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EXPERIMENTAL STUDY ON THE SULFURIC ACID RESISTANCE OF LOW CARBON CONCRETE

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In recent years, deterioration of concrete structures of sewerage facilities due to sulfuric acid attacks has been progressing. Therefore, it can be concluded that the demand for sulfur-acid resistant concrete is extremely high. In addition, concerning recent global warming countermeasures, research and development is underway on low-carbon concrete that reduced cement, which emits a large amount of carbon dioxide during the manufacturing process. The purpose of this study is to develop low carbon concrete with high sulfur-acid resistance by replacing cement with large amounts of blast furnace slag and various admixtures. As a result, it was found that the sulfur-acid resistance was improved when using blast furnace slag fine powder and fly-ash. In particular, when cement content was 20% of binder by mass, it was confirmed that the sulfur-acid resistance was excellent. What is more, there was no loss in compressive strength. It was considered that almost $Ca(OH)_2$ produced by hydration reaction of cement reacted with blast furnace slag and fly-ash, so the reaction of sulfur-acid and calcium hydroxide was suppressed.

Keywords: Blast furnace slag, Fly-ash, Durability, Corrosion depth.

1 INTRODUCTION

In recent years, deterioration of concrete about sewerage facilities due to sulfuric acid has been progressing. Deterioration of concrete by sulfuric acid is caused by reaction of $Ca(OH)_2$ and sulfuric acid in the concrete because the expansion pressure of products such as gypsum ill destroy the concrete (Asuo 1989). In addition, blast furnace slag fine powder has been widely used because it emits less CO_2 than ordinary cement in the manufacture. And since it can react with calcium hydroxide generated by hydration reaction of cement due to its latent hydraulic properties, it causes low environmental load and it has excellent resistance to sulfuric acid, so it is widely used. The purpose of this study is to develop durable low carbon concrete by replacing most of the cement content with blast furnace slag.

2 MATERIALS AND METHODS

2.1 Materials

The binders were ordinary Portland cement (C, density: 3.16), fly ash (FA, density: 2.20), silica fume (SF, density: 2.25) and blast furnace slag fine powder whose Blaine specific surface area are 4000 cm^2/g (BS4, density: 2.90) and 12000 cm^2/g (HBS, density: 2.91). Crushed sand (S, density: 2.64) was used as fine aggregates. Crushed stone (S, density: 2.64 g/cm3) was also used as coarse aggregates. Tap water (W) was used for mixing. A superplasticizer (SP, density: 1.09), a deformer (DF, density: 1.00), and an air entraining agent (AE, density: 1.06) were also used.

2.2 Mix Conditions

Table 1 presents the mixing conditions of the tests. Table 2 presents powder compositions and specified mix proportions. The amounts of deformer and reducing admixture reducing admixture were appropriately adjusted to satisfy the target values.

Table 1. Mixing conditions in the tests.

Mortar Series	water-to-brinder ratio (%)		30
	sand binder ratio		1.0
	Target values	air amount (%)	Under 3.0
		mortar flows (mm) of 0 hit	200±20
Concrete Series	water-to-brinder ratio (%)		30
	sand aggregate ratio (%)		45
	Target values	air amount (%)	4.5±1.5
		slump (cm)	15±2

Table 2. Specified mix proportions.

	Symbol	W/B (%)	Mass ratio (%)					Unit quantity (kg/m^3)							
			C	BS4	HBS	FA	SF	W	C	BS4	HBS	FA	SF	S	G
Mortar series	C10HBS10				10	-	-	299	100	797	100	0	0	899	0
	C10FA10		10	80	-	10	-	292	97	779	0	97	0	908	0
	C10SF10				-	-	10	293	98	781	0	0	98	907	0
	C20HBS10				10	-	-	301	200	701	100	0	0	897	0
	C20FA10		20	70	-	10	-	294	196	686	0	98	0	906	0
	C20SF10	30			-	-	10	295	196	687	0	0	98	905	0
Concrete series	HBS10			70	10					397	57	0	0	704	854
	HBS20			60	20	-				340	113	0	0	704	854
	HBS30		20	50	30		-	170	119	283	170	0	0	705	855
	FA10			70		10				397	0	57	0	676	845
	FA20			60	-	20				340	0	113	0	669	836
	FA30			50		30				283	0	170	0	661	827

2.3 Mixing Method

In the mortar test, a 10 litter capacity Omni type mixer was used for mixing. Firstly, the powder and fine aggregate were added and mixed for 30 seconds, then water and superplasticizer were added and mixed for 120 seconds. Finally, the deforming agent was added and mixed for 60 more seconds.

