



PII S0008-8846(96)00008-7

## RELATIONSHIP BETWEEN MECHANICAL PROPERTIES AND POROSITY OF WATER-RESISTANT GYPSUM BINDER

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(Refereed)

(Received November 5, 1993; in final form December 5, 1995)

### ABSTRACT

The paper describes an experimental investigation involving pore structure of blended gypsum binder. The pore structure was investigated by using mercury porosimeter. A relationship between structure and mechanical properties has been established. It has been found that the principal factor of porosity governs the development of structure and strength of the blended gypsum binder. The pore size distribution was characterised by a reduction in the volume of the pores whose diameters are larger than 500 Å and an increase in the volume of those smaller diameters. An interpretation of the development in strength vis-a-vis porosity of the blended gypsum binder is presented.

### Introduction

The use of portland cement must be restricted in developing countries due to the high cost of energy associated with industrial manufacture and transport of the material. Low cost housing requires consumption of cheap and low energy industrial by-products such as granulated blast furnace slag, flyash, red mud and phosphogypsum to get hardened binders with sufficient strength.

The gypsum plaster ( $\beta$ -CaSO<sub>4</sub> · 1/2H<sub>2</sub>O) does not show any significant performance concerning resistance to water because its solubility (2g/litre) and porosity are high. Attempts have been made to make gypsum water repellent (1-2). The processes developed so far could not be adopted due to the high expense of these treatments. Therefore, a water-resistant gypsum binder suitable for plaster, masonry work and fibre reinforced gypsum composites has been developed by blending the phosphogypsum plaster (70-80%) with granulated blast furnace slag/flyash, cement and a small quantity of organic retarder (3).

In India about 5.0 million tonnes of phosphogypsum is being produced annually from over a dozen phosphoric acid fertilizer plants. It contains impurities such as phosphate, fluoride, organic matter and alkalies which adversely affect the setting and hardening of plaster products. Several processing techniques and uses of phosphogypsum have been suggested by various workers (4,5). The hydraulic properties responsible for the water-resistance of gypsum plaster and durability have been reported elsewhere (3,6). The strength and durability properties of

blended gypsum binder showed that it has much higher strength and better water resistance than the plain plaster. These properties can be correlated with the reduction in porosity of the matrix.

This paper presents an experimental investigation into the changes in the pore structure of water resistant blended gypsum binder and plain plaster with curing period. The changes in the pore structure were determined by measuring the porosity and pore size distribution with mercury intrusion porosimetry technique. A comparison between the strength and the porosity and the pore structure of blended gypsum binder vis-a-vis plain plaster has been discussed.

## Experimental

**Production of Water-Resistant Gypsum Binder.** Water resistant gypsum binder was produced by blending the ground granulated slag, portland cement and an organic retarder with clacined phosphogypsum ( $\beta$ -hemihydrate) followed by grinding together in a ball mill to obtain a uniform product. The chemical composition of blended gypsum binder analysed as per IS: 1288-1983, Methods of testing of mineral gypsum is depicted in Table 1.

The physical properties of the binder tested according to IS: 4031-1968, Methods of physical testing for hydraulic cements and IS: 6909-1973, specification for supersulphated cement are reported in Table 2. The formation of hydraulic products in the blended gypsum binder responsible for the progressive enhancement in the strength was monitored by differential thermal analysis (Stantan Red Croft, U.K.), X-ray diffraction (Philips Diffractometer, Holland) and microscopic examination (Zeiss Petrographic Microscope, Germany) at different periods of its hardening.

Differential thermal analysis (DTA) of the blended gypsum binder showed formation of endotherms at  $145^\circ$  and  $790^\circ\text{C}$  due to ettringite ( $\text{C}_3\text{A}3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ ) and CSH besides double dehydration endotherms at  $197^\circ$  and  $235^\circ\text{C}$  due to gypsum respectively which increased on hydration.

X-ray diffraction of blended gypsum binder gave reflections at  $7.6880^\circ$ ,  $4.2872^\circ$ ,  $3.0455^\circ$  and  $1.4336^\circ$  A due to CSH and at  $5.6775^\circ$ ,  $3.8635^\circ$ ,  $3.3540^\circ$ ,  $2.7857^\circ$ ,  $2.2046^\circ$ ,  $2.1204^\circ$ ,  $2.0786^\circ$  and  $1.8937^\circ$  A due to ettringite intermingled with gypsum as the predominant phase.

