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PHOSPHOGYPSUM - FLY ASH CEMENTITIOUS BINDER - ITS HYDRATION AND STRENGTH DEVELOPMENT

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ABSTRACT

The paper deals with the formulation of a cementitious binder based on calcined phosphogypsum, flyash, hydrated lime and portland cement. Strength properties and hydration of the cementitious binder studied at room temperature and at 50°C in over 90% R.H are presented. It was found that the compressive strength of the cementitious binder was remarkably enhanced at 50°C than at 27°C. The hydration of the cementitious binder as studied by differential thermal analysis and scanning electron microscopy showed that the early age strength in the cementitious binder was due to the hardening of calcined gypsum and the hydration of portland cement while later age strength development was ascribed to the formation of ettringite and CSH.

Introduction

In many industrially developed countries the production of industrial by -products and waste such as fly ash and phosphogypsum often exceed the demand for use of these materials in other products such as cement and concrete. These excesses, if not treated properly, can pollute the water, air, land and the whole environment. However, many of these waste materials possess valuable inorganic compounds such as oxides of silicon, aluminium, calcium, iron and sulphate which have potential for utilization in the concrete, plaster , ceramic and cement industries. High early strength low energy cements containing C_4A_3S, C_2S or $C_5S_2S^-$ and CS^- phases were synthesized using raw materials composed of commercial materials and industrial wastes and by - products such as phosphogypsum, fly ash, blast furnace slag and bauxite (1,2). For reducing the exploitation of natural resources, protection of the environment and energy savings, phosphogypsum and fly ash available to the tune of 4.5 and 40.0 million tons annually from phosphoric acid manufacture and thermal power plants in India can be used as source of sulphate, silica and aluminiaum in building components. Phosphogypsum contains impurities of phosphate, fluoride, organic matter and alkalies which prevents its direct use as a building material (3). In an effort to circumvent these problems, several processing techniques and uses for phosphogypsum have been suggested by various workers (4 , 5). This paper describes the feasibility of the formation of cementitious binder based on (a) calcined phosphogypsum, flyash and lime and (2) calcined phosphogypsum, fly ash, lime and cement cured at 27^0 to 50^0C in greater than 90% R.H for different periods. The enhancemant in strength with hydration period and curing temperature was monitored by differential thermal analysis (DTA) (Stanton Redcroft, U.K) and scanning electron microscopy (SEM) (Model 501, Philips, Holland).

Experimental

Raw Materials:

The chemical composition of the raw materials used in the production of the cementitious binders is shown in Table 1.

TABLE 1

Chemical Composition of Raw Materials Used for Cementitious Binders

Constituents (%)	Calcined Phosphogypsum	Fly Ash	Portland Cement
CaO	38.00	02.60	62.50
SiO_2	01.10	70.60	24.76
R_2O_3 (Al_2O_3+Fe_2O_3)	00.04	24.40	07.50
MgO	Trace	00.73	03.00
K_2O + Na_2O	00.09	-	-
SO_3	52.10	-	-
P_2O_5	00.41	-	-
F^-	00.50	-	-
Loss on Ignition	06.10	00.20	00.46

Production of Cementitious Binder

The cementitious binder designated as 'A' was produced by blending calcined phosphogypsum (β-$CaSO_4$.1/2H_2O) (40%), fly ash (40%) and hydrated lime (20%) of fineness 3000 cm^2/g, 3100 cm^2g and 3400 cm^2/g Blaine respectively. The cementitious binder designated as 'B' was made by replacing 10 wt.% of the hydrated lime in binder 'A' with portland cement having specific surface area 3300 cm^2/g Blaine. The cementitious binders were uniformally ground in a ball mill to a fineness with a Blaine specific surface area of 3200 cm^2/g. The cementitious binders were tested and evaluated for their physical properties as per methods specified in IS:4031 - 1968, specification for methods of physical testing of hydraulic cement and IS:2542 (Part 1) - 1978, specification for methods of test for gypsum plaster, concrete and products. The 2.5 cm cubes of cementitious binders 'A' and 'B' made to evaluate different physical properties were cast at 39% and 34% consistency respectively. The cubes were cured under high humidity (90%RH) for different hydration periods up to 90 days at 27°, 40° and 50°C. The setting times of the cementitious binders 'A' and 'B' were initial 19, final 56 minutes, and initial 10 and final 50 minutes respectively.

