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Performance and Compatibility of Phosphonate-Based Superplasticizers for Concrete

Luigi Coppola ¹, Sergio Lorenzi ¹ , Patricia Kara ^{2,*} and Stefano Garlati ³

¹ Department of Engineering and Applied Sciences (DISA), Department of Engineering and Applied Sciences, University of Bergamo, 24044 Dalmine, Italy; luigi.coppola@unibg.it (L.C.), sergio.lorenzi@unibg.it (S.L.)

² Energy & Materials in Infrastructure & Buildings (EMIB), Faculty of Applied Engineering, University of Antwerp, 2020 Antwerp, Belgium

³ Giovanni Bozzetto S.p.A., 24040 Filago (BG), Italy; stefano.garlati@bozzetto.it

* Correspondence: patricija.kara@uantwerpen.be; Tel.: +32-3-265-8851

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Abstract: The paper deals with the effectiveness of an innovative phosphonate-based superplasticizer (PNH) for ready mixed concrete. Concrete specimens were manufactured by considering a constant initial workability, equal to 220 mm slump at the end of the mixing procedure. Workability was measured at 0, 30, and 60 min to evaluate the workability retention performances of the innovative superplasticizer. Compressive tests at 1, 7, and 28 days were carried out to evaluate the influence of the phosphonate-based superplasticizer on concrete setting and hardening. The concrete mixes were designed by considering 13 different cements to assess the superplasticizer-cement compatibility. The PNH-based admixture showed a better performance in terms of water reduction and workability retention with respect to naphthalenesulphonate based admixtures (NSF); however, a higher dosage of PNH with respect to polycarboxylate ethers (PCEs) was needed to get the same initial fluidity.

Keywords: concrete; phosphonate-based admixtures; compatibility; workability

1. Introduction

Since the last decade of the 20th century, advances in cement-based materials are mainly sustained by research activities focused on raw materials consumption, optimization of mixes, and the reuse of by-products to improve performances in a logic of sustainable development in the building industry [1–6]. All the studies in this field are characterized by the need to use admixtures tailored to improve concrete performance—both mechanical and rheological—in mixes characterized by high specificity due to the presence of a variable amount and nature of recycled raw materials. In such outlooks, superplasticizers can be considered ‘green additions’ because they permit the manufacture of sustainable and durable structures, further reducing the need of repair/rebuild and quarry raw materials. During the last 40 years, concrete technology has made considerable progress due to development and the use of very efficient admixtures designed in order to improve physical, rheological, mechanical properties of concrete and its durability [7]. Naphthalenesulphonate-based admixtures (NSF) have been used as chemical admixtures since approximately 1930. Since 2000, the development of an innovative class of superplasticizers—such as polycarboxylate ether-based plasticizers (PCE)—caused a big change in the field of concrete technology. PCEs significantly improved the performance of concrete in terms of workability retention up to a couple of hours, while also providing 2–3 times more effectiveness in terms of water reduction, cohesion, and rate of strength development than NSFs [8]. In addition, considering a relatively linear relationship over a significant admixture dosage range, it has allowed these chemicals to be used in a cost effective way to meet the requirements of concrete mix design.

The different performances of NSF and PCEs can be related to the different dispersion mechanism, which is driven almost entirely by electrostatic repulsion in the case of NSF, and significantly by steric hindrance in the case of PCEs [9–13]. Moreover, the possibility of changing several synthesis parameters of the PCEs (molecular weight, backbone length and flexibility, side-chain length, charge density) has led to the development of products characterized by tailored properties for specific applications. The higher efficiency of PCEs leads to a worsening of the well-known compatibility issues between superplasticizer and cement type [14–20]. It has also been reported that the performance variability of PCEs is dependent upon the cement production batch [8]. The incompatibility of the cement-superplasticizer system can lead to unexpected variability of the superplasticizer dosage needed to attain a sufficient workability, poor workability retention, and a compressive strength decrease at an early age.

