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Resistance of Concrete with Granulated Blast Furnace Slag Sand to Sulphuric Acid Attack

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ABSTRACT

This paper explains that granulated blast furnace slag sand can improve the resistance of concrete to sulphuric acid attack. When a part of cement is replaced with ground granulated blast furnace slag, and the granulated blast furnace slag sand is used for sand, the resistance of concrete to sulphuric acid attack can be improved because a coating of gypsum (calcium sulfate dihydrate) is formed on the mortar or concrete. A coating of gypsum is strong enough to prevent the corrosion caused by sulphuric acid attack. The relationships between the immersed depth of mortar or concrete by sulphuric acid attack and the product of soaking time and concentration of sulphuric acid are liner. This paper will show that the resistance to sulphuric acid attack of concrete with granulated blast furnace slag sand is 6 times higher than that of ordinary concrete. The exposure test on sulphuric acid in the sewer for one year has been done, and the superiority of concrete with granulated blast furnace slag sand has been confirmed.

INTRODUCTIONS

Inside sewers, living sewage decomposes producing hydrogen sulphide, ammonia, methane etc. In the presence of these gases, hydrogen sulphide reduced by sulphate-reducing bacteria is oxidized into sulphuric acid by aerobic sulphur-oxidizing bacteria on the concrete surface, which severely deteriorates the concrete [Japan Concrete Institute, 2007]. In the past, it was common to coat the concrete vulnerable to deterioration by sulphuric acid attack with an anticorrosion coating of a resin in order to prevent corrosion. However, in several cases where the coating was not sufficient, the problem of deterioration would surface just a few years after the coating. Therefore, there is an increasing trend to make the concrete itself resistant to sulphuric acid.

Methods for improving the resistance to sulphuric acid include a method that constrains the formation of calcium hydroxide, which is a base substance for ettringite; a method that does the hardening of cement precisely; and a method that constrains the formation of sulphuric acid using an antibacterial or antimicrobial agent. Among these, methods using substances that constrain the formation of calcium hydroxide and osmosis of acid are prevalent, and a method that uses the solidification of sulphur for portland cement, alumina cement, polymer cement and liquid glass was proposed [Hirata et al., 2006]. Blast furnace slag is produced

Table 1. Mixture proportions of cement paste, mortar and concrete.

G_{max} (mm)	W/B (%)	C/B (%)	Air (%)	s/a (%)	Unit content (kg/m^3) W	OPC	BF*1	RS*2	BFS*3	CS*4	HRWRA*5 (kg/m^3)
0	30.0	40.0	2.0	-	464	618	927	0	0	0	0.00
		100.0			476	1,587	0				
	60.0	40.0			629	419	629				
		100.0			641	1,068	0				
5	31.6	40.0		100.0	213	269	404	1,414	0		5.38
	30.0	100.0				710	0				12.78
	63.2	40.0			287	181	272				0.00
	60.0	100.0				478	0				
	31.6	40.0			213	269	404	0	1,500		5.38
	30.0	100.0				710	0				12.78
	63.2	40.0			287	181	272				0.00
	60.0	100.0				478	0				
20	25.0	40.0		50.0	150	240	360	0	872	863	1.60
				45.0	175	280	420		711	865	0.55
	35.0					200	300		795	965	
	40.0			42.5		175	263		799	793	0.50
	50.0	50.0		50.0		175	175		982	975	0.40
	60.0	40.0		42.5		117	175		856	850	0.20
	25.0	100.0		45.0		700	0	684	0	881	0.65

*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

about 290 kg per ton of pig iron. In 2008, 22 million tons of blast furnace slag was produced in Japan [Nippon Slag Association, 2009]. In this paper, it will be shown that resistance of mortar and concrete to sulphuric acid attack can be improved when both ground granulated blast furnace slag and granulated blast furnace slag sand are used.

