Research on Performance and Microstructure of Sewage Pipe Mortar Strengthened with Different Anti-Corrosion Technologies

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Abstract. Mostly urban underground sewage is the acidic corrosion environment with a high concentration of aggressive ions and microbe, which resulted in performance deterioration and service-life decrease of sewage concrete pipe. In order to effectively protect durability of the concrete pipe, the present paper briefly analysed the main degradation mechanism of concrete pipe attacked by urban underground sewage, and proposed that using penetrating and strengthening surface sealer based on inorganic chemistry. In addition, using index of compressive strength, weight loss and appearance level to investigate the influence of the sealer on corrosion resistance of mortar samples after different dry-wet cycles. Besides, comparative research on effect of the sealer, aluminate cement and admixture of corrosion resistance was also addressed. At last, the SEM technology was used to reveal the improvement mechanism of different technologies of corrosion resistance. The results indicated that the sealer and aluminate cement can significantly improve corrosion resistance of mortar. Besides, the improvement effect can be described as the descending order: the penetrating and strengthening surface sealer $>$ aluminate cement $>$ admixture of corrosion resistance. The mortar sample treated with the sealer displayed the condensed and sound microstructure which proved that the sealer can improve the corrosion resistance to urban underground sewage.

1. Introduction

Sewage pipe, as an important component of urban sewerage system, effectively assures the green and sustainability of urban development. At present, the sewage pipes are mainly made of concrete materials in China. Mostly organic and inorganic substances from municipal sewage are corrosive for concrete. In addition, the corrosion phenomenon developed slowly in a long term, therefore the damage resulted from the corrosion is slight in a short duration. However, it is worthy of notice that the difficulty of maintenance and rehabilitation for concrete pipe under the sewage $^{[1,2]}$. Based on deterioration mechanism of concrete pipe under sewage, the corrosion could be categorized into sulfate and acid attack.

As for the deterioration mechanism of concrete pipe, sulfate attack is a complicate corrosion which is composed of physical salt crystallization destruction under the role of drying and wetting cycles, expansion destruction from formation of ettringite and gypsum crystal, and decomposition destruction of C-S-H gel transformed into thaumasite at the condition of cold and moisture (the environmental temperature is lower than 15 °C) $^{[3,4]}$. 

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Acid corrosion is also a key factor for deterioration of concrete pipe under the sewage. Particularly, acid corrosion will accelerate precipitation of calcium ions and contribute to destructive reaction from sulfate attack on concrete. Based on the resource of acid corrosion, acid substance originated from polluted water in the sewage or from microbiological corrosion. The former acidity, originated from acetic acid, fatty acid, citric acid, lactic acid, etc. from industrial waste and domestic sewage, could result into concrete destruction at the bottom and lateral side of the sewage pipe. Although the organic acid mentioned above is weak, the corrosion mechanism from the weak acid is similar to the strong acid which reacted with the cement hydration products into dissolved salt. Finally, the calcium ion flowed away from the hydrated products and resulted in concrete destruction. The later acidity referred in particular to that hydrogen sulfide corrosion on concrete pipe resulted from microbiological role [5]. The microbiological corrosion can be categorized into as follows: firstly, sulfide-rich waste water are released into sewage pipe and resulted in microbiological corrosion; secondly, sludge precipitated on pipe bottom resulted in the corrosion. When the organic and inorganic substances precipitated on the bottom of concrete pipe and transformed into sludge, sulfate ion was reduced by sulfur reducing bacteria to produce hydrogen sulfide gas. Under the role of biochemistry, the gas transports into upper space of concrete pipe unsaturated with water, and the sulfuric acid by the gas oxidation resulted in corrosion destruction of upper part of concrete pipe [6].

Based on corrosion mechanism and deteriorated characteristic of concrete exposed to sewage, it is suggested that increasing densification and reducing porosity of concrete and decreasing transport rate of aggressive ions in concrete can increase resistance of concrete to sewage corrosion. At present, the main technical solution of improving concrete resistance to acid and sulfate attack is corrosion resistance concrete and surface protection materials. The corrosion resistance concrete is mainly made by corrosion resistance admixture or aluminat cement with an excellent ability to resist sulfate attack. Surface protection materials are composed of film-forming coating, hydrophobic liner and pore-blocker [7-9]. In addition, the pore-blocker is a liquid solution consisting of highly reactive components which can effectively penetrate into concrete surface and react with hydrated products and anhydrate cement particles so as to strengthen the concrete surface and protect from the corrosion. Based on the reaction mechanism, pore-blocker can effectively improve the corrosion resistance of existing concrete, such as concrete pipe. Besides, the pore-blocker mainly made by inorganic substances can form a firm barrier to aggrieve substance in concrete surface without ageing and adhesive problem of organic coating.

