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The Effect of Melamine Based Superplasticizers on the Properties of Concrete

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Abstract

Melamine based superplasticizer (high range water reducing agent) was synthesized in the laboratory conditions which was used in different percentages in concrete mixture to obtain the optimum dosage. The effect of different superplasticizer dosages on the performance of concrete was tested. The measurement of slump, slump loss, water reduction, air content, penetration resistance and compressive strength on 24 hours, 3 days, 7 days and 28 days were carried out on the melamine based superplasticizers in comparison to a reference mixture without admixture.

Moreover, addition of chemical compounds that are calcium nitrate, triethanolamine, calcium formate, naphthalene sulphonate and sugar to the melamine based superplasticizer were tested in varying dosages, respectively. The accelerating effect of calcium nitrate, triethanolamine and calcium formate and the retarder effect of naphthalene sulphonate and sugar were compared with the melamine based superplasticizers by applying penetration test.

The results confirm that melamine based superplasticizer with optimum dosage supplies good workability to the concrete mixture. They also indicate that sugar has retarder effect and calcium nitrate has accelerating effect on fresh concrete mixtures.

Introduction

Water Reducers

A water reducer can be defined as an admixture that reduces the amount of mixing water of concrete for a given workability. It improves fresh and hardened concrete properties in particular, increases strength and durability. Usually, according to the standards [1] the reduction of the mixing water by the use of these admixtures must be at least 5% and at most 12% . This range of reduction is the limit for normal plasticizers. Above of the upper limit of normal plasticizer is called as an superplasticizer.

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, [2,3] 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) [4,5] and steric hindrance between adsorbed polymer molecules and neighboring particles. [5]

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 C3A , and substantially reduce the initial surface hydration rate. [4,5] 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. [4] Superplasticizers are also reported to retard the hydration of C3S [6].These interactions have practical consequences because they can delay the setting time of the paste and significantly reduce mechanical properties at early ages. [4,7] The retardation effect of superplasticizers is roughly proportional to their concentration and is generally more pronounced with low C3A cements since less superplasticizer can react with C3A , leaving more superplasticizer to be adsorbed on other mineral phases (C3S) and reduce their surface reaction rate. [7] With cements containing normal amounts of C3A , 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 . [8]

Accelerators

Accelerating admixtures are used in cold weather concreting operations. A significant increase in the rate of early strength development at normal or low temperatures enables reduction in the curing and protection periods necessary to achieve specified strengths in concrete. Many substances are known to act as accelerators for concrete. They include alkali hydroxides, silicates, fluorosilicates, organic compounds, calcium formate, calcium nitrate, calcium thiosulphate, aluminum chloride, potassium carbonate, sodium chloride and calcium chloride. Of these, calcium chloride is the most widely used because of its ready availability, low cost, predictable performance characteristics and successful application over several decades. [2]

One of the limitation to the wider use of calcium chloride in the reinforced concrete is that, if present in larger amounts, it promotes corrosion of the reinforcement, unless suitable precautions are taken. There is hence a continuing attempt to find and alternative to calcium chloride one equally effective and economical but without its limitations. Calcium nitrate, calcium formate and triethanol amine have been used in the research as an accelerators.

Retarders

The rheological properties of fresh concrete, such as workability and pumpability, and the other properties of plastic concrete such as finishing, setting and plastic shrinkage can be modified significantly by adding water reducing admixtures. The changes is mainly due to the chemical and physical affects of the organic molecules of water reducers on the surface of hydrating cement.

Many mechanisms have been suggested to explain the fluidifying effect of water reducer added to concrete at a given w/c. a) reduction of interfacial tension b) multi layer adsorption of organic molecules c) increase in electrokinetic potential d) protective adherent sheath of water molecules e) release of water trapped among cement particle clumps f) retarding effect on cement hydration g) change in morphology of hydrated cement. All mechanism except f) and g) based substantially on the dispersion of cement particles. [2] One of the main problem in the use of superplasticizer is slump loss. Adding sugar to superplasticizer slightly reduced the slump loss and delayed the setting time caused by melamine based superplasticizer.

