The Influence of Aggregate Type on the Physico-Mechanical Properties of Magnesia Cement Pastes

Medhat S. El-Mahlawy, Hassan A. Hassan and Ayman M. Kandeel

Abstract

The work concerns physico-mechanical properties of magnesia cement pastes—specially magnesium oxychloride (MOC) cement pastes—mixed with different types of aggregate. Fine and coarse carbonate quarry waste and sand dunes resulted in the six mixes were studied. Three mixes included the aggregates without water glass treatment while the remaining mixes contained aggregates treated with water glass. The influence of the aggregate types on the water absorption, bulk density, compressive strength and other properties of the magnesium oxychloride (MOC) cement pastes at 3, 7, 28 days of curing were determined. Also, water soaking at 90 days curing was measured. The results revealed that the water/solid ratio, aggregate type, aggregate size, and water glass additive affected greatly on the properties of the MOC cement pastes. Among the studied mixes, the mix containing treated sand dune aggregate is found the most suitable for using as a starting point in a suitable practice.

Index Terms—carbonate quarry waste, magnesium oxychloride cement, physico-mechanical properties, Sand dunes,

1. INTRODUCTION

Magnesia cements have been attracted attention for many years due to their properties and potential applications. One type of magnesia cement, magnesium oxychloride (MOC) cement, also known as Sorel cement, is a type of non-hydraulic cement formed by mixing powdered magnesium oxide (MgO) with a concentrated solution of magnesium chloride (MgCl\(_2\)).

The MOC cement has many superior properties compared to ordinary Portland cement. It has high fire resistance, low thermal conductivity, good resistance to abrasion and is unaffected by oil, grease and paints [1]. It is also distinguished by a high strength/bonding, quick setting time and does not require humid curing [2].

Magnesia (MgO) is mostly produced by calcination of magnesite (MgCO\(_3\)) at a temperature around 750°C. The quality or reactivity of the formed magnesium oxide powder is largely affected by calcination temperature, firing duration and particle size. The reactivity of MgO increases with decreasing crystal sizes through decreasing the firing temperature and increasing the surface area of crystals [3 and 4]. The thermal history of the magnesite is the main variable affecting surface area and reactivity of the magnesia; these both increase as temperature increases up to 900°C and then decrease [5]. This in turn influences both the reaction rate and the properties of the reacted product of magnesium oxychloride cement.

Calcination of magnesia limits its reactivity. In the range of 500-1000°C, magnesium carbonate is progressively transformed into magnesia. Between 1000-1250°C, a reorganization of the surface occurs. Above 1250°C, particles melt and agglomerate. The theoretical surface area as well as the reactivity of magnesia decreases [6].

The setting and hardening of the MOC cement takes place in a through-solution reaction and is based on the reaction between MgCl\(_2\) and MgO [7]. Four main reaction phases in the ternary MOC system are found; 2MgO (OH)\(_2\), MgCl\(_2\).4H\(_2\)O (phase2), 3Mg(OH)\(_2\), MgCl\(_2\), 8H\(_2\)O (phase3), 5Mg(OH)\(_2\).MgCl\(_2\).8H\(_2\)O (phase 5), 9Mg(OH)\(_2\), MgCl\(_2\).5H\(_2\)O (phase9), and Mg (OH)\(_2\), brucite. These phases exist as reinforced components in the ternary system at ambient temperature [8].

Magnesium oxychloride cement has many good engineering and mechanical properties, but it has a poor water resistance, causing significantly decreased strength of hardened MOC paste in water thereby limiting its engineering applications. Consequently, many investigations on the water resistance of MOC cements have been carried out over the years [9]. Additives that can greatly improve the water resistance of MOC cement are soluble silicates such as sodium silicate, phosphoric acid...
and soluble phosphates, including the phosphates of alkali metals, the phosphates of alkali earth metals, iron, aluminum, and the phosphates of ammonia. Small amount of these compounds can improve the water resistance of MOC cement pastes significantly. The presence of magnesium carbonate as an impurity in magnesia and grinding a powder allow a better reactivity, because the dissociation of magnesium carbonate is quicker than that of magnesia [6].

