Long-term Follow-up Survey on Sulfuric Acid Resistant Mortar

Background of the Follow-up Survey

FY	Background	JS Corrosion Prevention Manual*1
2000-2003	—	Development of 5x mortar*2 through joint research with two private companies
2003-2013	—	Test installation and follow-up of 5x mortar in the inflow channel of the actual treatment plant
2004-2007	Development of **10x mortar***3 through joint research with four private companies	—
2004-2014	—	Test installation and follow-up of 5x mortar in human pores infected of the actual treatment plant
2005-2007	—	Technical evaluation of sulfuric acid-resistant mortar anti-corrosion technology *Evaluated technology: 5X mortar
2008-2019	**Test execution** of four types of **10x mortar** in the primary settling tank of the WWTP. **Exposure tests of the specimens** since FY 2009.	—
April 2012	—	Second revision of the JS anti-corrosion manual added mortar lining method using sulfuric acid-resistant mortar (5x mortar)

*1: Guidelines and manuals for corrosion control and prevention technology for sewerage concrete structures.
*2: Mortar with a neutralization depth of 1/5th that of JIS mortar in a sulfuric acid immersion test under the same conditions.
*3: Mortar with a neutralization depth of 1/10th that of JIS mortar in a sulfuric acid immersion test under the same conditions.

- Report on the Follow-up survey on 10x Mortar Completed in 2019
- A need to review the design process indicated in the JS Corrosion Prevention Manual based on the results of the follow-up survey

Follow-up Survey Overview

◆sulfuric acid-resistant mortar with follow-up studies

*Used sulfuric acid-resistant mortar from the four companies involved in the joint research

Specimen used	Features
A	Uses alumina cement and special aggregate with high sulfuric acid resistance and improved densification to improve sulfuric acid resistance
B	Acrylic resin impregnation modifier is applied to sulfuric acid-resistant mortar to secure high sulfuric acid resistance by the combined effect
C	Improved sulfuric acid resistance by improving the densification of the hardened mortar and the sulfuric acid resistance of the hardened component itself
D	Sulfuric acid resistance has been improved by using a silicon compound as a binder of mortar

◆ Survey procedure

- Conducted a follow-up survey at the primary settling tank of real WWTP

◆ Survey items

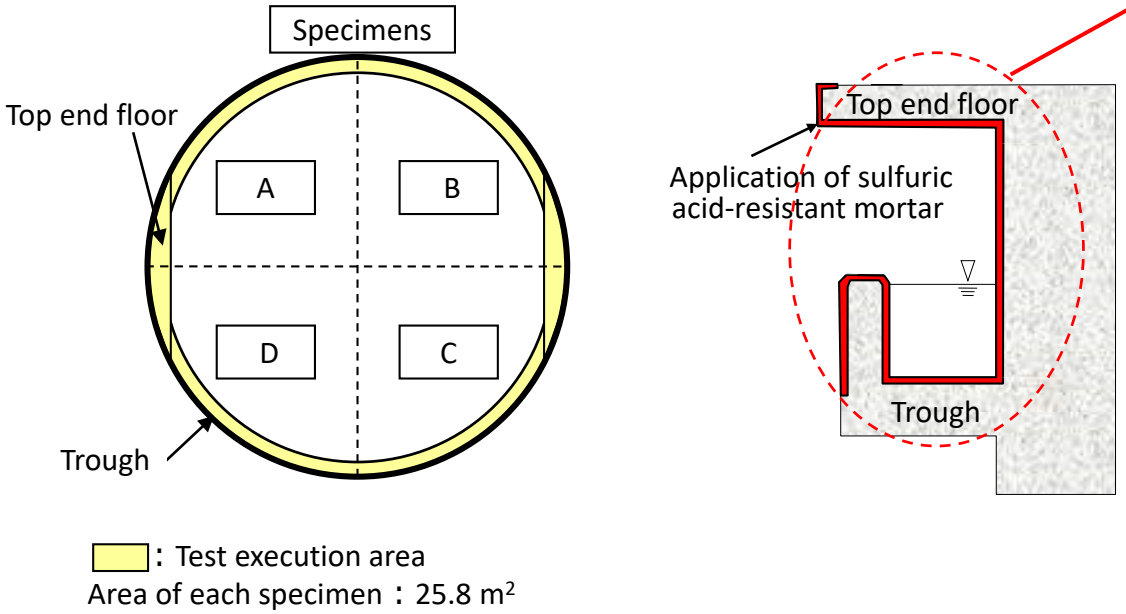
- Test execution: The above four specimens were tested in the overflow trough of the primary settling tank, and the aging process was investigated.
- Exposure test: Four materials and ordinary mortar cylindrical specimens were hung in the gas phase of the primary settling tank to investigate the appearance and aging of the neutralization depth.

