Effect of Admixing Fly Ash on Cementing Characteristics of Magnesium Oxychloride Cement

Rekha Sharma, R. N. Yadav

Abstract: Investigations pertaining to the effect of admixing different amounts of fly ash on setting characteristics and compressive strength of magnesium oxychloride cement has been carried out in this paper. For this purpose, two different dry mix compositions (1:0 and 1:1) of magnesia and dolomite were prepared and 5 %, 10 %, 15 % and 20 % fly ash were added in dry mixes. The dry mixes were then gauged with 24 °Be concentration of magnesium chloride gauging solution. It was observed that initial and final setting times of cement blocks tend to increase with increasing amount of fly ash in dry mix. MOC cement blocks of 1:1 composition admixed with fly ash displayed good cementing characteristics.

Keywords: Compressive strength, fly ash, Gauging solution, Inert filler, MOC, Setting time.

I. INTRODUCTION:

Magnesium oxychloride cement is an inorganic mineral binder which was introduced by a French chemist S. T. Sorel in 1867 [1]. It is prepared via an exothermic reaction between reactive MgO powder and concentrated MgCl₂. At room temperature phase-3 or [3Mg(OH)₂ • MgCl₂ • 8H₂O] and phase-5 or [5Mg(OH)₂ • MgCl₂ • 8H₂O] are the two chief hydrated phases that impart mechanical strength to the cement by intergrowth and interlocking tendencies of their needle like crystals [2]-[5]. This cement displays some very unique and diverse cementing properties that renders it superior in comparison to Portland cement, as reported by several researchers [6]-[10]. Due to very low specific gravity (~2.4), it is resilient and light in weight. It acts as a tough stone like, fire proof compound which is extensively used for both light and heavy floorings. MOC cement is characterized by rapid setting and high early strength. After setting it does not require humid curing. Owing to the low value of thermal expansion coefficient, it displays negligible volume changes during setting. MOC cement is also characterized by higher compressive strengths ranging in between 9000-45000 psi and tensile strength of over 800 psi as compared to conventional concrete [11]. Magnesium oxychloride cement possesses enormous load bearing capacity and can easily resist vibrations arising from heavy cast iron wheels, without displaying any cracks or fissures [5]. It shows better resistance towards oil, grease and paints and remains unaltered by the attack of acids or alkalis. It is resistant to abrasion also. Owing to its lower pH value (10-11) as compared to Portland cement with pH value (12-13), it could be used conveniently with glass without causing aging problems [12].

The manufacturing process of MOC binders is not only free from any carbon dioxide gas emissions, but due to carbon sequestration potential, these binders actually act as “sinks” for atmospheric carbon dioxide [13]. The important commercial applications of MOC binders include floorings of industries and hospitals, grinding wheels and wall insulation panels due to its marble like gloss. The industrial applications of MOC cement has been limited because of the associated problems of poor water resistance, volume instability, cracking and sweating etc. The magnesium oxychloride binder system exhibits excellent bonding capacity to a large variety of organic and inorganic substances. Different additives such as fillers, fibers, metals, wood, plastic, rubber, glass and even waste materials such as fly ash [14], granite [15] and asbestos wastes [16] etc. have been incorporated in it to get the desired properties in MOC binders. Effect of various additives on setting, strength and water resistance of magnesia cement has been studied by different researchers [8], [9], [14], [17]-[19]. Fly ash is a waste byproduct generated in coal based thermal power plants in huge amounts every year. The power plant ashes (or coal ashes) are generated as a mixture of coarse bottom ash (20 %) or finer pozzolanic fly ash (80 %) or flue ash. The word “pozzolanic” refers to the capacity of fly ash to react with lime and water at room temperature to form a water insoluble, solid cement like substance [20]. In cement and concrete technology, fly ash is defined as “pulverized fuel ash” [21]. The ministry of power, government of India estimates 1800 million tons of coal use every year and 600 million tons of fly ash generation by the year 2031-32 [22]. This surplus fly ash stock is posing a great threat in terms of precious land required for its disposal, detrimental impacts on environment and its inherent potential to cause health hazards. Hence in present scenario, the safe management and substantial utilization of this surplus fly ash generated, has become a major challenge. In recent years the intrinsic worth of fly ash for applications in diverse areas has been acknowledged. Construction industry is one such area which has a large potential to incorporate fly ash. Admixing of fly ash in concrete renders it an eco-friendly and energy efficient building material as it leads to a reduction in carbon footprint of concrete [14]. This addition also extends technical benefits of concrete, reduces its cost, saves virgin raw materials (coal, limestone etc.) and precious land resources required for fly ash disposal [22] - [23]. On the other hand, considering environmental concerns this incorporation of fly ash into concrete serves for an efficient method for its safe disposal and sustainable utilization.
As a result, fly ash earlier considered as “hazardous waste material” is now being treated as “valuable resource material and saleable commodity” [21].

