Experimental Study on Sulfate Attack Resistance of Cement Slurry with UEA Expansive Agent

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Abstract. Sulfate attack was one of the most important factors affecting the durability of cement slurry in mine corrosive environment. For water stopping and reinforcement projects in wellbore or working face under sulfate erosion environment, mineral admixtures were often used to improve the sulfate resistance of cement slurry. The physical and mechanical properties of cement mortar with 0, 4%, 8%, 12% and 16% UEA expansive agent content under the conditions of 0.6%, 3% and 15% sodium sulfate solution concentration were investigated through the full immersion test for 19 months in the laboratory. The results showed that the strength of mortar specimens decreased with the increase of UEA expansive agent content, but in the sulfate attack environment, the ability to resist sulfate attack could be significantly improved. In order to ensure the early strength of mortar and reduce the cost, the best effect of UEA expansion agent was 4%.

1 Introduction

Sulfate attack is considered to be one of the four main factors that cause failure and damage of concrete materials. Sulfate attack is also the most complex and harmful environmental water erosion. The main inclined shaft, the auxiliary inclined shaft and the return air inclined shaft of the mine in Gansu province cross the flowing sand layer. The water in this section is rich in SO_4^{2-} and Cl^- , and the concentrations are 4001mg/L and 4230mg/L, respectively. The total salinity of the water reaches 12,179 mg/L, and the pH of the water is 7.6, which is weakly alkaline. Corrosion and cracks in the three shafts occurred in different level, resulting in water inflow in the top, side and bottom of the shafts, especially in the section of water-rich sand layer.

Due to the insufficient understanding of sulfate attack shaft concrete, the project was carried that ordinary silicate cement slurry was injected into the sand layer of the section. But, 2 years later, the concrete of shaft in this section was still corroded seriously, and the effect of sealing water was getting worse (Fig. 1). As corrosion increases, its strength will be further reduced, and shaft safety and coal production will be seriously threatened. In the case of no reconstruction of the shaft, the shaft can only be plugged and strengthened by cement slurry grouting to delay the service life of the shaft. However, the conventional cement grouting solidified entity has weak sulfate corrosion resistance and poor durability, so it is urgent to carry out the research of sulfate corrosion resistance reinforcement methods for concrete shaft.

Figure 1. Corrosion failure mode of main inclined shaft

Sulfate erosion is an important factor affecting the durability of cement-based materials. The erosion mechanism and anti-erosion methods have been studied extensively by scholars at home and abroad [1,2]. The research mainly focuses on improving the corrosion resistance of cement-based materials in sulfate environment by reducing the content of tricalcium aluminate in cement, improving the permeability of cement-based materials and adding mineral admixtures such as fly ash, silica fume and slag [3-6]. UEA expansive agent is a kind of sulphur aluminate expansive agent, which can react with $\text{Ca}(\text{OH})_2$ in cement paste to form ettringite expansive component and produce appropriate expansion in concrete to compensate the shrinkage of concrete. Therefore, UEA expansive agent has been widely studied and applied in mortar or concrete engineering [7-9]. However, there are few researches on improving the corrosion resistance of cement-based materials by adding UEA expander in sulfate erosion

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environment^[10]. Therefore, through the full immersion erosion test of cement mortar in Na₂SO₄ solution, the effects of UEA expander on the mechanical properties of cement slurry stones and the effectiveness of sulfate resistance were analysed, which provided a basis for grouting reinforcement construction in this special environment.

2 Raw materials and test methods

2.1. Raw materials

Table 1. Chemical composition of raw materials

Name	Main chemical composition/%												
	SiO ₂	Al ₂ O ₃	TFe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	MnO	TiO ₂	FeO	Fe ₂ O ₃	loss on ignition
Cement	26.89	3.85	4.14	1.47	59.88	0.12	0.96	0.17	0.04	0.20	0.07	4.06	2.06
Fly ash	48.32	35.72	2.88	0.47	1.85	0.51	0.78	0.39	0.04	1.43	0.88	1.90	1.43
River sand	75.20	10.84	1.70	1.70	2.88	2.23	3.08	0.10	0.04	0.23	0.59	1.04	2.44

2.2. Test methods

Sulfate erosion shaft grouting reinforcement was to inject cement slurry into the internal and external strata of shaft concrete through drilling, and strengthen the shaft after cement slurry solidified. The cement slurry entered the sulfate attacked formation and was attacked by SO₄²⁻. The whole process of slurry coagulation was attacked by sulfate. In order to simulate the actual working conditions, the design water-cement ratio is 1.0, the cement and sand ratio is 1.0: 4.5, and the amount of fly