Phosphonic acids and their salts (phosphonates) are known to form complexes with inorganic species influencing the hydration reactions. Phosphonates appear to be much more efficient retarders than many other retarders normally used in concrete practice, for example, to retard the setting time of concrete in hot weather or in the case of long transportation times. The lower pH of aqueous acids improves their chelating or complexing ability, resulting in hindered growth and stabilization of the calcium silicate hydrate on the hydrating C_3S phase [21–23]. They have been used in cements, primarily soil/cement mixtures to improve the freeze–thaw properties and salt-resistance [24], in high temperature oil and gas plugging operations, gypsum plasters and as set time extenders for cements. Phosphonates may be classified as superretarders because of their efficiencies [23] and may find applications in controlling slump in superplasticized concrete, mainly in very hot climates or in cases of prolonged transport times. Ramachandran et al. [21] tested different phosphonates and found that diethylenetriamine-penta (methylenephosphonic acid), DTPMP, was the most efficient retarder in OPC pastes. He managed to increase the induction period of an OPC paste from 3 h (reference mix) to more than 72 h using only 0.09 % DTPMP by weight of cement. Gu et al. [25] reported that phosphonates produce a prolonged induction period and a delay of cement hydration ranging from 12 to 42 h at very low dosages (0.03–0.05%). The retarding effect of these admixtures promotes a delay in the setting time and improves the workability retention through a decrease of C_3S dissolution rate. Using electrical conductivity and AC impedance methods to investigate early hydration and setting behavior of OPC pastes containing phosphonates, [25] confirmed that phosphonates have strong chelating and complexing capability, and that this effect might hinder calcium hydroxide (CH) and calcium silicate hydrate (CSH) nucleation.

Most work related to phosphonate application is to be found only in patents and in the literature from the 1990s, their role in the hydration of Portland cement is not much studied lately. Considering that phosphonates have a super-retarding effect far more efficient than that of other products, their application nowadays in concrete could be a challenge for the future investigation. This present research focuses on the evaluation of the rheological and mechanical behavior of concrete manufactured by means of a new generation of phosphonate-based superplasticizer to improve the cement/admixture compatibility. This research is devoted to the study of an innovative superplasticizer for concrete with higher efficiency in terms of water reduction with respect to polycarboxylate-based admixtures and characterized by a higher compatibility upon different cement types/production batches than NSF-based admixtures.

2. Materials and Methods

Concrete mixes manufactured by using 13 different cement types produced by different cement plants were used to evaluate the compatibility of the phosphonate-based superplasticizer (mixed polymer made of poly amine and polyoxyethylene oxide where amminic chain constitutes the backbone and ethylen oxide constitute lateral chains) with respect to commercial naphthalene-based and polycarboxylate-based products.

The cements were specifically selected in order to cover the whole Italian production [26]. Chemical compositions of the cements are shown in Table 1. Different batches of cements from several cement plants were used. Tests on concrete were carried out using the following cements:

- CEM II/A-LL 42.5 R (Limestone Portland Cement)
- CEM II/A-LL 32.5 R (Limestone Portland Cement)
- CEM II/B-LL 32.5 R (Limestone Portland Cement)
- CEM II/B-S 32.5 R (Slag Portland Cement)
- CEM III/A 32.5 N (Blast-Furnace Slag Cement)
- CEM IV/A (P) 42.5 R (Natural Pozzolanic Cement)
- CEM IV/A (V) 42.5 R (Fly Ash Pozzolanic Cement)
- CEM IV/A (V) 32.5 R (Natural Pozzolanic Cement)

Table 1. Chemical composition (% by mass) of the cements.