Results and Discussion

Hydration of System

Fig. 1 (AI and A2) shows the thermograms of cementitious binder 'A' hydrated from 1 to 90 days at 27° and 50°C respectively. It can be observed (Fig. 1.A1) that ettringite is the main hydration product. It forms instantaneously and its intensity increased with increase in curing period up to 90 days accompanied by diminishing an endotherms for gypsum and lime. A small depression at 760 - 780°C indicates tobermorite. At 50°C (Fig. 1 A2) the reaction is much faster than that at 27°C. This is indicated by the enhancement in the intensity of the endotherms for ettringite and tobermorite and reduction in the intensity of the gypsum and lime endotherms. After 7 days of curing no lime andgypsum was detected.

Fig. 2 (B1 and B2) show the DTA of cementitious binder 'B' hydrated from 1 to 90 days at 27° and 50°C, respectively. The thermograms are similar to the thermograms of binder 'A' (Fig. 1). Ettringite is the main hydration product. However, in this binder at 27° and 50°C, gypsum and lime are both completely consumed with increased curing and the intensity of the ettringite and tobermorite endotherms are comparatively greater than those observed in binder 'A'. The tobermorite is formed as a result of hydration of both the portland cement and the pozzolanic reaction involving interaction of SiO_2 from the fly ash with the $Ca(OH)_2$. These results corroborate the findings of Chebukov (6).

Micrographs of cementitious binder 'A' cured at 27° and 50°C for 7 and 90 days are shown in Figs 3 (a, b) and 4(a, b). The SEM studies show the formation of anhedral to subhedral hydration products, unhydrated fly ash spheres coated with calcium hydroxide and agglomerated prismatic crystals of gypsum, and the formation of euhedral CSH crystals coated wih partially hydrated fly ash spheres.

Some typical micrographs of hydration products present in cementitious binder 'B' cured at 27° and

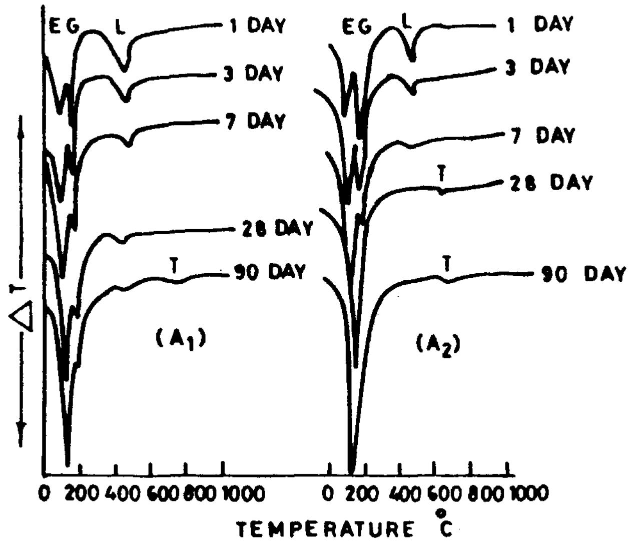


Fig. 1. DTA OF BINDER 'A' HYDRATED AT 27° (A_1) AND 50°C (A_2)
(E = ETTRINGITE, L = $Ca(OH)_2$, G = GYPSUM AND T = TOBERMORITE

