RESEARCH ON MgO-MgCl₂-H₂O SYSTEM CERAMSITE EXEMPTED FROM SINTERING

Ming-li Cao and Li-jiu Wang
School of Civil and Hydraulic Engineering, Dalian University of Technology, Dalian, 116024, PRC

Abstract

A new type of light aggregate from sintering is investigated. The aggregate has low apparent density, high strength, and high durability. This research introduces the MgO-MgCl₂-H₂O system to light aggregate production. The other point is that the closing technology will make a sealing course covering around the ceramsite to separate itself from those corrosive mediums effectively, so much as water.

Test results indicate that the strength of this ceramsite is at least one degree higher than those with the same degree of apparent density. The microstructure of the ceramsite sealing course has been testified by SEM testing. It shows remarkable economic and social benefits for using magnesite, halogen, and fly ash to develop new type light aggregate exempted from sintering.

1. Introduction

Since the 1990s, the research on light aggregate has been carried out in many fields. Light aggregate can be classified into sintered light aggregate exempted from sintering according to its production technology. When it comes to raw materials, light aggregate includes shale ceramsite, fly ash ceramsite, pumice ceramsite, glass ceramsite, diatomite ceramsite, etc. The MgO-MgCl₂-H₂O system ceramsite exempted from sintering discussed in this paper is different from normal man-made light aggregate. Its strength is at least one degree higher than the strength of those with the same degree of apparent density. High performance ceramsite cured in natural state is made from magnesite, MgCl₂, fly ash, and so forth. It is a kind of light aggregate, which can be produced through a series of manufacturing processes such as grinding, mixture making, foaming, ball-up, and natural curing. During foaming, gas is generated, which makes the ceramsite porous, light, and with a low density. It shows remarkable economic and social benefits by using magnesite, halogen, and fly ash to develop new type light aggregate exempted from sintering.
2. Experiment

2.1. Raw materials

2.1.1. Magnesite
The raw material in this test was made in Haicheng city, Liaoning Province. It was manufactured into magnesite after being calcined in the temperature of 600°C. The chemical composition of the raw material is displayed in Table 1. The raw material was calcined for 2 hours in silicon carbide rod electric-furnace with the temperature 850°C, and then it was cooled down to room temperature.

<table>
<thead>
<tr>
<th>MgO</th>
<th>CaO</th>
<th>Fe₂O₃</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>88.92</td>
<td>1.97</td>
<td>0.66</td>
<td>0.40</td>
<td>1.34</td>
<td>6.30</td>
</tr>
</tbody>
</table>

2.1.2. MgCl₂
In this test, the molecular expression of the raw material is MgCl₂·6H₂O. Industrial material will be used when produced in industry.

2.1.3. Fly ash
The fly ash used in this test was produced in Tieling. Its chemical composition is listed in Table 2.

<table>
<thead>
<tr>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Fe₂O₃</th>
<th>Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>53.19</td>
<td>6.16</td>
<td>28.52</td>
<td>1.91</td>
<td>1.47</td>
<td>8.75</td>
</tr>
<tr>
<td>47.84</td>
<td>6.69</td>
<td>25.23</td>
<td>1.24</td>
<td>1.55</td>
<td>17.45</td>
</tr>
</tbody>
</table>

2.1.4. Foaming
In this test, we use the foaming developed by our teaching and research section. Its chemical ingredients are organic oxidant and amid-based compounds.
2.2. Preparation of the pig-iron of the ceramsite
The magnesite and the magnesium chloride were mixed with the molar ratio of 4 to 6, and then fly ash and the foaming were added. As a result, the magnesian cement was obtained. The volume of the test sample was $200 \times 400 \times 600$ mm$^3$ (0.144 m$^3$), while the volume was 2 m$^3$ when the pig iron of the ceramsite was produced in industry.

After the initial setting of magnesian cement, the cement was distilled into the plate so it could turn into balls. Then a layer of acrylic acid waterproof paint was sprayed, which can lower the water absorbing capacity of the test sample remarkably. Before putting it to use, the balls must be cured in natural condition for a few days. The production process of the magnesian ceramsite is illustrated in Fig. 1.

![Fig. 1: Production process of the magnesian ceramsite](image)

3. Discussion and Results

3.1. Property test
The property test in this paper was carried out in accordance primarily with the new devised national standard, light aggregates, and methods of tests (GB17431-1998.)
3.1.1. Apparent density
The test sample, which volume was 4 liters, was screened with the size of sieve pore 5.00mm. Then the remnant was separated into two portions, and one of the portions was baked out. The mixture with weight from 300 to 500 g, which was composed of the two portions of the remnant, was weighed after being mixed uniformly. Then the mixture was put into a graduate and soaked in water for 2 hours. After this, the mixture was taken out and put into another graduate, with the volume of 1000 ml. Following this, 500 ml of water was poured into the graduate. The test sample, which was floating on the surface, was pressed into water with a known volume circular metal slab, and the water level was measured.

The apparent density of the ceramsite can be calculated according to the following equation:

\[
\gamma_k = \frac{g \times 1000}{V - V_1 - 500}
\]

In this equation, \(\gamma_k\) is the unit weight of the ceramsite, \(g\) is the weight of the test sample in milliliters, \(V_1\) is the volume of the circular metal slab in milliliters, and \(V\) is the water level of the graduate after adding the sample with the metal slab.

3.1.2. Strength of ceramsite
The strength of ceramsite is determined by the following equation:

\[
R_1 = \frac{P}{F}
\]

In this equation, \(R_1\) is the strength of the ceramsite, \(P\) is the stress value sustained by the circular metal slab at the depth 20 mm under the water, and \(F\) is the projected area (i.e. the area of ram model \(F\), 10000 mm\(^2\)).
3.1.3. Water absorbing capacity
The water absorbing capacity of the ceramsite is determined by the following equation:

\[ W_c = \frac{g_1 - g}{g} \times 100 \]

In this equation, \( W_c \) is the water absorbing capacity of the ceramsite (Mass %), \( g_1 \) is the weight of the test sample soaked in water, and \( g \) is the weight of the test sample baked out.

