Effects of active mineral admixture on mechanical properties and durability of concrete

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Keywords: concrete, mineral admixture, orthogonal test, mechanical properties, durability

Abstract

The purpose of this study is to figure out the effects of the active mineral admixture on the mechanical properties and the durability of the concrete. In this paper, the orthogonal test was adopted to study the effects of the metakaolin, the ultra-fine fly ash, and the silica fume on the compressive strength and the splitting tensile strength of the concrete at various curing ages, and to further determine the optimal mix ratio. After that, the ordinary concrete was taken as the control group, the Na₂SO₄ solution and the MgSO₄ + NaCl solution were used as the corrosive medium, and the dry-wet alternation method was adopted to make comparison and micro-analysis on the durability degradation processes of both the admixture concrete with optimal mix ratio and the ordinary concrete in the two solutions as mentioned above. The results show that: as for the concrete mechanical properties, the metakaolin shows the most significant and positive effects on the concrete cured for 7d–14d, while the silica fume affects the concrete with 28 d curing age most. The mechanical properties of the concretes at various curing ages reach their optimal levels when it is added with 10% metakaolin, 15% ultra-fine fly ash, and 3% silica fume. For the concrete durability, the application of mineral admixture could greatly improve the concrete capability in resisting the SO₄²⁻ corrosion. However the complex ions have destructive effects on the mineral admixture concrete. Compared with the ordinary concrete, it shows the most significant growth of corrosion product M–S–H, faster reduction of mechanical properties, and loose and porous micro-structure.

1. Introduction

The demand for concrete has been rising day by day due to the economic development and the population growing nowadays. The concrete is a widely used construction material. According to existing statistics [1], the demand for concrete in 2050 will reach at least 18 billion tons per year [2]. However the cement, as the main component of the concrete, would emit massive CO₂ during its production process. For every ton of cement production, there will be about 0.8 ton of CO₂ emitted to the air [3]. The CO₂ emitted therefrom accounts for 8% of the total CO₂ emission around the globe [4]. Therefore the most effective way to ease the environment pressure caused by cement production is to replace part of the cement by mineral admixture, thereby reducing the cement use. The fly ash is a mineral admixture that is commonly used. It is the main emission product of coal-fired power plant and can be cyclically utilized to minimize its impacts on the environment. However, since the fly ash is featured in large particle size and low activity, using fly ash to replace cement would have adverse effect on the mechanical properties of the concrete [5].

Therefore in order to guarantee the concrete performance, the active mineral admixture has been attracting more and more attentions in relative fields. For example, the ordinary fly ash can be made into ultra-fine fly ash by mechanical processing. The ultra-fine fly ash has comparatively large specific surface area, which can greatly enhance the bulk density of the cement paste when it is added in the concrete [6]. By doing so, it can effectively
improve the fluidity of the cement-based slurry with low water-binder ratio, and optimize the mechanical properties of the concrete at the latter stage [7]. Another example is the silica fume. It is a by-product of the large-scale industrial smelting and can also be cyclically utilized [8]. Its main component is the noncrystalline SiO2. Therefore adding the silica fume can help reduce the Ca(OH)2 content in the cement, and convert it into hydration product of calcium silicate, thereby improving the compactness and permeability of the concrete [9]. Compared with the silica fume, the metakaolin is also a mineral admixture with high pozzolanic activity. But being different from the silica fume, the main active components of the metakaolin still include a large number of noncrystalline Al2O3 besides the noncrystalline SiO2. Therefore the metakaolin can promote the cement hydration process [10].

In addition to the mechanical properties of the concrete, the durability is also an important index that determines the working performance of concrete. A large number of corrosive ions exist in the actual engineering environment, among which, SO42−, Cl− and Mg2+ are the ions having the greatest impacts on the concrete [11, 12]. SO42− could produce ettringite and gypsum, as well as other corrosion products inside the concrete, which forms expansion stress and damages the concrete [13, 14]; Mg2+ damages the concrete by softening the cement base [15]. As for the Cl−, it is featured in the widest spread in the environment and mainly damages the rebars inside the concrete. As a corrosive ion, Cl− can form synergism effect with Mg2+ and SO42− to damage the concrete together [16].

