

Portland Cement Hydration in the Presence of Admixtures – Black Gram Pulse and Superplasticizer

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Effect of admixtures such as black gram pulse (BGP) and sulfonated naphthalene based superplasticizer (SP) on the hydration of Portland cement has been studied. The hydration characteristics of OPC in the presence of BGP and SP were studied with the help of non evaporable water content determinations, calorimetric method, Mössbauer spectroscopic and atomic force microscopic techniques. Results have shown that both BGP and SP get adsorbed at the surface of cement and its hydration products. The hydration of Portland cement is retarded in the presence of both the admixtures and nanosize hydration products are formed.

Keywords: Mössbauer spectroscopy, black gram pulse, superplasticizer, nano size

1. Introduction

Concrete is one of the most widely used building material in the world, but the fundamental mechanisms underlying its behaviour are very poorly understood, due to its physical and chemical complexity^{1,2}. Cement is the main binding component of the concrete and the process of hydration proceeds in a very complex manner. In spite of a large number of research work the mechanism of cement hydration is still not fully understood^{1,2}. The hydration of cement involves series of reactions, which mainly depend on the cement composition, the water / cement ratio, surface area, particle size distribution, temperature and admixtures. Admixtures when added in small quantities make the hydration process much more complex. Organic admixtures are widely used in concrete and mortar for several decades to modify the properties of cement products^{3,4}. In recent times, advances in the field of cement products are related to the use of admixtures particularly organic polymeric materials. These additives modify physico – chemical, physico – mechanical and microstructural properties of cement and concrete. Many type of organic polymeric materials, known as superplasticizers, are being used in construction industries to alter the flow behaviour and the mechanical properties of concretes^{5,6}. Superplasticizers have a strong influence on the kinetics and setting characteristics of hydrating cement pastes and are introduced to cementitious systems in order to improve the rheological properties. The rheological properties of fresh cement paste are controlled by many factors, for instance by the dispersion characteristics between particles due to the mixing technique, type and amount of superplasticizers added, type and amount of hydration products, particle packing etc. They also modify the microstructures and change the particle size of the hydration products. The basic advantages of superplasticizers include i) high workability of concrete, resulting in easy placement without reduction in cement content and strength; ii) high strength concrete with normal workability but with lower water content; and iii) a concrete mix with less cement but of normal strength and workability. In addition to several of advantages of superplasticizers there are number of problems also. Some problems which could not

be solved or less understood, are: production of stiffness in concrete, variation of initial slump, and large slump loss of concrete prepared using some types of cement with a constant weight of the admixture, large variations in the flow of concrete prepared from some kind of superplasticizer with the same cement, etc.

However in recent years the superplasticizers are playing more important role in the preparation of ultrahigh performance concretes as compared to the cement itself. Since the amount of superplasticizers used in high performance concretes have increased, the cost is either comparable to that of the cement or even become higher. It is reported that new superplasticizers very often play more important role in concrete than new cements⁷. Further the role of superplasticizers during the hydration of cement is very complex and not fully understood⁸⁻¹⁰.

In view of high cost of the superplasticizers, it is essential to search some cheaper admixtures which may give effects similar to those of the superplasticizers and at the same time they should be ecofriendly. Many natural organic materials have been used as admixtures in cements and concretes in ancient times but the mechanism of their action was not known. Chandra and Aavik¹¹ tried to understand the role of black gram (natural organic material) as admixture in cement mortar and concrete. They found that black gram containing organic polymeric materials works parallel to the synthetic polymeric admixtures, say superplasticizers. However, they could not clarify the mechanism of action of naturally occurring admixtures. Further the emergence of nanoscience^{12,13} applications in cement chemistry seems to give a more significant impact on the understanding of classical reactions that occur in the cement-water system.

Therefore, there is a need to understand the mechanism of action of commercial superplasticizers (an industrial product) and naturally occurring ecofriendly admixture during the hydration of cement and to compare their effectiveness. In the present paper the effect of sulfonated naphthalene polymer, a superplasticizer (SP) and black gram pulse (BGP), a naturally occurring organic material (much cheaper

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than superplasticizer) on the hydration of Portland cement has been studied and the mechanism is discussed in the light of nanoscience.

2. Experimental

2.1. Materials

Ordinary Portland cement (Vikram premium OPC 53) commonly referred as OPC was used for the hydration studies. The cement contains 38.9% tricalcium silicate (C_3S), 31.8% dicalcium silicate (C_2S), 6.1% tricalcium aluminate (C_3A), 13.4% tetracalcium aluminoferrite (C_4AF) and 2.5% gypsum as SO_3 . Urad or black gram pulse (BGP) in fine powder form was used as a naturally occurring admixture and its chemical composition¹⁴ is given in Table 1.