3.1.4. Soften factor
The soften factor of the ceramsite is given as follows:

\[ K = \frac{R_f}{R_i} \]

In this equation, \( K \) is the soften factor of the ceramsite. \( R_f \) is the compressive strength of the ceramsite, which was soaked in water for 1 hour, and \( R_i \) is the compressive strength of the ceramsite kept in dry state.

3.1.5. Sturdiness
In this part, the sample test was weighted and then put into a network of triangle. A container with sodium sulfate liquid was prepared. After that, the test sample and the network, as a whole body, were soaked in the liquid. The volume of the liquid is at least 5 times the test sample, and the temperature of the test sample should be restricted to the range from 25°C to 35°C. Before laying the network of triangle into the container, the liquid should ascend and descend for 25 times in order to eject the bubble in the test sample. The distance between the bottom of the network of triangle and the bottom of the container should be kept at about 3cm. The distance between the networks should be no less than 3cm. The surface of the liquid should be higher by at least 3cm than the test sample counterpart.

Soaked in water for 24 hours, the network of triangle was taken out from the container and roasted in bake out furnace for 4 hours. So far, the whole cycle was
completed. When the test sample was cooled down to the temperature 25°C to 35°C, the next cycle started. In the second cycle, the time during which the test sample was soaked in water changed to 4 hours. This was repeated 5 times.

The test sample was soaked for an hour in water with the temperature lower than 25°C. Afterwards, it was rinsed in water with the temperature 60°C. The volume of the water was at least 10 times the test sample. Soaked in water like this, the test sample was roasted to get a constant weight. After being cooled down to the room temperature, the test sample was screened with the aperture that was one degree lower than the size category fraction. Then the remnant was weighted.

The weight loss of the test sample is calculated as follows:

\[ Q_j = \frac{g_1 - g_2}{g_1} \times 100 \]

In this equation, \( Q_j \) is the weight loss of the test sample (%), \( g_1 \) is the weight of the sample in dry state before the test, and \( g_2 \) is the weight of the sample in dry state after the test.

3.1.6. Particle diameter
The particle diameter of the test sample is in the range of 5 to 15mm, which has a good screen sizing.

3.2. Test results
The results of the test are listed in Table 3.

### Table 3: Results of the property test of the ceramsite

<table>
<thead>
<tr>
<th>Index</th>
<th>Apparent density (kg/m³)</th>
<th>Strength (MPa)</th>
<th>Water absorbing capacity (%)</th>
<th>Soften Factor (%)</th>
<th>Sturdiness</th>
<th>Particle diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Natural state</td>
<td>Absolutely dry state</td>
<td>Natural state</td>
<td>Absolutely dry state</td>
<td>2h</td>
<td>24h</td>
</tr>
<tr>
<td>750</td>
<td>650-680</td>
<td>8.5-9.0</td>
<td>9.0-10.0</td>
<td>10</td>
<td>15</td>
<td>0.9</td>
</tr>
</tbody>
</table>
3.3. Results discussion

3.3.1. Hydration phase of oxychloride magnesium cement
Oxychloride magnesium cement has series of characteristics, such as fast hardening, high strength, light weight, and good adhesion, and the hydration phase primarily is $5Mg(OH)_2\cdot MgCl_2\cdot 8H_2O$ (5-1-8 phase). The 5-1-8 phases have two fundamental structures: type I and type II. Type I is more stable than type II. The 5-1-8 phases, which are illustrated in Figs. 2 and 3, have a needle-like crystal and a compact structure. The needle-like crystal has a high strength.

![Fig. 2: Microstructure in SEM of the magnesian ceramsite](image)
(a) 1000 times  
(b) 2000 times

3.3.2. Theory of expansion and sealing
The expansion mechanism of the foaming is as follows: the organic oxidant and acid amides compounds produce many uniform small air bubbles, which expand the volume of the balls and make them porous. The diameter and content of the bubbles added, were connected not only with the content added, but also with the extend of mixing before forming, with temperature, and with time.

The purpose of the sealing the ceramsite was to prevent the permeability of oxychloride magnesium cement products with water. Using acrylic paint as
waterproof layer, the chlorine ions in the ceramsite, which make the ball permeable, were kept in the waterproof layer. This prevented more water molecules from entering into the ceramsite body. At the same time, the phase changes of $\text{MgCl}_2\cdot6\text{H}_2\text{O}$ were favorable to energy saving through adjusting the temperature of the building around. From Fig. 4, we can see that there is a compact layer between the ceramsite body and the fly ash coating, i.e. sealing layer.

Fig. 3: Microstructure in SEM of the magnesian ceramsite

Fig. 4: Sealing layer structure of the magnesian ceramsite
4. Conclusions

- The magnesian ceramsite exempted from sintering is superior to other normal ceramsite exempted from sintering in lower density, high strength, and low permeability. It is a new man-made light aggregate with high performance, which apparent density is 650-680 kg/m³. Its compressive strength comes out at 10.0 MPa, which is at least one degree higher than those with the same degree of the apparent density.
- Sealed by acryl waterproof layer, the magnesian ceramsite has a higher water-resistance. Moreover, its water absorbing capacity is reduced largely.
- The difficult point of shaping technique for the magnesian ceramsite is initial setting time control, which is related to temperature and mixing degree.
- It shows remarkable economic and social benefits for using magnesite, halogen, and fly ash to develop new type light aggregate exempted from sintering.

References