

Article

Effects of Various Corrosive Ions on Metakaolin Concrete

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Abstract: In order to study and verify if the three corrosive ions of SO_4^{2-} , Mg^{2+} , and Cl^- could promote or inhibit each other in concrete corrosion as time goes by, we take Metakaolin (MK) as the research object to explore the interaction mechanism among ions by testing the physical and mechanical properties, the ion content, the phase composition, and the microstructural changes of the MK concrete under the action of various ion combinations. The results show that during the initial and middle stages of the corrosion (40–80 days), SO_4^{2-} and Mg^{2+} are in reciprocal inhibition relation, Cl^- could inhibit the action of SO_4^{2-} , and Mg^{2+} could promote the diffusion of Cl^- . However, at the final stage of corrosion (120 days), SO_4^{2-} and Mg^{2+} could mutually promote each other, and both ions could promote the diffusion of Cl^- . Mg^{2+} could mainly produce magnesium hydroxide and M-S-H inside the concrete, SO_4^{2-} mainly generates the ettringite and gypsum, while Cl^- mainly produces Friedel salt and NaCl crystal.

Keywords: Metakaolin; complex ion; dry-wet alternation; microstructure; corrosion degradation



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1. Introduction

With the rapid development of the economy, large-scale infrastructure such as cross-sea bridges, expressways, and large-scale tunnels, have been increasing. However, concrete durability has always been a key problem to consider. External environmental factors propose formidable challenges to the reliability of large-scale infrastructure. Ions of Cl^- , SO_4^{2-} , Mg^{2+} , K^+ , and Na^+ exist in the northwest area or even in certain coastal areas of China [1,2]. In fact, Na^+ and K^+ have little effect on concrete properties [3], but Cl^- , Mg^{2+} , and SO_4^{2-} could be severely harmful [4,5]. The main damage of SO_4^{2-} to the concrete is the crystallized corrosion [6], such as conversion from thenardite crystals to mirabilite crystals [7], and the volume increase of ettringite crystal and gypsum crystal [8]. Both of the above could lead to a series of physical and chemical reactions inside the concrete, which could further induce concrete expansion and cracking [9–11]. The damage of Mg^{2+} is mainly represented by the weakening of mortar and aggregate on the surface of the concrete [12]. That is because Mg^{2+} generates magnetic $\text{Mg}(\text{OH})_2$ inside the concrete, which is features extremely low solubility. With the constant precipitation of $\text{Mg}(\text{OH})_2$, C-S-H cementing material keeps decomposing and generating non-cementitious M-S-H [13,14], which finally results in concrete adhesive performance reduction, or even loss [15,16]. On the other hand, Cl^- corrosion is the main reason causing the degradation of reinforced concrete [17]. To the Cl^- , it is the internal rebar instead of the concrete that is mainly eroded [18]. When the Cl^- reaches the critical corrosion concentration, it will induce rebar corrosion, thereby further damaging the concrete structure [19].

Besides, there are always the coupling effects of dry-wet alternation and salt corrosion in a sulfate environment, such as the high evaporation due to temperature differences in the saline soil of the northwest region and the tide-retardation alternation in the marine environment of China. Ions are not only physically erosive but also chemically erosive. Therefore, the damage caused by dry-wet alternation is much greater than totally or

semi-soaked concrete [20,21]. The fact is, multi-ion combination in a dry-wet alternation environment causes concrete damages more and more frequently. Reports say that in an environment containing SO_4^{2-} , Mg^{2+} could result in much more serious damage to the concrete [22–24], because the generated magnesium hydroxide would accelerate the production of gypsum crystal, making concrete cracking even worse. However, other studies prove that Mg^{2+} has a certain inhibitory effect on SO_4^{2-} corrosion [25,26] because the forming of an $\text{Mg}(\text{OH})_2$ layer is protective to the concrete [27]. For the interaction between Cl^- and SO_4^{2-} , Mas et al. [28] believed that the existence of SO_4^{2-} promotes the diffusion of Cl^- , and the concentration of SO_4^{2-} is the main factor causing such phenomenon, namely: the greater the SO_4^{2-} concentration, the faster the Cl^- diffusion. However, Chen et al. [29] held different ideas and believed that SO_4^{2-} can block the diffusion of Cl^- , because the increase of corrosion products inside the specimen would greatly reduce the porosity, thereby reducing the diffusion of the Cl^- . Stroh et al. [30] studied the interaction mechanisms of Cl^- and SO_4^{2-} and showed that Cl^- reacts with AFm prior to others to generate Friedel salt, and the forming of ettringite would lead to the decomposition of Friedel salt.

For this, there is still a lack of unified understanding about the interaction among the three ions of SO_4^{2-} , Cl^- , and Mg^{2+} . Most of the existing studies focused on the interaction of just two ions. Research on the interaction among the three ions is rarely seen. Besides, with the prolonging of the corrosion time, the increased corrosion products would definitely affect the interaction between ions. However, this variable of corrosion time is often ignored in most research. Moreover, replacing part of the cement with Metakaolin (MK), which is a new type of mineral admixture made of calcined kaolin, could not only greatly improve the durability and early-stage mechanical property of the concrete [31,32], but could also reduce the cement amount and protect the environment. In this case, the application of the above method has been attracting great attention in the marine concrete field [33,34], showing great value for study.

In this study, in order to verify if multiple types of ions could affect each other with the changes of corrosion time, we take the Metakaolin concrete as the test object and take NaCl solution, MgCl_2 solution, Na_2SO_4 solution, MgSO_4 solution, and $\text{MgSO}_4 + \text{NaCl}$ complex solution as the corrosion mediums, use clean water as the control group, and explore the physical property changes of the MK concrete in various corrosion medium, and its evolution information at the time of ion migration by the dry-wet alternation approach. Then, we further study the corrosion products and micro-morphology changing features of MK concrete under various ion combinations by X ray diffraction(XRD), thermo gravimetric analysis(TGA), Fourier spectrum analysis(FTIR), and scanning electron microscope(SEM), and analyze the affecting mechanism of multi-ion combinations on MK concrete as time goes by.

2. Test Overview

2.1. Test Materials

In this test, we utilized the PO42.5 Portland cement produced in Bagongshan of Huainan City, and the white-color Metakaolin with about 1.8 μm average particle size produced by Shanghai Lingdong Company. As for the cementing materials, please refer to Table 1 for their chemical compositions. For the aggregates, we used the 5–15 mm continuously graded limestone gravels as the coarse aggregate while using the medium sands from Huaihe River as the fine aggregate, for which, the fineness modulus was set at about 2.9. The Polycarboxylate-based superplasticizer produced by Shaanxi Qinfen Construction Materials Co., Ltd. (Nagqu, China) was used as the water reducer, which featured about 37% water reduction rate and 40% solid content in the liquid.

Table 1. Chemical Compositions of Cementing Materials in the Test(%).

Composition	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	Na ₂ O	MgO	SO ₃	P ₂ O ₅
Metakaolin	57.21	41.03	0.03	0.64	0.18	0.13	0.08	0.22	0.13
Cement	21.6	3.51	68.32	2.88	0.69	0.06	0.88	1.01	0.32

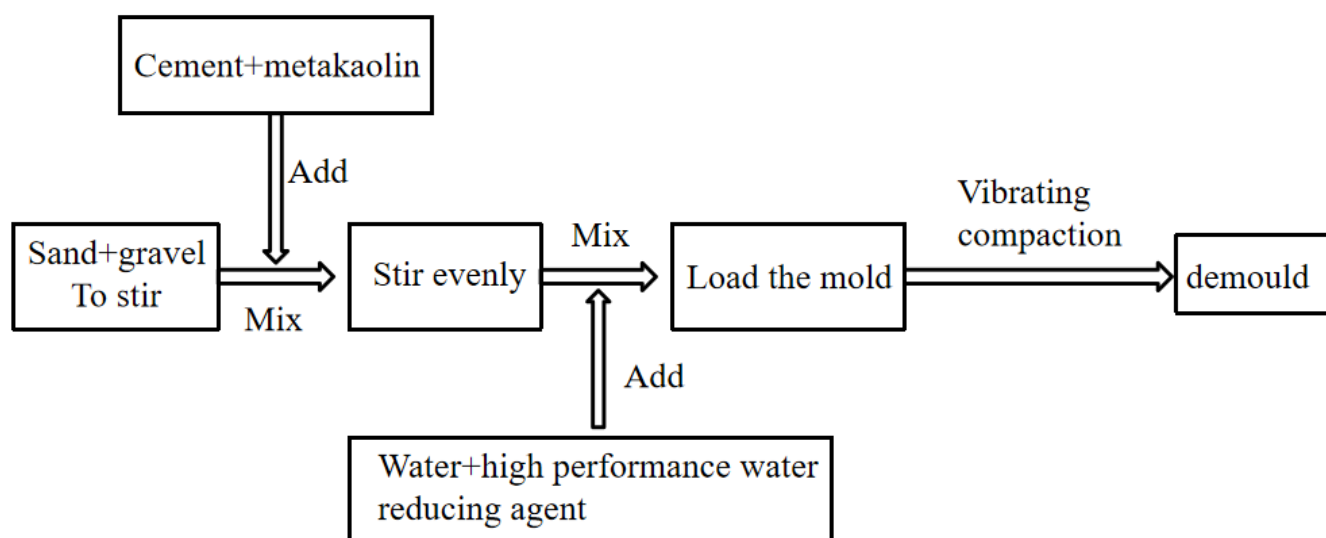
2.2. Testing Method

2.2.1. Test Block Production and Dry-Wet Alteration Operation

The concrete block made for the test was a non-standard block sized 100 mm × 100 mm × 100 mm. As for the MK concrete proportioning, please see Table 2. The process of making the concrete was: put the sand and gravel into a mixer and mix for over 1 min; then add cement and Metakaolin and mix for 2 min till the cementing material and the aggregates were mixed evenly; finally, mix the water reducer with the clean water, and put the mixture into the mixer to mix with other materials evenly. After finishing the mixing, put the mixture into the mold and then move the mold to the vibration table to have it vibrated and compacted (please refer to Figure 1 to see the vibration table). Then put the mold aside and wait for 24 h. After that, demold and put the concrete block in a standard curing room with (20 ± 2) °C temperature and 95% humidity for 28 days before carrying out the dry-wet alternation test. For an overview of making the concrete test block, please refer to Figure 1.

Table 2. Metakaolin (MK) Concrete Proportion Design (Kg/m³).

Component	Cement	Metakaolin	Sand	Aggregate	Water	Water Reducing Agent
Parameter	450	50	619	1101	180	4

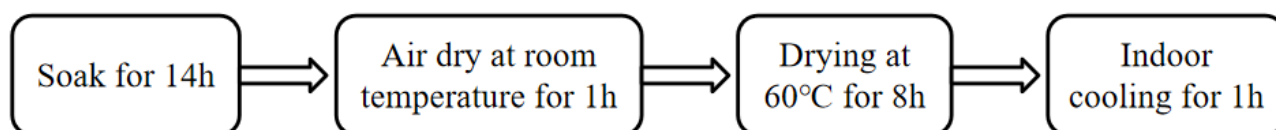
**Figure 1.** Flow chart of concrete production.