Lots of reports have proved that the mineral admixture can improve the mechanical properties and the durability of the concrete. Existing literature [17–19] show that the metakaolin and silica fume can produce a large number of cementitious materials, such as C–S–H and C–A–S–H, to fill up the capillary pores, destruct the connection among the pores, and enhance the concrete compactness. By this way, the metakaolin and the silica fume improve the mechanical properties of the concrete. Besides, the mineral admixture and the cement have different particle sizes, so the application of two materials in the concrete achieves micro-aggregate effects and better particle gradation, and forms more compacted stacking volume [20, 21]. Supit [22] conducted relative study and figured out that, adding 2% nano-silica fume in the ultra-fine fly ash concrete could greatly reduce the water absorption of the concrete and improve the performance of the test samples. About the durability of the concrete, Aghabag [23] conducted relative tests and proved that, when the concrete is subjected to the joint corrosion of Mg2+ and SO42−, the adding of metakaolin could weaken the damage from concrete expansion. But Lee [24] proposed opposite opinion, believing that the adding of metakaolin could worsen the concrete damage caused by corrosion of Mg2+ and SO42−.

As for the application of the mineral admixture, most existing researches focus on the replacement of cement by admixtures composed of single or double mineral components, lacking researches on compound admixture containing three types of mineral components. Meanwhile, researchers have expressed contradictory opinions on the complex ions corrosion to the active mineral admixture. Besides the corrosion caused by ions, the concrete is also subjected to the physical corrosion brought by dry-wet alternation. This is a corrosion type that is commonly ignored. Therefore in this study, the orthogonal test was adopted to study the influences of the three active admixtures on the mechanical properties of the concrete at various curing age, thereby figuring out the optimal mix ratio. Moreover in order to study the admixture concrete’s resistance to the compound salt, the 5%MgSO4 + 3.5%NaCl solution and the 5%Na2SO4 solution were taken as the corrosion medium, the admixture concrete with optimal mix ratio and the ordinary concrete were taken as the study objects, and the dry-wet alternation method was applied to conduct the durability tests. And then, the X-ray diffraction (XRD), the Fourier transform infrared spectrum (FTIR), the scanning electron microscope (SEM), and the energy dispersive spectrum (EDS), were applied to explore the degradation mechanism of the admixture concrete.

2. Test and method

2.1. Raw materials
The P.O. 42.5 ordinary Portland cement produced by Huainan Bagongshan, the ultra-fine fly ash (UFA) produced by Henan Huifeng New Materials Co., Ltd, the metakaolin (MK) produced by Shanghai Lingdong Company, and the silica fume produced by Zhengzhou Huaying Purification Materials Co., Ltd were used in this test. As for the chemical composition of the four cementitious materials, please see table 1; for the macro-morphology, please see figure 1; and for the micro-morphology, please see figure 2.

And for the aggregates, the mechanically crushed limestone with 5 mm–15 mm particle size were used as the coarse aggregates while the medium sands with 2.9 fineness modulus from Huaihe River were used as the fine aggregate; meanwhile, the Polycarboxylate-based superplasticizer was adopted in this test as the water reducer, which is featured in about 37% water reduction rate.
2.2. Test method

2.2.1. Orthogonal test design
The factors affecting the concrete performance at this time are the amounts of the three different mineral admixtures. To minimize the workload and improve the efficiency of the test, the orthogonal test design was used in this study. Three types of factors were selected: Factor A was the mass proportion of metakaolin (MK) which was used to replace cement; Factor B was the mass proportion of ultra-fine fly ash (UFA) which was used to replace cement; and Factor C was the mass proportion of silica fume (SF) which was used to replace cement (as shown in table 2).

2.3. Preparation of test samples
The concrete proportioning was determined according to JGJ55-2011 Specification for mix proportion design of ordinary concrete. As shown in table 3, the coarse and the fine aggregates were blended and put into the mixer to mix for 1 min; then the cementitious material was weighed and mixed with the aggregates under no-water condition for 2 min to mix the two materials sufficiently; after that, the water and the water reducer were put into the well-mixed materials to mix for 2–3 min. After that, the blended material was put into the 100 mm × 100 mm × 100 mm mold, which were then put onto the vibration table for being vibrated and compacted. Then the
molds were put in standard curing room with 20 ± 2 °C temperature and over 95% humidity. Finally, the materials were demold after 24 h, and kept cured till reaching required curing age.

2.4. Test method

2.4.1. Compressive strength test and splitting tensile test

The orthogonal test method was used to calculate the mix ratio of the concrete test samples, and the mechanical property tests were performed on 9 groups of concretes with various curing ages of 7d, 14d, and 28d respectively. These tests were in line with the requirements of the GB/T50081–2002[25] standard. Since the non-standard test sample sized 100 mm × 100 mm × 100 mm was applied in this study, the coefficient should be multiplied. The coefficient for the compressive strength conversion of cube is 0.95 while the coefficient for the splitting tensile strength is 0.85.

