# Sulfate Resistance of Mortar with Blast Furnace Slag Fine Aggregate

Graduate School of Engineering, Hokkaido University　Student Member　○WANG Lulin
Faculty of Engineering, Hokkaido University　Fellow　YOKOTA Hiroshi

## 1. Introduction

Blast Furnace Slag aggregate (BFS) is used widely as one of the substitute materials for natural aggregate, which contributes to environmental conservation. In practical engineering, blended fine aggregate of BFS sand and natural sand becomes popular to improve the quality of aggregate[1]. Concrete using BFS fine aggregate has a lower resistance to freezing and thawing when the air contents are the same, but the blended fine aggregate can enhance the durability against freezing and thawing according to the previous study[2]. Sulfuric acid-induced deterioration of concrete becomes a social problem in sewer structures because huge amount of waste sulfuric acid needs to be treated every day in many countries. It has been known that concrete using BFS sand has high sulfate resistance by forming a tight product layer. How the sulfate resistance could be enhanced by use of the blended aggregate was investigated in this research. Sulfate resistance of mortar using the combined aggregate with various BFS mixing ratios was investigated.

## 2. Experimental test procedures

### 2.1 Material properties

Cement used in the test was ordinary portland cement (OPC). Fine aggregate was river sand and BFS sand. Water-to-cement ratio and cement-to-fine aggregate ratio were 0.4 and 0.5, respectively. In this test five mixture types were prepared; that is, RS100 mortar was made with river sand only as the control mixture, RS-BFS30, RS-BFS50, and RS-BFS70 mortar were made with the blended fine aggregate of BFS sand and river sand with the BFS-to-fine sand mixing ratios of 30%, 50%, and 70%, and BFS100 mortar were made with BFS sand only. The details of the mixing parameters and mix proportions of mortar are listed in Tables 1 and 2, respectively.

### 2.2 Test method

The specimen used in this experiment is a cylinder measuring 50 mm in diameter and 100 mm in height. After casting the mortar, the specimens were cured in air for 1 day, and then demoulded. The specimens were subsequently immersed in saturated $Ca(OH)_2$ solution for 1 month in order to keep the amount of calcium in the specimen enough to react with sulfuric acid.

After the immersion, the top and bottom surfaces of the specimen were polished, and the specimen was cut into 3 pieces of 30 mm thick each by concrete cutter as shown in Figure 1.

Six specimens for each type of mixture were put into a containar with 3.5 L of sulfuric acid solution for the acid soaking test. A sponge was placed under the specimen in order to ensure the acid solution is thoroughly supplied to the bottom surface of specimen. To make sure the fully immersion into the acid solution, the top surface of the specimen was kept 20-30 mm deep from the solution surface.The test room temperature was kept at 20 ± 2 °C.

In this test, three concentrations of sulfuric acid solution were prepared: 3%, 1% and 0.5%. A pH meter was used to monitor pH variations of acid solution during the soaking period in order to keep the pH of acid solution almost constant. When the pH changed from 0.1 ~ 0.2, an appropriate amount of sulfuric acid was added or the solution was fully replaced.

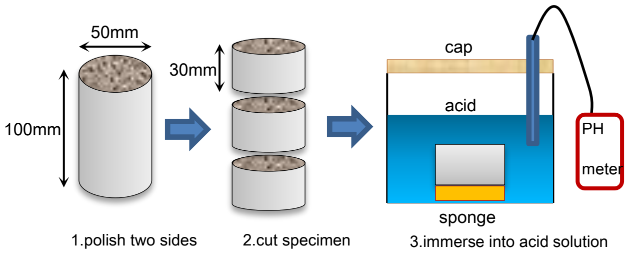


Figure 1　Specimen preparation and acid soaking test

Table 1　Parameters of mixing

| Mixture type | Cement | Fine aggregate | Mixing ratio (RS:BFS) | Content of BFS (%) |
|---|---|---|---|---|
| RS100 | OPC | RS | | 0 |
| RS-BFS30 | | RS and BFS | 7:3 | 30 |
| RS-BFS50 | | | 5:5 | 50 |
| RS-BFS70 | | | 3:7 | 70 |
| BFS100 | | BFS | | 100 |