Cement	Prod. Batch	LOI (500 °C)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	Cl
CEM II/B-LL 32.5 R	Lot 2	0.92	17.35	3.79	1.65	0.25	59.76	2.77	2.85	0.13	0.69	0.034
	Lot 4	0.96	16.59	3.89	1.73	0.12	60.01	2.42	2.67	0.13	0.62	0.020
CEM IV/A-V 32.5 R	Lot 2	1.18	26.65	8.49	3.23	0.29	50.27	2.53	2.5	0.30	0.97	0.030
	Lot 4	1.42	26.57	7.66	2.86	0.32	50.73	2.05	2.89	0.25	0.94	0.049
CEM II/A-LL 42.5 R	Lot 2	0.99	19.96	4.21	2.06	0.20	61.61	2.73	2.85	0.12	0.80	0.040
	Lot 4	1.06	18.59	4.11	1.79	0.19	61.41	2.34	3.62	0.10	0.68	0.040
CEM IV/A-P 42.5 R	Lot 1	2.52	27.64	8.38	3.83	0.41	49.02	2.04	2.87	0.41	2.02	0.010
CEM III/A 32.5 N	Lot 1	1.77	24.58	5.72	2.76	0.30	57.16	3.74	3.10	0.05	0.70	0.020
CEM II/B-S 32.5 R	Lot 1	3.07	22.16	5.64	2.54	0.28	56.40	3.78	4.19	0.45	0.85	0.060
CEM II/A-LL 42.5 R	Lot 1	6.27	18.74	4.98	2.22	0.28	59.43	3.40	3.28	0.45	0.90	0.050
CEM II/A-LL 42.5 R	Lot 3	1.09	18.90	4.63	2.78	0.24	57.02	3.52	3.24	0.25	0.78	0.074
CEM IV/A-V 32.5 R	Lot 3	0.60	25.28	7.56	4.43	0.36	52.95	1.94	3.62	0.39	1.12	0.078
CEM II/A-LL 32.5 R	Lot 3	1.59	18.53	4.54	2.65	0.25	57.33	3.35	3.17	0.28	0.72	0.024

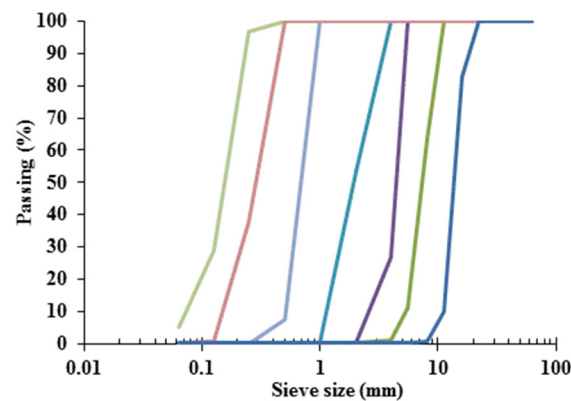
The performances of the new phosphonate-based superplasticizer (PNH1) were compared to commercial NSF (NSF3) and PCE-based (ACR1) products selected among those most widely used in Italy. The commercial products were tested in previous work [8,19,20]. The main properties of the NSF and PCE-based superplasticizers are summarized in Table 2. Concretes with w/c ratio equal to 0.52 and with a cement content of 325 kg/m³ were manufactured. The concrete mix composition is shown in Table 3. Particle size distribution of aggregates is shown in Figure 1. The superplasticizer dosage was adjusted to attain a constant slump with a value equal to 220–230 mm (UNI EN 12350-2) at the end of the mixing procedure. Workability was measured according to UNI EN 12350-2 and UNI EN 12350-5 at 0, 30 and 60 min. Air entrapping tendency and density were also evaluated on fresh concrete according to UNI EN 12350-6 and UNI EN 12350-7, respectively. The mixing procedure and all the measurements on fresh concrete were carried out at a room temperature of +20 °C and a relative humidity equal to 65%. Compressive strength was measured at 1, 7, and 28 days.

Table 2. Main properties of naphthalene, polycarboxylate-and the experimental phosphonate-based superplasticizers.

