Analysis of the Effect of Capillary Water Absorption on the Resistivity of Cementitious Materials

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Abstract: In a humid environment, the stray current generated by subway operation will corrode the underground pipe network and the internal steel structure of the track plate, which will seriously affect the service life of the subway track plate and increase the maintenance cost later. Groundwater in subway projects mainly enters the concrete interior through capillary action and affects the concrete resistivity, and there is a lack of research on the mechanism of groundwater effect on concrete resistance. In this study, the variation of cement mortar resistivity with capillary water absorption time for cement mortar with different amounts of mineral admixtures (fly ash, ground-granulated blast furnace slag, and silica fume) was measured by the four-electrode method, and the mechanism of the influence of the electrical properties of cementitious materials under the effect of capillary water absorption was analyzed based on the mercury-pressure method (MIP) and thermogravimetric method (TG-DTG). The results show that with the increase in capillary water absorption time, the change curve of cement mortar resistivity can be divided into two stages; in the first stage, capillary water absorption leads to gel pores and transition pores quickly connecting to capillary pores and other large pores to form a water-saturated conductive pathway, resulting in a rapid decrease in resistivity, when the gel pores and excessive pores have a greater impact on resistivity. The second stage is that of capillary water absorption, to a certain extent, after the specimen’s internal water upward development rate slows down; at this time, the formation speed of the conductive pathway decreases, resulting in the rate of change in resistivity decreasing and gradually stabilizing. The incorporation of silica fume can effectively improve the resistivity of cementitious materials under the action of capillary water absorption, in which the resistivity of specimens incorporated with 15% silica fume after 36 days of capillary water absorption is 10.39 times that of the reference group, which is mainly due to its lower porosity and a higher percentage of gel pores.

Keywords: electro-chemical corrosion; capillary water absorption; resistivity; mineral admixtures; cement mortar; pore structure

1. Introduction

Cement-based material is a typical porous material whose resistivity is closely related to its pore structure and pore water saturation [1–3]. In practical engineering, decreases in the resistivity of cementitious materials can lead to several problems, such as subway stray currents [4]. Studies have shown that the track insulation performance is excellent at the beginning of the metro opening [5], but with the dirty, wet, iron powder overlay or the aging of the surface of the operational insulation fasteners, the walking track current will leak into the surrounding soil and structures through the concrete roadbed, causing serious electrochemical corrosion of the main structure reinforcement and metal pipes along the line [6,7]. In addition, the main structure of the subway is often in a groundwater-rich environment, and the pore water saturation of the concrete roadbed rises rapidly under the invasion of moisture, and the resistivity decreases sharply, increasing the hazard of stray currents [8]; the subway, as an underground, hidden and complex project, is more...
difficult to renovate or repair [9]. Therefore, studying the preparation of highly insulating cementitious materials and their application in metro rail engineering is crucial.

There are various methods to improve the insulation (resistivity) of cementitious materials, of which the most common application is the incorporation of mineral admixtures. Research on mineral admixtures to improve the resistivity of cementitious materials has made some progress in recent years; Ehtesham et al. [10] found that the resistivity of concrete could be increased by a factor of 2.2 after replacing cement with a mass of 30% fly ash. Baweja et al. found that the resistivity of concrete after replacing cement with 25% fly ash equivalent mass underwent a large increase [11]. Bagheri et al. [12] found an eight-fold increase in 180d resistivity after replacing cement with 10% silica fume of equal quality. Dotto et al. [13] replaced cement with 6% and 12% silica fume of equal mass at 0.5 water-cement ratios, and found that the mortar replacement rate was increased by 2.5 and 5 times for 6% and 12% silica fume replacement, respectively. Yang et al. showed that the resistivity of concrete after replacing cement with 26% silica fume equivalent mass can be increased by 13.4 times and 17 times after 28 d and 60 d of curing, respectively [14]; Justnes et al. [15] found that calcined marl as a supplementary cementitious material was able to increase the resistivity of the mortar in a water-filled state. Liang, by comparing the effect of fly ash, slag, and partial high territory on the resistivity of cement mortar, found that the partial high territory has the best effect on the resistivity of cement mortar [13]. You found that the resistivity of concrete can be increased by 2.67 times after replacing cement with 15% silica fume of equal quality in experiment [16]. Cai et al. [17] found that electrical resistivity increased with the increase in the slag replacement ratio, since the addition of slag would consume more conductive ions. Li et al. [18] tested the resistivity of fly ash mixed in the early stage by a non-contacting electrical resistivity meter, and found that concrete mixed with 25–50% had high early stage resistivity. It is worth noting that most scholars currently test the resistivity of cementitious materials in a water-saturated state, but in actual working conditions, due to the specificity of the environment in which the subway is located, the pore water saturation of cementitious materials will fluctuate greatly, especially in rainy weather or groundwater-rich areas. Water mainly enters the interior of cementitious materials through capillary action so that its pore water saturation increases rapidly [19,20] and its resistivity decreases significantly, which is extremely unfavorable for the prevention and control of stray currents, and there are few reports on the changes in the resistivity of cementitious materials under different water-saturated states due to capillary water absorption.