The aim of this investigation is to determine the properties of melamine sulphonate based superplasticizer and the effect of adding different chemical compounds (as an accelerator and retarder) on the fresh and hardened concrete.

Experimental Test Program

At the beginning of this study, the optimum dosage of melamine sulphonate (MS) based superplasticizer (SP) was obtained by comparing with reference mixture. Then, the effect of different chemicals which were calcium nitrate (CN), triethanolamine (TE), calcium formate (CF), naphthalene sulphonate (NS), sugar (S) in varying dosages blending with MS were endeavored by testing on fresh and hardened concrete properties. Each series were compared with their reference concrete. The details of the experimental test program were given in Table 1.

Table 1 – Experimental Test Program

	Original	Acceleration			Retardation	
Tests	MS	MS+CN	MS+TE	MS+CF	MS+NS	MS+S
Water Reduction (%)	x	x	x	x	x	x
Air content (%)	x	x	x	x	x	x
Initial Penetration	x	x	x	x	x	x
Final Penetration	x	x	x	x	x	x
Compressive strength	x	x	x	x	x	x

Properties of Materials Used

In this investigation, only Type V portland cement, fine and limestone coarse aggregates were used. Melamine based superplasticizers which is MS was synthesized in laboratory conditions. Melamine, sodium metabisulphide and formaldehyde were used for condensation polymerization reaction . Condensation pH was kept at 4.0 and the polymerization reaction was below the 100 ^{0}C. After polymerization complete, pH of the solution was rised to 9.5. The effect of MS based SP on the microstructure of the concrete and mortar was researched by taking SEM (Scanning Electron Microscope) and presented elsewhere. [9] Properties of materials used in the test program are given in Table 2 and 3, respectively. The combinations of different chemicals in varying dosages blended with melamine sulphonate (MS) based SP.were given in Table 4.

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- Combinations of chemical compounds with MS based SP

Series	Nomenclature of Superplasticizers	Blend of the chemical compounds with MS	Addition of chemical amounts as an % of original MS based SP					
			A	**B**	**C**	**D**	**E**	**F**
0	Reference	Without admixture						
1	MS	Melamine Sulphonate	0	0	0	0	0	0
2	MS+CN	MS+ Calcium Nitrate	0.5	1	1.5	2	2.5	3
3	MS+TE	MS+ Triethanolamine	3	5	10			
4	MS+CF	MS+ Calcium Formate	0.4	0.5	1			
5	MS+NS	MS+ Naphthalene Sulphonate	1.5					
6	MS+S	MS+ Sugar	0.5	1	1.5	2		

Test Methods

Fresh concrete properties were tested to obtain water reduction, air content and slump. Compressive strength tests were performed for each series of concrete on a group of two cube moulds (15x15x15 cm) after 1, 3, 7 and 28 days of lime-saturated water curing in laboratory conditions.

Penetration resistance was done for each mixture of the series according to the standard. [1] Initial and final setting time were obtained and each series were compared according to their reference mixture. All the penetration resistance figures related to the initial and final setting time are given in Figure 1. Data given in the following tables were obtained by the mean values of at least three samples.

Test Results

The test results were given in the Table 5 and 6 . They include the composition and fresh properties of the concrete mixtures . The nomenclature of the following series is based on Table 4.