Properties	NSF3	ACR1	PNH1
Molecular weight (MW) (g/mol)	14,000	35,000	3000
MW/Mn	10	2.7	1.2
Side chain length (g/mol)		3000–5000	1000
Monomer type		Ester of acrylic or methacrylic acid	Amino-methane phosphonic polymer
Ionic groups/non-ionic side chains		5	3

Table 3. Concrete mix composition.

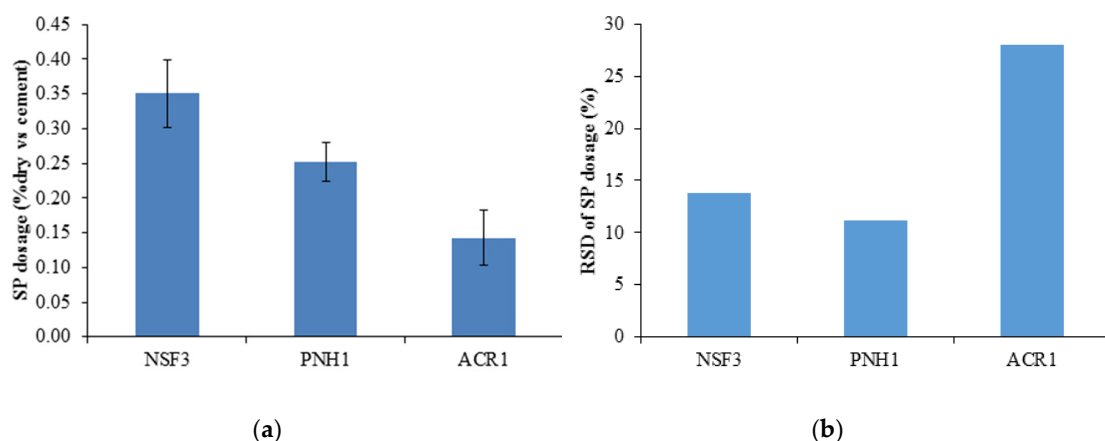
Materials	Grading Size Distribution (mm)	Dosage (kg/m ³)
Aggregates	10–20	600
	6–10	280
	3–4	295
	1.50–2.50	295
	0.6–0.8	110
	0.2–0.35	255
Filler	0.08–0.2	35
Cement		325
Water		169

**Figure 1.** Particle size distribution.

3. Results and Discussion

3.1. The Correlation between the Superplasticizer Dosage and Workability

Figure 2 shows the mean value of the superplasticizer dosage (the percentage of dry polymer vs. the cement mass) to attain the 220–230 mm slump at the end of the mixing procedure.

**Figure 2.** Mean value (a) and RSD (b) of the superplasticizer dosage (% of dry polymer vs. cement mass) to attain 220–230 mm slump on concrete.

The dosage used for the naphthalene-based superplasticizer is higher than for ACR1, therefore confirming that NSF3 superplasticizer has lower efficiency than ACR1 in terms of water reduction. The PNH1 admixture showed an intermediate dosage between the two different admixture product

families (NSF and PCE). The RSD (Relative Standard Deviation) values are sensibly lower in the case of PNH1, evidencing higher cement/superplasticizer compatibility compared to both NSF3 and ACR1 superplasticizers. ACR1 confirmed the highest dosage variability and, consequently, the highest dependence upon cement type/strength class. NSF3 showed, by contrast, a low performance variability, as expected.

Although the origin of the performance variability observed with different cements is not entirely understood, it must be considered that the adsorption of the superplasticizers onto the cement grains is driven by both enthalpic and entropic contributions [27]. In particular, for PCE superplasticizers at surface loadings close to the monolayer adsorption, the enthalpic contribution decreases and approaches zero, while the entropic contribution increases. In such conditions, it may happen that minor variations in cement chemistry or sulfate solubility, resulting in modifications of the solution ionic concentration, affecting the performance of PCE superplasticizers. On the other hand, phosphonate-based admixtures are known to have a higher adsorption energy and are thus less prone to variations in the solution chemistry.

