

Modifications in water resistance and engineering properties of β -calcium sulphate hemihydrate plaster-superplasticizer blends

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Abstract In this study, the effect of sulphonated naphthalene formaldehyde condensate (SNF) and polycarboxylate (PC) superplasticizers on the performance of β -calcium sulphate hemihydrate plaster has been discussed. A considerable improvement in the properties of β -hemihydrate plaster was observed with an increase in superplasticizer content. For 0.6 wt% SNF and PC content, a reduction of 18–20 % in water requirement is obtained and contributes 71–75 % enhancement in the compressive strength of modified pastes as compared to reference sample. The influence of superplasticizers on the hydration characteristics and morphology of the gypsum crystals have been studied using IR, SEM and Electrical Conductivity techniques. These studies indicate a significant influence of superplasticizers on the growth rates of the hydrates and leads to the formation of a dense and well compacted texture of crystals, thereby imparting high strength and better water resistance to the gypsum matrix than the reference material.

Keywords Superplasticizer · Phosphogypsum · Hydration · Strength · Morphology

1 Introduction

Gypsum is one of the oldest building materials widely used in the construction industry since time immemorial. It is a mineral which is available in the nature worldwide. The global annual production of gypsum in 2008 was estimated to be 250 million tonnes approximately [26]. Besides natural gypsum, various industries also generate gypsum as a by-product of their chemical processes such as phosphoric acid, hydrofluoric acid, tartaric acid and citric acid production. Phosphogypsum is an industrial by-product obtained during the manufacture of phosphoric acid. For every tonne of phosphoric acid produced, about five tonnes of phosphogypsum is yielded. The generation of the waste phosphogypsum is around 280–300 million tonnes per annum throughout the world. However, the average annual production of this material in India is about 6.5 million tonnes. Phosphogypsum has been studied as a starting material for making plaster products, as a set regulator in the manufacture of Portland cement, as a supplementary material in cementitious binders and in various building applications [12, 25]. Despite this, currently only about 15–20 % of phosphogypsum is used in soil and road stabilization. Usually, a huge amount of this waste is deposited in the open areas or is dumped

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elsewhere thus occupying considerable landfill space, creating environmental pollution and health hazards. As a measure to save natural gypsum resources, reduce the negative effects of disposal, offer environmental benefits and reuse industrial by-products for sustainable development, comprehensive utilization of phosphogypsum should be paid more attention.

Gypsum products have been used extensively as indoor building components because of their aesthetic characteristics, fine finish, easy fabrication feature, sound and thermal insulation behavior, etc. They are also environmental friendly since gypsum is a non-toxic mineral and is therefore, harmless to human life. Moreover, gypsum has a much lower calcination temperature than cement and thus requires much lower energy input, thereby conserving energy resources and offering greenhouse benefits. However, in spite of these advantages they are limited to interior applications and are not preferred for use in external moist or damp situations because of their sensitivity to water (solubility 2 g/l). For the wider application of gypsum elements in the construction industry, it is necessary to modify their properties so that they may exhibit longer service life. In recent years, several research studies have been conducted to explore the possibilities for improving the performance of phosphogypsum to adapt to various industry needs. The literature survey revealed that the mechanical properties and water stability of gypsum plaster were improved by the addition of supplementary cementitious materials such as granulated blast furnace slag, fly ash, lime, silica fume, etc. [16, 17, 22]. These systems acquired acceptable strength and water resistance during different curing conditions. Besides this, a wide variety of chemical admixtures including epoxy resins, latexes, metal stearates, siliconates, acrylics and methacrylate polymers have also been used by various researchers to improve the performance of gypsum based composite materials. Polymer impregnation has been used to improve the properties of gypsum products. Impregnating a monomer into the inorganic matrix, followed by polymerization not only improves the strength characteristics of the composite material, but also its durability due to the formation of a cross-linking network of polymer which coats the gypsum particles and fills the pores. Stav and Bentur [24] studied the hydration reactions and early-age properties of a system consisting of calcium sulphate hemihydrate and acryl amide monomer. In another

study [10] modification of plaster of Paris through filler additions like sand, cement, fly ash, epoxy, etc. followed by the impregnation of monomer and its subsequent polymerization lead to a perceptible improvement in the strength of the gypsum composites. Avalos et al. [3] reported that the addition of 10 % latex increased the flexural strength of the β -hemihydrate plaster from 8.9 MPa to 11.5 MPa. Studies undertaken by several research workers [4, 11] confirmed the significant increase in the mechanical characteristics of gypsum as a result of reinforcement using synthetic or natural fibres. Arikian and Sobolev [2] studied the effect of superplasticizer in conjunction with a retarding, air-entraining admixture and a water-soluble polymer on the engineering properties of gypsum composites. Kovler [16] studied the influence of superplasticizer on the temperature and setting expansion of gypsum-cement-silica fume blends. However, the literature survey revealed that considerable work has been done on the application of superplasticizer in cement, mortar and concrete [1, 8, 14] but with respect to gypsum based materials, the researches largely lag behind. Very limited studies [13, 20] have been attempted on the application of superplasticizer in gypsum plasters. Accordingly, the influence of superplasticizer on the performance of gypsum plaster needs to be extensively evaluated.

