Chloride Binding Capacity and Its Effect on the Microstructure of Mortar Made with Marine Sand

Congtao Sun, Ming Sun, Tao Tao, Feng Qu, Gongxun Wang, Peng Zhang, Yantao Li, and Jizhou Duan

Key Laboratory of Marine Environmental Corrosion and Bio-fouling, Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, China; ytl@qdio.ac.cn (Y.L.); duanjz@qdio.ac.cn (J.D.)
Center for Ocean Mega-Science, Chinese Academy of Sciences, 7 Nanhai Road, Qingdao 266071, China
Open Studio for Marine Corrosion and Protection, Pilot National Laboratory for Marine Science and Technology, Qingdao 266237, China
Nantong Research and Development Center of Marine Science and Technology, Institute of Oceanology, Chinese Academy of Sciences, Nantong 226004, China
School of Civil Engineering, Qingdao University of Technology, Qingdao 266033, China; sunmingfx@126.com (M.S.); peng.zhang@qut.edu.cn (P.Z.)
School of Civil Engineering, Hunan University of Technology, Xiangtan 411201, China; a791939465@hotmail.com (T.T.); wanggx@hnust.edu.cn (G.W.)
Correspondence: suncongtao@qdio.ac.cn (C.S.); qfkdl015@126.com (F.Q.)

Abstract: Chloride binding capacity and its effect on the microstructure of mortar made with marine sand (MS), washed MS (WMS) and river sand (RS) were investigated in this study. The chloride contents, hydration products, micromorphology and pore structures of mortars were analyzed. The results showed that there was a diffusion trend for chloride ions from the surface of fine aggregate to cement hydrated products. During the whole curing period, the free chloride content in the mortars made by MS and WMS increased firstly, then decreased and stabilized finally with time. However, the total chloride content of three types of mortar hardly changed. The bound chloride content in the mortars made by MS and WMS slightly increased with time, and the bound chloride content included MS, the WMS and the RS arranged from high to low. C₃Å·CaCl₂·10H₂O (Friedel’s salt) was formed at the early age and existed throughout the curing period. Moreover, the volume of fine capillary pore with a size of 10–100 nm increased in the MS and WMS mortar.

Keywords: marine sand; chloride binding; microstructure; mortar

1. Introduction

As a primary raw material of concrete, river sand (RS) has been overly exploited as fine aggregate because of the rapid growth of the construction industry. The overexploitation of RS has caused harmful environmental problems and has restricted the development of cement hydration industry. Given the advantages of abundant resources, uniform fineness modulus and low mud content [1,2], the utilization of marine sand (MS) to replace RS as a fine aggregate in concrete has been investigated by numerous scholars in recent years. Moreover, the concrete made by MS has excellent mechanical properties [3–7]. Therefore, it is hoped that the MS used in coastal environments could also reduce transportation costs and CO₂ emissions. However, the direct use of MS can increase the potential risk of steel bar corrosion and cause serious degradation of concrete structures [8–11]. To reduce the possibility of corrosion, MS desalination technology, such as washing, must be adopted, in which energy and fresh water could be consumed. However, some chloride ions can still be found on the surface of the washed MS (WMS), and the application of WMS can also increase the free chloride concentration in the pore solution of concrete. Meanwhile, it is well known that free chloride can bond with the use of hydration products, which can retard the occurrence of steel corrosion behavior [12]. Therefore, the chloride binding capacity is...
of great significance for the promotion of MS applications. The chloride binding capacity of concrete can be divided into two aspects [13–16]: a physical one, in which the chloride ions can be adsorbed by C-S-H gel because of its high specific surface values, and a chemical one, which denotes the reaction between chloride ions and C\textsubscript{3}A or AFm phase. However, chemical binding occupies the dominant position, and the contribution of chemical binding accounts for 70% of the total bound chloride capacity, whilst the contribution of physical adsorption remains stable between 25% and 28% [14]. Chemical binding is related to the chloride ions bound in C\textsubscript{3}A·CaCl\textsubscript{2}·10H\textsubscript{2}O (Friedel’s salt) or C\textsubscript{3}A·0.5CaCl\textsubscript{2}·0.5CaSO\textsubscript{4}·10H\textsubscript{2}O (Kuzel’s salt). However, Kuzel’s salt was generated when the chloride content was very low [17], and its stability needs further investigation. Therefore, chemical binding usually refers to the formation of Friedel’s salt [18,19].