After figuring out the optimal mix ratio, the SEM micro-performance test was adopted in order to find out the hydration mechanism of the mineral admixture concrete.

2.4.2. Dry-wet alternation test

First of all, the optimal mix ratio was figured out by the orthogonal test and the mineral admixture concrete with optimal mix ratio was prepared; then the dry-wet alternation tests were conducted on the mineral admixture concrete with optimal mix ratio, and the ordinary concrete. According to the ion composition in some certain saline areas and coastal areas, and on the basis of the Standard GB/T50082-2009[26], the 5%Na2SO4 solution and the 5%MgSO4 + 3.5%NaCl solution were taken as the corrosion medium of the study. The dry-wet alternation cycle applied in this paper is: soak in the corrosive solution for 14 h → dry in room temperature for 1h → dry in 60 °C dryer for 8 h → cool at room temperature for 1 h, which amount to 24 h per cycle. In order to maintain the concentration stability of all the solutions, we make and replace with new solutions every 10 days.

When the corrosion reaches 10d, 20d, 40d, 80d, and 120d, the compressive strength and mass of the concrete test samples were tested respectively. And comparisons were made on the mechanical properties and mass changes of the two different types of concretes in the two different solutions.

When reaching 120d corrosion, the XRD, FTIR, and SEM-EDS tests were carried out on the two groups of concretes in the two types of solutions. The D/max-2550 XRD machine produced by Japan, which is featured in 5°～95° scanning range and 0.02°scanning step, was used in this test. As for the FTIR test, NICOLET IS 50 infrared spectrometer with 350 cm⁻¹ ~ 7800 cm⁻¹ wave number range produced by American company was adopted in this study. And for SEM test, the Hitachi S4800 cold field SEM with 5 KV acceleration voltage and 10000 magnification power produced by Japan was used in this study.

| Table 2. Orthogonal test factor level table. |
|------------------|------------------|------------------|------------------|------------------|
| Level | Factor A MK(%) | Factor B UFA(%) | Factor C SF(%) |
| 1 | 2 | 15 | 1 |
| 2 | 6 | 20 | 3 |
| 3 | 10 | 25 | 5 |

| Table 3. Mix proportion design of each group of concrete (kg m⁻³). |
|------------------|------------------|------------------|------------------|
| Number | MK | UFA | SF | Cement | Sand | Aggregate | Water reducing agent |
| 1 | 10 | 75 | 5 | 410 | 619 | 1101 | 3.5 |
| 2 | 10 | 100 | 15 | 375 | 619 | 1101 | 3.5 |
| 3 | 10 | 125 | 25 | 340 | 619 | 1101 | 3.5 |
| 4 | 30 | 75 | 15 | 380 | 619 | 1101 | 4.5 |
| 5 | 30 | 100 | 25 | 345 | 619 | 1101 | 4.5 |
| 6 | 30 | 125 | 5 | 340 | 619 | 1101 | 4.5 |
| 7 | 50 | 75 | 25 | 350 | 619 | 1101 | 5.5 |
| 8 | 50 | 100 | 5 | 345 | 619 | 1101 | 5 |
| 9 | 50 | 125 | 15 | 310 | 619 | 1101 | 5.5 |
3. Results and analysis

3.1. Orthogonal test results

3.1.1. Range analysis

Figure 3 shows the test results of the mechanical properties of the mineral admixture concrete. It can be seen from the figure that Group 7 shows relatively better properties. However visual analysis may lead to significant error, and cannot explain the influences of various factors on the results, so the range analysis was conducted in this study. Table 4 shows the range analysis of the compressive strength and the splitting tensile strength of the concrete. For compressive strength, when reaching 7d-14d curing age, the Metalaolin replacement rate is the most significant factor affecting the compressive strength. When reaching 28d curing age, the range value of the silica fume exceeds the value of Metakaolin, indicating that the silica fume becomes the most significant factor affecting the concrete compressive strength at this time.

For the splitting tensile strength of the concrete, it can be seen that during the curing age of 7d ∼ 28d, the metakaolin volume has great impact on the tensile strength.