Along these lines, the present work aimed to analyze the effect of sulphonated naphthalene formaldehyde condensate and polycarboxylate type superplasticizers on the properties of β -calcium sulphate hemihydrate plaster. The microstructural characteristics, hydration and hardening processes of the SP-modified plasters were studied using the scanning electron microscopy (SEM), infrared (IR) spectroscopy and electrical conductivity techniques.

2 Experimental procedure

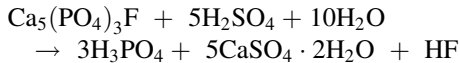
2.1 Raw materials

2.1.1 β -Calcium sulphate hemihydrate (β -CaSO₄·1/2H₂O)

In the commercial industrial process of phosphoric acid manufacturing, pulverized phosphate rock is treated with sulphuric acid. Besides the main product which is phosphoric acid (H₃PO₄), a small quantity of



hydrofluoric acid and by-product phosphogypsum are obtained:



Phosphogypsum (PG) primarily consists of calcium sulphate dihydrate with some impurities of phosphates, fluorides, alkalis, organic substances, etc. that adhere to the surface of the gypsum crystals or are built up in the crystal lattice. These impurities adversely influences the quality of plasters produced from phosphogypsum. It is therefore desirable that the reduction or inactivation of these impurities in PG should be done prior to its use. The process of beneficiation of phosphogypsum sample (procured from Ankleshwar, Gujarat) was carried out in the pilot plant installed at Central Building Research Institute, Roorkee which includes solubilization of impurities in water and rejection of coarse fraction (<10 %) retained over 300 micron IS sieve. The bulk of gypsum passing through the sieve is further washed, centrifuged to remove water soluble impurities and dried in the rotary drier as reported by Singh et al. [23]. The unbeneficiated and beneficiated PG samples were analyzed for their chemical constituents (Table 1) by X-ray fluorescence spectroscopy (Model: S8, Make: Bruker, German) and as per the standard test procedures (BIS 1288) [6].

β -hemihydrate gypsum plaster (β -CaSO₄·1/2H₂O) was produced by calcining beneficiated phosphogypsum at 150–160 °C. The calcination process was carried out for a period of 4 h in an electric oven with spatulation at regular intervals. On heating at 150 °C,

gypsum loses about 14.7 % of water of crystallization in the form of steam, resulting in the formation of β -hemihydrate plaster which contains about 6.0 % of the remaining water of crystallization. The plaster is then ground in a ball mill to a fineness passing 150 micron IS sieve.

2.1.2 Superplasticizers

Two commercially available superplasticizers (SPs), namely sulfonated naphthalene formaldehyde condensate (SNF) and spray-dried pure polycarboxylate (PC) were used for this study. SNF represents a traditional class of superplasticizer, whereas PC is a relatively new generation SP. The properties of the superplasticizers are presented in Table 2.

2.2 Methodology

2.2.1 Preparation of test specimens

Different compositions of samples were prepared in order to investigate the effect of addition of varying concentrations of SNF and PC superplasticizers on β -calcium sulphate hemihydrate plaster. These compositions, designated as N1–N8 and P1–P8, were prepared by adding SNF and PC superplasticizers, respectively in a dosage range of 0.1–1.2 % (by wt.) to gypsum plaster (Table 3). A control sample comprising of 100 % β -hemihydrate gypsum plaster to which no superplasticizer was added, is used as the reference (R) material. A homogeneous paste of the gypsum plaster containing the SPs was prepared manually by

Table 1 Chemical composition of phosphogypsum

Constituents (wt%)	Unbeneficiated phosphogypsum	Beneficiated phosphogypsum	IS: 12679 [5] Limits
P ₂ O ₅	0.52	0.25	Max. 0.40
F	0.42	0.20	Max. 0.40
Organic matter	0.05	0.02	Max. 0.15
SiO ₂ + Insoluble residue in HCl	0.95	0.80	–
Al ₂ O ₃ + Fe ₂ O ₃	0.45	0.32	–
CaO	31.10	32.40	–
MgO	0.09	0.06	–
SO ₃	44.90	45.60	–
Na ₂ O + K ₂ O	0.40	0.15	Max. 0.30
Loss on ignition	19.80	19.40	–
pH	3.5	6.5	Min. 5.0

Table 2 Characteristics of superplasticizers

Designation	SNF	PC
Chemical Origin	Sulfonated naphthalene formaldehyde condensate	Polycarboxylic ether
Form	Liquid	Solid
Color	Dark brown	Yellowish brown powder
pH value (20 °C, $c = 20\%$ solution)	6.5–8.5	6.0–8.0
Bulk density (kg/m^3)	–	500–600
Specific gravity	1.20 ± 0.02	–
Water content (%)	–	Max. 2.0
Air content (%)	<1.0	–
Chloride content (%)	Nil	0.01
Solid content (%)	<3.0	–

