

The Effect of Mg^{2+} on the Solidification of Chloride Ions in Portland Cement Paste

An Guo, Xuemao Guan*, Yifan Li, Songhui Liu

School of Materials and Science Engineering, Henan Jiaozuo 45400, Henan Polytechnic University, China

* Corresponding author: guanxuemao@hpu.edu.com

Abstract: In order to investigate the mechanism of the effect of Mg^{2+} on the solidification of chloride ions in hardened Portland cement slurry, a NaCl- $MgCl_2$ composite solution was used to soak and corrode the hardened Portland cement slurry. Under the condition of fixed total chloride ion concentration of 0.6mol/L, the effects of Mg^{2+} concentration (0.1mol/L, 0.2mol/L, 0.3mol/L) and soaking time in environmental solutions on Friedel salt production, leaching Ca^{2+} ion concentration, and leaching of hardened Portland cement were studied. The influence law of pH value and other properties in erosive environments. The results showed that in the early stage of immersion erosion, Mg^{2+} had little effect on the rate of pH increase of the erosion solution; After the pH value of the solution stabilizes, the final pH value of the solution decreases with the increase of Mg^{2+} concentration; As the concentration of Mg^{2+} in the erosion solution increases, Mg^{2+} promotes the dissolution of hydration product $Ca(OH)_2$ and the dissolution of Ca^{2+} , while generating $Mg(OH)_2$ precipitates, resulting in a decrease in solution alkalinity and an increase in the amount of chloride ions solidified; When the pH of the solution exceeds 12.1, a lower pH value will promote the formation of Friedel salts; When the pH of the solution is less than 12.1, higher concentrations of Mg^{2+} cause Friedel salt to decompose.

Keywords: NaCl- $MgCl_2$, Friedel salt, Chloride ion solidification, Tidal zone, Erosion reaction.

1. Introduction

Concrete has become the largest and most important engineering material in the 21st century, and it is widely used in various marine infrastructure construction. At present, marine engineering construction is in a new stage of development, and a large number of marine buildings are needed for national key strategies and maritime powers. However, in the marine environment, due to tides and other complex factors, the high content of inorganic salts leads to severe structural corrosion, especially the damage caused by chloride ion corrosion, which has a serious impact on the service life of building structures[1]. In order to gain a deeper understanding of the mechanism by which chloride ions penetrate concrete and cause deterioration of reinforced concrete, we divided the total chloride ions in the solution into chloride ions that combine with free chloride ions[2]. Free chloride ions refer to chloride ions that exist in pore solutions and can migrate within cement slurry. Combined chloride ions refer to chloride ions adsorbed on the surface of hydration products or chemically combined with hydration products[3]. Free chloride ions can move freely in cement slurry, and the combined chloride ions can be regarded as fixed chloride ions that can be released when the surrounding environment changes. Under normal circumstances, concrete buildings in marine environments are subject to erosion and destruction by various ions in seawater, including common corrosive ions such as Cl^- and Mg^{2+} . Concrete will be subject to the erosion of multiple ions, which will accelerate the entry of chloride ions into the concrete and lead to the corrosion of steel bars. The cement paste in the concrete can solidify chloride ions to generate Friedel salts, which can reduce the degree of erosion damage of reinforced concrete to a certain extent. Therefore, it is very meaningful to study the chloride ions solidified in concrete. At present, some studies on the solidification of chloride ions in cement slurry both domestically and internationally have found that the types of

chloride cations have a significant impact on the solidification of chloride ions in cement slurry. Zhu[5] studied the chloride ion content in concrete with different water binder ratios and found that in different types of chloride ion solutions, the ability to solidify chloride ions was in the order of $C_b(CaCl_2) > C_b(MgCl_2) > C_b(KCl) \approx C_b(NaCl)$. Tritthart's[6] study showed that the decrease in OH^- concentration in the pore solution of cement slurry immersed in $CaCl_2$ and $MgCl_2$ erosive solutions is due to the formation of $Ca(OH)_2$ and $Mg(OH)_2$ precipitates. In addition, it is found that the OH^- concentration of pore solution is inversely proportional to the chloride ion binding capacity of cement slurry, which indicates that the competitive adsorption between Cl^- and OH^- affects the chloride ion binding. B. Reddy[7] studied the effect of pH value on solidified chloride ions and believed that as pH value decreased, some of the bound chloride ions would be released. Cheng[8] found that Mg^{2+} in Portland cement mortar has a certain blocking effect on the chloride diffusion rate. The presence of Mg^{2+} reduces the pH value, and the decalcification dissolution of C-S-H gel greatly increases the chloride diffusion rate. The above related studies mainly considered the effects of some ions and pH changes on the solidification of chloride ions in cement slurry. Given that the concentration of Mg^{2+} significantly increases in tidal environments, the mechanism by which its concentration affects the solidification behavior of chloride ions in cement slurry is still unclear. Therefore, based on the above issues, this study conducted a study on the regularity of Mg^{2+} on cement solidification chloride ions in tidal environments.