Sulfonated naphthalene superplasticizer (SP) was used as an admixture and it is commercially available as Resikon SP 110 (brown liquid instantly dispersible in water). It was supplied by Anuvi Chemicals Private Limited, Badlapur, Dist., Maharashtra. Resikon SP 110 complies to IS 9103:1979 and IS 2645:1975 specifications.

2.2. Methods

2.2.1. Preparation of hydrated samples

10 g of Portland cement was taken in a polythene bag and mixed with 5 mL water so that water to cement (w/c) ratio becomes 0.3. It was thoroughly mixed in a mixer for 2 minutes. The air inside the polythene bag was removed to avoid carbonation and then sealed. The hydration reactions were allowed to continue at room temperature ($\approx 28^\circ C$). The hydrations at different intervals of time (1, 3, 7, 14 and 28 days) were stopped with isopropyl alcohol and diethyl ether. In a similar way, other samples were made in the presence of 2.0 and 5.0 wt. (%) BGP and 2.0 wt. (%) SP. The hydrated samples were heated at $105^\circ C$ for 1 hour in order to remove the adsorbed water. The dried samples were stored in polythene bags and kept in a desiccator.

2.2.2. Determination of non-evaporable water contents

Approximately one gram of the hydrated OPC in the presence and absence of 2.0 wt. (%) BGP and SP were weighed in ceramic crucibles and heated at $105^\circ C$ for 1 hour and then at $1000^\circ C$ for 1 hour. From mass losses the non-evaporable water contents were calculated.

2.2.3. Spectroscopic studies of adsorption of BGP and SP on OPC surface

Absorption spectra of 1 wt. (%) BGP and SP solutions were recorded with a Systronics Spectrophotometer in the wavelength range of 200–500 nm. 100 mL solutions were shaken well for 5 minutes

with 1 g OPC and filtered. The spectra of the filtrate were recorded. From the decrease in absorbance, the amount of BGP/SP adsorbed on cement surface was assessed.

2.2.4. Heat evolution measurements

The heats of hydration of OPC in the absence and presence of 2.0 wt. (%) BGP and 2.0 wt. (%) SP were determined with the help of 8 probe TAM AIR calorimeter at $20^\circ C$ in a way similar to that described earlier¹⁵. The water-solid ratio was kept to be 1.0. For this, following systems

10 g cement + 10 g water

9.8 g cement + 0.2 g BGP + 10 g water

10 g cement + 10 g water solution of 2.0 wt. (%) SP

Were taken in glass vials and vibrated for one minute in order to have homogeneous mixing and then kept in a calorimeter at $20^\circ C$. The heat flow as a function of time was recorded using quartz powder as a reference.

2.2.5. AFM studies

The surface topography of the cement hydrated for 3 days in the absence and presence of 2.0 wt. (%) SP were studied using AFM (Molecular Imaging, MI, USA with Model PICOSPM).

2.2.6. Mössbauer spectroscopic studies

Mössbauer spectroscopic data were recorded on anhydrous ordinary Portland cement and hydrated for 1 day in the absence and presence of 5.0 wt. (%) BGP and 2.0 wt. (%) SP. ^{57}Co source in Rh matrix with 25 mCi activities was used in Mössbauer spectrometer and the velocity drive was kept in constant acceleration mode. The calibration was done with an iron foil of natural abundance. The spectra were recorded at room temperature (298 K) and at low temperature (77 K). The absorbers for the measurements were prepared by taking 50 mg.cm⁻² of the powdered sample sandwiched between two cellophane tapes inside a copper ring. The scattering effects due to the presence of other non - Mössbauer constituents were compensated through improved statistics by storing more than ten lakhs of counts per channel in each case. Isomer shift is given relative to α -iron at room temperature. The evaluation of Mössbauer spectra were carried out by method of least-square fitting of Lorentzians.

3. Results and Discussion

Variations of non-evaporable water contents with hydration time in the absence and presence of 2.0 wt. (%) BGP and SP are shown in Figure 1. The non-evaporable water contents increased with hydration time and the values are lower in the presence of 2.0 wt. (%) SP and BGP as compared to that of control. This simply indicated that the admixtures retard the hydration. Lower the value of non-evaporable water content, higher the retardation. Thus for same concentration, BGP is a better retarder for OPC hydration than SP.

