THE SULFURIC ACID RESISTANCE OF CONCRETE WITH BLAST FURNACE SLAG

Paweena JARIYATHITIPONG
Research Engineer, Research and Development Labolatory, Landes Co.,Ltd, Japan

Kazuyoshi HOSOTANI
Manager, Technology Center, Landes Co.,Ltd, Japan

Takashi FUJII
Assistant Professor, Division of Environmental Science, Graduate School of Environmental and Life Science, Okayama University, Japan

Toshiki AYANO
Professor, Division of Environmental Science, Graduate School of Environmental and Life Science, Okayama University, Japan

ABSTRACT:

The deterioration of concrete by sulfuric acid attack in sewage environments has become a serious problem. In this study, it was shown that the resistance to sulfuric acid of mortar and concrete can be improved by using a blast-furnace slag fine aggregate to the total amount of fine aggregate. When mortar or concrete reacts to sulfuric acid, dihydrated gypsum film is formed around the particulate of the fine aggregate. This dihydrated gypsum film could retard the penetration of sulfuric acid, thus improving the resistance to sulfuric acid. However, the resistance to sulfuric acid depends on the hardness of the dihydrated gypsum film.

Keywords: sulfuric acid attack, blast furnace slag sand, ground granulated blast furnace slag, gypsum, sewerage

1. INTRODUCTION

Concrete has been used as the main material for constructing civil infrastructure systems such as sewage facilities. In facilities such as these, bacteria reacts with hydrogen sulfate, producing sulfuric acid which causes the concrete to rapidly deteriorate. There are many methods for protecting concrete from this effect; such as oxygen injection which prevents the production of hydrogen sulfate or the application of a product to the surface of the concrete which prevent direct contact with the sulfuric acid [1]. Although these methods are effective, they are mainly used to protect areas of the structure that are most prone to deterioration.

The most efficient way to extend the integrity of the concrete is to develop a concrete with an inherent resistance to sulfuric acid deterioration. This will protect the whole structure, not only the areas prone to deterioration. A sulfuric acid resistant concrete has been developed using blast furnace slag as an additional material.

Blast furnace slag is a by-product generated during the production of iron. It has been classified as an amorphous material when used as a binder material and called granulated blast furnace slag and classified as a crystalline material when used as a material for road paving, called gradually-cooled blast furnace slag. In Japan, the volume of granulated blast furnace slag produced is over 20 million tons per year and 90% of it is used as a material for cement and concrete production [2]. Concrete containing blast furnace slag is well known for improving some properties of concrete such as the watertightness, chemical resistance and chloride ion permeation resistance [3]. It also improves the resistance to sulfuric acid deterioration. However, when blast furnace slag is added to ordinary cement, such as Portland cement, higher compressive strengths yield a lower resistance to sulfuric acid. If ground granulated blast furnace slag is added to Portland cement it can improve the resistance to sulfuric acid.

It has been known that the sulfuric acid resistance can be improved when Portland cement is combined with ground granulated blast furnace slag. On the other hand, when the ground granulated blast furnace slag is used as a fine aggregate, it forms a dihydrated gypsum film around its own particle. These gypsum films could prevent the penetration of sulfuric acid into concrete. It has been proven in this study that a low water to binder ratio produces a higher amount of the dihydrated hardener which gives the concrete a higher resistance to sulfuric acid. In this study, the use of granulated blast furnace slag as a fine aggregate in high strength concrete improves the resistance to sulfuric acid.

2. SULFURIC ACID IMMERSION TEST

2.1 Materials

(1) Binder materials

Ordinary Portland cement (density: 3.15g/cm^3, Blaine

Table 1 Properties of Aggregate

Type of aggregate		Saturated density (g/cm^3)	Water absorption rate (%)	Fineness Modulus
Fine aggregate	River sand	2.61	1.97	2.96
	Blast furnace slag sand	2.77	0.72	2.15
	Crushed limestone sand	2.68	0.70	2.79
Coarse aggregate	Crushed sandstone	2.75	0.54	6.73

Table 2 Mix proportion of cement paste

Water to Binder ratio (%)	Cement to Binder ratio (%)
30.0	40.0
	100.0
60.0	40.0
	100.0

*Binder: Ordinary Portland cement and ground granulated blast furnace slag powder

