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Making of anhydrite cement from waste gypsum

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Abstract

The paper presents the results of research on the utilization of phosphogypsum produced as the waste of phosphoric acid manufacture. Phosphogypsum is a fine powder with high calcium sulfate content. The phosphatic and fluoride impurities present in phosphogypsum cannot be removed completely either by washing or chemical treatments. However, phosphogypsum, when heated at elevated temperature, produced an anhydrite and the impurities become inert. The formation of anhydrite cement was examined by microscopy and X-ray diffraction. Data showed that a stable anhydrite can be produced by heating phosphogypsum at 1000°C. The effects of different chemicals on setting and hardening of anhydrite cement and its hydration characteristics were studied. Results show that with the use of sodium sulfate and ferrous sulfate activators, maximum attainment of strength can be achieved. A correlation was established between hydration and chemically combined water. Microscopic studies revealed that formation of euhedral prismatic and rhombic shaped gypsum crystals govern high strength development in the anhydrite cement. Manufacture of anhydrite cement from phosphogypsum is recommended because of its lower energy requirements than the traditional building materials. Published by Elsevier Science Ltd.

Keywords: Thermal treatment; Acceleration; Microstructure; Physical properties; Cement

1. Introduction

Industrial advancement has led to brazen increase in the production of waste materials causing degradation of the environment. The accumulation of waste materials has harmed human health in addition to aggravating disposal problems. In India, over 100 million tons of waste materials are produced annually from the agro-industrial processes. Fly ash, slag, phosphogypsum, fluorogypsum, red mud, lime sludges, and mining tailings are the paramount industrial wastes that demand serious attention to save the fast deteriorating environment. Phosphogypsum, a waste product of phosphoric acid fertilizer, is produced up to 5.0 million tons/annum in India and not more than 10.0% is used at present. Efforts have been made in several countries to use phosphogypsum in making cement [1], gypsum plasters [2], building products [3], and binders [4].

Phosphogypsum is a rich source of calcium sulfate carrying impurities of phosphates, fluorides, organic matter, and alkalies. These impurities prevent direct use of phosphogypsum in building materials due to their bad effect on normal setting and hardening of cements as well as calcined gypsum. It is, therefore, essential to beneficiate phosphogypsum to get rid of innocuous impurities.

Processes based on washing, thermal, or chemical extraction have been investigated by many workers in India [3], Japan [5], Germany [6] etc. These processes are effective in reducing the impurities to a greater extent. However, these processes could not be adopted commercially due to their high cost of beneficiation.

Researches carried out by Simanovskaya [7], Gordashevskii and Broido [8], Berezovskii [9], Singh et al. [10] and Ostrowski [11] have shown that impurities can be made inactive by heating the phosphgypsum at high temperatures. At elevated temperature, phosphogypsum is transformed to the anhydrite. Different authors have suggested different temperatures for the preparation of anhydrite [12,13]. Studies by Wiedman [14] and El Hajjouji [15] have shown that high strength anhydrite cement can be produced from phosphogypsum just as from natural gypsum. However, due to disagreement among the annealing temperatures suggested by various workers, it has become almost imperative to understand the exact behavior of annealing phosphogypsum to obtain anhydrite cement of suitable

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properties. Investigations were, therefore, undertaken regarding calcination of phosphogypsum to form anhydrite at different temperatures. Data obtained for the morphology of anhydrite and its hydration in the presence of chemical activators are reported and discussed in this paper. The production of anhydrite cement from phosphogypsum is recommended due to its low energy requirements.

2. Experimental

Phosphogypsum, procured from Southern Petrochemical Industries, Tuticorin (India) with chemical composition cited in Table 1, was used for the entire work.