The microscopic studies of the blended gypsum binder revealed the formation of radiating needles, ettringite and hydrated plates of CSH interspersed with lath and prismatic crystals of

TABLE 1  
Chemical Composition of Blended Gypsum Binder

Constituents	Per cent
$\text{SiO}_2$ + insoluble in HCL	8.20
$\text{R}_2\text{O}_3$ ( $\text{Al}_2\text{O}_3$ + $\text{Fe}_2\text{O}_3$ )	9.00
CaO	37.30
MgO	1.80
$\text{SO}_3$	39.65
Loss on Ignition	4.10

TABLE 2  
Physical Properties of Water Resistant Gypsum Binder

Properties	Blended Gypsum Binder	Plain Gypsum Plaster
Fineness, cm <sup>2</sup> g <sup>-1</sup>	3100	3000
Setting time, min		
Initial	70	25
Final	145	-
Bulk density, G cm <sup>-3</sup>		
1-day	1.54	1.10
3-day	1.68	-
7-day	1.85	-
28-day	1.95	-
Compressive Strength,		
1-day	10.10	13.30
3-day	23.10	-
7-day	28.60	-
28-day	35.00	-
Soundness, mm	1.60	1.10
Water absorption, %	6.0	33.0
pH	11.5	6.9

gypsum. The formation of ettringite and CSH in the gypsum matrix are responsible for the gain in strength of the blended gypsum binder. The detailed hydration studies of the blended gypsum binder has been reported elsewhere by Singh and Garg. (3).

The performance of blended gypsum binder as studied by immersing the 28 days hardened 2.5cm cubes of the binder in water is shown in Table 3. It is evident from the Table that the increase in immersion period, the water absorption of blended gypsum binder increased without leaching of the matrix whereas plain phosphogypsum plaster exhibited leaching after 3 days of immersion. The superior behaviour of blended gypsum binder towards water may be ascribed to the filling of voids and pores of the gypsum matrix with ettringite and CSH.

The 25mm cubes of blended gypsum binder and plain plaster were cast at consistency 36% and 60% respectively for porosimetry test. The cubes were cured under high humidity (> 98% RH) for different hydration periods up to 28 days at 27°C.

For the measurement of pore parameters, a fragment of each specimen is taken from the inner one third of the 25 mm cube sample. The sample weighing between 0.5 and 1.0 g was taken and dried to constant weight in an oven at 42°C. The sample was then stored in a vacuum desiccator over silica gel until test. Pore size distribution was determined by using a mercury intrusion porosimeter of 206.8 MPa pressure capacity. The pressure applied (P) is related to the pore diameter (7) as

$$P = \frac{4\gamma \cos \theta}{d} \quad (1)$$

TABLE 3  
Performance of Blended Gypsum Binder in Water

Immersion Period (hr)	Water Absorption (%)	
	Blended Gypsum Binder	Phospho Plaster
2.0	1.86	27.94
8.0	2.09	30.73
24.0	2.89	32.09
72.0	3.77	34.31
168.0	3.91	Leaching
672.0	5.53	Leaching

Where  $\gamma$  is the surface tension of mercury,  $\theta$  is the contact angle and  $d$  is the diameter of the intruded pore. The value of  $\gamma$  was taken as 484 MN/m and  $\theta$  was 117°.

The total porosity ( $\Sigma$ ) of the blended gypsum binder is determined by using the relation.

$$\Sigma = \frac{W d_s}{d_w} \quad (2)$$

Where  $W$  is the weight loss on drying at 42°C until a constant weight,  $d_s$  is the dry density of blended gypsum binder and  $d_w$  is the density of water.

### Results and Discussion

**Relationship Between Porosity and Compressive Strength.** The mechanical properties of blended gypsum binder depend upon pore structure especially porosity. The development of compressive strength of blended gypsum binder with hydration periods is shown in Table 2. It can be seen that the strength at 1-day, 3 day and 7-day is 29% 66% and 82% of that of 28-day, respectively. These results clearly manifest that a porous structure is formed in the early period and after three days the matrix of the blended gypsum binder is being filled by hydration products (ettringite and tobermorite) and the structure becomes more dense attributing high strength. The attainment of high strength with hydration period may be correlated with porosity using the following relationship (8).

$$R = R_0 \exp (-BP) \quad (3)$$

Where  $R_0$  is the strength at zero porosity called intrinsic strength,  $P$  is the porosity and  $R$  is the strength at porosity  $P$  and  $B$  is an empirical constant. The  $R_0$  value obtained by extrapolation

TABLE 4  
R<sub>o</sub> and B Values for Blended Gypsum Binder

Hydration Period	Blended Gypsum Binder		Plain Plaster	
	R <sub>o</sub> , MPa	B	R <sub>o</sub> , MPa	B
1-day	67	0.08	32	0.025
3-day	72	0.63	32.05	0.025
7-day	80	0.06	32.50	0.025
28-day	83.01	0.056	32.50	0.02

from different porosity measurements and the B value by calculation using equation 3 for blended gypsum binder and  $\beta$ - hemihydrate plaster respectively are given in Table 4.

