Third International Conference on Sustainable Construction Materials and Technologies http://www.claisse.info/Proceedings.htm

# Evaluation of Sulfuric Acid Resistant Mortar as a Corrosion Protection Method for Sewerage Facilities

*Hiroyuki Fujimoto[1], Fumio Mishina[2], Kouji Onishi[3], Katsuichi Miyaguchi[4]*

*[1] Japan Sewage Works Agency, 5141 Shimo-Sasame,Toda, Saitama, Japan, 335-0037, E-mail: Fujimoto@jswa.go.jp*
*[2] Japan Concrete Erosion Prevent Association, Layered Ohtemachi Bldg., 1-4-5-401, Uchikanda, Chiyoda-ku, Tokyo, Japan, 101-0047, E-mail: f.mishina@ace-con.co.jp*
*[3] Ube Industries, Ltd., Seavans North Bidg.,1-2-1, Shibaura, Minato-ku, Tokyo, Japan, 105-8449, E-mail: k.ohnishi@ube-ind.co.jp*
*[4] Denki Kagaku Kogyo Kabushiki Kaisha, 2209 Omi, Itoigawa, Niigata, Japan, 949-0393,E-mail: katsuichi-miyaguchi@denka.co.jp*

## ABSTRUCT

Corrosion protection method for sewerage concrete facilities against sulfuric acid is mainly resin lining either painting type or sheet type in Japan. Recently, Japan Sewage Works Agency and private companies have jointly evaluated sulfuric acid resistant mortar for corrosion protection. This report describes evaluation of the corrosion protection method using the sulfuric acid mortar. Resign lining needs two processes; repairing concrete surface with sulfuric acid resistant mortar and application of resin lining. Sulfuric acid resistant mortar requires only one process; application of the mortar on concrete surface. Due to this fact, this method enables to simplify application and to reduce application period. When sewerage facilities are retrofitted or repaired, it is required to minimize application period to avoid inconvenience of wastewater treatment operation. Thus, this method is especially useful for retrofitting and repairing sewerage facilities.

**Keywords,** sulfuric acid resistant mortar, Portland cement based mortar, alumina cement based mortar, concrete corrosion, sewerage concrete facilities

## 1. MECHANISM OF SULFURIC ACID CORROSION IN SEWERAGE FACILITIES

Japan Sewage Works Agency has published ‘Technical guideline and manual on corrosion protection for sewerage concrete facilities’. According to this guideline, mechanism of sulfuric acid corrosion in sewerage facilities is summarized as follows.

The concrete corrosion is caused by carbonation, salt damage, frost damage, alkali-silica reaction and chemical attack of acid substance. Concrete corrosion in sewerage facilities is categorized as a chemical attack of sulfuric acid to concrete structures. Complex biological and chemical processes of sulfide generation and sulfuric acid corrosion, which takes place within sewer systems and covered tanks shown in Fig. 1, is shown as follows:

$$3Ca(OH)_2+3H_2SO_4+3CaO\cdot Al_2O_3+26H_2O \rightarrow 3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32H_2O\text{(ettringite)}$$
$$H_2SO_4+Ca(OH)_2 \rightarrow CaSO_4\cdot 2H_2O\text{(gypsum)}$$

