Investigation of a durable gypsum binder for building materials

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Abstract – An investigation was made to formulate a durable gypsum binder based on calcined phosphogypsum, fly-ash/granulated blast-furnace-slag and Portland cement. In this binder, phosphogypsum acts as the basic matrix and a source of sulphate in the mixture of calcium, alumina and silica derived from the fly-ash/granulated-slag. The strength development in the binder at an early age is due to the setting and hardening of calcined gypsum and Portland cement, and at a later age is due to the formation of ettringite and tobermorite. The formation of hydration products was confirmed by differential thermal analysis, X-ray diffraction and scanning electron microscopy. The gypsum binder based on fly ash exhibited lower compressive strength (22.0 N mm^{-2}) than gypsum binder based on granulated slag (35.0 N mm^{-2}). The effect of temperature (27–60°C) on strength development of gypsum binder in high humidity was studied. Data show that with increasing temperature, the strength of fly-ash-based gypsum binder is increased, whereas the strength of the slag-based gypsum binder is decreased. The enhancement in strength with increasing temperature is ascribed to the pozzolanic action of fly ash blended with the calcined gypsum. The fall in strength of slag-based gypsum binder can be attributed to the decomposition of ettringite with increasing temperature. The gypsum binder was found suitable for use in masonry mortars, bricks and glass-reinforced composites.

Phosphogypsum is a by-product of phosphoric acid manufacture. It presents a large disposal problem for which no satisfactory economical solution has yet been discovered, despite considerable research efforts.[1–3] Phosphogypsum contains a number of undesirable impurities such as phosphates, fluorides, organic matter and about 20 to 35% free moisture.[4] These impurities adversely affect the setting and hardening of calcined gypsum.[5]

In India, about 4.0 million tonnes of phosphogypsum are produced annually from over a dozen fertilizer plants. A small fraction of this material is used to produce cement, ammonium sulphate and in soil reclamation. Investigations made at the Central Building Research Institute, Roorkee, have shown that phosphogypsum after purification can be used in the production of ordinary Portland cement, blast-furnace granulated-slag cement and super-sulphated cement, calcined plaster and set plaster products.[6] The level of impurities, particularly of P_2O_5, F and organic matter, have been considerably reduced by wet sieving of phosphogypsum through 300 μm sieve. In addition to phosphogypsum, about 30 million tonnes of fly ash and 7 million tonnes of slag are produced as by-products from thermal power plants and the blast-furnace process of iron production. These industries provide potential centres in the country, where phosphogypsum, fly-ash/granulated-slag and ordinary Portland cement are closely available. Hence, utilization of these industrial by-products jointly to form any new building material would be an asset to the building industry.

Gypsum plaster and plaster products are not used externally because of their solubility in water. A durable water-resistant gypsum binder has been formulated based on calcined phosphogypsum (β-$CaSO_4.½H_2O$), fly ash, granulated blast-furnace slag, Portland cement and retarder. Hydraulic products responsible for the water-resistance of gypsum plaster have been identified with differential thermal analysis (DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The durability of gypsum binder and its utilization in masonry mortars, glass-reinforced gypsum boards and building bricks are described and discussed in the paper.

Experimental

Raw materials used

Phosphogypsum, granulated blast-furnace slag, fly ash and Portland cement clinker having the chemical composition shown in Table 1 were used. A small quantity of organic retarder was used to control the setting time of the gypsum binder.

Table 1 Chemical composition of phosphogypsum granulated slag, fly ash and Portland cement clinker

Constituents	Unprocessed phosphogypsum	Processed phosphogypsum	Percentage by weight Granulated slag	Fly ash	Portland cement clinker
P_2O_5	0.55	0.16	–	–	–
F	1.89	0.72	–	–	–
Organic matter	0.11	0.02	–	–	–
SiO_2	0.92	–	33.83	70.60	24.17
$Al_2O_3+Fe_2O_3$	0.48	–	22.93	24.40	6.77
CaO	32.40	–	34.93	2.60	62.42
MgO	0.07	–	7.46	0.73	3.21
SO_3	43.00	45.00	0.84	–	0.41
Mn_2O_3	–	–	0.099	–	–
Loss on Ignition	19.80	–	–	0.20	0.46
pH	5.00	6.10	–	–	–