This work aims to study the effect of different treated and non-treated aggregate types; carbonate quarry waste of two sizes and sand dunes made with different water/solid (w/s) ratios on the physico-mechanical properties of the hardened magnesium oxychloride cement pastes.

II. Experimental Procedures

A. Materials

The materials used in the current research are magnesite (M), sand dunes (SD) and carbonate quarry waste (CQW) as aggregates. Magnesite as a raw material is extracted from the southern Eastern Desert of Egypt associated with mafic and ultramafic serpentined rocks. Calcination of commercial Egyptian magnesite at about 750°C for 2h produced a white to light yellow color of magnesia (MgO) powder that was used in this investigation. The sand was collected from the Quataniya sand dunes at 6th October south Cairo, Western Desert of Egypt. The carbonate quarry waste was taken from Gebel Attaqa area, Cairo-Suez desert road, Egypt. Here, considerable amounts of carbonate quarry waste in the form of powder as by-product from the stone crushers are produced. This fine quarry waste is being collected, accumulated in the site, and the utilization of the waste is a big problem from aspects of safe disposal, environmental pollution and health hazards. In this study, two sizes were used, passed from 1 mm and 90micrometer sieves.

Also, additives were used in the present study; commercial grade of the available water glass (Na₂SiO₃) aqueous solution and the powder salt of ammonium dihydrogen phosphate (NH₄H₂PO₄) for improving the water resistance of the Sorel cement.

B. Sample Preparation

The mixtures were prepared with the aid of a laboratory bench top mixer first by dissolving the MgCl₂ and NH₄H₂PO₄ in sufficient quantity of water and secondly by adding the dry materials (magnesium oxide powder and the aggregate) incrementally to the mix and lastly by adding the residual water demand to achieve good workability; in case of water glass addition, it was added before pouring of the residual water. The water-to-solid ratio was different for all mixtures according to the type aggregates. It was controlled by obtaining good workability during the experiment. Following mixing, specimens were prepared by placing the MOC cement paste in steel cube molds of a size of 5x5x5 cm. The solidified specimens were demolded after 24h and then cured in the air at the ambient lab conditions (20±2°C and relative humidity 65 ± 5%) until testing at 3, 7 & 28 days. Care was taken to reduce the amount of air voids as much as practically possible. The mixing procedure was the same for all paste mixes each of which was represented by 20 cube samples. Six mixtures of different aggregates percentage (Tables 1 and 2) were prepared for studying the physico-mechanical properties of the air cured specimens at different ages. Mixtures A2, A4 and A6 (group A) were based on non-treated aggregates while mixtures A3, A5 and A7 (group B) were based on water glass treated aggregates.

C. Test Methods

The solid materials were tested as follows. The chemical analysis was performed on the ground pressed aggregates powder using Philips PW 1400 XRF as well as following the test method described in the American Society for Testing and Materials [10].

The particle size distribution was determined using the dry sieve analysis method of the International Organization for Standardization (ISO) for fine aggregates [11].

The mineralogical composition was characterized by X-ray diffraction (XRD). The XRD analysis was carried out on the powdered samples passed through the 25μm sieve using XRD apparatus of Xpert Pro type (Netherlands). The analysis was run using Cu Kα radiation in the range 2θ from 5°-50° with acceleration voltage condition of 40 kV and 40 mA. The interpretation of the obtained phases was achieved by the X'Port high score PDF-2 database software on CD-Release 2006. The semi-quantitative estimation of the obtained phases was calculated by the software based on the half width method of the detected main peaks.