Chloride binding is relatively complex and is influenced by various factors, such as chloride concentration, cement composition, cation of chloride salt, carbonation and sulfate ions [20]. Moreover, the intruding behavior of chloride ions is vital to the chemical binding mechanisms. The intruding chloride ions could be divided into two types: the external chloride ions intruded in the already hardened concrete, and the internal chloride ions introduced by raw materials [20]. For internal chloride ions, the chemical binding mechanism refers to the reaction between chloride ions and C\textsubscript{3}A, which can be explained by Equations (1) and (2), respectively [21].

\[
\begin{align*}
C\textsubscript{3}A + CaCl\textsubscript{2} + 10H\textsubscript{2}O &\rightarrow C\textsubscript{3}A·CaCl\textsubscript{2}·10H\textsubscript{2}O, \quad (1) \\
Ca(OH)\textsubscript{2} + 2NaCl &= CaCl\textsubscript{2} + 2Na\textsuperscript{+} + 2OH\textsuperscript{−}. \quad (2)
\end{align*}
\]

For external chloride ions, the chemical binding mechanism refers to bulk chloride ions in the pore solution adsorbed into the principal layers, [Ca\textsubscript{2}Al(OH\textsuperscript{−})\textsubscript{6}·nH\textsubscript{2}O\textsuperscript{+}], of the AFm structure to balance the charge [22].

For promotion of MS applications, several researchers have studied chloride binding using an approach that dissolves chloride ions in a water mix instead of MS [23,24]. Although both the chloride ions introduced by the water mix and MS are internal chloride, the influence on chloride binding, due to the two different approaches explained above, is still unclear. Therefore, the chloride binding investigated by the utilization of MS has more practical implications.

The objective of this research is to investigate the chloride binding behavior and mechanism of mortars made from MS and WMS, with the mortar made from RS being the control group. The free and total chloride contents at different curing ages were measured using titration methods. Subsequently, the bound chloride content was calculated accordingly, and the chloride binding process was analyzed on the basis of the curing age. Moreover, the hydration products and microstructure of mortars were tested on the basis of energy dispersive spectroscopy (EDS), scanning electron microscopy (SEM), X-ray diffraction (XRD) and thermogravimetric analysis (TGA). The pore size distribution that was influenced by MS and WMS was determined by mercury intrusion porosimetry (MIP). Based on this research, the chloride binding capacity of mortar made with MS exposed to a chloride salt solution will be investigated in a separate study.

2. Materials and Methods

2.1. Materials

Ordinary Portland cement (grade 42.5) was used in this research. The main chemical composition of cement is given in Table 1. For the fine aggregate, the typical MS was mined from the Zhoushan sea area (Zhejiang Province, China). The WMS was desalinated by the aforementioned MS, and the desalination process was as follows: the MS was immersed for 24 h, and the water was changed and washed for 20 min every 6 h. The RS was supplied by the Rizhao River Sand Factory (Shandong Province, China). The maximum particle size of the three types of sand (i.e., MS, WMS and RS) was 5 mm, and their properties are shown in Table 2.
Table 1. Chemical composition of cement.

| Content | SiO₂ | CaO  | MgO  | Fe₂O₃ | Al₂O₃ | SO₃  | Loss |
|---------|------|------|------|-------|-------|------|------|
| wt%     | 19.9 | 63.27| 1.6  | 2.82  | 4.14  | 4.49 | 0.55 |

Table 2. Primary properties of fine aggregates.

| Sand Type | Chloride Content (wt%) | Shell Content (wt%) | Fitness Modulus |
|-----------|------------------------|--------------------|-----------------|
| RS        | 0.005                  | 0                  | 2.73            |
| MS        | 0.236                  | 2.4                | 2.75            |
| WMS       | 0.058                  | 2.2                | 2.75            |

2.2. Mix Proportions and Specimen Preparation

The proportion of mortar is referred to as GB/T1761-1999 (Test Method for Cement Mortar Strength). For all mortars, the mass ratio of cement, sand and water was 1:3:0.5, respectively. All specimens were demolded after curing for 24 h. After demolding, the specimens were placed in a curing room at 20 ± 2 °C with 98% relative humidity (RH) until tested. The specimens measuring 70.7 mm × 70.7 mm × 70.7 mm were crushed at the ages of 3, 7, 28 and 56 d, respectively; two pieces were randomly selected from different areas for grinding into powder. Powders that could pass through a sieve of 0.85 mm were used to measure the chloride content. The specimens measuring 40 mm × 40 mm × 160 mm were also crushed at the ages of 3, 7, 28 and 56 d, respectively. Some pieces were selected for EDS and MIP, which were dried at 50 °C after being immersed in ethanol to stop hydration. Other pieces that were prepared for the analysis of hydration products (e.g., XRD, TGA) were grinded into powders with a particle size of less than 0.08 mm after stopping hydration.