OUTLINE OF EXPERIMENT

Materials and mixture proportions. Table 1 shows mixture proportions of cement paste, mortar and concrete used in this study. Ordinary Portland cement (Density: 3.15g/cm^3, Blaine fineness: 3,300cm^2/g) and ground granulated blast furnace slag (Density: 2.89g/cm^3, Blaine fineness: 4,150cm^2/g) are used for binder. As a fine aggregate, river sand (Density: 2.61g/cm^3, Water absorption: 1.96%) and granulated blast furnace slag sand (Density: 2.77g/cm^3, Water absorption: 0.72%) are used. As a coarse aggregate, crushed sandstone (Density: 2.75g/cm^3, Water absorption: 0.54%), crushed limestone (Density: 2.71g/cm^3, Water absorption: 0.35%) and blast furnace air-cooled slag stone (Density: 2.63g/cm^3, Water absorption: 4.71%) are used.

Test Method. Cylindrical specimens of ϕ50 × 100 mm and ϕ100 × 200 mm were used for sulphuric acid immersion test of mortar and concrete, respectively. After casting the mortar, the specimen was cured in water for 7 days and then soaked in sulphuric acid of 5% and 10% concentration to the solution by mass. After every 7 days, the specimen was washed with water and then weighed after removing degraded parts. Moreover, using a dry-type cutter, we cut the specimen that was immersed in sulphuric acid for 56 days. After that, we sprayed it with phenolphthalein solution and measured the diameter of the area of the cut surface that changed color. One specimen was used for one mixture in the experiment.

Inside sewers, concrete suffers from drying and wetting. In order to examine the effect of drying on deterioration by sulphuric acid attack, some specimens in the experiment were soaked in the sulphuric acid permanently, and some specimens were alternately dried in the air and soaked in the sulphuric acid.

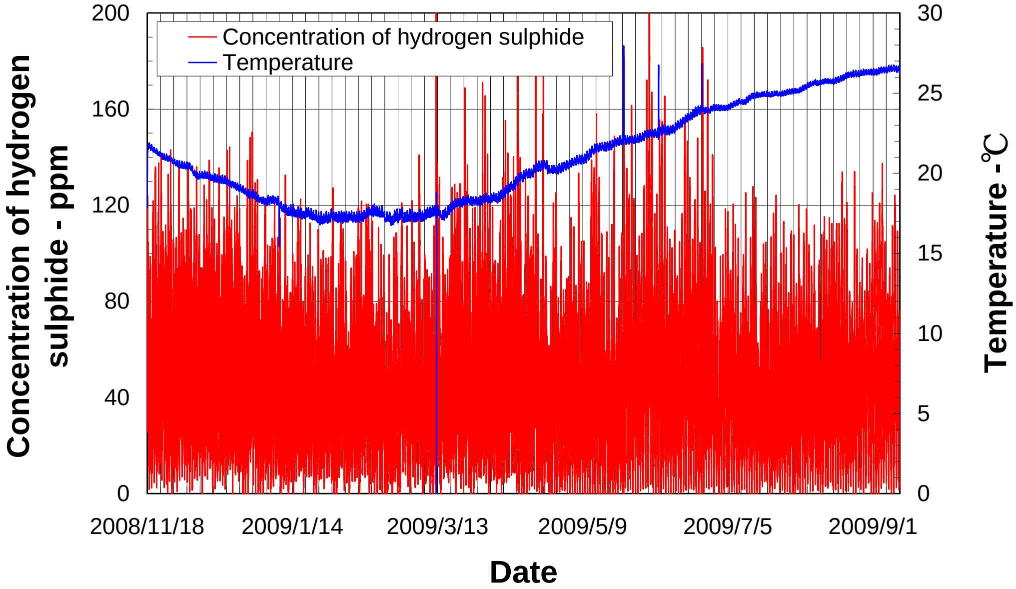


Figure 1. Environment of the sewer for exposure testing.

The environment of the sewer for the exposure test is shown in Figure 1. The temperature is 14C in winter and 27C in summer. The annual difference in temperature is small, compared with outside. The average concentration of hydrogen sulphide is 49.6 ppm, and the highest concentration of hydrogen sulphide is 200 ppm. This environment is classified into the severest environment.