The physico-mechanical properties of the hardened blended magnesium oxychloride cement paste mixtures were studied after 3, 7 and 28 days of curing. The water of consistency, bulk density, water absorption and compressive strength were determined according to ASTM standards [12-15]. Also, the durability of MOC cement specimens air cured for two weeks was determine by water soaking for 3 months at the lab ambient conditions.
Table 1. Mix composition of mixtures with non-treated aggregates (Group A)

<table>
<thead>
<tr>
<th>Mix code</th>
<th>Mix composition</th>
<th>Quantity % by wt.</th>
<th>W / S ratio</th>
<th>Remarks on aggregate</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2</td>
<td>- MgO&lt;br&gt;- Carbonate quarry waste&lt;br&gt;- MgCl₂&lt;br&gt;- NH₄H₂PO₄&lt;br&gt;- Mixing water</td>
<td>33.80&lt;br&gt;33.80&lt;br&gt;16.90&lt;br&gt;0.24&lt;br&gt;15.26</td>
<td>0.18</td>
<td>CQS: Passed from 1mm sieve diameter (Coarse aggregate).</td>
</tr>
<tr>
<td>A4</td>
<td>- MgO&lt;br&gt;- Carbonate quarry waste&lt;br&gt;- MgCl₂&lt;br&gt;- NH₄H₂PO₄&lt;br&gt;- Mixing water</td>
<td>35.62&lt;br&gt;35.62&lt;br&gt;17.81&lt;br&gt;0.25&lt;br&gt;10.70</td>
<td>0.12</td>
<td>CQS: Passed from 90 µm sieve diameter (Fine aggregate).</td>
</tr>
<tr>
<td>A6</td>
<td>- MgO&lt;br&gt;- Sand dunes&lt;br&gt;- MgCl₂&lt;br&gt;- NH₄H₂PO₄&lt;br&gt;- Mixing water</td>
<td>36.94&lt;br&gt;36.94&lt;br&gt;18.47&lt;br&gt;0.26&lt;br&gt;7.39</td>
<td>0.08</td>
<td>SD: Natural.</td>
</tr>
</tbody>
</table>

Table 2. Mix composition of mixtures with water glass treated aggregates (Group B)

<table>
<thead>
<tr>
<th>Mix code</th>
<th>Mix composition</th>
<th>Quantity % by wt.</th>
<th>W / S ratio</th>
<th>Remarks on aggregate</th>
</tr>
</thead>
<tbody>
<tr>
<td>A3</td>
<td>- MgO&lt;br&gt;- Carbonate quarry waste&lt;br&gt;- MgCl₂&lt;br&gt;- NH₄H₂PO₄&lt;br&gt;- Mixing water</td>
<td>33.60&lt;br&gt;33.60&lt;br&gt;16.80&lt;br&gt;0.24&lt;br&gt;9.04</td>
<td>0.11</td>
<td>CQS: Passed from 1 µm sieve diameter and treated with water glass.</td>
</tr>
<tr>
<td>A5</td>
<td>- MgO&lt;br&gt;- Carbonate quarry waste&lt;br&gt;- MgCl₂&lt;br&gt;- NH₄H₂PO₄&lt;br&gt;- Mixing water</td>
<td>34.40&lt;br&gt;34.40&lt;br&gt;17.20&lt;br&gt;0.24&lt;br&gt;6.88</td>
<td>0.08</td>
<td>CQS: Passed from 90 µm sieve diameter and treated with water glass (100 ml).</td>
</tr>
<tr>
<td>A7</td>
<td>- MgO&lt;br&gt;- Sand dunes&lt;br&gt;- MgCl₂&lt;br&gt;- NH₄H₂PO₄&lt;br&gt;- Mixing water</td>
<td>35.00&lt;br&gt;35.00&lt;br&gt;17.50&lt;br&gt;0.24&lt;br&gt;5.26</td>
<td>0.06</td>
<td>SD: Natural and treated with water glass (100 ml).</td>
</tr>
</tbody>
</table>

III. Results and Discussion

A. Characterization of the Aggregate Raw Materials

The chemical composition of the used aggregates is listed in Table 3. As expected, MgO is the main oxide in magnesite, SiO₂ is the main oxide in sand dune while SiO₂, CaO and MgO are the main oxides in the carbonate quarry waste. The high value of loss on ignition (L.O.I) for magnesite and carbonate quarry waste is due to the releasing of a high content of CO₂ during ignition. The chemical composition of the carbonate quarry waste refers to including the aggregate on quartz, calcite and dolomite as shown subsequently.