In order to simulate the physical and chemical corrosion in ocean and saline areas, based on the Standard for test methods of long-term performance and durability of ordinary concrete (GB/T50082-2009) and according to the chemical compositions of ions in soils and underground water in offshore and western areas of China, the 5% NaCl solution, 5% MgCl₂ solution, 5% Na₂SO₄ solution, 5% MgSO₄ solution, and 5%MgSO₄ + 5%NaCl complex solution were taken as the corrosion medium for the test, while clean water was used as the control group (for the types and specific ionic compositions of various solutions, please refer to Table 3).

Table 3. Types and Ionic Compositions of Corrosion Solutions.

Solution Type	Cl [−]	Mg ²⁺	SO ₄ ^{2−}
Clear water			
5% NaCl	+		
5% MgCl ₂	+	+	
5% Na ₂ SO ₄			+
5% MgSO ₄		+	+
5% MgSO ₄ + 5% NaCl	+	+	+

The durability test of concrete is performed by the dry-wet alternation (see Figure 2). The operation process of the test was: soak each group of concrete blocks in the solution for 14 h → dry at room temperature for 1 h → dry in a 60 °C dryer for 8 h → cool at room temperature for 1 h, accumulating 24 h as a cycle. See Figure 3 for test instrument. In order to maintain the concentration stability of all the solutions, we made and replaced them with a new solution every 10 days. The test was counted by the number of dry-wet alternations. In total it composed 4 cycles, which were respectively: 20 times, 40 times, 80 times, and 120 times. During each cycle (20 times, 40 times, 80 times, and 120 times), we took three parallel test blocks from each set of concrete to test their concrete compressive strength, mass, and dynamic elastic modulus (see Section 2.2.2). We then tested the ion content when it reached the 40th, 80th, and 120th time of alternation (see Section 2.2.3), and we tested the phase composition and conducted a microstructure test when it reached the 40th and 120th time of alternation (see Section 2.2.4). For the specific test flow chart, please refer to Figure 4.

**Figure 2.** Wet-dry cycle test flow.**(a)** Wet state**(b)** Dry state**Figure 3.** Dry-wet Alternation Test.

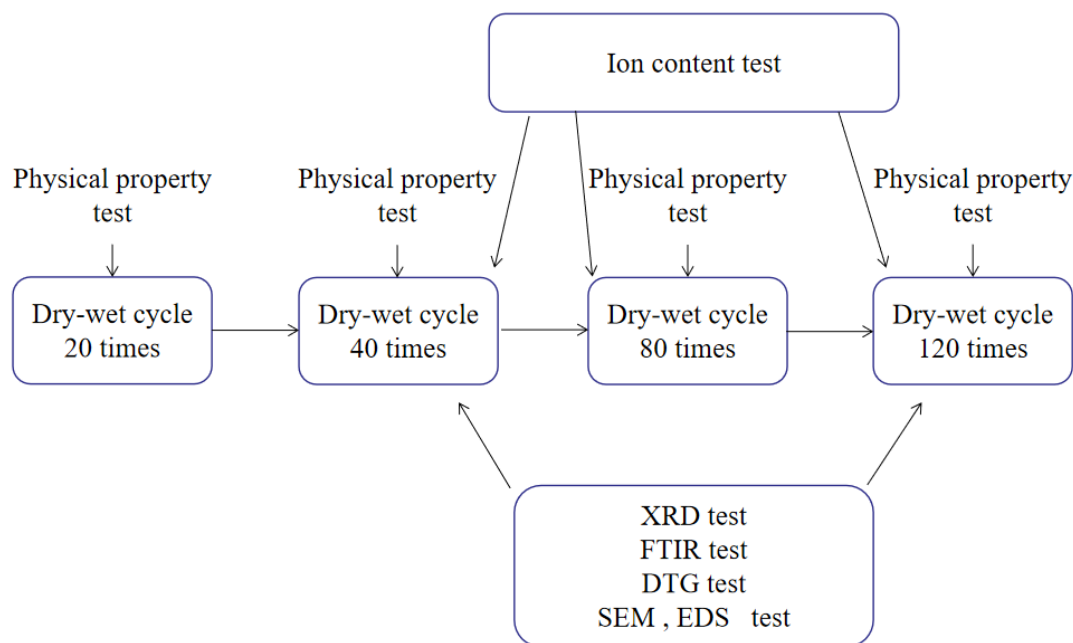


Figure 4. Specific test flow during the dry-wet cycle.

2.2.2. Physical Property Test

(1) Computing the Relative Compressive Strength

Compressive strength tests were carried out on all sets of test blocks in each cycle. For the uniaxial compression test performed on the concrete, the compression machine needed to maintain a stable and even speed with a loading rate of 3 mm/min. The uniaxial compression test was carried out based on the Standard for test method of mechanical properties on ordinary concrete (GB/T 50081-2002). Since the concrete block we adopted in the study was a non-standard block sized 100 mm × 100 mm × 100 mm, we needed to multiply the conversion factor of 0.95 in the computing. The relative compressive strength of the concrete should be calculated according to Equation (1)

$$F_{\alpha} = \frac{F_N}{F_0} \times 100\% \quad (1)$$

where F_{α} is the relative compressive strength, F_N is the compressive strength of concrete after n times of dry-wet alternation, F_0 is the MK concrete compressive strength that has been cured for 28 days but not corroded yet.

(2) Mass Change Rate

When we reached the specified cycles, we put the concrete test block in a dryer to dry it for 48 h and then cool it for 1 h. After that, we use the electronic balance (accurate to 0.1 g) to test the concrete block mass. The mass change rate of the concrete block was calculated according to Equation (2).

$$M_{\alpha} = \frac{M_N - M_0}{M_0} \times 100\% \quad (2)$$

where M_{α} is the mass change rate of the MK concrete block, M_N is the MK concrete block mass after n times of dry-wet alternations, and M_0 is the MK concrete block mass before corrosion.

(3) Relative dynamic elastic modulus

We used the ultrasonic detector to test the relative dynamic elastic modulus. For MK concrete, the relative dynamic elastic modulus was calculated according to Equation (3).

$$E_{rd} = \frac{t_0^2}{t_n^2} \times 100\% \quad (3)$$

where E_{rd} is the relative dynamic elastic modulus, t_0 is the initial ultrasonic time of concrete block before corrosion; t_n is the ultrasonic time of concrete block after different erosion periods.

2.2.3. Test of Concrete Ion Content

(1) Tests for Magnesium Ion and Chloride Ion Content

The ion chromatograph was produced by Shanghai Wufeng Instrument Company, which is equipped for the National Key Laboratory, was used for the test. Before starting the test, the core-drilling method was adopted to drill from the surface of the concrete block to its inside for every 4 mm distance in order to obtain the concrete powder, which was then dissolved in distilled water. After that, the above solution was put in the oscillator to shock for 1 h and then set aside to wait for 23 h, then filtered to obtain a clear liquid. Finally, the ion chromatograph was used to test the concentration of corrosive ions, and calculate the contents of magnesium ion and chloride ion inside the MK concrete at different depths according to Equation (4).

$$C\% = 100\% \times \frac{10^{-X}cV}{m} \quad (4)$$

where: $C\%$ is the mass percentage of magnesium ion or chloride ion; c is mole mass of testing solution ions; X is the mole concentration of testing ions; V is the solution volume, and; m is the sample mass of MK concrete powder.

(2) Test for Sulfate Ion Content

The test of sulfate ions was carried out on the basis of the Test Code for Hydraulic Concrete (SL352-2006) and the Methods for Chemical Analysis of Cement (GB/T 176-2008) by means of the barium sulfate precipitation method. The sulfate ions content inside the MK concrete was calculated according to Equation (5).

$$C\% = 100\% \frac{c \times (M_3 - M_2)}{M \times M_1} \quad (5)$$

where $C\%$ is the mass percentage of the sulfate ion; c is mole mass of testing ions; M is the mole mass of the barium sulfate; M_1 is the mass of the soaked concrete powder; M_2 is the mass of the crucible, and; M_3 is the total mass of the barium sulfate and the crucible.

2.2.4. Phase Composition and Microstructure Test

The D8-ADVANCED X-ray diffraction analyzer which is made by Brooke, Germany (scanning speed: $5^\circ/\text{min}$, scanning range: $5^\circ \sim 75^\circ$), NICOLET IS 50 Fourier infrared spectrometer which is made by American thermoelectric company (wavenumber region: $350 \sim 7800 \text{ cm}^{-1}$), and the STA449C thermal analyzer which is made by Germany naichi instrument company (thermogravimetric analysis range: $30 \sim 800^\circ\text{C}$), which were equipped for the key national lab, were used in this study to analyze the phase compositions of the MK concrete at the time when the concrete was corroded by various ions. Meanwhile, the S-3000N SEM and EDS which is made by Hitachi, Japan were applied to observe the post-processing slice under 5 KV accelerating voltage.

3. Test Results

3.1. Changes of Physical and Mechanical Properties

3.1.1. Degradation Law of Physical and Mechanical Properties of MK Concrete under Corrosion of SO_4^{2-}

For the SO_4^{2-} corrosion, as shown in Figure 5, all the three physical properties of concrete blocks in Na_2SO_4 solution showed the changing tendency of ascending stage $\rightarrow$ descending stage $\rightarrow$ rapid descending stage. However, the same properties in either MgSO_4 solution or $\text{MgSO}_4 + \text{NaCl}$ complex solution showed a tendency of ascending stage $\rightarrow$ descending stage. During the 0–20 days corrosion period in Na_2SO_4 solution, the compressive strength of the medium relative compressive strength of the concrete reached as high as 1.09. Since the cement was still at the hydration stage at this time, plus the secondary hydration and the micro-aggregate effect of MK, the physical properties of the MK concrete rose during this stage. Besides, the SO_4^{2-} corrosion at the beginning would generate a little amount of ettringite, which resulted in no obvious damage, instead, the proper amount of ettringite could fill in the apertures inside MK concrete to enhance the concrete block performance. However, as the reaction progressed, the amounts of ettringite and gypsum increased, which lead to the reduction of concrete mechanical properties. After reaching 120 cycles, the relative compressive strength reduced to only 0.92 while the relative dynamic elastic modulus reached only 0.91. When SO_4^{2-} and Mg^{2+} combined, the concrete blocks were corroded in MgSO_4 solution and $\text{MgSO}_4 + \text{NaCl}$ complex solution. At this time, the Mg^{2+} and the C-S-H inside the concrete co-generated non-cementitious M-S-H, which could soften the concrete surface and lead to the slow rising of physical and mechanical properties. On the 20th day of corrosion, the relative compressive strengths in the MgSO_4 solution and the $\text{MgSO}_4 + \text{NaCl}$ complex solution were only 1.02 and 1.04. With the increase of corrosion days, the C-S-H kept decalcifying and turning towards M-S-H, which lead to the peeling-off of mortar from the surface of the concrete, migration of corrosive ions from apertures, and acceleration of the gypsum and ettringite producing amount. This was the second round of damage to the concrete. As shown in Figure 5, the relative compressive strength of MK concrete in the MgSO_4 solution was only 0.80 while the relative dynamic elastic modulus was only 0.87, showing a much faster reduction than that in the Na_2SO_4 solution. In the $\text{MgSO}_4 + \text{NaCl}$ complex solution, the physical property of the concrete block reduced slower than that in the MgSO_4 solution. That was mainly because the Cl^- would react with SO_4^{2-} prior to the others to generate Friedel salt, thereby preventing the forming of ettringite [35]. The generated Friedel salt would fill up the apertures to further ease the invasion of SO_4^{2-} into the concrete channels. Therefore, Cl^- , to a certain extent, could inhibit the SO_4^{2-} corrosion. To sum up, the corrosion severity of solutions containing SO_4^{2-} are: $\text{MgSO}_4 > \text{MgSO}_4 + \text{NaCl} > \text{Na}_2\text{SO}_4$.

