What Makes More Effective Polycarboxylates Comparing to Lignosulphonates? Differences on Adsorption Mechanisms

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Abstract

The adsorption of chemical admixtures onto cement particles is a key factor in the mechanisms of action of water-reducer admixtures that controls the dispersion ability and, consequently, the rheology of cement suspensions. Along these lines, the dispersion ability of polycarboxylates is significantly higher when comparing to lignosulphonates.

Polycarboxylates are completely adsorbed on cement particles at dosages lower than the saturation dosage. Beyond this dosage, no more surface is available and, consequently, part of the admixture remains in the solution. Accordingly, at low dosages, the entire admixture is working on dispersing cement particles. However, the percentage of adsorption of lignosulphonate remains invariable whatever the dosage is and, consequently, high dosages of lignosulphonate are needed to achieve a significant degree of cement dispersion. Results indicate that different mechanisms control the adsorption of polycarboxylates and lignosulphonates and the ability of polycarboxylates to be strongly adsorbed on cement particles contributes to improve its effectiveness at very low dosages.

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1 Introduction

As described in the literature, water reducer admixtures exhibit affinity towards the surface of the cement particles [1-5] and, consequently, the molecules of the admixture are adsorbed onto the cement surface due to electrostatic or Van der Waals type interactions. The adsorption of water reducer molecules depends on several factors related to the chemical structure of the polymer, the composition of the clinker, the type and amount of sulfates and the mixing procedure.

Regarding the chemical structure of the polymer, the adsorption of water reducer molecules onto the cement surface depends mainly on the type and density of functional groups of the admixtures [1,6], the molecular weight distribution [7-10], the length of the main chain, as well as length and density of the side chains [11-12] and the electrical charges [13-14].

On the other hand, the composition of the clinker influences the adsorption of admixture onto cement, especially the type and amount of C_3A [15-17]. Along these lines, the admixture seems to adsorb preferentially on the aluminates rather than the silicates [2,19]. This was demonstrated [16] through Auger Electron Spectroscopy by measuring the thickness of the adsorbed layer of a naphthalene based superplasticizer, which was of 50 nm and 300 nm on the alite (C_3S) and aluminates, respectively.

Moreover, the type and amount of sulfates added to the clinker play an important role in the effectiveness of the water reducers [20] and influences the admixture adsorption [15,18]. Along these lines, the amount of admixture adsorbed depends on the quantity of alkaline sulfate present, which reduces the adsorption on the aluminates in favor of the adsorption on the silicates [15]. This implies the existence of an optimum sulfate content in the cement for optimizing the adsorption and, consequently, maximizing the fluidity.

The amount of admixture adsorbed depends also on the instant in which is incorporated in the cement-water system. Several authors [11, 16, 21-22] state that this amount is lower when the admixture is added after mixing the cement with water, providing a significant improvement in the workability. The literature [23] suggests that the superplasticizer should be added two minutes after the water, which coincides with the beginning of the dormant stage. Along these lines, the initial hydrolysis of Ca^{2+} alters the surface of the cement reducing the adsorption of admixture and increasing the amount of free admixture in the aqueous solution for further activity [16].

Also, the way in which the admixture is adsorbed depends on its type. According to the literature [24], the admixtures with long chains adopt a

complex configuration, whereas naphthalene-based admixture is adsorbed in a monolayer due to its strong interaction.

The present work summarizes the results of an experimental study performed in BASF Construction Chemicals with the aim of evaluating the possible differences in the mechanism of adsorption between polycarboxylates, naphthalene based admixtures and lignosulphonates. Along these lines, the amount of admixture adsorbed was determined in cement paste using different dosages of each admixture. This provides information about the adsorption of different types of admixtures at dosages lower and higher than the saturation dosage.

2 Experimental Details

2.1 Materials

Cement of type CEM I 42.5R (European Standard ENV 197-1:2000) and distilled water were used throughout the study. The composition of the cement is shown in Table 1.