Figure 3 shows the superplasticizer dosage and the workability at 60 min. ACR1 based admixtures are represented in the upper-left zone of the graph, meaning that they have higher efficiency in terms of water reduction and workability retention. On the contrary, NSF3 is in the lower-right zone due to lower effectiveness in terms of water reduction and poor workability retention compared to ACR1. PNH1 is in the middle-high zone of the graph, because they have intermediate efficiency between NSF3 and ACR1, but outstanding workability retention at 60 min. Looking through each class of superplasticizer, dosage does not significantly affect fluidity at 60 min. This trend is particularly evident in the case of ACR1 and PNH1. NSF3 presented a high variability upon different cement type/strength class. PNH1 superplasticizer showed poor workability at 60 min only for one cement (75 mm slump) and the performance variability is substantially in the 125–180 mm slump range. ACR1 presented under-performances on three different cements and the range is almost similar to the experimental admixture.

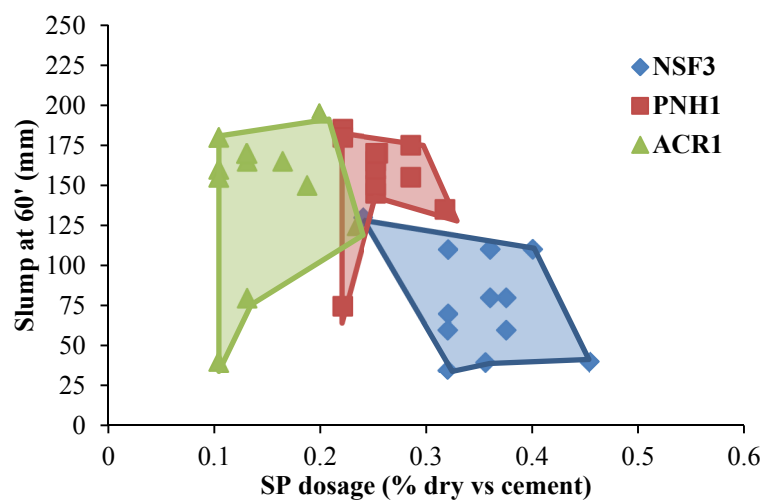


Figure 3. Slump value after 60 min as a function of the superplasticizer dosage.

3.2. Workability

Figure 4 shows the mean value of slump after 60 min. Workability is lower for NSF superplasticized concrete with respect to mixes manufactured with PCE products, as expected.

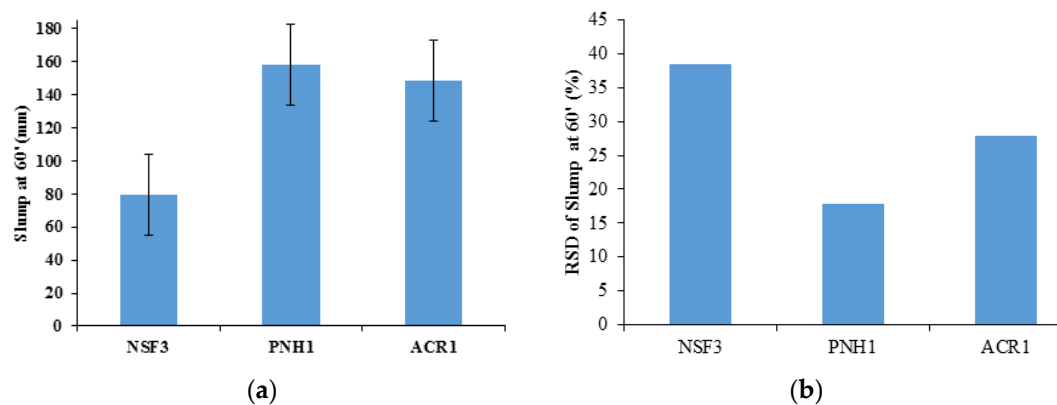


Figure 4. Slump mean value (a) and RSD (b) after 60 min since mixing procedure.