Testing and evaluation of gypsum binder

Gypsum binder prepared by blending the calcined gypsum ($\beta-CaSO_4.½H_2O$), specific surface 3200 cm^2 g^{-1} (Blaine's), with the ground granulated slag, 4200 cm^2 g^{-1} (Blaine's), or fly ash, 4000 cm^2 g^{-1} (Blaine's), and a retarder was tested for different properties as per IS:4031-1968, methods of physical testing for hydraulic cements, and IS:6909-1973, specification for supersulphated cement.

The formation of hydraulic products in gypsum binder was monitored by DTA (Stanton Red Croft, UK), X-ray diffraction (Philips diffractometer, Holland) and microscopy (Philips Model 501, Holland).

Durability of binder

Performance of gypsum binder was studied by immersion of 2.5 cm cubes of gypsum binder (28 days cured) in water. The effect of increasing temperature (27 – 60°C) on the hardening of gypsum binder in 90% relative humidity was studied. The

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Table 2 Physical properties of gypsum binder

Designation of binder	Properties											
	Fineness ($cm^2 g^{-1}$) (Blaine's)	Setting time (min)		Bulk density ($g\ cm^{-3}$)				Compressive strength (MPa)				Soundness cold expansion (mm)
		Initial	Final	1d	3d	7d	28d	1d	3d	7d	28d	
Binder A												
(a) Based on untreated phosphogypsum	3150	10	40	1.52	1.67	1.83	1.91	3.5	11.0	16.2	22.0	3.50
(b) based on processed phosphogypsum	3100	70	145	1.54	1.68	1.85	1.95	10.1	23.1	28.6	35.0	1.60
Binder B												
(a) Based on untreated phophogypsum	3200	45	90	1.53	1.66	1.64	1.65	8.0	13.7	19.0	19.6	1.10
(b) based on processed phosphogypsum	3180	95	150	1.55	1.68	1.69	1.69	13.7	19.0	20.9	21.3	0.88
Selenite gypsum	3050	65	126	1.57	1.57	1.60	1.70	9.8	21.0	32.3	34.2	1.20
Plain gypsum plaster (β-hemihydrate)	3000	25	–	1.10	–	–	–	13.3	–	–	–	–

cm cubes of gypsum binder after 24 h curing were osed to different temperatures in the sealed desiccator water for a period up to 28 days. The bulk density and pressive strength of gypsum binder was determined. DTA made to ascertain the effect of increasing temperature he gypsum binder. The durability of gypsum binder by nate wetting and drying and heating and cooling cycles 27-60°C has already been studied.[7]

paration of masonry mortars

gypsum binder based on phosphogypsum, fly ash and tland cement was mixed with sand (fineness modulus 1) in different proportions. Cubes (5 cm × 5 cm × 5 cm) re cast at 105% flow for the compressive strength test. ter retentivity of the mortar and bond strength were ermined as per IS:4031-1968 and by using cross couplets bricks according to the method suggested by Rehsi *et* [8], respectively.

paration of glass-reinforced boards

ass-reinforced gypsum binder boards of size 400 mm × m x 112 mm were prepared by reinforcing E-type glass diameter 10 μm, tensile strength 1750 MPa) in the psum binder slurry by using a spray suction technique veloped in the laboratory. The glass fibre was spread at ndom in two layers, *ie* one layer of gypsum binder slurry lowed by glass-fibre reinforcement. The gypsum boards re tested for bulk density, flexural strength, tensile strength, pact strength and thermal conductivity according to the ocedures laid down in IS:8273-1976, the specification for rous gypsum plaster boards, and IS:2380-1977, the ecification for methods of tests for wood and particle boards m other lignocellulosic material.