2.3. Test Methods

The contents of free chloride and total chloride in the mortars were tested using silver nitrate titration method in accordance with the standards of ASTM C1218/C1218M-99 (Standard Test Method for Water-Soluble Chloride in Mortar and Concrete) and ASTM C1152/C1152M-04 (Standard Test Method for Acid-Soluble Chloride in Mortar and Concrete), respectively. The free chloride content (Cₐ) and total chloride content (Cₜ) were calculated on the basis of the titration result, and each titration was conducted twice. The difference between the two experimental results should not exceed 0.0037%, and the average was taken as the final result.

In this work, EDS was used to test the elements of mortars. The tested sample was prepared using hardened mortar pieces, followed by vacuum drying, polishing and covering with gold film. The instrument for this examination provided by EDAX Inc. (USA), and it was used with an acceleration voltage of 20 keV and a working distance of 10 mm. The morphology of the mortar was observed using a scanning electron microscope (QUANTA Q400, FEI Inc, Hillsboro, OR, USA). The pieces that reflected the real internal structure were dried in an oven, and each section was cleaned and covered with gold film. Then, their morphologies were observed. Phase assemblage was characterized by an X-ray diffractometer (D8 Advance, AXC Inc, Karlsruhe, Germany) with Cu radiation and a current of 40 mA and 40 kV, respectively. The test rate was 0.1 s/step with a step of 0.02°. Phase assemblage was verified by TGA using the comprehensive thermal analyzer (SDT Q600, TA Inc, New Castle, DE, USA). The specimen was heated from room temperature to 900 °C in an N2 atmosphere. According to the characteristic weight loss peak in the DTG pattern, the content of Friedel’s salt could be obtained from TGA data. MIP was conducted to characterize the pore size distribution. The samples were prepared with 3–5 mm dried in an oven at 50 °C to achieve a constant weight before testing. The instrument used was an AutoPore IV 9510 from the MICROMERITICS INSTRUMENT CORPORATION, USA. The maximum pressure was 420 MPa, the contact angle was 140° and the surface tension was 480 mN/m.
3. Results and Discussion

3.1. Diffusion of Chloride Ions from Fine Aggregate to Cement Hydrated Products

Liu et al. [25] found that chloride diffusion occurred from the surface of the sand to the inner parts of the hydrated cement products during the cement hydration process. However, simulated marine sand was used in the Liu et al. investigation. Whether this process existed in the mortars made with MS or WMS remains to be explored. The chloride contents of two areas that were different distances away from the sand at 3 d were tested. Figure 1 shows the scanning area location of mortars. Spectrum 1 is closer to the sand, while Spectrum 2 is farther away from the sand. Figure 2a,b show the EDS test results of the surface of the hydrated products around fine aggregate particles in MS and WMS mortars, respectively. In the MS specimen, the chloride contents in scanning areas 1 and 2 are 2.31% and 1.59%, respectively. In the WMS specimen, the chloride contents in scanning areas 1 and 2 are 1.05% and 0.69%, respectively. The chloride content in area 1 is obviously higher than that in area 2. This result is consistent with the results obtained by Liu et al. [25]. The chloride ions introduced by fine aggregates were not completely dissolved in a mix of water during the specimen preparation. In the early ages, only a part of the chloride ions entered into the pore solution and participated in the hydration process. Another part of the chloride ion dissolved gradually in the pore solution during the curing process.

3.2. Free Chloride Content of Mortars at Different Curing Ages

Figure 3a presents the free chloride content of mortars made with three types of fine aggregate at different curing ages. During the whole curing period, the free chloride content in MS specimens was always much higher than that in others, the WMS specimens were second, whilst the RS specimens had the lowest free chloride content, which was stable at about 0.005%. The free chloride content in the MS and WMS specimens increased first, then decreased and finally stabilized during the curing period. The free chloride content in the MS specimen was 0.052% at 3 d, 0.060% at 7 d, 0.058% at 28 d and 0.057% at 56 d, and that in the WMS specimen was 0.015%, 0.025%, 0.016% and 0.015%, respectively. This also indicates that the chloride diffusion process exists in the mortar made with MS and WMS. The free chloride content increased in the early age because the chloride ions had not been absolutely released from the fine aggregate and the chloride binding capacity was not fully able to perform. Due to the completion of the chloride release process and free chloride ions gradually bound by hydration products, the free chloride content decreased and stabilized with age.