2. Test

2.1. Raw materials

The experimental materials were fly ash (FA) produced by Gongyi Longze Water Purification Materials Co., Ltd. and ground granulated blast furnace slag (GGBS) produced by Gongyi Longze Water Purification Materials Co, Ltd. The

Portland cement used in the experiment was produced by Jiaozuo Qianye Cement Co, Ltd. Its chemical composition and physical and mechanical properties are shown in Tables 1 and 2. The mineral composition and content of Portland cement are shown in Table 3. The chemical composition of fly ash and mineral powder is shown in Figure 4. Fly ash is

industrial solid waste discharged from fossil-fuel power station, which has micro aggregate effect and chemical activity effect. Mineral powder is a powder material obtained by grinding the slag discharged from an ironmaking blast furnace after quenching and quenching with water. The design of cement paste mix proportion is shown in Table 5.

Table 1. Chemical Composition of Portland Cement (wt.%)

Oxide	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	f-CaO	Cl ⁻	LOI
Content	21.192	5.03	3.38	63.32	2.01	2.06	0.55	0.68	0.018	1.76

Table 2. Physical Properties of Portland Cement

Fineness(0.08/%)	Density(g/cm ³)	Specific surface area(m ² /Kg)	Standard consistency(%)	setting time(min)	
				Initial setting	Final set
0.4	3.12	354	24.60	95	155

Table 3. Mineral Composition Content of Portland Cement (wt.%)

Mineral	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	other
Content	57.55	17.82	7.54	11.19	5.9

Table 4. Chemical composition of fly ash and blast furnace slag (data presented by mass %)

Mineral	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	MgO	Na ₂ O	LOI
FA	7.26	50.26	33.14	4.16	2.16	0.23	0.45	2.34
GGBS	34.00	36.56	17.70	1.03	1.64	8.01	0.22	0.84

2.2. Specimen Forming and Curing

In order to eliminate the impact of aggregate interface on erosion, this article uses the GB/T1346-2011 "Cement Standard Viscosity Water Consumption, Setting Time, and Stability Testing Method" standard to prepare clean slurry test blocks with a water cement ratio of 0.4 as the research object. The formed slurry is demolded and cured in saturated lime water for 28 days. The hardened cement slurry cured for 28 days is broken into cement powder with a particle size of 200 mesh, and the obtained samples are placed in a vacuum drying oven at 40°C for 3 days. Finally, immerse the dried sample in

an erosion solution in a constant temperature chamber, with a solid-liquid mass ratio of 1:20. In order to simulate the ion concentration in the tidal zone environment and accelerate the testing process, the Cl⁻ concentration in the erosion solution was fixed at 0.6mol/L. Choose three concentration gradients for Mg²⁺ concentration: 0.1mol/L, 0.2mol/L, and 0.3mol/L. A detailed combination of erosion solutions is shown in Tables 5. A total of four sets of erosion solution environments were designed to study the erosion damage mechanism of cement slurry under the coupling effect of different concentrations of Cl⁻ such as Mg²⁺.