eparation of gypsum binder bricks

quettes of size 7 cm × 5 cm × 3 cm were cast by hand- ng using gypsum binder and two types of sand: mainly adarpur (Fineness modulus 1.95) and Ranipur sand ineness modulus 1.25) in different proportions at 105% flow. e briquettes were cured at 27°C under more than 90% ative humidity, up to a period of 28 days, dried at 40°C d tested for bulk density, compressive strength and rability.

sults and discussion

aluation of gypsum binder

e binder based on phosphogypsum plaster, granulated ag and Portland cement has been designated 'A', while nder based on phosphogypsum plaster, fly ash and Portland cement has been designated 'B'. Their physical properties are reported in Table 2. The binder based on unprocessed phosphogypsum shows less retardation of the setting time and low strength development, whereas binder based on processed phosphogypsum plaster shows prolongation of the setting time and considerable improvement in the strength. The improvement in the quality of the binder is attributed to the removal of impurities from the gypsum. The soundness of the binder determined as cold expansion according to IS:6909-1973 is within the maximum specified value of 5 mm.

DTA and XRD of the gypsum binder confirmed formation of ettringite ($C_3A.3CaSO_4.32H_2O$) and calcium silicate hydrate (CSH).[7] The clusters of euhedral needles were enhanced with the formation of lath and prismatic crystals with increasing curing period. The formation of $C_3A.3CaSO_4.32H_2O$ and CSH are primarily responsible for the increase in the strength of binders A and B. The attainment of higher strength in binder A over the binder B may be ascribed to the formation of a greater amount of CSH gel in the former than in the latter.

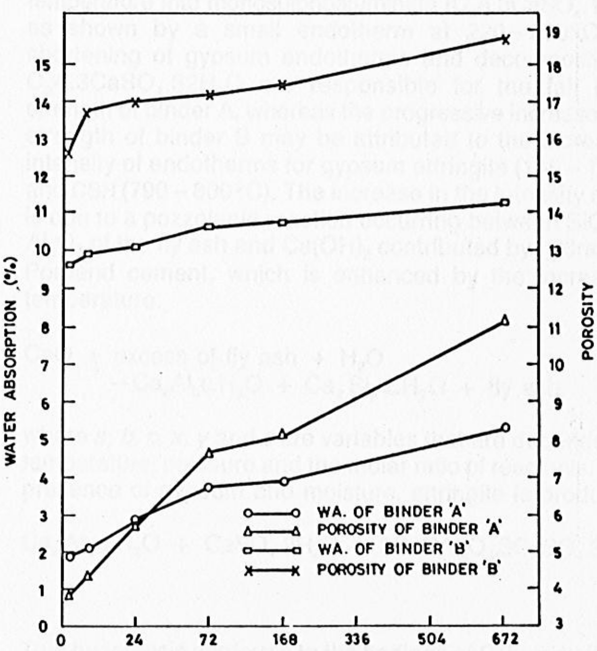


Fig1 Relationship between water absorption and porosity with immersion period

Performance of gypsum binder in water

Data on water absorption and porosity of hardened gypsum binder are reported in Fig 1. It can be seen that with increasing immersion period, the water absorption and the porosity of the gypsum binder increase. The level of increase in the water absorption and the porosity in binder A is much lower than the binder B. However, the plain gypsum showed an increase in water absorption up to three days after immersion in water (27.94%, 30.73%, 32.09%, 34.31% at immersion for 2 h, 8 h, 24 h and 72 h, respectively) and then leaching of the matrix took place, indicating thereby a better water-resistance of the gypsum binder than the plain gypsum plaster. The higher stability of gypsum binder towards water is due to the formation of $C_3A.3CaSO_4.32H_2O$ and CSH, which fill up the voids and pores of the binder.