Summary of the Test Execution

◆ Test execution locations

- Conducted a test execution at the overflow trough of the primary settling tank
- As the test execution site had concrete corrosion, the deteriorated parts were removed by chipping before the test.

Plane and cross-sectional views of the primary settling tank



Before application
(chipping condition of the frame)

Completed application of sulfuric acid-resistant mortar

The thickness of sulfuric acid-resistant mortar was set to 10mm, based on the prediction of deterioration.
The thickness of cross-sectional restoration material (10mm) plus sulfuric acid-resistant mortar (10mm) or sulfuric acid-resistant mortar (20mm) was used, depending on the performance of each material.

Summary of the Test Execution

- Confirm floats and cracks with a percussion stick and make a visual inspection of the exterior, annually.
- At the same time, a corrosive environment survey was conducted.

◆ Test execution

Content	Test item	Frequency
Apperance	Visual inspection and confirmation of lifting and cracking with a percussion stick	Once a year

◆ Corrosive Environment Survey

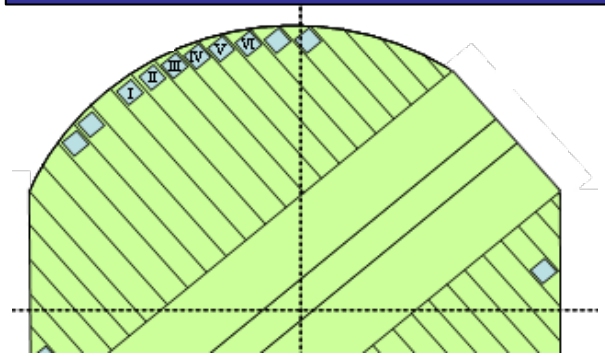
Content	Test item	試験個所	Frequency
Water quality	pH, SS, BOD, chloride ions, sulfate ions, free carbon dioxide, errosive free carbon dioxide, etc.	Overflow of primary settling tank trough Condensation in the primary settling tank	Twice in summer and winter
Hydrogen sulfide gas concentration	Hydrogen sulfide gas concentration in gas phase	In the primary settling tank	Summer to winter
Temperature	Gas phase temperature	In the primary settling tank	Summer to winter

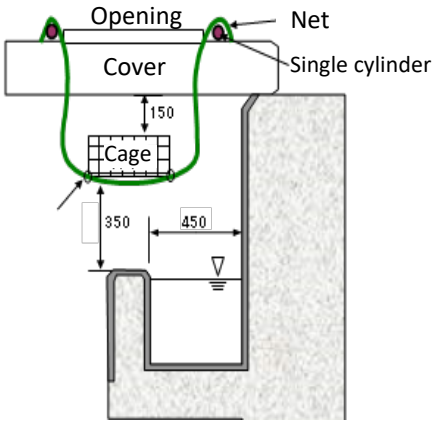
Summary of Exposure Test

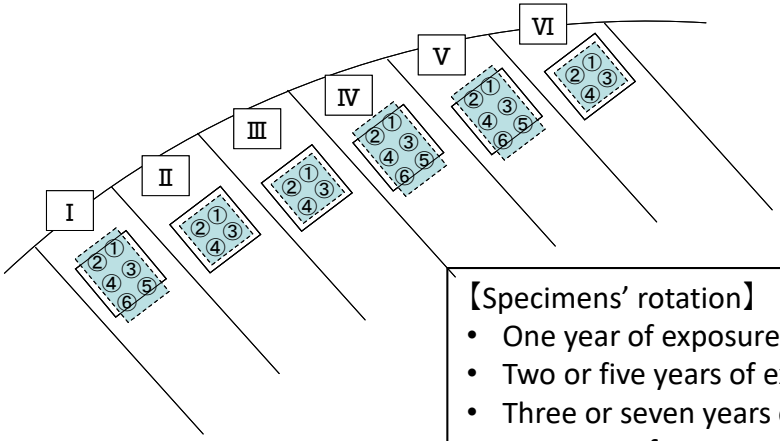
◆ Location of the exposure test

- Installed in the gas phase of the six apertures (I to VI) of the cover of the specimen
- Installation locations were rotated every year.