Figure 1. Schematic diagram of scanning area.
3.2. Free Chloride Content of Mortars at Different Curing Ages

Figure 2. Scanning result from the energy disperse spectroscopy (EDS) of mortars: (a) marine sand (MS) mortars, (b) washed marine sand (WMS) mortars.

3.3. Total Chloride Content of Mortars at Different Curing Ages

Figure 3a presents the free chloride content of mortars made with three types of fine aggregates at different curing ages. The MS specimens had the highest total chloride content. During the whole curing period, the free chloride content decreased and stabilized with age. This also indicates that the chloride diffusion process exists in the mortar made with MS and WMS. The free chloride content increased in the early age because the chloride ions had not been absolutely released from the fine aggregate and the chloride binding capacity was not fully able to perform. Due to the completion of the chloride release process and free chloride ions gradually bound by hydration products, the free chloride content decreased and stabilized with age.

The amount of Friedel's salt in hydrates is related to chemical chloride binding. The XRD results for hydration products of mortars made using the three types of fine aggregates at different curing ages are shown in Figure 4. As can be seen in Figure 4a, the hydrates of mortars at different curing ages were characterized by XRD and TGA. Chemical chloride binding typically results from the formation of Friedel's salt, and the chloride ions had not been absolutely released from the fine aggregate and the chloride binding capacity was not fully able to perform. Due to the completion of the chloride release process and free chloride ions gradually bound by hydration products, the free chloride content decreased and stabilized with age. This also indicates that the chloride diffusion process exists in the mortar made with MS and WMS. The free chloride content increased in the early age because the chloride ions had not been absolutely released from the fine aggregate and the chloride binding capacity was not fully able to perform. Due to the completion of the chloride release process and free chloride ions gradually bound by hydration products, the free chloride content decreased and stabilized with age.

Figure 3b illustrates the total chloride content of mortars made with three types of fine aggregates at different curing ages. The MS specimens had the highest total chloride content. During the whole curing period, the free chloride content decreased and stabilized with age. This also indicates that the chloride diffusion process exists in the mortar made with MS and WMS. The free chloride content increased in the early age because the chloride ions had not been absolutely released from the fine aggregate and the chloride binding capacity was not fully able to perform. Due to the completion of the chloride release process and free chloride ions gradually bound by hydration products, the free chloride content decreased and stabilized with age.

The total chloride content in the MS specimens was 0.171% at 3 d, 0.175% at 7 d, 0.177% at 28 d and 0.176% at 56 d, and that in the WMS specimens was 0.015%, 0.025%, 0.016% and 0.015%, respectively. This also indicates that the chloride diffusion process exists in the mortar made with MS and WMS. The free chloride content in the MS and WMS specimens increased with curing age and that in the WMS specimens was 0.027%, 0.030%, 0.040% and 0.041%, respectively, whilst the RS specimens were stable at 0.015%.

56 d, and that in the WMS specimens was 0.015%, 0.025%, 0.016% and 0.015%, respectively, whilst the RS specimens were stable at 0.015%.

Figure 3c shows the bound chloride content. The bound chloride contents included the MS, the WMS, and the RS specimens. The bound chloride content was calculated on the basis of the total chloride content minus the free chloride content. The bound chloride content was not fully able to perform. Due to the completion of the chloride release process and free chloride ions gradually bound by hydration products, the free chloride content decreased and stabilized with age. This also indicates that the chloride diffusion process exists in the mortar made with MS and WMS. The free chloride content in the MS and WMS specimens increased with curing age and that in the WMS specimens was 0.027%, 0.030%, 0.040% and 0.041%, respectively, whilst the RS specimens were stable at 0.015%.

56 d, and that in the WMS specimens was 0.027%, 0.030%, 0.040% and 0.041%, respectively, whilst the RS specimens were stable at 0.015%.

Figure 3. Chloride content of mortars at different curing ages: (a) free chloride content, (b) total chloride content, (c) bound chloride content.

