



# Sulphuric acid resistance of soluble soda glass–polyvinyl acetate latex–modified cement mortar

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## Abstract

In order to develop a sulphuric-acid-resistant mortar at a low cost a new idea to modify cement mortar by using soluble soda glass (sodium silicate) and polymer latex as main and supplementary modifying materials, respectively was proposed. In light of an exploratory test including five kinds of polymer latexes, the polyvinyl acetate latex was chosen as the supplementary modifier. Four different mortars, namely soluble glass–polyvinyl acetate modified mortar, polyvinyl acetate modified mortar, soluble glass modified mortar and unmodified mortar were then made for a detailed contrast research. The contrast results showed that the sulphuric acid resistance of the soluble glass–polyvinyl acetate modified mortar was significantly higher than that of the other kinds of mortars. © 2001 Elsevier Science Ltd. All rights reserved.

**Keywords:** Mixture proportioning; Microstructure; SEM; Corrosion; Polymers

## 1. Introduction

In many parts of the world most of the expenditure on sewerage is allocated for improving the structural performances and the capacity of the existing network. Most collapses and stoppages of sewers are the results of sulphuric acid attack. This is because sewage from chemical industry may contain sulphuric acid and one of the final products of interaction between bacteria and domestic sewage is also sulphuric acid [1]. Good sulphuric acid resistance, therefore, is of vital importance for sewers. Reinforced mortar is a suitable construction and repairing material for relining of sewers. Small aggregate size enables the mortar to be of better durability. Small overall thickness has relatively little influence on the flow ability and the relining is easy to make. In order to further increase the durability of the relining at a low cost the authors put forward a research project for developing a new kind of mortar.

Many polymer latex-modified mortars have been developed for improving corrosion resistance [2–5]. However, all polymers are expensive. Soluble glass is cheaper than polymer latex and the acid resistance of soluble glass mortar is generally higher than that of polymer latex modified mortar. This is mainly because amorphous  $\text{SiO}_2$  forms after the setting of soluble glass. However, soluble glass mortar has a high porosity, a low strength and is brittle. The existence of nonreacted sodium silicate leads to a decrease of the water resistance of the mortar. Further, because the soluble glass was used as the only gelling material the price of the soluble glass mortar was still relatively high.

In view of these facts, the authors proposed a new idea to modify the cement mortar by using soluble glass and polymer latex as main and supplementary modifying materials, respectively. The soluble glass–polymer latex modified mortar was expected to have good properties (such as a high sulphuric acid resistance and a relatively high strength and density) at a low cost. Five polymer latexes were chosen as supplementary modifying materials, respectively, in an exploratory test and the polyvinyl acetate was proved to be the best. Based on these four different mortars, namely soluble glass–polyvinyl acetate modified mortar, polyvinyl acetate modified mortar, soluble glass modified mortar and unmodified mortar, were made for a

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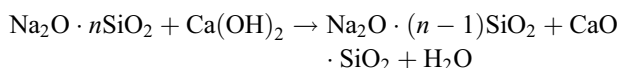
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contratest research. Both the corrosion resistance and mechanical behavior were compared and the modifying mechanism was discussed.

## 2. Basic idea for developing soluble glass–polymer latex modified mortar

Hardened conventional mortar contains larger and weaker preferentially oriented crystals of  $\text{Ca(OH)}_2$  with small surface area, leading to a high porosity.  $\text{Ca(OH)}_2$  is also the weakest component easily leached out by water flow or is attacked by sulphuric acid. In order to enhance the corrosion resistance of a mortar the content of  $\text{Ca(OH)}_2$  and interconnected capillary pores should be decreased.

Noting this, soluble soda glass was chosen as the main modifying material because: (1) the sulphuric resistance of soluble glass is higher than polymers and can bind up a part of cement and sand; and (2) soluble glass can react with  $\text{Ca(OH)}_2$  to form impermeable precipitate of C–S–H which fills the pores of mortar [6,7], and thus results in a decrease of permeability and an increase of sulphuric acid resistance.



It should be noted that many particles with various diameters of 1–6  $\mu\text{m}$  may form during the setting process of soluble glass, leading to the formation of a great amount of large air bubbles in the mortar and consequently, a decrease in corrosion resistance [8]. To eliminate this unfavourable factor, the following measures were taken: (1) dispersant was introduced to decrease the sizes of soluble glass particles and air bubbles; (2) a small amount of polymer latex was added into the mix with the expectation that the polymer film will seal various pores in the mortar. In the meantime, a bubble-eliminating agent was used to eliminate air bubbles (generated due to the use of polymer and soluble glass) [9]; and (3) fly ash was added

into the mix so that the microstructure of the mortar could be further improved with time in consequence of a secondary pozzolanic reaction between the  $\text{Ca(OH)}_2$  present there and fly ash.

