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Study on Alumina cement based sulfuric-acid-resistant mortar

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ABSTRACT

Ube Industries, Ltd. and the Japan Sewage Works Agency have jointly developed sulfuric-acid-resistant mortar, which eliminates corrosion and prevents coating with resin. The authors focused on alumina cement and special aggregate, which have superior sulfuric-acid resistance and promoted the development of sulfuric-acid-resistant mortar using such materials. They confirmed that such mortar has excellent basic properties in addition to sulfuric acid resistance. To confirm the workability and durability of sulfuric-acid-resistant mortar when used in an operating sewerage facility, the mortar was tested by repairing the wall of intermediate slab in a sewerage manhole under a corrosive environment. It was found that the mortar's workability (and its basic performances as mortar) was as good as that of general-purpose repairing mortar. It was also confirmed that the area where sulfuric-acid-resistant mortar was applied still maintains excellent durability even in a follow-up survey conducted eight years after the test construction.

Keywords. sulfuric-acid-resistant mortar, alumina cement, test construction, sewerage facility, durability

INTRODUCTION

Corrosion by sulfuric acid degrades properties of concrete in sewerage facilities. Sulfuric acid corrodes concrete far faster than neutralization by carbon dioxide, causing serious damage to structures. The diffusion rate of sewerage in Japan reached 75% in recent years, and the number of deteriorating sewerage facilities aged 30 years or more is increasing. Measures against corrosion by sulfuric acid caused from micro-organisms were not common when those facilities were constructed, therefore extreme corrosion of concrete by sulfuric acid seriously damages duct lines and sealed sewerage facilities. Resin lining method for corrosion protection is employed most frequently to prevent corrosion by sulfuric acid. However, if the concrete or repair mortar itself can be made sulfuric-acid resistant, repair work could be simplified and costs reduced.

In this joint study, we noted that corrosion resistance could be improved more than that of conventional repairing materials if alumina cement and special aggregate, which have superior sulfuric-acid resistance, are used as basic materials. This joint study seeks to promote the development of repair materials that can assure a standard useful life for concrete structures through the independent use of sulfuric-acid-resistant mortar, without using other corrosion-prevention coating materials such as resin.

DEVELOPMENT OF SULFURIC-ACID-RESISTANT MORTAR

Materials and formulation. Table 1 lists the materials for sulfuric-acid-resistant mortar, and Table 2 lists the formulations for the mortar. Shown in Table 2, a formulation using special aggregate was examined for sulfuric-acid-resistant mortar (Formulation A). To compare the performance of sulfuric-acid-resistant mortar with common mortar, the test was also conducted on a general-purpose formulation that uses ordinary portland cement (Formulation N).

Table 1. The materials for sulfuric-acid-resistant mortar

Materials		symbol
Cement	Alumina cement	AC
	Ordinary portland cement	NC
Aggregate	Special aggregate	X
	Quartz	Q

Table 2. The formulations for the mortar

Formulation	Cement	Aggregate	C/S (%)[1]	W/C (%)[2]
N	NC	Q	33	50
A	AC	X	67	35

[1] C/S : cement/aggregate ratio, [2]W/C : water/cement ratio

Experimental.

Mixing: The mortar was mixed in 1 litter on a batch in a Hobart mixer (5L) at 139rpm for 2min.

Test of basic properties on mortar: The test of basic properties performed on the mortar is shown in table 3.

Table 3. The test of basic properties performed on the mortar

Test items	Test method, specimen size and curing method	
Compressive strength	Test method	JIS A 1108
	Specimen size	50 mm in diameter and 100 mm tall
	Curing method	underwater curing in 20 deg C
Dimensional stability	Test method	JIS A 1192
	Specimen size	40 mm long, 40 mm wide and 160 mm tall.
	Curing method	atmospheric curing in 20 deg C

Sulfuric acid immersion test: The concentration of sulfuric acid used in the sulfuric acid immersion test was 5%. During the first month after starting the test, the entire volume of sulfuric acid was replaced every week. One month after the start of the test, the entire volume of sulfuric acid was replaced every month. At the predetermined age of material, the surface of the specimen was washed with water, the specimen was cut, and the neutralization was measured by the phenolphthalein method.