Therefore, in this paper, three typical mineral admixtures are selected: fly ash, mineral powder, and silica fume, and changes in cement mortar resistivity with capillary water absorption time and different admixtures are measured by the four-electrode method. The influence mechanism is analyzed by combining microscopic testing techniques, and the obtained research results can provide a reference for the prevention and control of stray currents in metro projects.

2. Materials and Methods
2.1. Materials

The cementitious material adopts P.I 42.5 cement (C) produced by Fushun Aosier Technology Co., Ltd. (Fushun, China), first-grade fly ash (FA), S95 ground granulated blast furnace slag (SL), and silica fume (SF) produced by Henan Hengyuan New Materials Co. (Xinxiang, China). The chemical composition of the cementitious material and the results of particle size tests (average particle size $D_{50}$) are shown in Table 1. The fine aggregate is ordinary river sand (S) with a fineness modulus of 2.72; the mixing water is ordinary tap water (W).
Table 1. The chemical compositions of raw materials (calculated by mass fraction %).

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>SO₃</th>
<th>Na₂Oeq</th>
<th>TiO₂</th>
<th>f-CaO</th>
<th>D₅₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>20.58</td>
<td>4.97</td>
<td>3.76</td>
<td>63.57</td>
<td>2.29</td>
<td>2.00</td>
<td>0.53</td>
<td>-</td>
<td>0.75</td>
<td>17.763</td>
</tr>
<tr>
<td>FA</td>
<td>55.7</td>
<td>28.39</td>
<td>4.695</td>
<td>3.424</td>
<td>0.751</td>
<td>0.885</td>
<td>0.949</td>
<td>1.15</td>
<td>-</td>
<td>7.911</td>
</tr>
<tr>
<td>SL</td>
<td>30.48</td>
<td>15.46</td>
<td>0.322</td>
<td>37.45</td>
<td>8.12</td>
<td>2.36</td>
<td>0.46</td>
<td>1.16</td>
<td>-</td>
<td>11.895</td>
</tr>
<tr>
<td>SF</td>
<td>93.7</td>
<td>0.329</td>
<td>0.0957</td>
<td>0.478</td>
<td>0.248</td>
<td>1.35</td>
<td>0.893</td>
<td>0.017</td>
<td>-</td>
<td>14.860</td>
</tr>
</tbody>
</table>

2.2. Mixture Proportion Design

This test mainly considers the type and dosage of mineral admixtures and adopts a control variable method to design four groups of specimens; they are reference group (JZ group), fly ash group (FA group), ground-granulated blast furnace slag group (SL group), and silica fume (SF group), respectively. The water–binder ratio of the specimen was fixed at 0.40, and the comb–sand ratio was 1:2. The content of mineral admixture is the percentage of the mass of the admixture in the mass of cement, and the specific test mix design is shown in Table 2.

Table 2. Mix proportions of cement mortar.

<table>
<thead>
<tr>
<th></th>
<th>Cement</th>
<th>FA</th>
<th>SL</th>
<th>SF</th>
</tr>
</thead>
<tbody>
<tr>
<td>JZ</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>FA-1</td>
<td>95</td>
<td>5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>FA-2</td>
<td>90</td>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>FA-3</td>
<td>80</td>
<td>20</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>FA-4</td>
<td>70</td>
<td>30</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SL-1</td>
<td>95</td>
<td>-</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>SL-2</td>
<td>90</td>
<td>-</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>SL-3</td>
<td>80</td>
<td>-</td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td>SL-4</td>
<td>70</td>
<td>-</td>
<td>30</td>
<td>-</td>
</tr>
<tr>
<td>SF-1</td>
<td>95</td>
<td>-</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>SF-2</td>
<td>90</td>
<td>-</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>SF-3</td>
<td>80</td>
<td>-</td>
<td>-</td>
<td>20</td>
</tr>
</tbody>
</table>