3.1.2. Variance analysis

Since the range analysis cannot distinguish the data fluctuation caused by test conditions and errors, the variance analysis was adopted in this study (as shown in tables 5 and 6). And in order to further verify the factor influences on the indicators, the factor contribution ratio was calculated and analyzed as well.

Generally, the three types of mineral admixtures have far greater effects on compressive strength than splitting tensile strength of the concrete. During 7d-14d curing age, for the compressive strength, the metakaolin which is the factor with the biggest contribution rate, is equivalent to 42.60 times of the error contribution rate, but is only 15.12 times of tensile strength. When reaching 28d curing age, silica fume becomes the factor with the
biggest compressive strength contribution rate, which is 30.86 times of error contribution rate. And for the splitting tensile strength, it is the metakaolin that has the biggest contribution rate at this time. Its contribution rate is only 3.90 times of the error contribution rate. Since the three types of highly active mineral admixtures are of different particle sizes, they help obtain excellent internal particle gradation inside the concrete, and form compacted filling structure and stacking structure inside the concrete. This is the reason why the highly active mineral admixture have great impact on the compressive strength, but small impact on the splitting tensile strength.

For the concrete compressive strength, during the 7-14d curing age, the metakaolin contains a large number of Al$_2$O$_3$ and can rapidly react with the cement hydration product of Ca(OH)$_2$, thereby reducing the alkalinity of the body, and accelerating the hydration process. It can be known that the metakaolin could enhance the concrete strength at early stage. According to the variance analysis, such effects are significant during 7-14d, which is conform to the results obtained by the range analysis. For the silica fume, it seems to have significant effect on the concrete with 7d curing age, and have highly significant effect on the concrete when reaching 14d-28d curing age.

For the splitting tensile strength, the Metakaolin has the greatest effect on the splitting tensile strength. However the effects reduces with the curing age increase. And the error contribution rate also increases with the increase of curing age.

3.1.3. Factor index analysis method
Range analysis and variance analysis can be used to figure out the factor influences on the final results accurately. However it cannot make comparison on the result differences caused by the changing of factor levels. Therefore

| Examination index | Factor | Degree of freedom | Mean square | F Value | Significance | Contribution rate |
|-------------------|--------|-------------------|-------------|---------|--------------|-------------------|
| 7-day compressive strength | A | 2 | 49.308 | 171.340 | ** | 64.33% |
|                     | B | 2 | 15.788 | 54.862 | * | 20.34% |
|                     | C | 2 | 10.815 | 37.579 | * | 13.81% |
|                     | Error | 2 | 0.288 | 1.51% | | 1.51% |
| Sum | 8 | | | | | |
| 14-day compressive strength | A | 2 | 39.443 | 155.697 | ** | 49.48% |
|                     | B | 2 | 13.870 | 54.750 | * | 17.19% |
|                     | C | 2 | 25.644 | 101.224 | ** | 32.05% |
|                     | Error | 2 | 0.253 | 1.28% | | 1.28% |
| Sum | 8 | | | | | |
| 28-day compressive strength | A | 2 | 31.574 | 124.092 | ** | 33.02% |
|                     | B | 2 | 13.068 | 51.359 | * | 13.51% |
|                     | C | 2 | 49.951 | 196.314 | ** | 52.40% |
|                     | Error | 2 | 0.254 | 1.07% | | 1.07% |
| Sum | 8 | | | | | |

Table 5. Results of variance analysis of compressive strength.

| Examination index | Factor | Degree of freedom | Mean square | F Value | Significance | Contribution rate |
|-------------------|--------|-------------------|-------------|---------|--------------|-------------------|
| 7-day splitting tensile strength | A | 2 | 0.358 | 61.528 | * | 74.23% |
|                     | B | 2 | 0.080 | 13.767 | η | 15.66% |
|                     | C | 2 | 0.031 | 5.249 | Δ | 5.21% |
|                     | Error | 2 | 0.006 | 4.91% | | 4.91% |
| Sum | 8 | | | | | |
| 14-day splitting tensile strength | A | 2 | 0.238 | 26.964 | * | 57.36% |
|                     | B | 2 | 0.125 | 14.077 | e | 28.89% |
|                     | C | 2 | 0.029 | 3.222 | — | 4.91% |
|                     | Error | 2 | 0.009 | 8.84% | | 8.84% |
| Sum | 8 | | | | | |
| 28-day splitting tensile strength | A | 2 | 0.117 | 16.384 | Ω | 45.12% |
|                     | B | 2 | 0.048 | 6.782 | Δ | 16.74% |
|                     | C | 2 | 0.072 | 10.173 | e | 26.56% |
|                     | Error | 2 | 0.007 | 11.58% | | 11.58% |
| Sum | 8 | | | | | |

Table 6. Variance analysis results of splitting tensile strength.