The heat flow as a function of time during the hydration of cement in the absence and presence of 2.0 wt. (%) BGP and SP are shown in Figure 2. In the case of reference, the curve is divided into five parts: 1) rapid heat evolution due to cement wetting, dissolution of alkalis, dissolution of hemihydrates and hydration of C_3A and its reaction with gypsum 2) induction period where the hydration products acquire certain critical size 3) as soon as the critical size is reached, the nucleation and crystal growth starts, hydration accelerates with time and reaches to a maximum value. In this stage mainly the hydration of alite phase occurs. One of the hydration products

Table 1. Composition of Indian Black gram (BGP)¹⁴.

Constituents	Amount (g/100 g)
Reducing sugar	0.2
Non reducing sugar	3.1
Starch	49.1
Protein	20.2
Fat	1.7
Crude fibre	7.2
Moisture	11.1
Ash	3.6

is C-S-H, which may be of nanometer size. 4) deceleration period where the rate of heat evolution decreases with hydration time due to the formation of large amount of hydration products and 5) the last stage in which the rate of reaction is very slow and the reaction is diffusion controlled. 2.0 wt. (%) SP and BGP modify different stages of rate of heat evolution, the induction period increased and the maximum rate of heat evolution shifted towards much longer time. The results show that for the same concentration, BGP is a better retarder than SP. Spectroscopic studies have shown that both BGP and

SP get adsorbed at the surface of cement and its hydration products. Extent of retardation indicates that probably the adsorption of BGP is more than that of SP on the cement surfaces. Thus the retardation of hydration of cement is due to adsorption of BGP/SP at the surface of cement/hydration products.

In addition to silicate and aluminate phases Portland cement also contains 4CaO, Al_2O_3 , Fe_2O_3 (C_4AF) mineral phase. X ray crystallographic studies have shown that iron occupies both octahedral and tetrahedral sites. However, due to the presence of other mineral phases in the cement, the bonding of iron may be altered resulting into distortion of the octahedral and tetrahedral sites. Due to hydration in the presence and absence of BGP and SP, there may be some changes in the iron environment which have been studied with the help of Mössbauer spectroscopy.

Mössbauer spectra of anhydrous OPC and hydrated for 1 day in the absence and presence of 5.0 wt. (%) BGP and 2.0 wt. (%) SP were recorded at 298 K and 77 K (Figure 3). Mössbauer parameters viz; Quadrupole splitting (ΔEQ), Isomer shift (δ) and line width values are given in Tables 2 and 3. Results showed that iron is in +3 state with an octahedral and tetrahedral environment in C_4AF phase of OPC. Mössbauer parameters of OPC hydrated for one day at 298 K shows a combination of two doublets. The first doublet with higher value of quadrupole splitting seems to be due to Fe^{3+} at the octahedral site, while the second doublet with smaller value of quadrupole splitting¹⁶ is due to the tetrahedral Fe^{3+} .

Mössbauer spectra of OPC, hydrated for one day in the presence of 5.0 wt. (%) BGP show only one doublet instead of two as found in the absence of BGP. The Mössbauer parameters of the doublet correspond to Fe^{3+} in octahedral sites in both the cases. The absence of another doublet corresponding to Fe^{3+} in tetrahedral sites may be due to retardation of hydration in the presence of BGP. In the presence of 2.0 wt. (%) SP Mössbauer spectra gives two doublets. The Mössbauer parameters in the presence of BGP and SP are different. This indicates different extent of adsorption on cement surfaces and retardation of hydration.

Low temperature (77 K) and room temperature (298 K) Mössbauer spectra of anhydrous OPC are almost identical. Mössbauer spectra of OPC hydrated for 1 day at 77 K show a combination of two doublets. The first doublet seems to be due to Fe^{3+} at the octahedral site, while the second doublet may be due to tetrahedral site of Fe^{3+} . The Mössbauer spectra of OPC hydrated for 1 day in the presence of 5.0 wt. (%) BGP show one doublet and one sextet. In the sextet, the first and sixth lines clearly show that the particles are small enough to show the supermagnetic phenomenon. As we go to lower temperature i.e. below the blocking temperature, the spins of the atoms get blocked, meaning thereby that the relaxation time is of the order of 2.5×10^{-9} sec. The blocked spins at this stage appear like a magnetic material showing magnetic sextet. The presence of doublet and sextet indicate wide particle size distribution in the cement. Supermagnetic doublet shows that the major fraction is in single domain range and

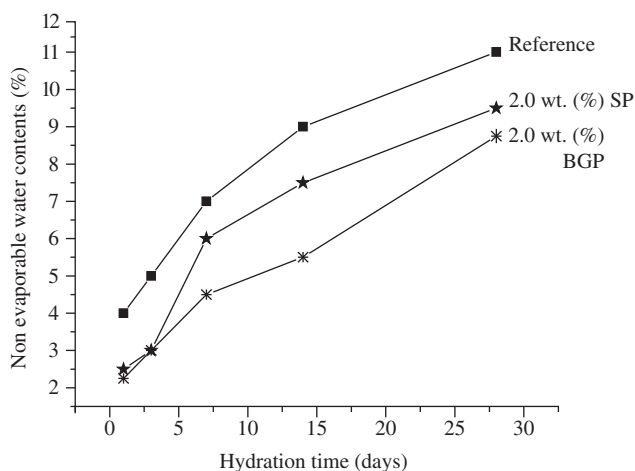


Figure 1. Non-evaporable water contents of OPC hydrated for different days in the absence and presence of 2% SP and 2% BGP.