Table 3 Mix proportion of mortar experimenting on reaction of sulfuric acid to fine aggregate

W/B (%)	C/B (%)	Air (%)	Unit Content (kg/m^3)						HRWRA^{*5} (kg/m^3)
			W	OPC	BF^{*1}	RS^{*2}	BFS^{*3}	LS^{*4}	
30.0	100.0	2.0	213	710	0	1,414	0	0	12.78
						0	1,500		
							0	1,451	
31.6	40.0			269	404	1,414	0	0	5.38
						0	1,500		
60.0	100.0		287	478	0	1,414	0		0.00
						0	1,500		
63.2	40.0			181	272	1,414	0		
						0	1,500		

^{*1} BF: Ground granulated blast furnace slag powder, ^{*2} RS: River sand, ^{*3} BFS: Blast furnace slag sand, ^{*4} LS: Limestone sand,
^{*5} HRWRA: High-range water reducing admixture

Table 4 Mix proportion of mortar on experimenting of deterioration rate of sulfuric acid

W/B (%)	C/B (%)	Air (%)	Unit Content (kg/m^3)					HRWRA^{*4} (kg/m^3)
			W	OPC	BF^{*1}	RS^{*2}	BFS^{*3}	
25.0	100.0	2.0	220	880	0	1,250	0	13.20
	40.0			352	528	0	1,271	
60.0	100.0			367	0	1,673	0	0.00
	40.0			147	220	0	1,740	5.51

^{*1} BF: Ground granulated blast furnace slag powder, ^{*2} RS: River sand, ^{*3} BFS: Blast furnace slag sand,
^{*4} HRWRA: High-range water reducing admixture

Table 5 Mix proportion of concrete

G_{max} (mm)	W/B (%)	C/B (%)	Air (%)	s/a (%)	Unit content (kg/m^3)						HRWRA^{*5} (kg/m^3)
					W	OPC	BF^{*1}	RS^{*2}	BFS^{*3}	CS^{*4}	
20	25.0	100.0	2.0	45.0	175	700	0	684	0	881	0.65
		40.0				280	420	0	711	865	0.55
	60.0	100.0				292	0	834	0	1,074	1.17
		40.0				117	175	0	869	1,066	

^{*1} BF: Ground granulated blast furnace slag powder, ^{*2} RS: River sand, ^{*3} BFS: Blast furnace slag sand, ^{*4} CS: Crushed stone,
^{*5} HRWRA: High-range water reducing admixture

size: 3,300 cm^2/g) and ground granulated blast furnace slag (density: 2.89g/cm^3, Blaine size: 4,150 cm^2/g) are used.

(2) Aggregate and additional admixture

River sand, ground granulated blast furnace slag (called blast furnace slag sand) and crushed limestone sand are used as fine aggregates. Crushed stone is used as a coarse aggregate. The properties of the aggregates are shown in Table 1. The polycarboxylate type of high range water reducing admixture is used as an additional admixture.

(3) Mixed proportion

Mixed proportions of cement paste, mortar and concrete are shown in Table 2 to Table 5. The dosage of admixture is determined by a decided flow for mortar and slump flow for concrete. Decided flow values for mortar are about 250 mm for 25% and 30% of water to binder ratio mortar specimens and about 180 mm for

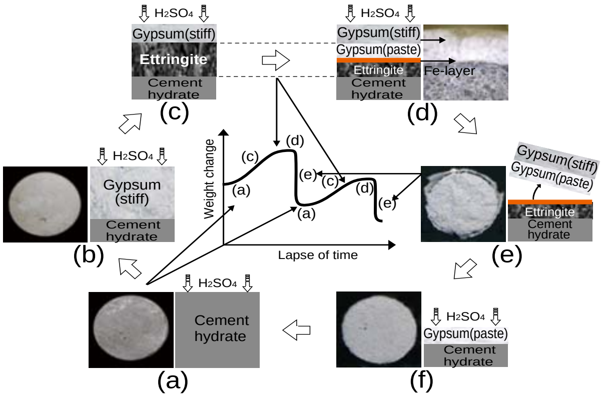

Fig. 1 Cycle of deterioration of cement paste due to sulfuric acid immersion test

60% of water to binder ratio mortar specimens. The decided slump flow value for concrete is about 650 mm for 25% of water to binder ratio concrete specimens, and the decided slump value for concrete is 5 cm for 60% of water to binder ratio concrete specimens.

