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Behavior of water glass–polymer hybrid-modified mortars under flowing sulfuric acid solution environment

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Abstract

As the second part of a research program, a comparison test research on the flowing sulfuric acid resistance of four kinds of mortars (namely water glass–polyvinyl acetate hybrid-modified mortar, water-glass-modified mortar, polyvinyl-acetate-modified mortar and unmodified mortar) was performed so that laboratory simulation matched site condition better. The test results show that the flowing sulfuric acid attack is much more severe than the static one. Both microscopic and macroscopic test results indicate that the behavior of the hybrid-modified mortars under the flowing sulfuric acid solution is significantly better than that of the control mortars.

Keywords: Microstructures; Corrosion; Mortar; Polymers; Mixture proportioning

1. Introduction

In order to develop a sulfuric-acid-resistant mortar at a low cost, water glass (sodium silicate) and polyvinyl acetate latex (chosen from five kinds of polymer latexes) were used as main and supplementary modifying materials, respectively, for producing a hybrid-modified mortar as the first part of a research program [1]. A mass loss comparison test showed that the static sulfuric acid resistance of the water glass–polyvinyl acetate hybrid-modified mortar was significantly higher than that of the other kinds of modified and control mortars [1].

It should be noted that some deterioration of concrete/mortar is mainly due to flowing sulfuric acid attack (such as sewers) [1,2]. In order that laboratory simulation matched site condition better, the authors further proposed a comparison test research on the behavior of the hybrid-modified mortars under a flowing sulfuric acid solution as the second part of this research program. To obtain a better understanding of the influence of flowing sulfuric acid environment on hybrid-modified mortars, not only mass loss, but also the microstructures and main chemical compositions of various mortars after flowing acid attack were investigated.

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2. Experimental program

2.1. Materials

Based on the first part of this research [1], the following materials were used. A water glass with a density of 1.44 g/cm^3 and a viscosity index of 1.6 was chosen as the main modifying material. Na_2SiF_6 was used as a hardener for the water glass. Polyvinyl acetate latex was used as a supplementary modifying material. Ordinary Portland cement, sand and Class II fly ash in accordance with Chinese standards were used. Lignosulfonate was used as a dispersing agent, and tributyl phosphate as an antifoamer.

2.2. Specimen groups and comparison test program

Based on an exploratory test [1], four kinds of mortars (with six mixture proportions) were chosen as shown in Table 1.

For Groups 1–4 of mortars, the specimens of each group were composed of three 100-mm cubes and 12 prisms of $40 \times 40 \times 100$ mm. The three cubes were tested for density, compressive strength and microstructures before corrosion. The 12 prisms were divided into four sets. The first set of three prisms was tested for flexural strength. The second set of three prisms was tested for porosity of large pores (mainly connected pores). The third set of three prisms was tested for mass loss versus time in a static sulfuric acid

Table 1
Mixture proportions for different groups of mortars (by mass)

Material	Mortar group					
	Group 1, water glass–polyvinyl acetate hybrid-modified mortar-1	Group 2, water glass-modified mortar	Group 3, polyvinyl acetate-modified mortar	Group 4, unmodified mortar-1	Group 5, water glass–polyvinyl acetate hybrid-modified mortar-2	Group 6, unmodified mortar-2
Cement	100	100	100	100	100	100
Water glass/ lignosulfonate*	7/0.05	7/0.05			7/0.05	
Na_2SiF_6	1.05	1.05			1.05	
Polyvinyl acetate latex	3		5		3	
Lignosulfonate	0.5	0.5	0.5		0.5	
Tributyl phosphate	6	1	10		6	
Fly ash	15	15	15	15	15	15
Sand	200	200	200	200	200	200
Water	55	55	55	55	45	45

* Water glass and lignosulfonate were mixed before producing hybrid-modified mortar.

solution. The last set of three prisms was tested for mass loss versus time in a flowing sulfuric acid solution. After flowing sulfuric acid attack, the microstructures and main chemical compositions of the central parts (about 20 × 20 × 20 mm) of the last three prisms were measured by using scanning electron microscopy (SEM) and X-ray diffractometry (XRD), respectively.

For Groups 5 and 6 of mortars, the specimens of each group of the mortars were composed of six cubes of dimensions 100 × 100 × 100 mm. The six cubes were divided into two sets and tested for compressive strengths before and after flowing sulfuric acid attack.

2.3. Curing conditions

Immediately after casting, the specimens were covered with hessian polyethylene sheeting for 24 h at a temperature of about 19 °C. The specimens were then demoulded and transferred to the curing room for further curing of 27 days at 20 ± 1 °C and 98% RH. Due to the rearrangement of the equipment in the laboratory, the specimens for flowing sulfuric acid corrosion test were stored in the curing room for 30 weeks before the test.