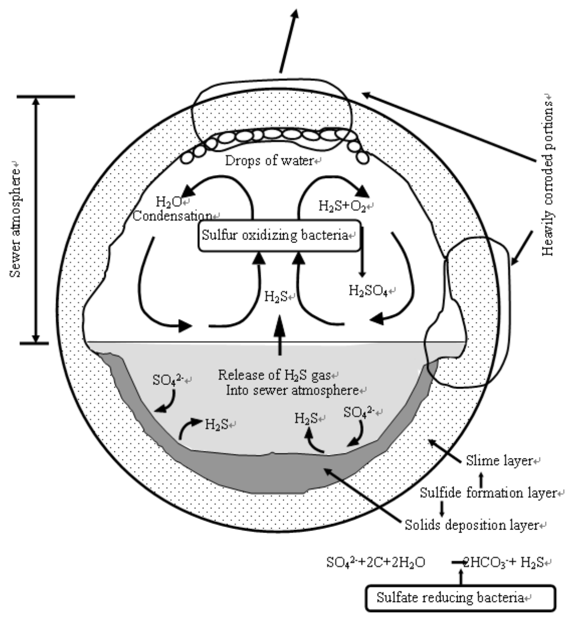


**Figure 1. Processes of sulfide generation and sulfuric acid concrete corrosion in sewer systems**

Under anaerobic conditions, sulfate reducing bacteria in wastewater or sludge reduce sulfate ($SO_4^{2-}$) to sulfide ($S^{2-}$). Hydrogen sulfide ($H_2S$) gas is released from the wastewater or sludge to the atmosphere in sewers or tanks. Turbulence can cause its rapid release. Released $H_2S$ gas combines with moisture on the non-submerged concrete surfaces of the pipes or tanks, and is oxidized to sulfuric acid by aerobic sulfur oxidizing bacteria. Sulfuric acid attacks the non-submerged concrete surface. Finally, reaction of sulfuric acid and hydrated Portland cement in concrete structures surface forms ettringite ($3CaO\ Al_2O_3\ 3CaSO_4\ 32H_2O$) and gypsum ($CaSO_4\ 2H_2O$), and corroded portion of the surface, a soft corrosion product at less than pH 1, is easily washed away by wastewater or torn off.

The rate of concrete corrosion is generally affected by the characteristics of wastewater such as sulfuric ion concentration and the local conditions for each sewerage facility. Many variables directly or indirectly affect sulfide generation, $H_2S$ gas release and the rate of corrosion, but the rate is varied from one location to another location significantly due to $H_2S$ gas concentration, relative humidity and temperature in the atmosphere. The $H_2S$ gas concentration varies from 0 ppm to 1,000 ppm and more and is considered as the most influencing factor among many variables.

In the sewerage systems, pumping stations and wastewater treatment plants, the structures and portions that tend to have severe hydrogen sulfide corrosion damages can be summarized in Table 1 based on the past technical reports and field surveys.

**Table 1. Structures and portions that tend to have severe sulfuric acid corrosion**

| Facilities | Structures and portions with severe sulfuric acid corrosion |
|---|---|
| Sewer system | - Junction and manhole with large drop or turbulence<br>- Upstream and down stream of inverted siphon<br>- Connection from building wastewater holding tank<br>- Outlet of force main into gravity sewer |
| Pumping station<br>(covered facilities) | - Inlet<br>- Outlet into gravity sewer |
| Wastewater treatment plant<br>(covered facilities) | - Receiving tank and connecting channel<br>- Distribution tank and connecting channel<br>- Effluent weir and flume of primary settling tank<br>- Inlet into aeration tank<br>- Overflow weir and flume of gravity thickener and effluent pit<br>- Sludge storage tank<br>- Supernatant holding tank of anaerobic digestion tank<br>- Transportation facility of recycle flow from sludge handling units |

The rates of hydrogen sulfide concrete corrosion in sewerage facilities are much higher in summer than in winter or in the areas with higher annual average temperature than in the areas with lower annual average temperature.

The two year exposure test using mortar test pieces at six corrosive atmospheric environments in Japan revealed that without any corrosion preventing methods the maximum concrete corrosion rates could be 10 mm/year and 6mm/year for the average $H_2S$ concentrations of 100 mg/l and 10 mg/l, respectively.

## 2. CORROSION PROTECTION TECHNOLOGIES DEVELOPED AND APPLIED IN JAPAN

Japan Sewage Works Agency has conducted research projects on the mechanism of sulfuric acid concrete corrosion in the sewer systems and wastewater treatment plants. According to the 'Technical guideline and manual on corrosion protection for sewerage concrete structures', corrosion protection technologies are summarizes as follows.

The sulfide control techniques and the approaches to prevent concrete structures from sulfuric acid corrosion, which have been developed and applied in Japan, are categorized in Table 2 in terms of classification of technology, principles and purposes, and facilities.

