Surface Finishing of Concrete Structures by a Silane Series Solvent

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In many parts of the sewage line, concrete structures have been used. In those environments, hydrogen sulfide gases are very easy to be evolved. The gases are often changed to sulfuric acid, being aided by biofilims' action on the concrete. The sulfuric acid penetrates into the concrete structures and deteriorates them gradually due to the decrease of pH. Conventionally, the epoxy resin was used to protect the penetration of sulfuric acid. However, the thickness of the epoxy coating requires several millimeters. Therefore, we developed a silane compounds which could protect the penetration with the thickness of 300 micrometers. The performance and problems were testified and discussed in this study.

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1. INTRODUCTION

In Japan, sewage lines have been developed and maintained very rapidly since 1970s. Nowadays, the number of miles was about 221,000 (355,000 km) and the part of concrete rebar pipes reached about 40,000 miles (64,000 km)[(1)]. The corrosion and the following deterioration phenomena for sewage line concretes were already observed at sewerage pipes in Los angeles, USA, 1900. And also in Japan, laboratory and fields tests about the technical problem have been carried out so far. In 1987, "Guideline & Manuals for Protective Concrete Coating of Sewage Line" about the problem was established by Japan Sewage Works Agency[(2)-(4)]. Nowadays, most of Japanese engineers in this field are trying to solve the problems according to this guideline.

The corrosion and deterioration of concrete in sewage lines are originally induced by sulfate reducers and sulfur oxidizing bacteria reacting with hydrosulfate flowing into waste water. The reaction changes hydrosulfate into sulfuric acid via hydrogen sulfide and the sulfuric acid decreases the pH of concrete which leads to the structure collapse finally, since the concrete loses alkalescency. Therefore, the guideline mentioned above describes the coating-type resin lining technique in detail as one of effective corrosion protection methods. However, the technique requires the multiple repetition of coating which increases the thickness as a result and leads to high cost, particularly when the concrete structure would be used in high concentration of hydrogen sulfide.

In this paper, we investigated a silane compound for the application to coating materials which can be used for corrosion protection in sewage environment as well as for filling spray coated films' micro pores, since it might shorten the term of works by saving the repetition number and cut the cost by decreasing the thickness of coating.

2. CORROSION OF CONCRETE IN SEWAGE LINES AND ITS COUNTERMEASURE

Generally speaking, the corrosion of concrete in sewage line occurs and becomes advanced as follows:

#1: The sulfate ion which comes from cleaning substances for domestic use, shampoo, aluminum sulfate in filtration plants etc. mixes into sewage water.

#2: The biological reactions between sulfate ion and anaerobic sulfate reducing bacteria occur and hydrogen sulfide (H_2S) forms.

#3: Hydrogen sulfide gas diffuses into air through turbulence of sewage water or polluted mad.

#4: Hydrogen sulfide gas is absorbed into water condensed on side walls or ceilings made of concrete in sewage system.

#5: In the condensed water, sulfuric acid forms through the reaction between hydrogen sulfide and aerobic sulfur oxidizing bacteria.

#6: The formed sulfuric acid reacts with calcium hydroxide ($Ca(OH)_2$), ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) etc. from concrete to form gypsum ($CaSO_4 \cdot 2H_2O$), which deteriorate concrete structures finally.

The following countermeasures against the corrosion phenomena mentioned above are now investigated.

#1: Mitigation of occurrence: Inhibition of sulfate ion into sewage water, restraint of anaerobic environment etc.

#2: Inhibition of corrosion: inhibition of hydrogen sulfide diffusion, dilution of hydrogen sulfide in gas phase etc.

#3: Corrosion protection: Application of anti-sulfuric acid materials, the increase of anti-sulfuric acid property of concrete, coating of concrete surfaces. As maintenance and anti-corrosion technique for new concrete, coating-type techniques were often used. The guideline for anti-corrosion by Japan Sewage Works Agency(3) defines four ranks according to the performances, A, B, C, D_1. And D_1 is used for the severest environment. The properties required for D_1 are shown in the following table (Table 1).

