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Effects of Erosion Form and Admixture on Cement Mortar Performances Exposed to Sulfate Environment

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Abstract: The effects of the admixtures, erosion age, concentration of sulfate solution, and erosion form of sulfate attack on the mechanical properties of mortar were investigated. Simultaneously, the microstructure, pore characteristics, kinds and morphologies of erosion products of mortar before and after sulfate attacks were performed by Mercury Intrusion Porosimetry (MIP), Environment Scanning Electronic Microscope and Energy Dispersive Spectrometer (ESEM-EDS). In addition, the crystal form and morphology characteristics of crystallization on mortar surfaces attacked by partial immersion form were studied. The results showed that the compressive and flexural strengths of mortar attacked by sulfate for four months decreased with the increase of the replacement of cement with fly ash, and the corresponding strength of mortar containing slag first increased and then decreased. The admixtures can improve the microstructure and mechanical properties of mortar within the replacement ratio of 10%. Although the change laws of the mortar specimens containing different admixtures were similar, the mortar containing slag had an excellent sulfate resistance under the same condition. Compared with the complete immersion form, the strength variation of the mortar containing fly ash attacked by semi-immersion form was less. The porosity and average pore diameter of mortar attacked by sulfate for four months increased, and the percentage of micropore with the pore diameter less than 200 nm increased. Plenty of rod-like and plate-like erosion products were generated in mortar attacked by a sulfate solution with a high concentration. A larger number of fibrous and flocculent crystallization covered the mortar's surface containing fly ash, but it was a granular and dense crystallization formed on the mortar's surface containing slag. Much dendritic erosion product was generated in the mortar attacked by semi-immersion form, and ESEM-EDS analysis revealed that it may be scawtite, spurrite, and residue of the decomposed calcium silicate hydrate (CSH) in the inner mortar; however, the crystallization sodium sulfate was crystallized on mortar surface.

Keywords: degradation; mechanical properties; mechanisms; diffusion; material properties

1. Introduction

Concrete and mortar are the most commonly used construction materials in civil engineering [1–3]. Many environmental influencing factors affect the performance variation of concrete structures, and the sulfate attack is one of the most important factors in the deterioration of concrete structures [4]. The performance deterioration of cement-based materials is not only because of the expansion effect of sulfate erosion products but also due to the sulfate attack, which causes a reduction in the adhesion forces of the structure by destroying the major cementitious products of the hydrated cement, i.e., calcium aluminate hydrate (CAH), calcium hydroxide (CH), and calcium silicate hydrate (CSH) [5,6]. Therefore, the sulfate attack of cement-based materials is a complex physical and chemical process including crystallization and reaction. The concrete can be treated as the combination of mortar and coarse aggregates, so the performance variation of concrete can be indirectly characterized by the property evolution of the mortar. Sulfate attack can affect the various performance of the mortar, such as strength, length change, long-term behavior, and durability [7–11]. Therefore, it is very significant to investigate the performance variation of the mortar under sulfate environment.

Many studies on sulfate attack of mortar have been conducted which mainly focus on the concentration and kinds of sulfate solution [12,13], mechanical properties and microstructure of mortar [14–16], material composition, and exposure conditions [17]. For example, Aziez et al. [18] investigated the effect of temperature and type of sand on the magnesium sulfate attack in sulfate-resisting cement mortars, and the results indicated that high temperature improved some physical and mechanical properties. Ghafoori et al. [19] discussed the effects of the fineness and tricalcium aluminate (C_3A) content on the sulfate resistance of mortars, and the results showed that microsilica increased sulfate resistance more effectively than nanosilica and increasing cement fineness proved beneficial in combination with either pozzolan regardless of the cement's C_3A content. Kim and Baek [20] studied the weight and strength of cement mortars under sulfate attack, and their results showed that the cement mortar using crushed sand had a good resistance against sulfate compared with river sand. Akpinar and Casanova [21] conducted a combined study of the length-change, tensile strength evolution, and durability of high- and low-C_3A Portland cements, and they proposed a novel approach to assess the performance under severe and moderate sulfate attack. In general, the effective way for protecting mortar from damage of sulfate attacks is to reduce the mortar's permeability or to use mineral admixtures to reduce the amount of CH formed during the cement hydration [22]. Many studies regarding the replacement of mineral admixtures to an amount of cement have been carried out [23–25]. Simultaneously, the effects of mineral admixtures including fly ash, slag, limestone, silica fume, ground bagasse ash, micro-particle additives on the mechanical properties of mortars were investigated [1,26,27]. For example, Ryou et al. [28] represented the relationship of the replacement ratio and limestone on durability of mortar, and the results demonstrated that both the high fineness level and the replacement ratio had a negative effect in resisting sodium sulfate attacks. Chindaprasirt et al. [29] discussed the effect of fly ash fineness on strength, drying shrinkage, and sulfate resistance; they presented that the fly ashes can have a significant improvement in drying shrinkage and resistance to sulfuric acid attack. Marvila et al. [30] studied the replacement of the hydrated lime by kaolinitic clay in mortars, and their results showed that with up to 50 wt.% of the hydrated lime replacement, it was perfectly feasible to fulfil with technological parameters of standards. Markssuel et al. [31] evaluated the durability of mortars with external coating containing incorporation of 0%, 1.5%, 3.0%, and 5% of fiber, the durability results proved that the mortars with 1.5% fiber showed a better behavior than the reference mortar in all situations, including in salt spray attack. Tosun and Kim et al. [32,33] investigated the influence of the admixtures' contents on resistance to sulfate attack, and the results indicated that the low temperature and limestone replacement ratio played a little effect on the sulfate resistance of cement mortars. Lee and Kim [34,35] represented the effects of admixtures including limestone and alpha-calcium sulfate hemihydrate on variation of the setting time, strength, and strain of mortar; their results indicated that the samples incorporating higher replacement levels of limestone filler were more susceptible to sulfate attacks. However, the deterioration modes were significantly dependent on the types of sulfate solutions. Plenty of other studies also showed that nano-silica replacement in the production of cement-based materials results in outstanding performance in terms of improved mechanical properties and durability [36]. In addition, Marvila et al. [37–39] carried out many works on mortar such as preparation of gypsum plaster mortar, eco-friendly mortars, and paper mortar. Although a larger number of the existing achievements regarding influence of partial replacement of cement by admixtures on the mortars' performance were carried out [40], the coupled effects of concentration of sulfate solution, types and contents of admixtures, erosion age and form on the microstructure and mechanical property have not been discussed in detail.

The aim of this study was to evaluate the resistance to sulfate attacks of the mortars with different replacements of cement by admixtures. The effects of concentration of sulfate solution, kinds and contents of admixtures, and erosion age and form of sulfate attack on the mechanical properties of mortars were investigated. In addition, the microstructure, pore characteristic, type, and morphology of erosion products were also studied. The results of this study will be useful in the efficient selection of the admixtures that provide a positive effect on sulfate resistance in mortars and can also provide a theoretical support for the durability assessment of structural engineering under sulfate attack environment.

2. Experimental Procedure

2.1. Raw Materials

Portland cement (PC) of grade P·O 32.5 was purchased from Pingtang Cement Plant of Hunan. Class I fly ash and S95 slag were provided by Hunan Xiangtan power plant and Hunan Lianyuan Steel Group Co., Ltd., respectively. The fineness modulus of ISO standard sand is 3 (Xiamen Aisiou Standard Sand Co., Ltd., Xiamen, China). In addition, the industrial grade sodium sulfate with a purity of 99% was purchased from a local market. Table 1 lists the chemical compositions of the cementitious materials, and Table 2 lists the physical properties of cementitious materials.

Table 1. Chemical compositions of cementitious materials/%.

Items	CaO	SiO_2	Al_2O_3	P_2O_5	Fe_2O_3	MgO	K_2O	Na_2O	Loss
Portland cement	65.61	19.89	4.73	2.88	1.45	2.01	1.14	0.21	1.98
Fly ash	2.52	54.63	26.81	-	6.11	1.12	1.05	0.38	2.53
Slag	35.52	32.41	12.22	0.15	-	-	-	-	1.27

Table 2. Physical properties of cementitious materials.