**Table 2. Sulfide control methods and approaches to prevent sulfuric acid corrosion**

| Classification of Methods | Principle and purpose | Facilities | Methods and approaches |
|---|---|---|---|
| Control of sulfuric acid formation | Reduction of $SO_4^{2-}$ concentration in wastewater | Sewer system | Reduction of sulfide generation potential:<br>- regulation for industrial or hot spring wastewater discharge with high $SO_4^{2-}$con.<br>- prevention of sea water infiltration |
| | Control of biological sulfide generation in wastewater and sludge | Sewer system | Prevention of anaerobic condition in wastewater:<br>- air injection, oxygen injection and nitrate salt injection into force main<br>- structural modification of inverted siphon<br>- cleansing of concrete surface and flushing of sediments in gravity sewer system |
| | | Pumping station and wastewater treatment plant | Prevention of sulfide generation potential:<br>- optimum operation of pumps<br>- optimum operation of units process in wastewater treatment plants |
| | Prevention of $H_2S$ gas release into atmosphere | Sewer system, pumping station and wastewater treatment plant | Oxidation and precipitation of sulfide:<br>- ferric chloride feeding, polyferric sulfate feeding<br>Structural modification to reduce $H_2S$ gas release:<br>- modification of inlet pipe and large hydrological flow drop |
| | Inhibition of sulfur oxidizing bacteria activity forming sulfuric acid | Sewer system, pumping station and wastewater treatment plant | Reduction of $H_2S$ gas concentration:<br>- ventilation and deodorization<br>Drying of concrete surface:<br>- ventilation<br>Inhibition of sulfur oxidizing bacteria activity:<br>- mixing of bacteriostatic agents into concrete |
| Prevention of concrete corrosion | Upgrading of sulfuric acid resistance in concrete | Sewer system, pumping station and wastewater treatment plant | Resin lining on concrete surface:<br>- painting type<br>- sheet type<br>Upgrading sulfuric acid resistance of concrete itself:<br>- sulfuric acid resistant concrete |

In this table, technologies related to biological sulfide generation control, $H_2S$ gas release prevention into atmosphere and sulfur oxidizing bacteria activity inhibition are defined as the sulfuric acid formation control technology. And other technologies related to sulfuric acid resistant concrete and resin linings are defined as the concrete corrosion prevention technology.
Among those technologies classified in Table 2, only resin lining method on the concrete surface in sewerage facilities is the commonly applied anti-corrosion technology. However, air injection and oxygen injection for preventing anaerobic condition in wastewater, and chemical feeding for sulfide oxidation or precipitation are applied in case that a large amount of hydrogen sulfide might be generated and built up in sewer systems such as force mains.

## 3. SULFURIC ACID RESISTANT MORTAR FOR CORROSION PROTECTION

Resin lining method, painting type and sheet type, has been generally adapted for corrosion protection method for concrete structures of sewerage facilities. In case of retrofitting of sewerage facilities or machineries, application of corrosion protection method is strictly limited to change operation temporally. Sulfuric acid resistant mortar can be applied directly on wet concrete surface, and it can be applied at one time for both surface repairing and protection layer; thus, application period can be reduced significantly. Japan Sewage Works Agency and private companies have studied the application of sulfuric acid resistant mortar as a corrosion protection method for concrete structure of sewerage facilities. In this study, Portland cement based mortar and alumina cement based mortar were tested as sulfuric acid resistant mortar.

### 3.1 Corrosion Mechanism of Sulfuric Acid Resistant Mortar

Sulfuric acid resistant mortar is corroded itself by sulfuric acid, but corrosion rate is very slow compared to concrete or ordinary mortar. Corrosion mechanism of sulfuric acid resistant mortal is described below.

### 3.1.1 Portland Cement based Mortar

Sulfuric acid resistant mortar based on Portland cement reduces its calcium hydroxide content to several % (usually around 20%) by containing blast furnace slag fine powder and fly ash; thus, inhibits production of gypsum dehydrate. Also, silica fume, which has specific surface area of 40 to 70 times as much as that of Portland cement, is mixed to compact mortar structure; thus, inhibits intrusion of sulfuric acid into the mortar. Based on the inhibition mechanism, the rate of corrosion can be decreased. Corrosion mechanism and chemical reactions are shown in Figure 2.