Table 3 Mix compositions of β -hemihydrate gypsum plaster with SNF and PC superplasticizers

S.No.	SNF Superplasticizer (%)	PC Superplasticizer (%)
1	0.1 (N1)	0.1 (P1)
2	0.2 (N2)	0.2 (P2)
3	0.4 (N3)	0.4 (P3)
4	0.5 (N4)	0.5 (P4)
5	0.6 (N5)	0.6 (P5)
6	0.8 (N6)	0.8 (P6)
7	1.0 (N7)	1.0 (P7)
8	1.2 (N8)	1.2 (P8)

admixing it with water for a period of 60 s. Prior to mixing, water was allowed to soak into the dry plaster powder for a minute. This allowed easy and lump-free mixing. The quantity of water required to produce a paste giving standard consistency was determined according to Indian Standard (BIS 2542—[7] Part I). The test is carried out by filling the sample paste into the ring mould followed by lifting it up to allow a free flow of the paste and spread over a clean, dry and non-sticky horizontal base plate. The diameter of the spread measured using a scale should lie within a range of 100 ± 3 mm for standard consistency. Immediately after mixing, the pastes were cast into cubes of size $25 \times 25 \times 25$ mm for the compression and water absorption test. The rectangular specimens of size $100 \times 25 \times 25$ mm were cast for the flexural strength test. After 2 h, the specimens were demoulded and kept at room temperature for 24 h and then dried in an oven at 42 ± 2 °C for two days.

Thereafter, the specimens were cooled at room temperature and then tested for different properties.

2.2.2 Testing

The setting times of the reference and SPs modified β -hemihydrate plasters were determined in accordance with the test method given in Indian standard (BIS 2542-[7] Part I) using a Vicat apparatus.

The strength characterization of the reference and SPs modified gypsum plasters was evaluated in terms of compressive strength. Compressive strength tests were performed using dried $25 \times 25 \times 25$ mm cube specimens on Universal testing machine with a capacity of 25 kN pressure and a loading rate of 0.1 kN/s. Six samples were used for each test from different compositions and their arithmetic means are reported. The results obtained were within a 5 % variation level of the arithmetic average.

For the determination of water absorption, the cubic specimens were dried to a constant weight at 42 ± 2 °C and then cooled. This was followed by the immersion of specimens in tap water for different periods up to 28 days. The temperature of the tap water was maintained at 25 ± 2 °C. At the end of the respective immersion period the cubes were taken out from water, the surface water was wiped off and weight of the cubes was taken. The water absorption was calculated by using the relationship as given in the Indian Standard (BIS 2542—[7] Part II). The bulk density of the dried cubic specimen was calculated by dividing the mass of the specimen by its overall

volume. An average value of three specimens of each composition is reported.

2.3 Conductivity measurements

The electrical conductivity of the paste of β -calcium sulphate hemihydrate was measured with the help of a Toshcon Autoranging Conductivity Meter at room temperature (21 ± 2 °C). The paste was prepared by adding 100 ml of distilled water to 10 gm of β -hemihydrate plaster followed by stirring for a period of 30 s with the help of a glass rod. The readings were taken after different time intervals. Similar experiments were also performed in the presence of SNF and PC based superplasticizers. At the end of each experiment, the conductivity cell was carefully removed, washed with conc. HCl and thereafter with distilled water.

2.4 XRD, IR and SEM analyses

A combination of X-ray Diffraction, Scanning Electron Microscopy and Infrared spectral studies were used to investigate the mechanism for enhancement in the properties of SPs-modified gypsum plasters. The diffraction patterns of beneficiated and calcined PG samples were measured at 30 kV and 40 mA on a Rigaku D-Max 2200 X-ray Diffractometer using $\text{Cu-K}\alpha$ radiation.

A LEO-438 VP Scanning Electron Microscope at an accelerating voltage of 20 kV was used to observe the morphological attributes of the hydration products. The IR spectra of some selected hydrated samples were recorded with the Spectrum GX FT-IR spectrometer in KBr phase. One milligram of the powder sample was ground with 99 milligram of potassium bromide in an agate mortar to produce a homogeneous mixture. Additionally, for these analyses, samples are taken from the centre of the crushed specimens. The samples are then ground to fine powder and dried in an oven at 42 ± 2 °C up to constant weight.