Effect of temperature on gypsum binder

The effect of increasing temperature on the compressive strength of gypsum binder is given in Table 3. Data show that with increasing temperature (40–60°C) and curing period (1 to 28 days), the compressive strength of binder B increased while that of binder A decreased. The fall and rise in the strength of binder A and B are demonstrated by DTA and microscopic studies. Figures 2 and 3 show DTA of binder A and B, respectively, cured at 40, 50 and 60°C for a period of 28 days. For binder A it can be seen that as the temperature is increased (40 – 60°C), the intensity of double dehydration endotherms at 150 – 160°C and 190 – 200°C for the gypsum decreased, while the enotherm at 760 – 770°C due to CSH remained constant. The endotherm at 140°C is due to $C_3A.3CaSO_4.32H_2O$, which decomposes with increasing temperature into monosulphoaluminate ($C_3A.3CaSO_4.12H_2O$) as shown by a small endotherm at 220 – 230°C. The shortening of gypsum endotherms and decomposition of $C_3A.3CaSO_4.32H_2O$ are responsible for the fall in the strength of binder A, whereas the progressive increase in the strength of binder B may be attributed to the increase in intensity of endotherms for gypsum ettringite (135 – 140°C) and CSH (790 – 800°C). The increase in the intensity of CSH is due to a pozzolanic reaction occurring between SiO_2 and Al_2O_3 of the fly ash and $Ca(OH)_2$ contributed by hydration of Portland cement, which is enhanced by the increase in temperature.

Table 3 Effect of temperature on the strength of gypsum binder

Binder Designation	Curing period (days)	Compressive strength (MPa) 27°C	40°C	50°C	60°C
A	1	10.1	10.4 (103.00)*	9.6 (95.00)	84.0 (83.40)
	3	23.1	19.0 (82.48)	18.8 (81.30)	18.5 (80.40)
	7	28.6	22.5 (78.70)	20.4 (71.30)	19.8 (69.30)
	28	35.0	26.2 (75.00)	21.6 (61.71)	22.6 (64.70)
B	1	13.7	8.4 (61.70)	8.5 (62.04)	8.8 (64.67)
	3	19.0	9.5 (50.20)	11.6 (61.31)	11.7 (61.57)
	7	20.9	10.0 (47.80)	15.9 (76.34)	16.7 (77.51)
	28	21.3	20.4 (95.70)	21.0 (98.68)	21.41 (100.46)

*Values in the parentheses are percentages of strength to the original strength for the respective curing period.

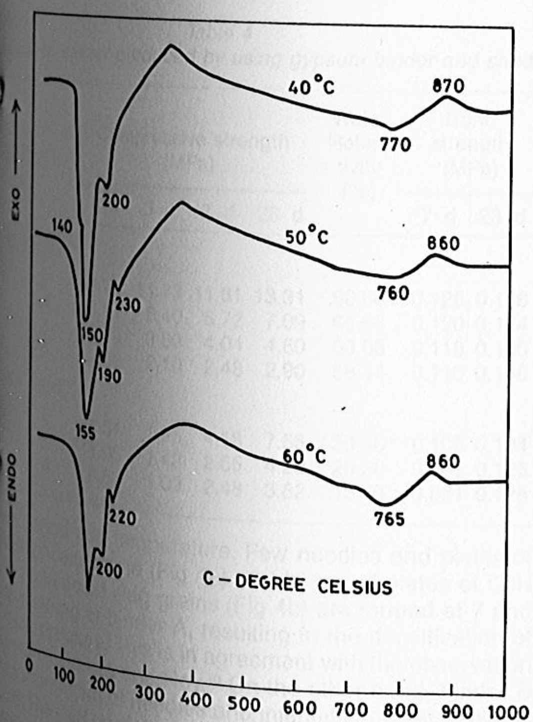


Fig 2 Differential thermogram of gypsum binder A hydrated at different temperatures for 28 days

