Effects of Different Superplasticizers on Early Strength of Concrete

By Tandırlı E., Akalın Ö., Arca E.

Synopsis: Four types of superplasticizers which have different functional groups and dispersion mechanisms were used in concrete mixture and cement mortar. One of them is a new generation of superplasticizer whose dispersion mechanism is by electric repulsion and steric hindrance, others have electric repulsion only. These superplasticizers were used to compare the mechanical properties and permeability resistance. The superplasticizer dosages (ranging from 0.6 to 1.5 percent, expressed as dry mass of superplasticizer per mass of cement) were selected to produce concretes having different slumps at the same W/C . Compressive strength, flexural strength of mortar, penetration resistance, water permeability of concrete were tested. In addition, at the same W/C cement mortars have been prepared to compare mechanical properties. SEM (Scanning Electron Microscope) photos have been taken on the samples of concrete and cement mortars to obtain knowledge about their microstructures.

Keywords: compressive strength, penetration resistance, permeability, microstructure, superplasticizer, scanning electron microscope

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INTRODUCTION

Nowadays, qualitative demands toward the concrete are increasing and the concrete structure to be designed and constructed becoming larger and more complicated. So, the concrete is expected to have higher compressive strengths and durability , and contribute to the rationalization of the construction work. High range water reducing agents, so called superplasticizers (SP) which mainly consist of melamine formaldehyde condensates (MS), naphthalene formaldehyde condensates (NS), the blend of melamine and naphthalene condensates (MNS) and new range superplasticizer which is polycarboxylate (PC) based are the main tools to reach this objective.

Superplasticizers are polymers that can interact physically and chemically with cement particles. The physical interaction occurs when a superplasticizer is used to disperse cementitious fine powder. This type of interaction includes three modes of interaction : 1) adsorption of superplasticizer molecules by Van der Waals and electrostatic forces on the particles,[1,2] 2) reduction of the attractive forces between oppositely charged particles (deflocculation) and induction of interparticle repulsive forces due to the high negative charge conveyed to the particles by the adsorbed superplasticizer (dispersion) [3,4] and steric hindrance between adsorbed polymer molecules and neighboring particles.[4]

The high concentration of cement particles in the mixing water requires relatively high superplasticizer dosages to completely deflocculate and disperse the suspension of cement particles. Superplasticizers can also chemically interact with the hydration of cement particles. It has been found that naphthalene-based superplasticizers can react with the most reactive sites of cement particles, particularly with C_3A , and substantially reduce the initial surface hydration rate.[3,4] According to Uchikawa et.al., naphthalene-based superplasticizers are more preferentially adsorbed by the interstitial phase and free lime than by the calcium silicate phases.[3] Superplasticizers are also reported to retard the hydration of C_3S [5]. These interactions have practical consequences because they can delay the setting time of the paste and significantly reduce mechanical properties at early ages.[3,6] The retardation effect of superplasticizers is roughly proportional to their concentration and is generally more pronounced with low C_3A cements since less superplasticizer can react with C_3A , leaving more superplasticizer to be adsorbed on other mineral phases (C_3S) and reduce their surface reaction rate.[6] With cements containing normal amounts of C_3A , a significant retarding effect may also occur if unnecessarily high superplasticizer dosages are used.

These results emphasize the fact that determining superplasticizer dosage can be a relatively complex task with implications on cost , rheology of fresh concrete, and mechanical properties at early ages. An optimal dosage will produce a concrete with a good workability maintained during the required amount of time, but without any major effect on setting time or initial mechanical properties .[7]

The aim of this research is to evaluate the effects of different superplasticizers on early strength at the same mixture proportions. For this purpose, compressive strength, flexural strength, water permeability and SEM (Scanning Electron Microscope) were performed on the series of concrete and mortar with and without admixtures.

EXPERIMENTAL

Test Program

The mixtures prepared were divided into three series. Two of them are related to concrete while the other is a mortar. Samples from these series were subjected to different experimental investigations are early compressive strength, flexural strength, penetration resistance, water permeability, microstructure photography.

Total amounts of water, amount of cement and W/C were kept constant for all of the series. The difference between the two series of concrete has been the expression of the SP dosage.

The principle of the mortar series has conformed to the second series of concrete. Compressive strength tests were common to all of the series, while flexural strength was limited to only mortar series. Water permeability was obtained just for the second series of the concrete.

Finally, SEM photos were taken on the mortar phase of the first concrete series and on the mortar series. Experimental program is given in Table 1.

