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Effect of Super Plasticizers on Fresh and Hardened Properties of Concretes made with Special Cement OPC 53-S

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ABSTRACT: This paper presents a comparative study on compatibility and Heat of Hydration of Super plasticizers with OPC 53 and OPC 53-S cements. To the best of the knowledge of the authors this is the first attempt in India at studying the heat of hydration of OPC 53-S cements and their compatibility with Super Plasticizers. The experimental investigators have revealed that MCE group and SNF group of super plasticizers can be considered to be better suited for use with OPC 53-S grade cement.

KEYWORDS: Cement, super plasticizer, flowability, heat of hydration.

I. INTRODUCTION

Portland cement concrete has clearly emerged as the material of choice for the construction of a large number and variety of structures in the world. Today, there is a marked shift towards using higher strength concretes and precast technologies in such structures. When structures are designed to be constructed using precast concrete technology, it is necessary to have not only high 28-day strength but also a relatively high early strength to facilitate quick turn over of moulds. In such cases OPC will have to be preferred over PPC. Among the recent advancements, most noteworthy is the development of super plasticised concrete mixtures which gave very high fluidity at relatively low water contents.

Superplasticizers are chemical admixtures, which enormously increase the workability of concrete to a fixed water cement ratio and allow a large water reduction to be achieved at constant slump. For production of high strength concrete that is characterized by a low water-cement ratio and a high dosage of superplasticizer, loss of workability properties may be more rapid than that of normal strength concrete. The effect of superplasticizer depends on both the surface forces of the particle system and on the mechanism of hydration. Slump loss of superplasticized concrete is affected by a number of factors namely the properties of the consistent materials, the compatibility between them, the mixing procedure in particular the time for addition of the super plasticizing admixture. The amount of superplasticizer is also an important factor, which significantly effects the total surface of solid particles in the particle system.

The present study investigated the suitability of three types of superplasticizers based on flow test and heat of hydration with OPC 53 and OPC 53-S cements necessary for high early strength of concrete and required compressive strength at 28 days.

Significance of Research

IS 12269:2013 [1] which stipulates the specifications for OPC 53 Grade Cement has in its fold (since 2000 as an amendment and since 2013 as part of the regular code) another type of cement designated as OPC 53-S Grade Cement. This is exactly the same as the so called "Sleeper Cement" which for the last 35 years was being

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manufactured by a few cement factories in India according to the Indian Railway specifications IRS/T-40-1985 [2]. Tables 1 and 2 give a comparison of the chemical and physical characteristics to be satisfied by the two types of 53 cements. As the 53-S cement was and is being used almost exclusively only by the prestressed concrete sleeper manufacturing factories, most of the engineers other than those connected with the sleeper manufacturing are not conversant with the use of 53-S cement.

From a comparison of the properties required of 53 and 53-S grade cements as shown in Tables 1 & 2, it can be seen that i) the fineness of 53-S cement is much higher than that of 53 cement ii) the 53-S cement contains certain amount of C_3A (not exceeding 10%) and iii) it is required to have a minimum of 45% of C_3S . All these differences can be expected to contribute to a more rapid rate of growth of concrete strength in initial stages when OPC 53-S cement is used in place of OPC 53 cement even when subjected only to normal curing. But no test reports are available so far which quantify these differences. The studies reported in this paper contribute to provide such a comparison.

II. RELATED WORK

The IS Code requirements of chemical and physical properties of OPC 53 and OPC 53 - S cements are given in Table 1 & Table 2 along with IRS specifications.