In the concrete test, a 60 litter capacity forced action biaxial mixer was used for mixing. Firstly, only the powder and fine aggregate were added and mixed for 30 seconds, then water and admixture were added and mixed for another 120 seconds. Finally, coarse aggregate was added and mixed for 90 more seconds.

2.4 Test Items

2.4.1 *Fresh properties tests*

In the mortar test, the 0 hit mortar flow test and the air content test were carried out. Mortar flow test was carried out in accordance with ISO 9597. The spread distance of the test specimen when not dropped is taken to be the mortar flow value. The air content test was carried out in accordance with ISO 4848.

In the concrete test, the concrete slump test was carried out in accordance with ISO 4109 and air volume measurement was carried out in accordance with ISO 4848.

2.4.2 *Compressive strength test*

Compressive strength test of mortar was carried out in accordance with ISO 1920-4 for mortar and ISO 1920-4 for concrete. The target value was set at 45 N/mm^2 or more, after they were cured in water (20 °C) for 28 days.

2.4.3 *Sulfuric acid immersion test*

Mass change rate test and Corrosion depth test were carried out. The mortar test specimens were φ50 mm × h100 mm in size and the concrete test specimens were φ100 mm × h200 mm in size. The number of specimens was three for each condition. In this study, after demolding, specimens were cured in water at 20 °C, and after 28 days the specimens were soaked in sulfuric acid solution of 5% mass percent concentration at 20 °C.

In the mass change rate test, the specimens were removed from sulfuric acid immersion solution after 7, 28, 56 and 91 days. After that, the specimens were washed with water, and their mass was measured. The average value of three specimens was taken as mass change rate.

About the corrosion depth by sulfuric acid attack test, the specimens were removed from sulfuric acid immersion solution after 28 and 91 days. After that, specimens were washed with running water. Then specimens were cut in half in the direction of height with a diamond cutter. After that, the phenolphthalein was sprayed on the cut surface, the uncolored part was regarded as the part which was eroded by sulfuric acid. The diameters of colored part of 5 different places were measured and the average value was calculated. 1/2 of the difference between this average value and initial value of the specimen diameter was taken as corrosion depth.

The target values were made to be within ± 10% of mass change rate and within 3 mm of corrosion depth, after it was soaked in sulfuric acid solution for 28 days, referring to the target level of Manual of corrosion control and corrosion prevention technical for sewage concrete structure (Japan Sewage Works Agency 2017).

3 RESULTS

3.1 Fresh Properties Tests Results

The results are shown in Table 3. All results satisfied the target value. As can be seen from Table 3, in the mortar series, for obtaining the target flow values of mortar containing SF, the amount of SP mixed is more than that when HBS or FA was mixed. It was confirmed that because the specific surface area of SF is 200,000 cm^2/g (Kurashige and Uomoto 2001), so more

SP was necessary to satisfy the flowability. And, much air was entered when a large amount of SP was used, so the amount of DF was increased together.

Table 3. Fresh properties test results.

	Symbol	SP (%)	DF (%)	AE (%)	Fresh properties tests results		
					0 hits of mortar flows (mm)	SL (cm)	Air content (%)
Mortar series	C10HBS10	2.0	1.0	-	180	-	0.2
	C10FA10	2.2	1.0	-	190	-	0.3
	C10SF10	3.0	1.2	-	195	-	0.4
	C20HBS10	2.0	1.0	-	215	-	0.4
	C20FA10	2.2	1.0	-	210	-	0.6
	C20SF10	3.0	1.2	-	200	-	0.5
Concrete series	HBS10	0.85	-	0.90	-	16.5	4.5
	HBS 20	0.96	-	0.50	-	17.0	3.0
	HBS 30	0.94	-	0.50	-	16.5	3.0
	FA10	0.98	-	0.50	-	14.0	6.0
	FA20	0.90	-	0.50	-	15.5	3.5
	FA30	0.96	-	0.40	-	17.0	5.0

3.2 Compressive Strength Test Results

The results of the compressive strength test are shown in Figure 1. As shown in Figure 1, the target values were satisfied for all mix proportions. In addition, compressive strengths increased in the condition of 20% cement content. Furthermore, as can be said for all mix proportions, the mix proportions mixed with FA showed slightly lower compressive strength than the other mix proportions at 7 days' material age. However, at 91 days' material age, the mix proportions mixed with FA showed equivalent compressive strength when compared with other mix proportions. This is thought to be due to the long period of time because of slow pozzolanic reaction, which is a characteristic of FA, resulting in a dense and strong internal structure with excellent strength expression.

