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Cement and Concrete Research 33 (2003) 1663–1668

CEMENT AND CONCRETE RESEARCH

# Experimental study on urban refuse/magnesium oxychloride cement compound floor tile

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Received 19 December 2001; accepted 10 April 2003

**Abstract**

This article is a study on the production technology of urban refuse magnesium oxychloride cement compound floor tile by taking urban refuse and magnesium oxychloride cement as main raw materials. We experimentally studied the influence of the concentration of magnesium chloride solution and the fineness of magnesium oxychloride cement on the property of the product by means of experiments and analyzed the microstructure of hydration product using SEM.


*Keywords:* Magnesium oxychloride cement; Urban refuse; Composite; Fineness; SEM

## 1. Introduction

Magnesium oxychloride cement is one type of magnesia cement. This kind of cement has many excellent performances such as rapid hardening rate, very high strength, good cohesiveness, shaping convenience, easy to be colored, good fire-resistance, and ability to resist high temperature condition. However, its property of water-resistance is relatively poor. In the last century, researchers [1] attempted to solve two problems in the application of magnesium oxychloride cement. The first one is to improve its property for water-resistance; another one is to improve its service life. Since the 1980s, material scientists [2] from various countries have made great progress on the research of magnesia cement. By changing plaster's curing condition, adding chemical modifying agent, carrying on surface treatment, controlling the content of active magnesium and magnesium chloride effective composition, mixing fiber-reinforced materials, we improved magnesia cement's durability, antipermeability, wearability, mechanical strength, and impact durability performance a lot. China has extremely abundant magnesium oxide resources, the already verified reserves are nearly 3 billion tons, accounting for one-third of the world's magnesium oxide reserves and occupying the first place in the world. The magnesium chloride resources, which incorporate magnesium oxide, are also quite abundant. Golmud Salt Lake of Qinghai province alone stores nearly 1900 million tons of magnesium chloride. Also there is a large amount of by-products of magnesium chloride in every coastal salt field. They offer sufficient guarantee of raw materials for the development of the magnesium oxychloride cement trade in China.

The urban refuse is the accessory substance brought in by industrialization and urbanization. With the promotion of industrialization and urbanization and the increase of urban population, the amount of urban refuse also increases constantly. The statistics [2] show that every year the newly produced waste in the whole world is more than 10 billion tons. In China, because of the great population and size of cities, the issue of rubbish is particularly important. Relevant data [3] indicate that annual generation of urban refuse reaches 140 million tons in China, and increases progressively at a rate of 8–10% every year. Urban refuse has already led to great environmental problem and it is essential to look for a rational and effective way to deal with it and utilize it. At present, the treatment method [4] for the urban refuse in China relies mainly on burning. This method produces a large amount of pernicious gases as well as air pollution of inflammable inorganic composition that are still not dealt with. Urban refuse is a harmless disposal and its resource

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doi:10.1016/S0008-8846(03)00136-4

Table 1
Compositions of magnesite (wt.%) used in this experiment

| Analyzed items | | MgO | CaO | Ignition loss | 125 μm sieve residue |
|---|---|---|---|---|---|
| Content (%) | 75# | 68.33 | 2.28 | 29.37 | < 10% |
| | 85# | 79.48 | 2.86 | 17.66 | |

utilization is one of the great subjects in China's sustainable development strategy at present. The urban refuse/magnesium oxychloride cement compound colorful floor tile developed in this project is a kind of new-type road surface material made by moulding technology using magnesium oxychloride cement and urban refuse as main raw materials. The production of this product can utilize various kinds of urban refuse in a large amount. By this method, we can solve the problems of urban refuse such as the land taken up by urban refuse and environment pollution. At the same time, the urban refuse is converted into a product again, beautifying the city and promoting the well-being of mankind.

## 2. Experiments

### 2.1. Materials

#### 2.1.1. Magnesite

The magnesite used in this experiment comes from Laizhou magnesium mineral in Shandong province. The results of the composition analysis are shown in Table 1. As shown in Table 1, the magnesite we used complies with the enterprise criterion [5]. The compositions of magnesite used in the criterion are shown in Table 2.