## 3. Experimental

### 3.1. Materials

#### 3.1.1. Materials chosen directly

A soluble soda glass with a specific gravity of 1.44 and a viscosity index of 1.6 was chosen.  $\text{Na}_2\text{SiF}_6$  was used as hardener for the soluble glass. Ordinary Portland cement, sand and class II fly ash used were in accordance with Chinese standards. Lignosulphonate was used as dispersing agent and tributylphosphate was used as bubble-eliminating agent.

#### 3.1.2. Materials chosen from exploratory test

An exploratory contratest was carried out first. Seven categories of mortar cube specimens were made with the above mentioned soluble soda glass, five kinds of polymer latexes (including, polyvinyl acetate, polyacrylic ester, polyethylene-vinyl acetate, chloroprene rubber and epoxy resin). Strength and unit weight were used for evaluating the modifying effects of the different categories of specimens. It is shown that the polyvinyl acetate latex was the best supplementary modifying material compared with the other latexes. Test results of various modified mortars with 3, 5, 7 and 9 wt.% of soluble glass (on cement weight) showed that the mortar with 7 wt.% of soluble glass had relatively highest strength and unit weight.

### 3.2. Contratest

#### 3.2.1. Test programme

Based on the results of the exploratory test, a detailed contratest research was carried out to study the mechanical

Table 1  
Mix proportions for different groups of mortar specimens (on weight)

Material	Specimen group			
	Group 1, soluble glass–polyvinyl acetate modified mortar	Group 2, soluble glass modified mortar	Group 3, polyvinyl acetate modified mortar	Group 4, unmodified mortar
Cement	100	100	100	100
Soluble glass/lignosulphonate <sup>a</sup>	7/0.05	7/0.05		
$\text{Na}_2\text{SiF}_6$	1.05	1.05		
Polyvinyl acetate latex	3		5	
Lignosulphonate	0.5	0.5	0.5	
Tributylphosphate	6	1	10	
Fly ash	15	15	15	15
Sand	200	200	200	200
Water	55	55	55	55

<sup>a</sup> Soluble glass and lignosulphonate were mixed before producing modified mortar.



Fig. 1. SEM micrograph of unmodified mortar. 2800 × 2K; Arrow 1: large crystal; Arrow 2: large pore.

properties and sulphuric acid resistance of the soda soluble glass–polyvinyl acetate latex modified cement mortar. Four groups of mortar specimens (with different mixture proportions) were made, as shown in Table 1. Each group of specimens was composed of three 100 mm × 100 mm × 100 mm cubes and twelve 40 mm × 40 mm × 100 mm prisms. The three cubes were tested for unit weight, compressive strength and microstructure. The 12 prisms were divided into two sets. The first set of three prisms was tested for bending strength. The other set of nine prisms was tested for weight loss versus time in dilute sulphuric acid solution and content of  $\text{SO}_4^{2-}$  ions after sulphuric acid attack.

### 3.2.2. Curing conditions

Immediately after casting, the specimens were covered with Hessian polythene sheeting for 24 h at a temperature of about 19°C. The specimens were then demoulded and

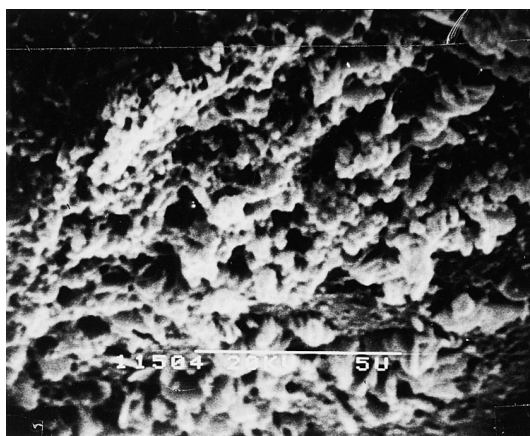


Fig. 2. SEM micrograph 1 of soluble glass–polyvinyl acetate modified mortar. 5500K (without large crystal and pores).

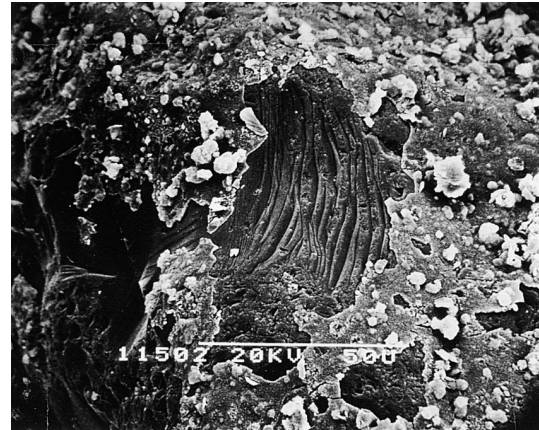


Fig. 3. SEM micrograph 2 of soluble glass–polyvinyl acetate modified mortar. 550K (with polymer film).

transferred to the curing room for further curing of 27 days at  $20 \pm 1^\circ\text{C}$  with relative humidity of 98%.