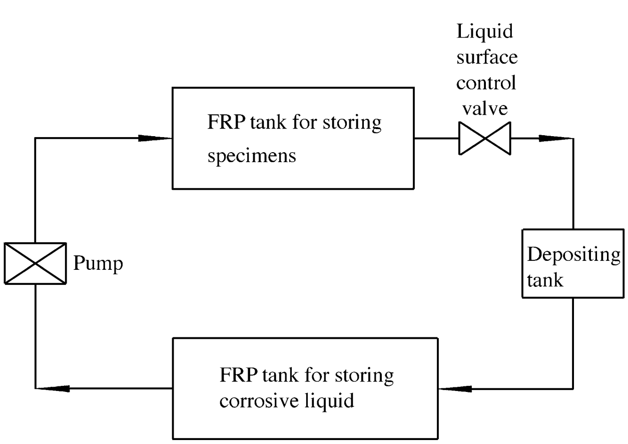


Fig. 1. Flowing corrosion system.

2.4. Static and flowing sulfuric acid attack environments

Based on a primary test for selecting the concentration of sulfuric acid solution[1], a 1% sulfuric acid solution was chosen, and put into glass beakers as the static sulfuric acid environment. The flowing sulfuric environment is shown in Fig. 1. The lower glass-fiber-reinforced plastic (FRP) tank was used for storing a 1% sulfuric acid solution at room temperature. A water pump worked for 8 h every day with a current velocity of 40 l/min so that the specimens stored in the upper FRP tank were subjected to flowing sulfuric acid attack. The solution in the tank was changed every week.

3. Results and discussion

3.1. Physical and mechanical properties of different mortars

The strength properties, density, porosity, mass loss and strength after 10-week sulfuric acid attack of mortars are presented in Table 2. It is shown that the 28-day compressive strength, flexural strength and density of water glass–polyvinyl acetate hybrid-modified mortar-1 (Group 1) are higher than those of the polyvinyl-acetate-modified mortar (Group 3) and water-glass-modified mortar (Group 2) [1].

The porosities of large pores of different mortars were roughly measured as follows. The prisms were put into a water tank to absorbing water until saturation. The saturated specimens were allowed to be in a saturated-surface-dry state, then weighed (W_1). After that, the saturated-surface-dry specimens were dried in a drying oven at a temperature of 45 °C. Next, the dried specimens were ground into grains. Finally, the grains were allowed to be in a surface-dry state and reweighed (W_2). The porosity of large pores of every specimen is estimated by the ratio between the mass difference ($W_1 - W_2$) and the volume of the prism. The

Table 2
Strength properties, density, porosity and mass loss after 10-week sulfuric acid attack of different groups of mortars

Test item	Mortar group					
	Group 1, water glass–polyvinyl acetate hybrid-modified mortar-1	Group 2, water glass-modified mortar	Group 3, polyvinyl acetate-modified mortar	Group 4, unmodified mortar-1	Group 5, water glass–polyvinyl acetate hybrid-modified mortar-2	Group 6, unmodified mortar-2
28-Day compressive strength (MPa)	20.7	15.1	15.0	20.3	23.3	24.8
28-Day flexural strength (MPa)	3.0	2.8	2.9	3.2		
28-Day density	1.87	1.79	1.78	1.94		
28-Day porosity of large pores (ml/ml)	17.4	22.9	19.9	18.7		
Mass loss after 10-week flowing sulfuric acid attack (%)	4.05	9.81	23.11	35.12		
Mass loss after 10-week static sulfuric acid attack (%)	1.1	2.92	5.11	7.75		
Compressive strength after 10 week flowing sulfuric acid attack (MPa)					22.7	17.2

porosities of large pores of mortars of Groups 1, 2, 3 and 4 are 17.4%, 22.9%, 19.9% and 18.7%, respectively. There is evidence that hybrid modification leads to a denser mortar.

Decreases in the compressive strengths of water glass–polyvinyl acetate hybrid-modified mortar-2 (Group 5) and unmodified mortar22 (Group 6) were 2.6% and 30.6%, respectively, after 10-week flowing sulfuric acid attack, indicating a significant improvement in flowing sulfuric acid resistance by hybrid modification.

3.2. Mass losses of different mortars in flowing and static sulfuric acid solutions

For Groups 1~4 of mortars, the specimens were weighed once a week in such a way that the specimens were brushed softly under water with a nylon brush to remove loose surface debris before weighing.