For the production of anhydrite plaster, phosphogypsum was calcined in a muffle furnace of dimensions 1.5 × 0.8 m in the temperature range of 500–1000°C. The retention time of calcination was maintained at 4.0 h. After desiccation, the properties of anhydrite cement like density, specific surface area, pH and loss on ignition were studied as per the Indian Standard IS:2542 (Part I)-1978 [16]. The mineralogical studies of anhydrite cement were determined by X-ray diffraction (Philips diffractometer, Netherlands) and scanning electron microscopy (SEM Model 508, Philips). The anhydrite cement was ground in a ball mill and the effect of different types of chemical activators, namely sodium sulfate, ferrous sulfate, ammonium sulfate, potassium sulfate, potassium dichromate, calcium chloride, and calcium hydroxide was studied on the properties of anhydrite as per the ASTM Standard:C 61-1993 [17] as well as IS: 2542 [16]. The strength development of anhydrite cement was evaluated with differential thermal analysis (Stanton Redcroft, UK) and X-ray diffraction. The chemically combined water of hydrated anhydrite was determined as per the ASTM Standard:C 471-76 [18].

3. Results and discussion

3.1. Properties of anhydrite cement

In the production of anhydrite from phosphogypsum, the behavior of impurities, particularly P_2O_5 and F, play an important role. As we know, these impurities are of different types, namely: (a) water soluble—a large portion of P_2O_5 and F exist on the surface of gypsum crystals and in the interstices of agglomerated crystals as H_3PO_4, $Ca(H_2PO_4)$. H_2O, NaF and Na_2SiF_6 [19], (b) a portion of P_2O_5 and F in the gypsum lattice which has entered in to solid solution with gypsum by substitution of HPO_4^{--}, FPO_3^{--} and AlF_5^{--} ions for SO_4^{--} ions because these crystals have identical lattice parameter and belong to the analogous space group [20,21], and (c) insoluble form as $Ca_3(PO_4)_2$ and CaF_2 [22].

Table 1
Chemical composition of phosphogypsum

Constituents	Contents (%)
P_2O_5	0.47
F	0.86
Organic matter	0.59
SiO_2 + insoluble in HCl	0.29
$Al_2O_3 + Fe_2O_3$	0.54
CaO	31.09
MgO	1.31
SO_3	43.21
Na_2O	0.29
Loss on ignition	18.38

Table 2
Impurity contents in anhydrite cement

	Constituents (%)	
Materials	P_2O_5	F
Phosphogypsum (as such)	0.47	0.86
Phosphoanhydrite prepared at (°C)		
500	0.54	0.92
600	0.56	0.95
700	0.56	0.96
800	0.57	0.97
900	0.57	0.97
1000	0.58	0.98

The water soluble impurities of P_2O_5 and F can be easily removed from phosphogypsum by washing with ordinary tap water. However, the P_2O_5 occluded ($CaHPO_4 \cdot 2H_2O$) in the gypsum crystals is rather difficult to be removed due to its low solubility 0.0286 g/100 cm^3 water at 35°C. The strength of cement and calcined gypsum are adversely affected by slow dissolution of $CaHPO_4 \cdot 2H_2O$ with the progressive hydration. It has been observed that during the heating of phosphogypsum at high temperature, the impurity $CaHPO_4 \cdot 2H_2O$ gets converted into calcium pyrophosphate (CaP_2O_7) which is water insoluble and thus harmless [23,24]. This was confirmed by obtaining the absence of phosphate in the extract prepared by shaking the anhydrite prepared from phosphogypsum in saturated lime water for 4 h. The phosphoanhydrite samples were tested for impurity contents. The results are reported in Table 2. It can be seen that there is no appreciable change in the phosphate content but fluorides have volatilized to some extent. The organic matter was largely eliminated on annealing of phosphogypsum. Results indicate that stable anhydrite is formed at temperatures between 800°C to 1000°C due to the close proximity of P_2O_5 and F contents. Other properties such as density, specific surface area, pH, and loss on ignition of anhydrite cement are listed in Table 3. Data shows that with enhancement in calcination temperature, the values of specific gravity, pH and specific surface area increased and that of $CaSO_4 \cdot 2H_2O$ content reduced. The increase in pH values beyond 800°C is probably due to formation of free lime from the partial decomposition of gypsum. The loss on ignition of anhydrite at 800°C, 900°C and 1000°C

Table 3
Characteristic properties of the anhydrite produced from phosphogypsum

Temperature of calcination (°C)	Properties			
	Density (kg/m^3)	Specific surface area Blaine (m^2/kg)	pH	Loss on ignition (%)
500	2650	260	7.1	3.0
600	2700	266	7.1	2.5
700	2780	270	7.1	2.3
800	2800	275	7.2	2.0
900	2810	280	7.3	1.8
1000	2900	288	7.3	1.6

was within the maximum specified value of 2.0% laid down in IS:2547 (Part I)-1976 [25], thereby, establishing the formation of stable anhydrite cement.