Experimental results.

Basic properties: Table 4 lists the relevant basic properties. The compressive strength of each formulation increased with an increase in the curing period until the third month. Formulation A of sulfuric-acid-resistant mortar exhibited a higher strength than Formulation N, and its compressive strength after three months reached 89.9N/mm^2. One of the main reasons for this result is that the strength of binding between the cement and the aggregate was improved by the use of special aggregate.

As for dimensional stability, both formulations exhibited shrinkage, but Formulation A exhibited slightly less shrinkage.

Table 4. The relevant basic properties

Formulation	Compressive strength (N/mm^2)			Dimensional stability (%)		
	7 days	1 month	3 months	7 days	1 month	3 months
N	19.4	28.1	31.1	- 0.06	- 0.04	- 0.08
A	58.2	71.8	89.9	- 0.06	- 0.04	- 0.06

The sulfuric acid immersion test: The measurement results for neutralization after sulfuric acid immersion test are shown in Figure 1. For Formulation N, the specimen itself disappeared after six to nine months of immersion. In contrast, the neutralization of sulfuric-acid-resistant mortar after 12 months of immersion in Formulation A was 10.0mm, and that corrosion by sulfuric acid was suppressed. This was caused by calcium hydrate, a factor in the corrosion of hardened cement paste by sulfuric acids, not being generated when alumina cement is used and by it having higher acid neutralizing capacity than Portland cement.

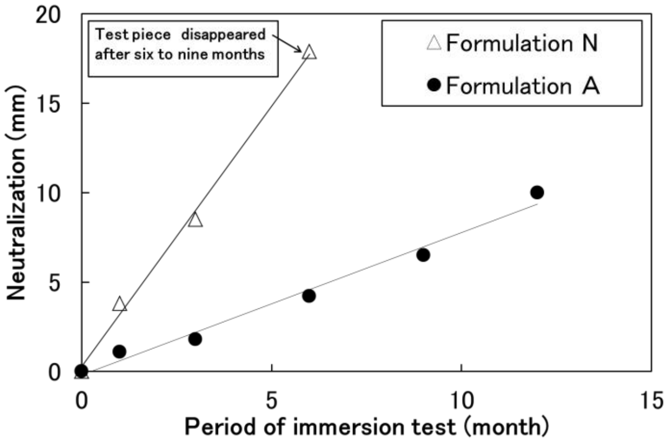

Figure 1. Neutralization after sulfuric acid immersion test

TEST CONSTRUCTION IN SEWERAGE FACILITIES AND FOLLOW-UP SURVEYS

Survey content. As described above, we confirmed that the sulfuric-acid-resistant mortar that we developed has excellent basic properties and strong sulfuric-acid resistance, based on the results of various tests conducted in the laboratory. To further confirm the workability and durability of the sulfuric-acid-resistant mortar at a field site, it was used in a trial repair for the wall of intermediate slab in a sewerage manhole under a corrosive environment. The environmental conditions at the field site correspond to corrosive environment class II as specified by the Japan Sewerage Works Agency (annual average concentration of H_2S: 10ppm to 50ppm). For the sulfuric-acid-resistant mortar, an improved formulation prepared by using the above mentioned formulation as the base and adding emulsion, etc. was used. The mixing performance, troweling performance, surface conditions, hardening, etc. were checked during the construction.

To evaluate the durability, we will implement follow-up surveys for the next 10 years. In this report, we will mainly describe the result of a follow-up survey conducted eight years after the construction. During the follow-up surveys, peeling, cracks and corrosion of the sulfuric-acid-resistant mortar, was visually inspected. Moreover, samples were collected to check directly the state of the sulfuric-acid-resistant mortar at the field site. The surface of the mortar was scraped to collect samples of the surface layer. Small-diameter cores (20mm) were collected to sample in the inside of the mortar. The cores were collected after preliminarily exploring the positions of the reinforcing steel with RC radar so that the reinforcing steel would not be cut. The samples of the surface layer on the mortar were carried out XRD analysis and the core specimens were carried out neutralization measurement and XRD analysis.

