Effect of formaldehyde as an additive on some properties of magnesium oxysulphate cement

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ABSTRACT

A French scientist Sorel S.T., discovered magnesium oxysulphate cement (magnesia / Sorel’s Cement) in 1867. In this work the effect of formaldehyde as an additive is studied on some properties of Sorel’s cement. It is found that incorporation of formaldehyde in the matrix increases setting periods but does not contribute to the water tightness of the cement, though compressive strength of the product improves by its incorporation in small amount. Minor contractions in the linear beams are also noticed with passage of time.

Key words: Magnesium oxysulphate cement, Compressive strength, Water tightness, Setting periods, Weathering effects, linear changes.

INTRODUCTION

Sorel cement, which is named for its inventor, Frenchman Stanislas Sorel who first produced it in 1867, is a hydraulic cement mixture of magnesium oxide (burnt magnesia) and magnesium chloride with the approximate chemical formula Mg₄Cl₂(OH)₆(H₂O)₈, corresponding to a weight ratio of 2.5-3.5 parts MgO to one part MgCl₂. This material, which is also called “Magnesia Cement,” is usually combined with filler materials such as sand or crushed stone. Magnesia cements are a variety of cements based on magnesium oxide (MgO). This variety includes magnesium oxychloride cement¹ ¹², magnesium oxysulphate cements³, magnesium phosphate cements⁴ ⁵, Morover, adding magnesium oxide to Ordinary Portland Cement (OPC), yields more durable composite cement⁶ ⁷. Magnesite cements (or magnesium carbonate) is one of the more promising magnesia cements that has recently attracted considerable interest from industry⁸.

Its chief drawback is its poor water resistance, making it unsuitable for construction applications. Additionally, it is expensive compared to standard concrete and gypsum.

Sorel has highlighted the use and potential of Magnesium oxysulphate as a binder material since the invention of magnesia cements in 1867¹ ¹² ¹⁰. Sorel cements show many properties that are superior to those of OPC¹¹. For example, it has high fire resistance, low thermal conductivity, high abrasion resistance, high transverse and crushing strengths and does not require wet curing. It is being considered for nuclear applications also⁴ ¹² ¹³. Magnesium oxysulphate cement has a very distinct difference from Oxychloride cement that it does not present a potential source for corrosion of reinforcing steel. Magnesium oxysulphate cements, formed by the reaction of magnesium sulphate solution with magnesium oxide, have similar properties, as of magnesium oxychloride cements³.
According to temperature ranges and preparation conditions, five types of Oxysulphate cements are known. They are 5Mg(OH)$_2$.MgSO$_4$.3H$_2$O (or2H 2O), 3Mg(OH)$_2$.MgSO$_4$.8H$_2$O, 5Mg (OH)$_2$.MgSO$_4$.8H$_2$O, Mg(OH)$_2$.MgSO$_4$.5H$_2$O and Mg(OH)$_2$.2MgSO$_4$.3H$_2$O [14,15]. Hall et. al has also identified the presence of 5Mg(OH)$_2$.MgSO$_4$. 3H$_2$O [16]. Magnesium Oxysulphate cement of 5Mg(OH)$_2$.MgSO$_4$.8H$_2$O composition is most commonly found17-19.

The Oxysulphate cement category is normally considered to be weaker than the oxychloride types of cement. But studies reveal that many weak cementing materials can be made to have higher strengths by modifying certain conditions of manufacture or preparation20,21. In case of Portland Cements²², strength remains unchanged during its exposure to water23,24. The oxysulfate cement system is not in the wide use because of loss of strength on prolonged exposure to water.

Additives or admixtures play an important role to modify the properties of oxysulphate cement either in positive or in negative direction and also nullify the pernicious effects of the impurities present in the raw materials. Incorporation of Green additives has been reported for sustainable cement production to improve its properties25. Green Chemistry is placed in the frontier areas of research and has been focused for considerable recent research26. Use of green additives involve considerable decrease in emissions of green house gases (CO2 and SO2) during the production of cement27,28. It opens new doors of possibilities to produce sustainable cements.