Table: 1 IS Code requirements of Chemical Properties of OPC 53 and OPC 53- S grade Cements along with IRS specifications

S.No	Particulars	Requirement of OPC 53 grade As per IS:12269-1987	Requirement of IRS/T-40 -1985	Requirement of OPC 53-S grade, as per IS:12269-1987, Amendment No.6, June 2000,
1	Lime Saturation Factor (LSF)	0.66 to 1.02	0.80 to 1.02	0.80 to 1.02
2	Alumina to that of Iron oxide Ratio % (A/F)	0.66 Min.	0.66 Min.	0.66 Min.
3	In soluble Residue (% by mass)	3.00 Max	2.00 Max	2.00 Max
4	Magnesium Oxide (% by mass)	6.00 Max	5.00 Max	5.00 Max
5	Sulphuric Anhydride (% by mass)	3.00 Max	5.00 Max	5.00 Max
6	Total Loss on Ignition (% by mass)	4.00 Max	4.00 Max	4.00 Max
7	Total Chloride (% by mass)	0.10 Max. (for N.C.) 0.05 Max. (for P.C.)	--	0.10 Max. (for N.C.) 0.05 Max. (for P.C.)
8	Tricalcium Aluminate (C_3A) %	--	10.00 Max.	10.00 Max.
9	Tricalcium Silicate (C_3S) %	--	45.00 Min.	45.00 Min.

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Table: 2 IS Code requirements of Physical Properties of OPC 53 and OPC 53-S grade Cements along with IRS specifications

S.No	Particulars	Requirement of OPC 53 grade As per IS:12269-1987	Requirement of IRS/T-40 -1985	Requirement of OPC 53-S grade, as per IS:12269-1987, Amendment No.6, June 2000,
1	Fineness (m ² /kg) Blaine's specific surface area	225 Min.	370 Min.	370 Min.
2	Setting Time (Min.) Initial Setting Time Final Setting Time	30 Min. 600 Max.	60 Min. 600 Max.	60 Min. 600 Max.
3	Expansion Le.Chatelier (mm) Auto Clave (%)	10.00 Max. 0.8 Max.	-- 0.8 Max.	5.00 Max. 0.8 Max.
4	Compressive strength (MPa) 3 Days 7 Days 28 Days	 27 Min. 37 Min. 53 Min.	 Not specified 37.5 Min. Not specified	 Not specified 37.5 Min. Not specified

Properties of cements used

OPC 53 and OPC 53-S grade cements were procured from the market. The mechanical properties and strengths of the cements used in the study are given in Tables 3. It can be seen that the two samples each of OPC 53 and OPC 53 S have fully satisfied the codal requirements for strength. The fineness of both the OPC 53 samples (330 Blaine) was much higher than the minimum specified (225 Blaine) and almost close to the value specified for 53 S. The properties of OPC 53 and OPC 53-S cements are given in Table 3 (Tests are carried out as per IS: 4031-1968)[3]

Table: 3 Properties of OPC 53 and OPC 53-S grade cements

	OPC 53 grade cement	OPC 53-S grade cement
Fineness of cement	330 m ² /kg*	402 m ² /kg*
Normal Consistency	28%	29.5 %
Initial Setting Time	110 minutes	130 minutes
Final Setting Time	180 minutes	220 minutes
Soundness as per Le-chatelier	1.0mm	1.0mm

* Reported by the supplier

The compressive strength of 3 samples of OPC 53 and 2 samples of OPC 53-S grade cements tested in the laboratory are given in Table 4 and Figure 1. From the results it can be seen that in the initial days after casting, the rate of gain in strength of samples of 53-S Grade cements is significantly higher than in samples of 53 Grade cement. For example,

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the one-day strength of 53 S samples is as high as 43% of the 28-day strength whereas it is only 19.5% in the OPC 53 samples.

The basic difference in the chemical specifications of OPC 53 and OPC 53-S cements is that there is a special provision for Tricalcium Aluminate (C_3A) and Tricalcium Silicate (C_3S) in the case of OPC 53-S cement which is responsible of giving high early strength to the cement. Similarly, the differences in the physical properties of those two cements include higher fineness of OPC 53-S cement which is of $370 (m^2/Kg)$ against $225 (m^2/Kg)$ of OPC-53 cements.