2.2 Experimental Method

(1) Sulfuric acid immersion test of fine aggregate

Particle sizes 0.3-5.0 mm of fine aggregates were used. The samples were prepared in an absolutely dry state. A sample of 120 g of each aggregate and 200 ml of 5% by mass concentration of sulfuric acid were used for each test. After the samples were immersed in sulfuric acid for 14 days, each sample was removed from the container, washed of sulfuric acid by running water, then dried out in a 105±5 degree Celsius temperature controlled oven for 12 hours. The dried samples were sieved, weighed and measured; while the samples remaining at the 0.3 mm sieve were weighed as well.

(2) Sulfuric acid immersion of cement paste and mortar

The specimen is a cylinder specimen with a 50 mm diameter and 100 mm height for cement paste and mortar. The concrete specimen is a cylinder specimen with a 100 mm diameter and 200 mm height. The specimens were cured in the water after remolding up to age 7 days.

The concentrations 1%, 3%, 5% and 10% by mass of sulfuric acid were prepared. The volume of sulfuric acid for each test was calculated by a 1:2 mass ratio of sulfuric acid to specimen. The total amount of sulfuric acid was replaced every 7 days. The mass of specimens were measured every 7 days as well. At a predetermined date, the specimens were cut and sprayed with a phenolphthalein solution on the cutting face and were measured for the diameter of the coloration area.

3. RESULT OF SULFURIC ACID IMMERSION TEST

3.1 Deterioration of Sulfuric Acid to Cement Paste

The cycle of deterioration of sulfuric acid to cement paste is shown in Figure 1. Figure 1(a) shows the condition of the cutting surface of the specimen after immersion in sulfuric acid. Figure 1(b) shows a state where dihydrated gypsum film is formed by the reaction of calcium and sulfuric acid. Figure 1(c) shows a state where ettringite is generated at the contact surface of cement and dihydrated gypsum when tricalcium aluminate in cement reacts with dihydrated gypsum. Figure 1(d) shows a state where formed ettringite changes to become a paste-type gypsum when ettringite comes into contact with penetrated sulfuric acid, making a lower pH in the cement paste. Figure 1(e) shows a state where ettringite reacts with penetrated sulfuric acid. The reaction increases the paste-type of dihydrated gypsum and it peels away from the cement surface. Figure 1 (f) shows the state where the left ettringite makes direct contact with sulfuric acid, becoming a paste-type dihydrated gypsum and finally peels away from the cement surface. This entire cycle is then continually repeated. The result of a mass change of cement paste specimen when 5% concentration of sulfuric acid was used in the immersion tests is shown in Figure 2. The red-white circle and solid red circle marks represent the result of W/C 30% and W/C 60% of ordinary Portland cement