II. MATERIALS AND METHODS:
The raw materials used in the study were calcined magnesite, magnesium chloride, dolomite powder and fly ash.

A. Calcined Magnesite
Magnesia used in this study was of Salem, Chennai origin with following characteristics: (1) Bulk density 0.85 kg/l (2) 95 % passing through 75-micron (200 IS sieve) (3) minimum magnesium oxide 90 % (4) CaO < 1.5 % (5) Ignition loss at 100 °C ~ 2.5 ± 0.5 %.

B. Magnesium Chloride (MgCl₂.6H₂O)
Magnesium chloride used in present study was of Indian Standard Grade 3 of Indian Standard: 254-1973 with following characteristics: (1) Colorless, crystalline, hygroscopic crystals. (2) Highly water soluble. (3) Magnesium chloride hexahydrate minimum 95 % (4) Magnesium sulphate, calcium sulphate and alkali chlorides (NaCl) contents < 4%.

C. Dolomite (Inert Filler)
Dolomite dust was used as an inert filler having following grading: (1) 100 % passing through 200-micron Indian Standard sieve (2) 50 % retained on 125-micron IS sieve (3) CaO ~ 28.7 % (4) MgO ~ 20.8 % (5) Insoluble and other sesquioxide contents < 1.0 %.

D. Fly Ash (Additive)
Fly ash was procured from Dadri thermal power plant, Uttar Pradesh. It had following characteristics: (1) SiO₂ - 62.58 % (2) Fe₂O₃ - 13.50 % (3) Al₂O₃ - 8.50 % (4) CaO - 1.68 % (5) MgO - 1.60 % (6) Na₂O - 0.18 % (7) K₂O - 0.21 % (8) SO₃ - 9.00 % (9) LOI - 1.45 %. Physical Characteristics- (1) Whiteness - 43.30 % (2) oil absorption – 26.20 ml /gm (3) water absorption – 33.80 % (4) pH - 7.20 (5) bulk density- 1.11 gm /cc (6) moisture- 0.06 %.

E. Preparation of magnesium chloride solution
Magnesium chloride solution was prepared by transferring magnesium chloride flakes into plastic containers and then adding potable water to it to obtain concentrated solution. This solution was kept overnight to allow insoluble impurities to settle down at the bottom. The supernatant concentrated solution was then transferred into other plastic container and well stirred after each dilution prior to the determination of specific gravity. Concentration of the solution is expressed in terms of specific gravity on Baume scale (Be).

F. Preparation of dry-mix compositions
Dry mixes were prepared by mixing lightly calcined magnesite (magnesia) and dolomite (inert filler) in the ratio 1:0 and 1:1 by their weight and then admixing fly ash in different amounts (5 %, 10 %, 15 % and 20 %) in each dry mix composition.