Table: 4 Compressive Strength of the OPC 53 and OPC 53-S grade cements at different ages

Compressive Strength in N/mm^2	Age of Testing			
	1 Day	3 Days	7 Days	28 Days
OPC-53 Sample, C-I	9.8	28.4	39.2	54.4
OPC-53 Sample, C-II	10.2	28.8	38.6	55.0
OPC-53 Sample, C-III	11.2	29.2	38.4	54.6
OPC 53-S, Sample I, (SC-I)	23.2	35.4	48.4	56.0
OPC 53-S, Sample II, (SC-II)	25.7	36.6	49.2	58.2
Requirement of OPC 53 and OPC-53 S grade cement, as per IS: 12269 -1987, Amendment No.6, June 2000.	OPC 53	--	27	37
	OPC 53-S	--	37.5	--

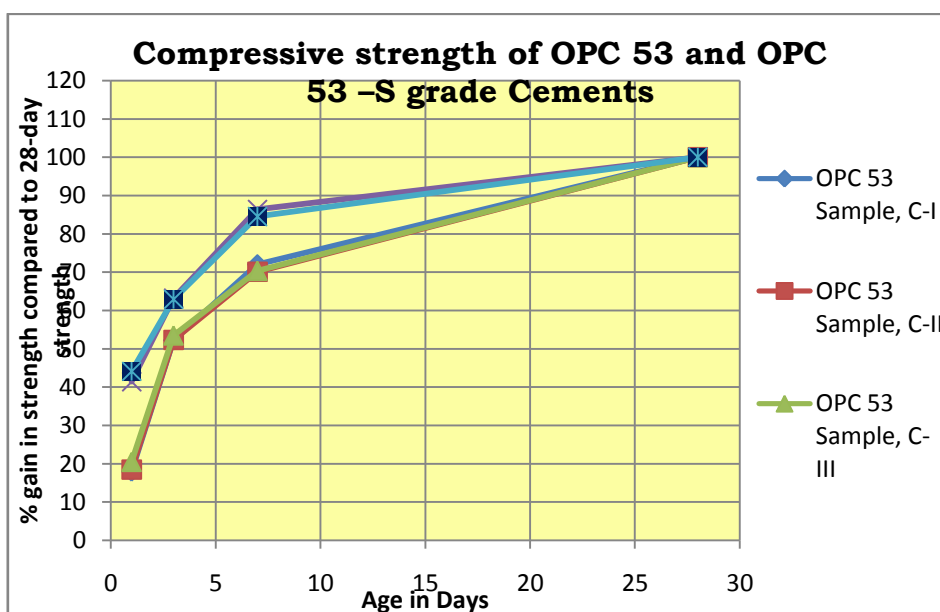


Figure: 1 Compressive strength of OPC 53 and OPC 53-S grade Cements at different ages

As a second study, the rates of hydration of the two varieties of cements were also compared by measuring the temperature rise during the first 22 hours of hardening of the cement paste For the tests a cement paste consisting of

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200 g of cement and 70 g of water (water/cement ratio of 0.35) was mixed in a plastic beaker. Immediately after mixing, the beaker was placed in a thermos container and equipped with a thermo-wire. In this test set-up a number of 4 specimens could be tested at a time by connecting it to a multi thermostat. The temperature rise was recorded for about 22 hours. The profiles of temperature rise observed are shown in Fig. 2. From the results presented in Fig.2 it can be seen that the peak temperature measured in samples from 53-S Grade cements was about 70% larger than in samples from 53 Grade cements and that this peak temperature was attained within about 10 hours and 13 hours respectively for the 53-S Grade and 53 Grade cements. This trend observed is in conformity with the pattern of the increase in strengths of cement in the early ages of the two types of cements as presented in Table 4.