## 4. Results and discussion

### 4.1. Microstructure

The microstructures of the various mortars were studied by using SEM. It is seen in Fig. 1 that the unmodified mortar contained many larger crystals of  $\text{Ca}(\text{OH})_2$ , and pores. However, the soluble glass–polyvinyl acetate modified mortar contained mainly C–S–H, with no clear crystalline morphology and large pores (Fig. 2). Fig. 3 shows a polymer film, indicating a denser microstructure.

### 4.2. Mechanical properties

The test results are presented in Table 2. It is shown that the cube strength, bending strength and unit weight of the

Table 2  
Contratest results of different groups of mortar specimens

Test items	Specimen group			
	Soluble glass–polyvinyl acetate modified mortar	Soluble glass modified mortar	Polyvinyl acetate modified mortar	Unmodified mortar
Cubic strength (MPa)	20.7	15.1	15.0	20.3
Bending strength (MPa)	3.0	2.8	2.9	3.2
Unit weight	2.43	2.19	2.22	2.45
Weight loss after 25-week sulphuric acid attack (%)	4.9	11.4	29.5	47
$\text{SO}_4^{2-}$ content after 25-week sulphuric acid attack [BaSO <sub>4</sub> /mortar (%)]	1.8	3.0	3.3	3.98

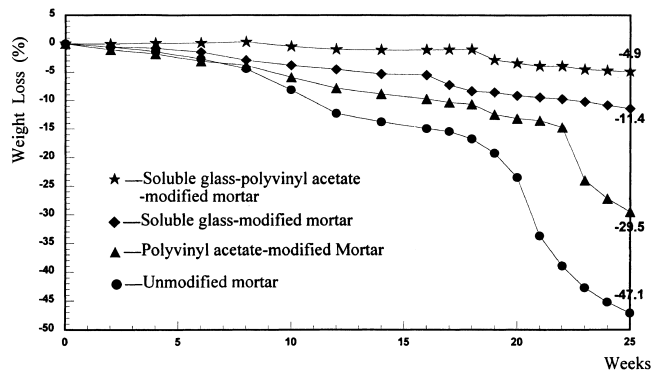


Fig. 4. Curves of weight loss versus time in sulphuric acid solution.

soluble glass–polyvinyl acetate modified mortar were higher than those of the polyvinyl acetate modified mortar and soluble glass modified mortar. The higher strength of the soluble glass–polyvinyl acetate modified mortar mainly resulted from its dense microstructure.

#### 4.3. Sulphuric acid resistance

##### 4.3.1. Weight loss in diluted sulphuric acid solution

Primary weight loss tests of mortar prisms in 0.5%, 1% and 2% sulphuric acid solution showed that the weight loss was too quick for specimens in 2% sulphuric acid solution and too slow for specimens in 0.5% sulphuric acid solution. Therefore, 1% concentration was chosen as the medium of accelerated corrosion test. The solution was put into glass beakers and changed every week. The samples were weighed once a week. The specimens were brushed softly under water with a nylon brush to remove loose surface debris before weighing.

Fig. 4 shows the test results of weight loss versus time for different kinds of mortars. The 25-week weight losses were 4.9%, 11.4%, 29.5% and 47% for soluble glass–polyvinyl acetate modified mortar, soluble glass modified mortar, polyvinyl acetate modified mortar and unmodified mortar, respectively. The weight loss of the soluble glass–polyvinyl acetate modified mortar was only 10.4% that of the unmodified mortar. The significantly higher sulphuric acid resistance of the soluble glass–polyvinyl acetate modified mortar mainly stemmed from the noticeable improvement of its microstructure and ingredients used as starting materials.

It should be noted that the sulphuric acid resistance of the low-cost soluble glass–modified mortar was noticeably higher than that of the high-cost polyvinyl acetate modified mortar in this research.

##### 4.3.2. $\text{SO}_4^{2-}$ content

After 25-week weight loss test the central parts of the different mortar specimens were taken as samples for the  $\text{SO}_4^{2-}$  content test. Ion titration was used for determining

the content of  $\text{SO}_4^{2-}$  (mainly coming from water-soluble  $\text{CaSO}_4$  by-product formed by the reaction between the Ca in cement and  $\text{H}_2\text{SO}_4$ ). As shown in Table 2 the test results had good agreement with those of the weight-loss test. The  $\text{SO}_4^{2-}$  content of the soluble glass–polyvinyl acetate modified mortar was only 45.2% that of the unmodified mortar, indicating a slower progress of formation of  $\text{CaSO}_4$ .

## 5. Conclusions

- (1) The mortar modified with 7 wt.% of soluble glass and 3 wt.% of polyvinyl acetate had a significantly higher sulphuric acid resistance compared with that modified with 5 wt.% of polyvinyl acetate and 7 wt.% of soluble glass.
- (2) The cube compressive strength, bending strength and density of the soluble glass–polyvinyl acetate modified mortar were higher than those of the polyvinyl acetate modified mortar and soluble glass modified mortar.
- (3) The sulphuric acid resistance of the 7 wt.% of soluble glass modified mortar was noticeably higher than that of the 5 wt.% of polyvinyl acetate modified mortar.

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