Figure 3a presents the free chloride content of mortars made with three types of fine aggregates at different curing ages. The MS specimens had the highest total chloride content. During the whole curing period, the free chloride content decreased and stabilized with age. This also indicates that the chloride diffusion process exists in the mortar made with MS and WMS. The free chloride content increased in the early age because the chloride ions had not been absolutely released from the fine aggregate and the chloride binding capacity was not fully able to perform. Due to the completion of the chloride release process and free chloride ions gradually bound by hydration products, the free chloride content decreased and stabilized with age. This also indicates that the chloride diffusion process exists in the mortar made with MS and WMS. The free chloride content in the MS and WMS specimens increased with curing age and that in the WMS specimens was 0.027%, 0.030%, 0.040% and 0.041%, respectively, whilst the RS specimens were stable at 0.015%.

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Figure 3c shows the bound chloride content. The bound chloride contents included the MS, the WMS, and the RS specimens. The bound chloride content was calculated on the basis of the total chloride content minus the free chloride content. The bound chloride content was not fully able to perform. Due to the completion of the chloride release process and free chloride ions gradually bound by hydration products, the free chloride content decreased and stabilized with age. This also indicates that the chloride diffusion process exists in the mortar made with MS and WMS. The free chloride content in the MS and WMS specimens increased with curing age and that in the WMS specimens was 0.027%, 0.030%, 0.040% and 0.041%, respectively, whilst the RS specimens were stable at 0.015%.

56 d, and that in the WMS specimens was 0.027%, 0.030%, 0.040% and 0.041%, respectively, whilst the RS specimens were stable at 0.015%.

Figure 3. Chloride content of mortars at different curing ages: (a) free chloride content, (b) total chloride content, (c) bound chloride content.
3.3. Total Chloride Content of Mortars at Different Curing Ages

Figure 3b illustrates the total chloride content of mortars made with three types of fine aggregates at different curing ages. The MS specimens had the highest total chloride content. The total chloride content in the MS specimens was 0.171% at 3 d, 0.175% at 7 d, 0.177% at 28 d and 0.177% at 56 d, and that in the WMS specimens was 0.042%, 0.055%, 0.056% and 0.056%, respectively, whilst the RS specimens were stable at 0.015%.

3.4. Bound Chloride Content at Different Curing Ages

To clarify the chloride binding behavior of mortars at different curing ages, the bound chloride content was calculated on the basis of the total chloride content minus the free chloride content (Figure 3c). The bound chloride contents included the MS, the WMS and the RS that were arranged from high to low. The higher chloride content was introduced and the higher bound chloride content was generated. The bound chloride content in the MS specimens was 0.115% at 3 d, 0.116% at 7 d, 0.119% at 28 d and 0.120% at 56 d, and that in the WMS specimens was 0.027%, 0.030%, 0.040% and 0.041%, respectively, whilst the RS specimens were stable at 0.009%. A slight increase in bound chloride content existed in the mortar made with MS and WMS. This is mainly due to the free chloride ions that are bound by hydration products gradually with time.

3.5. Chloride Binding Mechanism of Mortars at Different Curing Ages

The amount of Friedel’s salt in hydrates is related to chemical chloride binding. The chemical chloride binding typically results from the formation of Friedel’s salt, and the hydrates of mortars at different curing ages were characterized by XRD and TGA.

The XRD results for hydration products of mortars made with the three types of fine aggregate at different curing ages are shown in Figure 4. As can be seen in Figure 4a, the Friedel’s salt diffraction peak appeared throughout the whole curing period. The Friedel’s salt diffraction peaks also appeared in the WMS mortars (Figure 4b). However, in RS specimens, the Friedel’s salt diffraction peak was barely visible throughout the whole curing period (Figure 4c). The results indicate that the chloride ions introduced by fine aggregates were combined with hydration products to form Friedel’s salt at early curing ages, and that Friedel’s salt always exists in mortars throughout the whole curing period.

![Figure 4. Cont.](image-url)
Figure 4. XRD diffraction patterns of specimens at different curing ages: (a) MS mortars, (b) WMS mortars, (c) RS mortars.