Table 2　Mix proportion of mortar

| Mixture type | W/C (%) | Unit content (kg/m$^3$) | | | |
|---|---|---|---|---|---|
| | | W | C | RS*1 | BFS*2 |
| RS100 | 40 | 275 | 687 | 1374 | |
| RS-BFS30 | | | | 970 | 416 |
| RS-BFS50 | | | | 696 | 696 |
| RS-BFS70 | | | | 420 | 979 |
| BFS100 | | | | | 1410 |

*1 RS: density 2.71 g/cm$^3$, water-absorption 1.98%, FM 2.69
*2 BFS: density 2.77 g/cm$^3$

### 2.3 Measuring and evaluation

During the acid soaking test, changes in the mass and diameter of the specimen were measured every 7 days. For the measurement, the specimens were taken out from the container and were washed with water carefully to clean up particulaly to remove deteriorated parts. Then the specimen was weighed to obtain its mass loss, which is used as a macro index to evaluate sulfate resistance.

The diameter of the specimen was measured in the middle section by vernier caliper. To consider the variations in the diameter caused by surface deterioration, the measurement was made at 3 points and their average is taken to evaluate the acid invasion as a macro index.

## 3. Test results and discussions

### 3.1 Mass change

Figures 2-4 show the changes in the masses of the specimens over the soaking period. The mass change curves vary due to the differences in the BFS mixing ratio, and the sulfate resistance is enhanced with increase in the BFS mixing ratio.

As shown in Figure 2, when the test specimen is subjected to 3% acid (pH=0.2), it quickly reacts with sulfuric acid, and changes in the mass of mortar in each mixture type are obvious during the whole soaking period.

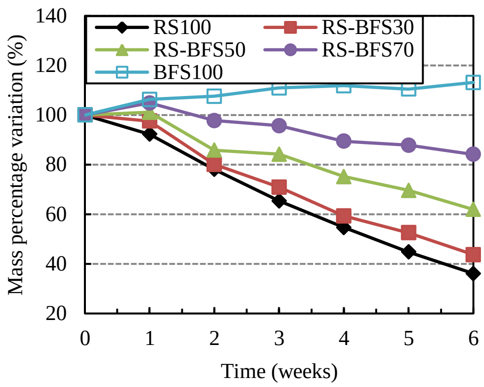


Figure 2　Mass change in 3% acid during soaking period

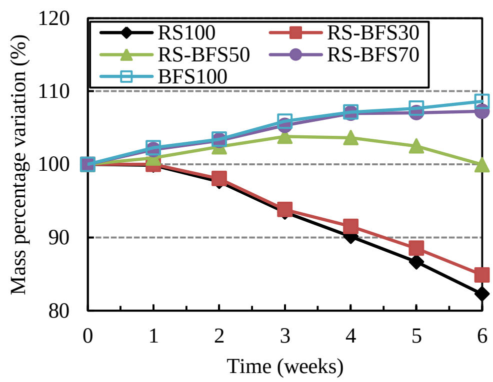


Figure 3　Mass change in 1% acid during soaking period

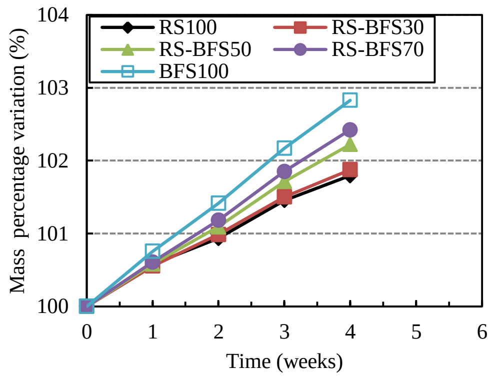


Figure 4　Mass change in 0.5% acid during soaking period

The masses of RS100 mortar and RS-BF100 mortar obviously decrease from the 1st week in the 3% acid solution, and continue to decrease with almost the same rate until the 6th week. In the mixture type RS-BFS50 and RS-BFS70, the mass increases obviously in the 1st week when they are subjected to the 3% acid solution, but due to the high concentration of acid, the corrosion product layer is unsteady and is easy to fall off, which makes more serious mass loss after the 1st week.