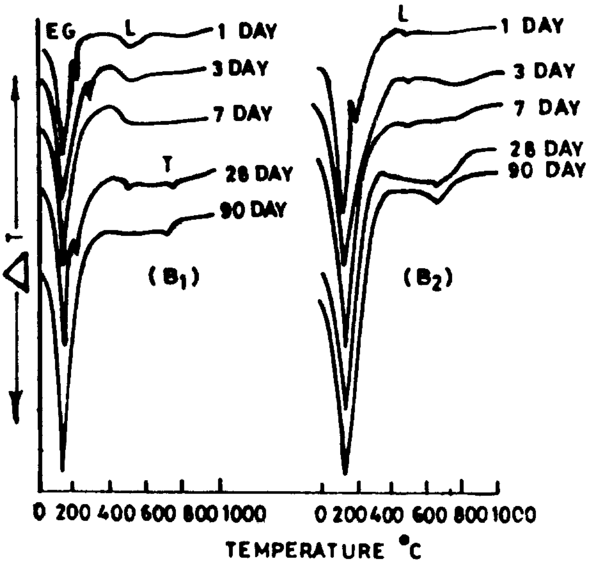
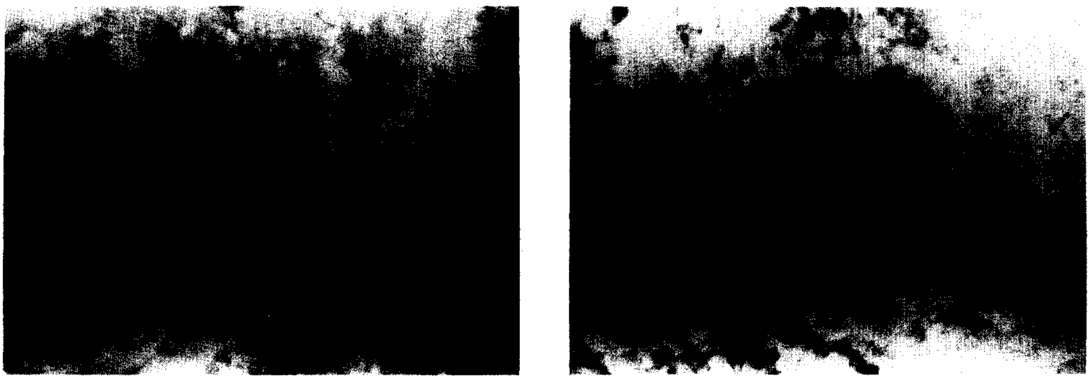


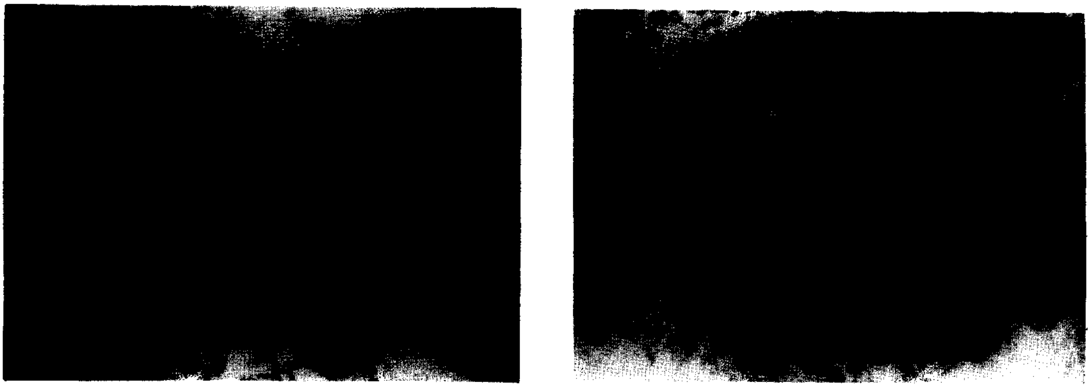
Fig. 2. DTA OF BINDER 'B' HYDRATED AT 27°(B_1) AND 50°C(B_2)

50°C, are shown in Figs 5 and 6. Fig.5(a) and (b) illustrate the formation of euhedral to subhedral prismatic and needle shaped crystals of gypsum and agglomerated needles of ettringite interspersed with fly ash. Unreacted lime and the CSH crystals coated with unhydrated fly ash particles can also be seen in Fig 5(b). Fig. 6(a) and (b) showed that 7 and 90 days cured binder 'B' develops subhedral to anhedral crystals of tobermorite agglomerated with cubic $Ca(OH)_2$, as well as lath and prismatic shaped crystals of gypsum and ettringite.



(a) (b)

Fig. 3 Micrographs of cementitious binder 'A' cured for 7 (a) and 90 (b) days at 27°C (original magnification : x 1250)



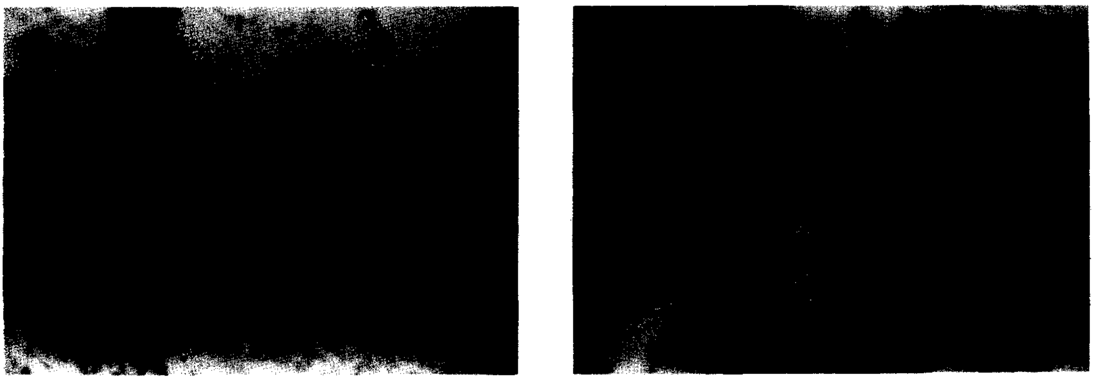
(a) (b)