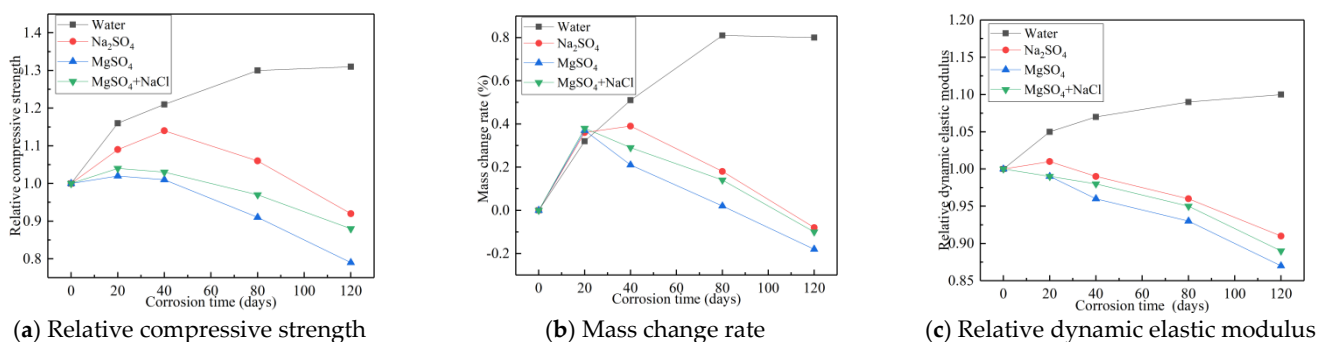


Figure 5. Influences of SO_4^{2-} on the Physical Properties of MK Concrete.

3.1.2. Degradation Law of Physical and Mechanical Properties of MK Concrete under Corrosion of Mg^{2+}

Figure 6 shows the corrosion of Mg^{2+} to the concrete. At the initial phase when the $MgCl_2$ solution eroded the concrete, the $MgCl_2$ could react with OH^- to generate the protective layer of magnesium hydroxide, thereby slowing down the diffusion of Mg^{2+} . At the same time, the Cl^- could also react with C_3A in the concrete to produce a certain amount of Friedel salt, making the concrete more compacted. Therefore the relative compressive strength reached 1.14 on the 20th day of the corrosion, achieving a 14% increase rate; and the mass then increased by 0.37% while the relative dynamic elastic modulus reached 1.015. With the increase of corrosion days, the physical performance of MK concrete in three types of solutions containing Mg^{2+} kept reducing. That was mainly because of the M-S-H forming, which was not only related to the decalcifying of C-S-H but also related to SiO_2 . As a matter of fact, MK concrete contains a huge amount of active SiO_2 , which can react with the hydrated SiO_2 to produce M-S-H gel, promoting the dissolution of $Mg(OH)_2$ and SiO_2 . The forming of the M-S-H gel will last till the amorphous SiO_2 or $Mg(OH)_2$ totally disappears. Therefore, Mg^{2+} is quite significant to the MK concrete. When reaching the 120th corrosion, if Mg^{2+} combined with Cl^- , the mass of the concrete block in the $MgCl_2$ solution would reduce by 0.02% while the relative dynamic elastic modulus was only 0.93. Since both the $MgSO_4$ solution and the $MgSO_4 + NaCl$ complex solution contained SO_4^{2-} , the secondary damage resulted by SO_4^{2-} and Mg^{2+} to MK concrete accelerated its physical performance reduction: the relative compressive strength in $MgSO_4$ solution reached only 0.81, the mass reduced by 0.18%, and the relative dynamic elastic modulus was only 0.87. However, in the $MgSO_4 + NaCl$ solution, the relative compressive strength reached only 0.86, the mass reduced by 0.10%, and the relative dynamic elastic modulus was only 0.89. The corrosion severity of the three solutions containing Mg^{2+} was $MgSO_4 > MgSO_4 + NaCl > MgCl_2$, which proved that Mg^{2+} could somewhat promote the SO_4^{2-} corrosion at the final corrosion stage.

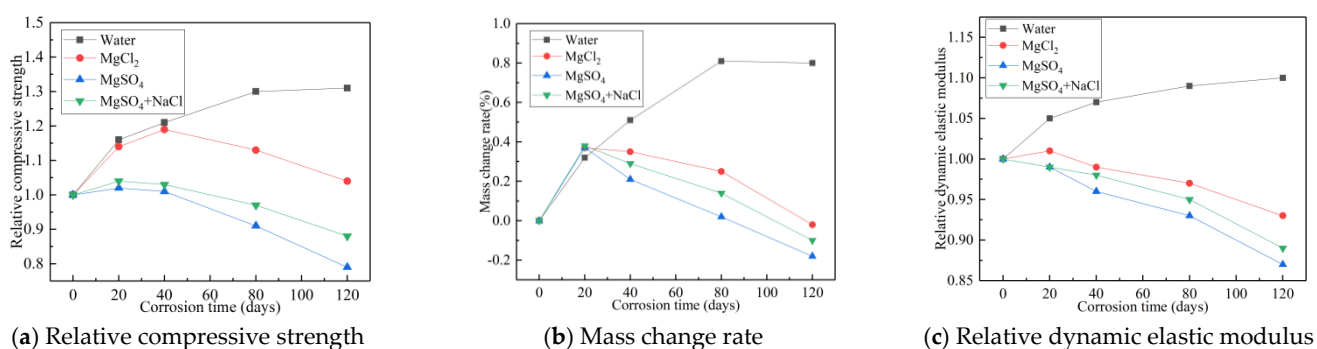


Figure 6. Influences of Mg^{2+} on Physical Properties of MK Concrete.

3.1.3. Degradation Law of Physical and Mechanical Properties of MK Concrete under Corrosion of Cl^-

The Cl^- corrosion effect on MK concrete is mainly manifested by chemical binding and physical adsorption effects in the concrete block. The former means that Cl^- reacts with C_3A inside the concrete to generate Friedel salt ($3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$), while the latter means that Cl^- is absorbed by C-S-H, C-A-S-H, or even M-S-H in the concrete. Since the MK is featured in high pozzolanic activity, besides the huge amount of contained active SiO_2 and Al_2O_3 , it can also greatly promote the generating of hydrated cementitious materials inside the concrete. Meanwhile, the A1-phase inside the MK concrete can also promote the generating of Friedel salt [36], please see Figure 7 During the 0–80 dry-wet alternation cycles under NaCl corrosion, the hydration effects of the cement and the generating of Friedel salt made the pores refined and compacted, which further lead to continuous increase of physical performance. When the alternation reached 80–120 cycles,

the mass and the compressive strength of the MK concrete dropped slowly. That was because the cement pH value reduced at the final stage of its hydration, decomposing part of the Friedel salt and releasing Cl^- again to form free Cl^- . When the dry-wet alternation reached 120 cycles, the relative compressive strength of the MK concrete in NaCl solution reached 1.25, and its mass increased by 0.78% while its relative dynamic elastic modulus reached 1.09. It could be determined from the comparison of the physical property changes of concrete in clean water that Cl^- itself has almost no corrosion effect on MK concrete. However, when MK concrete is corroded by the MgCl_2 solution, there were plenty of non-cementitious M-S-H results in the peeling-off of cement and aggregate, leading to the generation and expansion of pores. Therefore, the physical property of MK concrete in MgCl_2 solution were lower than that in the NaCl solution. If all the Cl^- , Mg^{2+} , and SO_4^{2-} invaded the concrete, the physical properties of the MK concrete would further reduce. The appearance of lots of corrosion products, such as M-S-H, ettringite, and gypsum, resulted in the expansion and cracking of the concrete, which further reduced the physical property greatly. Therefore, the corrosion severity of the three types of corrosive solutions containing Cl^- were: $\text{MgSO}_4 + \text{NaCl} > \text{MgCl}_2 > \text{NaCl} = \text{Clean Water}$.

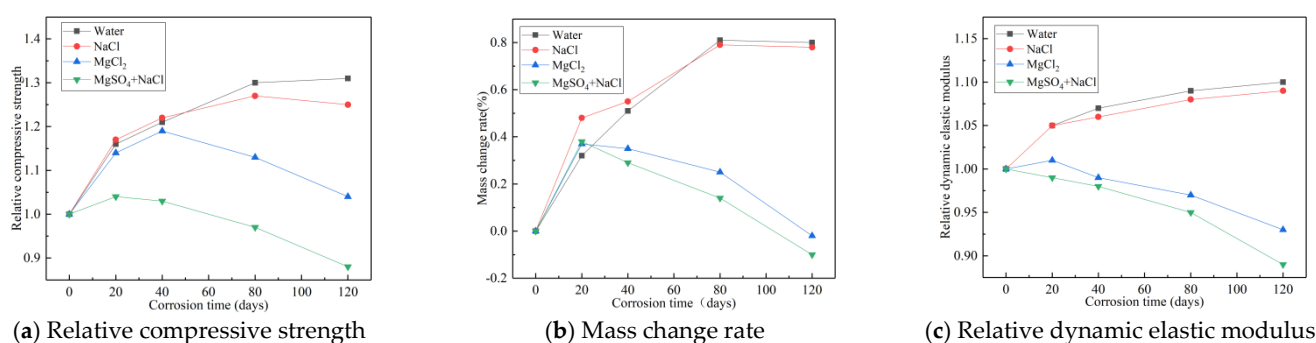


Figure 7. Influences of Cl^- on Physical Properties of MK Concrete.

3.2. Analysis of Ion Content

For SO_4^{2-} (As shown in Figure 8), when MK concrete was corroded by separated SO_4^{2-} in Na_2SO_4 solution, the ion content enhanced with the increase of corrosion time, but decreased with the deepening of corrosion depth. Since MK concrete has a certain amount of pores on the surface, various ions in the corrosive solution gathered together on the concrete surface and diffuse towards the inner side of the MK concrete due to the concentration gradient effects. However, during the diffusion process, lots of free SO_4^{2-} reacted inside the MK concrete and generated corrosion products of ettringite. In this case, the ion concentration gradient dropped sharply. Moreover, with the deepening of the corrosion, pore tortuosity increased while pore saturation reduced, which resulted in the increase of diffusion resistance and ion content reduction. It could be seen from the comparison between the Na_2SO_4 solution and MgSO_4 solution that when the dry-wet alternation reached 40 cycles if, at the same depth inside the concrete, the SO_4^{2-} contents of concrete blocks in MgSO_4 solution were all lower than those in the Na_2SO_4 solution. In fact, the maximum SO_4^{2-} content in the Na_2SO_4 solution reached 0.55% while the same data in the MgSO_4 solution was only 0.45%. This was mainly due to the generation of $\text{Mg}(\text{OH})_2$, which blocks the diffusion of SO_4^{2-} . When the dry-wet alternation reached 80–120 cycles, the maximum SO_4^{2-} contents of the concrete in the Na_2SO_4 solution increased from 0.92% to 1.14%, while the same data in the MgSO_4 solution increased from 0.96% to 1.20%. At this time, the SO_4^{2-} contents of MK concrete in the MgSO_4 solution gradually exceeded the data in the Na_2SO_4 solution. That was because, on the one hand, the increase of M-S-H and the expansion of $\text{Mg}(\text{OH})_2$ and ettringite made the expansion force greater than the tensile strength of the substrate and generated new cracks. On the other hand, $\text{Mg}(\text{OH})_2$ was formed prior to the gypsum, so when the corrosion times reached 40, the forming of gypsum in Na_2SO_4 was faster than in MgSO_4 . With the corrosion time increasing, the

continuous accumulation of gypsum turned lots of free SO_4^{2-} to combined SO_4^{2-} and clogged the pores. This led to an increase of SO_4^{2-} diffusion resistance and content reduction. For the $\text{MgSO}_4 + \text{NaCl}$ complex solution, due to the inhibiting effect of Cl^- to SO_4^{2-} , when alternation reached 40–80 cycles, the SO_4^{2-} contents of the concrete blocks in the complex solution were all lower than in Na_2SO_4 and MgSO_4 . When 120 cycles were reached, Mg^{2+} showed comparative severe damage to the MK concrete. At this time, the maximum SO_4^{2-} content in the complex solution reached as high as 1.19%, while the same data in the Na_2SO_4 solution was only 1.14%. This indicates that the SO_4^{2-} content in the complex solution started to exceed the content in the Na_2SO_4 solution from this moment.

