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# Investigation of properties of fluorogypsum-slag composite binders – Hydration, strength and microstructure

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ABSTRACT

A composite binder of high strength and low water absorption has been developed using industrial by-products fluorogypsum, granulated blast furnace slag and Portland cement. The development of strength in the binder at an early age is attributed to the conversion of anhydrite into gypsum and at later age is due to the formation of ettringite and tobermorite, as a reaction of slag with lime produced during the hydration of cement. These cementitious phases fill in pores and voids of the hydrating gypsum crystals to form a dense and compact structure of low porosity and low pore volume. The reaction products formed during the hydration period were confirmed by scanning electron microscopy and X-ray diffraction. The reduction in porosity and low pore volume of binders, as studied by mercury intrusion porosimetry, are responsible for attainment of high strength and better stability towards water in composite binders than the conventional gypsum plaster.



## 1. Introduction

Every year, more than 300 million tonnes of industrial solid wastes are being produced by various industries in India and governments are seeking ways to reduce the dual problems of disposal and health hazards from the accumulation of by-products. In recent years, the use of waste materials in the construction industry has become an important option, as it offers cost reductions, energy savings, and reduced $CO_2$ emissions from the production of Portland cement, as well as reduced environmental impacts of construction materials. The predominant industrial by-products that can be effectively used include chemical gypsum, slag, fly ash and lime sludge.

Out of different waste materials being generated, the use of by-product gypsum is significant not only from the point of view of its disposal, but to avail the dross for conserving high quality natural gypsum and to produce new building materials. By-product gypsum is available to an extent of about 13.0 million tonnes per annum in India from phosphoric acid, hydrofluoric acid and intermediate dye industries and not more than 15.0% is utilized by the cement industries, soil reclamation etc. The limited application of the by-product gypsum is due to the adverse impacts of certain undesirable impurities present in the gypsum on the engineering properties and performance of building materials. Gypsum products are known for their fire resistance, thermal insulation and acoustic properties. However, due to its low water resistance and mechanical strength, gypsum is not a suitable material for external construction works [1–3]. The protection of gypsum requires prevention against penetration of moisture to avoid any damage to the plaster. The gypsum obtained from different sources can be utilized as supplementary raw materials in the production of composite binders as investigated by various researchers. Some attempts were made to produce gypsum-cement-pozzolana binders [4–6] with phosphogypsum. Investigations revealed that a gypsum binder made of a phosphogypsum anhydrite and blast furnace slag mixture 70–24% with appropriate activators achieved 23 MPa strength after 28 d curing at 27 °C under high humidity [7] and a mixture composed of 75% gypsum, 20% OPC and 5% micro silica as cementitious binder developed a strength of up to 17 MPa after 200 d under water [2,8]. Other researchers reported that blends of 41% gypsum, 41% OPC and 18% natural pozzolana gained 22 MPa strength after 95 d; blends of 50–80% fluorogypsum, 15–50% OPC and 0–5% fly ash achieved 32 MPa strength after 180 d and blends of 75% fluorogypsum with blast furnace slag and metakaolin samples showed 14 MPa strength after 360 d of curing in wet conditions [9–11]. The above quoted references reported cementitious systems of various compositions using different sources of gypsum, which developed strength during various curing periods.

In India about 4.0 million tonnes of fluorogypsum, a cardinal waste material of the hydrofluoric acid industry, is produced per annum and poses the problem of disposal and pollution hazards

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as it sets too slowly to form any useful building materials, thus creating an environmental nuisance. The literature survey revealed that not much work has been done on the utilization of fluorogypsum as a main component in composite binders. The objective of this research was to convert fluorogypsum into a composite binder by enhancing its hydration properties and performance through the use of an appropriate processing method. Underlining this, a systematic study is undertaken for the utilization of fluorogypsum, as a main component, by admixing it with blast furnace slag and ordinary Portland cement into a composite binder suitable for construction work. The mechanical properties, hydration mechanism, microstructure and durability under water of the composite binders are discussed in the paper. A comparison between the strength and performance in water of the composite binders and commercially available gypsum plaster (β-$CaSO_4.1/2H_2O$) used as a reference material is also presented.