Table 1 Specification for D1 category

Inspection Item	Test Method	Specification for D_1

Appearance	JIS K5600-1-1:1999	No wrinkles, irregularity, peeling, cracking of coating
Adhesiveness	JIS A6909	>1.5MPa at standard state >1.2MPa at water absorption state
Acid tolerance	JIS K5600-6-1	No bunch, cracking, softening, dissolution of coating after 60 days immersion in 10% sulfuric acid solution
Penetration depth of sulfuric acid	EPMA	<5% penetration depth of the designed thickness And <100 μm, After 120 days immersion in 10% sulfuric acid solution
Alkali resistance	JIS K5600-6-1	No bunch, cracking, softening, dissolution of coating after 60 days immersion in calcium hydroxide saturation solution
Permeability	JIS A1404	<0.15g of transmissibility coefficient

It should be noted that the penetration rate of sulfate acid ion into the coating layer is rgulated. In fact, the guideline describes that the appropriate technique compatible with the specification should be thick coating and multiple repeated coating processes [3]. In this experiment, we applied a silane compound based sealer to concretes for sewage lines and tried to reduce the thickness of coating down to 300 micro meters and also decrease the repetition numbers of coating down to two times, so that the thinner silane compound coating would satisfy the specification for D_1 category (Table 1).

3. EXPERIMENTAL

3.1 Inorganic sealer

Conventionally, epoxy and polyurethane resins have been mainly diluted by thinner and the resin part of them has been used for the purpose of sealing(5). However, they could not seal the micro pores of thermal spray coating perfectly, since the solid concentration was low. And as a result, they failed to increase the coating performances. Therefore, we used other sealer based on silane compounds in the series of investigation to overcome the defects of conventional sealers. One of the authors has already investigated the sealer in the past(6) to increase the corrosion resistance of thermal spray coating and it was already patented by D & D Corporation (7). Now in Japan, it is often used for highway bridges, runaway lights and bridge of airports etc. and earns a good reputation. At the same time, it is still investigated on laboratory scale(8). The inorganic sealer is based on a silane compound and a curing catalyst is added to it. It absorbs moisture components in air to form a polymer through hydrolysis – condensation reactions (7). In the series of experiments, we have applied this kind of silane compound sealer to the protection of deteriorated concrete in sewage lines.

In this investigation, four kinds of silane compounds were tested by changing the molecular weights of oligomers which was composed of methyl silane and phenyl silane to fix the composition of silane compound sealer. The samples were describes in Table 2.

Table 2 Molecular weight of silane compounds used in this experiment

specimen number	average molecular weight
1	360
2	760
3	1,500

4	1,700

As curing catalyst, two kinds of titanium complex, a kind of aluminum complex, and zirconium complex were tested to evaluate the curing rate and protection capability against sulfuric acid penetration. In order to choose an appropriate filler, titanium oxide, talc, aluminum borate whisker, glass flake, burned kaolin, attapulgite and burned scallop shell were tested. According these evaluations, the composition of silane compound sealer was fixed to apply to the coating of concrete.

3.2 Evaluation tests

Evaluation tests for the silane compound were classified into four categories in this study. The first one was carried out to fix the molecular weight of silane compound applicable to the concrete. Various compounds were coated (200g/m^2) to mortar plates (70mm x 70mm, the thickness: 20mm), hardened and kept at room temperature in 7 days. Then they were immersed into 10% sulfuric acid and the surface conditions were observed by naked eyes. And the protection capability against the penetration of sulfuric acid was also evaluated by the penetration rate of sulfate ion.

The second test was carried out to fix a curing catalyst appropriate for the coating. The four kinds of chemicals mentioned in 3.1 were added to a certain kind of silane oligomer. Then the curing rates and protection capability against sulfuric acid penetration were measured.