Table 1. Mineralogical composition of cement CEM I 42.5R

Mineralogical Composition, in %	
C_3S Alite *monoclinic*	64,1
b-C_2S Belite *monoclinic*	12,1
C_3A	4,4
$C_4(A,F)$ *Ferrite*	8,9
$CaSO_4$ *Anhydrite*	0,3
$CaSO_4 * 0.5\ H_2O$ *Hemihydrate (Bassanite)*	0,8
CaSO4 * 2 H_2O *Dihydrate (Gypsum)*	0,2
K_2SO_4 *Arcanite*	0,0
CaO *Free Lime*	0,7
MgO *Periclase*	1,0
$CaCO_3$ *Calcite*	5,9
$CaMg(CO_3)_2$ *Dolomite*	0,9
SiO_2 *Quartz*	0,7
$Ca(OH)_2$ *Portlandite*	0,0

Three different admixtures belonging to the main chemical families have been used in the study. These admixtures are pure polymers or raw materials instead of formulations of these products that are available commercially. Along these lines, no secondary raw materials can interfere with the measurements. Some properties of these admixtures are shown in Table 2, along with the designation of the admixtures used in the present work.

Table 2. Admixtures used

Designation	LS	BNS	PC
Type	Calcium Lignosulphonate	Sodium Naphthalene based	Polycarboxylate
Density (g/cm^3)	1.260	1.200	1.100
Solid content (%)	50.5	41	44
pH	7	7	6.5
Average Molecular Weight	N.A.	N.A.	42900

2.2 Cement paste fluidity

The fluidity of cement pastes was determined using a metallic cylinder with a diameter of 30 mm and a height of 50 mm. The cylinder is placed over a glass and filled with the cement paste. The cylinder is lifted causing it to spread. The average final base diameter is taken as the fluidity of the paste.

Tests were performed on cement paste using cement CEM I 42.5R and water/cement ratio of 0.4. The dosages of admixture by active material used to prepare the pastes ranges from 0 to 1.5%. The water in the admixtures has been accounted as part of the water/cement ratio.

2.3 Adsorption measurements

Cement pastes with w/c = 0.4 and different dosages of the admixtures were prepared for adsorption measurements. The amount of admixture adsorbed was determined at 5, 15 and 30 minutes.

Along these lines, the paste is filtrated at the time of the test using a vacuum pump and the adsorption of admixture remaining in the solution is determined through a Total Organic Carbon (TOC) analyzer. The amount of admixture adsorbed is calculated by deducting it from the amount of admixture added. Note that the paste is continuously stirred up to the filtration at 5, 15 and 30 minutes.

3 Results and Discussion

Figure 1 shows the initial fluidity of cement pastes prepared with different dosages of the admixtures described in Table 2. The dosages used range within 0 to 1.50% of solid residue of the admixture by cement weight.
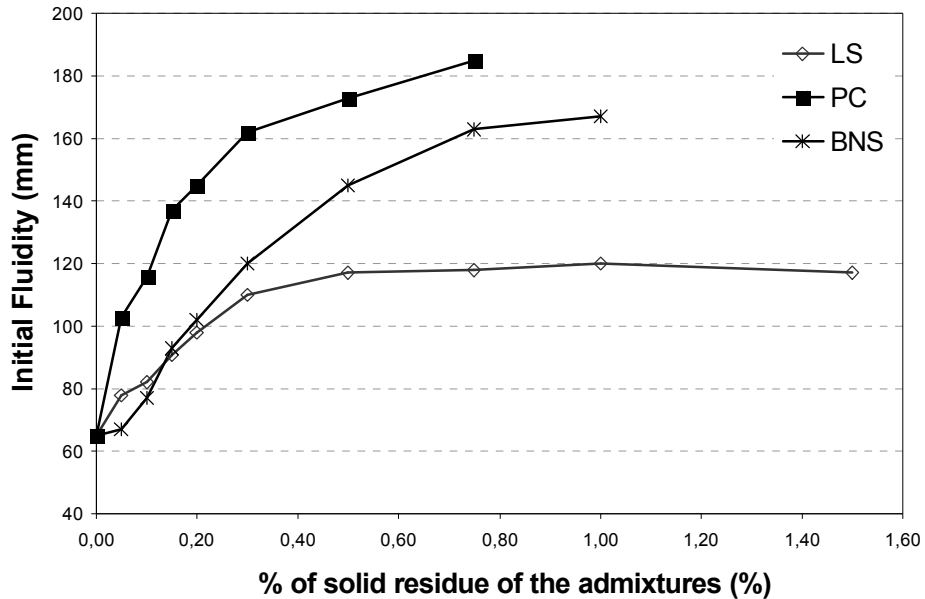