## 2. Experimental and materials

### 2.1. Raw materials

#### 2.1.1. Fluorogypsum

The sample of fluorogypsum was analysed for various constituents such as $SiO_2$, $Al_2O_3$, $Fe_2O_3$, CaO, MgO, $SO_3$, $CaF_2$ and pH as per standard test procedures [12,13] and characterised by differential thermal analysis (DTA) (Stanton Red Croft, UK), X-ray diffraction (Rigaku D-Max 2200) and scanning electron microscopy (SEM) (LEO 438 VP, UK). The results of the chemical analysis given in Table 1 show that fluorogypsum possesses a high purity along with free acid (pH 2.8), which is responsible for its hygroscopic nature and may corrode the grinding media. Therefore, the pH of the fluorogypsum was adjusted to 8–8.5 by addition of 0.5–1.0% of lime ($Ca(OH)_2$) and then ground in a ball mill to a fineness of 90% passing through a 90 μm IS sieve.

#### 2.1.2. Granulated blast furnace slag

The chemical analysis of granulated blast furnace slag tested as per IS:4032-2005 [14] is shown in Table 2. The composition of blast furnace slag satisfied the requirements of IS: 12089-2008 [15] as the ratio of CaO + MgO + $Al_2O_3$ to $SiO_2$ was found to be 1.6, which was greater than a minimum value of one as specified in the standard. Therefore, it was found suitable for making Portland slag cement and other cementitious materials [16,17].

#### 2.1.3. Portland cement

The physical and chemical analysis of Portland cement tested as per Indian Standards [14,18] are given in Table 3.

### 2.2. Preparation and testing of composite binders

The mixture composition of composite binders prepared by blending the beneficiated ground fluorogypsum with granulated blast furnace slag (Fineness 400 $m^2$/kg (Blaine), Portland cement and activators in different proportions followed by inter-grinding in a ball mill to a fineness of 410 $m^2$/kg (Blaine) are given in Table 4. The composite binders were tested for different properties as per methods specified in Indian Standards and compared with properties of conventional gypsum plaster or Beta-hemihydrate plaster (β-$CaSO_4.1/2H_2O$).

**Table 1**
Chemical composition of fluorogypsum.

| Constituents | (%) |
|---|---|
| $CaF_2$ | 1.32 |
| $SiO_2$ + insoluble in HCl | 1.65 |
| $Al_2O_3$+$Fe_2O_3$ | 0.65 |
| CaO | 42.2 |
| MgO | 0.05 |
| $SO_3$ | 55.1 |
| Loss on ignition | 0.31 |
| pH | 2.8 |

**Table 2**
Chemical composition of granulated blast furnace slag.

| Constituents | (%) |
|---|---|
| Silica | 36.8 |
| $Al_2O_3$ | 16.5 |
| $Fe_2O_3$ | 0.36 |
| CaO | 34.9 |
| MgO | 7.46 |
| $Na_2O + K_2O$ | 1.7 |
| S | 0.92 |
| MnO | 0.85 |
| $SO_3$ | 0.37 |
| Insoluble residue | 0.039 |

**Table 3**
Physico-chemical properties of Portland cement.

| Property studied | |
|---|---|
| *Chemical constituents (%)* | |
| Silica | 24.2 |
| $Al_2O_3$ | 3.39 |
| $Fe_2O_3$ | 3.2 |
| CaO | 62.62 |
| MgO | 3.21 |
| $Na_2O + K_2O$ | 1.7 |
| $SO_3$ | 1.8 |
| Loss on ignition | 0.45 |
| *Physical properties* | |
| Specific gravity | 3.1 |
| Setting time (min) | |
| Initial | 240 |
| Final | 300 |
| *Compressive strength (MPa)* | |
| 3 d | 33.0 |
| 7 d | 45.0 |
| 28 d | 56.5 |

### 2.3. Testing

#### 2.3.1. Setting time

The initial and final setting times of composite binders were determined using a Vicat needle as per Indian Standard [18].

#### 2.3.2. Compressive strength and bulk density

To determine the compressive strength and bulk density of the composite binders, cubes of size 25 mm were cast at normal consistency. The samples were cured for 24 h at room temperature and then placed at 27 °C ± 2 °C in a sealed desiccator containing water for different hydration periods up to 90 d. The specimens cured for respective hydration periods were dried at 42 °C ± 2 °C for 2 d and the compressive strength was determined as per IS: 4031(2002). The average value of six specimens is reported. The compressive strength of composite binders was within a 5% variation level of the arithmetic average. The bulk density of the dried specimen in kg/$m^3$ was calculated by dividing the mass of the specimen by the overall volume of the cube.

#### 2.3.3. Transverse strength

The specimens of size 200 mm × 25 mm × 25 mm hydrated for 28 d were tested for transverse strength under three point load-