It is interesting to record here that anhydrite cement produced at 1000°C is less energy intensive than for Portland cement and various other building materials. The fuel energy consumed per kilogram of the anhydrite cement production vis-a-vis other building materials is projected in Table 4. Data shows that gypsum anhydrite can be produced at much lower fuel requirement than the traditional building materials.

X-ray diffraction patterns of unprocessed phosphogypsum and the phosphoanhydrite obtained by firing at 500°C, 600°C, 700°C, 800°C, 900°C, and 1000°C are shown in Fig. 1. It can be seen from X-ray diffraction patterns that compared to unprocessed phosphogypsum, shifting of the most intense lines/reflections takes place in case of anhydrite cement obtained at 500°C, 600°C, and 700°C. As the calcination temperature is increased, no shifting in lines occurs which shows the absence of secondary rearrangement of the gypsum crystal lattice. An increase in the intensity of some reflections and decrease in others reflections are found. Major reflections were noticed at 3.549, 2.849, 2.3298 and 2.2115 Å which confirm the conversion of phosphogypsum into anhydrite of stable configuration.

The microstructure of fractured surface of anhydrite cement produced at, 500°C, 600°C, 700°C, 800°C, 900°C, and 1000°C are shown in Fig. 2, denoted by a, b, c, d, e, and f, respectively. At 500°C, 600°C, and 700°C (Fig. 2a–c), anhedral to euhedral prismatic and rhombic shaped crystals of irregular boundaries and stackings are formed. The formation of small-size pseudoamorphous particles has largely enhanced. The anhydrite produced at 800°C, 900°C, and 1000°C (Fig. 2d–f) shows appearance of euhedral to anhedral prismatic and rhombic shaped crystals of platy structure binding the smaller anhydrite grains. The pseudoamorphous gypsum crystals break down into microcrystals with the increase in calcination temperature. These results corroborate the findings of Berezovskii [9]. The pseudoamorphous crystals may be attributed to the crystals of soluble anhydrite (γ-$CaSO_4$) which are transformed to

Table 4
Energy requirements for various building materials in India

Materials	Basic	Energy (kcal)
Gypsum anhydrite	kg	0.52×10^3
Cement	kg	1.93×10^3
Wood particle board	kg	0.74×10^3
Quick lime	kg	1.51×10^3
Mild steel	kg	6.30×10^3
PVC	kg	27.75×10^3
Aluminium	kg	34.30×10^3

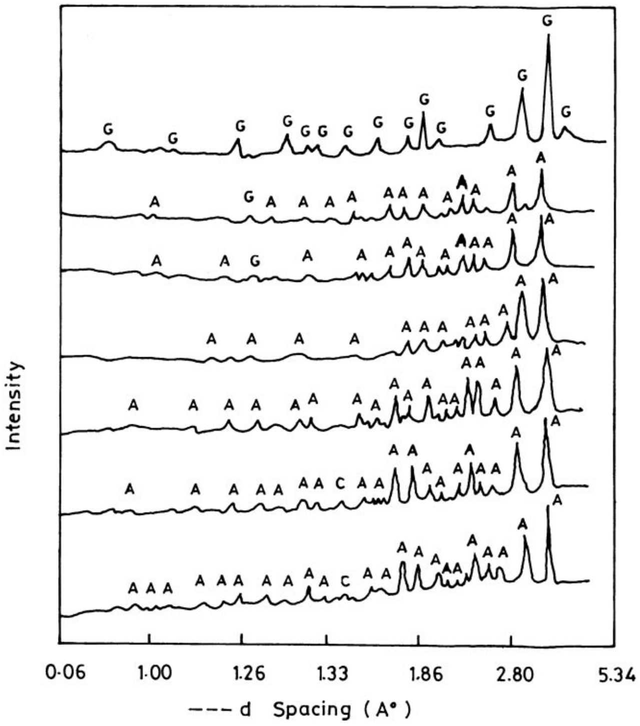

Fig. 1. X-ray diffractograms of phosphogypsum calcined at different temperatures (G=gypsum ($CaSO_4 \cdot 2H_2O$), A=anhydrite ($CaSO_4$) and C=lime (CaO)).

