Chloride Ion Penetration Resistance and Pore Structure of Magnesium Silicate Hydrate (M-S-H) Mortars

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Abstract—The main purpose of this paper is to study the chloride ion penetration resistance and pore structure of magnesium silicate hydrate cement (MSH) mortars. The chloride ion penetration resistance of MSH mortars with different water-to-cement ratios (0.5, 0.55, 0.6) and different sand rates (25%, 50%, 75%) was studied and compared to ordinary Portland cement (OPC) mortars. The pore structure of magnesium silicate hydrate mortar was tested using mercury intrusion porosimetry (MIP). The results indicate that the chloride ion diffusion coefficient becomes larger with an increase in the water-to-cement ratio and sand rate; the coefficient of MSH mortars is much smaller than that of OPC mortars. The results of MIP show that MSH mortars generally have gel pores measuring less than 10nm; however, the pore size of OPC mortars is dominated by pores measuring 10nm to 100nm. Finally, MSH mortars were found to be less porous than OPC mortars.

Keywords- magnesium silicate hydrate mortar; chloride ion penetration resistance; pore structure

I. INTRODUCTION

Magnesium silicate hydrate cement (MSH) is a new type of cementitious material. Literature has indicated that the hydration products of MgO-SiO\textsubscript{2}-H\textsubscript{2}O system are primarily composed of Mg(OH)\textsubscript{2} and MSH gel, which is formed by the reaction of MgO and amorphous silica in the presence of sodium hexametaphosphate (Na-HMP) [1-3]. The properties of magnesium silicate hydrate cement have also been studied by some scholars[4,5].

The pH of MSH cement is lower than that of ordinary Portland cement (OPC) and is therefore better suited to encapsulating nuclear waste and some heavy metal ions[6]. It is also used in wall insulation materials, refractory castables, and other fields due to its light weight, excellent mechanical properties, and high raw material temperature[7].

Although MSH cement has been theoretically improved, its durability has not been empirically tested; therefore, its durability is worth studying. There are many forms of deterioration that threaten the durability of cement-based materials, most of which is related to the intrusion of water and chlorinated salts[8]. There are many methods to prevent corrosion in concrete, but the most basic and effective way is by improving the properties of cement-based materials[9].

Extensive research has been done on OPC with regard to chloride ion penetration[10-11], but in the case of MSH cement, its performance under chloride ion penetration remains unknown. As a new type of building material that also has sound development prospects, MSH’s performance under chloride ion penetration warrants further study. Therefore, the main aim of this paper is to study the effect of the water-to-cement ratio and sand content on the chloride ion diffusion coefficient of MSH mortars. The study also intends to compare MSH and OPC mortars under the same impermeability conditions. The pore size distribution of cement mortars is measured using mercury intrusion porosimetry (MIP).

II. EXPERIMENTAL

A. Materials

This study used commercially available MgO (MgO; MagChem 30, M.A.F. Magnesite B.V., The Netherlands), silicate fume (SF; Elkem Materials Ltd., Shanghai, China), OPC (P.O 42.5R, Onoda Cement Co., Ltd., Dalian, China), and sodium hexametaphosphate (Na-HMP, chemical grade, >95% purity; Sinopharm Chemical Reagent Co., Ltd., Shanghai, China). According to previous research[12], fine silica sand was used in the preparation of all samples. The chemical compositions of the raw materials are reported in Tab. 1.

| Chemical Composition (wt.%) | SiO\textsubscript{2} | Al\textsubscript{2}O\textsubscript{3} | Fe\textsubscript{2}O\textsubscript{3} | CaO | P\textsubscript{2}O\textsubscript{5} | MgO | K\textsubscript{2}O | Na\textsubscript{2}O | SO\textsubscript{3} |
|-----------------------------|---------------------|-----------------|-----------------|-----|----------------|-----|----------------|----------------|----------------|
| Silica fume                 | 94.71               | 0.23            | 0.24            | 0.68| 0.37           | 1.19| 1.74           | 0.35           | 0.36           |
| MgO                         | 0.35                | 0.07            | 0.15            | 0.87| -              | 98.3| -              | -              | 0.05           |
| OPC                         | 21.45               | 5.24            | 2.89            | 61.13| -              | 2.08| -              | 0.77           | 2.50           |
TABLE II. Mixture Proportions of Mortar