Items	Average Diameter, μm	Specific Surface Area, (m^2/kg)	Bulk Density, (g/cm^3)	Initial Setting Time, min	Final Setting Time, min	Water Requirement for Standard Consistency, %
Portland cement	34.6	345.2	1.35	172	251	28
Fly ash	41.3	332.7	0.78	-	-	-
Slag	31.7	432.5	1.18	-	-	-

2.2. Experimental Process

According to Chinese standard (GB/T 17671-1999, Method of Testing Cements-Determination of Strength), the mortar specimens of 40 mm × 40 mm × 160 mm were prepared with water:cement:sand ratio of 0.5:1:3 by weight [41]. Fly ash and slag were used as admixture to replace the cement with replacement ratios of 5%, 10%, 15%, 20%, and 30% by weight. The specimens were cured at a temperature of 20 ± 1 °C and a relative humidity of 95% ± 3%. Subsequently, all specimens were demolded after 24 h and cured in saturated lime water for 28 d at a temperature of 20 ± 1 °C. Without special instructions, the control sample (KB) in this study was defined as the mortar specimen cured in a standard condition (i.e., temperature of 20 °C and a relative humidity of 95%) for the same curing age without sulfate attack. Simultaneously, the blank sample was the mortar specimen cured in a standard condition (i.e., temperature of 20 °C and a relative humidity of 95%) for the same curing age without admixtures, termed as KB.

The experimental process of complete immersion form of the mortar attacked by sulfate was conducted as follows. Firstly, the sulfate solutions with different concentrations (i.e., 1%, 5%, 10%, and saturated solution) were prepared. The mortar specimens were immersed in sulfate solution. The distance of mortar specimens was set to be no less than 2 cm to ensure the uniformity of sulfate solution. Secondly, the sulfate solution boxes were all covered with plastic film to prevent the water from evaporation. Moreover, in order to ensure identical concentration, the sulfate solution should be changed once a week. Then, the mortar specimens were taken out from the sulfate solution and placed in air for 3 d at room temperature, when the sulfate erosion age reached the erosion ages of two and four months. Finally, the mechanical properties of mortar were tested. The experimental process of the sulfate attack of the mortar with semi-immersion form was as follow: a half of the mortar specimen was vertically immersed into the sulfate solution, and another half part of the mortar specimen was exposed to air. In order to study the salt crystallization on specimen surface, the specimens attacked by partial immersion form were carried out, that is, the mortar specimen of 1/5 length was immersed into sulfate solution, and the other part of the mortar specimen was exposed to air.

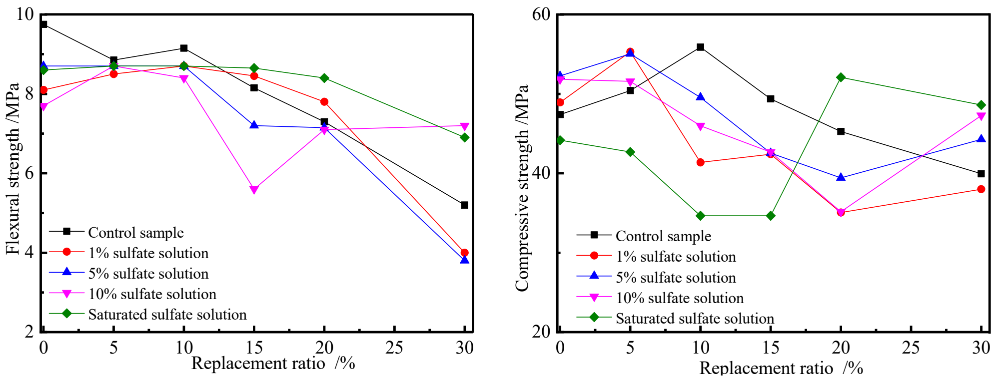
The preparations process of mortar sample for micro properties test was as follows. Firstly, the specimens were broken into particles with sizes of 2~5 mm. Secondly, the broken particles were immersed in alcohol for 24 h to terminate reaction. Then, the broken particles were dried at 60 °C for 48 h. Finally, the processed particles were stored in the dryer. The broken particles were sprayed with gold for Environment Scanning Electronic Microscope and Energy Dispersive Spectrometer (ESEM-EDS) analysis. The samples particles of 3~5 g were weighted and put into sample cells for the Mercury Intrusion Porosimetry (MIP) analysis.

The Quanta-200 Environment Scanning Electronic Microscope and Energy Dispersive Spectrometer (ESEM-EDS) produced by FTI Company from the Czech Republic was used to measure the microstructure. The Autopore-9500 Mercury Intrusion Porosimetry was produced by Microtrac Inc. of USA. Moreover, the YAW-300D produced by Jinan Kesheng Test Equipment Co. Ltd. of China was used to measure the strength of mortar specimens.

3. Results and Discussion

3.1. Effects of Admixture and Erosion Age on Strength of Mortar Attacked by Sulfate

The effects admixtures, concentration of sulfate solution, and erosion age on the strength of the mortar attacked by sulfate were investigated. The compressive and flexural strength of the mortar attacked by the complete immersion form for two months was tested. Figure 1 shows the variation curves of mortar strength with the replacement of cement by fly ash.

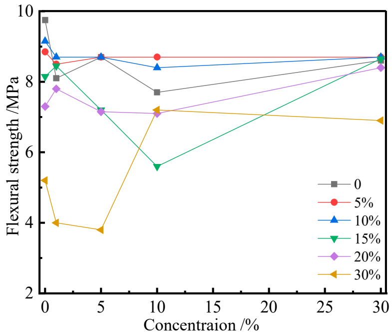


(**a**) Flexural strength (**b**) Compressive strength

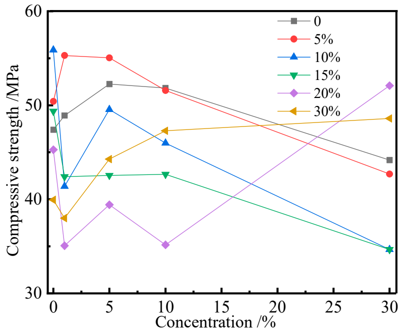
Figure 1. Variation curves of mortar strength with replacement ratios of cement by fly ash exposed to sulfate solution for 2 months.

As seen from Figure 1, the flexural strength of the control sample decreased with the increase of the replacement ratio of cement by fly ash. However, the flexural strength of the mortar specimens containing fly ash attacked by different concentrations of sulfate solutions first increased and then decreased with replacement ratios of cement by fly ash. The compressive strength of the control sample first increased and then decreased, and there existed a maximum value of compressive strength with the replacement ratio of 10%. Although the change laws of the flexural strength of the mortar specimens attacked by different concentrations of sulfate solution were similar, the variation of compressive strengths differed. At a low concentration of sulfate solution (i.e., less than 10%), the compressive and flexural strength of mortar specimens containing fly ash first increased and then decreased with the increase of the replacement ratio. However, the compressive strength of the mortar specimens attacked by saturated sulfate solution first decreased and then increased, and its corresponding value was less than that of the control sample. Hence, the mechanical properties of the mortar reduced with the increase of the replacement ratio. When the fly ash was used as admixture to replace a certain amount of cement in mortars, the effects of fly ash enhancing sulfate the resistance of the mortar were in terms of replacement, pozzolanic, shape, and tiny aggregate [1]. The fly ash was composed of active compositions, such as amorphous silicon oxide and aluminum oxide, which can react with calcium hydroxide (CH) and generate cementitious substances. As a result, the cement matrix became denser, and the mechanical properties of the mortar were enhanced. If there is an overly excessive replacement of cement by fly ash, the fly ash cannot completely react with CH. Thus, the amount of the hydrated products formed by fly ash is less. Therefore, a proper amount of fly ash to cement can improve the microstructure and mechanical properties of mortar specimens. However, the quantity of cementitious hydration products generated in mortar decreases when the cement in mortar was replaced by abundant of fly ash. In general, the main erosion products of sulfate attack were ettringite (AFt), monosulfoaluminate (AFm), gypsum, and salt crystal [42] which have double effects on mortar performance, i.e., positive and negative effects. On the one hand, the expansive erosion products fill in the micropores, reduce the crystallization and orientation of CH, improve the microstructure, and decrease the porosity; so, the sulfate attack had a positive effect on the performance of the mortar. On the other hand, the sulfate attack consumed the amount of CH, reduced the pH value, and decomposed the cementitious hydration products which induced the generation of coarse expansive erosion products and results in the generation of the micro damage and cracks, so it plays a negative effect on the performance of mortar. The variation of the mechanical properties of the mortar exposed to sulfate is a comprehensive result under the coupled effects of sulfate attack and admixture. If there exists a positive effect on the performance of mortar, the mechanical properties and sulfate resistance of mortar are enhanced. Conversely, the various performances of the mortar are reduced.