#### 2.1.2. Urban refuse

Urban refuse in China contains more inorganic materials and less organic materials. The content of inorganic materials is about 70–85% and organic materials about 15–30%. The inorganic materials mainly consist of building debris such as sands, stones, soil, and fragment of bricks, etc. Organic materials are mostly wasted papers, dish leaf, melon peel, plastic bags, etc. Plastic materials are selected and removed by wind; most of the other organic materials are left rotten to take the form of fiber materials. The urban refuse is broken down into pieces smaller than 5 mm and preserved for use. The SEM micrograph is shown as Fig. 1.

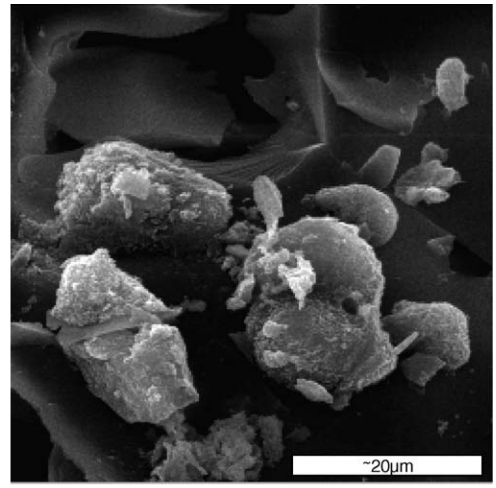


Fig. 1. SEM micrograph of urban refuse.

#### 2.1.3. Magnesium chloride

The magnesium chloride used in this experiment was produced by Dajiawa chemical plant in Weifang, Shandong. Its chemical compositions are shown in Table 3.

### 2.2. The production technology of compound floor tile

The urban refuse/magnesium oxychloride cement compounded floor tile is produced by moulding technology. The production technological flow chart is shown in Fig. 2.

Considering the ornament effect and the production costs of compound floor tile, we adopt two moulding technologies for the moulding of the surface and bottom layers of the floor. The surface layer was made up of high-grade raw materials, pigment, hard filler, etc. The bottom layer was made up of urban refuse and magnesite.

To make the test sample for physical property test, the required raw materials were weighed exactly as the following ratio: magnesite/urban refuse/haloid powder = 1:3:0.5. Then water was added in the order shown in Fig. 2 and mixed adequately. The paste was poured into the mould of the size $40 \times 40 \times 160$ mm and vibrated slightly to get rid of the air bubble inside the paste. Delamination, segregation, and leakage were not allowed to occur in the paste. The test samples were cured for 24 h at room temperature before its demoulding. Then the samples were placed in a room with temperature at $20 \pm 0.5$ °C and relative humidity of 60–70% for 28 days. Its properties were tested according to the floor tile's relevant criterion [6].

Table 2
Compositions of magnesite (wt.%) used in Q/LJU 14001-88

| Analyzed items | MgO | CaO | Ignition loss | 125 μm sieve residue |
|---|---|---|---|---|
| Content (%) | ≥ 68 | < 3 | < 30 | < 10% |

Table 3
The chemical compositions of magnesium chloride (wt.%) used in this experiment

| Analyzed items | $MgCl_2 \cdot 6H_2O$ | NaCl | KCl | $MgSO_4$ |
|---|---|---|---|---|
| Content (%) | 96.57 | 1.83 | 0.95 | 0.55 |

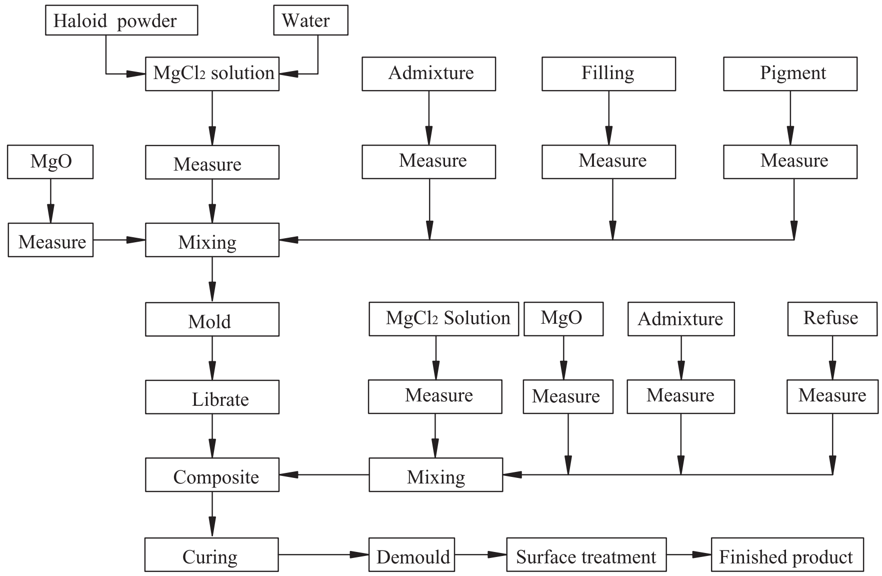


Fig. 2. The production technological flow chart of compound floor tile.