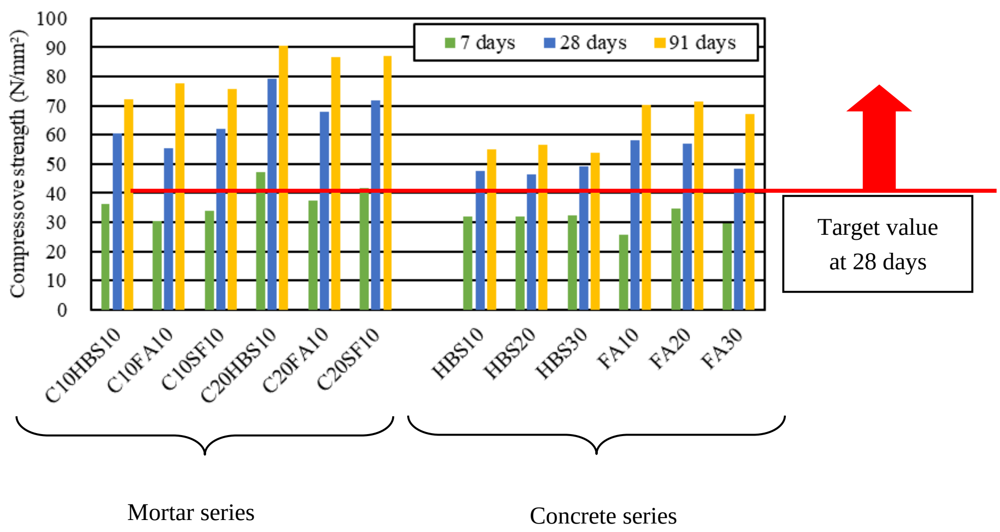

Figure 1. Results of compressive strength test.

3.3 Sulfuric Acid Immersion Test Results

3.3.1 *Mass change rate test results*

Figure 2 show the mass change rate test results.

From Figure 2, it can be seen that the target value was satisfied except for the mix proportions using SF. Also, in all cases, the mass increased up to 28 days of immersion in sulfuric acid. It is thought that the mass increased because unreacted $Ca(OH)_2$ in the hardened body reacted with sulfuric acid, and the substance that seems to be dehydrate gypsum was formed on the surface. However, the weight of some mix proportions decreased gradually from 28 days to 91 days. Moreover, on the surface of the actual specimens, cracks were confirmed due to expansion pressure generated when gypsum dehydrate appeared. Through the crack, sulfuric acid entered into the hardened body, and the substance formed on the surface peeled off, so that the mass greatly decreased.

In addition, in the mortar series, at a cement content of 20% the mass continued to increase in all mix proportions, and there was no reduction in mass even in 91 days. When 20% cement was contained, the amount of $Ca(OH)_2$ increased. Therefore, the cause for the penetration of sulfuric acid into the hardened body was suppressed due to the densification of the internal structure of the hardened body caused by the latent hydraulic property of BS and the pozzolanic reaction of FA and SF.

Furthermore, in the concrete series, in the case of the mixture with FA, the mass change rate was smaller as the FA mixing rate increased, and the improvement of the sulfur acidity resistance by FA mixing was also observed in the concrete. In addition, the higher the mixing ratio of HBS was, the smaller the mass change ratio was. Though this is considered to be affected by the filling rate of the whole system of the binder, future examination subject is necessary.

The weight change of the mixture containing FA tended to be slightly smaller than that of the mixture containing HBS except HBS10.