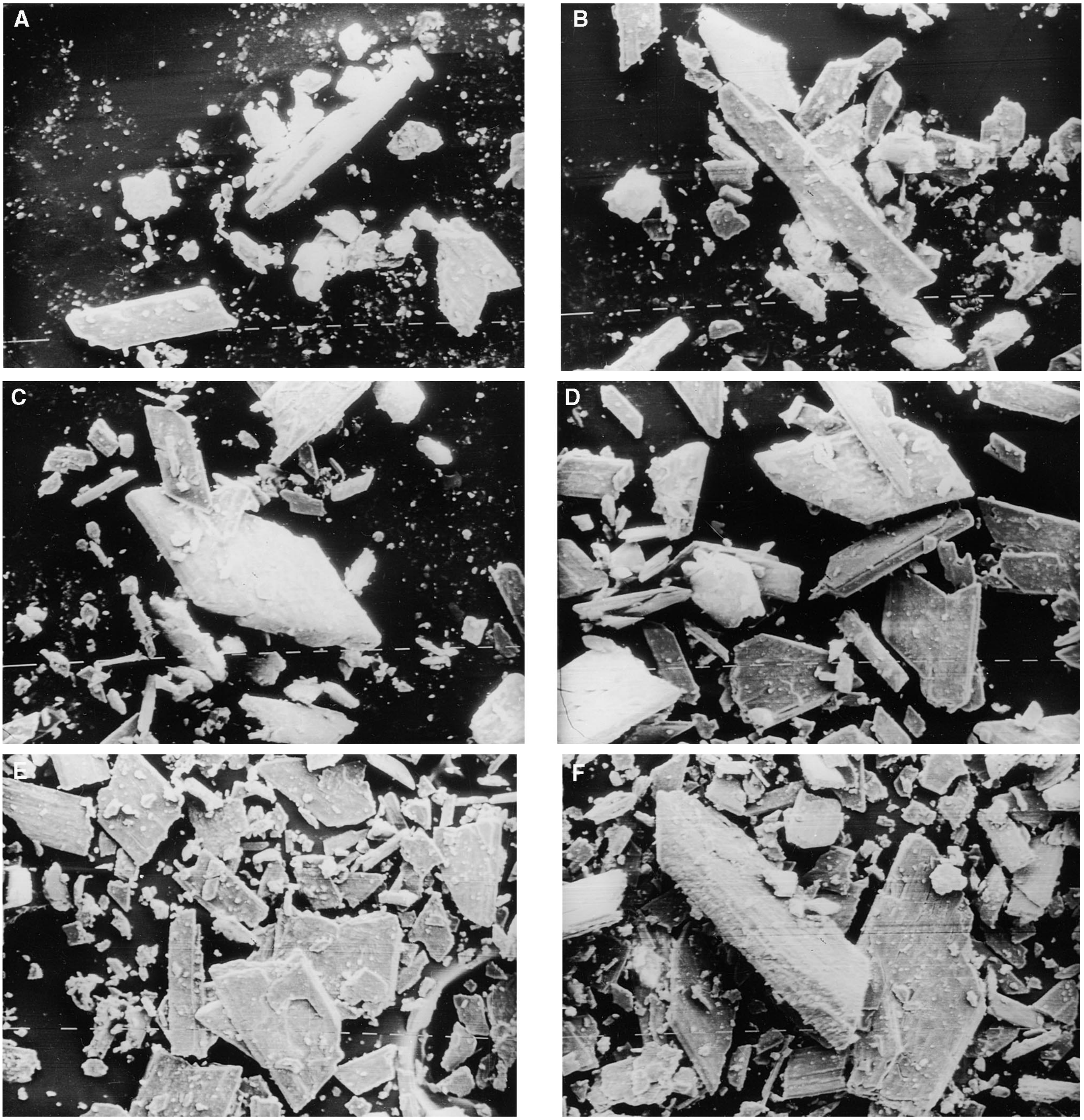

Fig. 2. Microphotographs of anhydrite cement produced at different temperatures: (a) 500°C, (b) 600°C, (c) 700°C, (d) 800°C, (e) 900°C, and (f) 1000°C (magnification × 1200).

anhydrite with the increase in temperature. At 900°C (Fig. 2e), the cavities and irregular boundaries with variable stacking of anhydrite crystals can be seen. However, the size of prismatic crystals increased in association with occasional formation of rhombic shaped crystals with sharp boundaries at 1000°C (Fig. 2f). The formation of euhedral prismatic crystals and transformation of pseudoamorphous crystals of soluble anhydrite into microcrystallites having sharp edges and uniform stackings could be the deciding factor for the optimum strength development in phosphoanhydrite cement.

3.2. Strength development in anhydrite cement

Anhydrite cement produced by calcining phosphogypsum at 1000°C was selected for further studies on account of achieving stable structure. The effect of different chemical activators on the setting time of anhydrite cement is

Table 5
Setting behavior of the anhydrite cement with different chemical activators