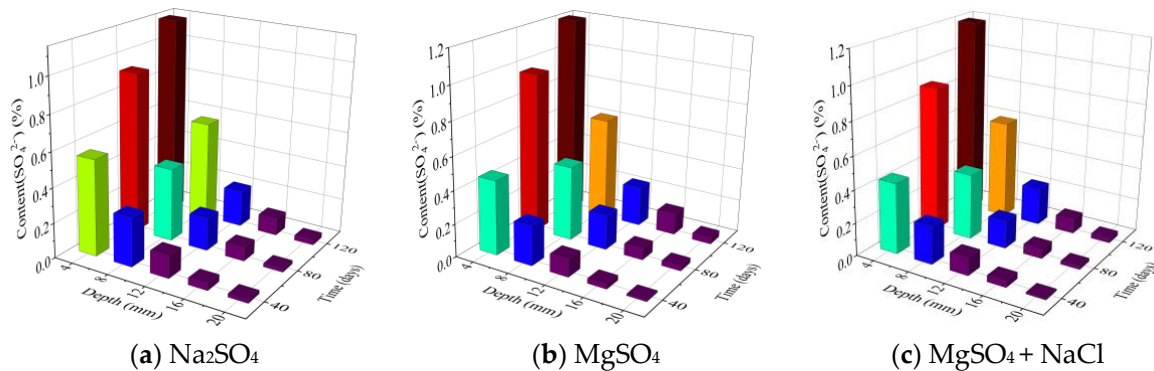


Figure 8. SO_4^{2-} Content in MK Concrete.

For Mg^{2+} , as shown in Figure 9, its distribution laws were the same as those of SO_4^{2-} : the ion content enhanced with the increase of corrosion time but decreased with the deepening of corrosion depth. After reaching 40–80 cycles of alternation, it could be observed that Mg^{2+} content was high at 0 mm–4 mm. The changes became more obvious with the increase of the cycles. However, the Mg^{2+} content decreased rapidly with the deepening of the corrosion and turned to reach internal stability. That was mainly because the Mg^{2+} has low mobility in a high pH value environment [37]. When reaching 120 cycles, the pH inside the concrete block greatly reduced, which resulted in severe concrete damage, and large cracks and pores. At this time, besides the increase of Mg^{2+} content on the surface, the content inside also increased sharply. According to the comparison among MgCl_2 , MgSO_4 , and $\text{MgSO}_4 + \text{NaCl}$, as shown in Figure 6, during the period of 40–80 cycles, the Mg^{2+} content in MgCl_2 reached the maximum, rising from 0.54% to 0.65%. In the MgSO_4 solution, the data rose from 0.50% to 0.61%. In the $\text{MgSO}_4 + \text{NaCl}$ solution, the data rose from 0.52% to 0.64%. Since there was no impact by fillers such as ettringite, the Mg^{2+} content in MgCl_2 was higher than in the other two solutions. Therefore, at the initial and middle stages of the concrete corrosion process (40–80 times), SO_4^{2-} slows down the Mg^{2+} diffusion to a certain extent; when the corrosion times reached 120, the contents of Mg^{2+} in various solutions were: $\text{MgSO}_4 > \text{MgSO}_4 + \text{NaCl} > \text{MgCl}_2$. That was because a great amount of gypsum can be formed in MK concrete when it is soaked in corrosive solutions containing SO_4^{2-} , which accelerates the pH reduction and promotes the ionic mobility of Mg^{2+} . So in the final stage of corrosion (120 times), the SO_4^{2-} could promote the Mg^{2+} penetration.

For Cl^- content, as shown in Figure 10, during the dry-wet alternation from the 80th day to the 120th day, Cl^- increased more than either SO_4^{2-} or Mg^{2+} . The test showed that in the three types of solutions, the maximum increase of Cl^- appeared in the $\text{MgSO}_4 + \text{NaCl}$ complex solution, which increased from 0.38% on the 80th day to 0.71% on the 120th day, achieving an 86.8% increase rate; the maximum increase of SO_4^{2-} was 35.22% while the data of the Mg^{2+} reached 29.51%. This was because in the final stage of corrosion, due to the reduced pH value in the concrete, the Friedel salt decomposed into free Cl^- , so that the Cl^- contents was increased obviously at this time. It could be found from the comparison between the MgCl_2 solution and NaCl solution that the maximum Cl^- contents of the

MK in the MgCl_2 solution increased from 0.38% to 0.67%, while the same data in NaCl increased from 0.29% to 0.61%. The content of Cl^- in the MgCl_2 solution was greater than that in the NaCl solution. On one hand, Mg^{2+} can react with the hydroxyl to reduce the pH value of the solution inside the apertures and accelerate the Cl^- penetration. On the other hand, the Metakaolin itself has lots of active SiO_2 and a high pozzolanic effect producing a huge amount of C-S-H during the hydration process. Therefore, the decalcification of C-S-H and the reaction between SiO_2 with Mg^{2+} and hydroxyl produced plenty of M-S-H, which could greatly improve the physical absorption capability, reduce combined ions that can participate in the reaction and produce Friedel salt, and promote the diffusion of free ions. Therefore, Mg^{2+} could promote the diffusion of Cl^- to some extent. When the MK concrete was soaked in the $\text{MgSO}_4 + \text{NaCl}$ complex solution, it could be seen that the Cl^- content at the 40th time of alternation was always lower than that in the MgCl_2 solution. That was because the ettringite formed by SO_4^{2-} at the initial stage made the internal structure of MK concrete compacted, which further slowed down the invasion of Cl^- ions. However, with the increase of corrosion time, during the 80th–120th cycles, the pores and cracks inside the block increased, which accelerated the penetration of Cl^- . At this time, the Cl^- content reached the highest level in the $\text{MgSO}_4 + \text{NaCl}$ complex solution.

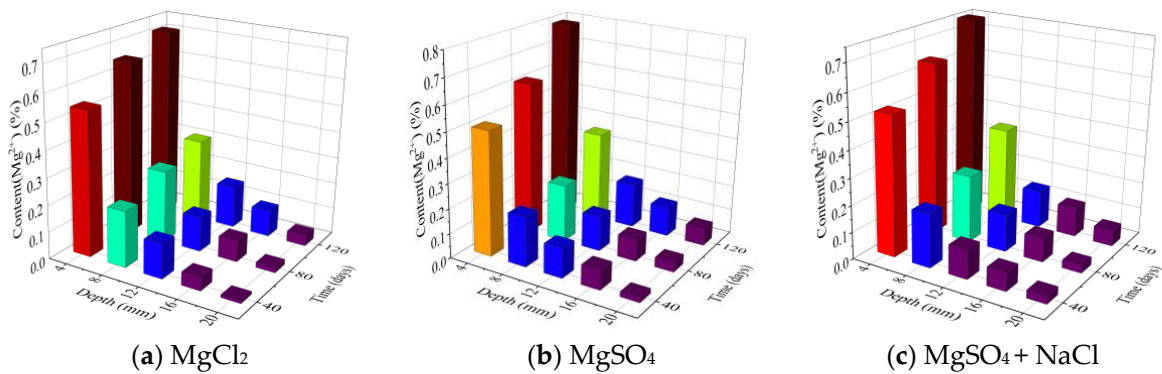


Figure 9. Mg^{2+} Content in MK Concrete.

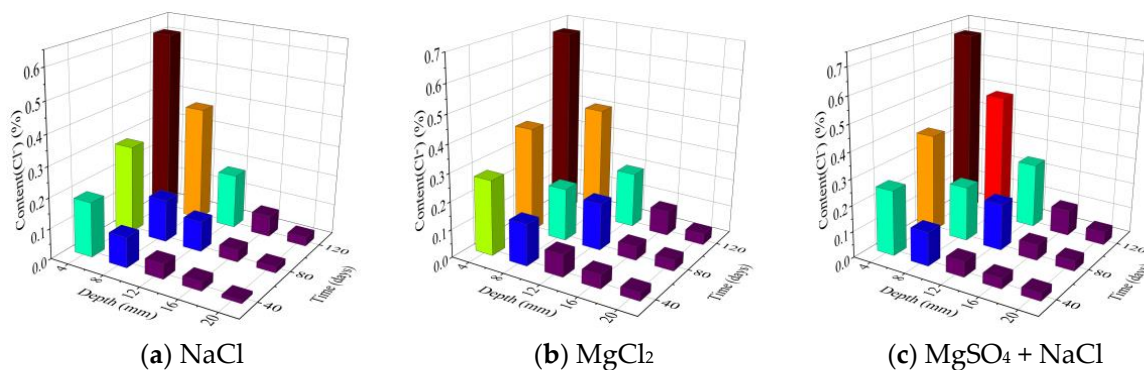


Figure 10. Cl^- Content in MK Concrete.

3.3. Phase Composition Analysis

3.3.1. X-ray Diffraction Analysis

Figures 11 and 12 are the XRD diffraction diagram when MK concrete accepts the corrosion of various solutions. In clean water, the phase composition of MK concrete mainly included quartz, quartz, calcite, ettringite, and $\text{Ca}(\text{OH})_2$. The largest diffraction peak in the figure is quartz, which, similar to calcite, is the aggregate of the concrete.

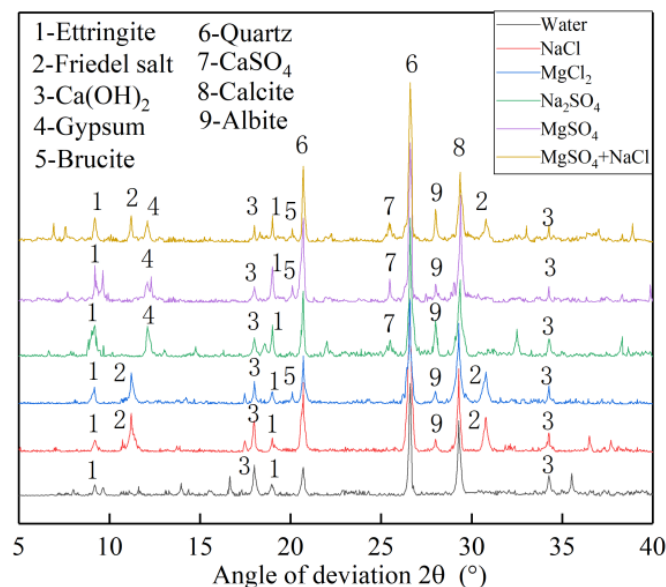


Figure 11. XRD diagram of 30 dry-wet cycles.