Situation of repairing. Photo 1 shows the application of sulfuric-acid-resistant mortar by trowel. We were able to complete the construction work from mixing to application without delays and without problems such as roughness, cracks, or peeling. As a result, we were able to complete the construction on schedule as planned initially. Furthermore, the hardening was excellent condition and did not influence the construction work on the following day.

Follow-up Survey Results.

Visual inspection of the repaired parts: Photo 2 shows the repaired parts in eight years after the test construction. A visual inspection revealed discoloration of the wall surface (to brown) that changed properties of the surface of mortar. However, examination by touch and

Photo 1. Application of sulfuric-acid-resistant mortar

Photo 2. Repaired parts in eight years after the construction

percussion with a test bar confirmed that the internal parts were strong, even though the surface was soft. Furthermore, no harmful cracks or peeling were detected in the repaired parts. In the photo, the trace of the sample collection and the trace of marking at the time of sample collection remain on the wall surface. Therefore the wall surface discolored because sulfuric acid generated on a resin sheet lining section of the ceiling concentrated and then dropped along the slant of the ceiling. Resin sheet lining has very high anti-corrosion performance. For this superior performance, it is considered that generated sulfuric acid is not neutralized and remains on the resin sheet lining. On the contrary, all of the mortar for Formulation N, placed at the field site for comparison, had changed into gypsum and disappeared by the second-year follow-up survey.

Visual inspection of core samples: Photo 3 shows a core specimen sprayed with phenolphthalein solution; Photo 4 shows the surface of the core specimen. As seen in Photo 3, the core specimen was approximately 40mm long in the depth direction. The sulfuric-acid-resistant mortar part was approximately 25mm long, and the original concrete part was approximately 15mm long. Sulfuric-acid-resistant mortar was initially applied with a thickness of 20 to 25mm depending on the unevenness of chipped original concrete surface. These facts suggest that the sulfuric-acid-resistant mortar was hardly affected by corrosion.

In confirming the neutralization with phenolphthalein, the whole side surface was colored purple-red by phenolphthalein, indicating that both the sulfuric-acid-resistant mortar and the original concrete were sound with no neutralization. The surface of the core specimen discolored and became whitish due to corrosion by sulfuric acid derived from microorganisms. However, the discoloration by phenolphthalein over the whole core suggests that only the surface layer was corroded by sulfuric acid.

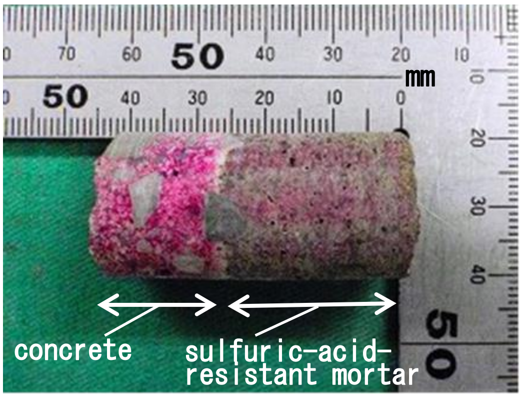

Photo 3. Core sample sprayed with phenolphthalein solution

Photo 4. Surface of the core sample

Results of XRD analysis: The surface of the sulfuric-acid-resistant mortar and the core specimens were carried out XRD analysis; Fig. 2 shows the results. XRD analysis for the surface of the sulfuric-acid-resistant mortar demonstrates that most of the analysis sample was gypsum. It can be inferred that calcium sulfate dihydrate generated when the calcium in the sulfuric-acid-resistant mortar reacted with sulfuric acid derived from microorganisms that was generated on the surface of the resin sheet lining. Calcium sulfate hemihydrate was detected instead of calcium sulfate dihydrate because the sulfuric-acid-resistant mortar was carried out a high-temperature drying process (at 100℃) during the preparation of the analysis samples.