To discuss the effect of sulfate solution concentration on mechanical properties of the mortar containing fly ash, the strength of mortars attacked by sulfate solution for two months was measured as shown in Figure 2.



(**a**) Flexural strength

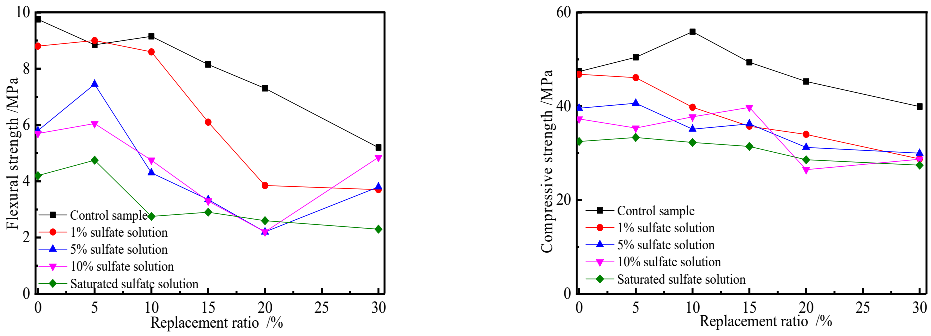


(**b**) Compressive strength

Figure 2. Strength variation of the mortar containing fly ash with sulfate solution concentrations.

With an increase in the concentration of the sulfate solution, the compressive and flexural strength of the mortar with the replacement ratio less than 15% decreased, but the corresponding strength of the mortar with a high replacement increased. The strength of the mortar containing more fly ash attacked by a high concentration of sulfate solution was larger than that of the control sample. This was due to the fact that the active composites of fly ash were activated by a sulfate attack and formed into plenty of expansive products which reduced the porosity and improved the microstructure of the mortar; so, the sulfate attack had a positive effect on the performance of the mortar specimens. Moreover, the filling effect of fly ash can also improve the microstructure of mortar which was proved by Reference [37]. Macroscopically, it expresses as the increase of compressive and flexural strength of mortar. Taking a mortar specimen with a replacement ratio of 30% fly ash as an example, it can be seen that the mechanical properties of the mortar first decreased and then increased with an increase of the concentration of the sulfate solution. The reasons may be as follows. On the one hand, the quantity of cementitious hydration products generated in mortar was reduced when more cement was replaced by fly ash. On the other hand, the sulfate ions of sulfate solution concentration less than 5% reacted with CH and reduced the pH value, which induced the decomposition of hydration products in mortar. Therefore, the mechanical properties of the mortar decreased. With the increase of concentration of the sulfate solution (i.e., 10%), the active compositions of fly ash are activated and generated into hydration products. Simultaneously, more expansive products, such as AFt, AFm, and gypsum are generated in mortar, which can improve the microstructure and consistency of mortar [43]. The sulfate attack and fly ash play a positive role on performance of the mortar, so the corresponding strength of the mortar specimens containing more content of fly ash attacked by a high concentration of sulfate solution increases. In addition, the mortar with a low content of fly ash attacked by low concentration of sulfate solution increases, which is due to the positive coupled effects of sulfate attack.

The erosion age also plays a significant effect on variation of the mortar strength. Taking the mortar specimens containing fly ash attacked by sulfate for four months as an example, the variation of compressive and flexural strength of the mortar with replacement ratio was investigated as shown in Figure 3.

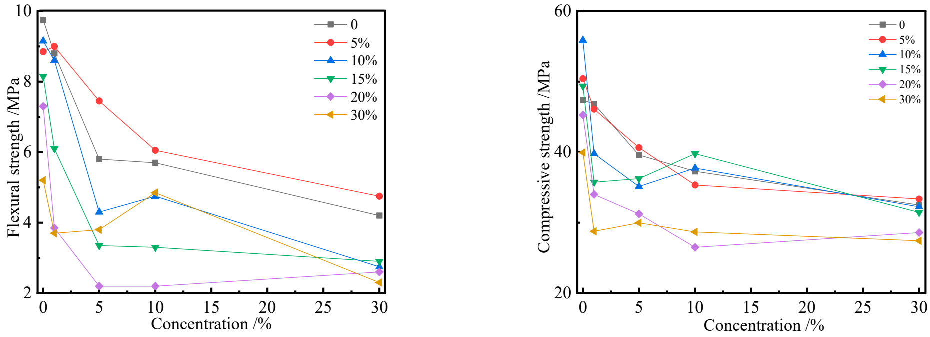


(**a**) Flexural strength (**b**) Compressive strength

Figure 3. Variation of mortar strength with replacement ratios of cement by fly ash.

The compressive and flexural strength of the specimens attacked by sulfate for four months decreased with the increase of the replacement of cement by fly ash, and the corresponding values were less than that of the control sample. With the same replacement of cement by fly ash, the mechanical properties of mortar reduced with increase of concentration of the sulfate solution. Compared with Figure 1, it can be seen that the regularity of strength variation of mortar attacked by sulfate for four months becomes more significant. Although the change laws of the mechanical properties of the mortar are similar, the corresponding percentages and variations are different. Compared with Figures 1 and 3, a conclusion can be drawn that the variation of mortars containing fly ash attacked by sulfate for four months are more significant. This is due to the fact that more and more sulfate ions intrude into mortar with erosion age. Therefore, more expansive products are generated, and plenty of hydration products are decomposed, which result in the damage and micro-cracks in the mortar.

To deeply investigate the effect of sulfate solution concentration on the mechanical properties of the mortar, taking mortar containing fly ash as an example, the variation of the compressive and flexural strength of mortar attacked by sulfate solution for four months was investigated as shown in Figure 4.



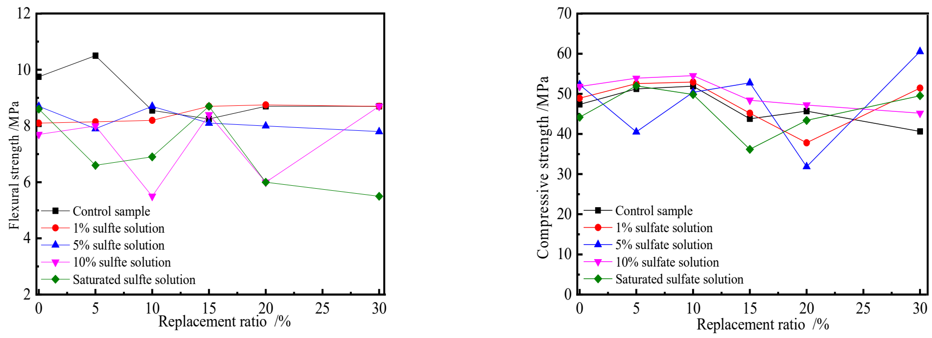
(**a**) Flexural strength (**b**) Compressive strength

Figure 4. Strength variation of the mortar containing fly ash attacked by different concentrations of sulfate solution for four months.

As seen from Figure 4, the compressive and flexural strength of the mortar specimens attacked by sulfate for four months decreased with an increase in the replacement ratio of cement by fly ash. The larger the content of fly ash, the more significant the variation in the strength of the mortar. In comparison with compressive strength, the effect of the sulfate solution concentration on the flexural strength of mortar is more obvious. The compressive strength of the mortar attacked by sulfate was basically the same when the replacement of the cement by fly ash was no more than 15%. Compared with the compressive strength, the variation of the flexural strength of the mortar was more significant. Moreover, the strength of the mortar with a replacement of 5% was better than that of the blank sample. This was due to the fact that the active compositions of fly ash can be activated by CH in the mortar, resulting in the reduction of porosity and improvement of microstructure. Compared with Figure 2, the compressive and flexural strength of the mortar attacked by sulfate for four months obviously decreased, and its regularity of strength variation became more remarkable. That may be related with the coupled effects of sulfate attack and fly ash. When their coupled effects are positive, the compressive and flexural strength of the mortar specimens increase. Conversely, the corresponding strength of mortar decreases.