### 2.3. Test methods

#### 2.3.1. Water absorb ratio (wt.%)

(a) Three 28-day samples were placed in an oven with temperature of 60 ± 5 °C;
(b) Samples were weighed every 2 h, and the value was recorded as $m_0$ if the difference between two successive weights is not more than 1 g;
(c) The samples were placed in water of 20 ± 0.5 °C and soaked for 24 h;
(d) The samples were removed from the water, the surface water was wiped off, then the samples were weighed as $m_1$, so water absorb ratio (wt.%)=$(m_1 - m_0)/(m_0) \times$ 100%.

#### 2.3.2. Softening coefficient

(a) Compressive strength of three 28-day samples was tested, and the average value was taken as $R_0$;
(b) Three 28-day samples were placed in water of 20 ± 0.5 °C for 28 days, and then the samples' compressive strength was tested;
(c) The average value was taken as $R_w$, so softening coefficient=$(R_w)/(R_0)$.

#### 2.3.3. Appearance of samples (namely, rehalogenation)

(a) Three 28-day samples were placed in an oven of 60 ± 5 °C for 48 h, then was taken out of the oven and cooled in a vacuum container;
(b) Samples were returned to a container plate with 3–4 mm thick fineness sand, and clean water was poured to make water surface and sand surface at the same level;
(c) Half of sample was embedded into the sand and water for 72 h;
(d) The samples were taken from water and placed into the oven to dry. The presence of white salt in the illumination condition was observed.

#### 2.3.4. Initial setting time

(a) The raw materials were weighed exactly as the following ratio: magnesite/haloid powder = 1:0.5. Then appropriate water was added and mixed round to make the net paste;
(b) The net paste was placed in a cone with an upside diameter of 70 mm, an underside diameter of 80 mm, and a height of 40 mm;
(c) The cone was positioned on the Vicat Apparatus, with the Vicat needle touching the surface of net paste, then letting the Vicat needle fall and inserting it into the net paste;
(d) The time was recorded as the initial setting time if the depth that the Vicat needle could reach is less than 5 mm in 30 s.

Table 4
The influence of concentration of $MgCl_2$ solution on the property of the product

| Order | Specific gravity of $MgCl_2$ solution ($g/cm^3$) | 7-day compressive strength (MPa) | Appearance of sample |
|---|---|---|---|
| 1 | 1.12 | 29.8 | Crack and no salt appearance |
| 2 | 1.20 | 60.9 | No salt appearance |
| 3 | 1.24 | 66.4 | No salt appearance |
| 4 | 1.26 | 68.1 | A little salt appearance |
| 5 | 1.32 | 69.9 | Some salt appearance |

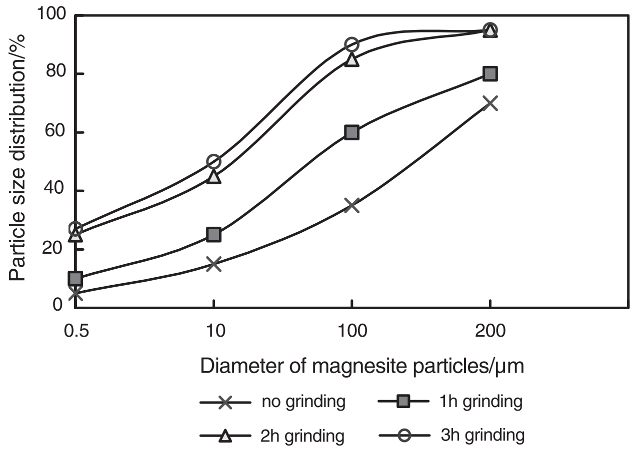


Fig. 3. Particle size distribution of unground and ground magnesite.

FAM laser particle analyses apparatus was used to test particle size distribution and HITACHI S-2500 scanning electron microscope was adopted to examine microstructure of samples.