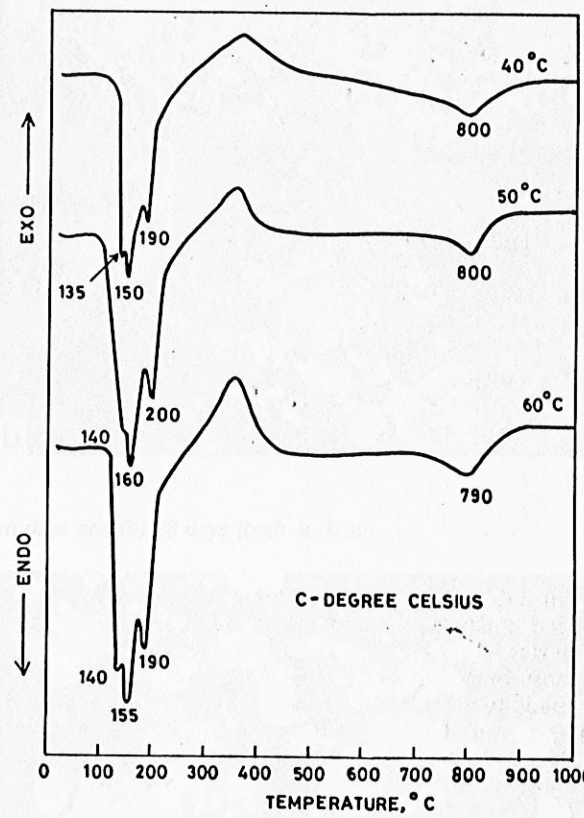


Fig 3 Differential thermogram of gypsum binder B hydrated at different temperatures for 28 days

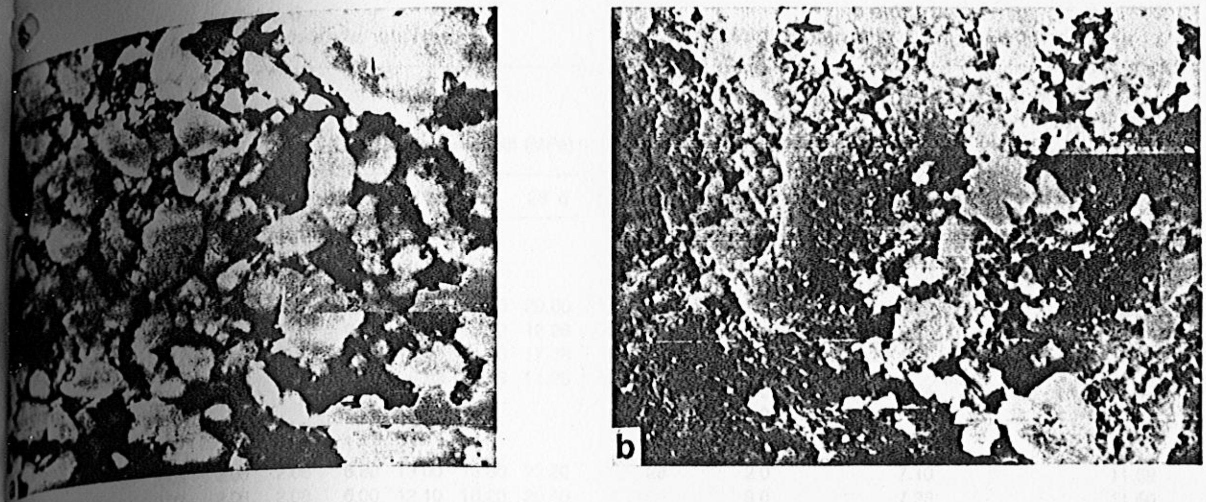
$$CaO + \text{excess of fly ash} + H_2O \rightarrow Ca_aAl_bc.H_2O + Ca_xSi_yz.H_2O + \text{fly ash} \quad (1)$$

where *a*, *b*, *c*, *x*, *y* and *z* are variables that are dependent on temperature, pressure and the molar ratio of reactants. In the presence of gypsum and moisture, ettringite is produced.

$$Ca_aAl_bc.H_2O + CaSO_4.2H_2O \rightarrow 3CaOAl_2O_3.3CaSO_4.32H_2O \quad (2)$$

This hypothesis conforms to the findings of Scholorholtz and Demirel.[9]

SEM corroborates the data obtained by DTA. For binder A the crystals of ettringite needles are reduced with increasing



Micrograph of gypsum binder A hydrated at 60°C for (a) seven days and (b) 28 days (both × 1250)