| Sample No. | Cement Type | Cement (wt.% | Water-to-Cement Ratio | Sand Content (wt.%)
|------------|-------------|--------------|-----------------------|---------------------|
| N1         | M-S-H†      | 75           | 0.5                   | 25                  |
| N2         | M-S-H†      | 50           | 0.5                   | 50                  |
| N3         | M-S-H†      | 25           | 0.55                  | 75                  |
| N4         | M-S-H†      | 50           | 0.6                   | 50                  |
| N5         | M-S-H†      | 50           | 0.6                   | 50                  |
| N6         | O-P-C       | 50           | 0.5                   | 50                  |

a. The composition of MSH paste is MgO: SF: Na-HMP = 40: 60: 2.

B Methods

According to the formulation in Tab. 2, specimens were cast in steel molds to create 40mm×40mm×160mm and φ100mm×100mm samples. The molds were covered with plastic wrap and moved to the standard curing room with a relative humidity of >95% RH to prevent samples from drying out while curing. Specimens were demolished within (24±2) hours and then placed in standard curing chambers to undergo strength and chloride ion penetration resistance tests, respectively. According to Chinese Standard GB/T50082-2009, the chloride ion diffusion coefficient was evaluated using an apparatus to determine the rapid chloride migration coefficient (RCM-NTB Beijing NELD Instrument Co., Ltd., China). Seven days before the test, specimens were taken to coring at φ100mm×50mm and cured until the test ages. After the mechanical properties of the specimen were tested, select the shape of the rules of crushed samples of about 2g placed in the sealed bag and terminate hydration with alcohol. The prepared crushed samples were placed in a vacuum oven at 50°C for 48 hours prior to the MIP and SEM tests.

III. RESULTS AND DISCUSSION

A. Mechanical Properties

Fig. 1(a) presents the results of the MSH mortars’ flexural and compressive strength after curing for 28 days curing with under different water-to-cement ratios. From Fig. 1(a), we can see that flexural and compressive strength decreased gradually over 28 days while the water-to-cement ratio increased. When the water-to-cement ratio reached 0.5 and the sand content reach 50%, the compressive strength of MSH mortar was 58.6Mpa; hence, MSH cement showed good mechanical properties. Fig. 1(b) displays the results the MSH mortars’ flexural and compressive strength of the MSH mortars after curing for 28 days with different sand contents. As shown in Fig. 1(b), the flexural and compressive strength of the MSH mortars after curing for 28 days increased gradually as sand content increased.

B. Chloride Ion Penetration Resistance Analysis

After the chloride ion penetration resistance test, the specimens were taken out and broken in half. The depth after color development with AgNO₃ is shown in Fig. 2. According to Chinese Standard GB/T50082-2009, the chloride ion diffusion coefficient was calculated using the following formula:

\[
D_{RCM} = \frac{0.0239 \times (273 + T) \times X_d}{(U - 2) \times L} \left( X_d - 0.0238 \times \sqrt[3]{\frac{(237 + T) \times L \times X_d}{U - 2}} \right)
\]

where \(D_{RCM}\) is chloride ion diffusion coefficient, \(U\) is the absolute value of the voltage (V), \(T\) is the average of the initial temperature and the end temperature of the anode solution (°C), \(L\) is the specimen height (mm), \(X_d\) is the average chloride ion penetration depth (mm), and \(t\) is the testing time (h). The MSH chloride ion diffusion coefficients are shown in Tab. 3.

From the results, we can see that the chloride ion diffusion coefficient of MSH mortar increased with an
increasing water-to-cement ratio and sand content, presumably because the pores in the mortar also increased; thus, impermeability was reduced. The chloride ion diffusion coefficient of the OPC mortars was about six times larger than that of the MSH mortars, indicating that MSH impermeability was better than that of OPC.