## 3. Experimental result and analysis

### *3.1. The influence of the concentration of $MgCl_2$ on the property of the product*

In this reaction system, magnesite and magnesium chloride worked as cement and the crushed urban refuse worked as filler. As to the hydration reaction of magnesite, studies [7–9] suggested that the main hydration products of this reaction are:

5.1.8 phase (also called 5 phase: 5 $Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$),
3.1.8 phase (also called 3 phase: 3 $Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$).

And the other products are $Mg(OH)_2$, unreacted MgO, $MgCl_2$, etc. The mainly crystal shape of 5 phase and 3 phase, especially the 5 phase, is needlelike and long-tree-like, they crossed mutually and connected into a net structure. This kind of structure allows the magnesite cement product to be of high mechanical strength. In the formation process of 5 phase and 3 phase, firstly, MgO dissolved in the $MgCl_2$ solution and turned into $Mg^{2+}$ and $OH^-$ ions. Subsequently, these two kinds of ions reacted with $Mg^{2+}$, $Cl^-$, and $H_2O$ in the system into 5 phase and 3 phase. So the concentration of $MgCl_2$ solution and the activity of MgO made a great influence on the rate of reaction.

Controlling the content of active MgO, using $MgCl_2$ solution with different concentrations to prepare the paste and form the test sample (using specific gravity of the solution to denote its concentration commonly in engineering application), the test results after 7 days standard curing are shown in Table 4.

According to the data shown in Table 4, we can easily conclude that the strength increased with the increase of concentration of $MgCl_2$ solution. The product is easy to crack when the concentration of $MgCl_2$ is too low and salt appearance (rehalogenation) on its surface is too high. Commonly, it is suitable when the specific gravity of $MgCl_2$ solution ranges between 1.20 and 1.26 g/cm$^3$. In this experiment, we choose $MgCl_2$ solution with 1.24 g/cm$^3$ as a basic parameter.

### *3.2. The influence of the fineness of magnesite on the property of the product*

The fineness of magnesite also has some influence on the hydration speed and the final degree of hydration, in addition to the concentration of $MgCl_2$ solution and the activity of MgO. In this experiment, we searched the influence of grain fineness distribution of magnesite on the property of the product, by comparing the property of ground magnesite and the original magnesite. The different grain fineness distributions of magnesite used in this experiment are shown in Fig. 3. Two kinds of magnesite with different grain fineness have been used to make test samples, and were tested for their strength with their difference analyzed using SEM. The strengths of compound floor tile test samples made of different fineness of magnesite are shown in Table 5. From the table, we can see that the samples made of ground magnesite have a remarkable improvement in compressive strength and flexural strength. At the same time, its water absorption ratio was reduced and its softening coefficient increased remarkably. In addition, the initial setting time was shortened from 26 to 22 min. The reason is mainly because the specific surface area of ground raw material had a remarkable increase and the larger specific surface area was

Table 5
The influence of the fineness of magnesite on the property of the product

| Kind of magnesite | 7-day compressive/ flexural strength (MPa) | 28-day compressive/ flexural strength (MPa) | Water absorbance ratio (wt.%) | Softening coefficient | Appearance of sample |
|---|---|---|---|---|---|
| No grinding | 68.1/11.75 | 76.3/17.88 | 17.6 | 0.72 | A little salt appearance |
| 1 h grinding | 73.2/13.55 | 91.6/21.97 | 13.6 | 0.78 | No salt appearance |
| 2 h grinding | 75.5/14.10 | 95.8/23.10 | 9.6 | 0.81 | No salt appearance |
| 3 h grinding | 78.4/14.25 | 95.0/23.50 | 9.4 | 0.87 | No salt appearance |

very helpful in advancing the speed of MgO's dissolution and hydration. Especially on the interface of the newly ground magnesite, it is too late for MgO to react with the moisture water in the air and the ratio of active MgO was relatively higher. This would enhance the density of the 5.1.8 phase and make a tighter cross combination. This leads to a notable increase on the sample strength at every age. The porosity inside the sample is lowered and its water absorption ratio reduced. The appearances of samples show a notable improvement. In order to confirm this viewpoint, we used SEM (see Fig. 4).