$Ca(OH)_2$ + $H_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O$ (gypsum dihyrate)
$3Ca(OH)_2 + 3H_2SO_4 + 3CaO \cdot Al_2O_3 + 26H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ (ettringite)

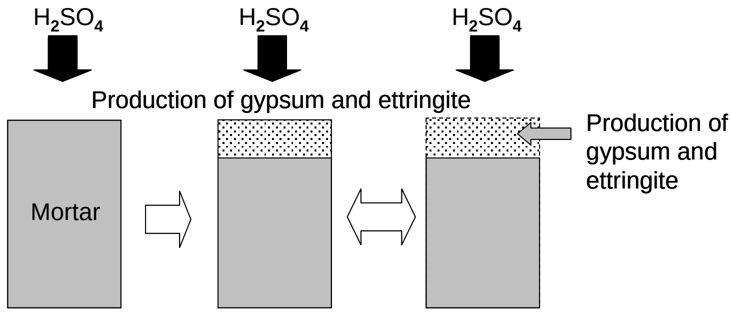


**Figure 2. Corrosion mechanism of Portland cement based mortar**

### 3.1.2 Alumina Cement based Mortar

Sulfuric acid resistant mortar based on alumina cement does not contain calcium hydroxide; thus, chemical reaction is different from that of Portland cement mortar. In case of alumina cement mortar, when pH decreases, aluminum hydroxide, which is stable substance, is formed. Aluminum hydroxide inhibits intrusion of sulfuric acid into mortar. When pH decreases less than 4, aluminum hydroxide will resolve as aluminum ion. At the same time, healthy mortar reacts sulfuric acid; then, aluminum hydroxide will be formed, and will inhibit pH declining. Corrosion mechanism and chemical reactions are shown in Figure 3.

1. pH>4

$C_3AH_6 + 3H_2SO_4 \rightarrow 3CaSO_4 \cdot 2H_2O + 2Al(OH)_3$ ($C=CaO$, $A=Al_2O_3$, $H=H_2O$)

2. pH<4

$2Al(OH)_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 6H_2O$

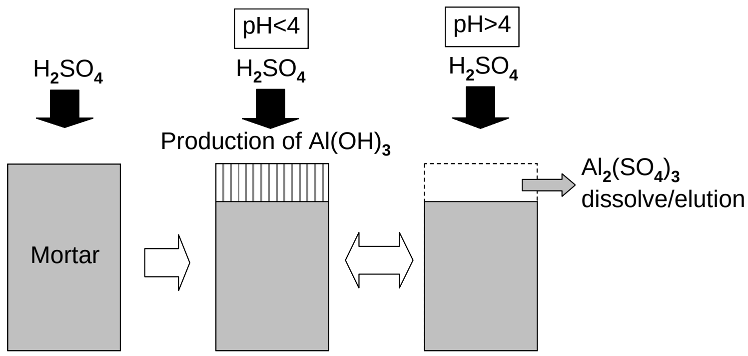


**Figure 3. Corrosion mechanism of alumina cement based mortar**

### 3.2 Sulfuric Acid Immersion Test

The concentrations of sulfuric acid in this sulfuric acid immersion test were 0.5%, 1%, 3%, 5% and 10%. The size of the test pieces was 50mm of diameter and 100mm height. Portland cement based mortar and alumina cement based mortar were tested.

Test samples were made as shown follows; first, ingredients were set in molds and put in the air (20℃) for 24 hours, second after removing molds, samples were put in water with 20℃ for 28 days. Then, these samples were put in sulfuric acid solutions, 0.5% to 10% with atmospheric temperature of 20℃. For 28 weeks, sulfuric acid solutions were exchanged every week. After that, sulfuric acid solutions were exchanged every 4 weeks.