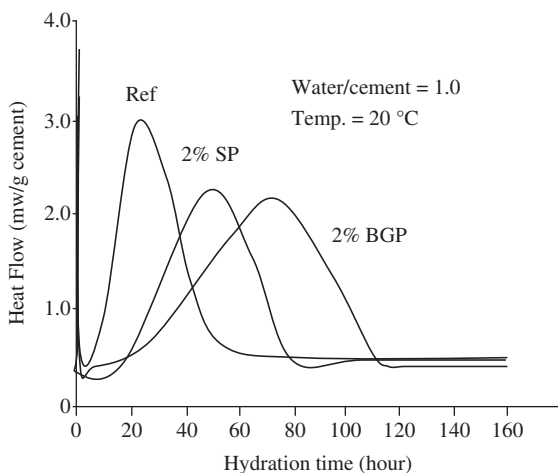


Figure 2. Variation of rate of heat evolution with hydration time in the absence and presence of 2.0 wt. (%) SP and 2.0 wt. (%) BGP.

Table 2. Mössbauer parameters of OPC samples at room temperature (298 K).

Samples	Iron sites	Isomer shift (δ) mm/s	Quadrupole splitting (EQ)mm/s	Width (Γ) mm/s	Area (%)
Anhydrous OPC	Doublet	0.297	1.658	0.549	100
OPC hydrated 1 day	Doublet 1	0.271	1.64	0.536	53
	Doublet 2	0.311	0.69	0.511	47
OPC hydrated in the presence of 5%BGP- 1 day	Doublet	0.296	1.652	0.552	100
OPC hydrated in the presence of 2%SP- 1 day	Doublet 1	0.28	1.75	0.46	53
	Doublet 2	0.26	1.06	0.50	47

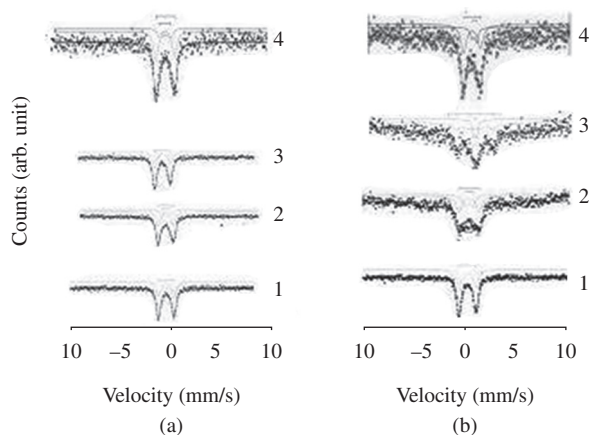


Figure 3. Mössbauer spectra of 1 - OPC, 2 - OPC hydrated for 1 day, 3 - OPC hydrated for 1 day in the presence of 5.0 wt. (%) BGP and 4 - OPC hydrated for 1 day in the presence of 2.0 wt. (%) SP: at a) 298 K and b) 77 K.

the particles are in nanometer size range. The high value of isomer shift also corroborates the ultrafine nature of the particles containing Fe^{3+} ions. The Mössbauer spectra of OPC hydrated for 1 day in the presence of 2.0 wt. (%) SP at 77 K is identical to that at 298 K. The isomer shift values at 77 K are higher than those of at 298 K indicating the presence of ultrafine particles containing Fe^{3+} ions. BGP and SP act in a different way.

Mössbauer spectroscopic studies clearly indicate that BGP and SP modify the hydration behaviour of C_4AF phase in such way that the electronic environment around Fe^{3+} ions becomes asymmetric and hydration products of nanometer size range are formed.

AFM images of Portland cement hydrated for 3 days in the absence and presence of 2.0 wt. (%) SP are shown in Figure 4. The photographs show that the hydration products are of nanometer size.

4. Conclusions

From the results following conclusions have been made.

Both the admixtures BGP and SP retard the hydration of OPC.