EXPERIMENTAL RESULT AND DISCUSSION

Figure 2 shows the change in weight of cement paste made from ordinary portland cement and ground granulated blast furnace slag. ○ and ● show the results for cement paste whose water to cement ratio is 30% and 60%, respectively. (From now, these cement paste are called OPC30 and OPC60, respectively) On the other hand, □ and ■ are results of paste made from ordinary portland cement and ground granulated blast furnace slag. Cement to binder ratio of both types of paste is 40%. Water to binder ratio of □ and ■ is 30% and 60%, respectively. (From now, these pastes are called BB30 and BB60, respectively.) The weight of OPC30 was linearly decreased. The weight loss of OPC30 at 56 days after testing was 72.0%. The weight of OPC60 was gradually decreased till 35 days, and from 35 days the weight was increased and decreased at 42 days, once again. On the other hand, the weight of BB30 was increased at the start of testing and was decreased from 28 days of immersing time. The weight loss of OPC60 continued to increase till 56 days of immersing time.

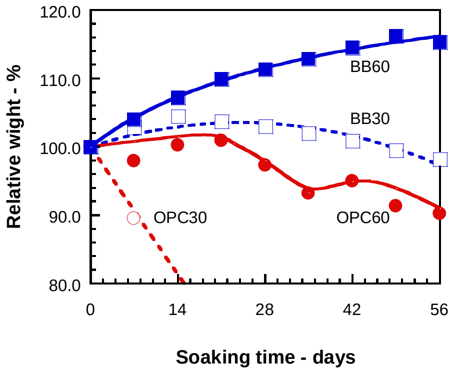


Figure 2. **Resistance for sulfuric acid of cement paste.**

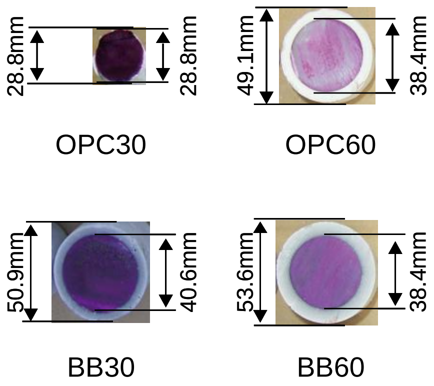


Photo 1. **Cement paste soaked in sulfuric acid during 56 days.**

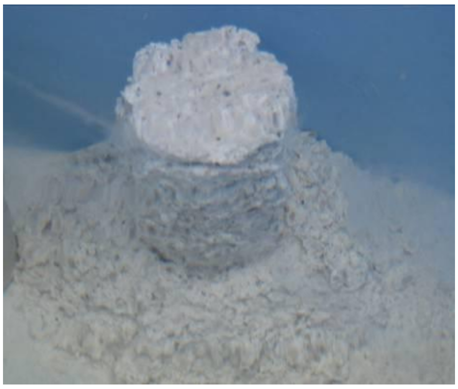


Photo 2. **Specimen of sulfuric acid attack resistance test.**

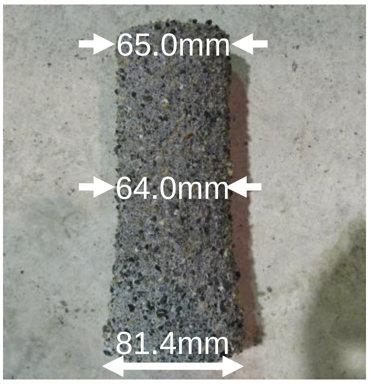


Photo 3. **Protection effect from sulfuric acid by gypsum.**

Photo 1 shows the results of spraying the phenolphthalein solution on the cut surface of paste immersed in sulfuric acid for 56 days. On the surface of OPC60, the white part indicates that it did not react with the phenolphthalein solution. However, on the surface of OPC30 whose water to cement ratio was small, the white part cannot be observed. On both surfaces of BB30 and BB60, the white part can be reserved. The corrosion of OPC30, which does not have the white part on the surface, is the worst of these pastes. The main content of the white part of OPC60, BB30 and BB60 is gypsum.