Table 5. Design and Combination of Corrosion Solutions

Concentration of exposed solutions	Chloride ion (mol/L)	Magnesium ion (mol/L)	Abbreviation
0.6mol/L NaCl	0.6	-	0.6NC
0.4mol/L NaCl+0.1mol/L MgCl ₂	0.6	0.1	0.4NC-0.1MC
0.2mol/L NaCl+0.2mol/L MgCl ₂	0.6	0.2	0.2NC-0.2MC
0.0mol/L NaCl+0.3mol/L MgCl ₂	0.6	0.3	0.0NC-0.3MC

2.3. Test methods

Use a pH meter to measure the pH value of each erosion solution at different immersion times. Before each use, the pH electrode is washed with deionized water and placed in the solution to be measured. At the same time, the solution is stirred gently with a glass rod. After the value is stable, the observed value is recorded. 0.22 passed before the test μ After filtering with the m filter membrane, 1mL of erosion solution and 9mL of dilute nitric acid solution with a mass fraction of 2% were added and mixed evenly. The solution was analyzed using spectral Arcos ICP-OES in semi quantitative analysis mode, and the concentration of Ca²⁺ was detected within the calibration range. Thermogravimetric analysis: Place the

soaked sample in a 40°C vacuum drying oven for 3 days, and use the HCT-3 microcomputer differential thermal balance produced by Beijing Science Instrument Factory to test and analyze the prepared sample. The temperature range for testing is 25~500°C, and the heating rate is 10°C/min. X-ray diffraction analysis: The X-ray diffractometer produced by Dandong Haoyuan Co., Ltd., manufactured in China, was used for testing and analysis, and the obtained samples were characterized for phase composition. Cu target and K were used in the experiment α Radiation, tube voltage 40KV, tube current 150mA, scanning area 5-70°, scanning speed 5°/min.

3. Results and Discussion

3.1. The effect of Mg²⁺ on the solidification of Cl⁻ in cement slurry

3.1.1. XRD analysis

Figure 1 shows the partial phase composition of cement slurry in four different Mg²⁺ concentration erosion solutions. Under pure NaCl corrosion environment, the composition of cement hydrate phase mainly includes Ca(OH)₂ and Friedel salt crystals, with characteristic peaks of Ca(OH)₂ at 18.0°, 34.1°, and 45.5°, respectively; The characteristic peak of Friedel is 11.2°. In the NaCl MgCl₂ erosive environment, in addition to Friedel salt and Ca(OH)₂ crystals, Mg(OH)₂ was also found, with characteristic peaks at 18.5° and 37.9°. At the same time, it was also found that with the appearance of the diffraction peak of magnesium hydroxide crystal, Ca(OH)₂ disappeared from the 18.0° diffraction peak, indicating that the generation of Mg(OH)₂ consumed a portion of Ca(OH)₂ in the solution.

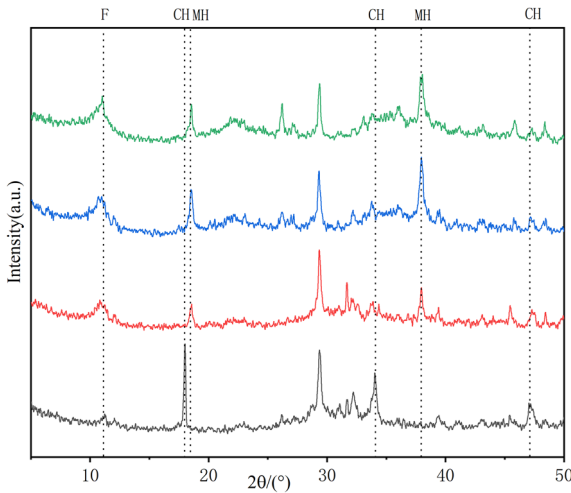


Figure 1. XRD diagram of cement slurry after soaking four erosion environments for 7 days

3.1.2. Thermogravimetric analysis

According to Figure 2, thermal analysis shows the phase composition of cement hydration products after erosion by Cl⁻ Mg²⁺ solution. Under the erosion environment of pure NaCl solution, the phase composition of cement hydration products mainly includes Friedel salt and Ca(OH)₂. Among them, the Friedel salt endothermic peak range is 250-410°C^[9], and according to the TG curve calculation, its weight loss is 7.67%. The endothermic peak range of Ca(OH)₂ is 410-520°C^[9], and calculated by TG curve, its weight loss is 20.9%. The phase composition of cement hydration products in NaCl MgCl₂ erosion solution not only includes Friedel salt and Ca(OH)₂, but also generates Mg(OH)₂. The endothermic peak range of Mg(OH)₂ is 350-420°C^[10]: Due to the partial overlap of the endothermic peaks of Mg(OH)₂ and Friedel salt, the weight within the range of 250-350°C is divided into Friedel salt, and the weight within the range of 350-420°C is divided into Mg(OH)₂. Therefore, the contents of Friedel salt, Mg(OH)₂, and Ca(OH)₂ calculated based on the TG curve are shown in Figure 2.