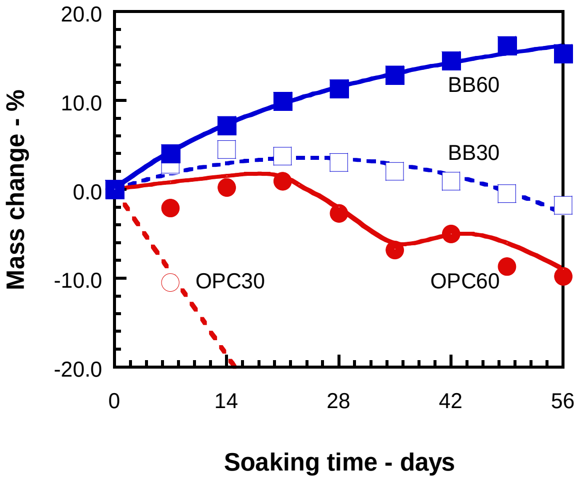

Fig. 2 Result of sulfuric acid immersion test

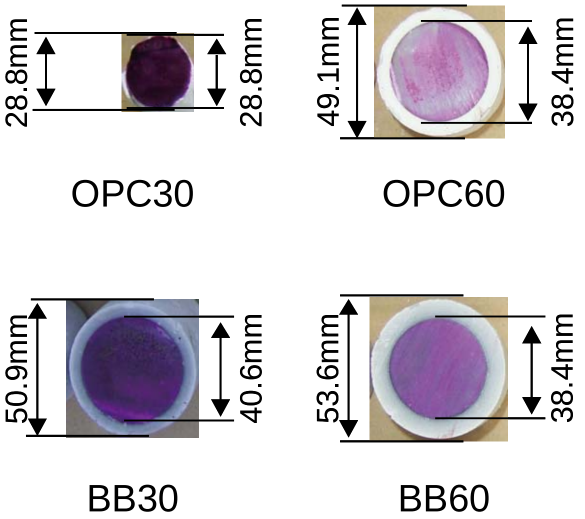

Photo 1 Cutting surface of cement paste specimens after 56 days of sulfuric acid immersion test

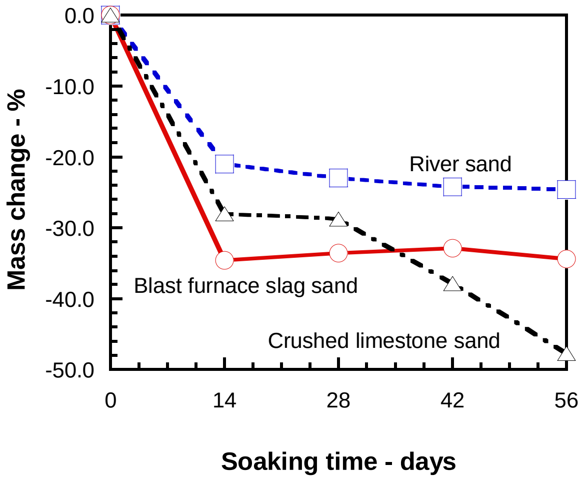

Fig. 3 Mass loss of fine aggregate due to the sulfuric acid immersion test

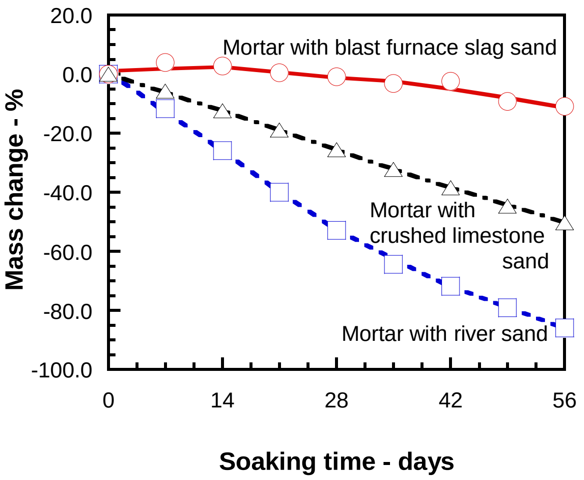

Fig. 4 Result of mass loss of mortar specimens

specimen. Ordinary Portland cement with 30% water to cement ratio shall be referred to as OPC30 and Ordinary Portland cement with 60% water to cement ratio shall be referred to as OPC60.

The blue-white square and solid blue square marks represent the result of W/B 30% and W/B 60% of cement containing blast furnace slag specimen. Cement containing blast furnace slag with 30% water to binder ratio shall be referred to as BB30 and cement containing blast furnace slag with 60% water to binder ratio shall be referred to as BB60. The ratio of cement and blast furnace slag is 4:6 by mass.

The mass loss tendency of OPC30 is linear. It reaches 28% when the immersion time is 56 days. While OPC60 has 2 cycles of gaining a little mass at the beginning and losing mass at 56 days. BB30 has a cycle of gain and loss of mass during the 56 day test; while BB60 gains mass and has no cycle of losing mass,

The results show that smaller water to cement ratios make a higher strength cement product, but there is also a higher rate of loss of mass. When blast furnace slag is used, the mass loss of the specimen is lower than the ordinary Portland cement specimen.

Photo 1 shows the cutting surface of a specimen after the immersion test has passed 56 days. The diameter of the specimen before the immersion test is 50 mm. There is no gypsum film remaining at the surface of the OPC30 specimen which shows a high deterioration of the specimen caused by sulfuric acid. OPC60 shows an amount of gypsum remaining around the specimen but the diameter of the coloration area has decreased. BB30 and BB60 show an amount of gypsum remaining, creating a larger diameter of the specimen compared with its diameter before the immersion test. The coloration by phenolphthalein solution shows the area that does not react with sulfuric acid. The BB is a larger diameter than the OPC.