2.3. Test Method

(1) Test material preparation: Test specimens of mortar strength and resistivity were made according to the Chinese standard: GB/T17671-2021 “Test Method for Cement mortar Strength (ISO Method)”. The size of cement mortar is 40 mm × 40 mm × 160 mm, and the strength test and resistivity test specimens are made, respectively. The electrical electrode of the resistivity test specimen is ordinary stainless steel mesh, and extends 20 mm out of the mortar surface for testing. The spacing between the mesh is 40 mm, and the distance between the two ends of the mesh is 20 mm from the end of the specimen. In the process of specimen pouring, four electrodes were inserted vertically into the bottom of the mold, and then the specimen was placed on the shaking table to vibrate and compact. To avoid water loss, the surface of the specimen was covered with a layer of plastic wrap immediately after the completion of vibration, and the specimen was demolded after being cured in the laboratory environment at 20 °C for 24 h, before being put into the saturated lime water solution at 20 ± 2 °C for curing to the corresponding age. The molded specimen is shown in Figure 1.

According to the mix ratio given in Table 2, six test pieces (three strength test pieces, and three resistivity test pieces) were made for each mixing ratio of cement mortar at the same time. The strength and resistivity test pieces of three strength test pieces and resistivity test pieces with the same ratio were tested. The average values of the three pieces were taken as the strength or resistivity test results of the test pieces under the mix ratio.
(2) Compressive strength test: The compressive strength of the cement mortar specimens of corresponding age was tested according to the Chinese standard: GB/T17671-2021 “Test Method for Cement mortar Strength (ISO Method)”.

(3) Resistivity test: At present, the commonly used methods of concrete resistance testing are the Wenner method [21], double-probe method [22], embedded four probe method [23], impedance spectroscopy [24], and ASTM C1760-12 method, etc. The four-electrode method is widely used because of its simple test method, uniform test electric field, and small error [21–23]. Therefore, this paper chooses the four-electrode method using ordinary stainless steel mesh as the electrode; a DC voltage of 24 V was used during the resistivity test. At the same time, to avoid the influence of temperature on the resistivity test [25,26], the whole test process was carried out in a laboratory environment of 20 °C.

(4) Capillary water absorption test: The capillary water absorption test was carried out according to ASTM C1585-13 standards. First, the 28 day aged mortar resistivity test specimen was removed from the saturated lime water solution, and the surface moisture of the specimen was dried with dust-free paper. The specimen was placed in a vacuum drying oven at 50 ± 2 °C, and the mass change was no more than 0.1% after 24 h. After that, silicone rubber and plastic film were used to seal all surfaces except the absorbent surface to ensure that capillary absorbent is only carried out on the absorbent surface [27], and to eliminate the influence of air humidity and carbonization, among which the absorbent surface is the opposite of the specimen-forming surface. After that, the specimen was placed at room temperature of 20 °C and stood for 1 d. After the temperature of the specimen remained constant, its mass (accurate to 0.01 g) was weighed and its resistivity was tested. Then, the specimen was placed in the water absorption device (as shown in Figure 2), and the depth of immersion was about 3 mm. Before testing, the specimen was first wiped with dust-free paper to remove any excess water from the suction surface, and then quickly weighed (±0.01 g). Its resistivity was then tested (control within 30 s to complete), and the specimen was placed in the suction device to continue the capillary suction test. The specific test time is shown in Table 3.

![Figure 1. Resistivity test specimen.](image1)

![Figure 2. Schematic diagram of capillary water absorption and resistivity testing of mortar specimens [28,29].](image2)
Table 3. Timing and tolerance of capillary water absorption quality tests.