![Fig. 1. X-ray diffraction patterns of the aggregates used](image-url)

The XRD patterns and their identified phases are shown in Fig.1. In the XRD diffractograms, several typical minerals are identified. The sand dune aggregate is composed of quartz mineral SiO₂ (100%). This is in agreement with observations by other researchers. The XRD of carbonate quarry waste is consistent with the chemical analysis showing a composition of approximately 40% quartz, 35% dolomite CaMg(CO₃)₂ and 25% calcite CaCO₃. The magnesite aggregate is composed essentially of pericale miner, approximately 90% MgO and 10% portlandite mineral Ca(OH)₂. The mineralogical analysis of each aggregate shows the same composition as that revealed by the chemical analysis.
The grain size distribution of the aggregates is illustrated in Fig. 2. The size of studied aggregates is less than 1.8mm and larger than 300 µm, i.e. the aggregate maximum size is 1.18mm. As seen, the sand dune is the finest aggregate followed by magnesite and carbonate quarry waste, in that order. The graded materials belong to the fine aggregate size [16]. Due to its fineness, sand dune, is expected to be more reactive than the other studied aggregates.

![Fig. 2. Grain size distribution based on dry sieves analysis of the aggregate used](image)

B. Physico-Mechanical Properties of the Hardened MOC Cement Specimens

In order to study the effect of aggregate on the physico-mechanical properties of hardened MOC specimens, tests were done to measure the consistency of paste, bulk density, water absorption, water soaking, and compressive strength (dry and wet).

C. Water Demand

In order to obtain the same workability, the water/solid ratios (w/s) of the glass non-treated mixes A2, A4 and A6 (group A) are 0.18, 0.12 and 0.08, respectively, cf. Tables 1-2 and Figure 1. In other words, the mix which contains coarse aggregate of dolomite requires the largest water/solid ratio followed by the mix which contains fine aggregate of dolomite and the mix containing sand dunes in that order. This is due to the larger water absorption of the coarse dolomite aggregate than the fine dolomite aggregate and sand dunes, so that the water/solid ratio increases with aggregate size. Moreover, the siliceous sand aggregate attains the lowest water absorption of the studied aggregates [17]. The water / solid ratio of water glass treated mixes A3, A5 and A7 (group B) are 0.11, 0.08 and 0.06, respectively. The lowest values of group B compared to group A are due to the aggregates of the former-as opposed to the latter- group being treated with water glass as reflected in the reduced w/s ratio. The cement pastes of the group B achieved the same arrangement of the group A with the non treated aggregates.

D. Bulk Density

The bulk density of the cement specimens of all mixes (groups A and B) as a function of the curing period (3, 7 and 28 days) is plotted in Fig. 3. The bulk density depends on the packing of the particles, which in turn depends on shape, density, surface texture, and grading of the particles.

The figure shows that for the hardened MOC cement pastes of group A mix A6 provides the highest bulk density followed by A4 and A2, in that order. This may be due to the higher specific gravity of sand dunes (= 1.40 -1.60 g/cm³) than the quarry waste (0.70 -1.20 g/cm³) [18]. Also, the bulk density is seen to increase with increasing curing period. Moreover, the bulk density of the cured cement paste of mix A4 gives higher values of bulk density than those of mix A2 at all curing times. This may be attributed to the specific gravity of fine dolomite aggregate being smaller than the coarse dolomite aggregate. This is confirmed by the material having a higher density in the solid state than the broken (crushed) state which in turns has a higher density than the pulverized (dust) state (the lowest). Group B followed the same trend as group A as specimens of mix A7 have the highest bulk density followed by A5 and A3, in that order. It is observed that the bulk densities of equal matures mixes of groups A and B containing the same aggregate are generally higher for the latter group. This may be explained by the solubility of silica in the alkaline media. Thus, MgO has high alkalinity, reaching a maximum pH value of 10 [19] which provokes the increase of amorphous silica solubility which in turn fills the voids and bonds the matrix together, so that the cement paste becomes harder than that without water glass. This is supported by the finding of others [20].

