greater in concretes containing cements with bihydrate than in those manufactured from cements with hemihydrate (Table 4)

Moreover, slump loss, as measured by the difference between the slump after mixing and that after 30 min, appears to be higher in concretes manufactured with cements containing hemihydrate. This effect is significantly emphasized by the presence of superplasticizers and this could be related with a different early hydration process of cements containing bihydrate or hemihydrate as shown in Fig. 2.

c) Ultrafiltered polymer

As it has been already said, the A industrial cement, when used in superplasticized concretes not only performed much better than other Portland cement, such as the B industrial cement, but it also appeared to be much more sensitive to small changes in the quality of superplasticizer. In order to confirm whether also this peculiar behaviour depends on the fact that in the A industrial cement gypsum is present almost completely as CSH_2 , the polymer as received and the ultrafiltered polymer were comparatively tested with the laboratory cements A_b and A_h , containing bihydrate and hemihydrate calcium sulfate respectively.

TABLE 4

Influence of sulfonated polymer (as received) on the characteristics of concretes manufactured from the laboratory cements.

CEMENT	GYPSUM STATE	POLYMER (%)	WATER/CEMENT RATIO	SLUMP (mm) just after mixing	SLUMP (mm) 30 min	COMPRESSIVE STRENGTH (MPa) AT:		
						1 day	7 days	28 days
A_b	CSH_2	0.4	0.41	220	185	43.0	66.7	76.2
A_b	CSH_2	---	0.56	225	185	20.5	40.8	53.4
A_h	$\text{CSH}_{0.5}$	0.4	0.48	225	110	32.8	56.3	66.3
A_h	$\text{CSH}_{0.5}$	---	0.55	220	170	20.6	42.2	54.1
B_b	CSH_2	0.4	0.41	215	180	44.5	73.1	82.0
B_b	CSH_2	---	0.56	225	185	22.8	45.9	57.8
B_h	$\text{CSH}_{0.5}$	0.4	0.46	210	100	36.8	63.5	73.8
B_h	$\text{CSH}_{0.5}$	---	0.54	220	165	24.6	51.2	60.3

The results shown in Table 5 indicate that the ultrafiltered polymer is more effective than the original polymer in increasing the fluidity of cement mixes. This is due to the change in the molecular weight distribution of the polymer (Fig. 1); however, at a given chemical composition of the clinker, the presence of CSH_2 instead of $\text{CSH}_{0.5}$ makes the improvement in the superplasticizing effect more significant, whereas no substantial difference is found in the change in zeta-potential or in the polymer adsorption between the A_b and A_h cements.

TABLE 5

Effect of sulfonated polymer as received (P) or treated by ultrafiltration (UF) on minislump, zeta-potential and adsorption on cements containing CSH_2 or $CSH_{0.5}$.

CEMENT	GYPSUM STATE	% OF POLYMER		MINISLUMP (cm ²)	ZETA POTENTIAL (mV)	ADSORPTION (%)
		P	UFP			
A _b	CSH_2	0.4	--	175	- 24.1	82
A _b	CSH_2	--	0.4	220	- 24.3	84
A _h	$CSH_{0.5}$	0.4	--	79	- 23.2	83
A _h	$CSH_{0.5}$	--	0.4	96	- 23.6	82

Conclusion

The results of the present paper allow us to draw some conclusions which could be useful, from a practical point of view, to manufacture cements which are more effective in superplasticized concretes:

1. When the grinding conditions into the mill hinder the thermal decomposition of the bihydrate into the hemihydrate calcium sulfate, Portland cements are produced which perform much better when used in the presence of superplasticizers, as the required mixing water, at a given concrete slump, is reduced.

2. Slump loss of superplasticized concretes is significantly reduced when cements containing bihydrate are used.

3. Cements containing gypsum almost completely in form of bihydrate appear to be much sensitive even to small changes in the quality of superplasticizers as those realized in the present work by ultrafiltration technique; therefore any improvement in the quality of superplasticizers becomes more effective when cements containing bihydrate are used.

On the other hand, from a scientific point of view, further development in the research work is required to elucidate the results of the present work. In particular further work is needed to examine:

1. The hydration process of the C_3A - CSH_2 - $CSH_{0.5}$ system with and without superplasticizers.

2. The chemical composition of the aqueous phase in the above mentioned system.

3. Optimization of the composition in the CSH_2 - $CSH_{0.5}$ system in relation-ship with the "reactivity" of the aluminate phase in different Portland cements in the presence of superplasticizers.

References

1. V.S. Ramachandran and V.M. Malhotra, "Superplasticizers" in Concrete Admixtures Handbook, pg 211, Noyes Publications, Park Ridge, (1984).
2. M. Collepardi, M. Corradi, G. Baldini and M. Pauri, "Influence of Sulfonated Naphthalene on the Fluidity of Cement Paste", VII Inter. Congr. Chem. Cements, Paris, Vol III, 20-25, (1980).
3. M. Collepardi, M. Corradi, M. Valente, "Influence of Polymerization of Sulfonated Naphthalene Condensate and its Interaction with Cements", Amer. Concr. Inst., SP-68, 485-498, (1981).