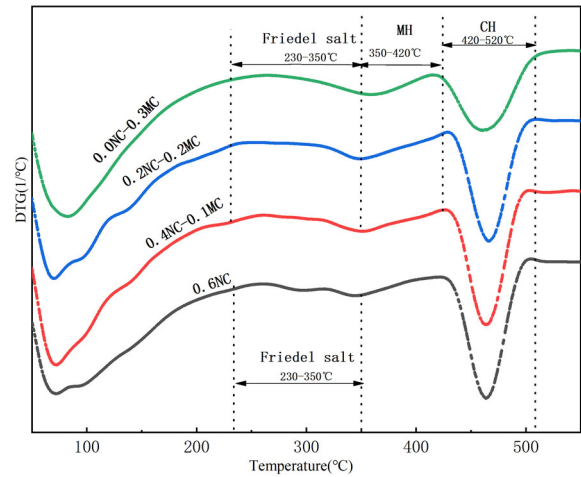


Figure 2. DTG map of cement slurry after 7 days of immersion in four erosion environments

From Figure 3, it can be seen that under the corrosion environment of 0.6mol/L Cl⁻ to 0.6mol/L Cl⁻ and 0.2mol/L Mg²⁺, the Friedel salt content in the corresponding environment samples increased from 7.67wt.% to 8.98wt.%; The content of Ca(OH)₂ decreased from 20.9wt.% to 11.68wt.%, and the content of Mg(OH)₂ increased from 0% to 8.77wt.%. This indicates that as the concentration of Mg²⁺ in the erosion solution increases, Mg²⁺ promotes the dissolution of Ca(OH)₂ and the dissolution of Ca²⁺, while generating precipitation of Mg(OH)₂ and promoting the formation of Friedel salts. In the corrosive environment of 0.6mol/L Cl⁻ and 0.2mol/L Mg²⁺ to 0.6mol/L Cl⁻ and 0.3mol/L Mg²⁺, the Friedel salt content in the samples decreased from 8.98wt.% to 8.75wt.%, the Ca(OH)₂ content decreased from 11.68wt.% to 10.77wt.%, and the Mg(OH)₂ content increased from 8.77% to 9.50% by weight. Therefore, it indicates that as the concentration of Mg²⁺ increases in the eroded environment, the Friedel salt content first increases and then decreases, the Ca(OH)₂ content gradually decreases, and the Mg(OH)₂ content continues to increase, indicating that the following reactions have occurred:

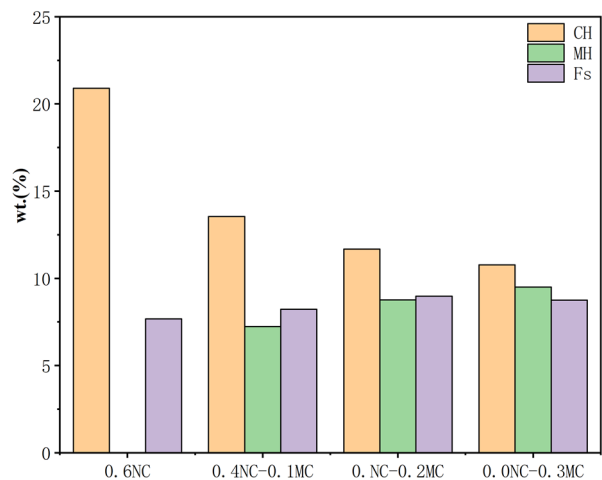
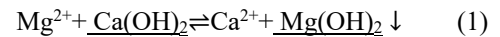


Figure 3. The cement slurry is composed of the main phase after soaking it in four erosion environments for 7 days