It is known that the solubility of quartz in pure water at 25 °C is about 6 parts per million whereas that of vitreous silica is at least 10 times greater. The high solubility of silica, especially the amorphous type, is obtained in alkaline media (pH value higher than 9) and particularly the solubility of amorphous silica at temperatures below 100°C has been the subject of many investigations [21].
E. Water Absorption

Water adsorption of the air cured specimens of the groups A and B after immersion in tap water for 24h are plotted in Fig. 4. It is observed that the hardened magnesium oxychloride (MOC) cement past of mix A2 provides higher values of water adsorption than mixes A4 and A6 at all curing times. This indicates that the coarse dolomite aggregate absorbs more water than the fine dolomite aggregate and sand dunes. Mix A6 which contains sand dunes affords lower values of water adsorption at all curing times. This is due to the physical properties of sand which commonly have lower water absorption than carbonate aggregate (quartz, calcite and dolomite). The MOC cement specimens of group B show lower water absorption than those of group A with the same aggregate but with and without water glass treatment, respectively. This could be attributed to various factors such as: (a) water glass acts as a bonding agent (b) water glass is a sodium silicate solution that in the presence of MgCl₂ produces very fine sized silicon chloride particles which can fill the pores acting as a water repellant, causing the water absorption to decreases (c) the amorphous silica may fill the voids between the grains reducing water absorption (d) a chemical reaction between the water glass and the aggregate permanently binding the silicates to the aggregate surface making them far more wearable and water repellant [22].

At any given curing time, mix A7 attained the lowest water absorption of all mixes. The sodium silicate may act as a glue producing a thin layer on sand grains to bond them together [23]. However, aggregate treated with sodium silicate solution significantly reduces porosity. In addition, water absorption increases as the curing progresses. This is likely ascribed to the escape of free water from the specimens as indicated by the decrease in weight of the air cured specimens with increasing curing time. This is shown by the experimental tests. From this point of view, the affinity of the cement specimens to absorb water is increased as the curing time increases.

F. Water Soaking

Table 4 shows the effect of soaking time on the splitting of soaked MOC cement specimens. All specimens sustained successfully the passive effect of water until 5 days of the immersion in water. Continued immersion in water until day 10 caused simple splitting on the specimen surfaces except for mixes A3 and A7. Further water immersion until day 15 resulted in clear cracks and sever splitting of all specimens, mixes A3 and A7 excepted. To verify the resistivity of specimens A3 and A7, they were immersed in water for 90 days. It may due to that the expansion effect according to formation of Mg(OH)₂ from non reacted MgO with water. The volume expansion due to the hydration of MgO has been linked to cracking [24]. However, such cracking only occurs provided the expansion of the material is constrained [25]. If a sufficient amount of MgO is used, the hydration occurs at a rate without causing cracking due to delayed hydration; this can be achieved by calcination of magnesite at low temperatures (< 750°C) forming products that are resistive to the breakdown in water [24].