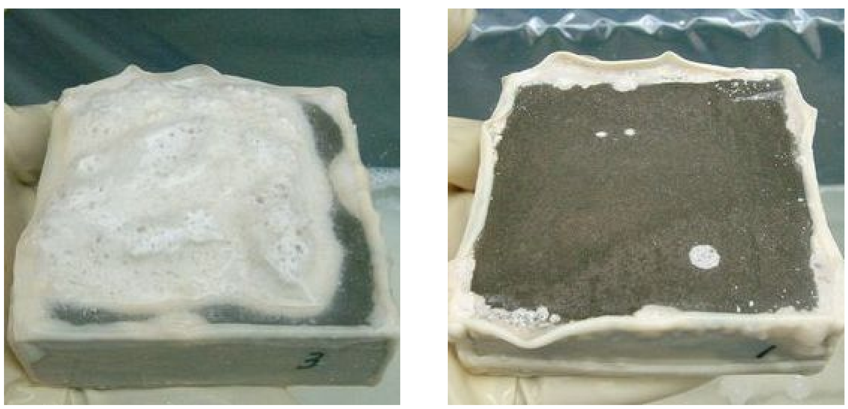
The third test was carried out to fix a kind of fillers appropriate for the coating. The seven kinds of materials as filler candidate were already mentioned in the previous section. They were added to a certain silane compound and the protection capability was investigated in the same way with the first test.

From all of these three kinds of tests mentioned above, a certain composition of silane compound for concrete coating was fixed. Then it was applied to concrete coating and the characteristics were investigated how it could be complied with the specification of D1. (The fourth evaluation tests)

4. RESULTS AND DISCUSSION

4.1 Composition determination of silane compound

The silane compounds having various molecular weights shown in Table 2 were coated on mortar plates and the surface appearances were observed by naked eyes. For all specimens from No.1 to 4, titanium complex (A type) was used as curing catalyst. All specimens were damaged and peeled off due to the penetration of sulfate ion to some extent. However, the extent differs from specimen to specimen. For specimen No.1, 100% of the coating was peeled off due to the penetration of sulfate ion. As for the specimen No.2, 90% of the specimen's surface was peeled off. For both No.3 and 4 or 5 % of their surfaces were



(1) specimen No.2 (2) specimen No.3

Fig.1 Surface apperances for specimen No.2 and 3.

peeled off. Fig. 1 shows the observation results by naked eyes for specimen No.2 and 3. As explained in the previous report by Japan Sewage Works Agency[(2)], penetrated sulfate ion reached the concrete surface through the coating layer and as a result, the concrete was deteriorated and heaved up. It suggests that the protection capability against sulfuric acid depended on the penetrate rate of sulfuric acid.

Fig 2 shows the correlation between the molecular weight of silane compound and the ratio of peeling area by the penetration of sulfuric acid. As shown in the figure, the protection capability increased with the molecular weight of silane compound.

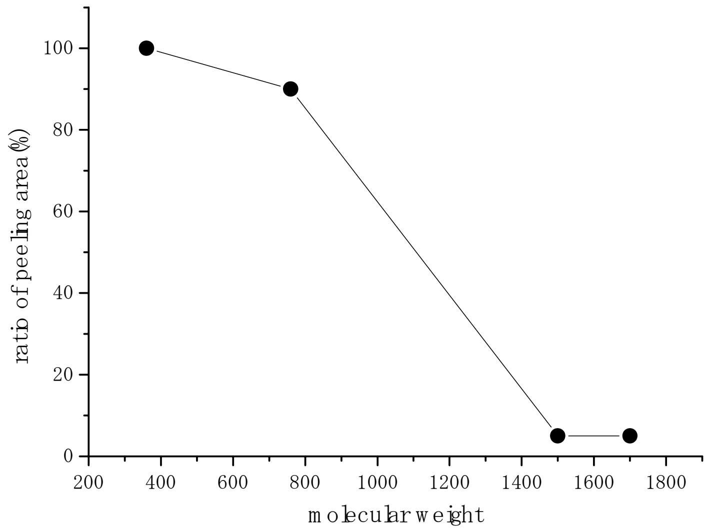


Fig.2 Correlation between ratio of peeling area and molecular weight of silane compound

On the other hand, the durability for all of these specimens was investigated by a complex cycle environmental test (the repetition of immersion in hot water at 80 degrees Celsius for two hours and drying at 80 degrees Celsius for four hours). The result indicates that the specimen No.4 showed the micro cracks in the coating layers at the very early stage of the tests. It suggests that the internal stress in the coating induced by the repetition of wetting and drying was accumulated and the coating layer was cracked when the internal stress exceeded over the tensile stress of coating layer. From all of these tests, we chose the specimen No.3 for the following tests.