<table>
<thead>
<tr>
<th>Time</th>
<th>60 s</th>
<th>5 min</th>
<th>10 min</th>
<th>20 min</th>
<th>30 min</th>
<th>60 min</th>
<th>Every Hour up to 6 h</th>
<th>12 h</th>
<th>24 h</th>
<th>Once a Day up to 36 Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tolerance</td>
<td>2 s</td>
<td>10 s</td>
<td>2 min</td>
<td>2 min</td>
<td>2 min</td>
<td>2 min</td>
<td>5 min</td>
<td>5 min</td>
<td>1 h</td>
<td>2 h</td>
</tr>
</tbody>
</table>

(5) TG: The cement water absorption test specimen at 28 d age was crushed into small pieces first. We took the pieces < 1.18 mm and immersed them in anhydrous alcohol for 7 days to terminate the hydration process, and then we put them in a vacuum oven for seven days. Finally, the specimens were ground into powder and 20 mg was selected for the TG test after passing through a 0.075 mm aperture sieve. The test temperature range was room temperature ~1000 °C, the test gas atmosphere was nitrogen, and the heating rate was 10 °C/min.

(6) MIP: Mortar was extracted from capillary water absorption test specimens of corresponding age for testing. The pore structure of the sample was tested by the automatic mercury injection instrument PoreMaster 33, produced by Konta company (Boynton Beach, FL, USA), and the pore size range was 5~106 nm.

3. Results and Discussion

3.1. Compressive Strength

Figure 3 shows the compressive strength test results of cement mortar after 28 d curing. It can be seen from the figure that compared with the specimens of the JZ group, the 28 d compressive strength of the specimens increased to different degrees after adding different amounts of mineral admixtures. The compressive strength of the FA group increased by 2.6%, 4.1%, 7.02%, and 8.3%, respectively. The compressive strength of the SL group increased by 5.2%, 6.89%, 7.72%, and 9.4%, respectively. The compressive strength of the SF group increased by 16.68%, 30.85%, and 45.81%, respectively, and the growing range increased with the increase in the admixture. This is because the admixtures can promote the secondary hydration reaction of the system and react with cement hydration products to generate more C-S-H gels. At the same time, the content of Ca(OH)₂ with low strength in the system is reduced, so the pore diameters of specimens in each group doped with admixtures are refined compared with those in the JZ group, and the structural system is more compact. This is evidenced in the Section 3.3 and 3.4 below. Among the three kinds of admixtures, SF has the best effect on enhancing strength, because SF has high chemical activity and can better promote the secondary hydration reaction of cement [30]. This led to a significant decrease in the porosity of the specimen along with the refinement of the pore size, resulting in a significant increase in strength. As shown in the Section 3.3, it can be seen that more gel pores and transition pores can lead to strength improvement in the case of similar porosity, and lower porosity has a significant effect on strength improvement at the point of large difference in porosity [31–33].

![Figure 3. 28 d compressive strength of cement mortar.](image-url)
3.2. Effect of Capillary Water Absorption on the Resistivity of Cement Mortar

Because in an underground environment, groundwater erosion on concrete through capillary action takes a long time, a longer capillary absorption test time of 36 d is chosen in this paper to restore the actual engineering situation as much as possible. Figure 4a,b show the resistivity of the cement mortar in the dry state and after 36 d of capillary water absorption, respectively. It can be seen in Figure 4a that in the dry state, the resistivity of the specimens in the JZ group is the highest, the resistivity of the specimens with admixture decreases to different degrees, and the resistivity of the specimens in the same group decreases with the increase of admixture. It can be seen in Figure 4b that after 36 d capillary water absorption, the resistivity of the specimens in the JZ group is the lowest, and the resistivity of the specimens doped with admixtures increases to different degrees. The resistivity of the specimens in the same group increases with the increase in the amount of admixture, and SF has the best effect on the resistivity of the specimens after improving water absorption. It can also be obtained from Figure 4 that after 36 d of capillary water absorption, the resistivity of specimens in the SF group decreases between 70% and 90%, while the resistivity of specimens in the other three groups decreases more than 90%, and the resistivity of specimens in the JZ group decreases the most, by 99.08%.

![Figure 4](image_url)

**Figure 4.** The resistivity of cement mortar: (a) Resistance in dry conditions; (b) Resistance after 36 d of capillary water absorption.