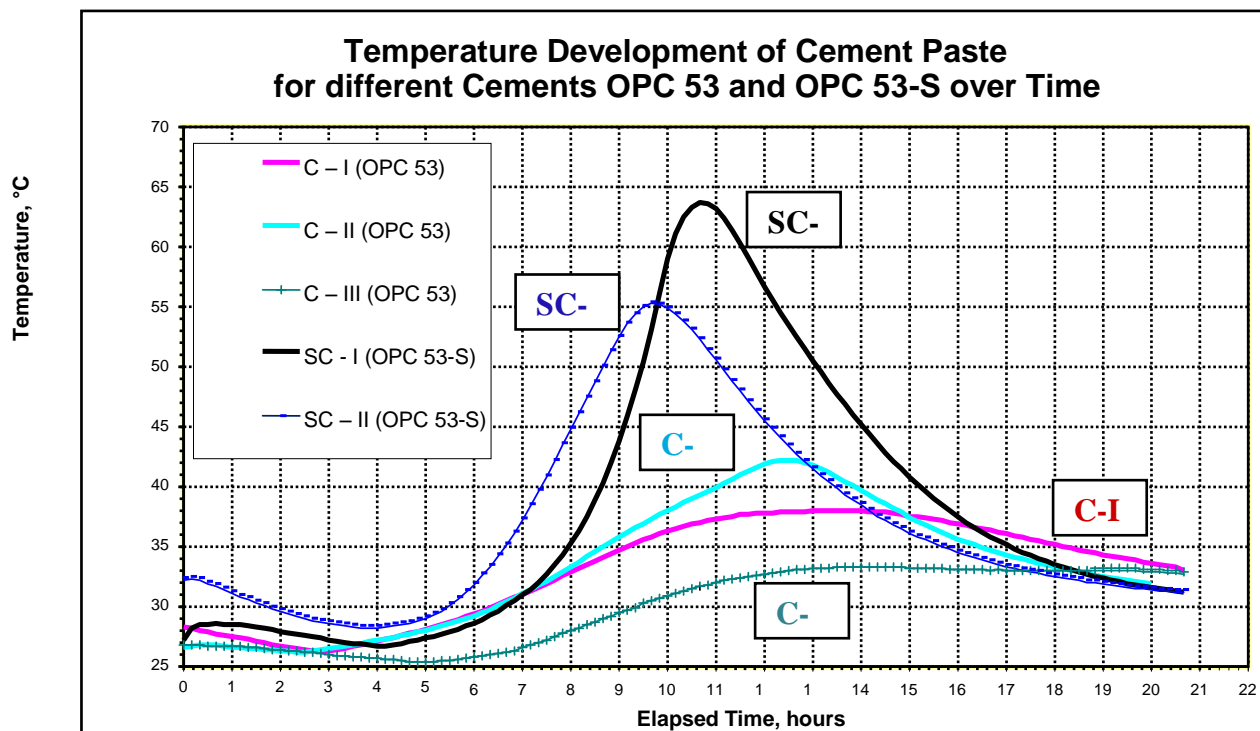


Figure: 2 Temperature rise during hardening of OPC 53 & OPC 53 –S Cements

From the Figure 2(C-I, C-II and C-III are different samples of OPC 53 cements and SC-I & SC-II are two samples of OPC 53-S cements) it can be clearly seen that the rate of temperature rise as well as maximum temperature reached during hydration are considerably higher for OPC 53-S cements as compared to those obtained in the case of OPC 53. The measured heat generation confirms the strength test results and shows that the sampled OPC 53-S cements are better suited than the OPC 53 grade cement for high early strength concrete.

Fine and Coarse Aggregates used

Fine aggregate was river sand conforming to Zone II as per IS 383 [4] with a specific gravity of 2.53 and Fineness Modulus of 2.91. Crushed quarried granite chips were used as coarse aggregate with a specific gravity of 2.96, fineness modulus of 7.36 and water adsorption of 0.4 %.

Super Plasticizer

11 super plasticizers were chosen, two from the Multi carboxylic ether (MCE) family, two from the Sulphonated melamine formaldehyde (SMF) family and 7 from the Sulphonated naphthalene formaldehyde (SNF) family. More number of samples were chosen from SNF family because they are more commonly available than the other types.

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Table: 5 Types of Superplasticizers Used.