PCE products present a higher workability retention than NSF-based products, confirming that the steric hindrance is far more effective than the electrostatic repulsion mechanism to grant a prolonged fluidity. PNH1 superplasticizer showed the highest mean value of the workability retention at 60 min. This fact could be ascribed to the set retardation effect of the phosphonate-based admixture. The lowest RSD value in terms of slump retention can be observed; PNH1 superplasticizer also displayed a more reproducible value despite the different cement types/strength classes.

3.3. Air Content and Density

All tested products showed low air entrapping tendency (see Figure 5), the values are below 1.5% for all products. PNH1 admixture showed a higher air content than the commercial products. This could be ascribed to the fact that a general purpose defoaming agent was adopted and it was not optimized for this specific experimental admixture. Nevertheless, it should be noticed that the values are typical for concrete and no anomalous air entrapping tendency of the experimental admixture was detected.

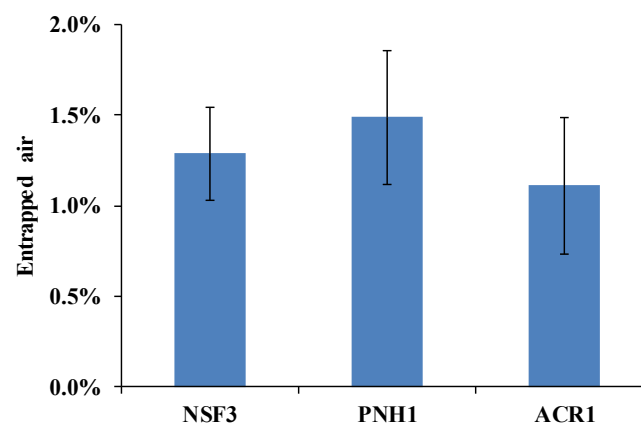


Figure 5. Mean value of entrapped air.

The density measurements conducted on fresh and hardened concrete (see Figure 6) confirmed the entrapped air data. The density values are substantially similar for all admixtures. PNH1 superplasticizer generally showed the lowest density value on fresh and hardened concrete compared to the commercial products. The commercial products generally showed higher density values on hardened concrete with respect to fresh concrete.

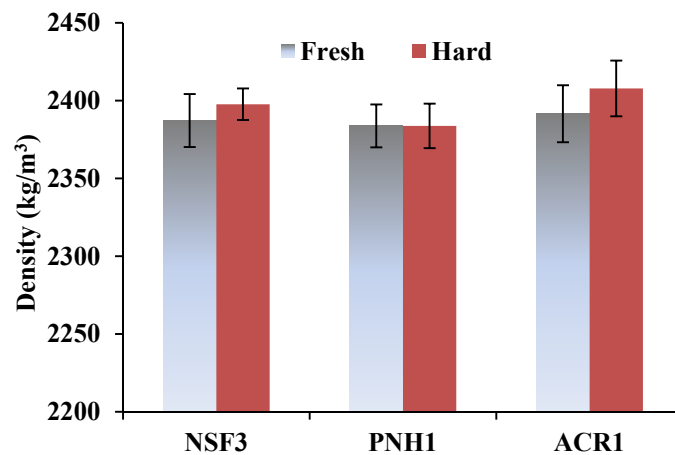


Figure 6. Density of fresh and hard concrete (mean value for all cements).

3.4. Compressive Strength

Figure 7 shows the normalized compressive strength values (R_c^*) of the three different admixtures. R_c^* is calculated as reported by Jolicouer et al. [9] in Equation (1)

$$R_c^* = R_c / R_{c,NSF} \quad (1)$$

where R_c is the compressive strength measured for each admixture at each curing times and $R_{c,NSF}$ is the compressive strength measured for NSF3 at 1, 7, and 28 days. Concrete manufactured with NSF3 generally showed higher compressive strength values at 1 day with respect to ACR1 (see Figure 7).