During the 1% acid (pH=0.6) soaking test as shown in Figure 3, there is no obvious mass change in the 1st week observed for the mixture types RS100 and RS-BFS30. However, their mass changes become obvious from the 2nd week, showing the similar trend each other. In the mixture types RS-BFS50 and RS-BFS70, the mass continuously increases from the beginning of the soaking. That of RS-BFS50 has a peak in the 3th week, and that of RS-BFS70 reaches a plateau from the 4th to 6th week.

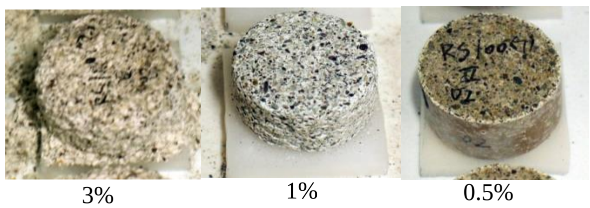


Photo 1　Acid corrosion of RS100 specimens in the 2nd week

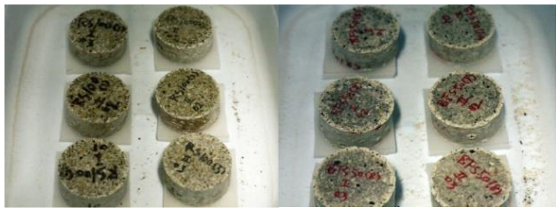

Photo 2　Acid corrosion of RS100 and RS-BFS50 specimens soaked in 0.5% acid solution in the 4th week

The trends of the mass change and acid corrosion in the 0.5% acid solution (pH=1) are considerably different from those in the 3% and 1% acid solutions, as shown in Figure 4 and Photo 1. The masses of all the specimens keep increasing during the whole soaking period. It means that a part of mortar was hardly fell off as shown in Photo 2 because the corrosion product formed by soaking in the 0.5% acid solution was very hard in all the mixture types.

The main chemical composition of BFS sand and cement hydrates reacting with sulfuric acid is CaO, because it is lighter than $CaSO_4{\cdot}2H_2O$. Once the corrosion product layer is formed and hardly falls off, the mass loss does not occur.

### 3.2 Diameter change

Figures 5-7 show the diameter variations of specimen during the soaking period. The diameter variation is affected by falling off or expansion of the outer surface of specimen. The diameter varies in proportion to the soaking period, which is similar to the mass variations. In the 3% acid solution, the diameters of RS-BFS50 and RS-BFS70 specimens increase in the 1st week, and decrease later due to falling off the corrosion product. In the 1% acid solution, their diameters increase continuously. In the 0.5% acid solution, the diameters increase continuously in all the mixture types.