3 Results and discussion

3.1 Material characterization

Phosphogypsum is a damp, powdery material which has very little or no plasticity. It is predominantly silt-

sized. The particle size of the PG sample used lies in the range of 1.0–0.1 mm and its specific gravity is 2.35. The results of chemical analysis given in Table 1 revealed that the unbeneficiated PG is acidic in nature (due to residual acid contents, pH 3.5) and contained P_2O_5 and fluoride impurities. However, beneficiated PG has comparatively lower levels of P_2O_5 , F, alkalis and higher pH (6.5) value than the unbeneficiated PG which lies within the maximum specified limits of the Indian Standard (BIS 12679) [5]. Figure 1 represents the XRD patterns of beneficiated and calcined PG samples. It can be seen from the figure that the prominent peaks of dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in the beneficiated PG appeared at 11.6° , 20.7° , 23.4° , 29.1° , 31.1° and 33.3° . Whereas, after calcination the major peaks of hemihydrate ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$) crystals were obtained at 14.7° , 25.7° , 29.7° , 31.9° , 49.4° , 54.1° and 55.1° along with the few small peaks of dihydrate at 43.3° and 47.8° . This confirms the subsequent conversion of phosphogypsum into β -hemihydrate plaster.

3.2 Water reduction rate

The water reduction rate of superplasticizers is an indicator of its capacity to lower the quantity of water (or water/hemihydrate ratio) required for standard consistency of the mixture being tempered and ultimately leads to improved strength and water absorption properties. Figure 2 present the results

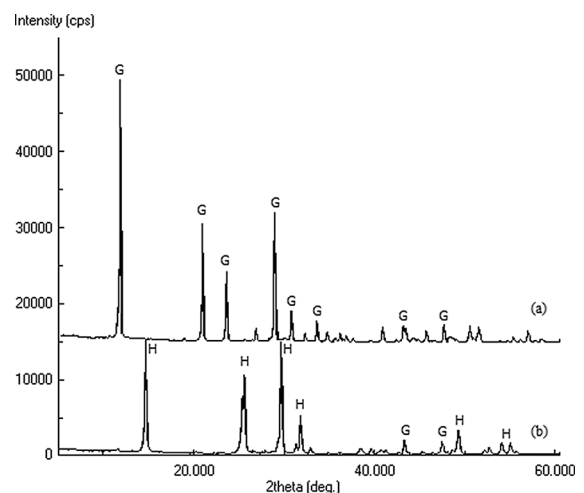


Fig. 1 X-ray diffractograms of *a* beneficiated, and *b* calcined phosphogypsum (*G* dihydrate gypsum, *H* hemihydrate gypsum)

concerning the water reduction rate at different concentrations of SNF and PC superplasticizers for β -hemihydrate gypsum plaster. The figure illustrated that the water reduction rate of SNF and PC superplasticizers increased from 4.0 to 19.5 and 1.0 to 25.5 %, respectively as their concentration increases from 0.1 to 1.2 wt%. It follows that the amount of water reduction varies greatly depending upon the content of SPs used. A small amount of SP (0.1–0.2 %) has little influence on the water reduction capacity. However, the addition of SPs begins to have a significant effect when their concentration exceeds 0.4 % and causes a dramatic increase in the water reduction rate. While considering the same content beyond 0.4 %, it was observed that the water reducing effect of PC superplasticizer is higher than that of SNF or it can also be said that for equal water reduction, more SNF than PC superplasticizer is required. For 0.6 wt% PC content, a reduction of 20 % in water requirement was obtained. On the other hand, the water reducing rate of SNF superplasticizer was nearly 20 % when its dosage is 1.0 %. These findings have been supported by other researchers also [27]. With further increase of SPs concentration beyond 0.8 %, not much reduction in the water demand of the gypsum plaster was observed. It was also noticed that besides reducing the water requirement of the plaster, the flowability, homogeneity and ease of application of the mixture is markedly improved due to the plasticizing, lubricating and dispersing effects of SPs. These effects are attributed to the adsorption of SP molecules on the surface of gypsum particles which causes the zeta potential to change from positive to negative. This leads to an electrostatic repulsion between the

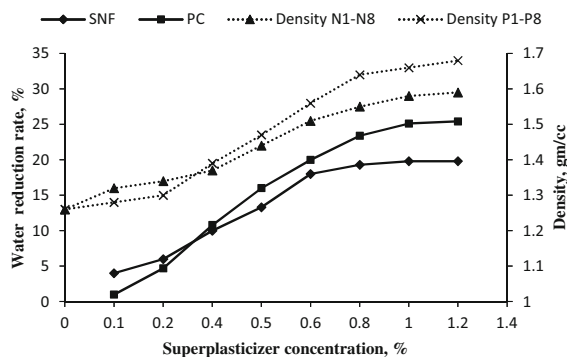


Fig. 2 Influence of superplasticizer content on water reduction rate and density of β -hemihydrate plaster

particles which avoids flocculation and brings about a rapid dispersion of the individual plaster grains. This finding is also supported by Peng et al. [19] who reported that the adsorption conformation of SNF is in the form of lying on gypsum surface and its dispersion capacity depends on the electrostatic repulsive forces that inhibit agglomeration of gypsum particles. While, PC is a comb-shaped polymer and its dispersion ability comes from a combination of steric hindrance and electrostatic repulsive forces. Owing to the strong steric hindrance generated by short side chains of PC, the water reducing capacity of PC is higher than that of SNF.