***represents highly marked, *represents marked, ○represents medium, Δrepresents slight — represents no marked
in order to figure out the primary/secondary factors, and the factor changing tendency in various level changes, the index analysis method was adopted in this study, please refer to figures 4 and 5.

For the compressive strength of the concrete, as shown in figure 4, when the metakaolin (Factor A) increases from 2% to 10%, the compressive strength of the test samples keeps rising, specifically: the compressive strength increases by 20.21% when reaching 7 days, increases by 15.32% when reaching 14 days, and increases by 11.67% when reaching 28 days. The metakaolin mainly improves the concrete mechanical properties by physical filling, hydration promoting, and Pozzolanic reaction promoting. The physical filling actually finishes at the initial stage of concrete hydration, while the Pozzolanic reaction mainly happens during 7d-14d [27]. Therefore the compressive strength of the concrete is greatly enhanced when reaching 7 days. However with the increase of curing age, the enhancement of the comprehensive strength reduces gradually. When the ultra-fine fly ash increases from 15% to 20%, and to 25%, the compressive strength of the test samples reduces gradually by 9.78%, 8.10%, and 6.90% respectively during the curing age of 7d-28d. At the initial curing stage, the ultra-fine fly ash is not quite active and only acts as a filling material. But with the increase of curing age, the cement hydration weakens and the Pozzolanic reaction of the ultra-fine fly ash is induced and activated, resulting in secondary hydration [28]. That explains why the performance reduction of concrete compressive strength slows down with the increase of curing age. Besides, when the silica fume increases from 1% to 5%, the compressive strength of the concrete enhances firstly, but then reduces. Therefore when the silica fume reaches 3%, it has the most significant effect on the improvement of the concrete compressive strength. For the compressive strength, according to the factor index analysis of figure 3, the optimal mix ratio of concrete should be A3B1C2. Compared to visual analysis, this conclusion obtained is much more accurate.

Figure 5 shows the splitting tensile strength of the concrete. With the metakaolin increase, the splitting tensile strength of the concrete enhances gradually. On the contrary, the splitting tensile strength keeps reducing with the increase of ultra-fine fly ash. Especially, when the ultra-fine fly ash increases from 20% to 25%, the reduction rate of the splitting tensile strength reaches as much as 10.21%; however when it increases from 10% to 15%, the maximum reduction rate of the splitting tensile strength is only 5.87%. It can be seen that the excessive ultra-fine fly ash has adverse effect on the splitting tensile strength of the concrete. With the increase of the silica fume, the splitting tensile strength always increases first and then reduces. Too much silica fume would
lead to the reduction of the concrete mechanical properties. However with the increase of curing age, when the silica fume enhances from 3% to 5%, the splitting tensile strength drops by 7.09% when reaching 3 days, drops by 3.30% when reaching 7 days, and drops by 0.28% when reaching 28 days. On the other hand, as shown in figure 4, the concrete compressive strength still follows such rule: as time goes by, when the admixture volume enhances from 3% to 5%, the curve tends to be flat. At the initial stage of the reaction, the active Pozzolanic material leads to continuous dissolution and reaction of Ca(OH)$_2$ crystals inside the test samples. The volume of unreacted crystals keep growing. And as the curing age goes by, the concrete interior becomes quite compact, so that the growing of the Ca(OH)$_2$ crystal is inhibited. As a matter of fact, the SiO$_2$, whose content inside the silica fume reaches over 90%[^29], can effectively reduce the content of Ca(OH)$_2$ at this time. Therefore the adverse effect of excessive silica fume could be eased with the increase of curing age. For the splitting tensile strength, the optimal mix ratio of the concrete is still A$_3$B$_1$C$_2$. When the metakaolin reaches 10%, the ultra-fine fly ash reaches 15%, and the silica fume reaches 3%, the admixture concrete is endowed with the optimal mechanical properties.

3.1.4. Micro-morphology analysis

In order to study the hydration mechanism of the highly-active mineral admixture concrete, the concrete A$_3$B$_1$C$_2$ with the optimal mix ratio was taken as the subject, and the SEM test was carried out on the concrete test samples with 7d, 14d, and 28d curing age which were cured under standard curing conditions.