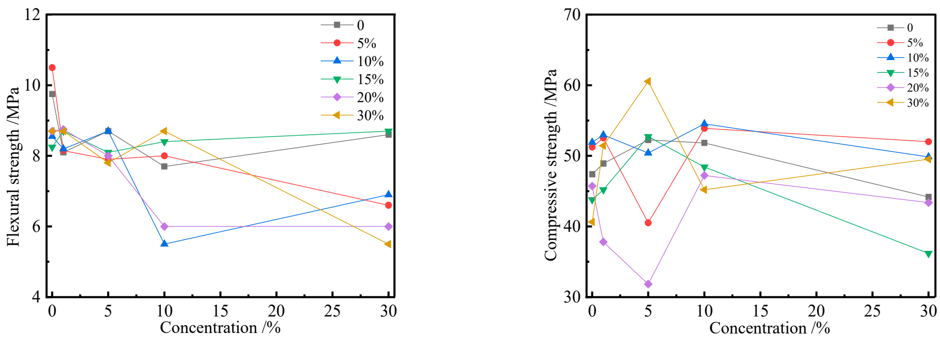
Moreover, the effects of solution concentration, slag content, and erosion age on the strength of mortar were also investigated. Taking the mortar attacked by sulfate for two months as an example, the variation curves of compressive and flexural strength of the mortar with the replacement ratio of cement by slag were plotted in Figure 5. Figure 6 shows the corresponding strength variation curves of the mortar with the concentration of the sulfate solution.

Figure 5 shows that the strength of the control sample decreased with the increase in the replacement of cement by slag. However, the variations of the strength of the mortar attacked by sulfate for two months differed from each other, as follows. The strength of the mortar increased with the increase of slag when the sulfate solution concentration was no more than 5%. Conversely, it decreased when the concentration of sulfate solution was more than 10%. Compared with Figure 1, the mortar had a higher strength and little variation, which revealed the mortar containing slag had an excellent sulfate resistance. The active compositions of slag were mainly calcareous and silicious ingredient, which can be easily activated by CH and generated into cementitious products. Those products can fill in the pores, reduce the porosity, and improve the microstructure of the mortar. Therefore, the strength of the mortar containing slag increased with the increase of slag content. The sulfate ions intrude into mortar and react with CH, which results in the generation of expansive products in the mortar. When the sulfate attack plays a positive effect on properties of mortar, the macro-characteristics of strength of the mortar increases. Conversely, the mechanical properties of the mortar decrease. In addition, there exist significant differences in the strength of the mortar specimens containing different replacement ratios of cement by slag or attacked by different concentrations of sulfate solution. That may be due to the fact that the sulfate attacks and slag content have the coupled effects on the performance of the mortar. The above discussion can be verified by the variation curves of strength of the mortar with different concentrations of sulfate solution for two months as shown in Figure 6.



(**a**) Flexural strength (**b**) Compressive strength

Figure 5. Variation curves of the strength of the mortars with replacement ratios of cement by slag.

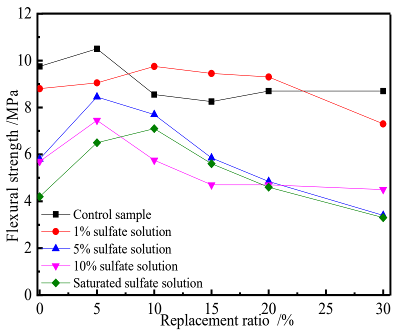


(**a**) Flexural strength (**b**) Compressive strength

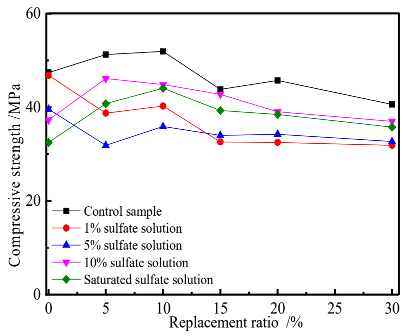
Figure 6. Variation curves of the strength of mortars containing slag attacked by sulfate solutions for two months.

The flexural strength of the blank sample decreased with the increase in the concentration of the sulfate solution, but the corresponding compressive strength first increased and then decreased. The flexural strength of the mortar containing slag decreased with the increase in the concentration of the sulfate solution. Moreover, Figure 6 also indicates that there exists a close relationship between compressive strength and slag content in the mortar attacked by sulfate solution. In addition, the compressive strength of the mortar specimen attacked by 5% sulfate solution differed from others. This was due to the coupled effects of sulfate attack and existence of slag. Compared with Figures 2 and 6, it can be seen that the compressive strength of the mortar containing slag attacked by sulfate for two months was higher which was due to the different active compositions and their sulfate resistance. In general, the slag contains more high-active substances than fly ash. Therefore, the change in the strength of the mortar containing slag was more significant.

To discuss the effect of erosion age on mechanical properties of the mortar containing slag well, the variations of mechanical properties of the mortar attacked by sulfate for four months were investigated as shown in Figure 7.



(**a**) Flexural strength



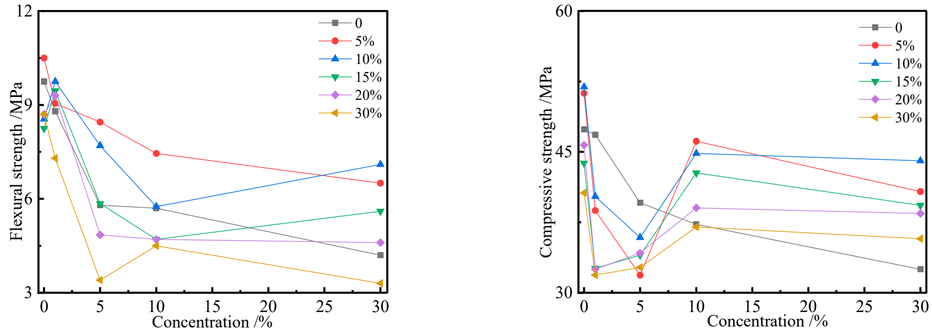
(**b**) Compressive strength

Figure 7. Variation curves of the strength of the mortar with slag content.

As seen from Figure 7, the compressive and flexural strength of the mortar attacked by sulfate for four months first increased and then decreased with the increase of the replacement ratio, and the corresponding strength values were less than that of the control sample. The variation of the flexural strength of the mortar attacked by sulfate was more sensitive. Although the change laws of the strength of the mortar attacked by sulfate were similar, the corresponding variations of the strength were different. There exists a maximum value of the strength of the mortar with a replacement ratio ranging from 5% to 15%. The above results indicate the sulfate solution concentration has a significant effect on the variation of the mortar's mechanical properties. In comparison with Figure 6, it can be seen that the variation of the strength of the mortar attacked by sulfate for four months was more significant and its regularity was better. This may be due to the fact that the sulfate attack plays a negative effect on the performance of the mortar. Compared with the strength variation of the mortar containing fly ash in Figure 3, the corresponding strength of the mortar containing slag was higher. Simultaneously, there exists a difference in the strength of the mortar specimens containing different replacement ratios of cement by slag. The above results indicate that the kinds and content of admixtures have a significant effect on the sulfate resistance of the mortar. Especially, the slag has better sulfate resistance performance than fly ash.

In order to reveal the effect of sulfate solution concentration on strength of the mortar, the variations of the compressive and flexural strengths of the mortar containing slag with concentrations of sulfate solution was investigated. Figure 8 shows the variation curves of the strength of mortar attacked by sulfate for four months.

The flexural strength of the mortar containing slag attacked by sulfate decreased with the increase in the concentration of the sulfate solution, but its compressive strength first decreased and then increased. The solution concentration of 5% had a significant effect on the compressive strength of the mortar specimen containing slag, but the variation of the flexural strength was not obvious. The flexural strength of the mortar specimens was more than that of the blank sample, when the replacement ratio of cement by slag was no more than 10%. The flexural strength variation of mortar became more significant under a high concentration of the sulfate solution. The corresponding compressive strength of mortar was larger than that of the blank sample when the sulfate solution concentration is larger than 10%. The variation of the compressive strength of the mortar becomes more significant with an increase of the sulfate solution concentration. Compared with two months, the strength of the mortar specimens attacked by sulfate for four months decreased obviously. In comparison with the strength variation of mortar containing fly ash in Figure 4, the strength of the mortar containing slag was higher with the same replacement ratio and sulfate solution concentration. The above results imply that the slag had an excellent sulfate resistance which was due to the active composition.