When gypsum shown in Photo 2 is not removed and continues the immersing test in sulfuric acid solution, the corrosion at the bottom which is covered by gypsum is smaller than that at top where is not covered with gypsum as shown in Photo 3. The diameter of the specimen at the top is 65.0 mm. The diameter of the specimen at the bottom is 81.4 mm. As can be seen from this result, gypsum can control the corrosion by sulfuric acid attack.

Photo 4 shows the results of spraying phenolphthalein solution on the cut surface of mortar with river sand immersed in sulfuric acid for 56 days. Except in the case in which the paste is BB60, every mortar does not have the white part that is not reacted with phenolphthalein solution. On the other hand, as shown in Photo 5, when ground granulated blast furnace slag sand is used, every mortar has white part which is not affected by phenolphthalein solution.

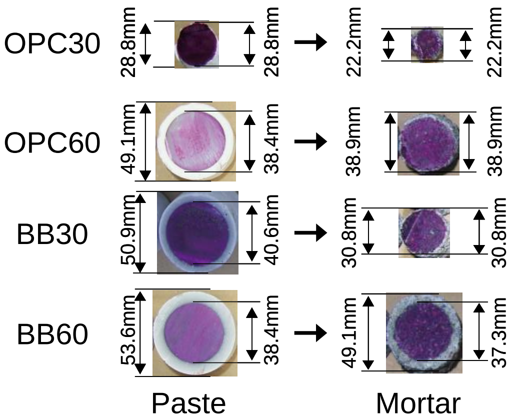


Photo 4. Test result of sulphuric acid attack resistance of mortar with river sand.

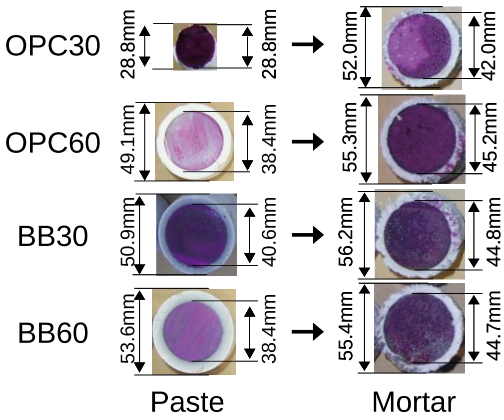


Photo 5. Test result of sulphuric acid attack resistance of mortar with blast furnace slag sand.

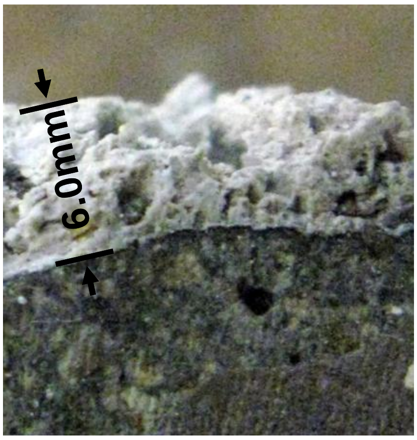


Photo 6. Surface layer of mortar with river sand.

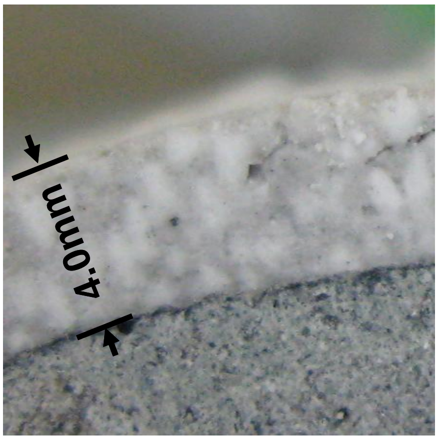
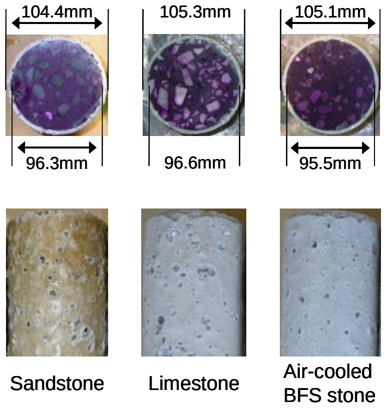


Photo 7. Surface layer of mortar with blast furnace slag sand.