Serial number	Chemical activators (by mass%)	Setting time (min)
1.	$(NH_4)_2SO_4$	
	1.0	275
	2.0	260
	3.0	240
2.	$Ca(OH)_2$(3%) + $CaCl_2$(0.5%) + Na_2SO_4(2%)	200
3.	$Ca(OH)_2$(3%) + $CaCl_2$(0.5%) + Na_2SO_4(2%)	180
4.	$K_2Cr_2O_7$(1%) + K_2SO_4(1%)	260
5.	Na_2SO_4(1.5) + $FeSO_4$(0.5%)	200

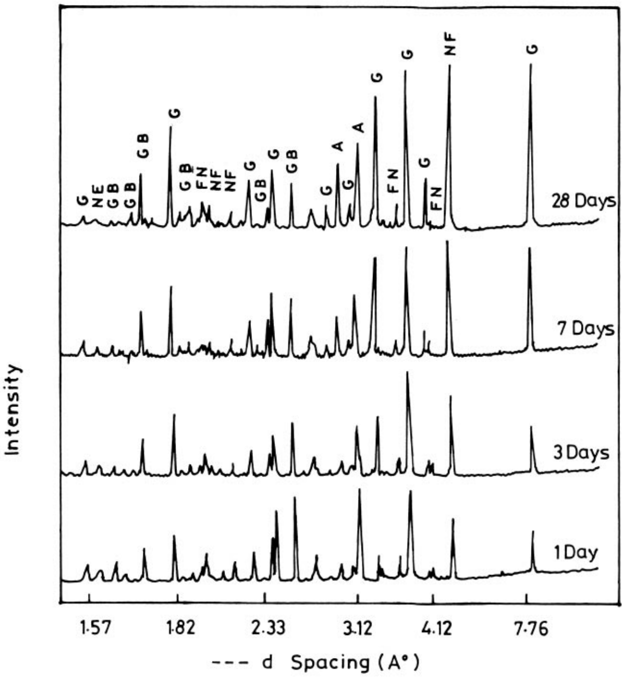

Fig. 3. X-ray diffractograms of anhydrite cement hydrated for different periods in presence of mixture of $Na_2SO_4 \cdot 10H_2O$ + $FeSO_4 \cdot 7H_2O$ activators (G = gypsum, NF = $Na_2SO_4 \cdot Fe_2(SO_4)_3$, FN = ferrinatrite ($Na_3 \cdot FeSO_4 \cdot 3H_2O$), GB = glauberite ($Na_2SO_4 \cdot CaSO_4$)).

shown in Table 5. According to ASTM:C61-1993 [16], the setting of anhydrite plaster is permitted within limit of 20–360 min. The phosphoanhydrite cement complied with the specified setting requirements of the standard cited above. The fast setting of anhydrite would be useful in early removal of components from the moulds. The percentage of chemical activators shown in the above table was chosen on the basis of attaining setting time as per standard requirements.