The cement used in this test was PO42.5 cement produced by Gezhouba Shimen special cement co., ltd. Expansive agent was the UEA concrete expansive agent produced by Anhui Wanke new technology development co., ltd. The sand used for mixing was Weihe sand in xi'an with fineness modulus of 2.1, which belonged to medium sand. The chemical composition of raw materials was shown in table 1. The sodium sulfate solution was prepared using chemical analysis reagents with mass fractions of 0.6%, 3%, and 15%, and the water was from the tap water of the laboratory.

ash is 0, 10%, 20%, 30% and 40% respectively (Table 2). The shaped specimens were placed in water and correspondingly prepared sulfate solution together with the molds to be immersed and cured, and the container was closed. After the final setting of the slurry, the molds were removed, and the test specimens were further cured. The solution was changed by every 2 months, the flexural and compressive strength test was performed after reaching the predetermined soaking age (1M, 3M, 5M, 10M, 12M, 14M and 19M).

Table 2. Mortar mix ratio and curing conditions

No.	Cement content	Fly ash content	Water	Sand	Curing conditions			
PO	100%	0	100%	450%	Water	0.6% Na ₂ SO ₄ Solution	3% Na ₂ SO ₄ Solution	15% Na ₂ SO ₄ Solution
UEA04	90%	10%						
UEA08	80%	20%						
UEA12	70%	30%						
UEA16	60%	40%						

The sulfate corrosion resistance of the test specimens is expressed by flexural and corrosion resistance coefficient.

The flexural and corrosion resistance coefficient is calculated according to Equation (1):

$$K=R_l/R_w \quad (1)$$

Where K is the flexural and corrosion resistance coefficient of the test corrosion; R_l is the flexural strength of the test corrosion when it is immersed in solution for a predetermined age, MPa; R_w is the flexural strength of the test specimens when it is immersed in water for a predetermined age, MPa.

3 Experimental results and discussion

3.1. Influence of UEA expansion agent dosage on mortar strength

The flexural and compressive strength of mortar specimens at different ages from 1 to 19 months under water conditioning were measured. It can be seen from Fig. 2 and Fig 3 that the flexural strength and compressive strength of mortar specimens with different dosage of UEA expansive agent increased with increasing age, at the curing age of 19 months, the flexural strength of mortar specimens with UEA expansion agent content of 0, 4%, 8%, 12% and 16% increased by 25.9%, 27.3%, 3.8%, 41.1% and 34.4%

respectively, and the compressive strength increased by 56.4%, 37.2%, 19.4%, 28.0% and 55.7% respectively. During the immersion period of 1-19 months, the flexural and compressive strength of mortar samples mixed with UEA expansive agent were all smaller than those without UEA expansive agent, and it was inversely proportional to UEA dosage, which decreased with the increase of UEA expansion agent. At the age of 19 months, the flexural strength of mortar specimens with UEA expansion agents of 4%, 8%, 12% and 16% decreased by 9.9%, 13.3%, 19.2% and 21.4% respectively compared with that of PO, and the compressive strength decreased by 14.5%, 25.2%, 28.8% and 35.9% respectively. This was because when UEA expansive agent was added to mortar for hardening, a large number of slender columnar or acicular ettringite crystals would be generated, and many gaps would be left in the crystal framework formed by lapping them together. Moreover, the samples were all in an unrestricted state. In the absence of constraints, ettringite crystals would grow larger, their porosity would increase, and their strength would be lower.

Figure 2. Flexural Strength Diagram of Mortar Specimens under Different Water Curing Ages

Figure 3. Compressive Strength Diagram of Mortar Specimens under Different Water Curing Ages

3.2. Effect of UEA expansion agent on sulfate resistance of mortar specimen

By measuring the flexural strength of mortar specimens of different ages from 1-19 months under water and sulphate solution immersion conditions, the flexural and corrosion resistance coefficient (abbreviation FCRC) was calculated according to formula 1. The effect of UEA expansion agent content and sodium sulfate solution

concentration on the sulfate corrosion resistance of mortar specimens was studied.

(1) Effect of UEA expansion agent dosage

Figure 4 shows the FCRC variation of mortar specimens with different UEA expansive agent content. It can be seen from the figure that the FCRC of ordinary Portland cement mortar specimens without UEA expansive agent increases first and then decreases significantly with the increase of immersion age in sodium sulfate solution with Different Concentrations, and after 19 months immersion, the FCRC is still greater than 1, and the surface of the specimens is intact without any sign of expansion damage. This is because the mortar specimens in the test have not been cured for 28 days but have been eroded directly, and the mortar strength has not yet developed. In Na_2SO_4 solution, SO_4^{2-} diffuses and penetrates into cement paste, and reacts with hydrated calcium aluminate and $\text{Ca}(\text{OH})_2$ to form ettringite, which fills the voids, gradually compacts the structure and enhances the strength of mortar specimens. With the continuous growth of immersion age, the number of ettringite is increasing, the expansion stress is increasing, the pore structure is damaged, micro-cracks begin to appear inside the mortar specimens, and the strength of the mortar specimens begins to decline, but at the same time, because of the consumption of calcium hydroxide, the ettringite formed during the later period of sulfate ion intrusion decreases, and the decreasing trend of the corrosion resistance coefficient of the mortar specimens slows down^[11].