During one year of this test, depth (from original surface) of neutralization dyed with phenolphthalein was measured. Figure 4a and 4b show the relationship between the depth of neutralization and testing period. Neutralization rate of alumina cement based mortar was significantly slower than that of Portland cement based mortar.

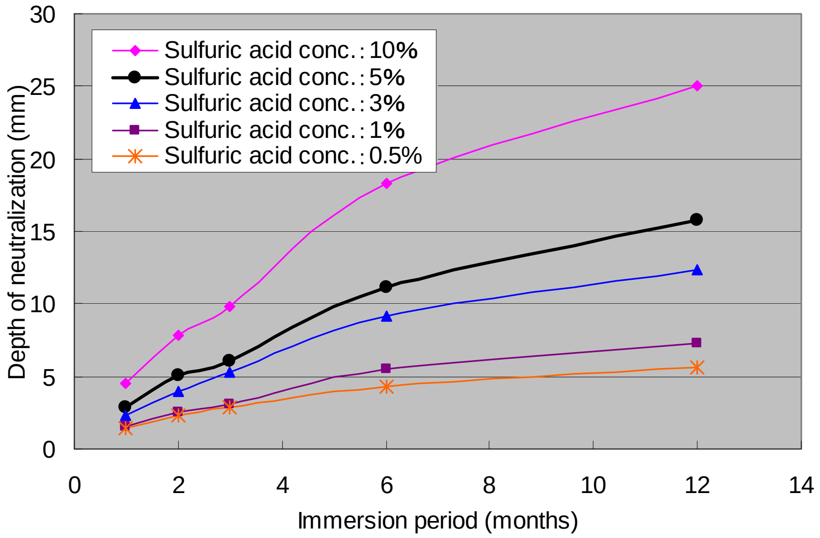


**Figure 4a. Sulfuric acid immersion test: Portland cement based mortar**

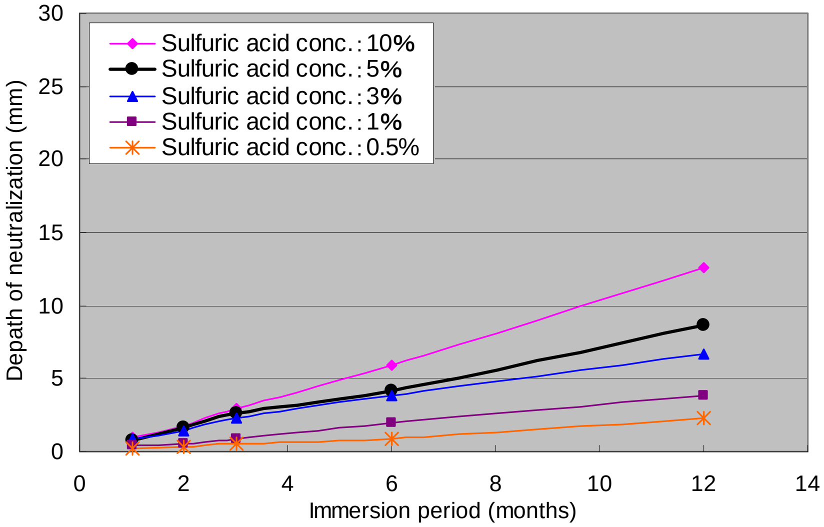


**Figure 4b. Sulfuric acid immersion test : alumina cement based mortar**

In comparison, ordinary mortar samples were also tested in 5% sulfuric acid solution. Ordinary mortar consisted of cement and sand (weight ratio of 1:3), and water (water/cement ratio 50%). Test samples were made as described before. Also, sulfuric acid solution was exchanged with same frequency as described before. Figure 5 shows the results of the test.