G. Determination of Standard consistency and setting times of cement pastes
Wet mixes were prepared by gauging dry mix composition with 24 °Be magnesium chloride gauging solution. The standard consistency, initial and final setting times were investigated as per IS 10132-1982 using Vicat apparatus [24]- [26]. The observed results are displayed in table-I and table-II.

H. Determination of Compressive strength
Influence of admixing fly ash on compressive strength of MOC cement was determined by using cubes (molds) of size 70.6 x 70.6 x 70.6 mm³ as per standard procedure [5], [25], [27]. Dry-mix compositions were prepared by mixing magnesia and dolomite in 1:0 and 1:1 ratio by their weight and adding 5 %, 10 %, 15 % and 20 % fly ash additive in dry-mix. These dry mixes were then gauged with 24 °Be gauging solution. All cubes were air dried at room temperature under lab conditions (75 ± 5 % relative humidity, 30 ± 2 °C temperature) and were tested for compressive strength after 30 days. The results obtained are recorded in table-III and table-IV.

I. Determination of Durability
To determine the durability of product, Le-Chateliers test was conducted as per the standard procedure [18], [24] and the results are recorded in table-V and table-VI.

III. RESULTS AND DISCUSSION
The effects of adding fly ash as an admixture, on setting characteristics of magnesium oxychloride cement having different dry mix compositions are displayed in table-1 and table-11 (fig. 1 and 2).

Table 1: Effect of fly ash on setting characteristics of 1:0 dry-mix composition of MOC.

<table>
<thead>
<tr>
<th>Fly Ash (%)</th>
<th>Without FA</th>
<th>5 % FA</th>
<th>10 % FA</th>
<th>15 % FA</th>
<th>20 % FA</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgCl₂ / Gauging Solution (ml)</td>
<td>94</td>
<td>92</td>
<td>91.5</td>
<td>90</td>
<td>88</td>
</tr>
<tr>
<td>IST (min.)</td>
<td>72</td>
<td>82</td>
<td>87</td>
<td>93</td>
<td>98</td>
</tr>
<tr>
<td>FST (min.)</td>
<td>210</td>
<td>225</td>
<td>236</td>
<td>250</td>
<td>262</td>
</tr>
</tbody>
</table>

Concentration of Gauging Solution: 24 °Be, Dry mix: 1:0* Humidity: 75 ± 5%

* One part by weight of magnesia and no dolomite IST: Initial setting time; FST: Final setting time, FA: Fly Ash
The small and spherical shaped fly ash particles reduce particle friction by exerting lubricating effect. This causes an increase in the fluidity (or workability) of the wet mix [29]- [30]. As a result, setting times tend to increase.

The results recorded in table I-II show the volume of gauging solution required for standard consistency. It was observed that volume of gauging solution required for standard consistency at different compositions of the dry mix (1:0 and 1:1) tends to decrease almost uniformly. Although dry-mix 1:0 requires more amount of gauging solution than dry-mix 1:1. The two factors, increasing inert filler content and amount of heat evolved are collectively responsible for the observed trends. Similarly, in each dry-mix composition, the amount of gauging solution decreases with increasing amount of fly ash. This can be related to the spherical shape of fly ash particles that lower particle friction and exert lubricating effect. This results in reduced water demand and improved workability (or fluidity) of the wet mix. Investigations pertaining the effect of fly ash admixture on compressive strength of MOC samples prepared with different dry mix compositions and gauged with 24 °Be concentration of gauging solution are summarized in the table III-IV and figure 3-4.