Changes in properties of Magnesium oxysulphate cement on admixing sodium bicarbonate as an additive have been studied separately, which reveals that sodium bicarbonate increases setting periods in all proportions within the experimental limits. It also improves the water tightness and strength of the cement when is added in powdered form. But in the form of saturated solution sodium bicarbonate is not a good additive29. In our research group we have tried many additives to magnesium oxysulphate cement and studied their effects on its various properties29-31.

In this study, formaldehyde is tried as an additive for magnesium oxysulphate cement. The molecular formula of formaldehyde is HCHO. It is highly water soluble and low boiling gas. Commercially it is available as formalin (40% solution in water containing a small amount of methanol). It is very reactive and prone to polymerization on account of the absence of bulky groups. This may contribute to some properties of magnesia cement. That is why formaldehyde has been tried as an additive for oxysulphate cement in the present work19.

The object of this study was to determine the effect of formaldehyde as an additive on Magnesium Oxysulphate Cement. Effect of formaldehyde on some properties of magnesium oxysulphate cement was studied by incorporating it in different amounts in the dry –mix (1:2 dry mix was prepared by weight of magnesia and dolomite), on the basis of: (i) Setting time investigations, (ii) Weathering effects, (iii) Moisture ingress (Steam tests), (iv) Compressive strength tests and (v) Linear changes (for soundness). The results are reported in the present article.

**EXPERIMENTAL**

**Raw materials**

The raw materials used in the preparation of magnesium oxysulphate trial blocks are magnesium oxide, magnesium sulphate and inert filler, dolomite³².

**Magnesia (magnesium oxide)**

Commercial grade magnesium oxide of Salem origin is used in the study with the following characteristics (i) MgO – 92% (ii) Active lime (CaO) < 1.9% (iii) Iron oxide (Fe$_2$O$_3$) < 1.4% (iv) Silica (SiO$_2$) < 8.2% (v) Alumina (Al$_2$O$_3$) 0.2 – 0.4% (vi) Bulk density 0.85 kg/l (vii) 95% passing through 75 micron (200 mesh) IS sieve (viii) Ignition loss 2.5 ± 0.5% at 110°C.

**Inert Filler (Dolomite- CaCO$_3$.MgCO$_3$)**

Uncalcined dolomite powder passing through 150-micron sieve and retained 50% on 75-micron sieve is used as inert filler in the preparation of magnesia cement³³. It was checked for reactive impurities like lime before use. Its incorporation in
the matrix absorbs the heat evolved during the exothermic formation of magnesia cement, which reduces thermal shocks in the structure. It contains 28.7% CaO, 20.8% MgO, insoluble and other sesquioxide contents less than 1.0% and loss on ignition 50%.

Magnesium Sulphate (Epsom Salt)

\[ \text{MgSO}_4 \cdot 7\text{H}_2\text{O} \] — Magnesium sulphate used in the study was according to Indian Standard Specifications\textsuperscript{34}. Technical grade magnesium sulphate is used in the study. On chemical analysis, magnesium sulphate content was found to be more than 98%, chlorides (as Cl), Lead (as Pb), Arsenic (as As\textsubscript{2}O\textsubscript{3}), Iron (as Fe), Zinc and matter insoluble in water were found to be present in traces.

Formaldehyde

Which is commercially available as Formiline.

METHODS

Effect of formaldehyde on setting, strength an moisture resistance of oxysulphate cement was studied by incorporating it in different amounts in the wet-mix and following experiments were conducted according to IS specifications [33-36].

Setting periods

Effect of formaldehyde on setting characteristics of the cement was studied by mixing formaldehyde in the gauging solution in varying proportions. The quantity of the additive was calculated by volume of gauging solution. Setting periods and consistency of the wet-mixes prepared by 1:2 dry mixes (1 part weight of magnesia and 2 parts by weight of dolomite) with magnesium sulphate solution of 25° Be having different quantities of additive were determined adopting the standard procedure by Vicat needle apparatus\textsuperscript{35}. The observed results are summarized in Table 1.

Weathering effects

Variation in weights of the setting time blocks were recorded after 24 hrs, 7 days, 30 days and 45 days respectively. Different weathering effects may increase or decrease the weights of the trial blocks with passage of time. Experimental findings are summarized in Table 2.

