The influence of added sulfates on the properties of cement paste, mortar and concrete

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ABSTRACT

Among the several parameters that characterize the chemical composition of cement, the sulfates content, especially soluble sulfates, is recognized in literature as one of the most critical, as a non adequate amount of sulfates could lead to problems of incompatibility between cement and superplasticizers. This behavior is particularly observed with polycarboxylate-type admixtures, which seem to be much more sensitive to the cement composition. In this work, five samples of cement containing different amounts of sulfates were selected. The influence of sufates content on the performances of BNS- and polycarboxylate-type supelasticizers was evaluated. A deeper investigation was carried out on the sample containing the lowest amount of soluble sulfates, evaluating its performances when different type of sulfates were added by means of adsorption tests, minislump tests, mortar and concrete tests.
Results of this study highlight that water reduction and workability retention are strongly influenced by the soluble sulfates content in the case of poycarboxylate, while BNS doesn't seem to be so sensitive to this parameter.

1. Introduction

The use of polycarboxylate-based superplasticizers nowadays represents a common practice in the production of concrete, both for pre-cast and for ready-mix applications. Compared to admixtures based on polynaphtalenesulphonate (PNS) and lignosulphonate, which were previously the most widely used in the market, polycarboxylates allow to reach performances once considered unachievable, namely extreme water reduction and meanwhile very good workability retention, as well as high early and ultimate compressive strengths. However, it is well known that these superplasticizers are characterized by a higher sensitivity to the conditions in which they are used, comprising not only the chemical and physical characteristics of the cement, but also the nature of aggregates and the conditions of use adopted (addition order, mixing procedure etc.).
Due to this sensitivity, some cases of incompatibility are sometimes met on site, where the use of these polycarboxylate-based admixtures is

inhibited by their performances, which are not as good as expected. Several studies have been published in recent years, concerning the causes of this incompatibility [1-4].

Many advancements have been achieved by the admixture science with the introduction of polycarboxylates-based superplasticizers; the challenge now is to assure a good robustness of these products, so as to guarantee the highest performances, both in the fresh and in the hardened state, in most of the applications. In order to be able to solve problems of incompatibility that may occur it is necessary a deep understanding of the reasons which lead to the problems.

Several works have focused, in the latest years, on the types and amounts of sulfates of cement, recognized as one of the key parameters which influence the performances of superplasticizers in concrete [5-16].

Magarotto et al [15, 17] have shown that polycarboxylkates-based superplasticizers (CE) and polynaphtalenesulphonate-based superplasticizers (PNS) respond in a different way when variations are made in the nature and content of soluble sulfates of the cement. This confirms that the two types of superplasticizers possess different mechanisms of action. As reported by Aïtcin [2], it is not the total amount of SO_3 in cement that is important, but rather the availability, or the rate of dissolution of SO_4^{2-} ions. Alkali sulfates, which are formed during Portland cement production in the clinkerization phase, are the most soluble among the sulfates contained in cement; together with calcium sulfate, added as set regulator, they provide the sulfate ions necessary for the reaction with C_3A in the early stages of cement hydration. This stages are extremely important since they determine the adsorption rate of the admixtures onto cement and consequently both the water reduction and the workability retention of concrete.

The present paper is focused on the effect that alkali sulphates play on the interaction between cement and superplasticizers; both polynaphtalenesulphonate-based (PNS) and polycarboxylate-base superplasticizers (CE) are considered. The work is divided into two parts: in the first part, a number of different cements, commercially available in Italy, are investigated, regarding both chemical composition, with particular attention to soluble sulfates, and interaction with admixtures, as given by minislump and mortar tests. The results show that these cements are quite different, especially concerning the content of alkali sulfates and the interaction with admixtures. The second part is focused on one cement, characterized by a very low content of alkali sulfates; practical performance tests are carried out with the purpose to highlight the impact that an external addition of soluble sulfates exerts on the performance of concrete, with both types of superplasticizers. The results presented here further confirm that alkali sulfates are of paramount importance for the efficacy of superplasticizers, representing a potential cause for the incompativbility problems sometimes occurring in the filed. It is also shown

that PNS ands CE admixtures behave differently in this respect, as explained by adsorption tests.