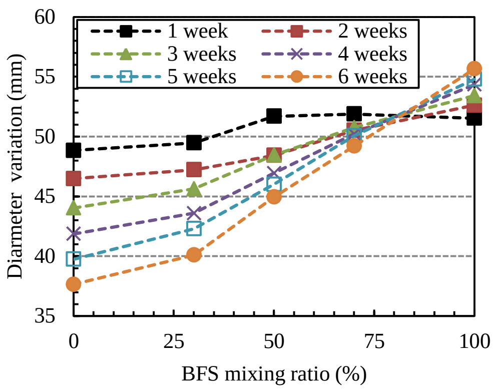


Figure 5　Diameter variations in the 3% acid solution

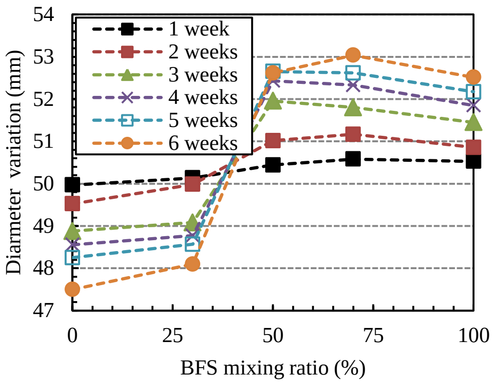


Figure 6　Diameter variations in the 1% acid solution

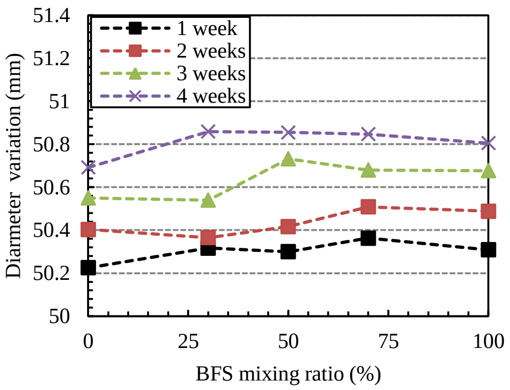


Figure 7　Diameter variations in the 0.5% acid solution

Increase in the diameters of RS-BFS50 and RS-BFS70 specimens is greater than that of BFS100 specimen because the acid invaded deeper in the specimen and more calcium reacted with sulfuric acid, which caused expansion. The expansion was caused by the increase in the volume of BFS sand and pop-out by ettringite formation[4)].

According to the test result, the effect of the blended aggregate on the mass and volume reduction is easy to appear when mortar is soaked by high concentration sulfuric acid.

### 3.3　Characteristic of acid corrosion

Because the molecular construction of corrosion product varies with concentration of sulfuric acid, the corrosion product layer exhibits different properties depending on the acid concentration. The product is rather soft when the concentration of acid is 3%, which leads to bursting and obvious mass loss. However, the product is hard and hardly falls off in every mixture type when the acid concentration is 0.5%, as shown in Photo 3, which results in mass increase.

Regardless of the BFS mixing ratios, the lower the concentration of acid is, the harder the corrosion product layer on the outer surface of mortar will be. Moreover, when the mixing ratio is low, a non-homogeneous corrosion layer is easy to be formed as shown in Photo 4.

## 4.　Deterioration mechanism

According to the previous studies[4, 5)], a siliceous particle has a compacted boundary with calcium. Accordingly, sulfuric acid can invade into cement matrix very quickly and makes mass loss prominent when mortar is made with normal river sand, as shown in Figure 8. Sulfate resistance of concrete can be enhanced by use of BFS sand, because the tight boundary existing between BFS sand and cement hydrates can effectively prevent the acid invasion.

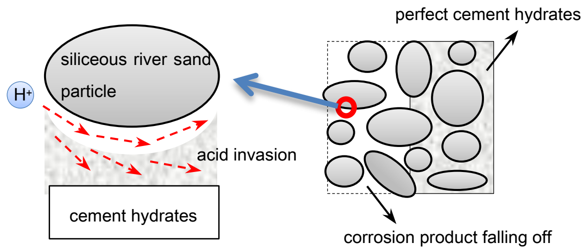


Figure 8　Sulfuric acid corrosion process of mortar using normal river sand

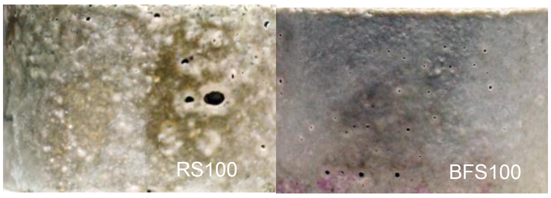


Photo 3　A hard layer formed on the outer surface of mortar in the 0.5% acid solution