The ordinary Portland cement mixture confirms that a smaller water to cement ratio yields a smaller diameter of coloration by phenolphthalein solution. However, the mixture containing blast furnace slag demonstrates an opposite tendency. The water to cement ratio has less influence on the loss of mass and carbonation of the specimen. When the gypsum is formed, it prevents the elution of decomposition of the product as well as the penetration of sulfuric acid into the specimen; thus, improving the sulfuric acid resistance of the specimen.

3.2 The Reaction of Fine Aggregate to Sulfuric Acid

Figure 3 shows mass loss of fine aggregate particle sizes 0.3 to 5.0 after the sulfuric acid immersion test. The black-white triangle , red-white circle and blue-white square marks represent the result of river sand, blast furnace slag sand and crushed limestone sand, respectively. The river sand shows 20% of mass loss for a 56 day immersion test. It is the lowest reactivity with sulfuric acid compared to another fine aggregate. On the other hand, when the crushed limestone sand was immersed into sulfuric acid, it generated carbon dioxide gas which illustrates a strong reaction. The mass loss is over 50% after the completion of the 56 days immersion test. The blast furnace slag shows a low number of mass loss; in fact, the mass actually increased after 14 days of the immersion period. This is due to a reaction of the blast furnace slag with sulfuric acid which produces dihydrated gypsum on the surface of the sample. It has been observed that, due to high amounts of calcium compounds in both blast furnace slag sand and crushed limestone sand contain, both aggregates have a strong reactions with sulfuric acid, though the products are different.

3.3 Deterioration of Mortar to Sulfuric Acid

Figure 4 shows the result of the sulfuric acid immersion test of 30% water to cement ratio mortar containing different types of fine aggregate. The ordinary Portland cement has been used as the binder material. The black-white triangle, red-white circle and blue-white square marks represent the result of river sand, blast furnace slag sand and crushed limestone sand, respectively. Among these three aggregates, river sand has the highest mass loss, followed by limestone and,

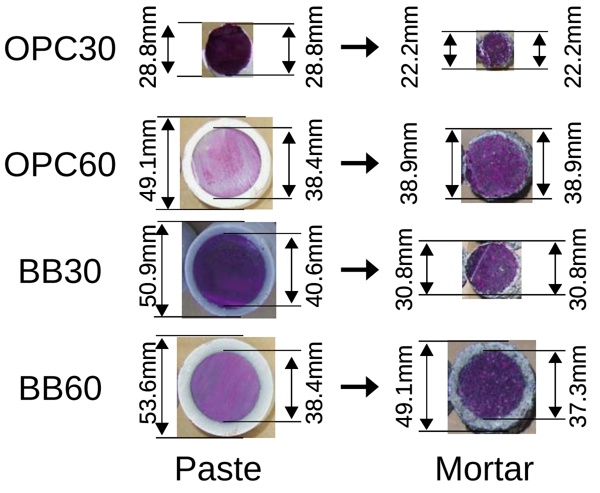

Photo 2 Result of sulfuric acid immersion test of cement paste and mortar with river sand

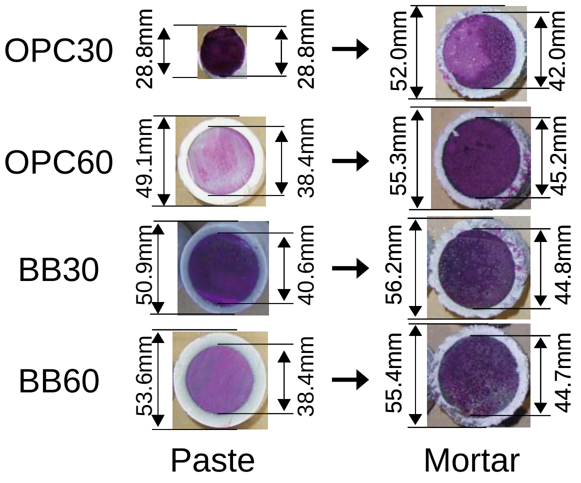

Photo 3 Result of sulfuric acid immersion test of cement paste and mortar with blast furnace slag sand