It can be seen Fig.1 that the total porosity determined by using equation 2 decreased with increase in the hydration period of blended gypsum binder. The rate of decrease of porosity was greater at early stages of hydration but became approximately linear after 7-days of hydration. These data clearly exhibited that reduction in porosity with curing period may be the reason behind the strength characteristics and durability performance of blended gypsum binder.

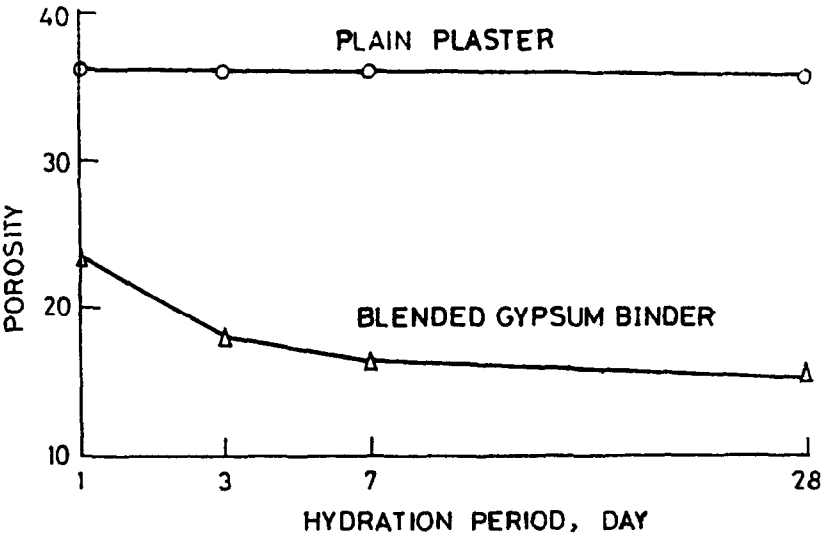


FIG. 1.  
Change in porosity with hydration period of Blended gypsum binder and plain plaster.

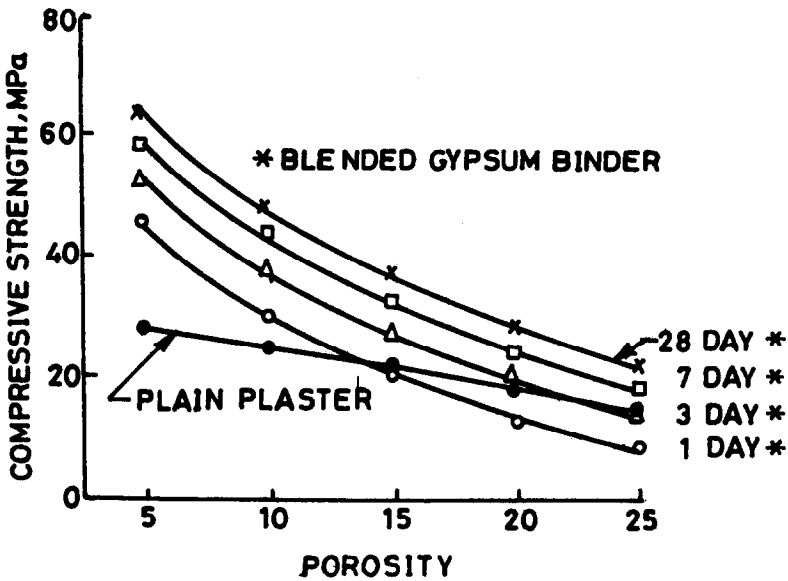


FIG. 2.

Relationship between compressive strength and porosity of Blended gypsum binder and plain plaster.

Figure 2 shows the relationship, between compressive strength (calculated from equation 3) and porosity of blended gypsum binder with different hydration periods and of plain plaster. It can be seen that this relationship is different from each other and follow different lines with hydration periods. It amply demonstrated the intrinsic strength values of blended gypsum binder increased with the increase in curing period.