Figure 1. Initial fluidity of cement pastes incorporating different dosages of the admixtures studied.

As can be seen in the figure, at any dosage, PC is more effective than LS and BNS in terms of fluidity provided. Note that, at very low dosages (i.e., up to 0.1%) PC is significantly more effective than LS whereas, in the case of BNS, the higher effectiveness is evident at higher dosages.

Note, also, that LS reaches the saturation dosage (i.e., the dosage beyond which the fluidity does not increase significantly) at a dosage of 0.4 - 0.5% approximately. In the case of PC and BNS, which provide a significantly higher fluidity, it is difficult to evaluate the saturation dosage since at fluidities higher than 160 mm the pastes show certain segregation. Along these lines, in highly fluid pastes, the use of Marsh cone [25] would facilitate the determination of the saturation dosage.

The amount of admixture adsorbed after 5, 15 and 30 minutes, in mg of admixture by g of cement, is shown in Table 3. In general, as can be seen in the table, the amount of admixture adsorbed does not change significantly with time up to 30 minutes, indicating quick adsorption of the admixture over the cement particles. This kind of behavior seems to correspond to water reducers that lead to good initial workability but without providing significant workability retention [26]. However, as shown in Table 4, the fluidity of the cement pastes does not change significantly over 30 minutes.

Table 3. Amount of admixture adsorbed at 5, 15 and 30 minutes in cement pastes incorporating different dosages of admixtures

Dosage*, in %	Amount of admixture adsorbed, in mg of admixture by g of cement								
	LS			BNS			PC		
	5 min	15 min	30 min	5 min	15 min	30 min	5 min	15 min	30 min
0,05	0,345	0,350	0,350	0,440	0,435	0,435	0,445	0,460	0,465
0,08	---	---	---	---	---	---	0,632	0,656	0,696
0,1	0,670	0,680	0,680	0,880	0,880	0,880	0,650	0,730	0,750
0,12	---	---	---	---	---	---	0,720	0,756	0,828
0,15	0,930	0,990	1,020	1,290	1,305	1,305	0,840	0,870	0,855
0,2	1,280	1,340	1,340	1,620	1,660	1,700	0,900	1,080	1,020
0,3	1,980	2,010	1,980	2,160	2,220	2,580	0,990	1,140	1,140
0,4	2,480	2,560	2,520	2,680	2,600	2,720	1,000	1,240	1,360
0,5	3,050	3,200	3,250	---	---	---	---	---	---
1	5,900	6,200	6,400	3,200	3,300	3,400	---	---	---
2	11,200	11,800	11,800	---	---	---	---	---	---

dosage in % of solid residue of the admixture by cement weight

The amount of admixture adsorbed after 5 minutes, in mg of admixture per g of cement, is shown in Figure 2. The adsorption was determined in several cement pastes incorporating different dosages of each admixture.