Plane and cross-sectional views of the primary settling tank





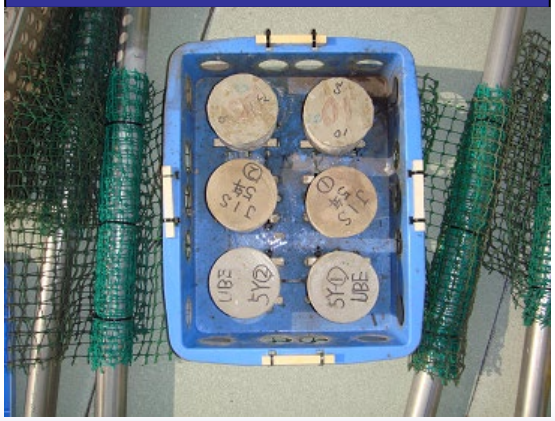


【Specimens' rotation】

- One year of exposure :Installed in II and IV
- Two or five years of exposure: Replace II and IV
- Three or seven years of exposure: Replace III and V
- Ten years of exposure: Replace I and VI

Specimen installation

Specimen placement



Exposure Test Overview

◆ Exposure test conditions

- Conducted at 1, 2, 3, 5, 7 and 10 years (6 years pf material age) after the start of exposure
- Installation year of the specimen was staggered according to the years of exposure

	FY	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019
Exposure test	Installation of specimens			Ten years of exposure									
				Three years of exposure			Seven years of exposure						
				One year	Two years		Five years of exposure						
	Appearance			●		●					●		●
	Weight change			●		●					●		●
	Depth of Neutralization			●		●					●		●

◆ Preparation of specimens

The conditions of specimens

- Ordinary mortar and 4 materials for comparison
- Φ100mm×H100mm Cylinder
- Curing in 20°C water before exposure, top and bottom surfaces are treated with anti-corrosive epoxy resin
- Number of specimens prepared : 2 for each age (5 types x 6 ages x 2) for a total of 60 pieces

◆ Exposure test item

Test item	Test procedure
Weight change	Measure the mass of specimens and compare them to the mass before the exposure
Depth of Neutralization	Cut into two equal parts parallel to the striking surface, and measure and photograph them by the phenolphthalein method

Results of Test Execution: Appearance

- As a result of the visual inspection, there were no floating or cracking problems in any of the companies
- Following are photos of the exterior at 1, 6 and 11 years after application

Survey year	Specimen A	Specimen B	Specimen C	Specimen D
First year				
Sixth year				
Eleventh year				

Results of Test Execution: Corrosion Environment

◆ Overflow of primary settling tank trough

- The concentrations of chloride and sulfate ions were higher than those of ordinary sewage, possibly due to the inflow of seawater.*50-100 mg/L for chloride ions (Japan Sewage Works Association: Sewerage O&M Guidelines, Part II, 2003, p. 750), 30-80 mg/L for sulfate ions
- It was considered that the potential for the generation of hydrogen sulfide was relatively high

	Water temperature°C	pH	SS(mg/L)	BOD (mg/L)	Chloride ions (mg/L)	Sulfate ions (mg/L)	Free carbon dioxide (mg/L)	Erosive free carbonate (mg/L)
Average	23.7	7.3	60.3	78.5	555	115	33.8	8.8
Maximum	30.2	8.0	82.8	125.0	880	160	69.2	32.7
Minimum	15.5	7.0	25.0	34.0	40	77.0	2.8	1.7

*Statistics of water quality analysis performed twice a year during the 2009-2019 study period

◆Condensation of primary settling tank

・The low pH and high concentration of sulfuric acid ions suggest that sulfur-oxidizing bacteria grow in the condensation and hydrogen sulfide is oxidized to sulfuric acid.