3.3 Setting time and bulk density

The crystallization of gypsum dihydrate from a suspension of calcium sulphate hemihydrate is well-known as the setting of plaster. Figure 3 depicted that the effects of SNF and PC superplasticizer on the setting time of gypsum plaster vary widely. The setting time of β -hemihydrate plaster incorporating SNF superplasticizer gradually decreased with an increase in its content. When its dosage is 0.6 %, the setting time reduced to 10 min and thereafter showed a stable trend with further increase in SP concentration. On the contrary, PC superplasticizer exhibited a significant retarding effect and prolonged the setting time of gypsum plaster. It can be seen that the addition of 0.8 % PC increased the setting time considerably from 28 to 52 min and this effect continued with further addition of SP. Such a high extension of setting time occurs due to the interactions between the two systems. The adsorption of SP molecules modifies

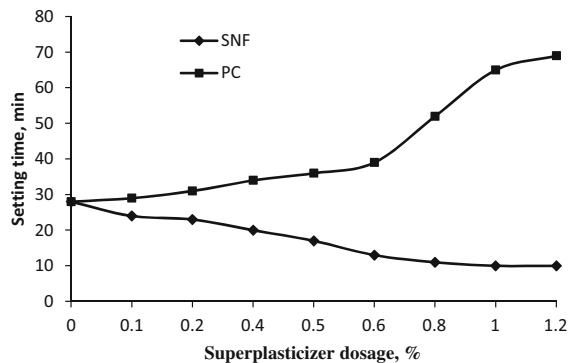


Fig. 3 The effect of superplasticizers content on the setting time of β -hemihydrate plaster

drastically the dissolution and crystallization rate of the gypsum crystals which is responsible for the setting of β -hemihydrate plaster.

Besides decreasing the water requirement and affecting the setting time of the gypsum plaster, the incorporation of SPs also exerted a substantial influence on the density of the hardened product. The relationship between the densities of hydrated β -hemihydrate plaster versus SPs concentration is illustrated in Fig. 2. The results showed a continuous increase in the bulk density values for all compositions that can be accredited to the decrease in water content of the gypsum plaster. This effect is even much more pronounced on the mix compositions with SPs content higher than 0.4 %. The density of the β -hemihydrate plaster was enhanced up to 23 and 30 % by the addition of 0.8 % SNF and PC content, respectively. However, density of the blends becomes nearly constant at SPs content beyond it.

3.4 Compressive strength

The strength characterization is one of the important indices to evaluate the quality of the solidified product for application in construction materials. Figure 4 illustrates the influence of SNF and PC type superplasticizers on the compressive strength and density of hardened β -hemihydrate plaster, respectively. The shadowed band represents the strength obtained for reference plaster. While considering the results obtained, it can be seen that superplasticizers enhance the compressive strength of the β -hemihydrate plaster up to varying degrees as compared to the unmodified reference sample. For 0.1 % addition of SPs, a slight

increment in the strength of gypsum plaster was observed. The strength subsequently increases further and exhibited a considerable improvement when the SPs content exceeds 0.2 %. At 0.6 %, the compressive strength increased reaching 14.2 and 13.9 MPa for SNF and PC superplasticizers, respectively. Up to this concentration, SNF made greater contribution towards improving the strength of plasters but attains an almost stable trend later on. However, PC continues to make an effort to increase the strength up to 1.0 % and the phenomenon becomes smooth thereafter. Analyzing the results, it follows that the remarkable increment in the strength of the β -hemihydrate plaster is attributed to the strengthening of gypsum matrix due to the interactions between the SPs particles and hydration products. Also, a decrease in the water requirement of gypsum plaster causes a reduction in the void fraction of the dihydrate gypsum crystals. This results in the formation of a more compact and dense structure of the matrix which contributes to the significant enhancement in the compressive strength of the hardened product. Similar findings were observed by Yu and Brouwers [26].

3.5 Water absorption

The effect of varying concentration of SNF and PC superplasticizer on the water absorption of the mix compositions designated as N1–N8 and P1–P8 (Table 3) measured after different immersion periods up to 28 days are depicted in Fig. 5a, b. The data revealed that the SPs modified specimens exhibited lower degree of water absorption compared to the unmodified reference (R) specimens. The results clearly manifest that with SPs content increasing, the water resistance efficiency also incremented. Furthermore, the water absorption of compositions N3–N8 increased with an increase in the immersion period but became almost constant after 7 days immersion in water. The trend remained unaltered for P3–P8 compositions too. The mix compositions N1–N2 and P1–P2 showed leaching of the gypsum matrix after 7 days immersion in water while in reference plaster (R) the leaching started after 3 days immersion period. The absence of leaching in SNF and PC modified β -hemihydrate plasters imparts an acceptable water resistance property to them and confirms their better performance over plain reference plaster. This is mainly ascribed to the formation and coagulation of