2. Experimental Details

2.1 Materials

Four Italian commercial portland cements type I 52,5 (according to EN 197/1) and one portland cement type I 42,5 were investigated, which will be named in the following as cement A, B, C, D and E respectively. Their complete chemical analysis was carried out according to the methods reported in EN 196/2. Total and soluble sulfates (within 2 minutes at w/c of 0.5) were determined by means of ionic chromatography. Three different superplasticizers were investigated, one based on β-naphtalensulphonate (BNS) and two based on ether polycarboxylates (PCE-1 and PCE-2). All the superplasticizers are water solutions with 38% solid content, pH 7.5 and density 1.195 ± 0.05 g/cm^3 for BNS, 35% solid content, pH 7 and density 1.095 ± 0.05 g/cm^3 for PCE-1 and 30% solid content, pH 7 and 1.060 ± 0.05 g/cm^3 for PCE-2. PCE-1 and PCE-2 are characterized by the same chemistry but different side chain length (PCE-1 has shorter side chains than PCE-2).

2.2 Minislump tests

A cement paste prepared with cement, water and superplasticizer (dosage 0.40% active bwc for BNS, 0.20% active bwc for PCE-1 and PCE-2) was poured, after mixing, into a metallic truncated cone mould (internal top diameter: 21 mm, external top diameter: 31 mm, internal base diameter: 40 mm, external base diameter: 50 mm) standing on a flat plexiglass surface; the cone was then lifted and the diameter of the collapsed paste measured. The right amount of water necessary to reach 150 mm diameter of the collapsed paste was determined.
A second series of minislump was carried out, only with cement B, adding the amount of $SO_4^=$ necessary to bring the soluble sulfate to the level of the reference sample A (0.77%): this addiction was done with gypsum dihyrate ($CaSO_4*2H_2O$), hemihydrate ($CaSO_4*0,5H_2O$), anhydrite ($CaSO_4$), K_2SO_4 and Na_2SO_4, in order to evaluate the influence of the degree of solubility of sulfates on the water reduction.

2.3 Adsorption analysis

The degree of adsorption onto cement of the β-naphtalensulphonate-based and polycarboxylate-based admixture was determined in cement

paste by T.O.C. analysis performed with a Shimadzu 5000-A. BNS was dosed at 0.40% active bwc, while PCE-1 and PCE-2 were dosed at 0.20% active bwc. The w/c was kept constant at 0.5. The samples were prepared according to the following procedure: powder and water, containing the admixture, were stirred for the defined time and then filtered by a vacuum pump. The amount of polymer adsorbed was determined by difference between the organic carbon originally contained in the polymer solution and the amount left in the solution filtered from the paste.

A second series of adsorption analysis was carried out by adding 0,77% $SO_4^=$ as $CaSO_4*2H_2O$, $CaSO_4*0,5H_2O$ and K_2SO_4.

2.4 Mortars

Standard mortars were prepared according to EN 196/1 with all the five cements studied, in the presence either of BNS and PCE superplasticizers. BNS was dosed at 0.40% active bwc, PCE-1 and PCE-2 at 0.20% active bwc. The flow was evaluated for each mortar according to the EN 413-2 after 15 shocks.

A second series of mortar tests was carried out by adding 0,77% $SO_4^=$ as $CaSO_4*2H_2O$, $CaSO_4*0,5H_2O$ and K_2SO_4.

2.5 Concrete tests

Concretes were prepared with cements A and B at 20°C, adopting the mixture composition shown in Table 1. The dosages of the superplasticizers were 0.40% active by weight cement for BNS, 0.20% active bwc for PCE-1 and PCE-2.

A second series of concrete mixes was carried out by adding 0,77% $SO_4^=$ as $CaSO_4*2H_2O$, $CaSO_4*0,5H_2O$ and K_2SO_4.