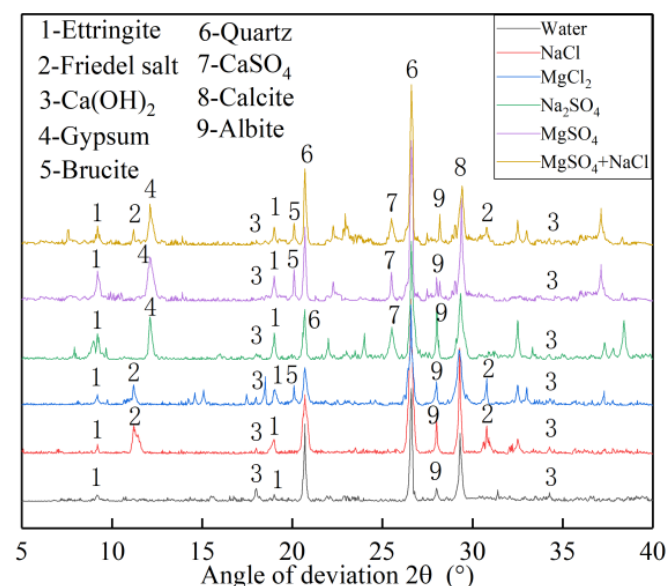
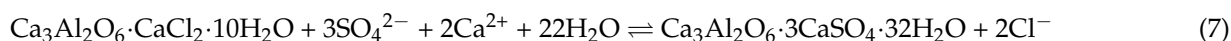
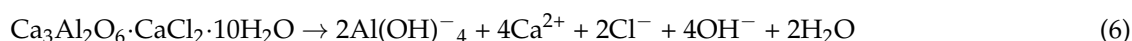


Figure 12. XRD diagram of 120 dry-wet cycles.

When reaching the 40th dry-wet alternation cycles, Ca(OH)_2 diffraction showed comparatively low peaks in various solutions. Since the Metakaolin contains Al_2O_3 , it can rapidly react with the CH produced by cement hydration, which reduced the pH of the hydration system. Besides, the forming of ettringite requires lots of Ca(OH)_2 , so that the three solutions containing SO_4^{2-} (Na_2SO_4 , MgSO_4 , $\text{MgSO}_4 + \text{NaCl}$) showed obviously less Ca(OH)_2 diffraction peaks than other corrosive solutions. Moreover, the ettringite diffraction peaks enhanced significantly and were accompanied by gypsum diffraction peaks. Since the Cl^- was featured in smaller volume and faster diffusion speed than SO_4^{2-} , it reacted with the aluminum phase prior to SO_4^{2-} , and generated Friedel salt which blocked the forming of AFt. Therefore, the ettringite diffraction peak of the $\text{MgSO}_4 + \text{NaCl}$ complex solution was lower than that of the MgSO_4 solution and Na_2SO_4 solution. For the gypsum diffraction peak, it can be seen from Figure 11 that since the Mg(OH)_2 would be produced before gypsum during the early stage of corrosion, the magnesium hydroxide layer inhibited the invasion of SO_4^{2-} to a certain extent, which further proves that Mg^{2+} has a certain inhibitory effect to SO_4^{2-} invasion at the early

stage of corrosion. Therefore, the diffraction peak of gypsum in Na_2SO_4 solution was greater than that in the MgSO_4 solution with $\text{MgSO}_4 + \text{NaCl}$ solution. For the corrosion solutions containing Cl^- , the Friedel diffraction peaks that appeared in NaCl solution, MgCl_2 solution, and $\text{MgSO}_4 + \text{NaCl}$ solution were different sizes. Cl^- reacted with C_3A to produce Friedel salt during the cement hydration process. The bicarbonate could also be converted to Friedel salt in the environment containing chloride [38]. Compared to the NaCl solution, the ettringite produced by SO_4^{2-} , and $\text{Mg}(\text{OH})_2$ and M-S-H produced by Mg^{2+} could inhibit the forming of Friedel salts to some extent. Therefore, it could be seen from the figure that the diffraction peak sizes of Friedel salts were: $\text{NaCl} > \text{MgCl} > \text{MgSO}_4 + \text{NaCl}$. According to that mentioned above, Mg^{2+} could promote Cl^- diffusion. However, only the chemical combined ions could participate in the formation of Friedel salt, further proving that it is the free Cl^- diffusion that the Mg^{2+} promotes [39].

When reaching 120 cycles of dry-wet alternation, the diffraction peak of the albite increased slightly. Since the albite is produced by N-A-S-H through bound water losing [40], the diffraction peak of $\text{Ca}(\text{OH})_2$ gradually disappeared. The ettringite diffraction peak in solutions containing SO_4^{2-} was higher than in other solutions. For the Na_2SO_4 solution, it could be seen that the diffraction peaks of CaSO_4 and gypsum gradually enhanced, while the peak of ettringite weakened. The reduction of pH lead to ettringite decomposition, accelerated the forming of CaSO_4 , and begun the conversion into gypsum. For the MgSO_4 solution and $\text{MgSO}_4 + \text{NaCl}$ complex solution, not only the gypsum and CaSO_4 diffraction peaks enhanced, but also the $\text{Mg}(\text{OH})_2$ diffraction peaks were improved. At this time, the pH reduction inside the concrete block inhibited the secondary forming of ettringite. The decalcification of the hydrated ettringite and the C-S-H made the contents of M-S-H and CaSO_4 increase. The ettringite diffraction of the two types of solutions was both lower than that of the Na_2SO_4 . However, the diffraction peak of the gypsum exceeded the Na_2SO_4 . For the corrosive solutions containing Cl^- , it could be seen that the diffraction peaks of the Friedel salt kept reducing. At the final stage of the corrosion, the Friedel salt in the environment became unstable and hydrolyzed. As for the reaction formula, please see Equation (6). Moreover, it can be seen from Figure 12 that the Friedel salt diffraction peak in $\text{MgSO}_4 + \text{NaCl}$ complex solution was lower than that in the NaCl solution and MgCl_2 solution. This may possibly be due to the mutual transformation of SO_4^{2-} and Cl^- [41,42]. It is a factor of ion concentration that when Cl^- concentration was comparatively higher, the ettringite would convert into Friedel, but if the SO_4^{2-} concentration was higher, the Friedel salt would decompose into ettringite, see Equation (7).

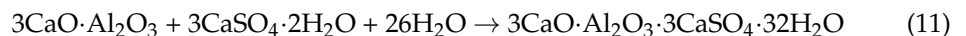
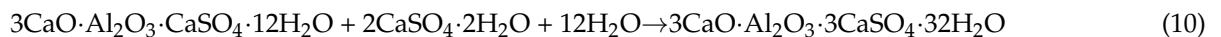
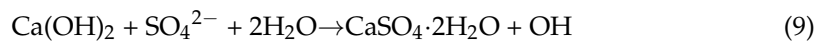
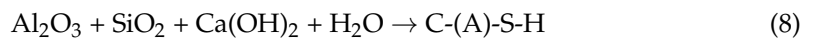


3.3.2. TG-DTG Thermal Analysis

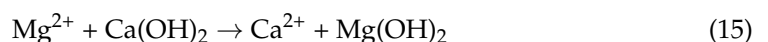
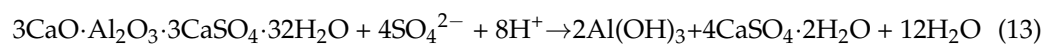
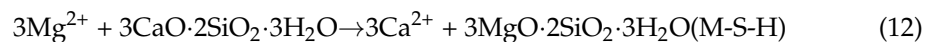
Figures 13–15 are DTG diagrams of MK concrete in various corrosive solutions, through which, we can make the comparison on the amount of not only corrosion products but also the hydration products. With the increase of dry-wet alternation, different corrosive solutions show different endothermic peaks on MK concrete.

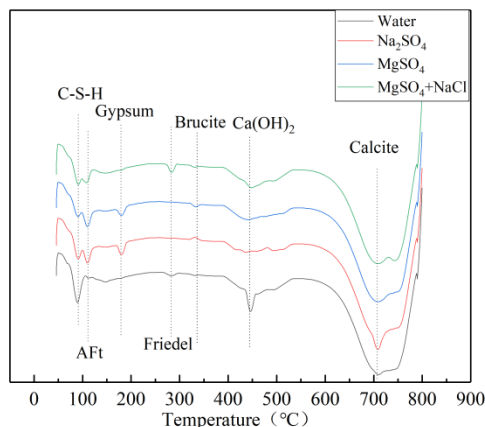
When the dry-wet alternation reached 120 cycles, the C-S-H dehydration endothermic peak appeared in the temperature range between 85–92 °C. The dehydration endothermic peak of the MK concrete soaked in clean water was much more obvious than that in other corrosive solutions. Without the corrosion of corrosive solutions, the C-S-H content inside the concrete increased greatly with the secondary hydration effects of the Metakaolin, see Equation (8). The endothermic characteristic peak of the ettringite appeared during the temperature range of 95–110 °C. The endothermic peak of $\text{Ca}(\text{OH})_2$ appeared during the temperature range of 412–500 °C. This proves that the $\text{Ca}(\text{OH})_2$ was disappearing at this time, see Equation (8) and (9). Besides, it could be seen that the ettringite endothermic peak of concrete in corrosive solutions containing SO_4^{2-} was much higher than that in other

types of corrosive solutions. This indicates that the corrosive ion of SO_4^{2-} could greatly promote the production of ettringite (Chemical Equation (9)–(11)). Meanwhile, Figure 13a shows that the gypsum had a weak endothermic peak. This was because the dihydrate gypsum loses crystal water and becomes the semi-hydrated gypsum. For the corrosive solution containing Cl^- , the dehydration endothermic peak of the Friedel salt appeared during the temperature range of 270 °C–300 °C. It can be seen from Figure 15a that the peak of the Friedel salt in the $\text{MgSO}_4 + \text{NaCl}$ complex solution was lower than that in other solutions containing Cl^- . The reason for causing the above phenomenon was, on one hand, the filling of ettringite, and on the other hand, it might be that the C-S-H could absorb more SO_4^{2-} in an environment containing both SO_4^{2-} and Cl^- [43]. Moreover, in the $\text{MgSO}_4 + \text{NaCl}$ complex solution, SO_4^{2-} could also reduce the binding of chloride, thereby converting Afm to Aft [44], and slowing down the formation of Friedel salt indirectly. Figure 14a shows that the dehydroxylation endothermic peak of Mg^{2+} appeared at around 330 °C, while the endothermic characteristic peak of the calcite (all calcite are from the concrete aggregate) appeared during the temperature range of 650 °C–720 °C [45].