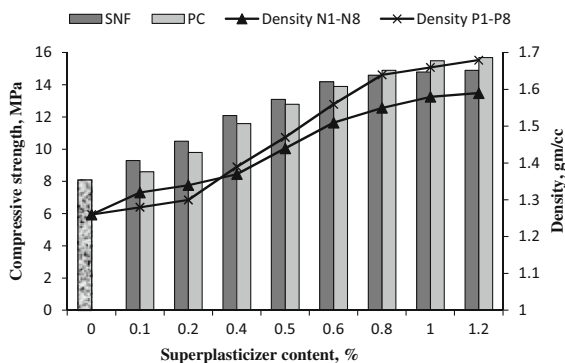


Fig. 4 Influence of superplasticizer content on the compressive strength and density of β -hemihydrate gypsum plaster

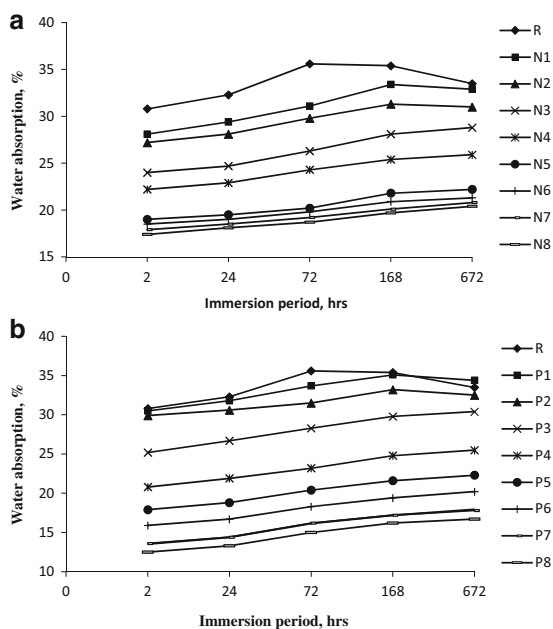
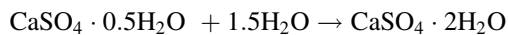


Fig. 5 Effect of water immersion period on the water absorption of β -hemihydrate gypsum plaster with **a** SNF (N1–N8), and **b** PC (P1–P8) superplasticizers

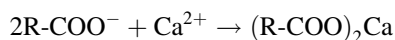
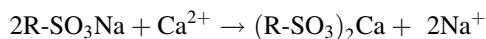
hydration products that accumulate in the pores of the matrix to form a compact body. This is responsible for the enhancement in the water resistance and mechanical properties of the hardened material. These results are in good harmony with the water reduction rate of SPs, bulk density and compressive strength values of the hardened β -hemihydrate plaster and correlate well with the findings of Colak [9].

3.6 Hydration of β -hemihydrate gypsum plaster

It is very well known that the hydration of calcium sulphate hemihydrate leading to the formation of calcium sulphate dihydrate occurs via different stages, i.e., dissolution of hemihydrate followed by germination and growth of gypsum crystals [18]. The hemihydrate dissociates into Ca^{2+} and SO_4^{2-} ions when mixed with water, making the solution initially saturated with respect to these ions. This saturated solution turns supersaturated with respect to calcium sulphate dihydrate, resulting in nucleation and crystallization of gypsum crystals as per the Le Chatelier's Principle [15]. The hydration reaction can be described as:



The addition of SPs to gypsum plaster affects the overall hydration processes. The mechanism for the action of SPs during the hydration of gypsum includes: (i) the adsorption of SPs molecules on gypsum surface modifies the hydration behaviour and morphology of the hydrate phases, and (ii) chemical interactions between the gypsum and SPs particles. Such interactions result in the formation of complexes which often accelerate or retard the hydration of calcium sulphate system. In fact, it is believed that during the hydration process, adsorption of compounds formed by the chemical interaction between the functional ion groups linked to the SPs molecules and calcium ions takes place. The ionic sulphonate (R-SO_3^-) of SNF and carboxylic group (R-COO^-) in PC superplasticizer interacts with the Ca^{2+} ions in the aqueous phase to form organic complexes as shown below:



Similar phenomenon has been observed by other workers also [21]. With the progress in hydration period, these complexes fill up the pore spaces in the gypsum matrix and improve the pore structure of hardened material to form a dense system as confirmed by SEM and IR studies.

3.7 Electrical conductivities

The effect of SNF and PC superplasticizers on the hydration of β -hemihydrate plaster has been studied by employing measurement of electrical conductivity through a dilute suspension of hemihydrate. The typical conductivity curves obtained for a suspension of pure (R) and SPs modified (N5 and P5) β -calcium sulphate hemihydrate systems are shown in Fig. 6. The sudden evolution and variation of electrical conductivity as a function of time is closely related to the physico-chemical changes continuously experienced by the hydrating system. Concerning the mechanism of hydration of gypsum hemihydrate, three different stages have been identified from the conductivity curves. The first plateau corresponds to the dissolution of β -hemihydrate plaster. As soon as calcium sulphate hemihydrate comes in contact with