Figure 5 shows the DTG results for the hydration products of mortars made with the three types of fine aggregate on different curing days. The types of hydration products from the three mortars were roughly the same because the same cement was used. The dehydration regions of C-S-H and AFt are overlapping; therefore, distinguishing them in the DTG curves is difficult [26]. The shoulder peaks around 150 °C result from the loss of water structure in AFm phases [27]. Some scholars have studied Friedel’s salt by TGA, but the results vary. Jin et al. [28] considered the endothermic peaks of Friedel’s salt to appear in the range of 340–350 °C. Csizmadia et al. [29] found that Friedel’s salt decomposed in the temperature range of 310–360 °C. Saikia et al. [30] suggested that the decomposition range of Friedel’s salt should be 310–385 °C. Although the decomposition range of Friedel’s salt cannot be given accurately, it can be suggested that Friedel’s salt decomposes in the temperature range of 310–385 °C. The endothermic peak between 390 °C and 500 °C accounts for the decomposition of Ca(OH)2, and the mass loss in this area can be used to generally determine Ca(OH)2 content [31]. The calcium carbonate endothermic peaks were observed in the temperature range of 650–750 °C.

Figure 5. DTG curves of powdered mortar samples: (a) MS mortars, (b) WMS mortars.
As shown in Figure 5, several evident endothermic peaks were observed in the MS and WMS specimens at different curing ages, and the corresponding substances included AFm, Ca(OH)$_2$ and calcium carbonate. The endothermic peaks of Friedel’s salt appeared at different curing ages, and the results were generally in good agreement with the analysis that was based on the XRD analysis. It was found that the intensity of endothermic peaks with Friedel’s salt slightly increases with time. In addition, the intensity of endothermic peaks with AFm increased significantly with time. This indicates that the contents of AFm are less in the initial period of curing, and that the AFm was generated in large quantities in the later period of curing with the hydration reaction proceeding. This phenomenon can also account for the change in free chloride content (Figure 3a). In the initial curing age, the chloride binding capacity of mortar was not yielding the highest because the AFm had not formed in large numbers. Therefore, the free chloride content increased with the diffusion of chloride ions from the MS. With the formation of AFm, the free chloride ions decreased and finally stabilized because of chloride binding by AFm.

3.6. Effects of Chloride Binding on Micromorphology and Microstructure

The micromorphology and pore structure of mortars may be influenced by the chloride binding product. Pore structure is considered a primary factor influencing chloride migration, and refined pore structure can resist the chloride migration physically by blocking the channel [23]. The micromorphology and microstructure of the mortars were characterized by SEM and MIP, respectively.

Figure 6 shows the micromorphology of the MS, WMS and RS mortars, including the hydration products of C-S-H, Ca(OH)$_2$ and AFt. Moreover, Friedel’s salt was observed in the MS and WMS mortars during the whole curing period, and the results were consistent with the XRD and TGA results.

Figure 6. Cont.
Figure 6. Micromorphology of mortars at different curing ages: (a) MS mortars, (b) WMS mortars, (c) RS mortars.

Figure 7 shows the relationship between the pore size and cumulative pore volume of the three types of mortars at 28 d. In addition, the porosity of the MS, WMS and RS mortars are 13.63%, 14.29% and 13.00%, respectively. These results indicate that the utilization of MS and WMS cause an increase in porosity. This may be attributable to the introduction of shell content with MS and WMS. MIP was also conducted to characterize the distribution of pore size at 28 d, and the results are shown in Figure 8. The curves illustrate that the volume of 10–100 nm fine capillary pores in the MS specimen was significantly the highest, followed by those in the WMS specimen and the RS specimen. This indicates that the utilization of MS and WMS could optimize the pore structure of mortars. On one hand, the chloride ions introduced by fine aggregate accelerate tricalcium aluminate (C₃A) hydrate by reacting with the cement clinker of C₃A to generate refractory chlorine aluminate hydration, such as Friedel’s salt, which can act as a filler in the pores of the concrete and improve its pore structure. On the other hand, chloride ions that react with Ca(OH)₂ and generate calcium chloride have low solubility in water, thereby further accelerating tricalcium silicate (C₃S) hydration to generate composite salt and increase the solid phase proportion in cement pastes [32,33]. In summary, the utilization of MS and WMS could increase the porosity of mortar; however, the pore structure is optimized.

Figure 7. Relationship between pore size and cumulative pore volume.
The utilization of MS and WMS could increase the porosity of mortars; however, the pore structure is optimized. The chloride ions introduced by fine aggregates can react with hydrates to form Friedel’s salt at the early ages, and the Friedel’s salt is stable throughout the whole curing period. The intensity of the endothermic peak with Friedel’s salt slightly increases with time, and the intensity of the endothermic peak with AFm increases significantly with time. The utilization of MS and WMS could increase the porosity of mortars. However, the pore structure is optimized, and the volume of fine capillary pores with sizes of 10–100 nm increases in the MS and WMS mortars.

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