The results of the investigations into the effect of various activators on the strength development of anhydrite are listed in Table 6. It can be seen that strength increased with the progress in the curing period in anhydrite cement with all types of activators. The strength complied with the minimum specified value of 17.0 MPa at 28 days as given in ASTM:C61-50-1981. However, maximum strength has been achieved with the mixture of Na_2SO_4 + $FeSO_4$ activators.

The strength development of hardened anhydrite was supplemented by X-ray diffraction and differential thermal analysis. The results are plotted in Figs. 3 and 4, respectively. X-ray diffractograms (Fig. 3) show reflections for the formation of glauberite ($Na_2SO_4 \cdot CaSO_4$), ferrinatrite ($Na_3FeSO_4 \cdot 3H_2O$), gypsum ($CaSO_4 \cdot 2H_2O$) and unconverted anhydrite ($CaSO_4$). The intensity of ferrinatrite and gypsum reflections increased while those of glauberite and anhydrite reduced with the increase in hydration of the anhydrite. Differential thermograms of the hardened anhydrite cement (Fig. 4) show an increase in the intensity of double dehydration endotherms of gypsum obtained at 130–150°C and at 170–190°C and that of inversion of γ-$CaSO_4$ into β-$CaSO_4$ at 360–380°C. The increase in the intensity of endotherms and exotherms confirm the formation of gypsum from anhydrite. Thus, DTA reaffirmed the results of X-ray diffraction data.

The chemically combined water of phosphoanhydrite cement plaster hydrated for different periods is reported in Fig. 5. Data show that chemically combined water increased with the development of hydration of anhydrite cement. The increase in chemically combined water with the progress of hydration confirmed increased inversion of

Table 6
Compressive strength of anhydrite cement with different activators

Serial number	Chemical activators (by mass%)	Compressive strength (MPa) 1 day	3 days	7 days	28 days
1.	$(NH_4)_2SO_4$				
	1.0	1.35	5.50	5.80	24.30
	2.0	1.30	5.40	8.60	32.23
	3.0	5.20	9.62	15.20	36.0
2.	$Ca(OH)_2$(3%) + $CaCl_2$(0.5%) + Na_2SO_4(2%)	13.16	18.42	28.70	37.20
3.	$Ca(OH)_2$(3%) + $CaCl_2$(0.5%) + Na_2SO_4(2%)	12.30	20.70	23.70	36.0
4.	$K_2Cr_2O_7$(1%) + K_2SO_4(1%)	2.10	13.0	3.30	32.90
5.	Na_2SO_4(1.5) + $FeSO_4$(0.5%)	5.50	12.50	25.30	38.90

anhydrite into gypsum which can be correlated with the periodical increase in the strength of anhydrite cement on curing (Table 6).

The plausible mechanism of transformation of anhydrite into gypsum in presence of chemical activators ($Na_2SO_4 \cdot 10H_2O$ + $FeSO_4 \cdot 7H_2O$) may be explained as follows.

(i) The chemical activators may retard the evaporation of water due to reduction in vapor pressure and therefore, gauge water is available for longer period to facilitate hydration for prolonged time and (ii) the solubility of anhydrite is increased in sulfate solution, thus hydration is augmented with gypsum crystallizing rapidly out of the calcium sulfate solution. The attainment of high strength in the gypsum anhydrite cement probably takes place by production of gypsum ($CaSO_4 \cdot 2H_2O$) through the formation of intermediate unstable salts such as ferrinatrite ($Na_3FeSO_4 \cdot 3H_2O$), $Na_2SO_4 \cdot Fe_2(SO_4)_3$ and glauberite ($Na_2SO_4 \cdot CaSO_4$). These salts are formed by the high concentration of colloidal particles of activators on the surface of anhydrite ($CaSO_4$) in an unsaturated solution. Consequently, active nucleating centers are created around which crystallization sets when the solution becomes supersaturated. The unstable intermediate salts decompose into Ca^{2+}, Na^{+}, Fe^{3+} and SO_4^{2-} ions which then bind water to anhydrite to form prismatic, tabular and rhombic shaped crystals, that in turn, cement the unconverted anhydrite grains to give high mechanical properties. It is, therefore, deduced that activators tend to increase the rate of dissolution of anhydrite through formation of intermediate compounds. The transformation of anhydrite into gypsum, thus involves a dissolution—nucleation—growth process. Several workers have reported the use of chemical activators that increase the hydration rate of the solid anhydrite [26–28].