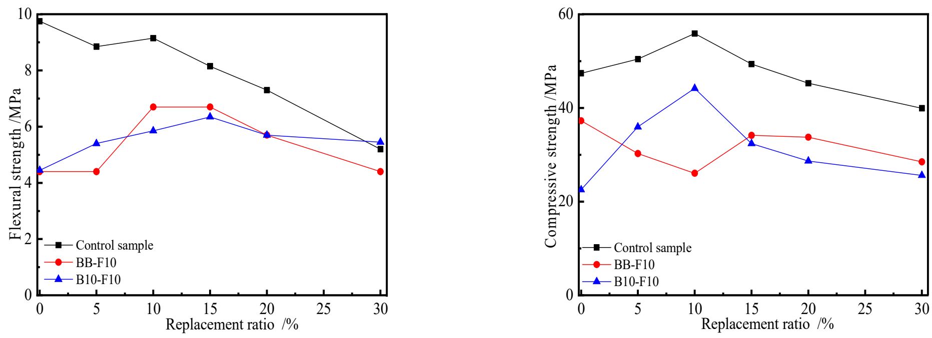


(**a**) Flexural strength (**b**) Compressive strength

Figure 8. Variation curves of the strength of mortar attacked by sulfate for four months with concentrations of sulfate solution.

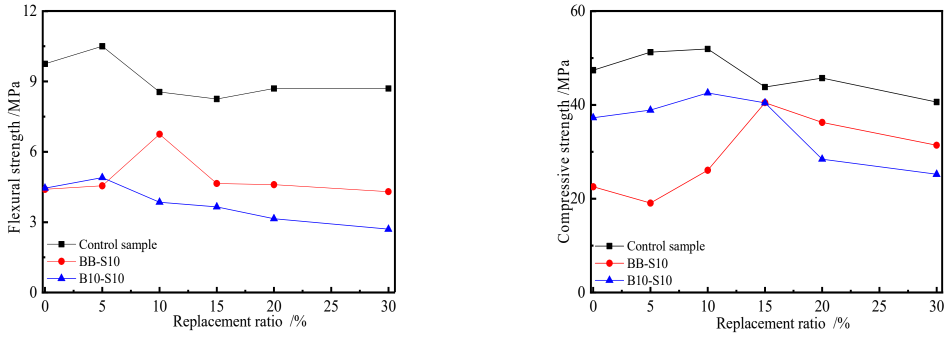
3.2. Effect of Erosion Form of Sulfate Attack on the Strength of the Mortar

The variation of the compressive and flexural strength of the mortar containing different admixtures attacked by semi-immersion form for four months was investigated, and 10% and saturated sulfate solution were used, respectively, to conduct the sulfate attack test. Figures 9 and 10 show the variation curves of the compressive and flexural strength of the mortar with the contents of fly ash and slag, respectively. The code numbers for the specimens mentioned below are explained as follow. Taken B10-F10 in Figure 9a as an example, the front part of letter and number stand for the immersion form (i.e., B is the semi-immersion form, C is the complete immersion from) and concentration of sulfate solution (i.e., the number stands for percentage, S is the saturated sulfate solution). The latter part of letter and number stand for the admixture and its substitute amount (i.e., F is the fly ash, S is the slag). Therefore, B10-F10 means the specimen containing 10% fly ash is attacked by 10% sulfate solution with semi-immersion form.



(**a**) Flexural strength (**b**) Compressive strength

Figure 9. Variation curves of the compressive and flexural strengths of mortar with the replacement of cement with fly ash.

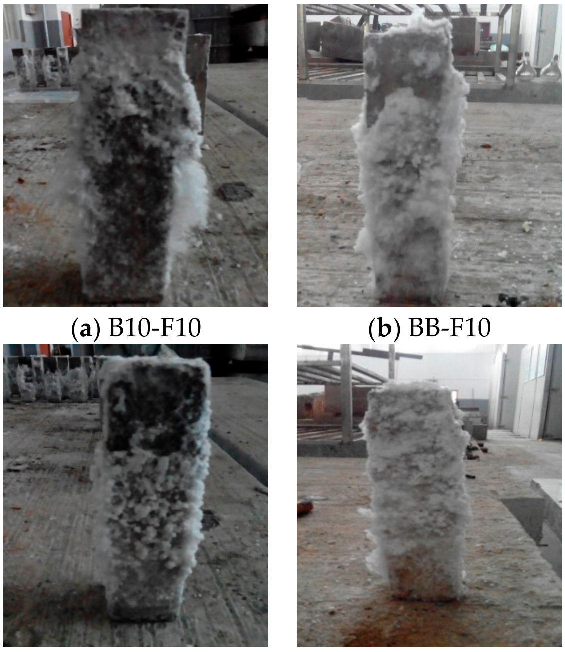


(**a**) Flexural strength (**b**) Compressive strength

Figure 10. Variation curves of the compressive and flexural strength of mortar with the replacement of cement with slag.

As seen from Figure 9, the flexural strength of the control sample decreased with the increase of the replacement of cement by fly ash, but the compressive strength first increased and then decreased. However, the flexural strength of mortar attacked by semi-immersion form for four months first increased and then decreased. There exists a maximum value of strength of the mortar containing fly ash, when the replacement ratio was of 10%. The change laws of the strength of the mortar attacked by different concentrations of sulfate solution were similar, but there also existed differences in terms of variations and percentages. The compressive and flexural strength of the mortar attacked by semi-immersion form were lower than the control sample. Compared with the solution concentration of 10%, the saturated sulfate solution had a more significant effect on the strength of the mortar specimens. Figure 10 also shows that the strength of the mortar attacked by semi-immersion form for four months first increased and then decreased with the increase in the replacement of cement by slag, and the strength value were all less than the control sample. That may be due to the fact that the sulfate attack had a negative effect on the performance of the mortar attacked by sulfate for four months. The compressive strength of the mortar attacked by sulfate increased with the replacement of cement by slag no more than 10%. The concentration of sulfate solution had a different effect on the variation of the strength of the mortar containing slag, that is, the higher the concentration of sulfate solution, the more significant the decrease of the strength. Compared with the variation of the strength of the mortar containing fly ash attacked by completed immersion form (i.e., Figures 3 and 7), the variation of the flexural strength of the mortar attacked by semi-immersion form was less, but the change of the compressive strength was more significant. The above results indicate the erosion form of the sulfate attack had a significant effect on the variation of the strength of the mortar. Under the evaporated and concentrated effects, much crystallized salt occurs on the mortar surface, which can result in the micro damage and cracks in the mortar. Therefore, the mechanical properties of mortar change. The above deduction can be verified by the crystallization on the mortar attacked by semi-immersion form for four months as shown in Figure 11.

Plenty of crystallization was formed on the mortar surface. Especially, more crystallization was observed on the mortar surface attacked by saturated sulfate solution. The morphology of the crystallization on the mortar's surface containing fly ash was fibrous and flocculent, but it was granular and dense salt covering the mortar's surface containing slag. The above results show that the admixture and concentration of sulfate solution had significant effects on the type and morphology of crystal. Compared with the solution concentration of 10%, there were more sulfate ions of saturated solution, so more crystallization was generated and crystallized on the mortar's surface under the effects of evaporation and capillary. The different active compositions of admixtures resulted in the difference of the thermodynamic equilibrium constants for different crystallized salts, so the kinds and morphologies of crystallization were different. The erosion mechanism and deterioration of mortar containing different admixtures differed from each other, so the variation of the mechanical properties and microstructure of the mortar was different. This was due to the fact that the effects of the admixtures and the solution concentrations on the performance of mortar were different.



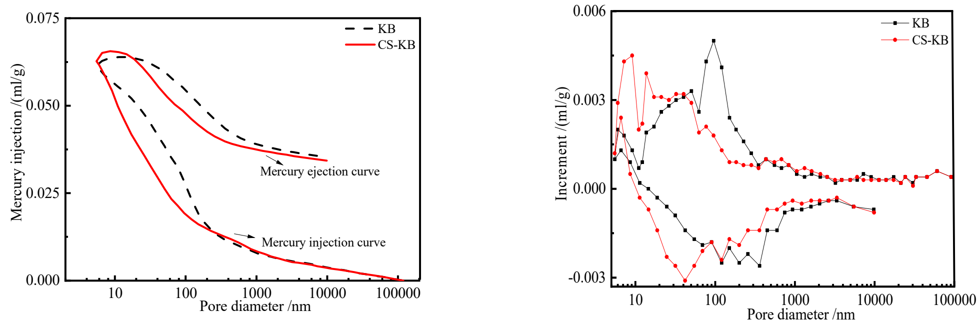
(**a**) B10-F10 (**b**) BB-F10

(**c**) B10-S10 (**d**) BB-S10

Figure 11. Crystallization on the surface of the mortar containing fly ash and slag attacked by semi-immersion form.