**Table III: Effect of Fly ash on compressive strength of 1:0 dry-mix composition of MOC.**

<table>
<thead>
<tr>
<th>Fly Ash (%)</th>
<th>Without FA</th>
<th>5 % FA</th>
<th>10 % FA</th>
<th>15 % FA</th>
<th>20 % FA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Load (Kg/N)</td>
<td>300</td>
<td>255</td>
<td>260</td>
<td>275</td>
<td>285</td>
</tr>
<tr>
<td>Compressive Strength (MPa)</td>
<td>60.188</td>
<td>51.16</td>
<td>52.163</td>
<td>55.173</td>
<td>57.179</td>
</tr>
</tbody>
</table>

Concentration of Gauging Solution: 24 °Be Dry mix: 1:0* Humidity: 75 ± 5 % * One part by weight of magnesia and no dolomite. FA: Fly Ash

![Fig. 1: Effect of fly ash on setting time of 1:0 dry mix of MOC.](image1)

It is quite evident that if the amount of magnesia in 1:0 dry mix is replaced by dolomite, as in dry mix (1:1), setting time tends to increase. This can be related to the nature of dolomite, an inert filler incorporated in the dry mix composition, which has a tendency to retard the evolution of heat (or exothermicity). For different compositions of wet mix, the increasing tendency of setting time may also be attributed to the property of crystalline phases present in the cement paste. Thus, the coupled effect of two factors, increasing amount of inert filler content and decreasing rate of heat evolution determines the observed trends. Final setting times are also following the same trend (table I-II, fig. 1-2). It was also observed that both setting times increased with increasing amount of fly ash.

**Table II: Effect of Fly ash on setting characteristics of 1:1 dry-mix composition of MOC.**

<table>
<thead>
<tr>
<th>Fly Ash (%)</th>
<th>Without FA</th>
<th>5 % FA</th>
<th>10 % FA</th>
<th>15 % FA</th>
<th>20 % FA</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgCl₂ Gauging Solution (ml)</td>
<td>80</td>
<td>77.5</td>
<td>76.5</td>
<td>75</td>
<td>74</td>
</tr>
<tr>
<td>IST (min.)</td>
<td>90</td>
<td>102</td>
<td>111</td>
<td>120</td>
<td>130</td>
</tr>
<tr>
<td>FST (min.)</td>
<td>230</td>
<td>250</td>
<td>265</td>
<td>282</td>
<td>300</td>
</tr>
</tbody>
</table>

* One part by weight of magnesia and one part by weight of dolomite

![Fig. 2: Effect of fly ash on setting time of 1:1 dry mix of MOC. IST: Initial setting time; FST: Final setting time, FA: Fly ash](image2)

In case of 1:0 dry mix (table III, fig. 3) gauged with 24 °Be of gauging solution, it was observed that addition of fly ash initially lowers the strength as compared to control block (without fly ash). The compressive strength for 5 % addition of fly ash is 51.160 MPa (255 Kg/N) which is lower than the strength of control mix 60.188 MPa (300 Kg /N). As the amount of fly ash addition is increased strength also increases gradually. For 15 and 20 % fly ash addition strength achieved is 55.173MPa (275 Kg /N) and 57.179 MPa (285 Kg /N) respectively.

![Fig. 3: Effect of Fly ash on compressive strength of 1:0 dry-mix composition of MOC.](image3)
Effect of Admixing Fly Ash on Cementing Characteristics of Magnesium Oxychloride Cement

This may be attributed to the fact that only magnesia is present in 1:0 dry mix, which reacts with magnesium chloride gauging solution to form strength giving phase-5. Incorporation of fly ash serves for dual role for strength development. The excess lime, released during hydration of cement, acts as a source for fly ash pozzolanic reaction and generates additional C-S-H gel having binding properties similar to that produced by hydration of cement paste. This reaction of fly ash with excess lime continues as long as lime is present in the pores of wet mix and imparts additional strength to it. On the other hand, the unreactive portion of fly ash behaves as “micro-aggregates” and fills up the matrix. This leads to enhanced packing effect and strength of cement [29]-[31]. Hence strength increases with increasing amount of fly ash.