The above phenomenon is related to the influence of mineral admixtures on the pore structure of cement mortar. Cementitious material is a typical gas–solid–liquid three-phase composite, and its electrical conductivity is mainly determined by the solid phase formed by the aggregate and cementitious material, and the gas phase and liquid phase in the pores, of which the conductivity of the gas phase is the worst, and the conductivity of the solid phase is also poor; their electrical conductivity is negligible, so the liquid phase in the pores is a key factor in determining the electrical conductivity of cementitious materials [16]. In the dry state, the pores inside the specimens are almost free of water and are all gas phase, and their connectivity is poor. The number of pores in the JZ group specimens is larger and larger (as shown in the Section 3.3); thus, their resistivity is the largest, and after mixing with mineral admixtures, the pore size of the specimens is refined, the number of large pores is reduced, and the resistivity decreases. This phenomenon is more obvious with the increase in admixture, wherein the specimens mixed with SF have the lowest porosity; thus, their resistivity is the lowest. Under the effect of capillary absorption, the pores inside the specimen are partially connected by water, the liquid phase replaces part of the gas phase, the electrical conductivity is greatly enhanced, the resistivity drops rapidly, the internal tortuosity of the specimen in JZ group is worse than the other three groups, the difficulty of forming the conductive pathway is reduced, and the number is higher; thus, its resistivity after water absorption is the lowest after the addition of mineral...
admixtures, as is the tortuosity of the pores inside the specimen. After the addition of the mineral admixtures, the degree of tortuosity of the internal pores of the specimens increased, the difficulty of forming conductive pathways increased, the number decreased, and the resistivity increased compared with that of JZ group.

Figures 5–7 show the change curves of capillary water absorption and resistivity with time for cement mortar with different FA, SL, and SF contents, respectively. It can be seen from the figure that the changes in the capillary water absorption resistivity of each group of specimens show two stages of rapid decrease and slow decrease, and tend to be stable; in stage I, in the early stage of capillary water absorption, a saturated area appeared at the bottom of the specimen, forming a large number of conductive paths, and the resistivity decreased rapidly. In stage II, after capillary water absorption reaches a certain level, water diffuses to the unsaturated region on the upper part of the specimen. At this time, capillary water absorption has little influence on the pore connectivity of the specimen, and it is difficult to form more conductive channels, so the resistivity decreases slowly until it is stable [34]. (Figure 8 shows the cross-section of the specimen after 36 days of capillary water absorption).

![Figure 5](image_url)

**Figure 5.** Changes in water absorption and resistivity of cement mortar with different FA contents over time: (a) Macroscopic damage; (b) Partially enlarged drawing.

![Figure 6](image_url)

**Figure 6.** Changes in water absorption and resistivity of cement mortar with different SL contents over time: (a) Macroscopic damage; (b) Partially enlarged drawing.

In addition, by comparing Figures 5–7, it can be observed that after FA or SL incorporation, the capillary water absorption and resistivity of the specimens with water absorption time are similar to those of the JZ group, while the specimens with SF incorporation are different. The resistivity of the specimens in the SF group decreased relatively gently with the increase in capillary water absorption time. The stage I process was significantly shorter than that of the other three groups. The resistivity of the samples doped with 5%, 10%, and 20% SF in the dry state was 41.3%, 37.5%, and 35.7% of that of the JZ group, respectively. However, after 36 d capillary water absorption, the resistivity of the SF group was 3.69, 6.45, and 10.39 times higher than that of the JZ group, respectively. The resistivity
of specimens in the SF group was significantly higher than that in the FA group and SL group after capillary water absorption. The capillary water absorption mass (g) and $t^{1/2}$ (s$^{1/2}$) of each group were linearly fitted according to the capillary water absorption data measured in the previous 6 h, and the fitted equations and the capillary water absorption coefficient data of each group were obtained, as shown in Table 4. It can be seen that the capillary water absorption coefficient of each group decreased after the addition of mineral admixtures compared with the reference group. With the increase in mineral admixture, the secondary hydration effect causes the internal pore structure of the specimen to be refined continuously, the degree of tortuosity increases, the internal pore connectivity becomes more difficult, the capillary absorption coefficient decreases continuously, and the capillary absorption coefficient of the SF group is the smallest. This explains the relatively gentle change in the second stage of capillary absorption in the SF group, and with the increase in the mineral admixture substitution, the SF group, being due to higher reactivity. The porosity of the specimens was significantly reduced (as shown in the Section 3.3), and the number of internal conductive pathways decreased significantly compared to other groups. Finally, the resistivity changes during the water absorption process are more gentle compared to the other groups. To a certain extent, it can be considered that the larger the initial water absorption rate, the lower the resistivity after capillary water absorption.