Materials

In this investigation, only Type V portland cement, fine and limestone coarse aggregates were used. Melamine based superplasticizers are MS and MNS were synthesized in laboratory conditions. The detailed synthesis procedure was given elsewhere [8]. A new generation type superplasticizer which is polycarboxylate based was kindly supplied by the producer. Properties of materials used in the test program are given in Table 2, 3 and 4, respectively.

Preparation of Mixtures

For all of the series, total amount of water was adjusted to be 180 kg / m^3 while the cement content has always been kept constant at 450 kg/m^3 . In the first series of the concrete SP's total mass was proportioned against cement however, in the other series the SP dosage was expressed as dry mass of superplasticizer per mass of cement. The details of mixture proportions are listed in Table 5, 6 respectively.

Test Methods

Compressive strength tests were performed for series 1 and 2 (Brc and Mdr) of concrete on a group of six cube moulds (15x15x15 cm) after 1, 7 and 28 days of lime-saturated water curing in laboratory conditions. Two samples that were taken to test after 24 hours were cured in different temperatures. One was held in 35 ^{0}C water in cure tank and while the other was held in 21 ^{0}C lime-saturated water.

Penetration resistance was done for each mixture of the Mdr series according to the ASTM C-803.

On the other hand for the third series of program cement mortars were prepared according to the ASTM C-305-94. Consequently flexural and compressive strengths were performed for each sample of the series according to the ASTM C-348-97 and ASTM C-349-97.

Water permeability test was applied only the samples of the second series which have the same admixture solid content and measurements were carried out after curing for 7 days in 21 ^{0}C . Then the concrete samples were connected to the water permeability apparatus and kept for 48 hours at 3 bar and 24 hours at 7 bar. The water permeability measurements were taken after cracking in the concrete compression machine in longitudinal axis.

For the series Brc and M, thin sections were cut from the concrete and mortar samples to obtain suitable dimensions for investigation in the SEM system. On concrete samples only the mortar phase was focused for the SEM photographs. Sample surfaces coated with gold , 100 A^0 at 10^{-3} bar by using

BIO-RAD Polaran Division SEM coating system. Their microstructures were investigated by JEOL JEM-1200 EX Model Scanning Electron Microscope .

Test Results

Compressive Strength— The results related to the compressive strengths, flexural strengths, water permeability and air content of the samples of each series are given in Table 7. The air content of all mixtures for all series of concrete (Brc, Mdr) varies between 0.5 and 3.0 percent.

The lowest values for the compressive strengths after 24 hours in 35 ^{0}C and 21 ^{0}C curing has been obtained for the series Mdr 3 as 31.7 Mpa and 16.8 Mpa, respectively. For this series NS based SP was used. On the other hand, the highest values (43 Mpa, 27.7 Mpa) for the compressive strengths obtained for the same conditions by using MNS based SP for the series Brc 2.

For the mortar series the highest compressive strength value was obtained with the MS based SP in M1 series. For both concrete and mortar series the lowest values were obtained for NS based SP.

After 28 days curing, series Brc 2 and Mdr 3 which contains MNS and NS respectively have the lowest values. Also similar results were seen for the mortar series.

Penetration Resistance- For the Mdr Series, initial and final set values (210~240 ; 330~ 360 respectively) of the mixtures except for the one with PC based SP were much earlier comparing to the reference. The earliest one among these was the mixture with MS based SP. Setting characteristics of the mixture with PC based SP were quite similar to that of the reference mixture. The results were given in Figure 1 .

Water Permeability – These results vary between the values of 1.5 and 2.0 for Mdr series. The lowest value was obtained for Mdr 1 which has MS based SP. The highest value was obtained for samples Mdr 2 and Mdr 3 were prepared with MNS and NS based superplasticizer.

Fresh and Mechanical Properties of Mortars— Flow values were obtained on each mortar mixtures by using the flow table top. M4 which was prepared by PC based SP has the highest flow value than the others. Compressive and flexural strengths of mortar series showed the same behaviour. That is after 1 day curing for two different temperatures (21 ^{0}C, 35 ^{0}C) compressive and flexural strengths of M1 was prepared by using melamine based SP gave the highest value while M3 prepared by using NS had the lowest value.