Figure 6(a) shows the micro-structure of the concrete with 7d curing age. It can be seen that part of the ball-shaped UFA are filling in the pores of the test samples at this time. A small number of UFA are wrapped with hydration products on their surface. At this time, the UFA actually plays a role of physical filling material. Besides, a lot of calcium hydroxide in tabular shape can also be seen. As shown in figure 6(b), a small number of needle-shaped ettringite appear when reaching 14d curing age. That’s because the metakaolin contains active Al$_2$O$_3$ that can produce a small number of ettringite during the initial stage of cement hydration. Proper amount of ettringite can fill up the pores inside the test samples and enhance the compressive strength of the admixture concrete at early stage. Compared with the micro-structure of concrete with 7d curing age, the concrete with 14d curing age contains lots of cementitious C–S–H and reduced amount of calcium hydroxide. That’s because the high pozzolanic effect of the metakaolin and silica fume accelerates the cement hydration, and further increases the consumption of calcium hydroxide crystals. When the curing age reaches 28d, the concrete compactness is further increased than that of 14d. At this time, the concrete surface is wrapped with a large number of cementitious C–S–H. And with the increase of curing age, the silica fume and the metakaolin induce secondary hydration and produce more hydration products, such as hydrated calcium aluminate and hydrated calcium aluminate sulfate[^30]. This could further enhance the mechanical properties of the admixture concrete at the latter stage. Therefore, the composite of mineral admixtures could significantly improve the mechanical properties of the concrete at various curing ages.

3.2. Effects of highly-active mineral admixture on concrete durability

To compare the durability of the mineral admixture concrete with the ordinary concrete when being subjected to the ion corrosion, the orthogonal test was applied to figure out the optimal mix ratio for the concrete: A$_3$B$_1$C$_2$, and the dry-wet alternation test was conducted with the control concrete.

3.2.1. XRD analysis

When reaching 120 cycles of corrosion, XRD test is carried out on concrete test samples in the two different solutions to figure out the laws of their phase transitions. It can be seen from figure 7 that different corrosive
solutions have different effects on the corrosion product compositions of the two different types of concretes. The differences are specifically represented by the intensity and width changes of the diffraction peaks.

The quartz and calcite, which possess the two highest diffraction peaks in the figure, are both from the aggregates of the concrete. The hydration product Na–A–S–H loses the combined water at the latter stage, and forms the albite \(A_3B_1C_2\). Figure 7(a) shows that the concrete mainly produces ettringite, gypsum, Friedel salt, and magnesium hydroxide when it is eroded by MgSO\(_4\) + NaCl solution. By comparing ordinary concrete with admixture concrete \(A_3B_1C_2\), it can be known that the diffraction peaks of ettringite, gypsum, and magnesium hydroxide of the ordinary concrete under corrosion of compound solution are all lower than those of the admixture concrete. That's mainly because of the M–S–H, which is generated due to the active SiO\(_2\) in the mineral admixture. The silica fume and the metakaolin contain a lot of active SiO\(_2\), so that the generating of M–S–H is promoted. The increase of M–S–H leads to the peeling-off of the aggregates on the concrete surface. This not only provides channels for SiO\(_2\) invasion, but also provides space for corrosion product stacking. Therefore the SiO\(_2\) can enter the test samples again to produce more ettringite and gypsum, thereby resulting in secondary damage to the concrete.

Figure 7(b) shows the XRD spectrum of two different types of concretes in Na\(_2\)SO\(_4\) solution. The concrete mainly produces ettringite and gypsum in Na\(_2\)SO\(_4\) solution. At this time, the size of the ettringite diffraction peak of the ordinary concrete in Na\(_2\)SO\(_4\) solution is similar to that of the admixture concrete. However the gypsum diffraction peak is much higher than that of the admixture concrete. Since it reaches 120 cycles of corrosion, with the increase of the corrosion products, the consumption of the Ca(OH)\(_2\) keeps rising while the pH value inside the concrete drops. This inhibits the generating of ettringite, but accelerates the generating of the gypsum \[32\]. The massive gypsum generating leads to concrete crack development and worsens the corrosion effects. Therefore compared with the admixture concrete, the ordinary concrete shows much more significant performance reduction in Na\(_2\)SO\(_4\) solution.

3.2.2. Infrared spectrum analysis
The XRD test can neither prove the existence of M–S–H, nor distinguish the thaumasite and the ettringite effectively. Therefore the Fourier transform infrared spectrum was adopted to further verify the phase compositions of the two different types of concretes in MgSO\(_4\) + NaCl solution.