As shown in Figure 2, in the case of PC and BNS, the increase in the dosage of admixture leads to an increase in the amount of admixture adsorbed onto the cement up to certain dosage. Beyond this point, the amount of admixture adsorbed does not increase significantly. This seems to indicate that, at low dosage, all the molecules of admixture

are adsorbed onto the cement surface. The increase in dosage leads to more adsorption up to certain point where a complete monolayer of molecules are adsorbed (i.e., the saturation dosage) covering the entire surface available for adsorption. After this point, the excess of water reducer admixture remains in the solution.

This can be clearly seen in Figure 3 where the adsorption is expressed as percentage of admixture adsorbed. As shown in the figure, in the case of BNS and PC, the entire water reducer admixture is adsorbed at low dosages and, after the saturation of the cement surface, the percentage of adsorption decreases with the dosage, indicating that part of the admixture remains in the solution without being adsorbed in the surface. This can indicate a mechanism of adsorption based on the formation of a monolayer of admixture on the cement surface. Along these lines, the main driving force of this kind of adsorption seems to be the surface available for adsorption.

Table 4. Initial fluidity of the cement pastes used for adsorption tests at 5, 15 and 30 minutes

| Dosage*, in % | Fluidity of the cement pastes, in mm | | | | | | | | |
| | LS | | | BNS | | | PC | | |
	5 min	15 min	30 min	5 min	15 min	30 min	5 min	15 min	30 min
0	67	67	67	67	67	67	67	67	67
0,05	67	68	67	63	67	68	91	93	98
0,08	---	---	---	---	---	---	115	120	122
0,1	75	74	72	74	76	72	115	122	119
0,12	---	---	---	---	---	---	121	128	124
0,15	79	80	78	78	80	82	120	128	130
0,2	82	81	82	85	90	85	137	138	140
0,3	85	83	85	110	115	111	145	148	145
0,4	101	89	87	120	122	122	141	145	143
0,5	108	89	84	---	---	---	---	---	---
1	115	105	92	145	143	141	---	---	---
2	113	115	111	---	---	---	---	---	---

dosage in % of solid residue of the admixture by cement weight

Interestingly, in the case of LS, the percentage of adsorption remains invariable (i.e., in the range of 60-70%) whatever the dosage of admixture is, as shown in Figure 3, and, consequently, the amount of

admixture adsorbed increases linearly with the dosage even at extremely high dosages (i.e., up to 2.0 % of solid residue of the admixture by cement weight), as shown in Figure 2. As can be seen in Table 3 and Figure 2, even at very low dosages, part of the molecules of admixture remains in the solution even when there is still surface available for adsorption. Moreover, at very high dosages, the amount of admixture adsorbed is significantly high comparing to the maximum admixture adsorbed in the case of BNS and PC.
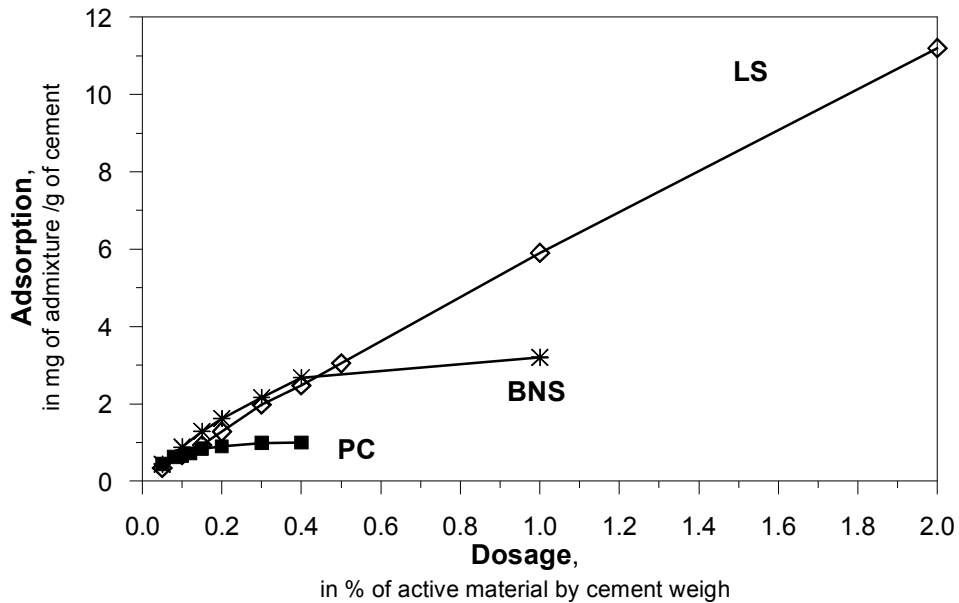