As show in these photographs, mortar with a coating of gypsum has high resistance to sulfuric acid attack.

Photo 6 shows a close-up photography of gypsum coating of mortar with river sand. Photo 7 shows the gypsum coating of mortar with granulated blast furnace slag sand. Paste of both mortars is BB60. Apparently, gypsum coating of mortar with granulated blast furnace slag sand is more rigid than that with river sand. As shown in Photo 4 and Photo 5, the diameter of the solid part of mortar with river sand and mortar with granulated blast furnace slag sand is 37.3mm and 44.7mm, respectively. The immersed depth by sulfuric acid of mortar with granulated blast furnace slag sand is much less than that with river sand. It can be deduced that resistance of mortar with granulated blast furnace slag sand to sulfuric acid attack is high because coating of gypsum is very rigid.



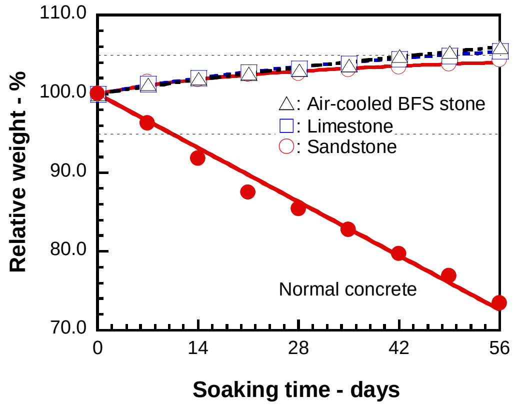


Photo 8. Cross section and surface of concrete with various gravel after soaking in sulfuric acid.

Figure 3. Effect of gravel on sulfuric acid resistance.

W/B: 25% W/B: 40% W/B: 60%

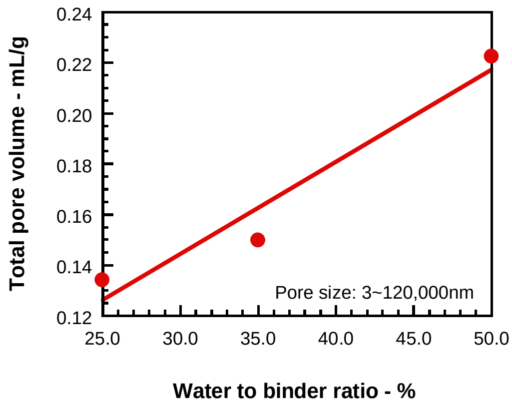


Photo 9. Effect of water to cement ratio on surface of concrete with ground granulated blast furnace slag.

Figure 6. Effect of water to cement ratio on total pore volume of gypsum.

Photo 8 shows the corrosion of concrete with crushed sandstone, crushed limestone and crushed air-cooled blast furnace slag stone. The fine aggregate of each concrete is granulated blast furnace slag sand. The corrosion of every concrete is almost the same because every coarse aggregate is not amorphous. That is, the same effect of granulated blast furnace slag sand can not be expected to crystallized coarse aggregate. However, when granulated blast furnace slag sand is used for fine aggregate, the immersed depth of every concrete is from 1.7mm to 2.3mm. It is much less than the immersed depth of concrete with river sand.

Figure 3 shows the comparison of weight change between concrete with granulated blast furnace slag sand and that with river sand immersed in sulfuric acid solution. ○, □ and △ in this figure show the result of concrete with crushed sandstone, crushed limestone and crushed air-cooled blast furnace slag stone, respectively. ● is the result of concrete whose binder is just ordinary portland cement, and whose fine and coarse aggregate are river sand

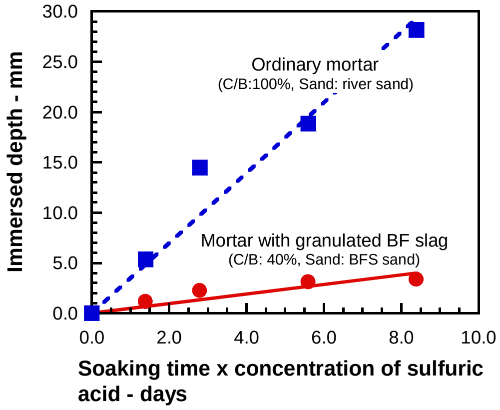


Figure 5. Relationship between immersed depth of mortar and product of soaking time and concentration of sulphuric acid.

