Phosphogypsum Based Composite Binders

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The physical properties of the composite binders have been tested and are reported. The composite binder containing slag and other constituents give maximum strength. The performance of the binder in water, as studied by the immersion method, is discussed. The composite binders have been subjected to their use in masonry and plastering and found to possess high strength and high workability than the conventional cement-sand mortars. The use of composite binders for masonry and plastering works, both in external and internal situations, is recommended. The techno-economic feasibility of the composite binder envisaged for a plant of capacity 50 t/d is presented.

Introduction

Development of industrial activities has led to accumulation of huge industrial wastes in the urban and semi-urban centres culminating into big problems of their disposal and health hazard. Several industrial wastes such as fly ash, phosphogypsum, red mud, blast furnace slag, nonferrous slags, lime sludges, mine tailings, etc., are produced in large quantities. Besides industrial wastes, agricultural wastes, hazardous wastes (electroplating, tanning, food products, distilleries, and pharmaceuticals), municipal and hospital wastes are also thrown away causing threat to the environment. Generally, these wastes are stockpiled near the industrial units. Sometimes they are trucked away to the disposal areas such as rivers, sea or open mines which involves huge expenditure. Recycling of industrial wastes is the only way of its waste management. Out of various industrial wastes mentioned above, the main focus is on the effective utilisation of phosphogypsum in both urban and rural areas as potential building material. It is interesting to note that building materials account for 70-75 per cent (Table 1) of the total cost of construction.

Phosphogypsum is a by-product of the phosphoric acid fertilizer plants which is available to the tune of over 5.0 mt/y in India. Phosphogypsum contains impurities of phosphates, fluorides, alkalis in addition to organic matter. The phosphate residue consists of the phosphoric acid, \( \text{Ca}_3(\text{PO}_4)_2 \), \( \text{Ca}((\text{H}_2\text{PO}_4)_2 \text{H}_2\text{O} \), and \( \text{CaHPO}_4 \). The fluoride containing compounds are \( \text{Na}_3\text{AlF}_6 \), \( \text{Na}_3\text{FeF}_6 \), and \( \text{CaF}_2 \) (ref. 2). Sometimes, phosphogypsum originating from phosphorites can be contaminated with radioactive elements. These impurities interfere with the normal setting and strength development of the building products made out of it. Since the impurities are both water soluble and insoluble in nature and vary in quantities, the treatment of phosphogypsum is imperative to meet the desired level of requirements laid down in the relevant standards. Several processes have been evolved by various researchers such as washing, wet sieving, treatment with lime water or even chemical leaching of the phosphatic and fluoride impurities to remove or inactivate the ill effect of impurities. Phosphogypsum has been utilized in the production of cement, plasters, building boards, and blocks.

The other important industrial wastes which can be used along with phosphogypsum are fly ash, slag, and red mud. The fly ash currently available to the extent of over 70 mt from the thermal power plants in India is not used more than 10 per cent compared to 45-70 per cent being used in countries like Germany, the Netherlands and Denmark. Besides fly ash, slag, and red mud are produced to a level of 10 and 2.5 mt/y, respectively. It is quite possible to synthesize new and durable materials by judicious blending of these wastes.

The study gives the development of low cost cementitious binders prepared from the calcined phosphogypsum, fly ash, slag, red mud, and other
Table 1 — Average cost break-up of building construction

<table>
<thead>
<tr>
<th>Materials (73 per cent)</th>
<th>Labour (27 per cent)</th>
<th>Component-wise (100 per cent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>18 Mason’s wages</td>
<td>10 Foundation</td>
</tr>
<tr>
<td>Iron and steel</td>
<td>10 Carpenter’s wages</td>
<td>5 Walls</td>
</tr>
<tr>
<td>Bricks</td>
<td>17 Unskilled labour</td>
<td>12 Roofs</td>
</tr>
<tr>
<td>Timber</td>
<td>13 Doors and windows</td>
<td>15 Roofing</td>
</tr>
<tr>
<td>Sand</td>
<td>7 Flooring</td>
<td>10 Finishing</td>
</tr>
<tr>
<td>Aggregate</td>
<td>8</td>
<td></td>
</tr>
</tbody>
</table>