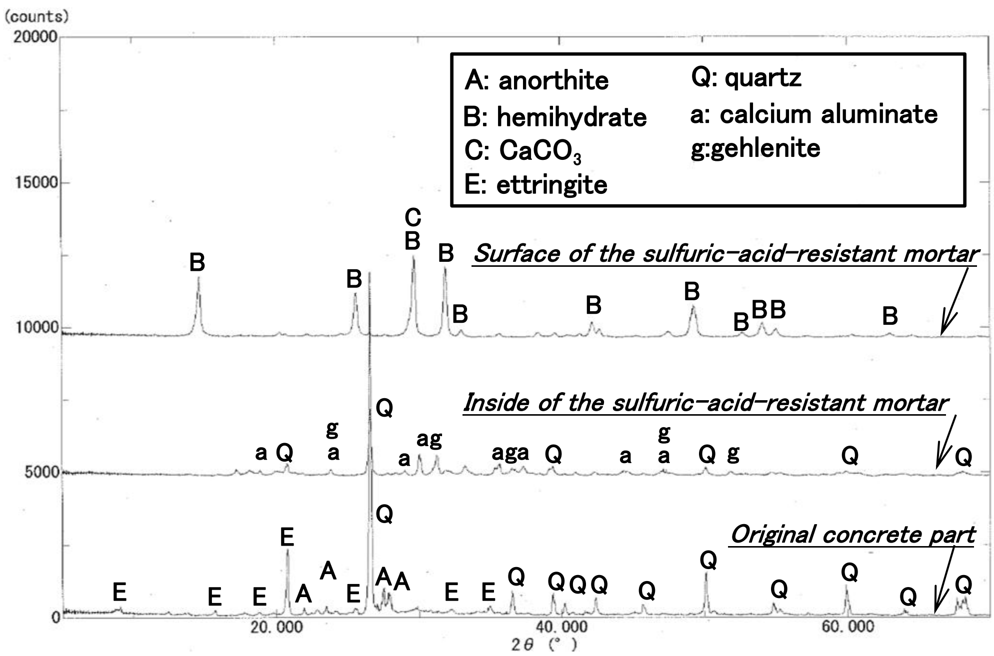

Fig 2. Results of XRD analysis

XRD analysis for the inside of the sulfuric-acid-resistant mortar shows quartz, calcium aluminate, gehlenite derived from the formulation of the sulfuric-acid-resistant mortar.

Furthermore, no gypsum, which was confirmed on the surface of the sulfuric-acid-resistant mortar, was detected in the XRD analysis. The results of these XRD analyses indicate that corrosion by sulfuric acid is confined exclusively to the outermost layer of the sulfuric-acid-resistant mortar.

XRD analysis for the original concrete part shows quartz and anorthite derived from the formulation of original concrete. Furthermore, as is the case with in above analysis for the inside of the sulfuric-acid-resistant mortar, there is no gypsum in the concrete part. These facts indicate sulfuric acid from the surface of the resin sheet lining is blocked by the sulfuric-acid-resistant mortar and doesn’t penetrate into the concrete part.

As described above, visual inspection of the repaired parts, core specimens and the XRD analyses indicate that the repaired parts of sulfuric-acid-resistant mortar are still in good condition eight years after the construction, with little corrosion in progress.

CONCLUSIONS

1. The sulfuric-acid-resistant mortar developed by us indicated excellent basic properties and strong sulfuric-acid-resistance.

2. During test construction in the operating sewerage facility, it was possible to apply sulfuric-acid-resistant mortar in the same method as for general-purpose repairing mortar. The surface conditions and hardening after the repair were good.

3. Based on a visual inspection of the repaired parts in 8 years after the construction, the inside was strong and no harmful cracks or peeling were detected, although the surface was discolored.

4. Visual inspection of core specimen indicated that corrosion of sulfuric-acid-resistant mortar in eight years after the construction was confined exclusively to the outermost surface layer, with the thickness of repair remaining almost as it was initially.

5. XRD analysis demonstrated that gypsum generated from corrosion by sulfuric acid existed only in the surface layer of the sulfuric-acid-resistant mortar, not inside sulfuric-acid-resistant mortar or in the existing concrete part.

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