Moisture ingress

In order to find out the effect of formaldehyde on moisture ingress of oxysulphate cement, all the setting time blocks with different proportions of the additive were cured for 2 months under identical conditions and then subjected to boiling water for at least 30 hrs as per standard procedure in a closed steam bath. Their relative moisture sealing efficacies were then studied as a function of time. Moisture ingress and soundness are inversely proportional\textsuperscript{37-40}. Results are shown in Table 3.

Compressive strength

To study the effect of formaldehyde on compressive strength of oxysulphate cement, standard 50 cm\textsuperscript{3} cubes were prepared from the standard consistency pastes having formaldehyde in different amounts. These cubes were tested after 30 days of curing under identical conditions with the help of compressive strength testing machine as per standard procedure\textsuperscript{35}. The practical out comings are recorded in Table 4.

Linear changes

The effect of formaldehyde on linear changes of magnesia cement was studied by preparing wet mixes having varying quantities of the additive and then filled into standard sized moulds (200mm\times25mm\times25mm). Trial beams were then kept under 90% relative humidity and 30±2°C temperature for 24 hrs. Initial length (after 24hrs) and final length (after 28 days) of the beams were measured using micrometer scale and then difference between the two was determined. This shows the linear change in the product by the incorporation of the additive\textsuperscript{37}. Results are enumerated in Table 5.

RESULTS AND DISCUSSION

The effect of mixing formaldehyde on setting characteristics of oxysulphate cement is summarized in Table 1. Incorporation of formaldehyde in the matrix increases initial setting periods. So is the case with final setting periods. Absence of steric hindrance in formaldehyde, its high reactivity and small size interfere with the normal setting process of oxysulphate cement. Also, at higher pH values, formaldehyde undergoes
autopolymerization to produce linear chains of polyformaldehyde (Eq 3). These chains entangle with lattice formation process and crystallization process of the product. During the crystallization process, position of water molecules may be replaced by small sized formaldehyde molecules, which in turn indirectly interfere with the setting process. Cumulative effects of all the above process retard setting process and increase setting periods. After final setting of the product, some uncombined moisture and formalin remain entrapped in the matrix, which may be given out with passage of time and results in decrease in weights of the trial blocks (upto 30 days) as is evident from the data shown in Table 2. At later stages, slight increase in weights is noticed. This may be due to factors like hydration, carbonation, etc of the unreacted or freely available basic

Table 1: Effect of formaldehyde on setting characteristics of oxysulphate cement

<table>
<thead>
<tr>
<th>S. No</th>
<th>Dry Mix Composition (%) Additive</th>
<th>Setting Time Initial (Min)</th>
<th>Setting Time Final (Min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0%</td>
<td>30</td>
<td>133</td>
</tr>
<tr>
<td>2</td>
<td>5%</td>
<td>32</td>
<td>223</td>
</tr>
<tr>
<td>3</td>
<td>10%</td>
<td>33</td>
<td>257</td>
</tr>
<tr>
<td>4</td>
<td>15%</td>
<td>35</td>
<td>275</td>
</tr>
<tr>
<td>5</td>
<td>20%</td>
<td>40</td>
<td>307</td>
</tr>
</tbody>
</table>

Table 2: Effect of formaldehyde on weathering characteristics of oxysulphate cement

<table>
<thead>
<tr>
<th>S. No</th>
<th>Dry Mix Composition (%) Additive</th>
<th>Weight of Blocks in gm after 24 hrs</th>
<th>7 days</th>
<th>30 days</th>
<th>45 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0%</td>
<td>258.870</td>
<td>251.163</td>
<td>243.322</td>
<td>241.440</td>
</tr>
<tr>
<td>2</td>
<td>5%</td>
<td>252.030</td>
<td>239.500</td>
<td>231.750</td>
<td>232.270</td>
</tr>
<tr>
<td>3</td>
<td>10%</td>
<td>255.360</td>
<td>242.100</td>
<td>231.100</td>
<td>231.500</td>
</tr>
<tr>
<td>4</td>
<td>15%</td>
<td>264.760</td>
<td>250.570</td>
<td>243.380</td>
<td>243.820</td>
</tr>
<tr>
<td>5</td>
<td>20%</td>
<td>246.350</td>
<td>231.200</td>
<td>224.090</td>
<td>224.800</td>
</tr>
</tbody>
</table>

g.s. = Gauging solution
ingredients of the matrix, which are responsible for gaining weights.