As shown in Fig. 2 and Table 2, the 10-week mass losses in the flowing sulfuric acid solution are 4.05%, 9.81%, 23.11% and 35.12% for the hybrid-modified mortar-1, water-glass-modified mortar, polyvinyl-acetate-modified mortar and unmodified mortar-1, respectively. It can be calculated that the relative mass losses of the four mortars are 1, 2.42, 5.71 and 8.67, respectively. It can be inferred that the flowing sulfuric acid resistance of the hybrid-modified mortar is significantly higher than that of the other mortars. The 10-week mass losses of the four mortars in static sulfuric acid solution are only 1.10%, 2.92%, 5.11% and 7.75%, respectively [1]. There is evidence that the flowing sulfuric acid attack is about 3.36–4.53 times as high as the static sulfuric acid attack.

3.3. Microstructures before and after flowing sulfuric acid attack

Investigation of the microstructures by using SEM before sulfuric acid attack [1] showed that the unmodified

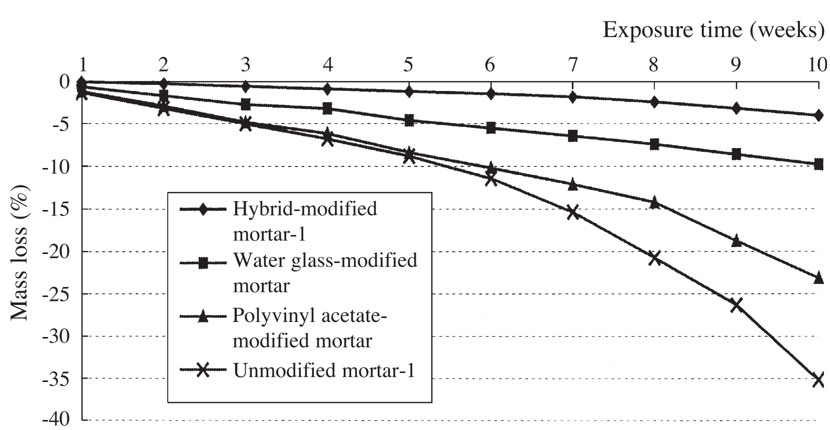
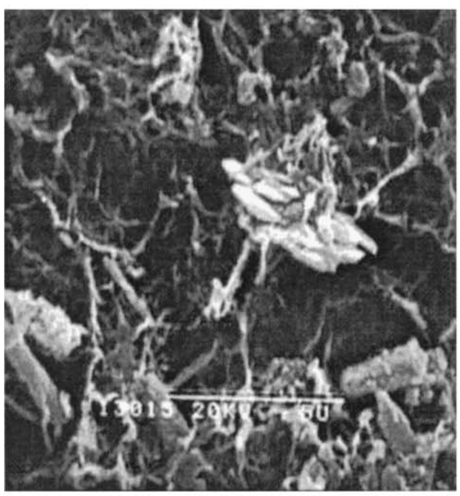


Fig. 2. Curves for mass loss versus exposure time in flowing sulfuric acid solution.

mortar contained many large crystals of $Ca(OH)_2$ and pores; however, for water glass–polyvinyl acetate hybrid-modified mortar, no clear crystalline morphology and large pores were observed, and a film composed of modifying materials was seen, indicating a denser microstructure.

Fig. 3 shows the SEM micrographs of mortars after 10-week flowing sulfuric acid attack. A considerable quantity of platelike, rice-shaped substance is seen in the central parts of the unmodified mortar after flowing sulfuric acid attack. Because the ricelike substance has an elliptical shape and large size, it can be inferred that the formation of such substance is responsible for a significant decrease in the strength. The ricelike substance is also seen in the polyvinyl acetate modified-mortar. Although polymer network can be seen in the polyvinyl-acetate-modified mortar, the microstructure of the mortar is porous. However, for the hybrid-modified mortar, no ricelike substance is found, and a relatively better network composed of modifying