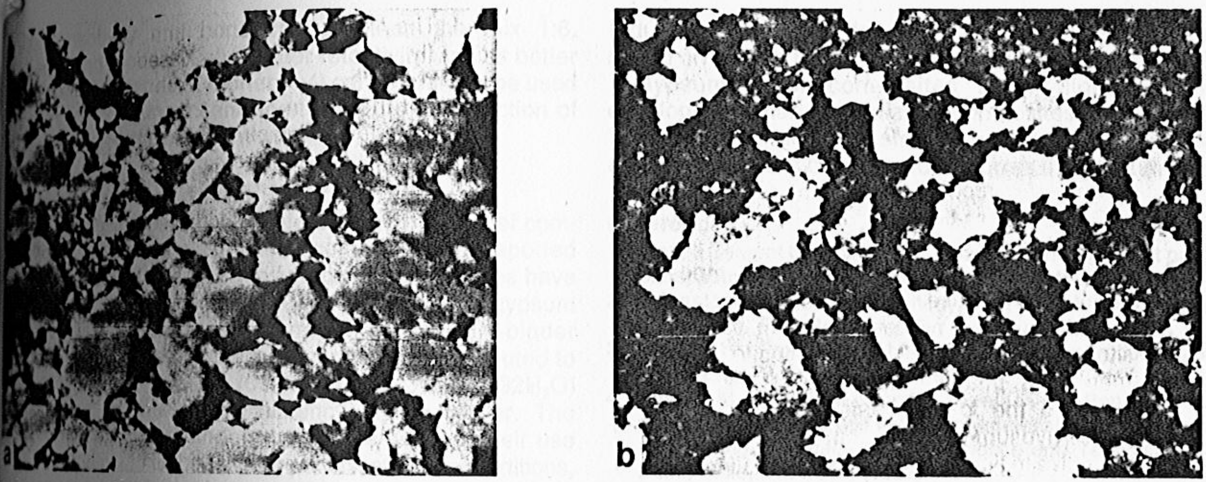


Fig 5 Micrograph of gypsum binder B hydrated at 60°C for (a) seven days and (b) 28 days (both × 1250)

Table 4
Properties of mortar produced by using gypsum binder and sand

Mix proportion (by weight)		Compressive strength (MPa)				Water Retentivity (%)	Bond strength (MPa)	
		1 d	3 d	7 d	28 d		7 d	28 d
Binder	Sand							
1	2	9.71	11.73	11.81	13.31	66.80	0.128	0.186
1	3	5.87	6.40	6.72	7.09	65.63	0.120	0.174
1	4	3.75	3.82	4.04	4.60	60.08	0.116	0.160
1	5	2.02	2.10	2.48	2.90	58.44	0.110	0.140
Cement	Sand							
1	4	1.54	1.95	4.18	7.56	30.40	0.106	0.134
1	5	1.05	1.42	2.65	4.20	20.20	0.096	0.126
1	6	0.85	1.02	2.48	3.82	16.40	0.081	0.128

Table 5
Properties of glass-fibre-reinforced gypsum-binder composites

Property	Gypsum-binder composites	Plain gypsum plaster composites
Bulk density (g cm^{-3})	1.62	1.20
Consistency (%)	65.00	81.00
Flexural strength (MPa):		
1 day	10.70	4.96
3 days	12.17	4.97
7 days	13.21	4.98
28 days	22.00	4.96
Tensile strength (MPa)	18.00	2.75
Impact strength (N mm mm^{-2})	18.60	10.20
Thermal conductivity (kcal $m^{-1}h^{-1}{}^{\circ}C^{-1}$)	0.09	0.12

curing period and temperature. Few needles and plates of monosulphoaluminate (Fig 4a) and hydrated plates of CSH coating unreacted slag grains (Fig 4b) are formed at 7 and 28 days curing of binder A, resulting in the densification of the microstructure. This is in agreement with the observation reported by Ogawa and Roy.[10] On the other hand, binder B exhibits formation of needles and interstitial hydrated plates of CSH. The CSH crystals coat the unhydrated fly-ash particles as shown in Fig 5a at 7 days of hydration of the binder. Fig 5b shows some fly-ash spheres that have been completely hydrated in 28 day-old specimens.