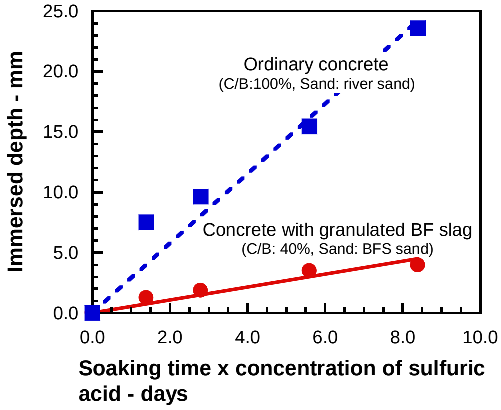


Figure 6. Relationship between immersed depth of concrete and product of soaking time and concentration of sulphuric acid.

and crushed sandstone. Even if granulated blast furnace slag sand is used, some small part on the surface of concrete is damaged and perfect gypsum coating can not be formed because coarse aggregate is crystallized. However, the weight change of concrete with granulated blast furnace slag sand is much less than that with river sand.

Photo 9 shows the effect of water to binder ratio on corrosion by sulfuric acid attack. Sand of every concrete is granulated blast furnace slag sand. As clear from this photograph, the less the corrosion of concrete surface is, the less water to binder ratio of concrete. Figure 4 shows the relationship between total pore volume of gypsum coating on the concrete surface and water to binder ratio of concrete. The observed range of pore diameter distribution is 3nm to 120,000nm by mercury intrusion porosimetry. Total pore volume is decreased with water to binder ratio. That is, when water to binder ratio is small, gypsum coating becomes rigid and the damage on the gypsum coating becomes little.

Figure 5 and Figure 6 show the relationships between the immersed depth of mortar and concrete by sulfuric acid and the product of soaking time and concentration of sulfuric acid, respectively. ● in Figure 5 and Figure 6 are the results of mortar and concrete with ordinary portland cement, ground granulated blast furnace slag and blast furnace slag sand, respectively. Cement to binder ratio of this mortar and concrete is 40%. (These mortar and concrete are called mortar with granulated blast furnace slag and concrete with granulated blast furnace slag, respectively in the following sentence.) ■ in Figure 5 and Figure 6 are the results of mortar and concrete with ordinary portland cement and river sand, respectively. (These mortar and concrete are called ordinary mortar and ordinary concrete, respectively in the following sentence.) Water to binder ratio of each mortar and concrete are 25%. Gravel of each concrete is crushed sandstone. As is clear from these figures, the relationships between the immersed depth by sulfuric acid and the product of soaking time and concentration of sulfuric acid are liner. The slopes of line shown in Figure 5 are 3.5mm/day and 0.5mm/day, respectively. It is clear that the resistance to suluric acid of mortar with granulated blast furnace slag is 6 times higher than that of ordinary mortar. And, the slopes of line shown in Figure 6 are 2.9mm/day and 0.5mm/day, respectively. The resistance to

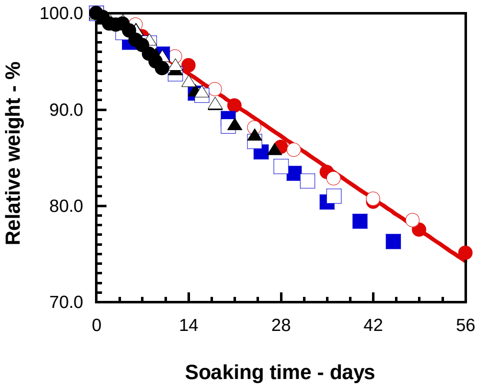


Figure 7. The effect of drying on deterioration of ordinary concrete by sulphuric acid.