![Figure 7](image7.png)

**Figure 7.** Changes in water absorption and resistivity of cement mortar with different SF contents over time: (a) Macroscopic damage; (b) Partially enlarged drawing.

![Figure 8](image8.png)

**Figure 8.** The capillary water distribution in the section of 1/2 length of the specimen (after 36 days of capillary water absorption).

Based on the above test results, the pore structure diagram of the cement mortar in the dry state and after capillary water absorption is given in Figure 9. In the dry state, the pore of the specimen is equivalent to the capacitance, which cuts off the conductive path, there is no connected pore inside the specimen, and the cement matrix is almost non-conductive, so the resistivity of the specimen is large. Under the action of capillary water absorption, the specimen can be divided into three areas according to the distribution of water inside the specimen: the saturated area, non-saturated area, and dry area. The bottom of the specimen is a saturated area, and the pores are connected by water to form a conductive path, which...
leads to a significant decrease in the resistivity of the specimen. However, the pores in the dry zone are hardly conductive.

### Table 4. Capillary water absorption coefficient fitting equation and parameters.

<table>
<thead>
<tr>
<th>Group</th>
<th>Equation</th>
<th>Correlation Coefficient</th>
<th>Capillary Absorption Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>JZ</td>
<td>$m = -0.0345 + 0.01984 t^{1/2}$</td>
<td>0.9976</td>
<td>0.01984</td>
</tr>
<tr>
<td>FA-1</td>
<td>$m = 0.00953 + 0.01644 t^{1/2}$</td>
<td>0.993</td>
<td>0.01644</td>
</tr>
<tr>
<td>FA-2</td>
<td>$m = -0.00631 + 0.01462 t^{1/2}$</td>
<td>0.999</td>
<td>0.01462</td>
</tr>
<tr>
<td>FA-3</td>
<td>$m = -0.0122 + 0.01267 t^{1/2}$</td>
<td>0.9917</td>
<td>0.01267</td>
</tr>
<tr>
<td>FA-4</td>
<td>$m = 0.01224 + 0.00992 t^{1/2}$</td>
<td>0.9956</td>
<td>0.00992</td>
</tr>
<tr>
<td>SL-1</td>
<td>$m = -0.00323 + 0.01568 t^{1/2}$</td>
<td>0.9957</td>
<td>0.01568</td>
</tr>
<tr>
<td>SL-2</td>
<td>$m = -0.00718 + 0.01402 t^{1/2}$</td>
<td>0.9987</td>
<td>0.01402</td>
</tr>
<tr>
<td>SL-3</td>
<td>$m = 0.03619 + 0.01105 t^{1/2}$</td>
<td>0.99551</td>
<td>0.01105</td>
</tr>
<tr>
<td>SL-4</td>
<td>$m = -0.00607 + 0.00983 t^{1/2}$</td>
<td>0.991</td>
<td>0.00983</td>
</tr>
<tr>
<td>SF-1</td>
<td>$m = 0.01867 + 0.00938 t^{1/2}$</td>
<td>0.9941</td>
<td>0.00938</td>
</tr>
<tr>
<td>SF-2</td>
<td>$m = -0.03766 + 0.00928 t^{1/2}$</td>
<td>0.9917</td>
<td>0.00928</td>
</tr>
<tr>
<td>SF-3</td>
<td>$m = 0.01172 + 0.0089 t^{1/2}$</td>
<td>0.99213</td>
<td>0.0089</td>
</tr>
</tbody>
</table>

![Figure 9. Diagram of a cement mortar opening pore: (a) Opening pore structure under dry conditions. (b) Opening pore structure under capillary water absorption.](image)

**3.3. Pore Structure Feature**

Figure 10 shows the MIP test results of the pore volume of the specimen, which can be divided into gel pore (5–10 nm), transition pore (10–100 nm), capillary pore (100–1000 nm), and macropore (>1000 nm) according to pore size [35].