S.No	Superplasticizer	Chemical Basis
1	SP-I	Multi carboxylat ether (MCE)
2	SP-II	Sulfonated Melamine Formaldehyde (SMF)
3	SP-III	Sulfonated Melamine Formaldehyde (SMF)
4	SP-IV	Sulfonated Naphthalene Formaldehyde (SNF)
5	SP-V	Sulfonated Naphthalene Formaldehyde (SNF)
6	SP-VI	Sulfonated Naphthalene Formaldehyde (SNF)
7	SP-VII	Sulfonated Naphthalene Formaldehyde (SNF)
8	SP-VIII	Sulfonated Naphthalene Formaldehyde (SNF)
9	SP-IX	Multi carboxylat ether (MCE)
10	SP-X	Sulfonated Naphthalene Formaldehyde (SNF)
11	SP-XI	Sulfonated Naphthalene Formaldehyde (SNF)

The relative compatibility of 11 different samples of super plasticizers were tested using the “Flow Table Method” as per Chinese standard GB 8076-1997 [5] at a water-cement ratio of 0.35. This w/c ratio was chosen because the w/c ratio in the mixes to be designed was expected to be in this region. For the test 100gms of cement was mixed with 35ml of water (water cement ratio of 0.35). After mixing, super plasticizer 1% by wt of cement, was added and the well mixed paste was poured onto a glass plate. The diameter of the spread paste which was used to compare the compatibility of the admixtures. The flow value of this was indicated by the average of the two perpendicularly crossing diameters of flow spread.

In the Marsh Cone Test or Mini Slump Test, after saturation dosage, the Marsh Cone flow time or Mini-Slump spread is more or less remain constant beyond the saturation dosage even up to 1% super plasticizer dosage (according to Jayasree et al. (2010) [6]. Hence the author has selected 1% dosage for each of the super plasticizer to compare the flow characteristics of different super plasticizers.

The flow tests were conducted for compatibility of the different super plasticizers namely Multi carboxylic ether (MCE) , Sulphonated melamine formaldehyde (SMF) and Sulphonated naphthalene formaldehyde (SNF) with OPC 53 grade cement of different samples C-I, C-II and C-III and OPC 53-S grade cement of samples SC-I and SC-II are shown in the Table 6. As many as 11 different super plasticizers were tested with each cement.

Table: 6 Flow Test results on Cement samples both OPC 53 & OPC 53-S with super plasticizers

Super Plasticizer	Cement Samples (Flow in mm)				
	OPC 53 Sample C-I	OPC 53 Sample C-II	OPC 53 Sample C-III	OPC 53-S Sample SC-I	OPC 53-S Sample SC-II
SP – I	18.3	23.2	20.3	20.3	23.0
SP - IX	22.0	20.5	22.0	23.0	24.0
SP – III	13.5	14.9	9.5	9.5	6.5
SP – II	11.8	16.8	7.3	7.3	9.5
SP – IV	17.0	19.3	19.0	19.0	18.3
SP – V	17.5	17.5	18.8	18.5	8.5
SP – VI	19.0	18.0	20.5	21.5	22.0
SP – VII	0.00	17.8	20.0	20.0	21.0
SP – VIII	18.5	17.8	19.8	22.0	22.0
SP – X	17.8	17.0	19.5	13.0	14.0
SP - XI	18.5	16.5	18.5	18.5	19.0

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From the flow characteristics shown in table 6, it can be seen that the Multi carboxylic ether (MCE) group of super plasticizers have shown very good characteristics for all cement samples, whereas the Sulphonated melamine formaldehyde (SMF) super plasticizers did not show much of a flow in all the 5 cement samples. The performance of the Sulphonated naphthalene formaldehyde (SNF) group also was good for 4 samples out of 5 cement samples but somewhat inconsistent in one sample. Hence for further studies super plasticizers from the two groups Multi carboxylic ether (MCE) group and Sulphonated naphthalene formaldehyde (SNF) group were considered. It was observed in general that the super plasticizers belonging to SMF group gave relatively lower flow compared to the super plasticizers of the other two groups.