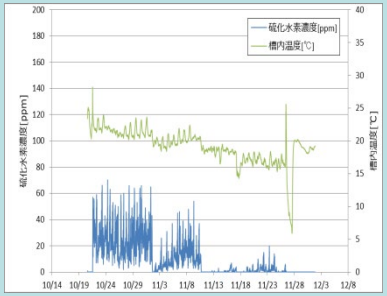
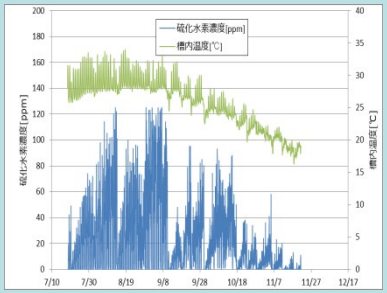
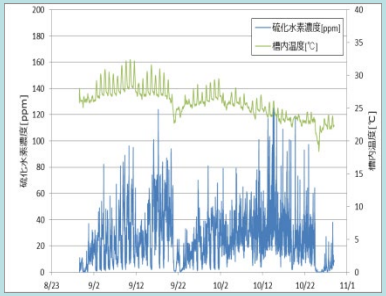
	Water temperature °C	pH	Chloride ions (mg/L)	Sulfate ions (mg/L)
Average	17.5	1.8	5	1,739
Maximum	17.5	2.5	17	9,250
Minimum	17.5	1.5	< 0.1	368

*Statistics of water quality analyses performed twice a year during the 2009-2019 study period

Results of Test Execution: Hydrogen sulfide gas concentration, In-tank temperature

- The peak of hydrogen sulfide concentration was relatively high when in-tank temperature was high, and it tended to be low when in-tank temperature was low.
- The average hydrogen sulfide concentration over the whole period was 11 ppm, which was classified as a corrosive environment category II.

◆ Examples of measurement results

Measurement period	Oct-Dec 2009	Jul-Dec 2012	Aug-Oct 2019
Graph			
Average	9ppm, 19°C	21ppm, 26°C	25ppm, 26°C
Maximum	70ppm, 28°C	125ppm, 34°C	125ppm, 32°C
Minimum	7ppm, 6°C	0ppm, 16°C	0ppm, 18°C

*The data shown in the above are extracted from three of the eleven measurements every year from the fiscal year 2009 to 2019.

◆ Measurement results for the whole period (2009-2019)

	Hydrogen sulfide concentration (ppm)	In-tank temperature(°C)
Average	11	22
Maximum	225	39
Minimum	0	6

Results of Exposure Tests : Appearance

・No significant changes were observed in any of the specimens from the previous conditions before exposure.

・The ordinary mortar for comparison did not show any significant changes in shape, but white precipitates, which appeared to be gypsum, were found on the surface.

Test year	Specimen A	Specimen B	Specimen C	Specimen D	Ordinary mortar for comparison
First year of exposure					
Fifth year 2014					
Tenth year 2019					

Results of Exposure Tests: Mass change, Neutralization depth

◆ Mass change

Each specimen had no swelling or flaking of the mortar and no significant mass change.