It can be seen from Figure 10 that compared with the JZ group, the pore volumes of the specimens in the FA group and the SL group after 28 days of curing are not very different, while the number of gel pores and transition pores is significantly increased, and the number of capillary pores and macropores is significantly reduced. Combined with the analysis in the Section 3.4, this is because FA and SL have lower activity and a lesser secondary hydration reaction, so their pore volume is very much different from that of the JZ group. Due to its physical filling effect and certain secondary hydration reaction, it has a certain refinement effect on the pores. This increases the tortuous degree of pores in the specimen to a certain extent, so the number of conductive pathways formed in the specimen under the effect of capillary water absorption is reduced and the resistivity of the specimen after capillary water absorption is increased; this phenomenon is more obvious with the increase in the doping amount. Under the same doping amount, the specimen doped with FA is stronger than that doped with SL group due to its secondary hydration effect (as can be seen from the Section 3.4, under the same doping amount, 28 d Ca(OH)₂ in FA group is lower than that in SL group), which leads to more gel pores and transition pores in FA specimens compared with SL group, and a better effect of the refining pore
structure. Therefore, the overall resistivity of FA specimens after capillary absorption is higher than that of SL group. In addition, combined with the test results of the resistivity of the specimens in the JZ group, the FA group, and the SL group, it can be found that when there is little difference in the pore volume, the resistivity of the specimens in the dry state increases with the increase in the number of capillary pores and macropores. According to this phenomenon, it is speculated that capillary pores and macropores contribute more to the resistivity of the specimens in the dry state.

![Pore volume distribution of cement mortar.](image)

Figure 10. Pore volume distribution of cement mortar.

It can also be seen from Figure 10 that compared with the JZ group, the pore volume of the specimen in the SF group was reduced by more than half. This is mainly related to the higher activity of silica fume; the stronger secondary hydration leads to a significant reduction in its pore volume. which greatly reduced the number of conductive channels formed in the specimen under the action of capillary water absorption, and greatly improved the resistivity of the specimen after capillary water absorption. In addition, with the increase in SF content, the pore volume of the SF group specimen decreased, but the difference was not large. With the same pore volume, the increase in pore-specific surface area increases the degree of tortuosity of pores within the specimen [36], while the significant increase in the number of gel pores and the significant decrease in the number of transition pores, capillary pores, and macropores increases the comparative area of their internal pores, which results in a significant increase in the degree of tortuosity of pores within the specimen. A more substantial increase was observed in the resistivity of the specimen after capillary absorption under the dual influence of the reduction in pore volume and the increase in internal tortuosity.

### 3.4. Hydration Products

In order to make the test results more prominent, the samples of JZ group and the three samples with the largest admixture content (FA-4, SL-4, SF-3) were, respectively selected to analyze the hydration products. Figures 11 and 12 show the TG-DTG curve of cement paste. It can be seen from the figure that when the DTG curve has an endothermic peak, the TG curve has a relatively obvious mass loss. The position of the endothermic peak of the slurry is the same, and there are three peak intervals: 70–350 °C (dehydration and decomposition of hydration products such as C-S-H, Ettringite, and Monosulfate (AFM)), 350–470 °C (dehydration and decomposition of hydration products \( \text{Ca(OH)}_2 \)), and 600–730 °C (decomposition of carbonate) [37]. The content of chemically bound water and
Ca(OH)$_2$ in the slurry can be quantitatively analyzed based on the TG-DTG curve [38], and the specific method is as follows.

$$m(H_2O) = m_A + m_B + m_C \frac{M_{H_2O}}{M_{CO_2}} \tag{1}$$

$$m(Ca(OH)_2) = m_B \frac{M_{Ca(OH)_2}}{M_{H_2O}} + m_C \frac{M_{Ca(OH)_2}}{M_{CO_2}} \tag{2}$$

In the above equation, $m_A$, $m_B$, $m_C$ are the weight loss rate (%) of the sample in the range of 70–350 °C, 350–470 °C, and 600–730 °C, respectively; $m(H_2O)$ is the content of chemically bound water (%); $m(Ca(OH)_2)$ is the content of Ca(OH)$_2$ (%); $M$ is the relative molecular mass, and the relative molecular masses of H$_2$O, CO$_2$ and CaOH$_2$ are 18, 44 and 74, respectively.