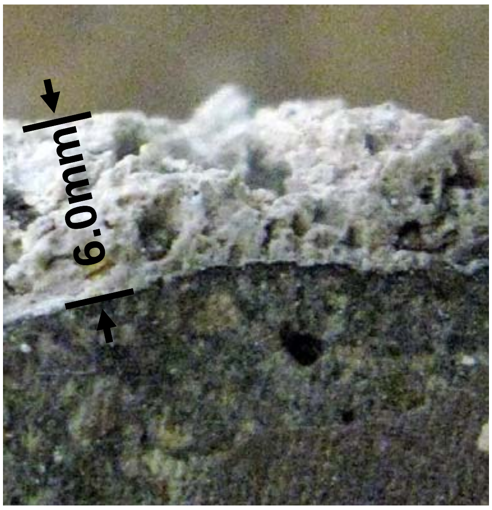

Photo 4 Surface of mortar with river sand

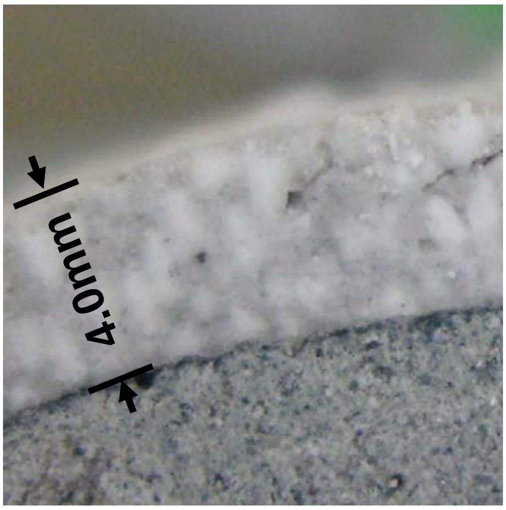

Photo 5 Surface of mortar with blast furnace slag sand

finally, with the lowest loss of mass, blast furnace slag. As a result, the lowest mass loss of a fine aggregate when it reacts with sulfuric acid is river sand, which has the highest mass loss of a specimen when it is used in mortar. While the higher reactivity of fine aggregates, such as crushed limestone stone and blast furnace slag sand, to sulfuric acid have a higher resistance to sulfates when they are used in mortar; especially, the mortar using blast furnace slag as a fine aggregate which shows insignificant data of mass loss during the 56 days of sulfuric acid immersion test.

Photo 2 shows the comparison of the cutting surface of cement paste and mortar specimens at the same water to binder ratio. River sand is used as a fine aggregate in the mortar specimen. The diameter of the specimen before the immersion test is 50 mm. The left side of the picture shows the test result of the cement paste specimens; the test result of the mortar specimens is shown on the right side. The mortar specimens show that there is no gypsum paste left on the surface of specimens; however, there is dihydrated gypsum film left on the same mixture of the cement paste specimen. In addition, the smaller water to binder ratio shows a greater effect of erosion by sulfuric acid.

Photo 3 shows the comparison of the cutting surface of the cement paste specimens and the mortar specimens at the same water to binder ratio. Blast furnace slag sand is used as a fine aggregate in the mortar specimens. The sulfuric acid immersion test results show that even the OPC30 cement paste specimen lost all trace of the dihydrated gypsum; however, the dihydrated gypsum is formed in the mortar specimen. The depth of carbonation becomes more shallow when blast furnace slag sand is used as a fine aggregate. Furthermore, the cement paste mixture which has dihydrated gypsum becomes resistant to sulfuric acid when blast furnace slag is used as a fine aggregate.