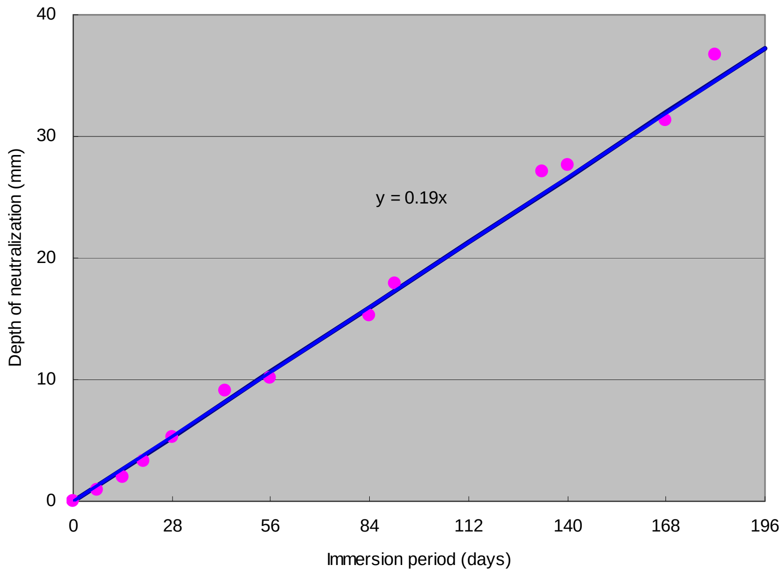


**Figure 5. Sulfuric acid (5%) immersion test: ordinary mortar**

### 3.3 Basic Concept of Design Method

Figure 6 shows the relationship between the depth of neutralization and immersion period in 5% sulfuric acid solution using alumina cement based mortar and ordinary mortar. Based on this result, thickness of alumina cement based mortar for corrosion protection is calculated. Basically, the ratio of neutralized depth of ordinary mortar and alumina cement based mortar is calculated; then, based on the actual neutralized depth of the objective concrete structure, necessary thickness of alumina cement based mortar will be calculated. As shown in Figure 6 concerning ordinary mortar:

$y_1$=0.19x (1)

where x: period (days) and $y_1$: neutralized depth (mm).

Also, concerning alumina cement based mortar:

$y_2$=0.024x (2)

where x: period (days) and $y_2$: neutralized depth (mm)

If ordinary mortar was neutralized 60mm for 10 years, x= $y_1$/0.19=60/0.19=316

Then, we get $y_2$=0.024*316=7.6mm.

Considering safety, for example, the thickness of alumina cement based mortar will be 10mm.

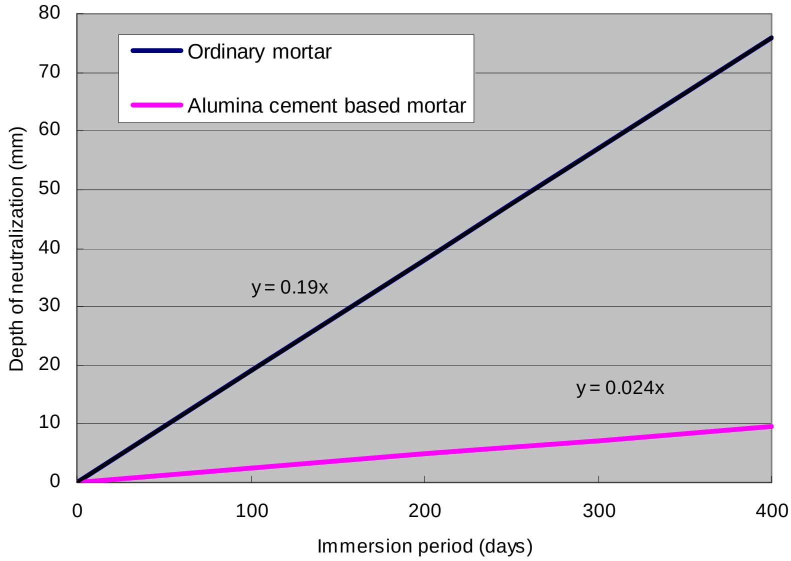


**Figure 6. Sulfuric acid (5%) immersion test**
**(Alumina cement based mortar and ordinary mortar)**

### 3.4 Exposure Test in Sewerage Facility

Exposure test in sewerage facility was conducted in two years. Test pieces of Portland cement based mortar, alumina cement based mortar and ordinary mortar were set in a sewerage manhole. The size of the test pieces was 100mm of diameter and 100mm height. In the manhole, average air temperature was 13℃ in winter and 25℃ in summer. Also, hydrogen sulfide concentration varied from zero to 220ppm, and average concentration was 20ppm.. After one year and two years, depth from original surface of neutralization (from original surface) dyed with phenolphthalein was measured (Table 3). After two years exposure, sulfuric acid resistant mortar was slower to be neutralized than ordinary mortar. Photo 1 shows cross-sections of test pieces dyed with phenolphthalein after two years of exposure. This test shows that neutralization of alumina cement based mortar was slowest of all.