Heat of Hydration of Cement Paste with Super Plasticizer

It is known that plasticizing admixtures have the tendency to retard the cement hydration to a certain extent. The retarding potential of the investigated admixtures were tested by measuring the temperature gain of a cement paste with and without admixture over time. The cement paste was prepared as mentioned for the measurement of the hydration heat. For the paste with super plasticizer, 1% of the respective super plasticizer was added. The temperature development was then measured in thermos containers as mentioned. The temperature developments for different super plasticizers for one particular cement SC-II of OPC 53-S grade are shown in Figures 3 to 5.

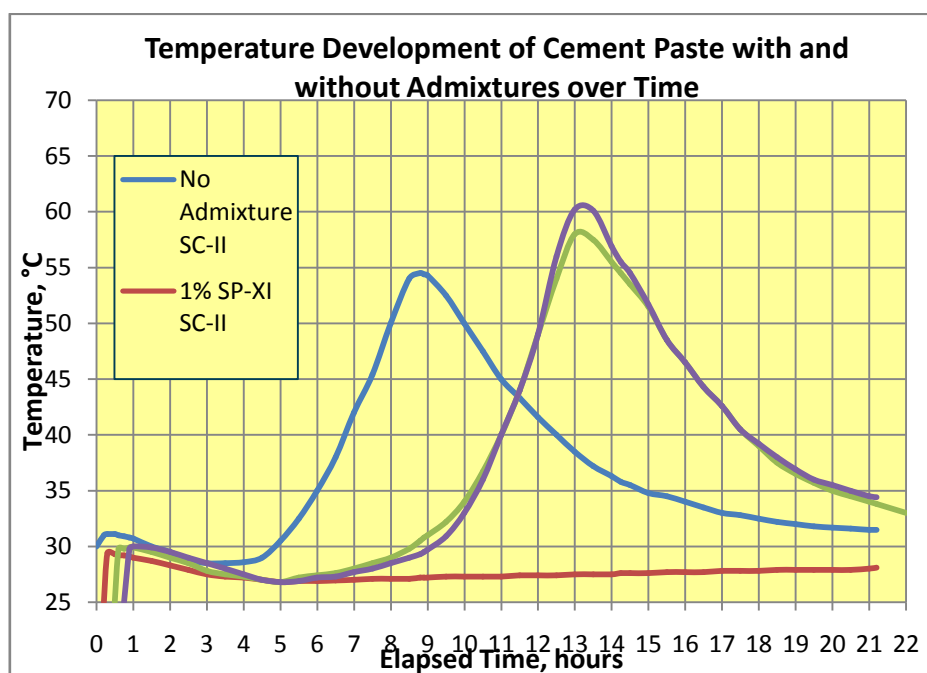


Figure:3 Retarding Effect of Super plasticisers with OPC 53-S cement of sample SC-II

In Figure 3 the cement paste with SP-XI is not gaining any temperature within 21 hours and subsequently no strength could be developed. The conclusion of the temperature graph could be confirmed by the still liquid cement paste extracted from the thermos container after 21hours. Hence super plasticizer SP-XI is not considered for further tests because of delay in attaining the temperature.

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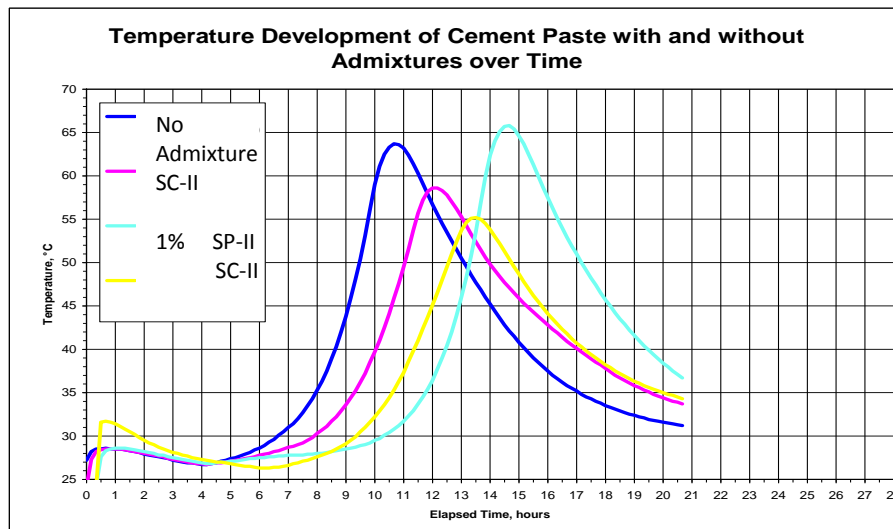