Table 5 – Composition and Fresh Properties of Concrete Mixtures

Series	Type of admixture	Cement kg/m^3	Water kg/m^3	W / C	SP, dosage %	Solid Content/m^3 %	Water Reduction %	Slump, mm	Air content %
0	Reference	310	190	0.61	-	-	-	9.0	1.2
1	MS	310	165	0.53	1	17.75	12	10	2.0
2	MS	310	157	0.51	1.5	26.89	18	9.5	2.1
3	MS	310	156	0.50	2.0	34.40	19	12	1.6
4	MS	310	151	0.49	2.3	39.56	22	11.5	2.2
5	MS	310	144	0.47	3.0	53.00	24	21	2.3
6	MS	310	137	0.44	3.5	61.55	29	18	0.9
0	Reference	310	191	0.62	-	--	-	10	1.5
2A	MS+CN	310	160	0.52	1.5	26.92	16	10	1.4
2B	MS+CN	310	158	0.51	1.5	27.31	18	10	1.4
2C	MS+CN	310	157	0.51	1.5	28.44	19	10	1.5
2D	MS+CN	310	167	0.54	1.5	28.97	13	9.5	1.7
2E	MS+CN	310	169	0.55	1.5	29.51	12	9.5	1.7
0	Reference	310	190	0.61	-	-	-	9	1.2
3A	MS+TE	310	158	0.51	1.5		17	9	2.0
3B	MS+TE	310	154	0.50	1.5		19	9	1.9
3C	MS+TE	310	152	0.49	1.5		20	9	2.0
0	Reference	310	190	0.61	-	-	-	9	1.2
4A	MS+CF	310	161	0.52	1.5		15	11	1.5
4B	MS+CF	310	157	0.51	1.5		18	10	1.7
4C	MS+CF	310	161	0.52	1.5		15	10	2.2
0	Reference	310	190	0.61	-	-	-	10	1.2
5A	MS+NS	310	150	0.48	1.5	40.00	23	10	1.8
0	Reference	310	189	0.61	-	-	-	10	1.2
6A	MS+S	310	154	0.49	1.5		19	11	2.1
6B	MS+S	310	154	0.50	1.5		19	12	2.0
6C	MS+S	310	153	0.49	1.5		19	14.5	1.7

Table 6 –Fresh and Hardened Concrete Properties

Series	Type of admixture	Compressive Strength (MPa)				Penetration Resistance	
		24 Hours	3 Days	7 Days	28 Days	Initial Set	Final Set
0	Reference	14.2	18.0	30	41.6	330	540
1	MS	22.4	30.5	43.7	53.3	330	510
2	MS	20.9	25.2	36.7	4.96	240	420
3	MS	21.0		40.7	50.0		
4	MS	24.6	35.0	47.2	53.5	270	390
5	MS	31.7	42.1	55.1	60.5	330	540
6	MS	30.9	33.0	50.6	62.9		
0	Reference	16.3	18.1	26.4	37.3	270	450
2A	MS+CN			34.7	49.5	330	510
2B	MS+CN			36.6	47.4	330	540
2C	MS+CN			48.3	56.8	240	390
2D	MS+CN			44.6	56.2	270	390
2E	MS+CN			44.7	54.3	240	360
0	Reference	14.2	18.0	30	41.6	240	420
3A	MS+TE			40.4	50.1	300	450
3B	MS+TE			41.6	53.8	330	540
3C	MS+TE			42.4	50.9	300	510
0	Reference	14.2	18.0	30	41.6	240	420
4A	MS+CF			43.6	53.1	330	480
4B	MS+CF			45.5	54.3	300	450
4C	MS+CF			46.2	55.9	360	540
0	Reference	13.0	18.0	26.7	35.3		
5A	MS+NS	22.7	31.5	41.7	53.9	240	270
0	Reference	16.3	18.1	26.4	37.3	270	450
6A	MS+S	24.8	29.7	38.0	53.0	300	480
6B	MS+S	25.8	32.1	44.1	57.2	360	540
6C	MS+S			38.8	53.1	450	630