At one year exposure, Portland cement based mortar was more neutralized than ordinary mortar. This result needs further investigation.

**Table 3. Depth of neutralization (mm)**

| Period | 1year | 2years |
|---|---|---|
| Portland cement based mortar | 3.3 | 11.3 |
| alumina cement based mortar | 0.0 | 0.4 |
| ordinary mortar | 2.1 | 17.9 |

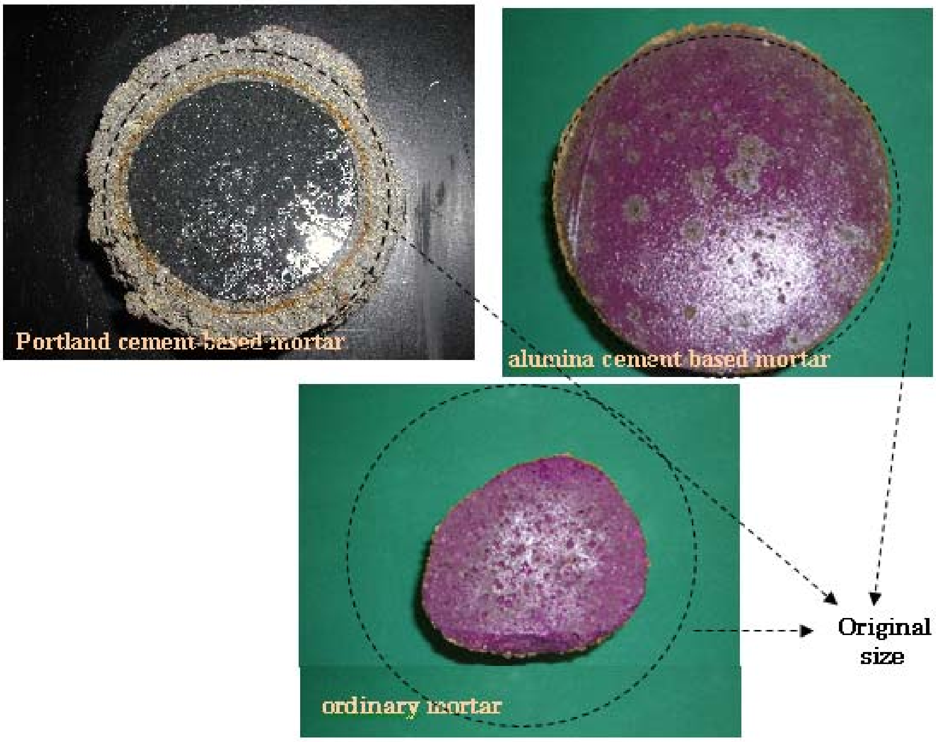


**Photo 1. Cross section spray dyed with phenolphthalein**

## 4. CONCLUSION

In addition to the resin lining method, painting type and sheet type, sulfuric acid resistant mortar was studied and evaluated. Base on the immersion test and exposure test, it was confirmed that the corrosion rate of sulfuric acid resistant mortar was slower than that of ordinary mortar. Corrosion resistance of alumina cement based mortar was significant. Also, based on the test results, basic concept of design method was developed. Because crack of sulfuric acid mortar layer causes severe risk to the concrete structure, sulfuric acid resistant mortar should be applied carefully.

## REFERENCES

Japan Sewage Works Agency (2012), Technical guideline and manual on corrosion protection for sewerage concrete structures

Japan Sewage Works Agency (2008), Report on technical evaluation of corrosion protection technology by sulfuric acid resistant mortar