Table 1 − Mix design for concrete tests

	Kg/m^3
Cement I 52.5	400
Limestone filler	15
Sand 0-1	380
Sand 0-2	234.4
Sand 2-4	316.6
Gravel 8-12	268
Gravel 12-19	632
K_2SO_4 (only in the second series)	5.58

3. Result and Discussion

3.1 Chemical Composition

In table 2 the chemical composition, using the methods reported in EN 196/2, and the phase composition, obtained by means of Bogue equation, of the five samples is reported: cement D shows the highest C_3A content (~ 11%).

Table 2 − Chemical composition of the cement samples (% by weight)

	CEM A I 52.5	CEM B I 52.5	CEM C I 52.5	CEM D I 52.5	CEM E I 42.5
Loss on ignition	1.44	3.28	1.59	1.85	3.61
SiO_2	19.51	20.66	19.85	19.17	20.20
CaO	64.77	62.01	65.18	63.73	63.76
MgO	1.55	3.29	1.16	2.25	1.09
Fe_2O_3	3.35	3.14	2.87	2.75	2.87
Al_2O_3	4.59	3.84	4.86	5.89	4.28
Na_2O	0.26	0.18	0.15	0.16	0.18
K_2O	0.54	0.19	0.14	0.50	0.33
Na_2O_{eq}	0.62	0.31	0.24	0.49	0.40
$SO_4^=$ (total)	**3.91**	**3.59**	**4.48**	**4.13**	**3.41**
$SO_4^=$ (soluble)*	**0.87**	**0.10**	**0.27**	**0.52**	**0.52**
Free CaO	0.28	0.22	0.13	1.26	0.17
I.R.	2.40	1.98	0.60	0.79	1.16
C_3S	70.41	56.55	67.03	60.37	65.19
C_2S	2.90	16.66	6.43	9.50	8.82
C_3A	6.50	4.87	8.03	10.96	6.49
C_4AF	10.18	9.55	8.72	8.36	8.72

* at 2 min and w/c = 0.5

The soluble sulfates content varies from 0.10% of CEM B to 0.87% of CEM A; sample C, D and E are in between of samples A and B. It is important to point out that the total sulfate contents of sample A and B are not so different. As the soluble sulfates are taken after two minutes of hydration, it is reasonable to suppose that most part of these sulfates are in the form of alkali sulfates, which are the most soluble.

3.2 Minislump tests

The results of the rheological evaluations from minislump measurements are reported in Fig. 1.
It can be seen from these results that the amount of soluble sulfates doesn't seem to be a key parameter for the water reduction capability of plain cement: samples A and B show the same w/c though having

completely different content of soluble sulfates, while CEM D and E, which have the same content of soluble sulfates, show different w/c. It is necessary to point out that the amount and type of sulfates can't be the only parameter to take into consideration when examining the mechanism of action of superplasticizers; several other ones, such as C_3A content and type, fineness etc., have a huge influence on admixtures performances, especially in terms of water reduction. Samples with the highest amount of soluble sulfates (CEM A, D and E) don't seem to be so sensitive to the chemistry of the admixtures: the water to cement ratio is in fact nearly the same for all the admixtures. Regarding the water reductions of the same superplasticizer on the different cements, it is clearly shown that the water reduction capability of polycarboxylates strongly depends on the amount of soluble sulfates: a high amount of soluble sulfates leads to a low water reduction, while a low amount of soluble sulfates leads to a high water reduction. The water reduction of BNS is almost independent from the soluble sulfates content, as it is similar for all the five samples studied, around 35%.

A second series of minislump tests was carried out with CEM B and the addiction of different types of sulfates; results are shown in Fig. 2. The addiction of calcium sulfates, although presenting different solubility rates, has no influence on the w/c both in plain and superplasticized pastes. When alkali sufates are added, BNS and PCE behave oppositely: the water reduction of BNS improves, while both PCE-1 and PCE-2 need more water (around 10-13 points) to reach the same fluidity.

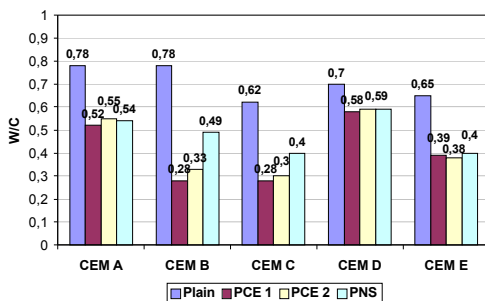It is important to underline that the water reduction obtained with CEM A always hinders the performances.