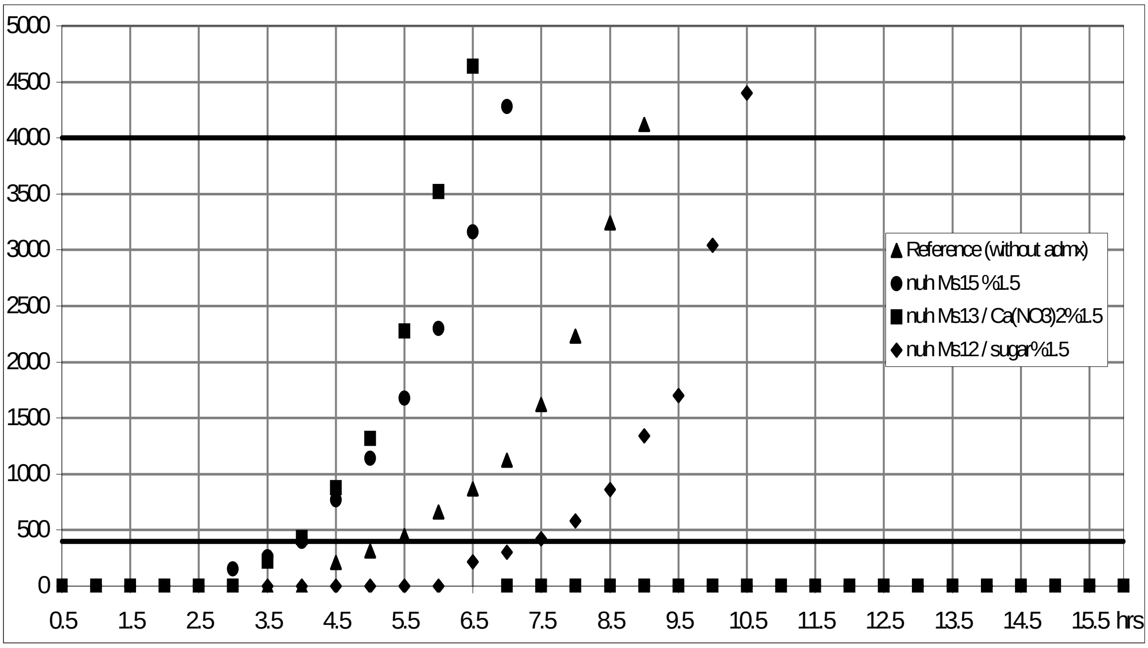

Fig.1. Penetration Resistances According to the Initial Setting Times

Discussion

In this research MS based SP was used as a high range water reducer. As can be seen from Table 5 optimum dosage for MS based SP was taken as 1.5 % due to the economical consideration. During this experiment the dosage of MS was changed within the limits of 1 % and 3.5 % , and the water reduction varied from the 12% to 29% , respectively.

Chemical compounds that are CN, TE and CF were used as an accelerator for this investigation. On the other hand using of CN with MS based SP showed slight reduction initial setting time compared to the reference. Optimum dosage of CN addition was found to be 1.5 % of the original SP. Addition of CN more than 1.5 % reached the plateau value for the penetration test. Sugar was used as an retarding agent and the optimum dosage for blending with Msbased SP was found as an 1.5 % . This amount of addition also satisfy the specifications of the standard.[1]

As can be found in literature naphthalene sulphonate addition to the melamine based superplasticizer showed slump retention rather than retardation. NS addition to MS based SP didn’t help retardation as much as sugar did. Nevertheless literature advises its usage for slump retention development.

Conclusion

The following conclusion can be drawn from this study ;

1. MS based SP shows significant accelerating effect by itself, while reducing the water content in a high range.
2. CN blended SP shows accelerating effect with respect to the reference.
3. Optimum dosage of CN addition was obtained with the value of 1.5 %.
4. Blending the sugar with MS based SP was enhanced water reduction comparing to the original MS .
5. Sugar blending MS based SP at the dosage of 1.5 % addition showed the retardation effect.
6. It is advisable to use of CN as an accelerating agent and sugar as a retarding agent for MS based SP.

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