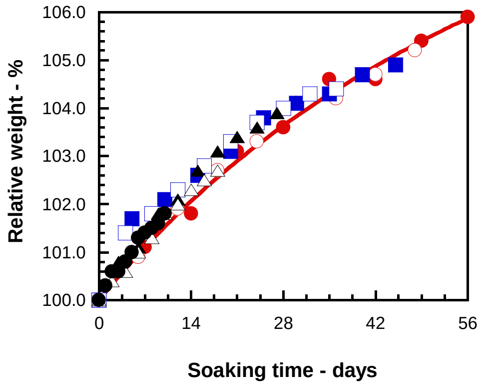


Figure 8. The effect of drying on deterioration of concrete with blast furnace slag by sulphuric acid.

sulfuric acid of concrete with granulated blast furnace slag is 6 times higher than that of ordinary concrete.

Figure 7 and Figure 8 show the effect of drying on deterioration by sulfuric acid attack. Figure 7 is the results of ordinary concrete whose water to cement ratio is 25%. Figure 8 shows the results of concrete with blast furnace slag whose water to binder ratio is 25%. In each figure, ● is the weight specimen in sulphuric acid for all time in the experiment. The specimen shown by ○ is dried for one day and soaked in 6 days. The specimen shown by ■ is dried for 2 days and soaked in 5 days. The specimen shown by □ is dried for 3 days and soaked in 4 days. The specimen shown by ▲ is dried for 4 days and soaked in 3 days. The specimen shown by △ is dried for 5 days and soaked in 2 days. The specimen shown by ● is dried for 6 days and soaked in one day. A horizontal axis of figure is total soaking time in sulfuric acid, that is, does not include drying time. From these figures, every data is plotted on the same line, irrespective of the type of concrete. That is, the effect of drying on deterioration by sulfuric acid attack is very small. The deterioration by sulfuric acid attack is affected by just soaking time in sulfuric acid.

(a) Ordinary concrete (W/C=30%)

(b) Ordinary concrete (W/C=60%)

(c) Concrete with granulated blast furnace slag (W/C=30%)

Photo 10. The specimens exposed in sewer for one year

Photo 10 shows the specimen exposure to sewer for one year. As clear from this photo, the damage of ordinary concrete with 30% water to cement ratio is big. As clear from Figure 9, the damage of concrete with granulated blast furnace slag is the smallest. Although the period of exposure test is just one year, the difference in the type of concrete is clear.

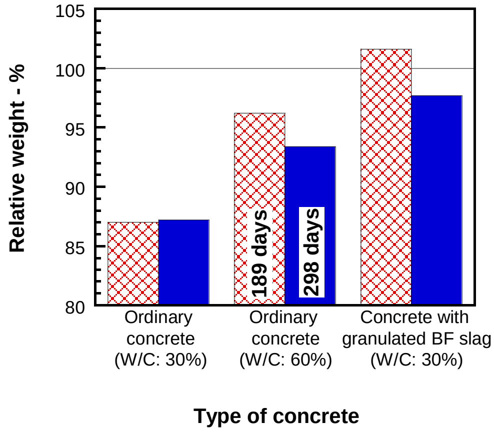


Figure 9. The weight change of each specimen in sewer.

CONCLUSIONS

When ordinary Portland cement is used, corrosion of cement paste due to sulfuric acid attack is big by low water to binder ratio. However, when both ordinary Portland cement and ground granulated furnace slag are used, corrosion of paste due to sulfuric acid attack is not different in water to binder ratio. Paste with high resistance to sulfuric acid attack forms a coating of gypsum on the surface of paste where sulphuric acid solution touches. Because of this coating, corrosion due to hydrogen ions and sulfuric acid ions is inhibited and paste becomes resistant to sulphuric acid. But, a coating of gypsum is lost, when river sand is used, even if ground granulated furnace slag is used. However, when granulated blast furnace slag sand is used, a coating of gypsum can be formed even if ground granulated blast furnace slag is not used. When coarse aggregate is used, perfect coating of gypsum can not be formed even if granulated blast furnace slag is used. However, resistance to sulfuric acid attack of concrete with granulated blast furnace slag sand is 6 times higher than that of ordinary concrete. The period of exposure test done in this study is short. However, the superiority of concrete with granulated blast furnace slag sand has been confirmed.

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