4.2 Determination of curing catalyst

Using silane oligomer having the molecular weight of 1,500, we evaluated the protection capability against the penetration of sulfate ion for the five kinds of curing catalysts by the same method with that in the previous section. As for aluminum based filler and zirconium based one, the curing process required several days more than 3 days and we concluded that they were inappropriate from the viewpoint of practical application. As for the two kinds of titanium complex, the complete curing times were 24 hours. However, the protection capability against the penetration of sulfuric acid for type A was better than that for type B and therefore, we chose titanium complex type A was chosen for the following test.

4.3 Determination of filler

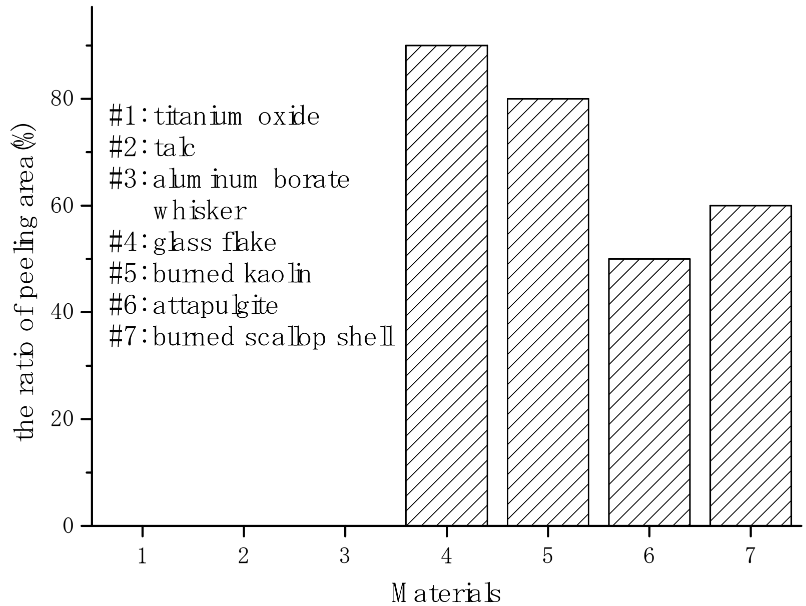


Fig.3 Change of protection capability against the penetration of sulfuric ion by the difference of fillers

Seven kinds of fillers were dispersed into the silane oligomer whose average molecular weight was 1,500, so that the weight ratio of filler to oligomer would be 0.25. And titanium complex of 2% was added to the compound as curing catalyst. The specimen's protection capability against the penetration of sulfate ion was evaluated by the same method mentioned above. The results were shown in Fig.3. They suggest that the positive effects for the protection capability of concrete were remarkable for titanium oxide, talc and aluminum borate whisker fillers. However, the cost of aluminum borate whisker is relatively high and inappropriate for the practical application. Therefore, we chose titanium oxide and talk as filler in this investigation.

As for the two kinds of filler (titanium oxide and talk), the filler ratios were changed in the following investigation to increase the protection capability against the penetration of sulfuric acid. Concretely speaking, the weight percentage of filler was increased to 40 % for both cases, and the same investigation was carried out. When the only titanium oxide was added as filler, the capability decrease slightly. When the mix of titanium oxide and talk (the weight ratio 1:1) were used on the other hand, the penetration capability showed the same very high value with those in Fig.3. Therefore, we chose the mix of two fillers for the following experiment.

4.4 Evaluation for the performance of the new concrete coating agent

From all of the investigations and discussion described from section 4.1 – 4.3, we decided the composition of the new silane coating agent in the following table (Table 3).

Table 3 Chemical composition of silane compound decided by this investigation.