Very poor watertightness is observed if formaldehyde is mixed as an additive in magnesia cement (Refer Table 3). Formaldehyde is highly water soluble and volatile compound. It is given out at high temperature during the steam test. This results in the formation of voids and makes the product less watertight on account of increased chances of moisture ingress.

Table 4 shows that incorporation of formaldehyde upto an optimum proportion (about 5%) improves compressive strength of the cement due to simultaneous formation of polyformaldehyde chains, which interlace and entangle with the main network of magnesia cement (Eq 3). On subsequent additions of the formaldehyde in the matrix, beyond optimum proportion, strength data show decreasing trends. This is attributable to the decreasing quantities of gauging magnesium sulphate solution with increasing additive proportions. Chances of formation of strength giving composition (magnesium oxysulphate) are thus reduced (Eq 5), which in turn reduce the mechanical strength of oxysulphate cement.

### Table 3: Effect of formaldehyde on moisturing ingress characteristics of oxysulphate cement

<table>
<thead>
<tr>
<th>Composition (% Additive)</th>
<th>0-5 Hrs</th>
<th>5-10 Hrs</th>
<th>10-15 Hrs</th>
<th>15-20 Hrs</th>
<th>20-25 Hrs</th>
<th>25-30 Hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 0%</td>
<td>N.E.</td>
<td>N.E.</td>
<td>N.E.</td>
<td>N.E.</td>
<td>C</td>
<td>-</td>
</tr>
<tr>
<td>2 5%</td>
<td>C</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3 10%</td>
<td>C</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4 15%</td>
<td>C</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5 20%</td>
<td>C</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

g.s. = Gauging solution, N.E. = No effect, C = Cracked

### Table 4: Effect of formaldehyde on compressive strength of oxysulphate cement

<table>
<thead>
<tr>
<th>Dry Mix Composition</th>
<th>0%</th>
<th>5%</th>
<th>10%</th>
<th>15%</th>
<th>20%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressive Strength (Kg/cm²)</td>
<td>275</td>
<td>340</td>
<td>310</td>
<td>300</td>
<td>270</td>
</tr>
</tbody>
</table>

g.s. = Gauging solution
Table 5: Effect of formaldehyde on linear changes of oxysulphate cement

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Dry Mix Composition (% Additive)</th>
<th>Length of Beams (mm)</th>
<th>Change in Length (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Initial</td>
<td>Final</td>
</tr>
<tr>
<td>1</td>
<td>0%</td>
<td>200.00</td>
<td>200.02</td>
</tr>
<tr>
<td>2</td>
<td>5%</td>
<td>200.00</td>
<td>199.37</td>
</tr>
<tr>
<td>3</td>
<td>10%</td>
<td>200.00</td>
<td>199.41</td>
</tr>
<tr>
<td>4</td>
<td>15%</td>
<td>200.00</td>
<td>199.48</td>
</tr>
<tr>
<td>5</td>
<td>20%</td>
<td>200.00</td>
<td>199.51</td>
</tr>
</tbody>
</table>

Steric effects being less pronounced in case of formaldehyde, causes contraction in volumes, for similar reasons (more association, more compaction) to greater extents (Eq 4). This is evident from the data shown in Table 5.

The following probable chemical changes are helpful in explaining the above discussion:

\[
\begin{align*}
\text{CaO} + \text{H}_2\text{O} & \rightarrow \text{Ca(OH)}_2 \\
\text{MgO} + \text{H}_2\text{O} & \rightarrow \text{Mg(OH)}_2
\end{align*}
\]

\[\text{pH}>7\]

\[n\text{HCHO} \rightarrow \text{[.....HCHO.....]}_n\]

Linear polymeric chain (hydrophobic)

\[5\text{Mg(OH)}_2 + \text{MgSO}_4 \cdot 7\text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow 5\text{Mg(OH)}_2 \cdot \text{MgSO}_4 \cdot 8\text{H}_2\text{O}\]

CONCLUSIONS

1. Incorporation of formaldehyde increases setting periods (initial and final, both).
2. Formaldehyde does not contribute to water tightness when mixed in the matrix.
3. Addition of formaldehyde improves mechanical strength of the product up to an optimum proportion (about 5%).
4. Minor contraction in trial beams is noticed on mixing formaldehyde in the matrix.

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