Table 2 — Chemical composition of raw materials

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Unprocessed phosphogypsum</th>
<th>Processed phosphogypsum</th>
<th>Granulated slag</th>
<th>Fly ash</th>
<th>Red mud</th>
<th>Portland cement</th>
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</thead>
<tbody>
<tr>
<td>P_2O_5</td>
<td>0.55</td>
<td>0.16</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>F</td>
<td>1.89</td>
<td>0.72</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Organic matter</td>
<td>0.11</td>
<td>0.02</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>SiO_2</td>
<td>0.92</td>
<td>—</td>
<td>33.83</td>
<td>70.60</td>
<td>13.80</td>
<td>24.17</td>
</tr>
<tr>
<td>Al_2O_3 + Fe_2O_3</td>
<td>0.48</td>
<td>—</td>
<td>22.93</td>
<td>24.40</td>
<td>65.20</td>
<td>6.77</td>
</tr>
<tr>
<td>CaO</td>
<td>32.40</td>
<td>—</td>
<td>34.93</td>
<td>2.60</td>
<td>—</td>
<td>62.42</td>
</tr>
<tr>
<td>MgO</td>
<td>0.07</td>
<td>—</td>
<td>7.46</td>
<td>0.73</td>
<td>—</td>
<td>3.21</td>
</tr>
<tr>
<td>SO_3</td>
<td>43.00</td>
<td>45.00</td>
<td>0.84</td>
<td>—</td>
<td>Tr.</td>
<td>0.41</td>
</tr>
<tr>
<td>MnO_2</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.20</td>
<td>8.10</td>
<td>—</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>19.80</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>pH</td>
<td>5.00</td>
<td>6.10</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Materials and Methods

Preparation of Composite Binder

The composite binders were prepared by mixing the ground calcined gypsum (calcium sulphate hemihydrate) (65 to 70 per cent) with the finely divided granulated blast furnace slag or fly ash or red mud, Portland cement, and small quantity of a chemical retarder in the ball mill to a fineness of 300-320 m^2/kg (Blaine). The chemical compositions of the raw materials are listed in Table 2.

Results and Discussion

Properties of Composite Binders

The properties of three different composite binders which were produced from the calcined phosphogypsum (with and without processing), fly ash, granulated slag, red mud, and other additives are shown in Table 3 and 4. It can be noticed that the compressive strength of composite binders increases with the advancement in the curing period. The composite binder, based on the phosphogypsum plaster blended with granulated slag shows highest attainment of strength. However, the setting time of the binders was quite fast. It can be attributed to the high concentration of SO_3 ions contributed by the calcined gypsum in the vicinity of
aqueous paste which combines with the $\text{Al}_2\text{O}_3$ ions in the presence of lime, thereby forming ettringite and gypsum dihydrate. The presence of impurities of phosphate and fluorides also modify the morphology of the calcined gypsum and affect the setting of the binder. In spite of rapid setting, the binders are sound as they show cold expansion within the maximum specified value of 5.0 mm laid down in IS: 6909-1989\textsuperscript{99}.

Due to rapid setting of the binders it was decided to process the phosphogypsum. The phosphogypsum was processed by washing and wet sieving of the phosphogypsum through 300 $\mu$m sieve and by rejection of the coarser fraction (not more than 10 per cent) retained over the sieve, rich in impurities of phosphate, fluoride, organic matter, and quartz present\textsuperscript{11}. The composite binders were prepared by blending the calcined gypsum...
made out of processed phosphogypsum at 150° to 160°C with the fly ash, granulated slag, and red mud, followed by grinding in the ball mill. Data given in Table 3, show an increase in strength values and improvement in the setting time. The cold expansion of the binders is also reduced. The increase in strength and prolongation of setting time can be linked with the reduction in impurities present in phosphogypsum.