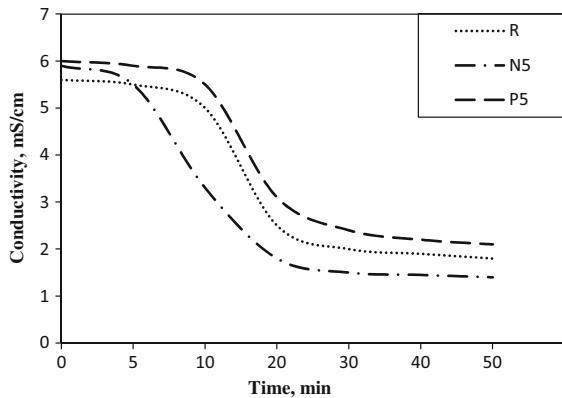


Fig. 6 Variation of electrical conductivity as a function of time during hydration of β -hemihydrate plaster with and without superplasticizers

water, it goes into the solution which becomes saturated with respect to calcium and sulphate ions. As a result, the conductivity increases rapidly and registers the maximum value. For a further few minutes, the conductivity remains constant. Once the phenomenon of setting of plaster starts, clustering of Ca^{2+} and SO_4^{2-} ions occurs and gypsum crystals starts growing due to which a notable decrease in the conductivity value is observed. This phase is considered as the period during which massive crystallization or precipitation of calcium sulphate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) takes place. The third stage is characterized by a very little change in the conductivity value, which implies a slow ending of the process of dihydrate crystallization from the suspension. Several effects of the addition of SNF and PC superplasticizer on gypsum hydration can successfully be characterized from the conductivity curves. The conductivity of the β -hemihydrate plaster with SNF superplasticizer, designated as N5, decreased immediately and after that exhibited a constant value. This early fall in the conductivity suggests that SNF accelerates the onset of plaster hydration. The superplasticizer increases the rate of dissolution of β -hemihydrate plaster and results in consequent nucleation and precipitation of dihydrate crystals. On the contrary, a delay in the fall of conductivity upon addition of PC superplasticizer (P5) confirms its rate retarding effect. This decelerating behaviour can be interpreted by the strong adsorption of PC molecules which blocks some of the growing sites and thus slows down the growth of dihydrate

crystallites. This phenomenon has been supported by Guan et al. [13] also.

3.8 SEM and IR studies

The microstructure of the hydrating system has a substantial influence on the performance of the solidified product. The scanning electron microscopic images of the mix composition R, N5 and P5 are shown in Fig. 7a–c, respectively. Figure 7a corresponds to the SEM image of a typical dihydrate gypsum matrix which presented a mass of randomly oriented flaky and needle shaped crystals. A few plate-like crystals are also visible in the loose crystal matrix. Also, the stacking of crystals is irregular and disordered. The examination of micrographs in Fig. 7b, c indicates that the addition of SNF and PC superplasticizer modifies the morphology of the resultant dihydrate gypsum crystals significantly. The β -hemihydrate paste mixed with SPs presented a crystalline network of well developed and distributed gypsum crystals. The hydrate formed in the presence of SPs is composed of a homogeneous structure of small and well shaped euhedral prismatic, cubic and hexagonal crystals having closer texture with interlocking arrangements. The gypsum matrix formed has a denser and compact structure and seems to be less porous than the reference specimen. This improvement in the pore structure of hardened gypsum is ascribed to the formation of gelatinous substances that fills the pores of the matrix, as exemplified in the figures. The superplasticizer particles increase the interface binding strength between the gypsum crystals and the space between them becomes narrow, resulting into a decrease in the average pore diameter of the set plaster [13]. This in turn leads to a stronger bond between the gypsum crystals which finally results in an improved strength and higher water resistance of the modified product.

Figure 8a–c shows the FT-IR patterns obtained for hydrated R, N5 and P5 samples, respectively. The characteristic peak belonging to the calcium sulphate is located at 605 cm^{-1} . A major and broad band appearing at 1120 cm^{-1} is assigned to the S–O stretching vibration of SO_4^{2-} group. This region becomes broader in the presence of SNF and PC superplasticizers. These changes are due to the interactions between SO_4^{2-} group and SP molecules and confirm the adsorption of complexes at calcium