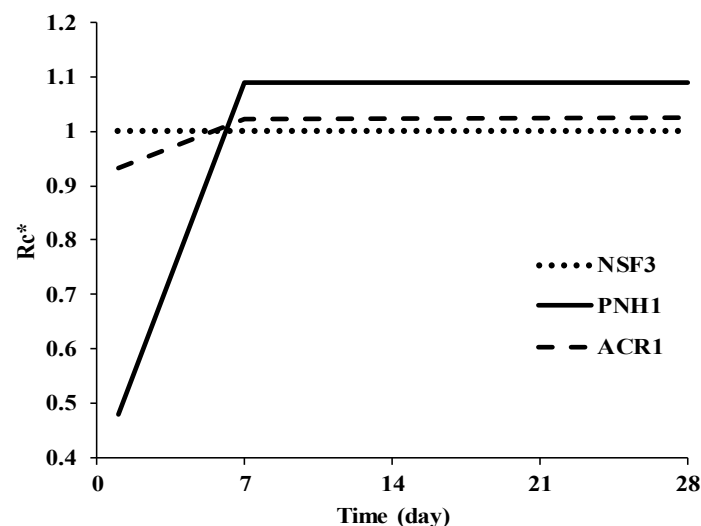


Figure 7. Mean values of compressive strength ($R_c^* = R_c / R_{c,NSF}$).

ACR1 admixture showed about a 10% decrease in the early compressive strength development due to a side effect of retardation that occurs in the case of overdose due to incompatibility. This side effect is evident only at an early age and disappears at the age of 7 and 28 days when the compressive strength becomes 2% higher with respect to that measured on NSF-superplasticized concrete. Retardation prevails on the dispersing effect at early age, whereas by contrast at the age of 7 and 28 days, dispersing action is dominant and the retardation effect becomes negligible. PNH1 admixture evidenced poor compressive strength at 1 day: a mean value of a 50% decrease can be noticed on all of the 13 analyzed cements (see Figure 8).

This fact could be ascribed to the super-retarding effect of the phosphonates [25] that causes a prolonged induction period and, consequently, produces poor early age compressive strength. At the age of 7 and 28 days, a 10% improvement in compressive strength can be evidenced (see Figure 9). While the decrease of compressive strength may be attributed to the retardation induced by the phosphonate, connected to the high adsorption energy and to the reduced C_3S dissolution rate, the higher compressive strength at later age should be related to the microstructure of the hydration products.

The variability of the compressive strength at early age is quite evident. Cements characterized by a lower hydration kinetic and a low compressive strength development generally presented lower early-age compressive strength with PNH-based admixture; this is the case for concrete manufactured by using CEM II/B-S 32.5R, CEM IV/A V 32.5R, CEM II/B-LL 32.5 R (see Figure 8). PNH1 superplasticizer showed higher compressive strength at 1 day with cements with higher strength class and rate of hardening. The highest compressive strength at 1 day was measured on cement belonging to lot 3. This might be related to the higher fineness of these cements, offsetting the retardation induced by the slower C_3S dissolution.