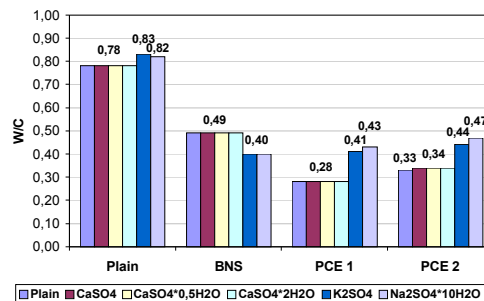**Fig. 1 −** Water-cement ratios of a given minislump test of 150 mm

Fig. 2 – Water-cement ratios for a given minislump test of 150 mm made with CEM B and 0,77% added $SO_4^=$

3.3 Adsorption tests

The results of the adsorption tests are shown in Table 3.
As shown in these results PCE admixtures are adsorbed in higher amount on cements that present lower soluble sulfates content, while BNS shows very high adsorption values that are nevertheless very similar in all the

cements. This behavior suggests that there is a competition between sulfates and polymer for the adsorption on cement particles onl y in the case of PCE, while BNS doesn't seem to be affected by the amount of sulfates. Of course, C_3A content and fineness of cement can't be neglected in evaluating the adsorption behavior of different admixtures. The higher C_3A content of CEM D in respect to CEM E, together with its higher fineness, could be an explanation for the higher adsorption vales observed with PCE admixtures.

Table 3 − Polymer adsorption onto cement

	Polymer adsorbed (%)								
	PCE-1			PCE-2			BNS		
	1'	30'	60'	1'	30'	60'	1'	30'	60'
cement A	52,0	54,5	60,5	40,9	37,2	44,0	97,4	87,5	83,3
cement B	72,1	73,9	78,2	67,9	77,2	76,2	79,5	90,3	93,4
cement C	62,9	80,7	89,1	53,4	68,7	59,6	88,2	93,0	92,2
cement D	53,1	60,2	58,3	57,4	57,3	62,8	88,3	90,8	86,8
cement E	44,9	53,7	61,0	29,2	31,7	42,7	81,0	84,8	85,3

A second series of adsorption tests was carried out on CEM B by adding different types of soluble sulfates; results are reported in Fig. 3-5.
The adsorption kinetics of all three admixtures slightly changes when calcium sulfates are added, showing good correspondence with minislump data. On the other hand, the addiction of K_2SO_4 causes a strong reduction in the adsorbed polymer, leading to a worse water reduction and possible better workability retention. It was observed by the lowering of adsorption that the competition between alkali sulfates and admixture to be adsorbed onto the cement particles was confirmed.
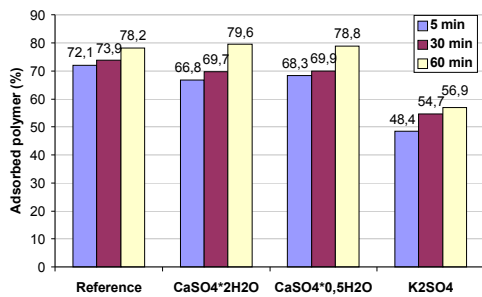
Fig. 3 – Adsorption of PCE-1 on CEM B
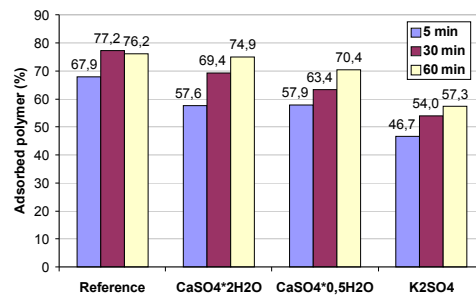
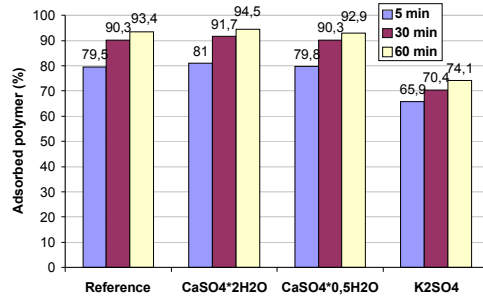**Fig. 4 −** Adsorption of PCE-2 onto CEM B