The FCRC of mortar specimens with UEA expansive agent is significantly higher than that without UEA expansive agent, but it shows different variation rules under different Na_2SO_4 concentration. It can be seen from Fig. 4 (a) that the FCRC of mortar specimens soaked in 0.6% Na_2SO_4 solution with UEA content of 4%, 8%, 12% and 16% increases gradually with the increase of soaking time. During the 1M-19M age, the mortar specimens with 8% UEA expansive agent had the greatest FCRC and the best sulfate corrosion resistance. The mortar specimens with 16% UEA expansive agent had relatively small FCRC, which indicated that the sulfate corrosion resistance was relatively poor. It can be seen from Fig. 4 (b) that the FCRC of mortar specimens soaked in 3% Na_2SO_4 solution with the addition of 4%, 8%, 12% and 16% increases first and then decreases gradually with the increase of soaking age, and tends to be stable. After 19 months immersion, the FCRC of mortar specimens with UEA expansive agent is significantly higher than that of ordinary Portland cement mortar specimens without UEA expansive agent, and the permeability coefficient of cement mortar specimens with 12% content is the largest, which indicates that the mortar specimens with UEA expansive agent have the best sulfate resistance. From 5 (c), it can be seen that the FCRC of mortar specimens soaked in 15% Na_2SO_4 solution with UEA expander dosage of 4%, 8%, 12% and 16% increases sharply within 1M-5M, increases slowly with the increase of soaking age in 5M-12M, and decreases slightly with the increase of soaking age in 12M-19M. It is stable and tends to be consistent.

Figure 4. Diachronic Variation of FCRC of Mortar Specimens with Different UEA Expansion Agent

When the cement is hardened with the addition of UEA expansive agent, the ettringite crystal formed by the interaction of cement and hydrate $\text{Ca}(\text{OH})_2$ is larger, which leads to the increase of porosity. At the same time, when soaked in Na_2SO_4 solution, SO_4^{2-} in solution reacts with cement hydration products to form new ettringite, filling the pore continuously. With the increase of soaking time, the number of ettringite increases continuously, the pore gets denser, which effectively prevents the diffusion and infiltration of SO_4^{2-} in the later stage, the amount of ettringite decreases, and mortar decreases. The strength of specimens tends to be stable.

(2) the influence of slurry concentration

Fig. 5 is a diachronic variation of the FCRC of mortar specimens in different concentrations of sodium sulfate solution. It can be seen from Fig. 5 (a) that the FCRC of PO mortar specimens without UEA expansive agent increases in the early stage and decreases after a certain age. In the rising stage, the FCRC of mortar specimens soaked in 0.6% sodium sulfate solution is the smallest, FCRC of mortar specimens with 3% concentration is the

largest, and the FCRC of mortar specimens with 15% concentration is between the two. In the descending stage, the FCRC of mortar specimens decreases with the increase of sodium sulfate solution concentration, which indicates that the higher the concentration of sodium sulfate solution, the more serious the mortar specimens are subjected to sulfate attack.

It can be seen from Fig. 6 (b) ~ (e) that the FCRC of UEA04, UEA08, UEA 12 and UEA16 mortar specimens with 4%, 8%, 12% and 16% UEA expansive agent increase gradually with the increase of immersion age, but there are different changing rules in different Na_2SO_4 solutions. When soaked in sodium sulfate solution for less than 5 months, the FCRC of mortar specimens is proportional to the concentration of sodium sulfate solution. That is to say, the higher the concentration of sodium sulfate solution is, the higher the fracture resistance coefficient of mortar specimens is. After 12 months immersion, the FCRC of mortar specimens with 0.6% sodium sulfate concentration is higher than that of sodium sulfate solution concentration of 3% and 15%.

Figure 5. Diachronic Variation of FCRC of Mortar Specimens in Different Concentrations of Na_2SO_4 Solution

4 Conclusion

By simulating the sulfate erosion environment in mines, the influence of UEA expansive agent on the sulfate corrosion resistance of cement mortar is studied. The following conclusions are drawn.

(1) When cured in water, the flexural strength and compressive strength of mortar specimens with different content of UEA expansive agent increased significantly with the increase of curing age.

(2) The addition of UEA expander will reduce the flexural and compressive strength of mortar, and decrease significantly with the increase of the amount of UEA expander, so the amount of UEA expander should not be too large.

(3) Cement grouting in sulphate-eroded environment can significantly improve its resistance to sulphate attack by adding 4%-16% UEA expansive agent. In order to ensure its early strength and reduce the cost, it is best to replace 4% cement in cement mortar.

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