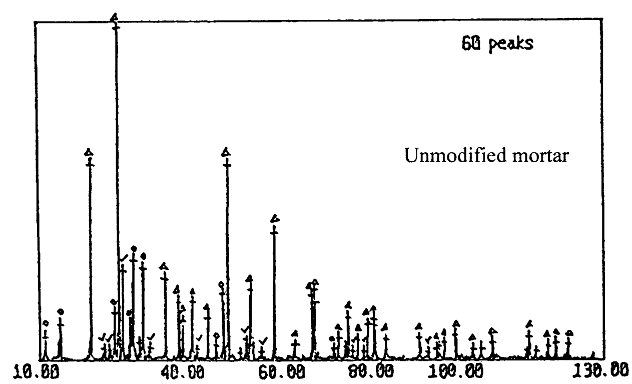
Unmodified mortar

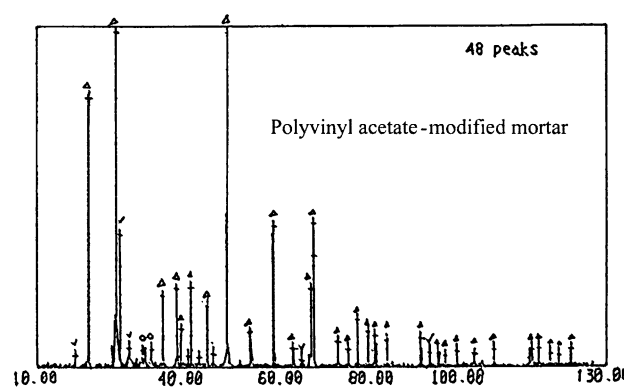


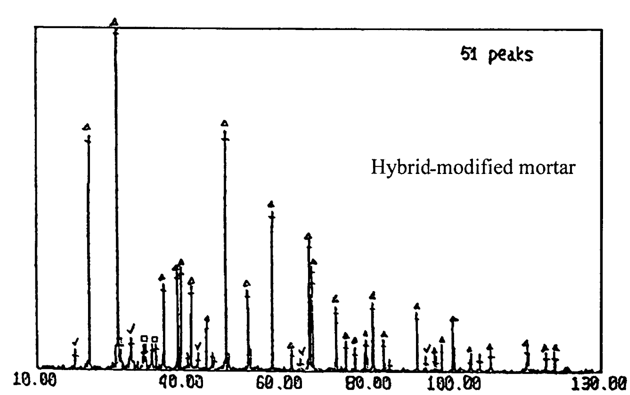
Polyvinyl acetate-modified mortar

Hybrid-modified mortar-1

Fig. 3. SEM micrographs of mortars after 10-week flowing sulfuric acid attack.







(△ –SiO_2, ○ –$CaSO_4 \cdot 0.6H_2O$, □ –Ca_2SiO_4, √ -$Mg_6Al_2Si_6O_{20}F_4$)

Fig. 4. XRD patterns of mortars after 10-week flowing sulfuric acid attack.

materials can be seen in Fig. 3, indicating good acid resistance. The benefit of the network is twofold. First, the network is highly acid resistant, leading to a significant increase in the flowing acid resistance of the mortar; second, the network may fill the large pores in the mortar (Table 2), leading to a denser microstructure.

3.4. Main chemical compositions after flowing sulfuric acid attack

Fig. 4 represents the XRD patterns of mortars after 10-week sulfuric acid attack. A large amount of $CaSO_4 \cdot 0.6H_2O$ is formed in the central part of the unmodified mortar as seen in this figure and the ricelike substance in Fig. 3, and its content is the second highest in the mortar after 10-week flowing sulfuric acid attack. $CaSO_4 \cdot 0.6H_2O$ is also found in the polyvinyl-acetate-modified mortar as seen in Fig. 4. This means that the central parts of the unmodified and polyvinyl-acetate-modified mortars were corroded. However, no $CaSO_4 \cdot 0.6H_2O$ is found in the central part of the hybrid-modified mortar in Fig. 4. It can be inferred that the central part of the hybrid-modified mortar was not corroded after 10-week storage in the flowing sulfuric acid solution.

4. Conclusions

In this study, the performance of four kinds (six groups) of mortars under flowing sulfuric acid environment is investigated. The test results indicate that the flowing sulfuric acid resistance of the hybrid-modified mortar is significantly higher than that of the other mortars. Within the scope of this study, particular conclusions may be summarized as follows:

1. The porosity of large pores of the hybrid-modified mortar is 7% lower than that of the unmodified mortar.
2. Decreases in the compressive strengths of the hybrid-modified mortar and unmodified mortar are 2.6% and 30.6%, respectively, after 10-week flowing sulfuric acid attack.
3. The relative mass losses of the hybrid-modified mortar, water-glass-modified mortar, polyvinyl-acetate-modified mortar and unmodified mortar in the flowing sulfuric acid solution up to 10 weeks are 1.00, 2.42, 5.71 and 8.67, respectively.
4. The mass losses of various mortars in the flowing sulfuric acid solution are about 3.36 to 4.53 times as high as those in the static one.
5. The network composed of modifying materials in the hybrid-modified mortar is highly sulfuric acid resistant, may fill the large pores, and thus leads to a significant improvement in the flowing sulfuric acid resistance.

Acknowledgements

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