Fig. 5 − Adsorption of BNS onto CEM B

3.4 Mortar tests

The results of mortar tests are presented in Table 4.
As observed in minislump tests, he water reduction capability of PCE admixtures depends strongly on the sulfates content of the clinker phase: cement with the lowest amount of soluble sulfates (CEM B and C) show the highest water reduction capability, while the opposite behavior is observed with cements containing the highest amount of soluble sulfates. The high water demand of CEM D could be due to its high C3A content, while the low water demand of CEM E could be also due to its lower fineness. Surprisingly, BNS performances with CEM D are better than with PCE admixtures. CEM A show nearly the same w/c with both PCE-2 and BNS, as it was previously observed in minislump tests. Different behaviors can be observed in the three admixtures as far as the workability retention is concerned: there seems to be an improvement in mortars made with PCE-1 when cements with higher soluble sulfates are used. The w/c for cements B and C is the same, but the workability retention is very different, as cement B, which contains the lowest amount of soluble sulfates, shows a fluidity loss within the first 30 minutes. Cement A, which contains the highest amount of soluble sulfates, retains workability better than cement D, although the water content of the mortar is lower. The same trend is observed with PCE-2, the mortar made with CEM B looses workability very quickly compared to CEM C even though they both contain the same amount of water, but CEM C has a higher amount of soluble sulfates. No clear correlation was found between the soluble sulfates content and the workability retention, as far as BNS is concerned.
A second series of mortar tests was carried out with CEM B by adding the amount of $SO_4^=$ necessary to bring the soluble sulfate to the level of the reference CEM A: results are summarized in Table 5.
The data show that the addiction of calcium sulfates has no effect on the performances of PCE admixtures, while potassium sulfate cause the w/c to increase significantly. Regarding BNS, calcium sulfates and potassium sulfate affect the water reduction in an opposite way with respect to PCE, as the fluidity increases when calcium sulfates are added.

Table 4 − Mortar tests

		CEM A	CEM B	CEM C	CEM D	CEM E
Plain	W/C	0,64	0,62	0,58	0,60	0,58
	Flow (%) 0'	124	123	125	129	123
	Flow (%) 30'	110	101	110	115	109
	Flow (%) 60'	105	88	103	108	100
PCE-1	W/C	0,47	0,42	0,40	0,50	0,42
	Flow (%) 0'	125	130	123	128	120
	Flow (%) 30'	105	60	90	95	100
	Flow (%) 60'	90	55	50	80	73
PCE-2	W/C	0,52	0,43	0,43	0,51	0,45
	Flow (%) 0'	130	133	123	128	132
	Flow (%) 30'	110	55	98	100	110
	Flow (%) 60'	90	35	60	84	87
BNS	W/C	0,53	0,57	0,48	0,46	0,51
	Flow (%) 0'	130	127	130	120	120
	Flow (%) 30'	103	114	70	102	90
	Flow (%) 60'	90	100	55	93	75

Table 5 − Mortar tests with CEM B and 0,77% added $SO_4^=$

			$CaSO_4$ $*2H_2O$	$CaSO_4$ $*0,5H_2O$	K_2SO_4
PCE-1	W/C	0,42	0,42	0,41	0,44
	Flow (%) 0'	130	135	135	129
	Flow (%) 30'	60	63	65	99
	Flow (%) 60'	55	55	53	87
PCE-2	W/C	0,43	0,43	0,42	0,49
	Flow (%) 0'	133	128	130	132
	Flow (%) 30'	55	50	55	89
	Flow (%) 60'	35	34	30	70
BNS	W/C	0,57	0,59	0,59	0,54
	Flow (%) 0'	127	130	130	130
	Flow (%) 30'	114	113	113	85
	Flow (%) 60'	100	98	103	75

3.5 Concrete tests

The results of concrete evaluations are reported in Table 6 and 7.
Regarding PCE admixtures, a very good correlation was found between the water reduction and the soluble sulfates content, as the water reduction obtained with cement B, which contains the lowest amount of soluble sulfates is considerably higher than the one obtained with cement

A. As previously observed in the mortar tests, PCE-1 seems to perform better than PCE-2 with cement A, while the performances of the two PCE admixtures are the same with cement B. It is important to point out that C3A content of CEM A and B are nearly the same.