Silane oligomer	Titanium oxide	Talc	Curing catalyst
60 wt%	20 wt%	20 wt%	2 wt%

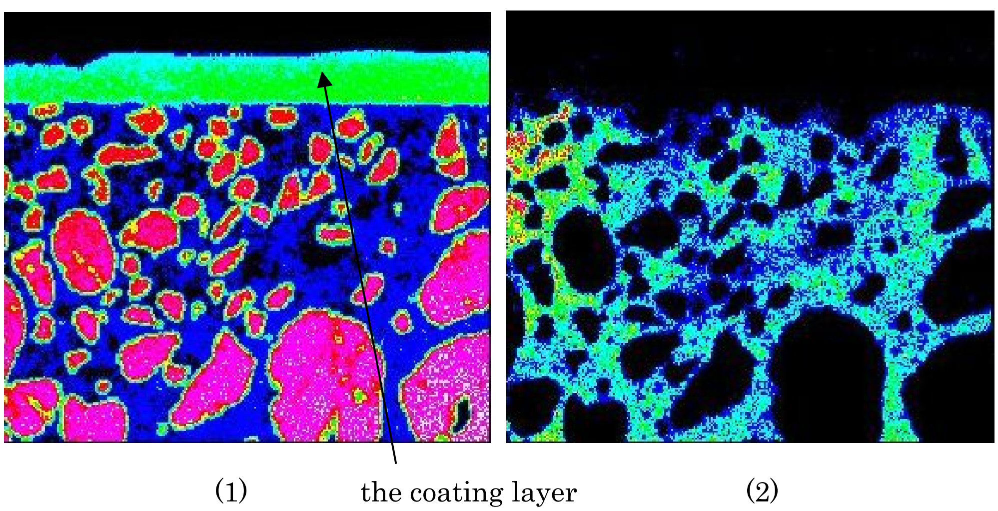


Fig. 4 EPMA results for the concrete specimen coated by the silane compound

The coating agent shown in table 3 was coated to the concretes. The amount of coating was 600g/m^2 corresponding to the thickness of 300 micro meters. And their performances for inspection items described by D_1 specification (Table 1) were investigated.

As for the appearance described JIS K5600-1-1:1999, no wrinkles, irregularity, peeling nor cracking of coating were observed. The adhesiveness test according to JIS A6909 indicates that it showed 3.1MPa at the standard state and 1.9MPa at water absorption state. Both values exceeded the standard value well. The peeling of coating was not observed, but the concrete itself was broken. The acid tolerance was achieved against sulfuric acid completely. When the coated concrete was immersed in 10% sulfuric acid for 60 days, the coating did not show any damages. As for the penetration depth of sulfuric acid corresponding to the protection capability against sulfuric acid penetration directly, the penetration of sulfur element in the coating layer was not observed after 120 days immersion. The result of EPMA analysis was shown in Fig.4. Fig.4-(1) shows the element analysis for silicon and the coating layer could be confirmed in the photo. However, sulfur level was almost zero in the corresponding area in Fig.4-(2) and it indicates that the coating layer did not contain sulfur and also that the penetration of sulfuric acid did not occur within 120 days after the beginning of immersion.

The concrete specimen was immersed into calcium hydroxide solution for 60 days to investigate alkali resistance. And any change was not observed after the immersion and it indicates that the alkali resistance satisfied D_1 specification. Finally, the water permeability was 0.01 g for the new coating agent and the result also satisfied D_1 specification.

5. CONCLUSIONS

We carried out a series of experiments to develop the concrete coating for the protection against the penetration of sulfuric acid. The developed chemical was silane based oligomer with fillers and curing catalyst. Being compared with the conventional coatings, the new coating chemical realized the complete protection against the penetration of sulfuric acid with thinner coating layer (300 micro meters) as well as other performances such as appearance, adhesiveness, acid tolerance etc., which could complied with the severest standard by Japan Sewage Works Agency completely. It should be further investigated and developed about many practical problems including coating techniques.

However, the significance of the silane compound based coating will be focused more in the near future.

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