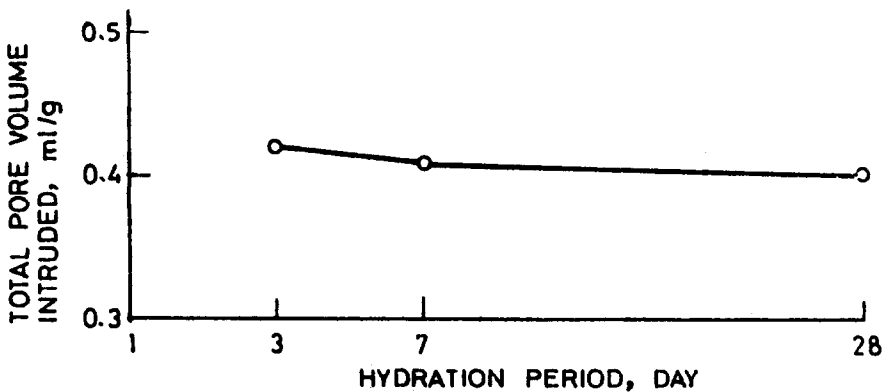


FIG. 3.

Effect of hydration period on the total pore volume intruded of Blended gypsum binder.

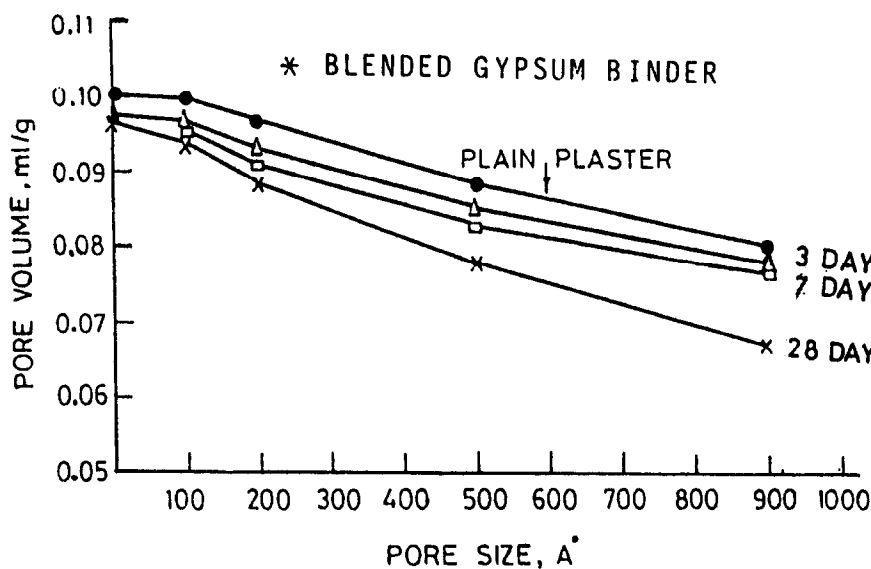


FIG. 4.

Effect of hydration period on comparative pore size distribution of blended gypsum binder.

**Pore Structure of Blended Gypsum Binder.** The total pore volume intruded by mercury also decreased with hydration period of blended gypsum binder (Fig. 3), whereas the porosity (Fig. 1) and total pore volume of  $\beta$ -hemihydrate plaster (0.50 ml/g) is much higher than blended gypsum binder. The higher porosity and pore volume of gypsum plaster implies that it possess higher quantity of pore spaces and coarser pores.

The pore size distribution results (Fig. 4) show that with the increase of hydration period, the pores of blended gypsum binder became finer. This may be ascribed to the filling of pores and voids with the hydrated products. At 28 days the pores larger than 500 A° in the blended gypsum binder are much less than those in the plain gypsum plaster.

### Conclusions

From the above study the following conclusions can be drawn:

1. The porosity and pore volume of blended gypsum binder are lower than those of the plain plaster.
2. The major parameter determining the development of strength, structure and durability of blended gypsum binder is porosity.
3. Enhancement in compressive strength of gypsum binder with hydration period can be correlated with the reduction in porosity of the blended gypsum binder matrix.
4. The total pore volume, porosity and the total intruded pore volume decreases with hydration period but density increases.

### Acknowledgement

The authors are thankful to Director, Central Building Research Institute, Roorkee for allowing publication of this paper. Thanks are also due to Shri R.P. Mehrotra, Scientist, Indian Institute of Petroleum, Dehradun (U.P).

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