SEM—SEM photographs for the series 1 and 3 (Brc and M) are given in Figures 2 - 3, Figures 4 - 5 respectively. SEM photographs were taken for Brc series after 7 days while they were taken for M series after 3 days in curing at 21 ^{0}C . Figures 2 and 3 are related to concrete series while the Figure 4 and 5 are for mortar series. SEM discloses local variations in the microstructure of the samples and it gives the possibility to distinguish between different phases and their distribution. The brightest phases are unreacted cement in the order ($C_4AF > C_3S > C_2S$) . C_2S is easy to identify by its commonly striped

structure. CH appears a light gray phase, while the amorphous CSH-gel is darker gray. Note that the porosity of CSH will influence the gray-tone. [9]

CONCLUSION REMARKS

The following conclusion can be drawn from this study;

1. Although this investigation was primarily focused on early strength effects of superplasticizers, no significant differences were observed in strength at any age.
2. However, there is a considerable acceleration in the setting duration of the mixture with MS based PC as refered in literature.[10]
3. Mortar and concrete series showed the similar behaviour in compressive strength development.
4. Although PC based concrete mixture has less entrapped air (0.5 %) than the others, melamine based (MS) concrete mixture has the lowest water permeability with 1.3 % air content.

Consequently the detailed investigation of the microstructure system and dispersion mechanisms of the superplasticizers will be our future program.

Acknowledgements

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Table 1 – Experimental Test Program

	Concrete		Mortar
Tests	Series 1 Brc	Series 2 Mdr	Series 3 M
SEM	x	-	x
Penetration resistance	-	x	-
Water permeability	-	x	-
Compressive strength	x	x	x
Flexural strength	-	-	x

Table 2 – Properties of Cement

Element	PÇ 42.5 , %
SiO_2	20.89
Al_2O_3	4.94
Fe_2O_3	4.50
CaO	62.34
MgO	1.20
$Na_2O + 0.658\ K_2O$	0.76
SO_3	2.51
C_3S	43.11
C_2S	27.37
C_3A	5.48
C_4AF	13.69
Unit weight (gr/cm^3)	3.12
Blaine (cm^2/gr)	3.302

Table 3- Properties of Aggregates

	Coarse aggregate		Fine aggregate	
Property	No 2	No 1	Crushed sand	Sand
Specific gravity, g/m^3	2.69	2.68	2.67	2.62
Fineness modulus	-	-	-	0.95
Absorption capacity, %	0.45	0.46	1.10	1.05
Maximum size, mm	20	12	8	5

Table 4- Properties of Superplasticizers

Properties	MS	MNS	NS	PC
Chemical content	Melamine	Melamine-Naphthalene	Naphthalene	Polycarboxylate
Solid content, %	28.05	40.14	39.61	35.04
Density, gr/ml	1.171	1.241	1.187	1.093

Table 5 – Composition and Fresh Properties of Concretes

Series	Type of admixture	Cement kg/m^3	Water kg/m^3	W / C	Fine aggregate, kg/m^3	Coarse aggregate, kg/m^3	SP, percent of C *	SP, dosage %	Slump, mm	Unit Mass kg/m^3
BrcR	-	450	180	0.40	757	998	0		1.0	2387
Brc1	MS	450	173	0.40	757	998	0.0042	1.5	6.5	2400
Brc2	MNS	450	173	0.39	757	998	0.0059	1.5	13.5	2381
Brc3	NS	450	173	0.39	757	998	0.0059	1.5	15.5	2388
Brc4	PC	450	177	0.40	757	998	0.0021	0.6	18.0	2381
Mdr1	MS	450	177	0.40	757	998	0.0028	1.0	10.0	2388
Mdr2	MNS	450	178	0.40	757	998	0.0028	0.7	9.0	2388
Mdr3	NS	450	178	0.40	757	998	0.0028	0.7	11.5	2381
Mdr4	PC	450	178	0.40	757	998	0.0028	0.8	28	2394

Table 6 – Composition and Fresh Properties of Mortar

Series	Type of admixture	Cement kg/m^3	Water kg/m^3	W / C	Sand	SP, percent of C *	Flow (cm)
Mdr1	MS	450	177	0.40	1080	0.0028	18
Mdr2	MNS	450	178	0.40	1080	0.0028	13
Mdr3	NS	450	178	0.40	1080	0.0028	8
Mdr4	PC	450	178	0.40	1080	0.0028	38

*Expressed as dry mass of superplasticizer per mass of cement

Series	Type of admixture	Cement kg/m^3	Water kg/m^3	W / C	Sand	SP, percent*	Flow (cm)
Mdr1	MS	450	177	0.40	1080	0.0028	18
Mdr2	MNS	450	178	0.40	1080	0.0028	13
Mdr3	NS	450	178	0.40	1080	0.0028	8
Mdr4	PC	450	178	0.40	1080	0.0028	38