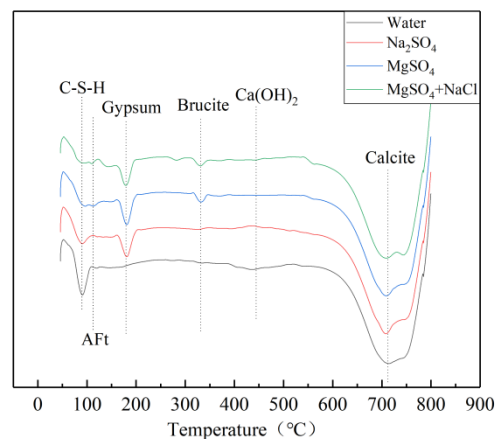


When the dry-wet alternation reached 120 cycles, as shown in Figure 13b: for the corrosive solution with SO_4^{2-} , it could be seen that the endothermic peaks at both 89 °C of the umber of Na_2SO_4 solution and 108 °C were significantly weakened than those in other corrosive solutions. Correspondingly, the ettringite and C-S-H contents were reduced. Through the above XRD test and ion content test, it could be seen that the reduction of the C-S-H was mainly because the C-S-H decomposition produced lots of M-S-H, see Equation (12). The reason why the ettringite content was reduced was because of the reduction of the pH value made the ettringite decompose, thereby accelerating the generation of gypsum, see Equation (13) and Equation (14). Besides, Figure 14b shows that the $\text{Ca}(\text{OH})_2$ diffraction peak at 445 °C reduced greatly, accompanied by an increase in hydration products. This corresponded to the magnesium hydroxide at 330 °C. The decomposition endothermic peak of the magnesium hydroxide at this time obviously increased more than that at the 40th cycle of the dry-wet alternation. This means that the corrosive solution containing Mg^{2+} continuously consumed $\text{Ca}(\text{OH})_2$ to produce $\text{Mg}(\text{OH})_2$ sediment during the circulation process, see Equation (15). For the solution containing Cl^- , due to the dehydration of Friedel salt, the Friedel endothermic peaks only weakened greatly at 28 °C.

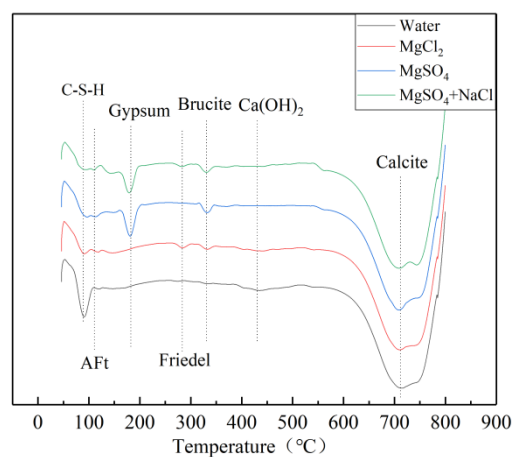
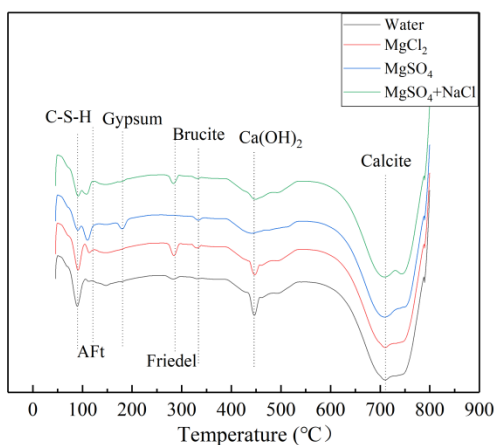
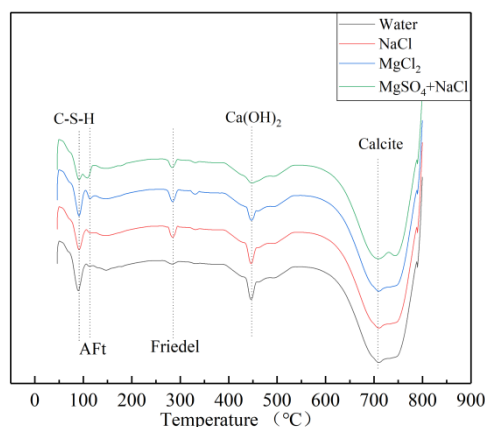




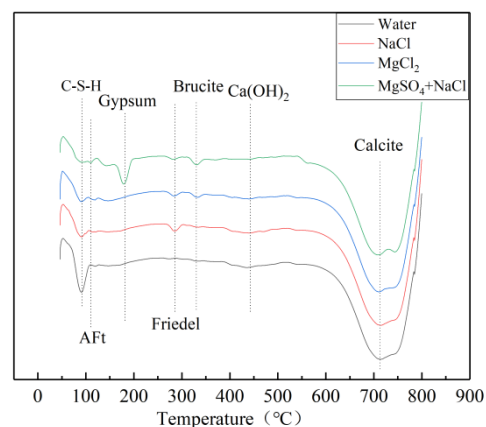
(a) Dry-wet cycle 40 times



(b) Dry-wet cycle 120 times

Figure 13. DTG diagram of erosion solution containing SO_4^{2-} .**Figure 14.** DTG diagram of erosion solution containing Mg^{2+} .

(a) Dry-wet cycle 40 times



(b) Dry-wet cycle 120 times

Figure 15. DTG diagram of erosion solution containing Cl^- .

3.3.3. Fourier Infrared Spectrum Analysis (FTIR)

To demonstrate the existence of M-S-H, three solutions containing magnesium ions, including MgCl_2 , MgSO_4 , and $\text{MgSO}_4 + \text{NaCl}$, were analyzed by the Fourier infrared spectrum. The corresponding infrared spectrum when dry-wet alternation reached 40 cycles

is shown in Figure 16a: the corresponding absorption peak of MK concrete at 3630 cm^{-1} was the O-H stretching vibration bond [46] in $\text{Ca}(\text{OH})_2$. At this time, the vibration peak of the oxhydroyl was weak. Besides, the bending vibration peak and the stretching vibration peak of the S-O bond were at 618 cm^{-1} and 1103 cm^{-1} respectively. The stretching vibration peaks of the Al-O bond existed at 531 cm^{-1} and 856 cm^{-1} , which proved the existence of ettringite. In addition, the vibration absorption peaks of the C-O bond and Si-O bond existed at 875 cm^{-1} and 774 cm^{-1} , based on which, it could be known that these were the quartz and calcite aggregates in MK concrete. What existed during the range of $964\text{--}970\text{ cm}^{-1}$ was the Si-O-T asymmetrical vibration in the hydrated product C-S-H [47]. The C-A-S-H stretching vibration peaks existed at 974 cm^{-1} , and the peak at 3696 cm^{-1} was related to the forming of $\text{Mg}(\text{OH})_2$ [48].

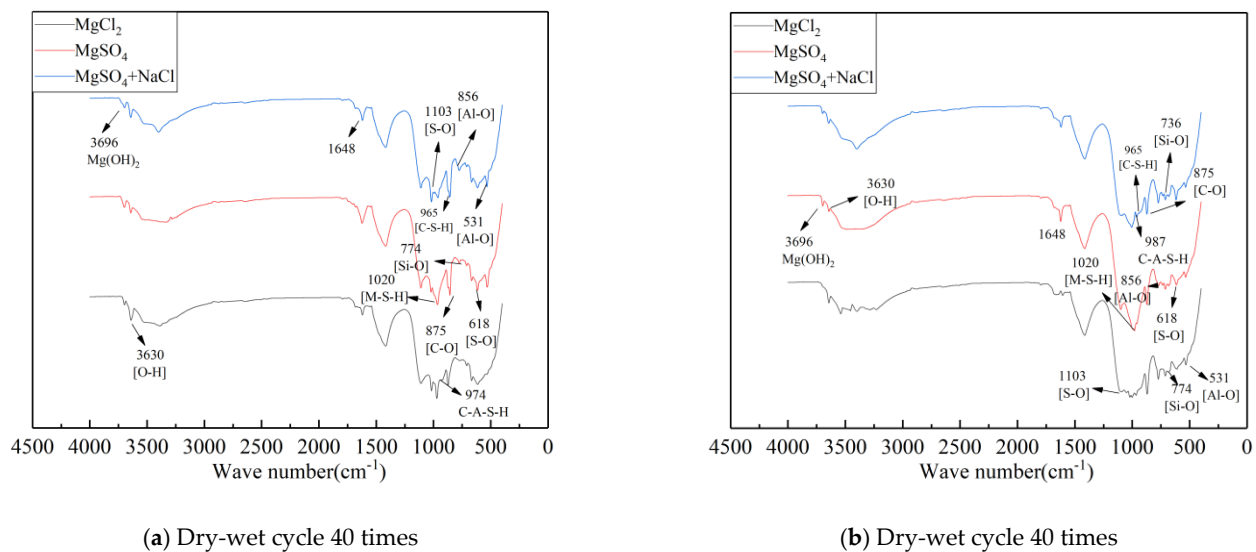


Figure 16. FTIR spectra of concrete corroded by Mg^{2+} solution.

With the increase of dry-wet alternation to 120 cycles, as shown in Figure 16b, the O-H stretching vibration peak at 3630 cm^{-1} weakened significantly, showing that the $\text{Ca}(\text{OH})_2$ was consumed. Due to the pH reduction in the pore solution, it could be seen that the vibration absorption peaks of the S-O bond and Al-O bond of the ettringite weakened, while the gypsum peak at 1648 cm^{-1} increased dramatically. The Aft decomposition increased the diffraction peak of the gypsum [49]. The stretching vibration peak of C-A-S-H moved from 974 cm^{-1} to 987 cm^{-1} , accompanied by a reduction of the diffraction peak. Besides, the Si-O bond of C-S-H at 945 cm^{-1} weakened while the characteristic absorption peak of M-S-H at 1020 cm^{-1} enhanced gradually [50], indicating the decalcification of C-A-S-H and C-S-H, and further proving that Mg^{2+} could react with MK concrete to produce a huge amount of M-S-H. Through the size of the M-S-H vibration absorption peak, the M-S-H contents in three types of solutions containing Mg^{2+} could be figured out: $\text{MgSO}_4 > \text{MgSO}_4 + \text{NaCl} > \text{MgCl}_2$. For the MgSO_4 solution and $\text{MgSO}_4 + \text{NaCl}$ solution, it could be known that Si-O vibration absorption peaks existed during $733\text{--}745\text{ cm}^{-1}$. Being different from the silicon-oxygen tetrahedra of the Si-O bond in the aggregate, the above was the silicon-oxygen hexahedra, coming from thaumasite [51]. Therefore, it can be known from the size of the vibration peaks and the types of the ion bonds that when corrosion occurred from MgSO_4 solution and $\text{MgSO}_4 + \text{NaCl}$ solution, the corrosion products of the MK concrete were mainly minerals of magnesium hydroxide, M-S-H, ettringite, gypsum, and thaumasite, as well as multiple types of crystal salts. However, the MK concrete produces more corrosion products in MgSO_4 solution than in $\text{MgSO}_4 + \text{NaCl}$ complex solution. When MK concrete is corroded in MgCl_2 solution, the main corrosion products were M-S-H and magnesium hydroxide with contents lower than those in the other two types of solutions.

3.4. Micro-Morphology Analysis

Figure 17 shows the micro-morphology of MK concrete in clean water. C-S-H with a large amount of the dense mesh structure can be seen in Figure 17a. That was because the adding of Metakaolin could accelerate the cement hydration process, thereby increasing the content of hydration product C-S-H. Besides, the unconsumed $\text{Ca}(\text{OH})_2$ which is in quadrilateral plate shape distributed in the slurry and inlaid in the pores together with a little amount of ettringite. When the dry-wet alternation reached 120 cycles, we zoomed in on it to see the overall MK concrete was more compacted than its condition at the 40th cycle. Due to the high pozzolanic activity of MK, its surface was covered by hydration products.