Utilization of gypsum binder

Masonry mortars

The data on compressive strength, water retentivity and bond strength of the mortars prepared with gypsum binder and sand are reported in Table 4. The results indicate that on increasing sand content, compressive strength, water retentivity and bond strength are reduced. A mix proportion of 1:4 binder:sand shows higher values of compressive strength,

Table 6
Properties of gypsum-binder bricks

Mix proportion (by weight)		Bulk density ($g\ cm^{-3}$)				Compressive strength (MPa)			
		1 d	3 d	7 d	28 d	1 d	3 d	7 d	28 d
Binder	Sand (Fineness modulus 2.0)								
1	1	1.98	2.02	2.03	2.06	10.46	11.20	16.06	20.80
1	1.5	2.05	2.07	2.07	2.08	9.60	10.40	13.33	18.26
1	2.0	2.13	2.14	2.14	2.15	10.20	10.90	11.26	17.38
1	2.5	2.07	2.08	2.10	2.11	3.26	5.93	6.53	11.25
Binder	Sand (Fineness modulus 1.25)								
1	1	1.95	2.03	2.05	2.06	6.80	13.00	18.80	23.20
1	1.5	2.01	2.03	2.06	2.08	6.00	12.10	16.20	20.40
1	2.0	2.03	2.06	2.07	2.09	5.86	8.93	12.00	15.20

Table 7
Water absorption of binder – sand bricks

Curing period (d)	Immersion period (h)	Water absorption (%)	
		Mix binder-sand (Fineness modulus 2.0) (1:2)	Mix binder-sand (Fineness modulus 1.25) (1:1.5)
1	2.0	9.89	13.93
	8.0	10.07	13.93
	24.0	10.25	13.93
3	2.0	9.27	12.27
	8.0	9.46	12.37
	24.0	9.65	12.45
7	2.0	9.04	11.48
	8.0	9.20	12.31
	24.0	9.30	12.45
28	2.0	7.10	11.59
	8.0	7.28	11.60
	24.0	7.40	11.65

water retentivity and bond strength than the mix 1:6, cement:sand mortar. Higher water retentivity implies better workability. Binder:sand mortar (1:4) can, therefore, be used in place of 1:6 cement:sand mortar for the construction of brick walls and for plaster work.

Glass-reinforced composites

The properties of glass-fibre-reinforced gypsum-binder composites in relation to plain-plaster composites are reported in Table 5. Data show that gypsum-binder composites have higher strength than those made with plain phosphogypsum plaster. The increase in strength in gypsum-binder composites over the plain-plaster composite is attributed to the cementitious phases (CSH and $C_3A.3CaSO_4.32H_2O$) formed and to the low consistency of the binder. The properties of gypsum-binder composites suggest their use as an alternative to timber in door panels, structural partitions, ceilings, cupboards, table tops, *etc.*

Gypsum binder bricks

The bulk density and compressive strength of briquettes (7.5 cm × 5.0 cm × 3.75 cm) produced by hand-moulding of gypsum binder and sand are reported in Table 6. It can be seen that with increase in sand content, the bulk density increased while the compressive strength decreased.

Table 7 gives the effect of immersion of hardened binder-sand mortars in water. The results show that with increasing hardening period (1-28 days), the water absorption decreases. However, the water adsorption increased with the length of immersion in water (2 – 24 h) for all the hardened mortar briquettes. These findings clearly indicate that there is no leaching of binder.

Conclusions

The strength of the gypsum binder increases with increasing curing period. However, the strength development at 27°C is more pronounced in the binder based on granulated slag than the binder based on fly ash.

With the increase in curing temperature from 27°C to 60°C, the compressive strength of the gypsum binder is reduced. The level of fall in strength was lower for binder based on fly ash than for binder based on granulated slag.

Gypsum-binder composites show higher strength development than plain-plaster composites.

Masonry mortar of high strength and high water-retentivity, and durable bricks can be produced from the gypsum binder.

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