Comparing Fig. 4a and b, we can see that the pore size on the sample surface made of ground magnesite is far less than that of the unground magnesite. But there still exist lots of pores on its surface. That is to say, it is not enough to resolve the phenomena of salt appearance of samples (namely rehalogenation) only by grinding the magnesite.

Comparing Fig. 4c and d, we can see that the 5.1.8 phase inside the sample made of unground magnesite is less and its structure is not compact. However, the 5.1.8 phase inside the sample made of ground magnesite has a large quantity and a uniform distribution. Its structure is very compact. This result is in agreement with the conclusion we got from the macro-physical property test.

## 4. Conclusions

1. It is a feasible technology to produce compound floor tile using urban refuse and magnesium oxychloride cement as main raw materials by moulding. This technology is simple and easy to manipulate. The various properties of the product can all measure up to the criteria [5,6] of concrete floor tile.
2. In the process of urban refuse/magnesium oxychloride cement compound floor tile production, controlling the content of magnesium chloride strictly according to the content of active magnesium oxide is an effective measure to assure the strength of the product and reduce salt appearance and rehalogenation.
3. An appropriate fineness of magnesite will enhance its reaction activity and is helpful to the formation of a stable phase—the 5.1.8 phase, and will advance on the product's strength and surface quality.

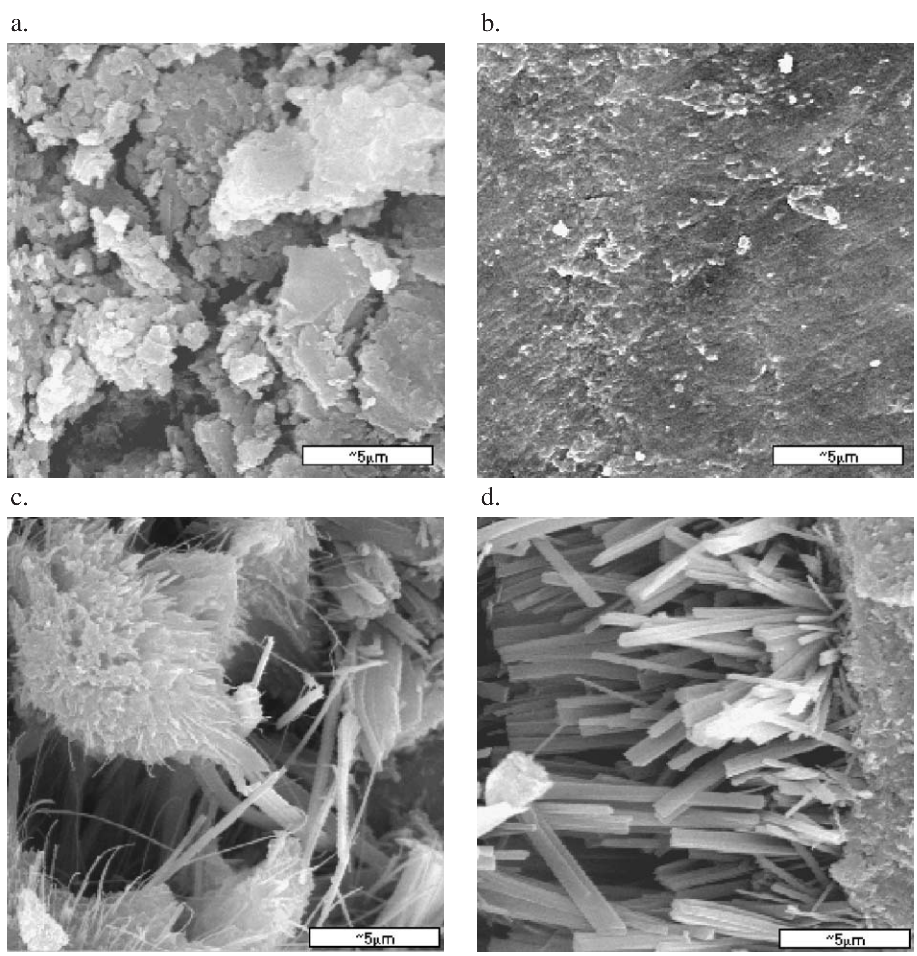


Fig. 4. SEM micrograph of samples surface and the hydration products. (a) Sample surface of unground magnesite. (b) Sample surface of ground magnesite. (c) Hydration products inside the sample made of unground magnesite. (d) Hydration products inside the sample made of ground magnesite.

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