![Figure 11. TG curve of cement mortar slurry.](image1)

![Figure 12. DTG curve of cement mortar slurry.](image2)

Figure 13 shows the calculated results of Ca(OH)$_2$ and the chemically bound water content of the sample. It can be seen from the figure that the content of Ca(OH)$_2$ in the four groups of samples is significantly different: JZ > SL-4 > FA-4 > SF-3. This well confirms the analysis in the Section 3.3, because the mineral admixture mixed with the cement hydration product (Ca(OH)$_2$)’s secondary hydration reaction, the consumption of Ca(OH)$_2$ content. As a result, the content of the mineral admixture mixed group Ca(OH)$_2$ is lower than in the JZ group. At the same time, the secondary hydration reaction and the filling effect of mineral admixtures together increased the number of gel pores or transition pores, reduced the number of large and capillary pores, and increased the tortuosity of pores,
so that the resistivity of the specimen after capillary absorption in the mineral admixture group was increased compared with that in the JZ group. The SF reaction activity was the highest among the three mineral admixtures, and the secondary hydration effect was the most significant, resulting in porosity of the SF group decreasing significantly. The percentage of gel pores and transition pores increased (as shown in Figure 10). In addition, the chemical binding water content of the sample with mineral admixtures decreased compared with that of the JZ group. This is the result of the comprehensive action of two factors. First, the content of cement clinker is reduced after cementing material replaces cement, resulting in a substantial reduction in the content of chemically combined water generated by cement clinker [39]. Second, compared with the JZ group, although the total amount of chemically combined water generated by cement clinker is greatly reduced after the addition of mineral admixture, the formation space of the cement clinker phase hydrate after the addition of mineral admixture is larger than that in the JZ group, and the surface of mineral admixture particles also provides a place for the non-uniform precipitation and generation of cement clinker hydration products, which promotes the hydration of the remaining cement clinker [40–42]. In addition, secondary hydration of mineral admixtures will also generate a portion of chemically combined water [43]. Combining the above two factors, the chemically combined water content of the mineral admixture group decreased compared with that of the JZ group, but there was little difference.

Figure 13. Content of chemically combined water and Ca(OH)$_2$ in cement mortar slurry.

4. Conclusions and Perspectives

4.1. Conclusions

(1) The secondary hydration of mineral admixture can increase the number of gel pores and transition pores in the specimen. The lower activity and certain filling effects of fly ash and SL can have a certain refining effect on the pore size. The silica fume can significantly reduce the porosity of the specimen and increase the proportion of gel pores and transition pores.

(2) In the dry state, capillary pores and large pores contribute to the resistivity; the more capillary pores and large pores in the specimen, the higher the resistivity, the highest resistivity was found in the dry state of JZ group cement mortar, and the resistivity of cement mortar mixed with mineral admixture had different degrees of decline.

(3) With the increase in the amount of mineral admixture and the increase in the number of gel pores and transition pores inside the specimen, the degree of curvature inside the specimen also increased, leading to a continuous decrease in the capillary water absorption coefficient of the specimen. The resistivity of the specimen after capillary water absorption increased with the decrease in the capillary water absorption coefficient. Among the three admixtures, the addition of silica fume has the best effect on improving the resistivity of cement mortar after 36 days of capillary water absorption, compared with the JZ group.
(4) With the increase in capillary water absorption time, the change curve of the resistivity of cement mortar can be divided into two stages: rapid decrease and slow decrease. It tends to be stable, while the resistivity of cement mortar with silica fume decreases relatively slowly with capillary water absorption. This is mainly due to the low porosity and high proportion of gel pores of the silica fume formation, which lead to a weakening of its water absorption capacity, a significant reduction in the number of conductive paths, and a slow change in resistivity after capillary water absorption.

(5) Under the action of capillary water absorption, the specimen can be divided into a saturated zone, an unsaturated zone, and a dry zone. The saturated zone causes the resistivity of the specimen to decrease greatly, while the unsaturated zone and dry zone have little effect on the decrease in the resistivity of the specimen.

(6) To improve the resistivity of cement-based materials after capillary water absorption, two aspects can be considered. One is to increase the number of gel pores (5–10 nm) and transition pores (10–100 nm) when the pore volume is not very different, because the contribution of gel pores to the resistivity after capillary water absorption is much higher than that of transition pores; the other is to greatly reduce the volume of pores. This is helpful for improving the resistivity of concrete elements in subways and reducing stray current corrosion.

4.2. Prospectives
Due to the complexity and diversity of the subway operating environment, there are often multiple factors acting together on concrete members in actual projects, and the current research is mainly focused on single-factor mechanism research. In future, studying the resistivity change mechanism of concrete members under multi-factor coupled environments is a possible research direction, and the evaluation of the durability performance of members under long-term current passage is also very important.

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