3.3. MIP Analysis

The effects of sulfate attack on the microstructure and variations in the pore characteristics of the mortar attacked by saturated solution for four months were studied as shown in Figure 12. Table 1 lists the characteristic parameters and distribution of pores in mortar.



(**a**) Pore characteristic curve (**b**) Pore diameter distribution curves

Figure 12. Curves of pore distribution characteristics of mortar before and after sulfate attack.

Figure 12 illustrates that the changes in the pore characteristics of the mortar before and after the sulfate attack were in terms of the porosity, average pore diameter, and pore distribution. The injection and ejection curves of mercury in Figure 12a show that the percentage of micropores with diameters less than 200 nm in the mortar attacked by sulfate for four months increased. Moreover, the difference between the mercury injection and ejection curves of the mortar attacked by sulfate decreased, which may be due to the erosion products generated by the sulfate attack refining the pores size. Compared with the blank sample, the variation of mercury curves of the mortar attacked by the saturated solution demonstrates that the number of micropores in the mortar increased. However, the variation of pores with a pore size larger than 1000 nm was not significant. The above results are in accordance with the measured data of pores listed in Table 3. The porosity and average pore diameter of mortar attacked by sulfate for four months were 13.24% and 35.1 nm, respectively. Simultaneously, the percentage of micropores in the mortar increased to 69.3%. This is due to the fact that the generated expansive products filled in some larger pores, which resulted in the decrease of the pore size. The increase in the porosity in the mortar was related to the micro damage and cracks caused by the sulfate attack.

Table 3. Characteristic parameters and distribution of pore in mortar.

Items	Porosity, %	Average Pore Diameter, nm	Porosity Distribution, %		
			5–100 nm	100 nm–10 μm	>10 μm
KBSJ	12.78	85.3	54.2	40.1	5.7
4KBSJ	13.24	35.1	69.3	24.7	6.0

To investigate the variation of the pore characteristics of mortar attacked by sulfate in detail, the pore distribution and characteristic curves of the mortar attacked by sulfate for four months were performed as shown in Figure 13.

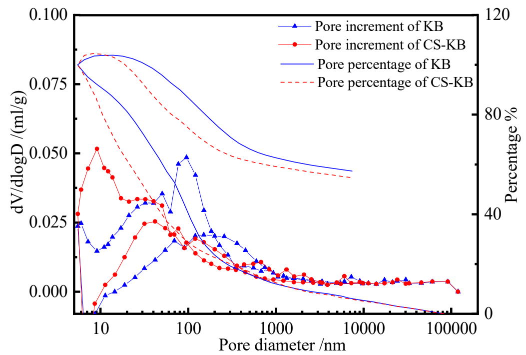
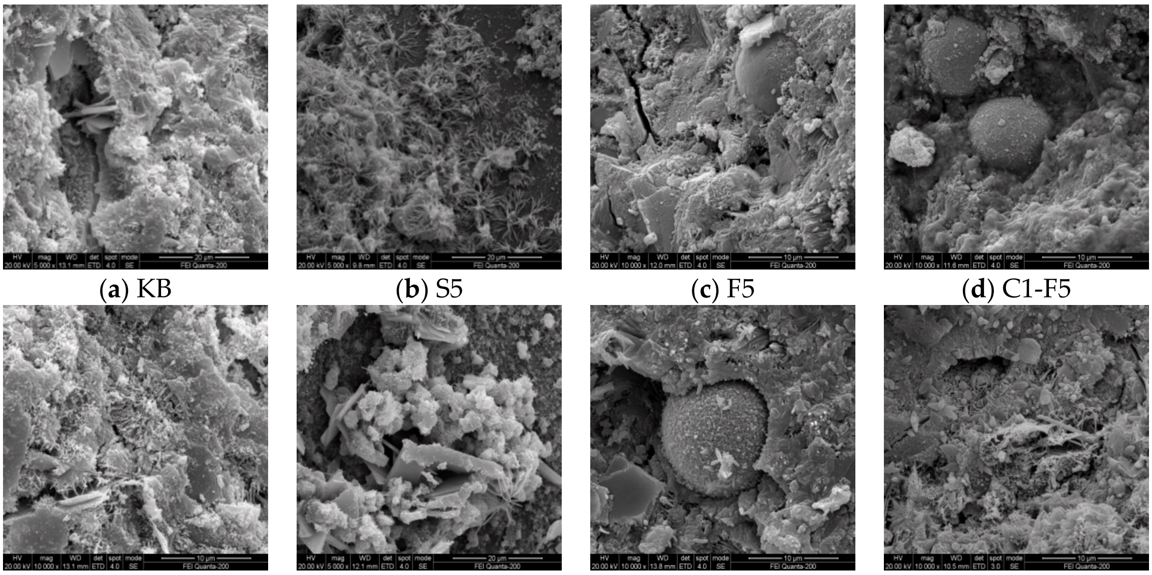


Figure 13. Curves of pore characteristics of mortar before and after sulfate attack.

Figure 13 shows that the porosity and the percentage of micropores with a pore diameter less than 100 nm increased when the mortar specimen was attacked by saturated sulfate solution for four months. Compared with the control sample, the percentage of macropores with a size larger than 200 nm in mortar attacked by saturated sulfate solution increased slightly, and the difference between the mercury injection and ejection curves of the mortar reduced. However, the deviation between the injection and ejection curves of the micropores with diameter less than 100 nm increased, which revealed that the micropores had a trend to translate into an ink bottle. As seen from the increment curves in Figure 13, the variations of the increment curves of the mortar specimens before and after attacked by sulfate are focused in the pore diameter less than 200 nm and 100 nm, respectively. This is due to the fact that the expansive products generated by sulfate attack in mortar fill and refine the pores, which results in the variation of porosity, compactness and crack of the mortar. Therefore, the mechanical properties of mortar specimens change before and after attacked by sulfate.

3.4. ESEM-EDS Analysis

The effects of admixtures and sulfate solution concentration on morphology and compositions of the mortar attacked by sulfate for four months were investigated, and the corresponding ESEM-EDS spectra are shown in Figure 14.



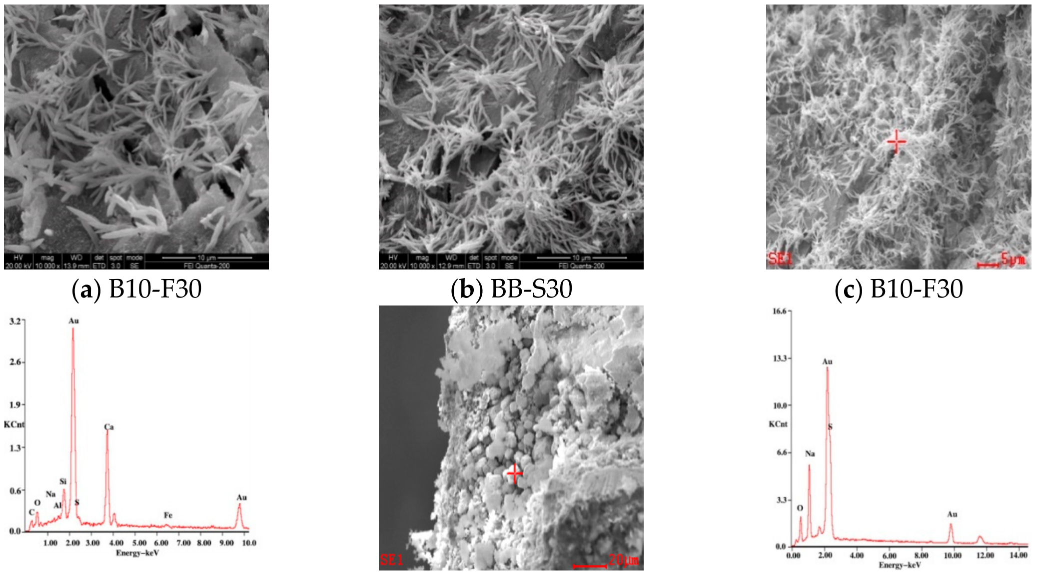
(**a**) KB (**b**) S5 (**c**) F5 (**d**) C1-F5
(**e**) C1-S5 (**f**) CS-S5 (**g**) CS-F10 (**h**) CS-S10

Figure 14. ESEM-EDS spectra of mortar specimens.