**Water—Resistance of Binder**

The performance of composite binder was studied by immersing 28 d cured 2.5 cm x 2.5 cm x 2.5 cm cubes in water. Data showed that with increase in immersion period, the water absorption of the binder enhanced without leaching of the matrix. However, the plain plaster of Paris showed increase in water absorption up to 3 d (32 per cent) and then leaching of the matrix took place, indicating thereby a better water resistance of the binder than the plain plaster. The water resistance of the composite binder may be ascribed to the development of cementitious products like C₃A₃CaSO₄·32H₂O (ettringite) and C-S-H (tobermorite) produced during hydration of the binder which fill up the voids and pores of the binder and improve the durability of the binder.

**Mortar Making Properties**

The properties of masonry mortars, made from the composite binder and sand (Fineness modulus 1.22) are listed in Table 5. Data show that mortar mix 1:4 binder-sand gives maximum strength, water retentivity, and bond strength than the conventional 1:6 cement-sand mortar. Due to high water retentivity, the mortar retains workability for longer time. The mortar is recommended for use in construction in masonry works.

**Use of Binder in Plastering**

A wall area of 1000 mm x 1000 mm x 12 mm was plastered with 1:5 binder-sand mortar (F.M. 1.22) (by volume), both in external and internal situations. The plaster developed excellent strength and hardness after 24 h of application. There were no cracks or leaching of the matrix even after 6 y. The cost of the materials used in mortar 1:5, binder-sand has been worked out to be Rs11.50/m² against Rs14.50/m² for the 1:6 cement-sand mortar traditionally used in construction, hence, cost may be effected.

**Process Flow Diagram**

The process flow diagram for the production of composite binder is shown in Figure 1. Various steps involved in production line are illustrated.

**Techno-economic Feasibility of the Composite Binder**

A plant having capacity of 50 t of the composite binder per day in three shifts has been envisaged for the commercial production on small-scale. The production line consists of separate grinding and blending of the raw materials. The major equipment are calcinator, roller or ball mill and a blender. The cost economics of the binder has been prepared on the basis of the processed
phosphogypsum. Details are given below:

(a) Capacity of the plant: 50 t/d, i.e., 15000 t/y of 300 working days

(b) Total Capital Investment
   (i) Fixed capital: Rs 25,80,000=00
   (ii) Working capital: Rs 5,16,000=00

(c) Total cost of production
   (i) Cost of production: Rs 157,00,000 =00
   (ii) Selling price per tonne: Rs 1115=00
   (e) Profitability: 34.46 per cent
   (f) Employment potential: 24 persons plus labour
   (g) Raw materials requirements
      (i) Processed phosphogypsum: 13452 t
      (ii) Fly ash: 2250 t
      (iii) OPC: 1500 t
      (iv) Retarder: 15 t

(b) Utility requirements
    (i) Electric power: 2, 68,560 kWh
    (ii) Coal: 630 t
    (iii) Water: 200 KL

Benefits of Composite Binder

The production of composite binder is very effective in disposing of large quantities of industrial wastes, particularly phosphogypsum, besides making available an alternative binder. The binder can be used in place of ordinary Portland cement in plastering and masonry mortars. The composite binder has great potential in making fibre reinforced boards of high strength and low water absorption, in making gypsum blocks, water resistant tiles etc. for various applications. The gypsum boards, based on the composite binder, can be used as the substitute for depleting wood. The cost of the binder is much less than the ordinary Portland cement, hence saving in the production cost of different products from the binder can be effected. The use of composite gypsum binder is recommended in the construction work.

Conclusions

The study arrives at the following conclusions:

(i) The composite binders may be prepared from beneficiated phosphogypsum and other ingredients such as fly ash, granulated slag, red mud, Portland cement and a retarder.

(ii) The composite binder based on calcined phosphogypsum and granulated slag develops maximum strength.

(iii) The composite binder shows better water-resistance than the plain gypsum plaster.

(iv) The composite binders are eminently suitable for masonry and plastering applications suited to different environments.

(v) There is an ample scope of composite binder for making fibre reinforced boards and building blocks as wood substitute.
References