Figure:4 Retarding Effect of Super plasticizers with OPC 53-S cement of sample SC-II

That an increase in the super plasticizer dosage leads to an increased retardation (1% SP-II and 2% SP-II) is shown in Figure 4.

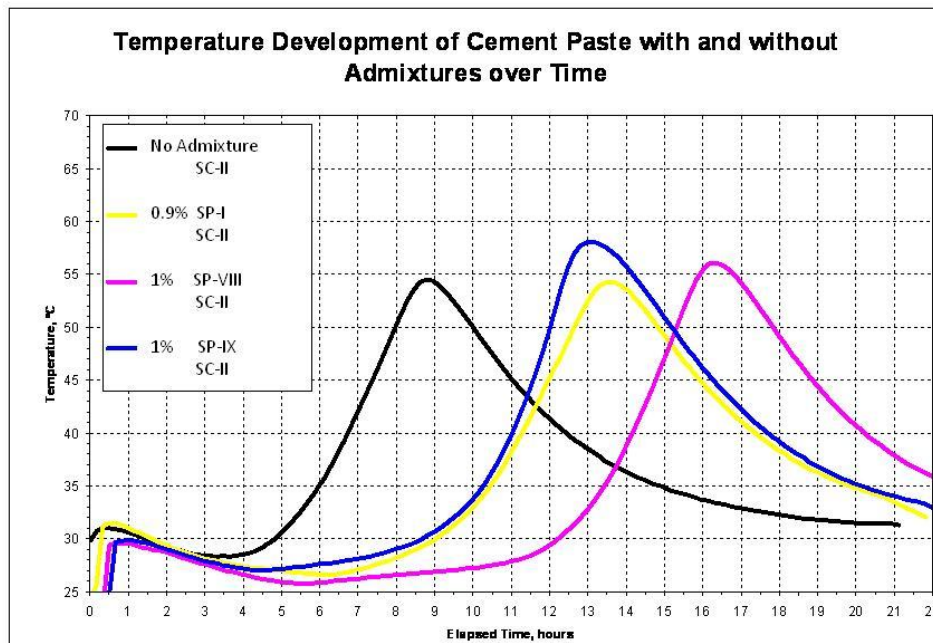


Figure:5 Retarding Effect of Super plasticizers with OPC 53-S cement of sample SC-II

All super plasticizers shown in Figure 5 are retarding, this can be seen by the delay in temperature increase compared to the reference mix without admixture. While SP-I and SP-IX retard the cement by about 3 – 4 hours and SP-VIII is retarding by 7-8 hours.

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III. EXPERIMENTAL RESULTS

Procedure for selection of Super Plasticizer

From the flow performance test and from the heat of hydration test shown in Figures 3 to 5 of different super plasticizers with OPC 53-S, the flow values and the temperature gain for the tested super plasticizers with the OPC 53-S cement are given in Table 7 and in Figure 6

Table: 7 Super plasticizer flow in mm and rate of gain of temperature with OPC 53-S Cement of sample SC-II

Super Plasticizer	Flow in mm	Dosage of super plasticizer	Rate of gain of temperature
No Super Plasticizer	--	--	55°C at 9 hrs
SP – I	23.0	0.9 %	55°C at 13.5 hrs
SP – II	9.5	1 %	58°C at 12 hrs
SP – II	9.5	2 %	65°C at 14.5 hrs
SP – V	8.5	0.9 %	55°C at 13.5 hrs
SP – VIII	22.0	1 %	55°C at 16 hrs
SP – IX	24.0	1 %	55°C at 13 hrs
SP – X	14.0	1 %	60°C at 13 hrs
SP – XI	19.0	1 %	No gain of temp.