The microstructure variations of the mortar containing admixtures before and after being attacked by sulfate were expressed as the compactness of microstructure, erosion products, and characteristic of pores [44] as shown in Figure 14. The major hydration products of the blank sample are a hexagonal plate CH and flocculent CAH, and some macropores can also be observed as shown in Figure 14a. The mortar containing admixtures had a more compact microstructure, less porosity, and a larger number of fibrous and flocculent hydration products as shown in Figure 14b,c. This is due to the fact that the admixtures can be activated by CH and formed into more cementitious substances. There exist differences in the microstructure of the mortar containing fly ash and slag, which is because of the difference of the active compositions and their chemical elements. Therefore, an appropriate number of admixtures added into mortar can enhance the microstructure and performances of mortar [45], which also accords well with the results in Figures 1 and 5. This is due to the fact that the actives substances of admixtures can react with CH and generate hydration products, so the microstructure and compactness of mortar are enhanced. The sulfate solution concentration plays a significant effect on microstructure, pore characteristics, erosion products. The microstructure of the mortar containing admixtures attacked by low sulfate solution concentration becomes denser, as shown in Figure 14d,e. Moreover, the fly ash particles eroded by CH can also be observed as shown in Figure 14d,g. There are plenty of rod-like and plate-like products generated by a high concentration of sulfate solution which may be considered as AFt, AFm, and gypsum based on their morphology characteristics. In addition, the replacement ratio of cement with slag also has a significant effect on erosion products as shown in Figure 14f,h.

The effect of erosion on the microstructure and morphology of mortar was studied, and the corresponding ESEM-EDS spectra of the mortar attacked by semi-immersion form for four months are shown in Figure 15.

The characteristics of microstructure and erosion products of the mortar containing admixtures were similar, and plenty of dendritic and rod-like products generated could be observed. Moreover, there were little CH and CAH. Compared with fly ash, the size of dendritic products generated by the sulfate attack in the mortar containing slag was smaller as shown in Figure 15a,b. The above morphology of erosion products in the mortar attacked by semi-immersion form differed from that of the mortar attacked by complete immersion form as shown in Figure 14. The EDS analysis showed that the major elements of dendritic products were Ca, Si, C, and O as shown in Figure 15c. Based on the morphology characteristics and composition elements, the dendritic products may be scawtite ($Ca_7(Si_6O_{18})(CO_3){\cdot}2H_2O$), spurrite ($Ca_5(SiO_4)_2(CO_3)$), and residue of decomposed CSH [46]. Simultaneously, plenty of crystallizations were formed on the mortar surface as shown in Figure 15e. The EDS analysis showed that the major elements of the crystallization were Na, S, and O as shown in Figure 15f. So. the crystallization may be sodium sulfate. Comparing with Figures 14 and 15, a conclusion can be drawn that the erosion form of sulfate attack affects the kinds and morphology of erosion products in the mortar.



(**a**) B10-F30 (**b**) BB-S30 (**c**) B10-F30

(**d**) EDS of B10-F30 (**e**) Crystallization on mortar surface (**f**) EDS of crystallization

Figure 15. ESEM-EDS spectra of mortar containing different admixtures attacked by different erosion forms.

4. Conclusions

(1) The effects of the admixtures, erosion age, concentration of sulfate solution, and erosion form on the mechanical properties of mortar were investigated. The results showed that the compressive and flexural strengths of the mortar specimens attacked by sulfate for four months decreased with the increase of the replacement of cement by fly ash. However, the strength of the mortar containing slag first increased and then decreased with the increase of the replacement of cement by slag. Although the change laws of the mortar specimens containing different kinds and contents of admixtures were similar, the strength variations and percentages of the mortar specimens were different. Compared with fly ash, the mortar containing slag had an excellent sulfate resistance under the same condition. The variation and regularity of the strength become more significant with the erosion age. An appropriate replacement of cement by admixtures can improve the mortar's microstructure and performances.

(2) The pore characteristics of the mortar, such as porosity and average pore diameter, were changed obviously after sulfate attack. The porosity and average pore diameter of the mortar specimen attacked by sulfate for four months increased, and the percentage of micropores with a pore diameter less than 200 nm increased. The mortar's microstructure became denser under a low concentration of sulfate solution, and there were plenty of plate-like and rod-like products in the mortar attacked by a high concentration of sulfate solution.

(3) The erosion form of sulfate attack played a significant effect on the erosion products and crystallization. The higher the concentration of the sulfate solution, the more crystallization on the mortar surface. Plenty of fibrous and flocculent crystallization were formed on the surface of the mortar containing fly ash, but they were the granular and dense crystallizations formed on the surface of mortar containing slag. Plenty of dendritic and rod-like products can be observed in the mortar containing admixtures attacked by semi-immersion form. The ESEM-EDS revealed that it may be

scawtite, spurrite, and residue of the decomposed CSH; however, the crystallization on the mortar specimen was mostly sodium sulfate.

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References

1. Arel, H.S.; Thomas, B.S. The effects of nano- and micro-particle additives on the durability and mechanical properties of mortars exposed to internal and external sulfate attacks. *Results Phys.* **2017**, *7*, 843–851. [CrossRef]
2. Azevedo, A.R.G.; Cecchin, D.; Carmo, D.F.; Silva, F.C.; Campos, C.M.O.; Shtrucka, T.G.; Marvila, M.T.; Monteiro, S.N. Analysis of the compactness and properties of the hardened state of mortars with recycling of construction and demolition waste (CDW). *J. Mater. Res. Technol.* **2020**, *9*, 5942–5952. [CrossRef]
3. Zanelato, E.B.; Alexandre, J.; de Azevedo, A.R.G.; Marvila, M.T. Evaluation of roughcast on the adhesion mechanisms of mortars on ceramic substrates. *Mater. Struct.* **2019**, *52*, 53. [CrossRef]
4. Jiang, L.; Niu, D.; Yuan, L.; Fei, Q. Durability of concrete under sulfate attack exposed to freeze-thaw cycles. *Cold Reg. Sci. Technol.* **2015**, *112*, 112–117. [CrossRef]
5. Grengg, C.; Mittermayr, F.; Baldermann, A.; Bottcher, M.E.; Leis, A.; Koraimann, G.; Grunert, P.; Dietzel, M. Microbiologically induced concrete corrosion: A case study from a combined sewer network. *Cem. Concr. Res.* **2015**, *77*, 16–25. [CrossRef]
6. Cohen, M.D.; Mather, B. Sulfate attack on concrete: Research needs. *ACI Mater. J.* **1991**, *88*, 62–69.
7. Tanyildizi, H. Prediction of compressive strength of lightweight mortar exposed to sulfate attack. *Comput. Concr.* **2017**, *19*, 217–226. [CrossRef]
8. Kilinc, K.; Uyan, M.; Arioz, O. Effects of sulfates on strength of Portland cement mortars. In Proceedings of the 15th International Offshore and Polar Engineering Conference (ISOPE 2005), Seoul, Korea, 19–24 June 2005.
9. Kim, M.S.; Baek, D.I.; Cho, K.S. Evaluation on basic properties of crushed sand mortar in freezing-thawing and sulfate attack. *J. Ocean. Eng. Technol.* **2009**, *23*, 54–60.
10. Skaropoulou, A.; Tsivilis, S.; Kakali, G.; Sharp, J.H.; Swamy, R.N. Long term behavior of Portland limestone cement mortars exposed to magnesium sulfate attack. *Cem. Concr. Compos.* **2009**, *31*, 628–636. [CrossRef]
11. Makhloufi, Z.; Aggoun, S.; Benabed, B.; Kadri, E.H.; Bederina, M. Effect of magnesium sulfate on the durability of limestone mortars based on quaternary blended cements. *Cem. Concr. Compos.* **2016**, *65*, 186–199. [CrossRef]
12. Senhadji, Y.; Mouli, M.; Escadeillas, G.; Khelafi, A.; Bennosman, A.S.; Chihaoui, R. Behavior of limestone filler cement mortars exposed to magnesium sulfate attack. In Proceedings of the International Congress on Materials & Structural Stability, Rabat, Morocco, 26–30 November 2013.
13. Lee, S.-T. Performance of mortars exposed to different sulfate concentrations. *KSCE J. Civ. Eng.* **2012**, *16*, 601–609. [CrossRef]
14. Tanyildizi, H. The investigation of microstructure and strength properties of lightweight mortar containing mineral admixtures exposed to sulfate attack. *Measurement* **2016**, *77*, 143–154. [CrossRef]
15. Binici, H.; Arocena, J.; Kapur, S.; Aksogan, O.; Kaplan, H. Microstructure of red brick dust and ground basaltic pumice blended cement mortars exposed to magnesium sulphate solutions. *Can. J. Civ. Eng.* **2009**, *36*, 1784–1793. [CrossRef]
16. Zhang, M.H.; Jiang, M.Q.; Chen, J.K. Variation of flexural strength of cement mortar attacked by sulfate ions. *Eng. Fract. Mech.* **2008**, *75*, 4948–4957. [CrossRef]
17. Lee, S.T. Evaluation on the sulfate attack resistance of cement mortars with different exposure conditions. *J. Korean Soc. Civ. Eng. A* **2012**, *32*, 427–435.