3.2. Changes in pH value and Ca²⁺ concentration in erosion solution

Figures 4 show the variation of pH value of erosion solution with erosion time in erosion environments with varying Mg²⁺ concentrations. Within 4 hours before soaking, the pH values in all four erosion solutions rapidly increased, and the rate of increase was similar. Therefore, before the pH of the solution stabilizes, Mg²⁺ has little effect on the rate of pH rise of the erosion solution. After the pH value of the solution stabilizes, the final pH value of the solution decreases with the increase of Mg²⁺ concentration. The decreasing state of the pH value of the erosion solution is obtained through XRD and thermal analysis. The addition of Mg²⁺ consumes a large amount of Ca(OH)₂ in the erosion solution, resulting in a decrease in the pH value of the solution. Figures 5 show the concentration of Ca²⁺ in the supernatant after 7 days of erosion in four different erosion environments. As shown in the figure, when the solution is stable, the Ca²⁺ concentration in each erosion solution increases with the increase of Mg²⁺ concentration, which proves that Mg²⁺ consumes a large amount of Ca(OH)₂, which is difficult to dissolve in water in the hydrate, resulting in a decrease in the pH value of the erosion solution and an increase in Ca²⁺ concentration.

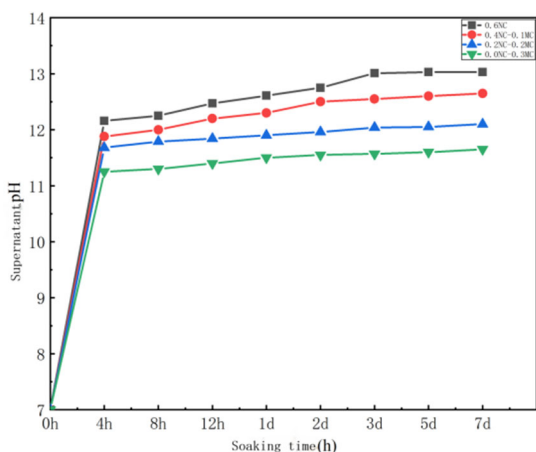


Figure 4. Changes in pH value of cement slurry immersed in four erosion environments

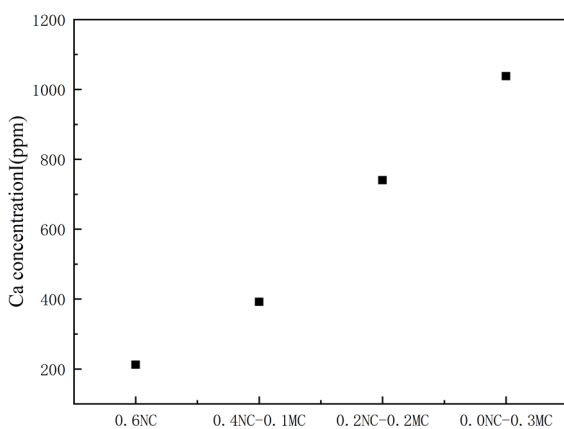
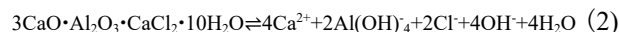


Figure 5. Supernatant Ca²⁺ concentration after 7 days of erosion of cement slurry in four erosive environments.concentration

3.3. Curve of pH Change in Friedel Salt and Erosion Solution under Different Mg²⁺ Concentrations

From Figure 6, it can be seen that the pH value of the pure cement slurry in the corrosive environment of 0.6mol/L Cl⁻ to

0.6mol/L Cl⁻ and 0.2mol/L Mg²⁺ decreased from 13.03 to 12.10, and the Friedel salt content in the corresponding environment samples increased from 7.67wt.% to 8.98wt.%, while the Ca(OH)₂ content decreased from 20.9wt.% to 11.68wt.%. The content of Mg(OH)₂ increased from 0% to 8.77wt.%. With the increase of Mg²⁺ concentration in the erosion solution, Mg²⁺ promotes the dissolution of Ca(OH)₂ and the dissolution of Ca²⁺, forming Mg(OH)₂ precipitation, and promoting the formation of Friedel salt, which indicates that the chloride ion binding capacity of cement paste decreases with the increase of pH value^[11] because of the competition between hydroxyl ion and chloride ion^[11]. Under the erosion environment of 0.6mol/L Cl⁻ and 0.2mol/L Mg²⁺ to 0.6mol/L Cl⁻ and 0.3mol/L Mg²⁺ in pure cement slurry, the pH value of the erosion solution decreased from 12.10 to 11.65, and the Friedel salt content in the corresponding environment decreased from 8.98wt.% to 8.75%. The Ca(OH)₂ content decreased from 11.68wt.% to 10.77wt.%. The content of Mg(OH)₂ increased from 8.77wt.% to 9.5wt.%. This indicates that as the concentration of Mg²⁺ in the erosion solution increases, Mg²⁺ promotes the dissolution of Ca(OH)₂ and the dissolution of Ca²⁺, resulting in the formation of Mg(OH)₂ precipitates and partial decomposition of Friedel salts. When the pH is too low, the solubility of Friedel salts increases^[12]. The reason can be explained by the following formula:



The above reaction consumes a large amount of OH⁻, and the chemical reaction shifts to the right, increasing the solubility of Friedel salts, which is not conducive to the solidification of chloride ions^[13,14].

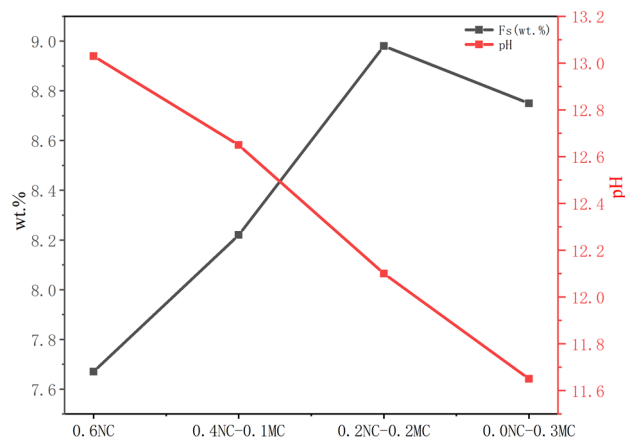


Figure 6. Silt slurry after 7 days of immersion in four erosion environments for Friedel salt-pH change curve

3.4. Microscopic morphology analysis

Figures 7 show the microstructure of pure cement slurry after immersion and erosion in four different erosion solutions for 7 days. From Figure 7(a), it can be seen that there is Friedel salt present in the control group sample, and its chemical composition can be demonstrated by energy dispersive elements (Figure 7(b)). It is not difficult to find from Figure 7(a) that the shape of Friedel salt is similar to a hexagonal plate shape^[15]. Figure 7(c) shows the microstructure of the sample surface in a 0.4mol/L NaCl-0.1mol/L Mg²⁺ etching solution. It is found that there are a large number of pores located on the sample surface, and

Mg(OH)₂ and Ca(OH)₂ are filled in the pores. When the sample is placed in an erosion solution with a high concentration ($\geq 0.2\text{mol/L}$), a large amount of Mg(OH)₂ phase is found in the erosion product (Figure 7(e)(g)). At the same time, it was found that when the concentration of Mg²⁺ in the erosion solution was 0.2mol/L, the samples in the erosion solution exhibited more cracks compared to the samples in the 0.6mol/L pure NaCl erosion solution (Figure 7(a)), and there

were Mg(OH)₂ with better crystalline morphology around the cracks. This is because the transformation of Ca(OH)₂ into the product Mg(OH)₂ led to the appearance of cracks, and the average width of the cracks in the erosion product of the sample under 0.2mol/L Mg²⁺ erosion solution was 116nm. Under 0.3mol/L Mg²⁺ corrosion solution, the crack width increases to 265nm, so an increase in Mg²⁺ concentration in the corrosion solution will lead to an increase in crack width.