In case of 1:1 dry mix composition (table IV, fig. 4) a decrease in strength was observed with initial addition of fly ash. The compressive strength of cement for 5 % addition of fly ash is 49.154 MPa (245 Kg /N) which is lower than the strength of control mix 58.182 MPa (290 Kg /N). Then it increased and maximum strength of 54.169 MPa (270 Kg /N) was obtained for 10 % addition of fly ash. After this strength reduced slightly with further addition of fly ash. Although strength obtained was higher than 45 MPa in all cases. For 15 % and 20 % fly ash addition strength obtained were 52.163 MPa (260 Kg /N) and 46.144 MPa (230 Kg /N) respectively. In 1:1 dry mix magnesia content is replaced by inert filler dolomite powder which is a double carbonate of calcium and magnesium. During the preparation of wet mixes, it gets converted into its respective oxides and expels carbon dioxide. Hence, compressive strength of molds reduces accordingly as the amount of inert filler increases in dry mixes of MOC samples.

\[ \text{Ca/MgO} \rightarrow \text{CaO + MgO + CO}_2 \]

**Table IV: Effect of fly ash on compressive strength of 1:1 dry-mix composition of MOC.**

<table>
<thead>
<tr>
<th>Fly Ash ((%))</th>
<th>Without FA</th>
<th>With 5% FA</th>
<th>With 10% FA</th>
<th>With 15% FA</th>
<th>With 20% FA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Load (Kg/N)</td>
<td>290</td>
<td>245</td>
<td>270</td>
<td>260</td>
<td>230</td>
</tr>
<tr>
<td>Compressive Strength (MPa)</td>
<td>58.182</td>
<td>49.15</td>
<td>54.16</td>
<td>52.16</td>
<td>46.14</td>
</tr>
</tbody>
</table>

Concentration of Gauging Solution: 24 °Be Dry mix: 1:1 * Humidity: 75 ± 5 %

* One part by weight of magnesia and one part by weight of dolomite. FA: Fly Ash

**Table V: Effect of Fly ash on soundness of 1:0 dry-mix composition of MOC.**

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Observations</th>
<th>Without FA</th>
<th>With 5% FA</th>
<th>With 10% FA</th>
<th>With 15% FA</th>
<th>With 20% FA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Weight of cement composition (gm)</td>
<td>38</td>
<td>38</td>
<td>38</td>
<td>38</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>(i) Magnesia</td>
<td>38</td>
<td>36.1</td>
<td>34.2</td>
<td>32.3</td>
<td>30.4</td>
</tr>
<tr>
<td></td>
<td>(ii) Dolomite</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>(iii) Fly ash</td>
<td>-</td>
<td>1.9</td>
<td>3.8</td>
<td>5.7</td>
<td>7.6</td>
</tr>
<tr>
<td>2</td>
<td>Amount of MgCl(_2) solution (in ml)</td>
<td>19.5</td>
<td>18.5</td>
<td>18.2</td>
<td>18</td>
<td>17.5</td>
</tr>
<tr>
<td>3</td>
<td>Distance between two pointers before starting (in mm)</td>
<td>9</td>
<td>11</td>
<td>14</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>Distance between two pointers after 7 days before boiling (in mm)</td>
<td>12</td>
<td>14</td>
<td>16</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>5</td>
<td>Distance between two pointers after boiling (in mm)</td>
<td>13.5</td>
<td>15.5</td>
<td>17</td>
<td>11</td>
<td>13</td>
</tr>
<tr>
<td>6</td>
<td>Expansion of cement (in mm)</td>
<td>1.5</td>
<td>1.5</td>
<td>1</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

**Concentration of Gauging Solution: 24 °Be**

**Dry-mix: 1:0**

* Humidity: 75 ± 5 %

As in 1:1 dry mix composition (table VI), the expansion in the volume of trial blocks tends to increase in comparison to 1:0 dry mix with no dolomite.
When fly ash is admixed expansion first increases and then reduces slightly for higher amounts of fly ash. The most plausible explanation of this trend is the fact that when ratio of inert filler increases in dry mix composition, the amount of residual active lime and unreacted magnesia content in the matrix also increases. These unconsumed contents undergo hydration during soundness test and cause volume expansion by converting into their respective hydroxides. Thus, positive volume changes are quite obvious under humid conditions.