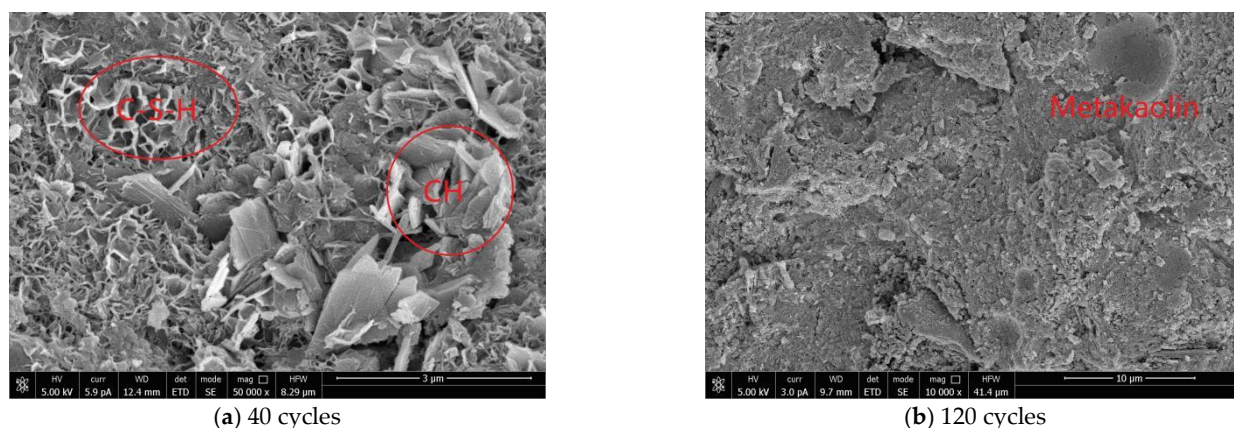


Figure 17. Microscopic morphology of MK concrete in clear water solution.

Figure 18a shows the micro-morphology of MK concrete in NaCl corrosive solution at the 40th dry-wet alternation cycle. It can be seen that the MK concrete surface has a small number of pores in which a small amount of $\text{Ca}(\text{OH})_2$ in plate shape was inlaid. When reaching the 120 cycles, and zoomed-in as shown in Figure 18b, we can see that lots of NaCl crystals were attached to the concrete surface. That was because the pH reduction makes the Friedel salt decompose, releasing lots of free Cl^- . These Cl^- ions bond with free Na^+ ions to form NaCl crystals. Compared with the concrete micro-morphology in clean water, both these two were of comparatively dense compaction, which further proves that separated Cl^- has no corrosion effect on concrete.

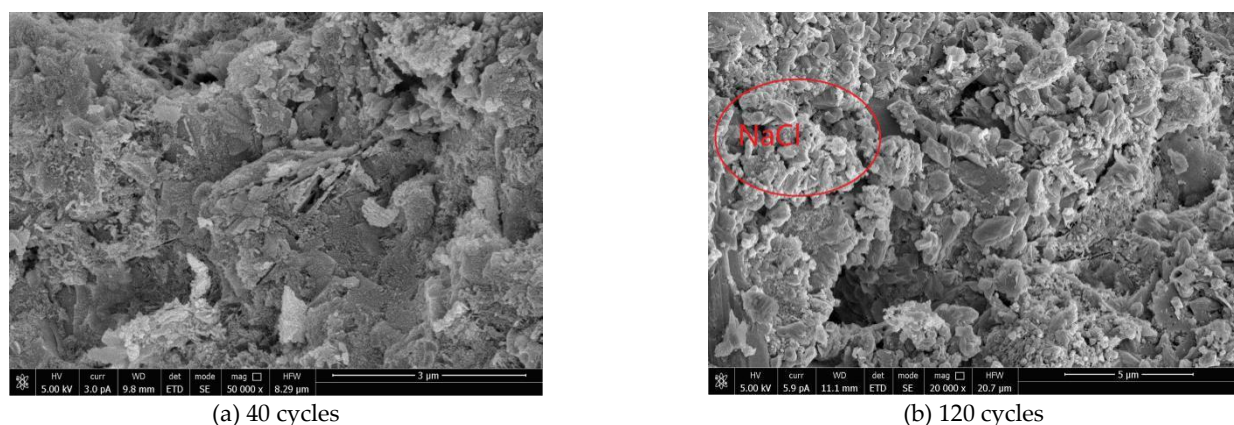


Figure 18. Microscopic morphology of MK concrete eroded by NaCl solution.

Figure 19a shows the micro-morphology of concrete in MgCl_2 solution at the 40th dry-wet alternation cycle. In addition to the C-S-H with a mesh structure, we could also see the worm-shaped cementitious materials. Based on EDS analysis (see Figure 20c), the main

composing elements of these corrosion products were Mg, O, Si, S, Ca. According to the M-S-H microscopic shape features [50,52], it could be seen that this was the non-cementitious M-S-H produced by the reaction between C-S-H and the Mg^{2+} invaded into MK concrete. With the increase of corrosion times, as shown in Figure 19b, M-S-H increased greatly, as did the pores inside the MK concrete, resulting in poor overall connection.

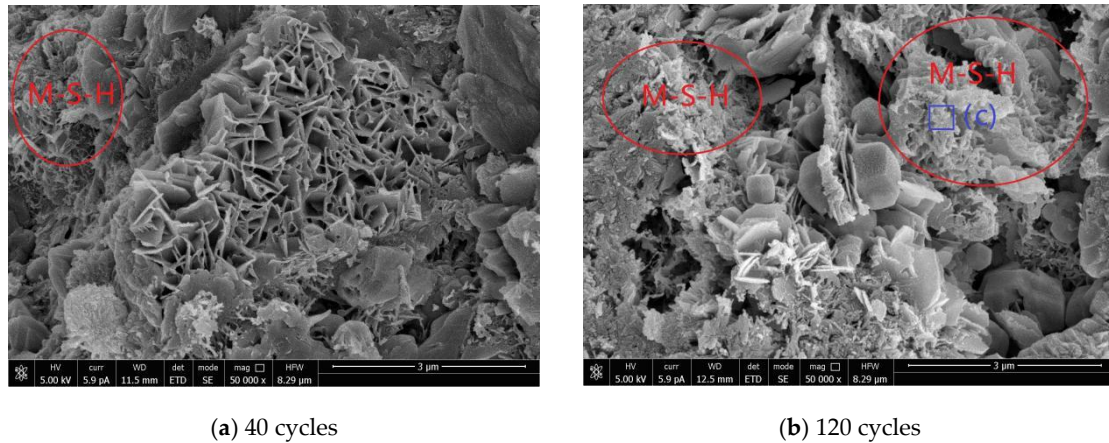


Figure 19. Microscopic morphology of MK concrete eroded by $MgCl_2$ solution.

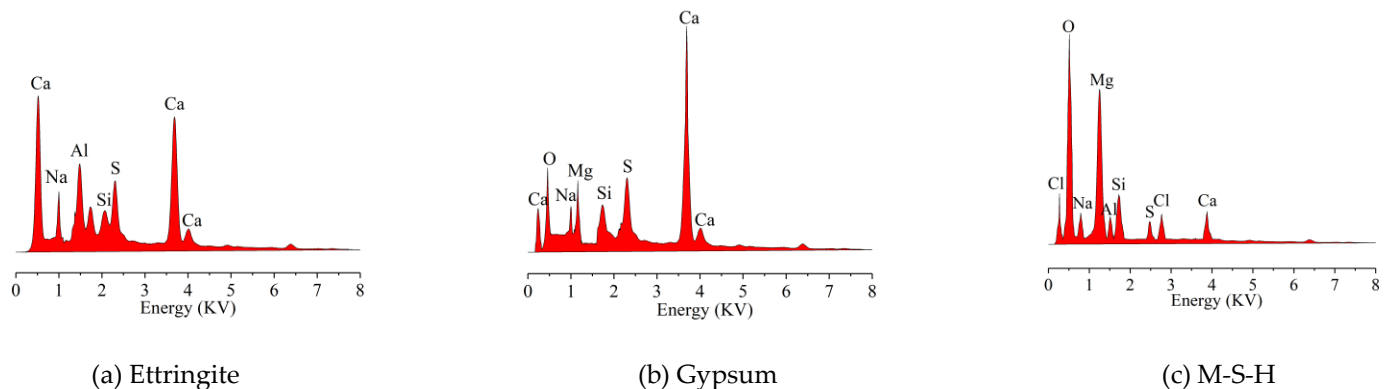


Figure 20. EDS energy spectrum image.

Figure 21 is a micro-morphology of concrete in Na_2SO_4 solution. When reaching 40 cycles of dry-wet alternation, we could see the needle-shaped ettringite inserted in the concrete with small radical and axial sizes. The ettringite at this time is of small size but dense distribution. When reaching 120 cycles, it could be known according to EDS analysis shown in Figure 20a that the main composing elements of this needle-shaped material included Ca, Al, S, Si, Na. Based on the knowledge in the literature [53,54], it was known that this corrosion product is still ettringite. We could see that the ettringite starts to expand in volume, and becomes a thicker bar shape. The expansion force inside the concrete causes cracking of concrete.

Figure 22 shows the micro-morphology of concrete in the $MgSO_4$ solution. As shown in Figure 22a, when dry-wet alternation keeps for 40 days, there is a certain amount of ettringite and M-S-H. Compared to the micro-morphology of MK concrete in Na_2SO_4 solution, the ettringite at this time in the $MgSO_4$ solution is featured in a lesser amount but greater volume. That was mainly because the generated M-S-H has no cementitious effect so the concrete structure is loose and leaves a larger internal space for the ettringite crystal to generate. When the dry-wet alternation reaches 120 days, lots of block-shaped or short column-shaped corrosion products could be found. Based on the EDS analysis in Figure 20b, it could be known that this was the material mainly composed of Ca, S, O,

Si. According to the microstructural features [55,56], it could be determined that this was gypsum. We could see that lots of gypsum crystals had developed as extremely big, layer by layer. That was because the pH reduction made the ettringite and C-S-H decompose, releasing Ca^{2+} ions. Besides, the generation of a large amount of M-S-H made the aggregate peel off, generating more cracks, and accelerating the ion diffusion towards the inside part of concrete. This further sped up the forming of gypsum crystal, resulting in secondary corrosive damage to the concrete.