Fig. 4 Micrographs of cementitious binder 'A'cured for 7 (a) and 90 (b) days at 50°C (original magnification : x 1250)

Properties of Cementitious Binder

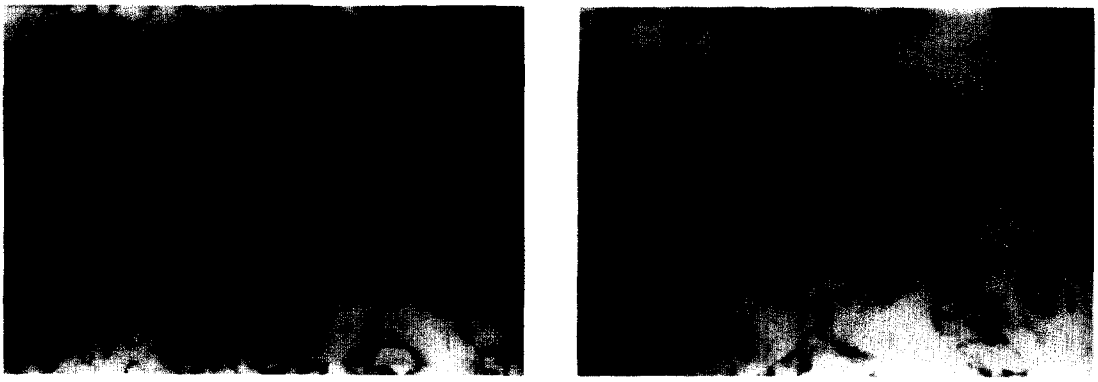
The properties of the cementitious binder 'A' and 'B' are given in Table 2.

It can be seen (Table 2) that the strength of the cementitious binder 'A' and 'B' increased with the increased curing temperature from 27° to 50°C and the hydration period from 1 to 90 days. The attainment of maximum strength in both binders 'A' and 'B' occured at 50°C. The strength development in binder 'B' is higher than that in binder 'A' due to the formation of ettringite and tobermorite and low consistency. The development of early age strength can be ascribed to the setting of calcined phosphogypsum and latter development of strength may be due to the formation of ettringite and tobermorite. The results showed that with an increase in curing temperature from 27° to 50°C, the water absorption



(a) (b)

Fig. 5 Micrographs of cementitious binder 'B' curedfor 7 (a) and 90(b) days at 27°C (original magnification : x 1250)



(a) (b)

Fig. 6 Micrographs of cementitious binder B' cured for 7 (a) and 90(b) days a 50°C (original magnification x 1250)

TABLE 2

Properties of Cementitious Binder

C.B.*	Curing Temp.. °C	Compressive Strength N/mm²					W.A.** % (24 hrs)
		1d	3d	7d	28d	90d	
A	27	1.82	1.98	2.01	2.97	8.50	23.30
	40	1.85	2.45	5.35	16.32	18.70	20.43
	50	1.92	3.04	7.71	20.07	22.53	17.38
B	27	1.96	2.50	4.50	8.78	12.06	19.46
	40	2.00	3.78	10.43	18.71	19.95	15.21
	50	2.81	5.89	13.72	22.41	23.68	11.63

* Cementitious binder ** Water absorption

decreased, probably due to the filling of voids and pores in the matrix by the enhanced formation of ettringite and tobermorite.

Conclusion

1. The cementitious binder containing equal proportions of calcined gypsum and fly ash and small quantities of hydrated lime and portland .cement attained higher strength than the cementitious binder containing hydrated lime and no portland cement.
2. The compressive strength of the cementitious binder was enhanced with increasing curing temperature from 27° to 50°C. Maximum strength was attained at 50°C.

3. The strength properties of cementitious binder achieved at elevated temperature are good enough so that these binders can be used for making building blocks, tiles, boards etc.

Acknowledgement

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