Photo 4 shows the formation of dihydrated gypsum film on mortar which has river sand as a fine aggregate. As there is a cavity between the bond of the particle of

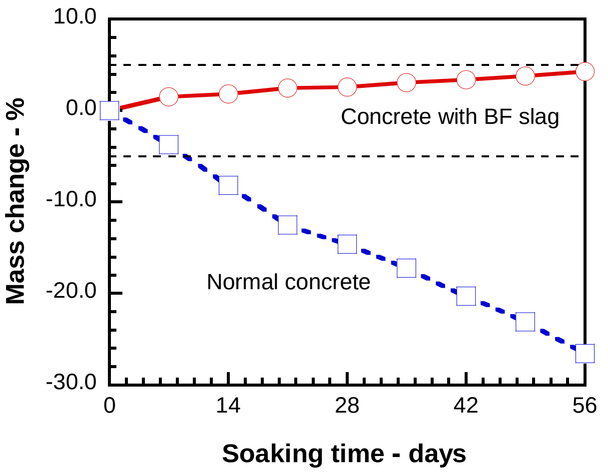

Fig. 5 Sulfuric acid resistance of mortar containing river sand and blast furnace slag

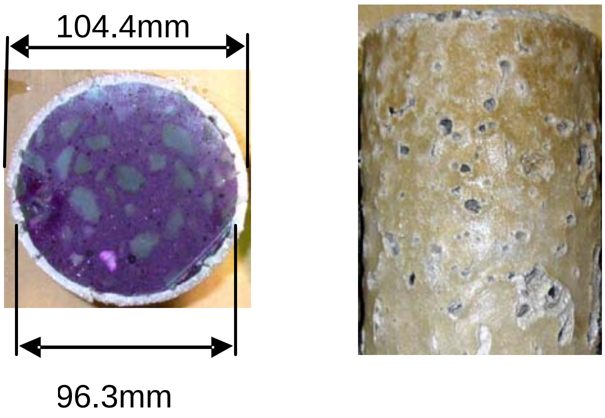

Photo 6 Carbonation of Concrete containing blast furnace slag after sulfuric acid immersion test

river sand and the dihydrated gypsum film, the gypsum is porous. Conversely, Photo 5 shows a highly dense dihydrated gypsum film at the surface of mortar which has blast furnace slag sand as a fine aggregate. It has been observed that, even when the ground granulated blast furnace slag powder has been combined with the binder, the density of the dihydrated gypsum film which is produced by the reaction of sulfuric acid is greatly different. The component of blast furnace slag sand is substantially the same as the component of cement and the reaction rate to sulfuric acid is almost the same. It is considered that the dihydrated gypsum film produced by the reaction of sulfuric acid and mortar which has blast furnace slag sand is homogeneous. On the other hand, when the river sand is used, the dihydrated gypsum film is heterogeneous at the boundary of the sand particle. Because of its cavity and heterogeneous formation, the dihydrated gypsum is not strong enough to prevent the penetration of sulfuric acid; thus, the mortar becomes more fragile than cement paste when under sulfuric acid attack.

3.4 Deterioration of Concrete to Sulfuric Acid

The result of the concentration 5% by mass of sulfuric acid immersion test of concrete are shown in Figure 5. blue-white square and red-white circle marks represent the results of normal concrete using river sand and blast furnace slag sand as a fine aggregate, respectively. Crushed sandstone is used as a coarse aggregate and the water to binder ratio of all mixtures is 25%. The ordinary Portland cement was used as a binder for the normal concrete mixture and ground granulated blast furnace slag powder was used as a binder material in concrete using the blast furnace slag sand mixture. The combination amount of blast furnace slag in the binder is 60%. The mass loss of normal concrete reached 30%, while the concrete with blast furnace slag powder and sand has a relatively small change in mass.

Photo 6 shows the cutting surface of concrete containing blast furnace slag after 56 days of the sulfuric acid immersion test. The size of the specimen was 100 mm in diameter before the test. It can be seen that the dihydrated gypsum was formed and that it prevented the penetration of sulfuric acid into the concrete. The sulfuric acid resistance has been improved.

4. CONCLUSIONS

(1) When river sand is used as a fine aggregate in mortar and concrete, the higher strength produces, the lower sulfuric acid resistance
(2) The resistance to sulfuric acid of blast furnace slag sand and crushed limestone sand are lower than that of river sand. But the sulfuric acid resistance of mortar with blast furnace slag sand and crushed limestone sand are higher than that of mortar with river sand.
(3) When blast furnace slag sand is used, the dihydrated gypsum film formed by the reaction of sulfuric acid and blast furnace slag sand is more dense and can prevent the penetration of sulfuric acid to the interior of the cement specimen. In addition, a lower water to binder ratio produces higher strength and sulfuric acid resistance.

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