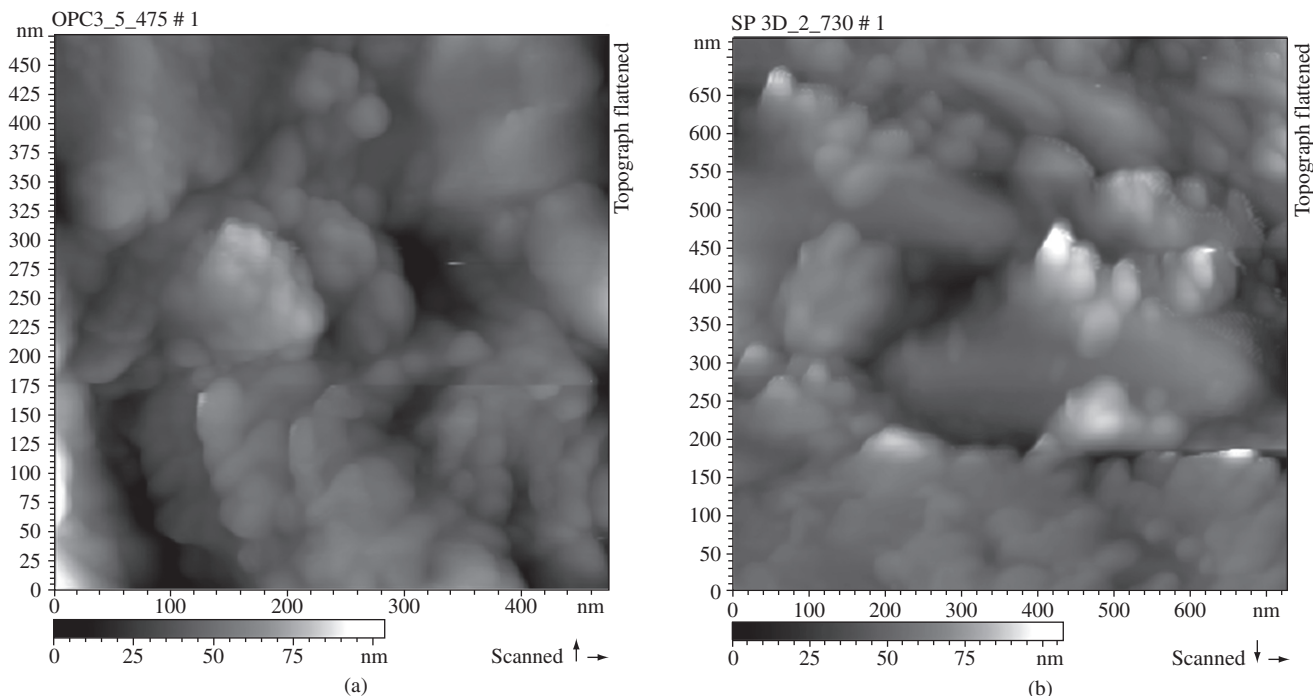


Figure 4. AFM pictures of a) OPC hydrated for 3 days b) OPC hydrated for 3 days in the presence of 2.0 wt. (%) SP.

Table 3. Mössbauer parameters of OPC samples at 77 K.

Samples	Iron sites	Isomer shift (δ) mm/s	Quadrupole splitting (ΔEQ) mm/s	Width (Γ) mm/s	Area(%)	Hyperfine field(H_f) Tesla
Anhydrous OPC	Doublet	0.38	1.66	0.55	100	-
OPC hydrated 1 day	Doublet 1	0.36	1.97	0.60	53	-
	Doublet 2	0.37	0.71	0.56	47	-
OPC hydrated in the presence of 5% BGP- 1 day	Doublet	0.380	0.316	0.317	80	-
OPC hydrated in the presence of 2% SP- 1 day	Sextet	0.40	0.13	0.829	20	19.11
	Doublet 1	0.65	0.50	0.39	16	-
	Doublet 2	0.42	1.77	0.70	84	-

For the same concentration (2.0 wt. (%)) BGP is better retarder than SP and the retardation is due to adsorption on cement/hydration products surfaces.

Mössbauer spectral parameters in the presence of BGP and SP are different, indicating different extent of adsorption on the cement surfaces.

Mössbauer spectroscopic studies have clearly indicated that BGP and SP modify the hydration behaviour of C_4AF phase of OPC in such a way that the electronic environment around Fe^{3+} ions becomes asymmetric and hydration products of nanometer size range are found.

AFM studies have shown that hydration products formed are of nanosize.

BGP being naturally occurring and ecofriendly admixture is much cheaper than superplasticizer and can act as a good retarder. However, before it is used as admixture, further work is needed.

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