According to figure 8, the S–O bond characteristic absorption peaks exist at positions of 1109 cm\(^{-1}\) and 621 cm\(^{-1}\), and the Al–O bond bending vibration peaks exist at positions of 549 cm\(^{-1}\) and 817 cm\(^{-1}\), which both prove the existence of ettringite. However the peak strength of the admixture concrete at 621 cm\(^{-1}\) is higher than that of the ordinary concrete. This indicates that the admixture concrete contains massive ettringite. This is in line with the XRD analysis results. Then at the wave numbers of 881 cm\(^{-1}\) and 1429 cm\(^{-1}\), there are bending vibration peak and stretching vibration peak of C–O bond; and at the wave number of 775 cm\(^{-1}\), there’s characteristic absorption peak of Si–O bond, which proves the existence of quartz and calcite. However a weak stretching vibration peak of Si–O bond exists at position of 741 cm\(^{-1}\), which is a silico-oxygen hexahedra different from the silico-oxygen tetrahedra of quartz \[33\]. This proves the existence of the thaumasite. And then by the sizes of the absorption peaks, it can be inferred that there’s just a few thaumasite inside the test samples. Moreover, M–S–H characteristic absorption peak is found at the position of 1002 cm\(^{-1}\) \[34\]. By comparing...
ordinary concrete with admixture concrete $A_3B_1C_2$, it can be known that the characteristic absorption peak of the admixture concrete at this position is wider and significantly higher than that of the ordinary concrete, so the amount of $M$–$S$–$H$ inside the admixture concrete is much greater than that in ordinary concrete. A comparatively weak characteristic absorption peak of O–H bond is found at wave number of 3644 cm$^{-1}$, which might be the absorption peak of calcium hydroxide $[35]$. Combining with XRD analysis results, it can be known that under the compound corrosion of $SO_4^{2-}$, $Mg^{2+}$, and $Cl^-$, the corrosion products of the mineral admixture concrete are mainly the ettringite, gypsum, Magnesium hydroxide, $M$–$S$–$H$, and thaumasite.

3.2.3. Micro performance analysis

As for the concrete, the durability is closely related to its micro-structure. Therefore when the corrosion reaches 120 cycles, the micro-morphology analysis was carried out on the two types of concretes in $Na_2SO_4$ solution and $MgSO_4 + NaCl$ solution (see figures 9 and 10) to study the corrosion products’ types by EDS (see figure 11), and explore the degradation mechanism.

Figure 9 shows the micro-morphology of the concrete in $Na_2SO_4$ solution. Admixture concrete usually has compact micro-structure. It can be seen that the ball-shaped UFA particles are filling up the pores inside the concrete at this time. Due to the large consumption of hydration products, the surface of the UFA is totally exposed, surrounded with no hydration product. Besides, it can also be seen that lots of needle-shaped materials are inserted around. Figure 11(a) EDS displays that these materials are mainly composed of Ca, O, Si, and S elements. According to Literature $[36]$, it is actually the ettringite, which is featured in small volume but dense distribution. Figure 9 (b) shows the micro-morphology of the ordinary concrete. Compared with the micro-structure of the admixture concrete, the ordinary concrete contains pores with various sizes. Meanwhile, its interior also has needle-shaped ettringite, which are featured in comparatively large volume and distributed on the concrete surface. Compared with the admixture concrete, the ordinary concrete bears great ettringite expansion stress at this time, which promotes the internal cracking and pore increase.

Figure 10 shows the concrete micro-morphology in $MgSO_4 + NaCl$ solution. As shown in figure 10(a), the mineral admixture concrete contains a lot of non-cementitious materials. It can be known from the EDS analysis of figure 11(b) that, Mg, O, Si, and S are the main elements of the aforesaid materials. According to the morphological characteristics $[37]$, it can be inferred that this kind of material is $M$–$S$–$H$. The concrete at this time contains lots of pores, so that the concrete shows very bad connectivity in general. And for the ordinary concrete, as shown in figure 10(b), it contains small-sized pores, but much higher compactness than that of the admixture concrete. But generally, the ordinary concrete structure is loose. Compared with the ordinary concrete, under the expansion stress of the corrosion products, and the surface tension formed by the corrosive solution migration in capillary pores during the dry-wet alternation process, the admixture concrete would have more internal cracks, which are interconnected and result in peeling-off of surface aggregate of the test samples.
Figure 9. Microscopic morphology of Na$_2$SO$_4$ solution after erosion for 120 days.