The study confirms that specimens made of mixes A3 and A7 submerged in water did not split. This may be due to the type of aggregate used, the low water absorption and the presence of water glass and ammonium dihydrogen phosphate in appreciable amounts. Other mixes may need enough amounts of these additives. Note that the addition of soluble phosphates to MOC improves the water resistance by precipitation of totally insoluble phosphate complexes [26] according to the following equations:

\[ \text{MgO} + \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 \]

\[ 3\text{Mg(OH)}_2 + 2\text{H}_3\text{PO}_4 \rightarrow 3\text{Mg}((\text{PO}_4)_2) + 6\text{H}_2\text{O} \]
Table 4. Visual observation of water soaked hardened specimens of the different mixes

<table>
<thead>
<tr>
<th>Specimens of the mix code</th>
<th>Splitting versus soaking time, days</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 - 5</td>
</tr>
<tr>
<td>A2</td>
<td>No evidence for splitting for the all specimens</td>
</tr>
<tr>
<td>A4</td>
<td>No splitting</td>
</tr>
<tr>
<td>A6</td>
<td>Simple splitting at the specimens surfaces.</td>
</tr>
<tr>
<td>A5</td>
<td>Severe splitting and clear cracks</td>
</tr>
<tr>
<td>A3</td>
<td>No splitting</td>
</tr>
<tr>
<td>A7</td>
<td>No evidence for splitting for the all specimens</td>
</tr>
</tbody>
</table>

G. Compressive Strength

The dry and wet compressive strength of the hardened MOC specimens of groups A and B at different air curing times up to 28 days are presented in Figs. 5 and 6, respectively. It can be seen that the strength of the MOC specimens of groups A and B increases with the increase of the curing times. It is revealed that the specimens of mix A7 have the maximum strengths at all curing ages, while the specimens of A2 have the minimum strengths. Also, the water glass treated specimens (A7, A5 & A3) provide higher values than the corresponding non treated specimens (A6, A4 & A2) i.e. specimens of the SD (treated and non treated aggregate) provide the highest values followed by CQW (treated and non treated aggregates) and then M (treated and non treated aggregates).

The wet compressive strength of the cured MOC specimens are lower than the dry compressive strength at the same curing age and follow the same trends of the dry specimens. Moreover, the lower w/s ratio, the higher the strength of the hardened MOC specimens. It is evident that the water to solid ratio plays an important role in the compressive strength property. Thus, the low strength values of mix A2 may be caused by the high content of free water which forming a large quantity of pores in the matrix. This is supported by the fact that the specimens of mix A2 attain the maximum water absorption at all curing times (2.39 – 7.35%). Thus, many pores inside the body skeleton are formed which soften the body.

It would appear that the prerequisites for achieving high performance MOC are: (1) the production of phase 5 (5Mg(OH)\(_2\)\_2MgCl\(_2\)_8H\(_2\)O), (2) reduction of the content of non reacted MgCl\(_2\) content, and (3) obtaining a reasonable workability with an appropriate setting time [3]. When MgO is mixed with MgCl\(_2\) solution, MOC gel paste is produced forming a network which strengthens the specimens as the curing time increases [27].

It is likely that upon the addition of water to the dry mix, the ammonium dihydrogen phosphate dissolves in the water to form an acidic solution which reacts with MgO at the surface of the magnesia particles. When sufficient hydrates are formed, the cement paste sets and hardens, thereby increasing the strength as observed by others [20].

IV. Conclusion

The influence of carbonate quarry waste and sand dune as aggregates on the physico-mechanical properties of hardened magnesium oxychloride (MOC) cement pastes was studied. The following conclusions can be drawn from the present study.

- The MOC mixes which contain water glass treated sand dunes provide the highest bulk density, compressive strength and water resistivity as well as the lowest water absorption.
- The mix which contains fine dolomite aggregate (water glass treated or non treated) attains improved physico-
mechanical values over those of mixes containing coarse dolomite aggregate even after treatment by water glass.
- Treatment of the aggregates by water glass improves the physico-mechanical properties for all mixes.
- The w/s ratio is an important parameter for controlling the properties of magnesium cement specimens containing water glass treated as well as non treated aggregates. This is in analogy with the increase in compressive strength of Portland cement specimens with the decrease in free water.
- The study suggested that mix A7 based on sand dune aggregate is a suitable starting point for the application of MOC, magnesium oxychloride cement.

References