Figure 2. Adsorption, in mg of admixture by g of cement, of the different water reducers studied according to the dosage.

All these trends seem to indicate that the mechanism of adsorption of LS is different than that of BNS and PC. Along these lines, the mechanism of LS adsorption seems not to be related directly to the surface available for adsorption as in the case of BNS and PC. This can be due to multilayer adsorption or changes in the configuration of the molecules of LS when adsorbed. Further testing will be needed to verify this.
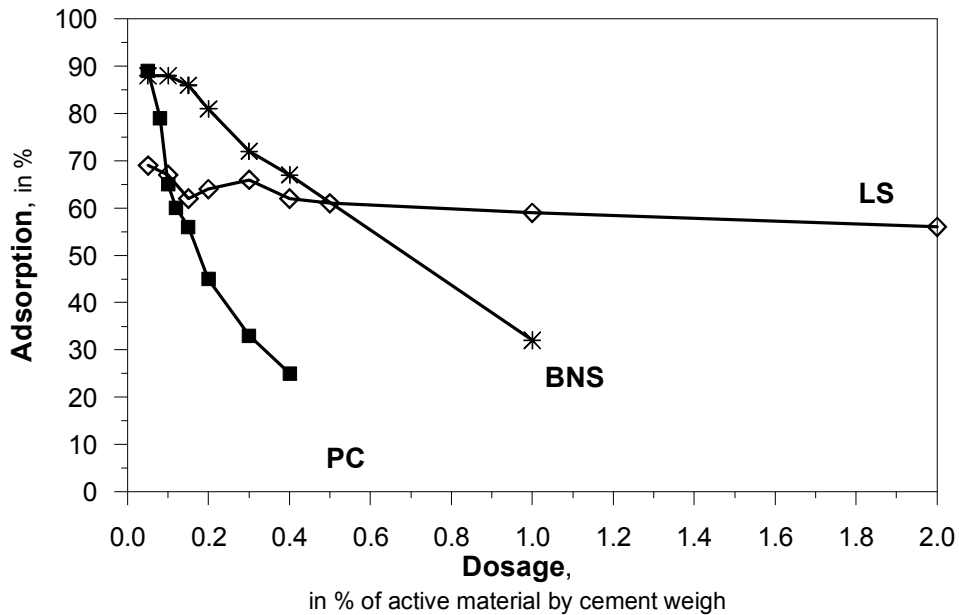
Figure 3. Adsorption, in percentage, of the different water reducer admixtures at different dosages.

4 Conclusions

The following conclusions can be drawn in the range of materials and variables studied:

- Two different mechanisms of adsorption have been identified according to the nature of the water reducer. Accordingly, BNS and PC shows a decrease in the percentage of admixture adsorbed with the dosage and, consequently, the amount of admixture adsorbed increases up to a maximum value. In these cases, the cement surface available seems to be the main driving force for the adsorption of the admixture molecules.

- Nevertheless, in the case of LS, the percentage of adsorption remains invariable whatever the dosage of admixture is and, consequently, the amount of LS adsorbed increases linearly with the dosage even at extremely (i.e., non used in the practice) high dosages. This seems to indicate that, in the case of LS, the mechanism of adsorption is not related directly to the surface available.

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