Figure 10. Micro-morphology of MgSO$_4$ + NaCl solution after erosion for 120 days.

Figure 11. EDS energy spectrum image.
3.2.4. Mechanical properties analysis

Figure 12 shows the mechanical properties changes of the two different types of concrete in different solutions. We can see the concrete degradation process clearly according to the changes of the concrete mechanical properties.

Figure 12(a) shows the changing laws of concrete mechanical properties in MgSO\textsubscript{4} + NaCl solution. During 0–20 corrosion cycles, the mechanical properties of both the two concretes rise because of two reasons: first, the cement is at the hydration stage at this time; and second, the ettringite and the magnesium hydroxide produced at the initial corrosion stage fill up the pores on the concrete surface; with the corrosion increases from 20 to 80 cycles, the compressive strength of the ordinary concrete reduces by 4% while the admixture concrete reduces by 12.3%. That’s because the high pozzolanic activity of the silica fume and the metakaolin inside the admixture concrete promote the formation of C–S–H, which is subjected to serious decalcification and generates M–S–H. This is kind of destructive damage to the concrete. During 80–120 cycles of corrosion, the compressive strength of the ordinary concrete drops by 9.4% while the same data of the admixture concrete drops by 13.2%. At this time, the admixture concrete is damaged jointly by the corrosion products of ettringite, gypsum, magnesium hydroxide, and M–S–H. This results in continuous crack emerging and developing on the concrete surface, which damages the micro-structure of the reaction area and leads to sharp reduction of the mechanical properties of the admixture concrete.

Figure 12(b) shows the mechanical properties changes of concrete in Na\textsubscript{2}SO\textsubscript{4} solution. Since the adding of the mineral admixture, which replaces part of the cement, results in C\textsubscript{3}A content reduction and higher compactness of the concrete, the mineral admixture concrete shows better corrosion-resistant performance than ordinary concrete in face of single SO\textsubscript{4}\textsuperscript{2−} corrosion. During 0–120 corrosion cycles, the mechanical properties of the admixture concrete reduces by 6.31%, while the compressive strength of the ordinary concrete reduces by 16.9%. Compared with conditions in MgSO\textsubscript{4} + NaCl solution, the mechanical properties of ordinary concrete only drops by 6.6%. That’s mainly because of the impacts brought by Mg\textsuperscript{2+} and Cl\textsuperscript{−}. For ordinary concrete, Mg\textsuperscript{2+} could only produce a small amount of M–S–H. And the magnesium hydroxide produced in ordinary concrete acts as the protective coating, which blocks the diffusion channels of SO\textsubscript{4}\textsuperscript{2−} to some certain extent; as for Cl\textsuperscript{−}, due to its smaller volume and faster diffusion, it could react with aluminum phase inside the test samples prior to SO\textsubscript{4}\textsuperscript{2−} to generate Friedel salt, thereby inhibiting the generating of ettingite. Therefore under the corrosion of compound ions, the ordinary concrete performance drops slower than under single SO\textsubscript{4}\textsuperscript{2−} corrosion, while the mineral admixture concrete shows opposite laws.

4. Conclusions

The metakaolin can greatly improve the mechanical properties of the concrete at the early stage (7–14d curing age); and the silica fume and the ultra-fine fly ash could improve the mechanical properties of the concrete at latter stage by secondary hydration (curing age after 28d).
The mix ratio: 10% metakaolin, 15% ultra-fine fly ash, and 3% silica fume, achieves best activities of the three mineral admixtures all through the whole curing period of the concrete, realizing optimal mechanical properties of concrete.

The mineral admixture concrete is quite resistive to single SO$_4^{2-}$ corrosion. However in practical construction sites, if Mg$^{2+}$, Cl$^{-}$ and SO$_4^{2-}$ exist in the environment at the same time, the adoption of mineral admixture concrete shall be decided based on prudent consideration. It can be known from the micro-analysis that, compared to ordinary concrete, the admixture concrete could produce more corrosion products, such as ettringite, gypsum, magnesium hydroxide, and thaumasite, among which, the increase of M$-$S$-$H is the most significant. Meanwhile at this time, the adixture concrete also show loose and porous micro-structure.

**Data availability statement**

All data that support the findings of this study are included within the article (and any supplementary files).

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