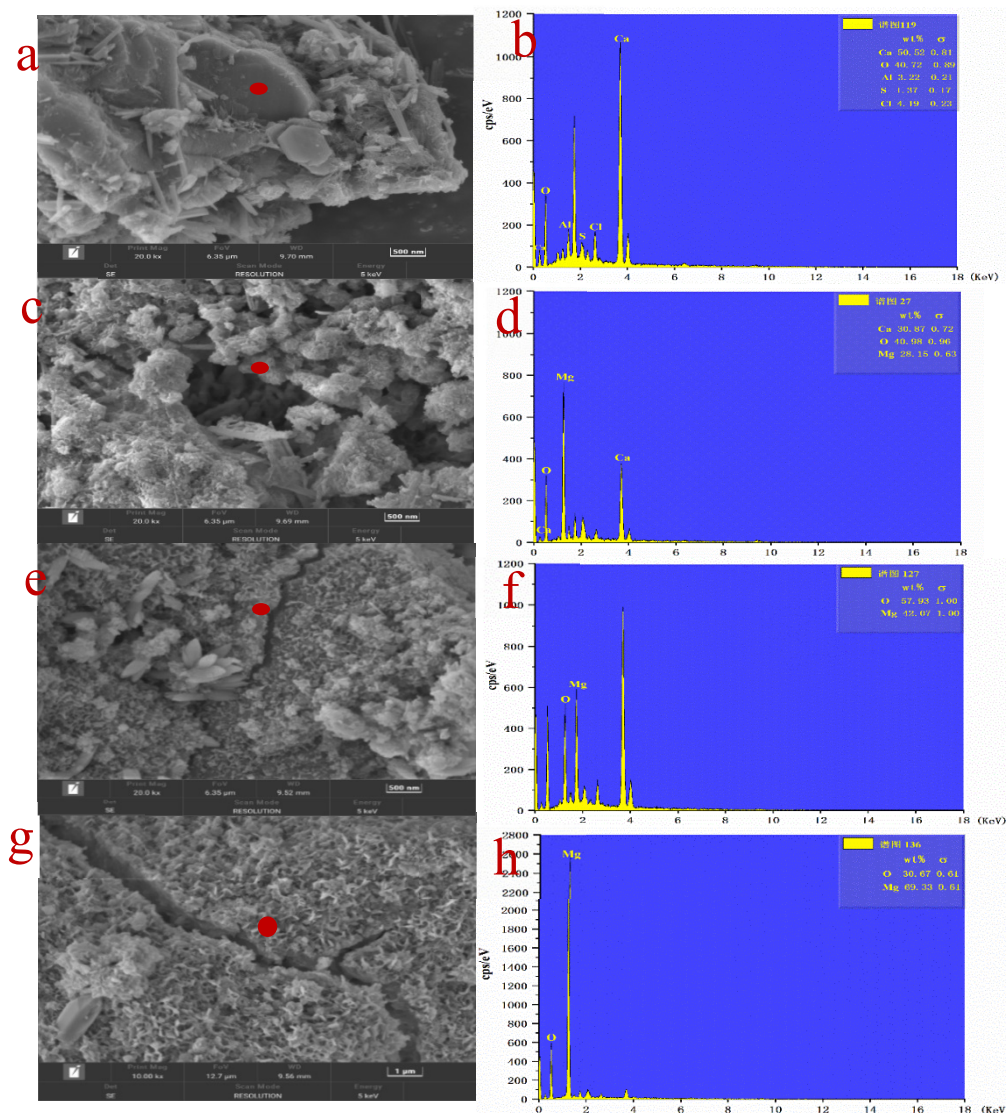


Figure 7. SEM EDS diagram of cement slurry after 7 days of erosion in four erosion environments: (a) SEM diagram of cement slurry under 0.6 mol/L NaCl erosion environment; (c) Scanning electron micrograph under the corrosive environment of 0.4mol/L NaCl-0.1mol/L MgCl₂; (e) Scanning electron micrograph under the corrosive environment of 0.2mol/L NaCl-0.2mol/L MgCl₂; (g) Scanning electron microscope image under 0.0mol/L NaCl-0.3mol/L MgCl₂ corrosion environment. (b) (d) (f) (h) correspond to the elemental analysis diagram of the energy spectrum points in (a) (c) (e) (g) respectively

4. Conclusion

(1) In the early stage of immersion erosion, Mg²⁺ has little effect on the rate of pH rise of the erosion solution; After the pH value of the solution stabilizes, the final pH value of the solution decreases with the increase of Mg²⁺ concentration.

(2) As the concentration of Mg²⁺ in the erosion solution increases, Mg²⁺ promotes the dissolution of hydration product Ca(OH)₂ and the dissolution of Ca²⁺, while generating Mg(OH)₂ precipitates, resulting in a decrease in solution alkalinity and an increase in chloride ion solidification.

(3) When the pH of the solution exceeds 12.1, a lower pH value will promote the formation of Friedel salts; When the pH of the solution is less than 12.1, higher concentrations of Mg²⁺ cause Friedel salt to decompose.

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