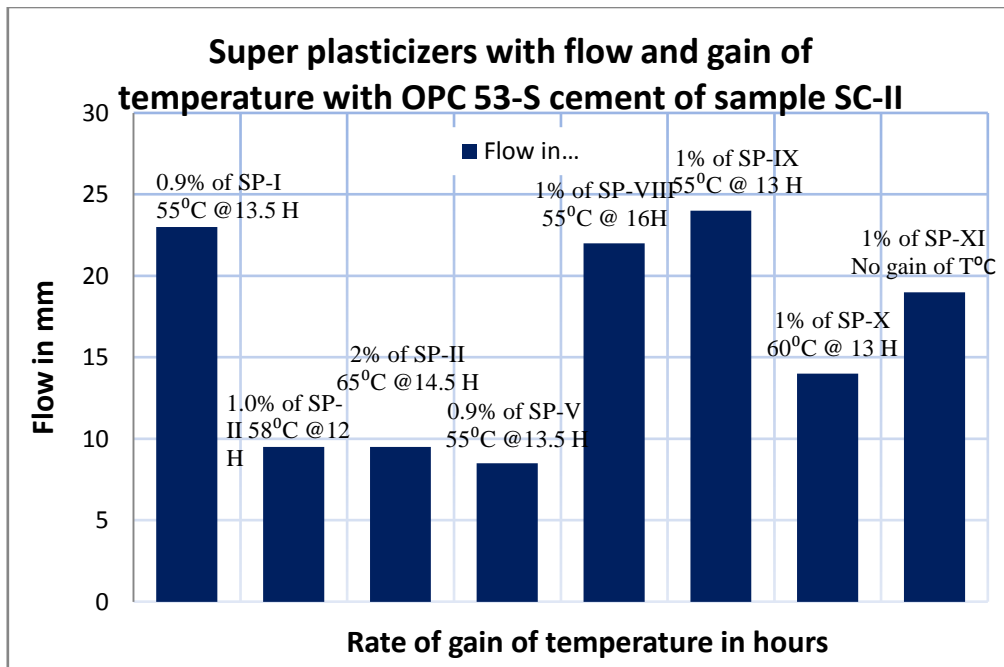


Figure: 6 Rate of gain of temperature and flow for the tested Super Plasticizers with dosages

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From the above graph the super plasticizers SP-I and SP-IX of MCE group and SP-VIII of SNF group are having higher flow as well as rate of gain of temperature is almost same. Hence from amongst the super plasticizers tested they can be considered to be better suited for use with OPC 53-S grade cement.

IV. CONCLUSION

1. The heat of hydration generated during hardening of OPC 53-S is much more than in the case of OPC 53 (Figure 3) and this is another characteristic highlighting the difference in the behaviour of OPC 53-S and of OPC 53. The is quite acceptable for making elements of relatively thinner dimensions where heat dissipation is quite large. But in case of mass concrete works proper attention should be taken with use of OPC 53-S cement.
2. Sulphonated melamine formaldehyde (SMF) super plasticizers did not show much of a flow in all the tested cement samples.
3. Multi Carbaxylat ether (MCE) super plasticizer [SP-I (or) SP-IX] gives higher flow with OPC 53-S cement and retard the cement by about 3 – 4 hours and SP-VIII of Sulfonated Naphthalene Formaldehyde (SNF) super plasticizer is retarding by 7-8 hours.
4. An increase in the super plasticizer dosage leads to an increased retardation (1% SP-II and 2% SP-II) was observed.
5. Investigations have shown that the results from cement-super plasticizer compatibility tests can be taken only as guidelines and final confirmation of the usefulness of the super plasticizer is to be proved only by a trial concrete mix.

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