Mortar is the main material at the internal surface of concrete pipe prepared by centrifugal compacting process. Considering corrosion characteristic of concrete pipe under sewage, the mortar is easily corroded by the aggressive substance from sewage water. Therefore, the present research mainly focused on effect of corrosion resistance on mortar sealed with the pore-blocker based on modified silicate technology, and the mechanism is also be discussed.

2. Raw Materials and Experimental Method
Considering the acid corrosion characteristic of concrete pipe under sewage, the present research conducted comparative research on effect of corrosion resistance admixture, aluminat cement for sewage corrosion, and modified-silicate based pore-blocker on corrosion resistance of mortar exposed to acid environment.

2.1. Raw Materials
Cement: Standard silicate cement conformed to the China National Standard GB 8076-2008 “Concrete admixture”.

Sand: Standard sand conformed to the China National Standard GB/T 17671-1999 “Method of testing cements-Determination of strength”.

Water: Tap water.

Corrosion resistance admixture (CY referred in the present research): CY admixture, yellow appearance and powder, conforms to the Chinese Industrial Standard JC/T1011-2006 “Sulfate corrosion resistance admixtures for concrete”, provided by an anti-corrosion company from Tian Jing.
city. Based on the product specification, the CY admixture is composed of surfactant, inorganic salt, organic promoter and carrier. The specification also claimed that the CY admixture, replaced cement content by 8 to 12 %, significantly improved the corrosion resistance of cementitious materials exposed to sulfate environment with content of 10000～15000 mg/l. In addition, CY admixture is recommended to use in some severe environment, for instance, salty soil, sewage.

Aluminate cement (KS referred in the present research): KS cement, grey appearance and conforms to the Chinese National Standard GB/T 201-2015 “Calcium Aluminate Cement”, provided by an anti-corrosion company from Tian Jing city. The specification of the cement indicated that KS cement is a hydraulic binder specially developed for concrete pipe, which contains approximately 50% alumina.

Modified-silicate based pore-blocker sealer (NF referred in the present research): NF sealer, as a translucent liquid solution with a pH value of 12, produced by Jiangsu SOBUTE New Materials Co., Ltd. In addition, density of the sealer is 1.15g/cm3, and measured solid content is about 26.1%. The sealer conforms to Chinese Industrial Standard JC/T1018-2006 “Water based capillary inorganic waterproofer”.

2.2. Mortar Preparation

Standard mortar sample: Mixture of standard mortar is described as follows: standard cement: standard sand: water = 1:3:0.5 (by weight). According to the Chinese National Standard GB/T 17671-1999 “Method of testing cements-Determination of strength”, the freshly mixed mortar was casted into steel mold with a size of 40×40×160 mm and vibrated until compacting. After 24 hours curing, the demolded mortar samples were put into standard curing room for 28 days.

Anti-corrosion mortar sample prepared by CY admixture (CY mortar mentioned in the present research): using the same mixture as the standard mortar, the standard cement replaced with CY admixture in the weight of 8 %. Besides, the CY mortar also adopted the same curing condition.

Anti-corrosion mortar sample prepared by KS aluminate cement (KS mortar mentioned in the present research): using the same mixture as the standard mortar, the standard cement replaced with KS aluminate cement in the weight of 100 %. Besides, the KS mortar also adopted the same curing condition.

Anti-corrosion mortar sample prepared by NF sealer (NF mortar mentioned in the present research): using the same mixture as the standard mortar, the NF sealer was firstly brushed the surface of standard mortar with usage of 0.5 kg/m2 and then cured at a room temperature condition for 8 days. Before the sealer brush, the standard mortar should be put into standard curing room for 20 days, and then wiped off the water on the surface of mortar samples until reaching the surface-dry condition.

2.3. Corrosion Test

Considering corrosion characteristic of concrete pipe under sewage, acid solution of sulfuric acid and acetic acid with pH value of 2 was prepared separately. When reached surface-dry condition after 28 days curing, the testing samples were kept into a room with the condition of 20±2℃and RH=65% for drying and wetting cycles of acid corrosion. The corrosion cycle persisted 24 hours as described as follows: drying for 16 hours at 50℃, cooling down for 2 hours at 20 ℃, and then immersing into acid solution for 6 hours. After reaching different cycles, the mortar samples were taken out and dried at room temperature, and then performance was evaluate with index of compressive strength, weight loss and appearance damage. Index of compressive strength was defined that the ratio of compressive strength of corroded mortar exposed to acid solution to that of the standard mortar cured at standard room at the same duration.