18. Aziez, M.N.; Bezzar, A. Effect of temperature and type of sand on the magnesium sulphate attack in sulphate resisting Portland cement mortars. *J. Adhes. Sci. Technol.* **2018**, *32*, 272–290. [CrossRef]
19. Ghafoori, N.; Batilov, I.; Najimi, M. Effects of blaine and tricalcium aluminate on the sulfate resistance of nanosilica-containing mortars. *J. Mater. Civ. Eng.* **2018**, *30*, 1–13. [CrossRef]
20. Kim, M.S.; Baek, D.I. Unit weight and compressive strength of cement mortars using crushed sand under sulfate attacks. *J. Korean Soc. Civ. Eng. A* **2007**, *27*, 585–591.
21. Akpinar, P.; Casanova, I. A combined study of expansive and tensile strength evolution of mortars under sulfate attack: Implications on durability assessment. *Mater. Constr.* **2010**, *60*, 59–68. [CrossRef]
22. Idiart, A.E.; Lopez, C.M.; Carol, I. Chemo–mechanical analysis of concrete cracking and degradation due to external sulfate attack: A meso–scale model. *Cem. Concr. Compos.* **2011**, *33*, 411–423. [CrossRef]
23. Huang, Q.; Wang, C.; Luo, C.Q.; Yang, C.H.; Luo, Y.L.; Xie, H. Effect of mineral admixtures on sulfate resistance of mortars under electrical field. *Adv. Cem. Res.* **2017**, *29*, 45–53. [CrossRef]
24. Lee, S.T.; Hooton, R.D. Influence of limestone addition on the performance of cement mortars and pastes exposed to a cold sodium sulfate solution. *J. Test. Eval.* **2016**, *44*, 414–423. [CrossRef]
25. Niu, Q.L.; Feng, N.Q. Effect of different mineral admixtures on sulfate attack to mortars. *Key Eng. Mater.* **2009**, *405*, 278–285. [CrossRef]
26. Hossack, A.M.; Thomas, M.D.A. Varying fly ash and slag contents in Portland limestone cement mortars exposed to external sulfates. *Constr. Build. Mater.* **2015**, *78*, 333–341. [CrossRef]
27. Chusilp, N.C.; Chai, J.; Kraiwood, K. Effects of LOI of ground bagasse ash on the compressive strength and sulfate resistance of mortars. *Constr. Build. Mater.* **2009**, *23*, 3523–3531. [CrossRef]
28. Ryou, J.; Lee, S.; Park, D.; Kim, S.; Jung, H. Durability of cement mortars incorporating limestone filler exposed to sodium sulfate solution. *KSCE J. Civ. Eng.* **2015**, *19*, 1347–1358. [CrossRef]
29. Chindaprasirt, P.; Homwuttiwong, S.; Sirivivatnanon, V. Influence of fly ash fineness on strength, drying shrinkage and sulfate resistance of blended cement mortar. *Cem. Concr. Res.* **2004**, *34*, 1087–1092. [CrossRef]
30. Marvila, M.T.; Alexandre, J.; Azevedo, A.R.G.; Zanelato, E.B.; Xavier, G.C.; Monteiro, S.N. Study on the replacement of the hydrated lime by kaolinitic clay in mortars. *Adv. Appl. Ceram.* **2019**, *118*, 373–380. [CrossRef]
31. Markssuel, T.M.; Afonso, R.G.A.; Daiane, C.; Jonatas, M.C.; Gustavo, C.X.; Dirlanede, F.C.; Sergio, N.M. Durability of coating mortars containing acai fibers. *Case Stud. Constr Mater.* **2020**, *13*, 00406.
32. Tosun, K.; Felekoglu, B.; Baradan, B.; Altun, I.A. Effects of limestone replacement ratio on the sulfate resistance of Portland limestone cement mortars exposed to extraordinary high sulfate concentrations. *Constr Build. Mater.* **2009**, *23*, 2534–2544. [CrossRef]
33. Kim, Y.S. Effects of pozzolanic admixture replacement ratio in ternary mortar on the sulfate attack resistance. *J. Arch. Inst. Korea Struct. Constr.* **2005**, *21*, 89–96.
34. Lee, S.T.; Hooton, R.D.; Jung, H.S.; Park, D.H.; Choi, C.S. Effect of limestone filler on the deterioration of mortars and pastes exposed to sulfate solutions at ambient temperature. *Cem. Concr. Res.* **2008**, *38*, 68–76. [CrossRef]
35. Lee, B.; Kim, G.; Nam, J.; Lee, K.; Kim, G.; Lee, S.; Shin, K.; Koyama, T. Influence of alpha-calcium sulfate hemihydrate on setting, compressive strength, and shrinkage strain of cement mortar. *Materials* **2019**, *12*, 163.
36. Said, A.M.; Zeidan, M.S.; Bassuoni, M.T.; Tian, Y. Properties of concrete incorporating nano-silica. *Constr. Build. Mater.* **2012**, *36*, 838–844. [CrossRef]
37. Marvila, M.T.; Azevedo, A.R.G.; Barroso, L.S.; Barbosa, M.Z.; de Brito, J. Gypsum plaster using rock waste: A proposal to repair the renderings of historical buildings in Brazil. *Constr. Build. Mater.* **2020**, *250*, 118786. [CrossRef]
38. Azevedo, A.R.G.; Alexandre, J.; Marvila, M.T.; Xavier, G.D.; Monteiro, S.N.; Pedroti, L.G. Technological and environmental comparative of the processing of primary sludge waste from paper industry for mortar. *J. Clean. Prod.* **2020**, 119336. [CrossRef]
39. Amaral, L.F.; Delaqua, G.C.G.; Nicolite, M.; Marvila, M.T.; de Azevedo, A.R.G.; Alexandre, J.; Vieira, C.M.F.; Monteiro, S.N. Eco-friendly mortars with addition of ornamental stone waste-A mathematical model approach for granulometric optimization. *J. Clean. Prod.* **2020**, *248*, 119283. [CrossRef]
40. Ghrici, M.; Kenai, S.; Said, M.M. Mechanical properties and durability of mortar and concrete containing natural pozzolan and limestone blended cements. *Cem. Concr. Compos.* **2007**, *29*, 542–549. [CrossRef]

41. State Bureau of Quality Technical Supervision. *Method of Testing Cements-Determination of Strength, GB/T 17671–1999*; China Standard Press: Beijing, China, 1999.
42. Mehta, P.K. Mechanism of sulfate attack on Portland cement concrete—Another look. *Cem. Concr. Res.* **1983**, *13*, 401–406. [CrossRef]
43. Liu, P.; Chen, Y.; Wang, W.L.; Yu, Z.W. Effect of physical and chemical sulfate attack on performance degradation of concrete under different conditions. *Chem. Phys. Lett.* **2020**, *745*, 137254. [CrossRef]
44. Skaropoulou, A.; Tsivilis, S.; Kakali, G.; Sharp, J.H.; Swamy, R.N. Thaumasite form of sulfate attack in limestone cement mortars: A study on long term efficiency of mineral admixtures. *Constr. Build. Mater.* **2009**, *23*, 2338–2345. [CrossRef]
45. Liu, T.J.; Qin, S.S.; Zou, D.J.; Song, W. Experimental investigation on the durability performances of concrete using cathode ray tube glass as fine aggregate under chloride ion penetration of sulfate attack. *Constr Build. Mater.* **2018**, *163*, 634–642. [CrossRef]
46. Zhang, Y.Q.; Radha, A.V.; Navrotsky, A. Thermochemistry of two calcium silicate carbonate minerals: Scawtite, $Ca_7(Si_6O_{18})(CO_3)\cdot 2H_2O$, and spurrite, $Ca_5(SiO_4)_2(CO_3)$. *Geochim. Cosmochim. Acta* **2013**, *115*, 92–99. [CrossRef]