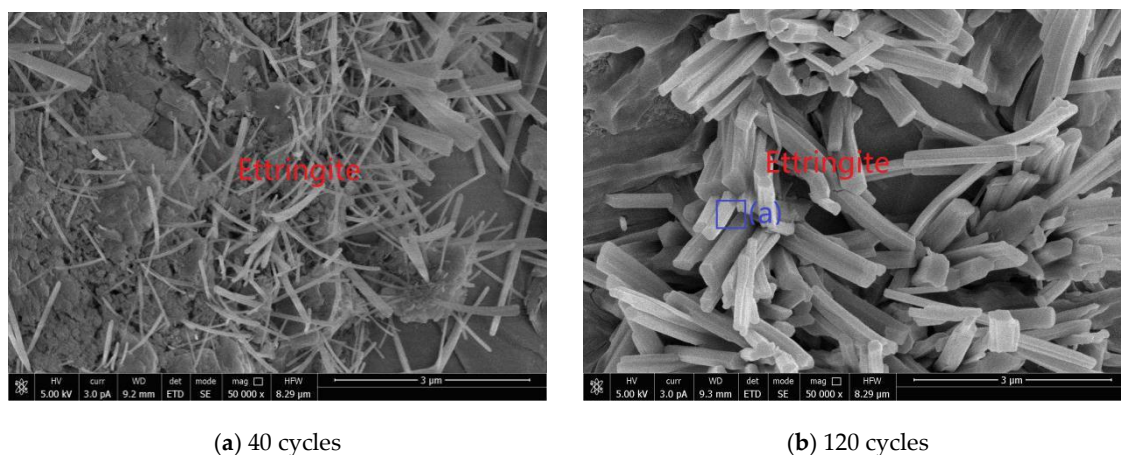


Figure 21. Microscopic morphology of MK concrete eroded by Na_2SO_4 solution.

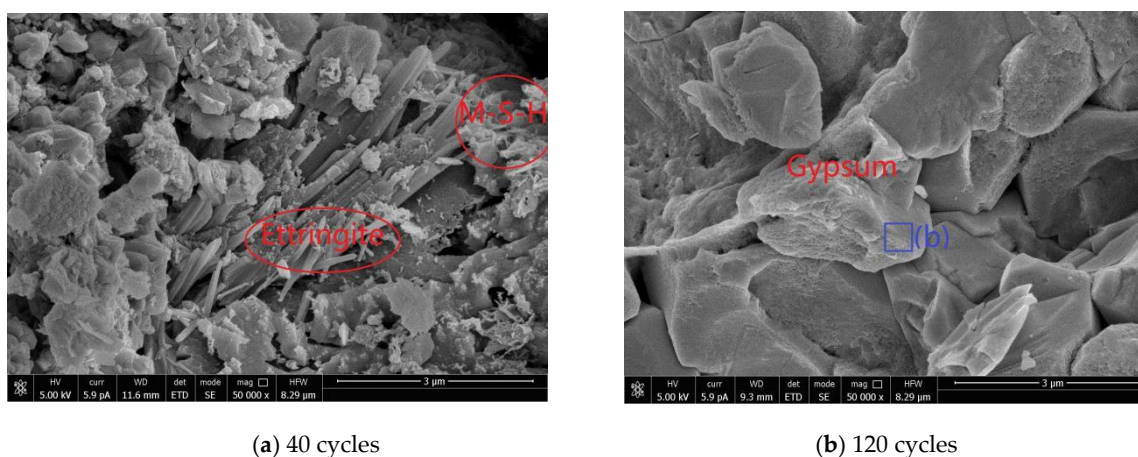


Figure 22. Microscopic morphology of MK concrete eroded by MgSO_4 solution.

Figure 23 shows the micro-morphology of MK concrete when suffering corrosion of $\text{MgSO}_4 + \text{NaCl}$ complex solution. It can be seen from Figure 23a that there was a small number of pores inside the concrete, in which, the ettringites were inserted. The ettringite was featured in a small amount and needle-shaped. When the dry-wet alternation reached 120 cycles, it showed that the ettringite started to expand and was disorderly inlaid in the concrete block accompanied by a small amount of NaCl crystals and M-S-H. However, the ettringite volume was smaller than the expansion volume of the concrete block in the Na_2SO_4 solution. The possible reason for this may be that the $\text{Mg}(\text{OH})_2$ volume with small solubility at this time was already big enough. Additionally, the generation of NaCl crystal inhibits the development space of ettringite. Similar to the conditions in the Na_2SO_4 and MgSO_4 solutions, the concrete block would have significantly more cracks inside due to the expansion stress of the corrosion products, and the surface tension formed by the corrosive solution migration in pores during the dry-wet alternation process. The cracks would connect and result in the peeling-off of the concrete surface.

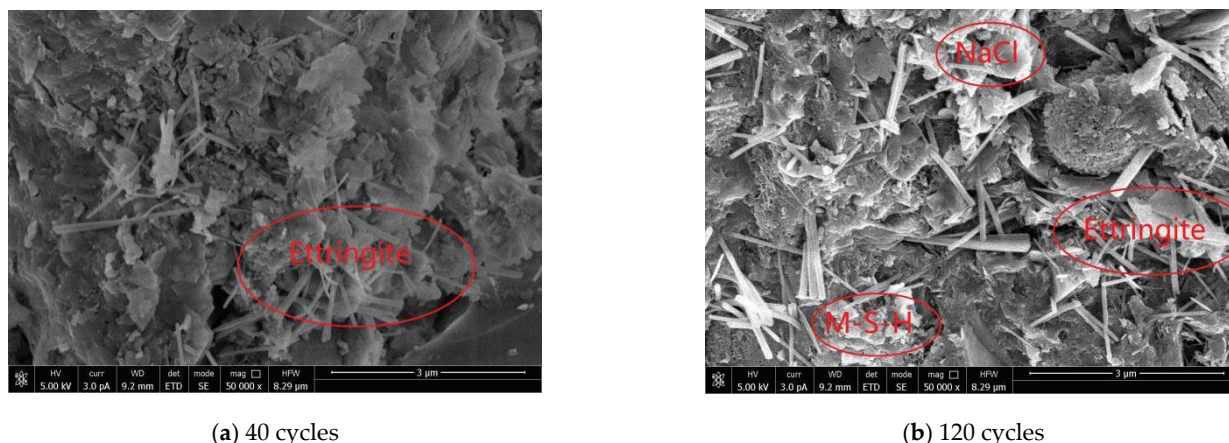


Figure 23. Microscopic morphology of MK concrete eroded by $\text{MgSO}_4 + \text{NaCl}$ solution.

4. Discussions

4.1. Effects of Test Block Preparation on Results

This test was performed under an ideal lab environment. In practical engineering scenes, in order for the convenience of construction and material acquisition, the cast-in-situ concrete structure is applied in lots of bridge, road, and tunnel construction projects. As for the subterranean work, in saline areas or even some offshore cities, the groundwater or even local lake water is usually used to prepare concrete. Compared to water used in the lab, these types of water contain certain chloride salt, so that the prepared concrete would suffer internal chloride corrosion [57,58]. The Cl^- ion would affect the materials of the cast-in-situ concrete because it can affect the cement hydration. Zhao et al. [59] showed in their test that the internal chloride salt corrosion would slow down the development of concrete strength, and induce more initial cracks in the test blocks, promoting the entry of external ions.

Besides the effects of raw materials, the concrete preparation is also subject to the surrounding environment. In the test, the concrete is cured once being prepared. However, in practical engineering scenes, the cast-in-situ concrete structure would be surrounded by a corrosive environment once being poured, leading to a quicker reduction of concrete durability.

4.2. Effects of the Cement and Cementitious Material Changes on the Results

It is the MK concrete that is used in this test. From the test results perspective, the MK concrete is highly subject to Mg^{2+} . To common concrete made of cement, the above ion has little effect. Wang et al. [35] took a complex solution and Na_2SO_4 solution as the corrosive solution to study the durability of the common shotcrete. The results show that Mg^{2+} has protective effects on common concrete to a certain extent and can slow down the reduction of test block performance. The reason for causing different results is still the mineral admixture, which can not only enhance the concrete mechanical properties but also improve the concrete frost/heat resistance. Therefore, a mineral admixture is widely used in the cement production industry, such as portland slag cement, portland pozzolana cement, and portland fly-ash cement. These types of cement have been largely used due to the cheap price and easy production process. The mineral admixture, such as slag, pozzolana, fly-ash, and Metakaolin, contains lots of active SiO_2 and Al_2O_3 , which could produce lots of C-S-H during the concrete hydration period to enhance the test block strength. Once eroded by Mg^{2+} , the M-S-H would be produced in a significant volume. A previous study [60] shows that although mineral admixture is highly resistant to mono SO_4^{2-} corrosion, its property drops quickly when encountering Mg^{2+} . Compared to Metakaolin, Mg^{2+} seems less effective to property reduction of fly-ash or slag, so that the commonly seen portland slag cement and portland pozzolana cement show the same rule.

Therefore in practical engineering, if the surrounding environment is featured in high Mg^{2+} content, the proportion of Metakaolin should be reduced correspondingly.

5. Conclusions

These tests study the degradation mechanism and corrosion products of MK concrete under the effects of corrosive solutions made of different ion combinations and the effects of the dry-wet alternation. The results show that:

- (1) Being corroded by various corrosive solutions, the physical properties of the MK concrete increase firstly and then reduce. Separated Cl^- almost has no corrosive effect on MK concrete. Mg^{2+} has the greatest impact on MK concrete. The combination of Mg^{2+} and Cl^- is corrosive to the concrete. The combination between Mg^{2+} and SO_4^{2-} could greatly enhance the damages to the concrete block. Therefore, the SO_4^{2-} shows the most significant damage effect on concrete. However, it can also relieve the damage to the concrete by combining with Cl^- . The corrosive effects of various solutions on the concrete, from severe to mild, are: $\text{MgSO}_4 > \text{MgSO}_4 + \text{NaCl} > \text{Na}_2\text{SO}_4 > \text{MgCl}_2 > \text{NaCl} = \text{Clean Water}$.
- (2) The corrosive ions are mutually promoted and inhibited and are closely related to the corrosion time. At the early and middle stages of corrosion (40–80 cycles of dry-wet alternation period), Mg^{2+} and SO_4^{2-} are mutually inhibited. Cl^- can inhibit the invasion of SO_4^{2-} . Mg^{2+} could promote the diffusion of the free Cl^- . When entering the final stage of corrosion (80–120 cycles of dry-wet alternation period), Mg^{2+} and SO_4^{2-} could promote each other, and SO_4^{2-} becomes promotive to the diffusion of Cl^- . Meanwhile, at this time, Mg^{2+} could also promote the Cl^- . However, it is not clear whether Cl^- can promote or inhibit the diffusion of SO_4^{2-} . This may be related to the concentrations of the two ions.
- (3) The main corrosion products of SO_4^{2-} on MK concrete are mainly gypsum and ettringite. When SO_4^{2-} is combined with Mg^{2+} , the generating speed and amount of the gypsum and ettringite are both low in the early and middle stages. But at the final stage of corrosion (120 days), the gypsum content becomes more than the amount of single SO_4^{2-} corrosion. The corrosion products of Mg^{2+} mainly include M-S-H and $\text{Mg}(\text{OH})_2$. Its combination with SO_4^{2-} would generate ettringite and gypsum, as well as a small number of thaumasite. The main corrosion products of Cl^- are Friedel salt and NaCl crystals. Either Mg^{2+} or SO_4^{2-} could inhabit the forming of Friedel.
- (4) The micro-analysis of SEM indicates that, for separated Cl^- corrosion, the concrete block shows many NaCl crystals on its internal surface and comparatively compacted microstructure. The combination of Cl^- and Mg^{2+} results in lots of M-S-H on the surface, which further leads to a loose and porous microstructure of the concrete block. When encountering SO_4^{2-} corrosion, ettringite could be generated greatly. After combining with Mg^{2+} , the ettringite at the early stage of corrosion is featured in a small amount but a relatively large volume, which further increases in both amount and volume in the final stage. After combining with Cl^- and Mg^{2+} , there would be multiple types of corrosion products, among which, ettringite shows proper volume.

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