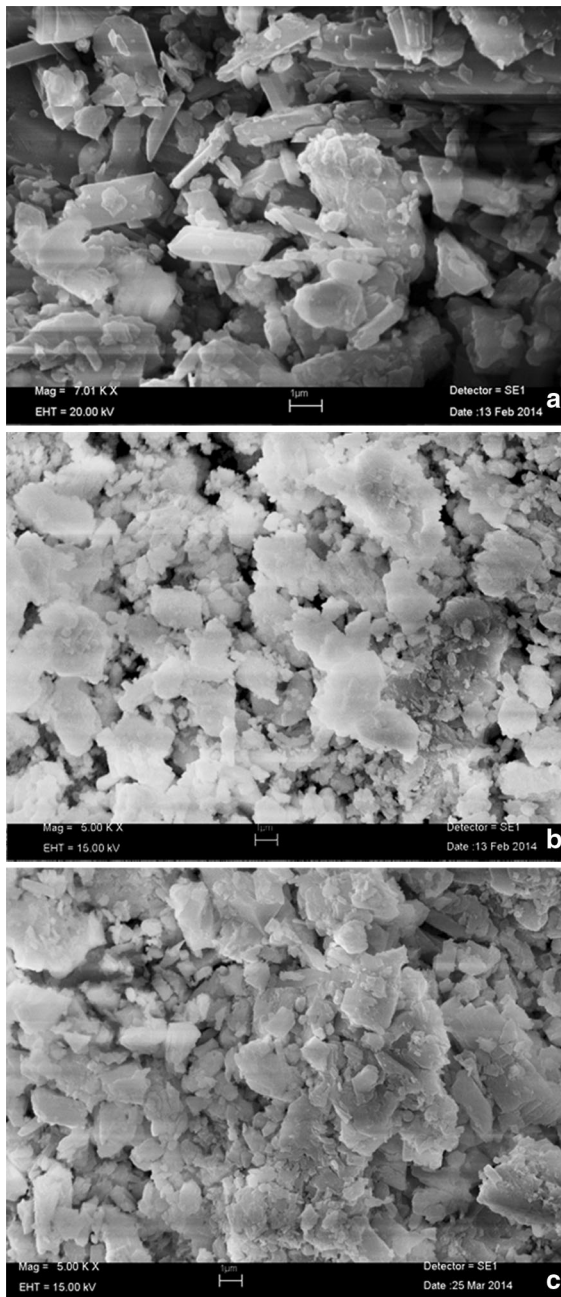


Fig. 7 Scanning electron micrographs of hydrated β -hemihydrate plasters, **a** R, **b** N5, and **c** P5

sulphate dihydrate crystal face. The additional absorptions at 1502 and 2514 cm^{-1} were identified for SNF and carboxylate group, respectively. The group $-\text{SO}_3\text{Na}$ manifests itself by valence vibration at $1220\text{--}1190\text{ cm}^{-1}$ and thus provides an evidence for the formation of complexes.

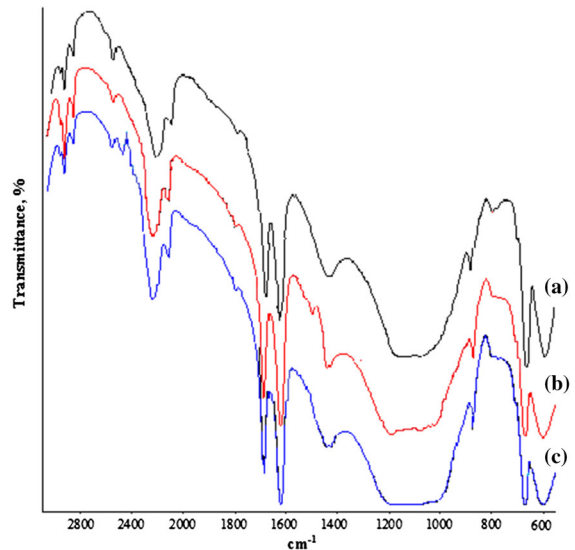


Fig. 8 FT-IR spectra of hydrated β -hemihydrate plasters, **a** R, **b** N5, and **c** P5

4 Conclusions

In the context of the influence of SNF and PC superplasticizers on the properties of β -hemihydrate gypsum plaster studied in the present work, the following conclusions can be drawn:

1. Incorporation of SPs caused a remarkable reduction in the water requirement of gypsum plaster due to better dispersion of the particles in the mixing water.
2. The 0.6 % SNF and PC content contributed 75 and 71.5 % to an enhancement in the compressive strength of the plaster as compared to reference sample, respectively.
3. The results of electrical conductivity measurements revealed that the addition of SPs modified the hydration process of β -hemihydrate plaster governed by adsorption and chemical interactions of the superplasticizer molecules.
4. The lower degree of water absorption and absence of leaching in modified β -hemihydrate plasters imparts an acceptable water resistance property to them and confirmed their better performance over unmodified plaster.
5. SEM studies showed formation of a dense and well compacted texture of crystals in the modified gypsum matrix due to accumulation of gelatinous substances in the pores of the matrix. This is

responsible for the enhancement in the water resistance and mechanical properties of the hydrated product.

6. The result obtained from this experimental investigation underlines the potential of SNF and PC superplasticizers to be used as a water reducer admixture for β -hemihydrate gypsum plaster and consequently its compatibility with the plaster.
7. The improvement in the engineering properties of gypsum plaster suggests that it can be used in plastering, pre-fabricated panels, load-bearing blocks and boards in the construction industry.
8. The use of phosphogypsum for preparation of gypsum plaster offers a solution to the current global issues concerning waste disposal, environment pollution, and depletion of natural resources and is a movement towards greener construction.

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