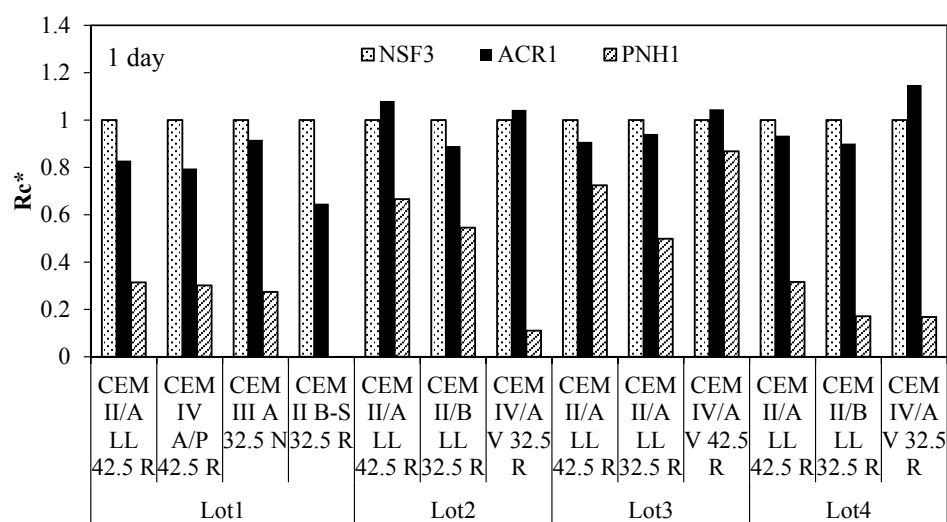


Figure 8. Normalized compressive strength at 1 day.

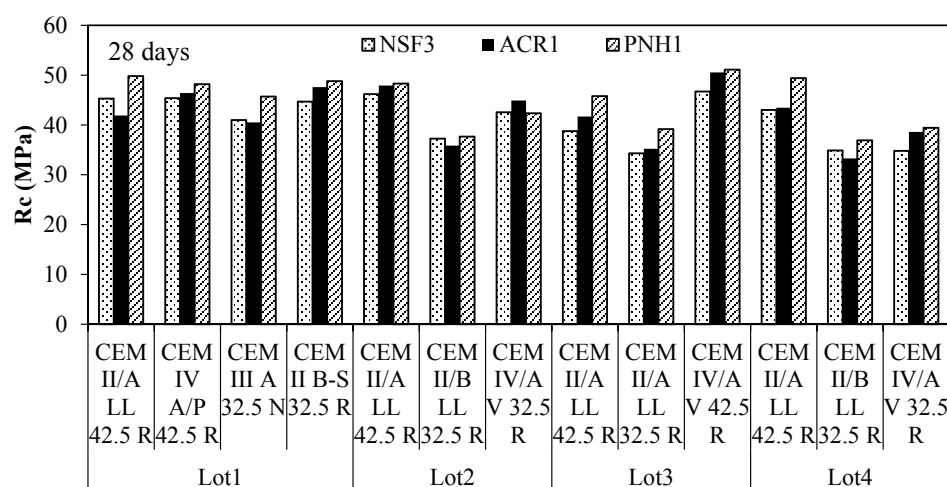


Figure 9. Compressive strength at 28 days.

4. Conclusions

A new phosphonate-based superplasticizer was synthesized by using amino-methane phosphonic polymer. Rheological and mechanical behaviors of concrete manufactured with superplasticizers belonging to NSF and PCE families and a new experimental phosphonate-based admixture were compared. The experimental tests were carried out on 13 different cement type/strength classes from three different cement producers to evaluate the superplasticizer compatibility. Experimental data collected showed that the new synthesized phosphonate-based superplasticizer is characterized by:

- higher efficiency in terms of water reduction with respect to NSF product, but lower than PCE-based admixtures;
- lower dosage variability for mixes made with different types of cement and strength classes, with respect to both PCE and NSF-based admixtures;
- higher workability retention at 60 min with respect to both PCE-based and NSF-based admixtures;
- lower workability change upon cement type/strength class with respect to both PCE and NSF products;
- no anomalous air-entrapping tendency;
- improvement of compressive strength at one day is relative in comparison to those at 7 and 28 days.

Despite phosphonate-based admixture showing lower efficiency with respect to PCE-based admixtures, higher compatibility of different cement was evidenced in terms of dosage and workability retention. The results are promising and an increasing interest in the study of this kind of admixture is expected.

Author Contributions: L.C. and S.L. conceived and designed the experiments; S.L. performed the experiments; S.L. and P.K. analyzed the data and managed the literature searches; S.G. contributed reagents/materials/analysis tools; L.C. wrote the first draft of the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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