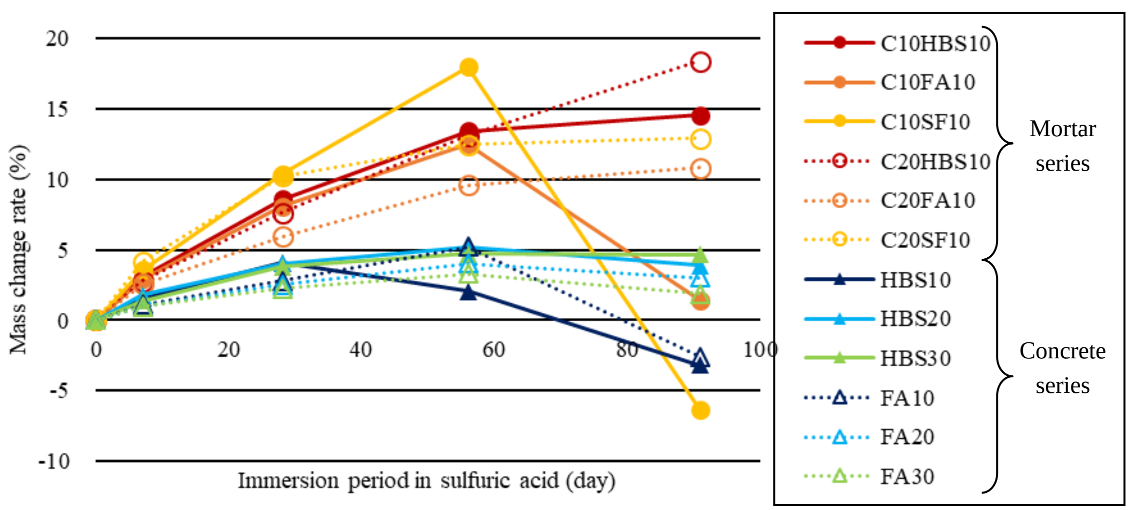

Figure 2. The mass change rates.

3.3.2 *Corrosion depth by sulfuric acid attack test results*

The results of the corrosion depth test are shown in Figure 3.

In the mortar series, the case containing SF was over the target range. In particular, although the C20SF10 was mixed with 20% of cement, the corrosion depth was not within the target range after the immersion period of 28 days. It is considered that because the pozzolanic reaction of SF was not sufficiently reacted at the time of the immersion period of 28 days and the infiltration of sulfuric acid was easy. However, it is necessary to study more about microstructure.

In the HBS or FA mixed mix proportions all of the measurement results for the immersion period of 28 days were within the target range of the corrosion depth. Therefore, by using HBS or FA, the substance formed on the surface of the specimens when immersed in sulfuric acid can be made denser, and it is considered that the infiltration of sulfuric acid can be suppressed even after 91 days of the immersion period.

In the concrete series, from Figure 3, it can be seen that the target value was satisfied except for the FA10. It is found that the degree of deterioration by sulfuric acid tends to decrease as the replacement ratio of each admixture, FA and HBS increases. In addition, it seemed that FA is more effective to suppress the deterioration for long time.

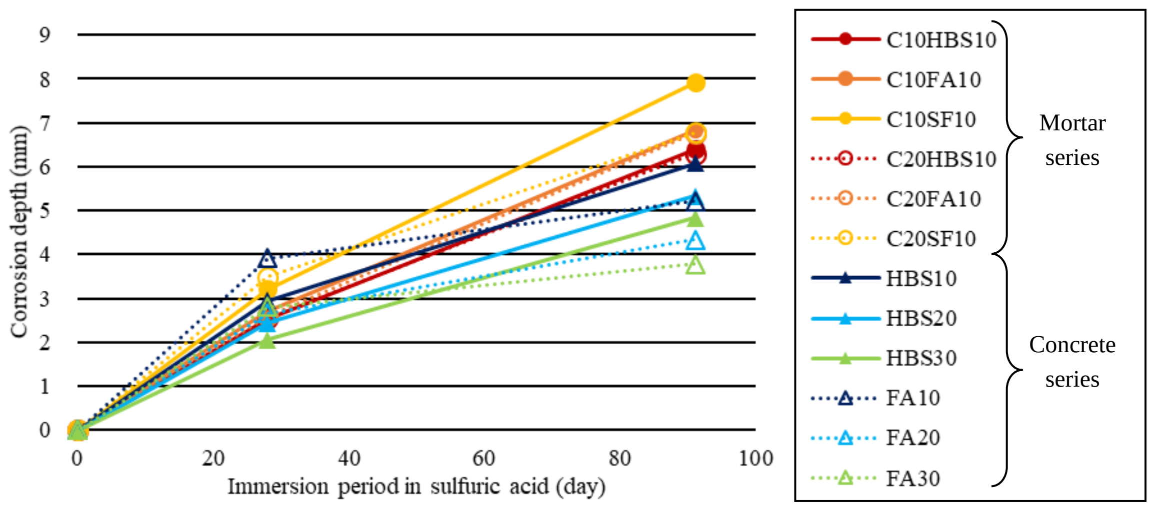

Figure 3. The corrosion depth.

4 CONCLUSIONS

From this study, in the experiment of mortar, sulfur acidity resistance was obtained when the cement content was reduced and a large amount of blast furnace slag and FA were mixed. Furthermore, when the same mixing condition of mortar was used at the concrete level, compressive strength and sulfur acid resistance did not decrease. In particular, the effect of preventing deterioration due to sulfuric acid erosion was confirmed by mixing HBS and FA when cement content was 20%.

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