3. Results

3.1. Index for Compressive Strength

The results from Figure 1 indicated that the sealer NF and aluminate cement KS significantly improved corrosion resistance of mortar to sulfur acid with the pH value of 12. After 90 days of corrosion cycles, NF and KS mortar exhibited a good result of index of compressive strength higher than 0.75 (required value for sulfate attack from the China National Standard GB/T 50082 “Standard
for test methods of long-term performance and durability of ordinary concrete”) and almost reached at 0.9, which meant high resistance to attack of sulfur acid on mortar. When mortar brushed with NF sealer, the reactive component reacted with hydration products and anhydrate cement particles to block the transport channel of aggressive ions and protect from acid attack on mortar. With increasing number of corrosion cycles, the continuous hydration of mortar sample will also improve its ability to resist corrosion by means of microstructure optimization. Therefore, the improved role of pore-blocker sealer NF and aluminate cement KS became more significant when increasing the exposure duration. By contrast, The CY admixture firstly increased the index for compressive strength of mortar but then decreased. The reason could be in that incorporation of CY admixture had a poor resistance to inhibit transportation of sulfate ions into the mortar samples, which could contributed to formation of ettringite resulted from reaction between sulfate ions and hydrated products. The ettringite improved compressive strength of the mortar at the early age of corrosion cycles, which appeared as increased index of compressive strength. However, hydration products could be decomposed in that increasing acidity with increased corrosion cycles deteriorated alkality environment which is important for stability of cement hydration products. Finally the decomposition of hydration products decreased the index of compressive strength.

3.2. Weight Loss

Figure 3 shows that NF and KS mortar also effectively decreased weight loss of the mortar samples exposed to sulfur acid solution, but the CY mortar had a significant weight loss. The weight loss of aluminate cement KS could ascribe to crystallization transfer of hydration products which also resulted in decrease of strength of aluminate cement.

Figure 1. Index of compressive strength for mortar exposed to sulfur acid condition at pH=2.

Figure 2. Index of compressive strength for mortar exposed to acetic acid condition at pH=2.
The results from Figure 4 indicated that CY admixture, KS aluminate cement and NF sealer had a good performance to resist corrosion from acetic acid with the pH value of 2. When the corrosion cycles reached at 90 days, weight loss of mortar sample was lower than 5% which is regarded as the critical value for weight loss of concrete exposed to frost condition according to the China National Standard GB/T 50082. Therefore, the acetic acid with a pH value of 2 had a slight influence on mortar performance.

Appearance of mortar samples exposed to sulfur acid solution was showed in Figure 5. By contrast, mark of NF mortar can be observed from the appearance, but the marks of KS and CY mortar were disappeared. In addition, it has been observed that peeling and sand leakage. Therefore, the results demonstrated that NF sealer significantly improved corrosion resistance of mortar samples than KS aluminate cement and CY admixture.
3.3. SEM
FEI Quanta 250 Scanning Electron Microscope was used to observe morphology of mortar surface after 90 days of corrosion in sulfur acid solution. The SEM images of CY, KS and NF mortar were showed in Figure 6 to 8 separately. The SEM results indicated that hydration product of CY mortar was loosed and porous, and CPS value of calcium ion was lower than that of KS and NF mortar with a magnification of 1000 times. Therefore, acid solution with the pH value of 2 resulted in significant decomposition and destruction. By contrast, KS mortar displayed a denser microstructure than CY mortar. However, some micro-cracks were observed on KS mortar surface, which indicated that sulfur acid or crystallization transformation of hydration products resulted in destruction of KS mortar. NF mortar has a denser microstructure than other mortar, no cracks and large pores were observed on the mortar surface. In addition, high value of CPS proved that NF sealer effectively improved microstructure of mortar and inhibited calcium leaching from hydration products.

Figure. 5 Corrosion appearance for mortar exposed to sulfur acid condition at pH=2.

Figure. 6 Microstructure morphology and chemical composition of mortar appearance protected by corrosion resistance admixture CY (×1000).
Figure. 7 Microstructure morphology and chemical composition of mortar appearance protected by aluminate cement KS ($\times 1000$).

Figure. 8 Microstructure morphology and chemical composition of mortar appearance protected by NF sealer ($\times 1000$).

4. Conclusions
(1) In the present research, the mortar sample sealed with modified silicate-based pore-blocker NF or the mortar sample made by aluminate cement KS displayed an excellent resistance to acid solution with a pH value of 2 respectively. However, corrosion resistance admixture CY, conforms to the Chinese Industrial Standard JC/T1011-2006 “Sulfate corrosion resistance admixtures for concrete”, had a poor performance to improve corrosion resistance of mortar exposed to acid solution. In addition, the corrosion resistance could be described in the following descending order: NF $>$ KS $>$ CY

(2) Results from SEM images also indicated that the mortar coated with NF sealer displayed denser microstructure than CY and KS mortar. In addition, no cracks and large pores were observed on NF mortar, and EDAX results demonstrated that calcium leaching is slight when compared with other mortars mentioned above.

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