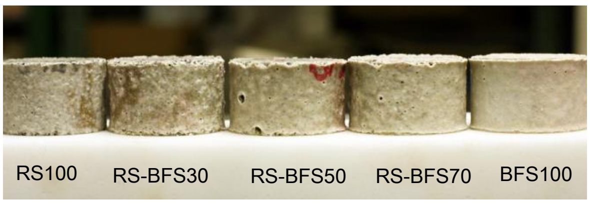


Photo 4　Appearance of specimens in the 0.5% acid solution for 4 weeks


Photo 5　Appearance of specimen after 1 week soaking in the 3% acid solution

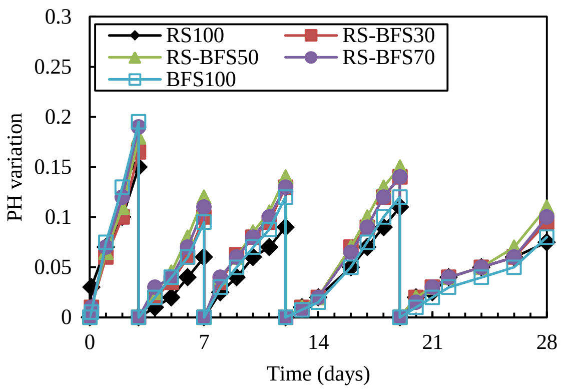


Figure 9　pH change of the 3% acid solution during soaking period

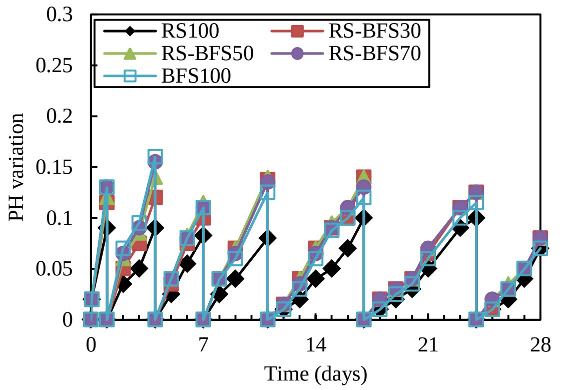


Figure 10　pH change of the 1% acid solution during soaking period

The mortar made with the blended aggregate has the characteristics of normal river sand and BFS sand because the particle of siliceous sand included in the river sand has an uncompacted boundary. It makes the corrosion product layer falling off more easily compared with the use of BFS sand only. As shown in Photo 5, the layer of $CaSO_4 \cdot 2H_2O$ fell off in the place where river sand particles existed, which made the outer surface of mortar more porous.

The boundary of BFS sand and river sand is not tight enough to prevent acid from invading easily although a hard corrosion product layer has been formed. Thus, sulfuric acid can invade inside along the space of the boundary because the mortar made with the combined aggregate always expands more than that made with BFS sand only in the sulfuric acid environment. The pH of acid solution of BFS100 changed greatly at the beginning when using the blended aggregate (especially RS-BFS50 and RS-BFS70) after a period of reaction as shown in Figures 9 and 10.

## 5. Conclusions

The following conclusions were drawn in this research:

1. Sulfate resistance of mortar made with BFS sand is enhanced with increase in the BFS sand mixing ratio.
2. Changes in mass and diameter of mortar specimen during acid soaking period are varied depending on the concentration of acid solution.
3. Behavior of corrosion product varies depending on the concentration of acid solution in all the mixture types.
4. Sulfuric acid can invade into mortar made with the blended aggregate more easily than to that made with BFS sand only.

Acknowledgements

The authors would like to express their gratitude to Dr. Yasuhiko Sato, Hokkaido University for his support to the procurement of the BFS sand. The authors also thank Dr Hai Yen Thi Nguyen, ex post-graduate student of Hokkaido University, for her help during the experimental test.

References

1) Architectural Institute of Japan: Recommendation for Practice of Concrete with Blast-Furnace Slag Fine Aggregate, 2013.
2) Uemoto, H., Abe, M., Kage, T. and Asano, K.: Research on effective utilization of blast furnace slag fine aggregate to concrete, Report 3.1-1, Research Center for Urban Disaster Mitigation, Kogakuin University, 2011.
3) Jariyathitipong, P., Hosotani, K. , Fujii, T. and Ayano, T.: Improvement of resistance to sulfuric acid attack of concrete by use of blast furnace slag sand, Doboku Gakkai Ronbunshuu, E, Vol. 69, No. 4, 337-347, 2013.
4) Fujii, T., Hosotani, K., Matsunaga, H. and Ayano, T.: Resistance to sulfuric acid of cement hydrate with blast furnace water-cooled slag, Proceedings of the Japan Concrete Institute, Vol. 31, No. 1, 847-852, 2008.
5) Ayano, T., Kogochi, M., Fujii, T. and Iriya, K.: Effect of type of fine aggregate on sulfuric acid attack of mortar, Proceedings of the Japan Concrete Institute, Vol. 30, No. 2, 559-564, 2008.