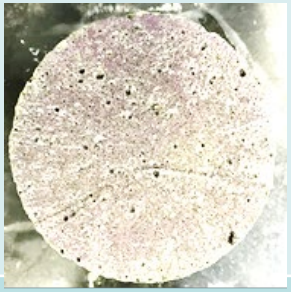
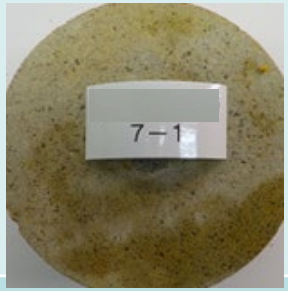
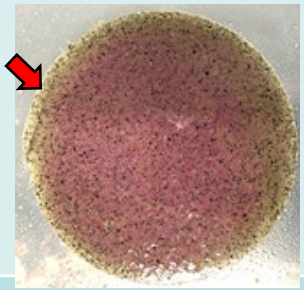
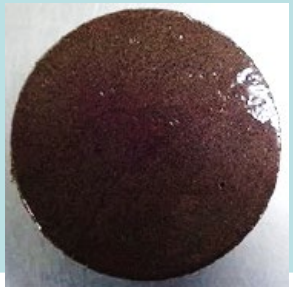
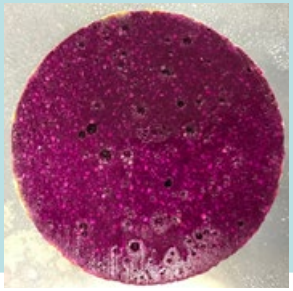
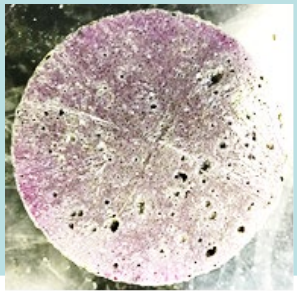
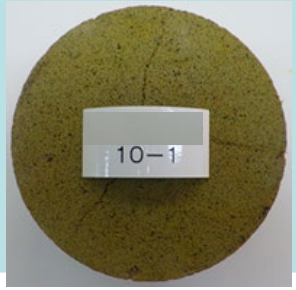
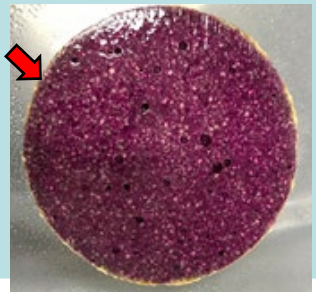
Test item	Period of exposure	Specimen A	Specimen B	Specimen C	Specimen D	Ordinary mortar for comparison
Mass change (%)	1 year	1.0	-0.2	1.2	0.1	-0.4
	2 yeas	1.6	0.3	1.6	0.1	0.9
	3 years	2.1	-0.1	1.6	0.1	0.1
	5 yeas	1.6	0.1	2.2	0.3	2.6
	7 years	2.0	0.2	2.5	0.5	2.2
	10 years	2.8	-0.1	2.7	0.3	0.4

◆ Neutralization depth

- sulfuric acid-resistant mortar specimens had no sulfuric acid penetration (neutralization)
- The specimens of ordinary mortar had a maximum of 6.1 mm of sulfuric acid penetration (after 7 years of exposure).

Test item	Period of exposure	Specimen A	Specimen B	Specimen C	Specimen D	Ordinary mortar for comparison
Depth of neutralization (㎜)	1 year	0.0	0.0	0.0	0.0	0.0
	2 yeas	0.0	0.0	0.0	0.0	0.0
	3 years	0.0	0.0	0.0	0.0	0.0
	5 yeas	0.0	0.0	0.0	0.0	0.0
	7 years	0.0	0.0	0.0	0.0	6.1
	10 years	0.0	0.0	0.0	0.0	0.3

Results of Exposure Tests: Neutralization depth

Period of exposure	Specimen A	Specimen B	Specimen C	Specimen D	Ordinary mortar for comparison
1 year					
7 years					
10 years					

*Since specimen D is neutral mortar, the depth of neutralization was checked using a 1% methyl orange solution, which shows a red color reaction at pH 3 and below

Conclusion of the Follow-up Survey

We carried out test execution and exposure test of 10x mortar for ten years, which was developed at our joint research, to confirm its durability in an actual WWTP.

◆ Environment of the test site

The gas phase of the primary settling tank had **an average hydrogen sulfide concentration of 11 ppm**, classified as **category II of the corrosion environment**. Sometimes, it showed over 200 ppm at maximum.

Test execution

The sulfuric acid-resistant mortar of test execution **did not show any floating or cracking** under such a corrosive environment.

◆Exposure test

The exposed specimens neither significantly change mass nor were neutralized and remained in **excellent condition**.

◆ Evaluation of Sulfuric Acid Resistant Mortar

The results of 11 years of testing execution and 10 years of exposure tests demonstrated **the performance of sulfuric acid-resistant mortar (10x mortar)**

◆ The Need to Review the JS Corrosion Prevention Manual

In this survey, neither sulfuric acid penetration nor cross-sectional defects were observed in the 10x mortar. It is unnecessary to consider "allowance for corrosion," which is supposed to be required in the mortar lining design. The necessity of reviewing the design procedure will be discussed in the future.