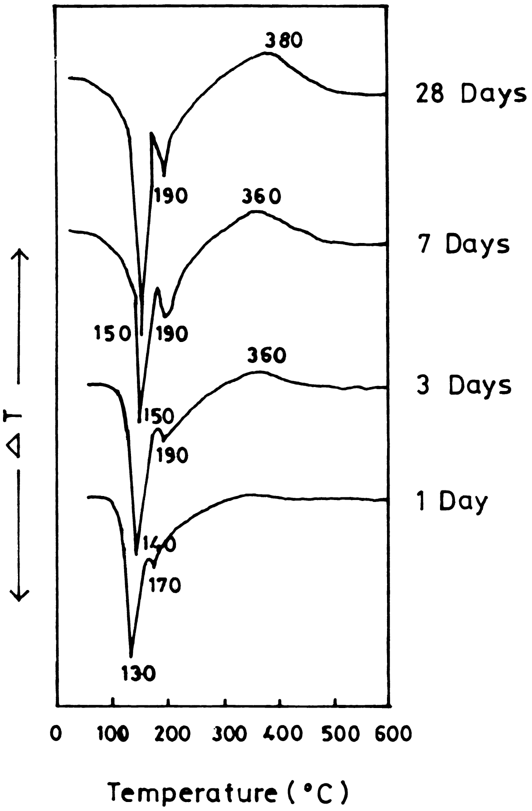

Fig. 4. Differential thermograms of anhydrite cement hydrated for different periods.

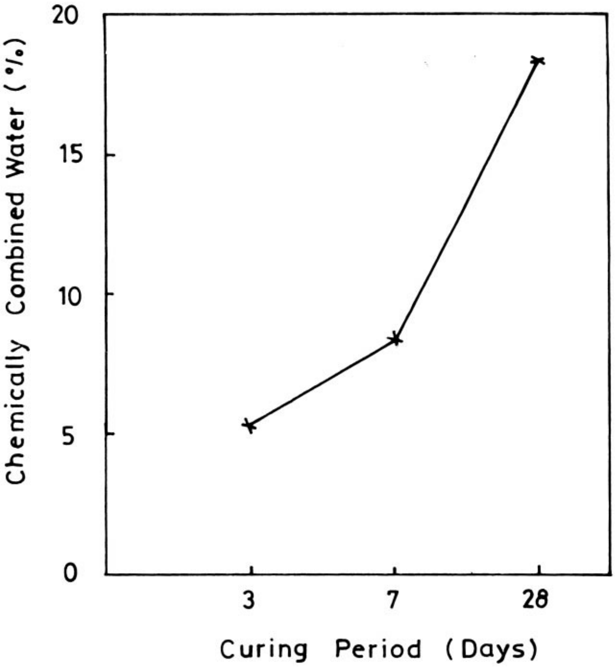

Fig. 5. Correlation between chemically combined water and curing period of anhydrite cement.

4. Conclusions

1. The stable anhydrite cement can be produced by heating phosphogypsum at 1000°C.
2. The microstructure of anhydrite cement shows the formation of euhedral prismatic and rhombic shaped crystals of platy structure.
3. Maximum attainment of compressive strength in anhydrite cement is achieved with the use of sodium sulfate and ferrous sulfate activators together.
4. The chemically combined water increases with the increase in hydration of anhydrite cement that is related to progressive increase in compressive strength.

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