Water reduction capability of BNS doesn't seem to be so affected by the amount of soluble sulfates again, although its behavior is opposite to PCE, according to what also mortar tests have shown.

Table 6 − Concrete tests with CEM A

Admixture	Water (l/m^3)	W/C	Slump (cm)		Volumic Mass (Kg/m^3)	Compressive strenghts (MPa)		
			5'	30'		1 day	7 days	28 days
	256	0,64	20	14	2337	22,9	29,5	36,2
PCE 1	180	0,45	21	15	2445	45,4	54,7	62,9
PCE 2	196	0,49	21	11	2405	38,1	48,3	53,2
BNS	232	0,58	20	15	2386	28,6	35,5	40,8

Table 7 − Concrete tests with CEM B

Admixture	Water (l/m^3)	W/C	Slump (cm)		Volumic Mass (Kg/mc)	COMPRESSIVE STRENGTHS (MPa)			Notes
			5'	30'		1g	7gg	28gg	
	260	0,65	20	16	2404	22,7	35,7	39,8	
	253	0,63	20	19	2362	24,8	30,3	36,7	Added 0,77% SO$_4^=$
PCE 1	150	0,38	21	1	2448	51,6	63,5	72,5	
PCE 1	183	0,46	21	17	2440	44,7	54,5	59,3	Added 0,77% SO$_4^=$
PCE 2	160	0,40	20	--	2433	48,8	62,9	72,0	
PCE 2	190	0,48	20	5	2393	39,3	45,2	52,7	Added 0,77% SO$_4^=$
BNS	240	0,60	20	11	2352	29,1	39,3	46,2	
BNS	228	0,57	21	15	2370	28,2	36,7	41,4	Added 0,77% SO$_4^=$

Further concrete tests were made with cement B adding the amount of soluble sulfates (0.77% of SO$_4^=$ as K$_2$SO$_4$) necessary to bring the soluble sulfate to the level of sample A.

The addiction of soluble sulfates causes a dramatic increase in the w/c when PCE admixtures are used, while the water reduction capability of BNS improves by adding the same amount of sulfates.

The w/c obtained with CEM B and sulfates addiction are nearly the same as the ones obtained with CEM A for all the admixtures, meaning that the

soluble sulfates content is a key parameter for the understanding of the interaction between cement and admixture.

No conclusions can be drawn in regards to the workability retention when considering the trials with and without sulfates addiction, as the water content before and after the addiction is too different. However, it is interesting to notice that the workability retention of PCE-1 and PCE-2 after sulfates addiction is very different, although the w/c ratio is nearly the same.

4. Concluding Remarks

Among the chemical parameters that characterize the cement composition, the amount and type of sulfates seem to play a key role for the interaction between cement and admixures. In particular, the soluble sulfates content (alkali sulfates in the clinker phase) are recognized as crucial in determining the performances of superplasticizers. The efficacy of polycarboxylate-type superplasticizers was proved to be strongly affected by the presence of soluble sulfates, which compete against polymers for the adsorption on cement particles. It was demonstrated that the higher the amount of soluble sulfates in the clinker phase is, the lower the water reduction capability of a PCE admixture is. Workability retention could be improved in these situations, as the superplasticizer which remains in the pore solution can act as a dispersant for a longer time. BNS-type superplasticizers seem to be much less sensitive to the soluble sulfates content, even though no clear correlation between water reduction, workability retention and sulfates content was found.

Of course, several other chemical parameters, such as C_3A content and type, have to be taken into consideration for a deeper understanding of the mechanism of action of superplasticizers.

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