The cumulative pore area distribution of the mortars is shown in Fig. 3(b). It can be seen that the cumulative pore area of the different types of cement mortars was composed primarily of pores smaller than 100nm increased with a decrease in pore size diameter. For MSH mortar, when the pore size diameter was less than 10nm, the cumulative pore area increased significantly, indicating that the MSH mortar was mainly composed of pores smaller than 10nm. For OPC mortar, when the pore size diameter was less than 100nm, the cumulative pore area increased significantly, indicating that OPC mortar was composed primarily of pores smaller than 100nm.

C. Pore Structure Analysis

MIP has been widely used to measure medium-to-large pore structures in porous materials[13]. In this experiment, pore structure was studied via MIP (AutoPore IV 9500 Series, Micromertics Instrument Corp, USA). We obtained data for sample N2 and sample N6; results appear in Tab. 4. It was observed that the MSH cement mortar had lower porosity and total intruded volume content than OPC mortar. The porosity of MSH mortar was 9.249%, about 52.7% lower than the OPC mortar. This is because the hydration products of MSH cement are mainly MSH gel, and the structure is dense. The OPC hydration products have more crystals, so the structure is loose.

The pore size distribution of the MSH and OPC cement mortars is shown in Fig. 3(a). MSH mortar shows a peak value of 0.036ml/g at a pore diameter of 91082.6nm and a peak of 0.031ml/g at a pore diameter of 554.0nm. During mixing, the vibration process may be insufficient, leaving air in the specimen. When the pore diameter was less than 17.1nm, the amount of total intruded volume increased gradually as pore diameter decreased; this indicates that the pore size diameter of MSH mortar is mostly less than 17.1nm. The total intruded volume of OPC mortar was mainly between 10nm and 100nm and reached a maximum of 0.192ml/g at a pore diameter of 77.1nm.

D. Relationship Between Porosity and Penetrability

The pore structure and chloride ion transport properties of concrete has been reported thoroughly in research[14]. After identifying the pore structure parameters affecting chloride ion permeability, porosity is the main factor affecting chloride ion permeation. The pores that affect the chloride ion permeability of cement-based materials are capillary pores; gel pores are not substantially affected[15]. Thus, we can conclude from the chloride ion permeation test and pore structure results that gel pore-based MSH mortars have greater impermeability than do OPC.
IV. CONCLUSION

(1) With an increase in the water-to-cement ratio, the mechanical properties decrease. When the sand content gradually increased, mortars’ mechanical properties also increased. The compressive strength of MSH mortar was 58.6 MPa when the water-to-cement ratio was 0.5 and the sand content was 50%. As a consequence, MSH mortar demonstrated good mechanical properties.

(2) As for MSH cement, with an increase in the water-to-cement ratio and sand content, the chloride ion diffusion coefficient gradually increased. Compared with water-to-cement ratio and sand content, the chloride ion diffusion coefficient of two kinds of cement mortar under the same conditions, we found the impermeability of MSH mortar to be better than that of OPC.

(3) The porosity of MSH mortar is lower than that of OPC mortar. MSH mortar was mainly composed of gel pores smaller than 10 nm, whereas OPC mortar was mainly composed of capillary pores smaller than 100 nm. The permeability results showed that the MSH mortar with gel pores had better impermeability than OPC mortar.

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TABLE III. THE PENETRATION COEFFICIENT OF MORTARS (×10⁻¹² m²/s)

| Sample NO. | Total Intrusion Volume (mL/g) | Median Pore Diameter (Area) (nm) | Average Pore Diameter (4V/A) (nm) | Porosity (%) |
|------------|-------------------------------|---------------------------------|---------------------------------|--------------|
| N1         | 1.261                         | 1.602                           | 1.523                           | 1.580        | 8.802        |

TABLE IV. MIP RESULTS

| Total Intrusion Volume (mL/g) | Median Pore Diameter (Area) (nm) | Average Pore Diameter (4V/A) (nm) | Porosity (%) |
|-----------------------------|---------------------------------|---------------------------------|--------------|
| N2                          | 0.092                           | 7.2                             | 18.9         | 9.249        |
| N6                          | 0.108                           | 17.1                            | 36.6         | 19.572        |