\[
\begin{align*}
\text{Ca} / \text{MgCO}_3 & \rightarrow \text{CaO} + \text{MgO} + \text{CO}_2 \quad (1) \\
\text{CaO} / \text{MgO} + \text{H}_2\text{O} & \rightarrow \text{Ca(OH)}_2 / \text{Mg(OH)}_2 \quad (2)
\end{align*}
\]

On boiling the trial blocks, active lime and magnesia are formed by the decomposition of inert filler dolomite with the expulsion of carbon dioxide. Hence under humid conditions significant volume changes are observed due to the formation of calcium and magnesium hydroxides. When fly ash is admixed in concrete, these alkalis are consumed by the reaction occurring between the siliceous glass of fly ash and the alkali hydroxide of the cement paste. Hence, their availability for causing expansion reaction with reactive aggregates is reduced. Also, when cementitious material is partly replaced by fly ash, amount of heat evolution is low. This liberated heat is consumed during pozzolanic reaction of fly ash. As a result, micro-cracking is reduced with increased soundness of cement binders.

### Table VI: Effect of Fly ash on soundness of 1:1 dry-mix composition of MOC.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Observations</th>
<th>Without FA</th>
<th>With 5% FA</th>
<th>With 10% FA</th>
<th>With 15% FA</th>
<th>With 20% FA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Weight of cement composition (gm)</td>
<td>38</td>
<td>38</td>
<td>38</td>
<td>38</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>(i) Magnesia</td>
<td>19</td>
<td>18.05</td>
<td>17.1</td>
<td>16.2</td>
<td>15.2</td>
</tr>
<tr>
<td></td>
<td>(ii) Dolomite</td>
<td>19</td>
<td>19</td>
<td>19</td>
<td>19</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>(iii) Fly ash</td>
<td>-</td>
<td>0.95</td>
<td>1.9</td>
<td>2.8</td>
<td>3.8</td>
</tr>
<tr>
<td>2</td>
<td>Amount of MgCl₂ solution (in ml)</td>
<td>14.5</td>
<td>14.5</td>
<td>14</td>
<td>13.5</td>
<td>13</td>
</tr>
<tr>
<td>3</td>
<td>Distance between two pointers before starting (in mm)</td>
<td>12</td>
<td>11</td>
<td>8</td>
<td>7</td>
<td>14</td>
</tr>
<tr>
<td>4</td>
<td>Distance between two pointers after 7 days before boiling (in mm)</td>
<td>16</td>
<td>15</td>
<td>11</td>
<td>10</td>
<td>17</td>
</tr>
<tr>
<td>5</td>
<td>Distance between two pointers after boiling (in mm)</td>
<td>18.5</td>
<td>18</td>
<td>13.5</td>
<td>12</td>
<td>19</td>
</tr>
<tr>
<td>6</td>
<td>Expansion of cement (in mm)</td>
<td>2.5</td>
<td>3</td>
<td>2.5</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

*Concentration of Gauging Solution: 24 °Be Be*  

**Dry-mix: 1:1**  
**Humidity: 75 ± 5%**

IV. CONCLUSION

1. Admixing of fly ash in 1:0 and 1:1 dry-mix compositions improves workability of the wet mix.
2. Dry mix compositions (1:0 and 1:1) display similar trends for increase in setting time characteristics by incorporation of fly ash. Although setting times are prolonged in presence of dolomite.
3. Dry mix composition 1:1 (equal amounts of magnesia and dolomite) with incorporation of fly ash also exhibits good cementing characteristics such as compressive strength and durability.
4. Thus 1:1 dry mix composition has a potential to be used as a cost-effective cementing material.

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