Table 7 – Air Content and Mechanical Properties of Concrete and Mortar Series

			Compressive Strength, MPa				Flexural Strength, MPa				Water Permeabiliy mm
Series	Type of SP	Air, %	1 day 35 ^{0}C	1 day 21 ^{0}C	7 days	28 days	1 day 35 ^{0}C	1 day 21 ^{0}C	3 days	28 days	7 days
BrcR	-	1.5	35.4	29.4	59.4	64.7					
Brc1	MS	1.7	41.7	27.0	58.8	60.0					
Brc2	MNS	2.0	43.0	27.7	58.2	60.5					
Brc3	NS	3.0	39.6	26.1	60.2	69.5					
Brc4	PC	2.0	41.7	26.7	65.1	70.2					
Mdr1	MS	1.3	32.6	17.2	51.0	62.3					15
Mdr2	MNS	1.7	32.7	18.8	47.2	66.9					20
Mdr3	NS	1.8	31.7	16.8	46.5	60.6					20
Mdr4	PC	0.5	32.5	17.5	60.6	70.8					18
M1	MS		7.5	4.5	11.7	16.7	0.61	0.31	0.67	0.72	
M2	MNS		7.2	3.8	9.7	14.8	0.51	0.28	0.62	0.87	
M3	NS		5.7	1.8	6.9	12.8	0.17	0.03	0.29	0.64	
M4	PC		7.5	2.7	13.9	17.7	0.42	0.12	0.39	0.81	

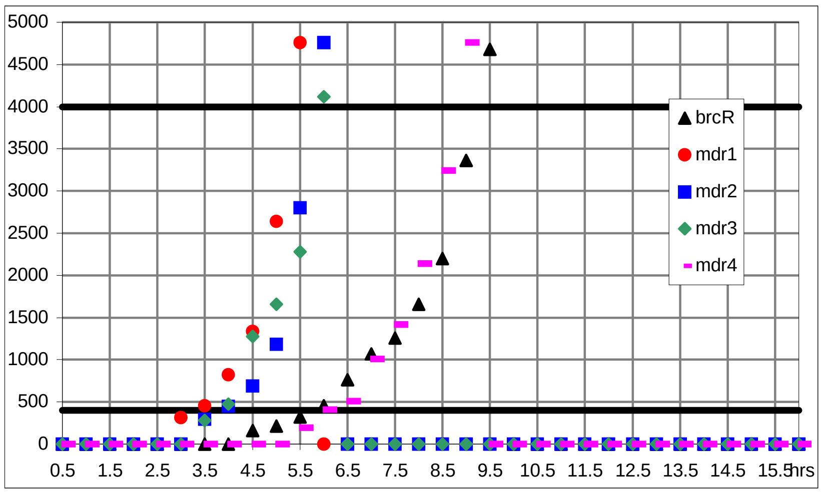

Fig. 1.a Penetration Resistances According to the Initial Mixture Times

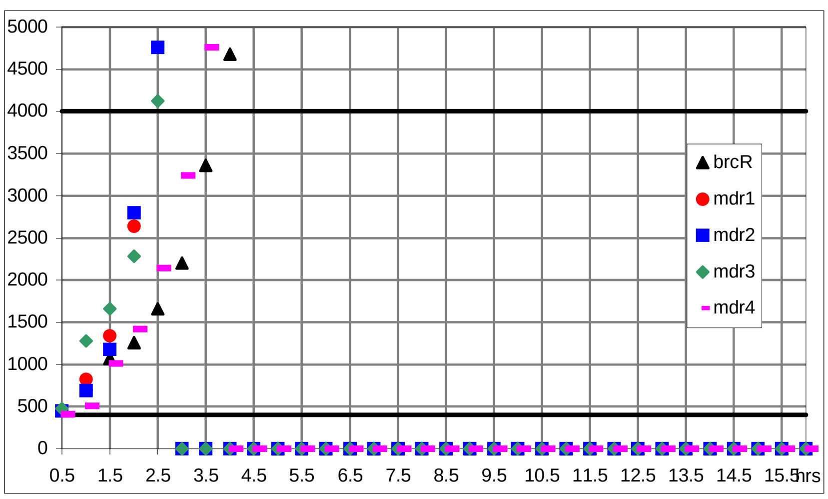

Fig. 1.b Penetration Resistances According to the Initial Setting Times

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Please enclosed find one original and one photocopy entitled with 'Effects of Different Superplasticizers on Early Strength of Concrete' for the conference which will be held in Barcelona

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Yours sincerely,

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