

# Sulfate Resistance of Concrete using Ground Granulated Blast-furnace Slag for Recycling

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## Abstract

Recently, ground granulated blast-furnace slag (GGBFS) has been increasingly used as additive for concrete. Many researchers reported that concrete using GGBFS had a better resistance under severe environments, such as marine or sulfate-rich soils, than Portland type cement concrete.

The aim, therefore, of this study is to evaluate on the effectiveness of concrete using GGBFS when the concrete exposes to sulfate-rich environment. The detailed items for experiments show 2 series consisted of sulfate immersion test with mortar and sulfate diffusion test with concrete.

The sulfate immersion test was performed for 400 days and contained reduction of compressive strength, length change and XRD analysis.

For sulfate diffusion test, sulfate ions diffusivity was calculated on the consideration of electrochemical theory by the diffusion cell test.

As the results of this study, it was found that the concrete using GGBFS as additive was superior to portland type cement concrete. Consequently, the use of concrete with GGBFS for recycling may expect the durable and economical benefits.

*Keyword* : . ground granulated blast-furnace slag, sulfate immersion test, XRD, sulfate ions diffusivity

## 1. Introduction

The development of cement and concrete capable of resisting sulfate attack has been the subject of research and development for many years. The deterioration of concrete structural components exposed to soils and groundwater contaminated with sulfate salts is a serious problem in durability of concrete.

It is generally accepted that sulfate attack of hydrated cement takes place by the reaction of sulfate ions with calcium hydroxide and calcium aluminate hydrate to form gypsum and ettringite. The formation of the two products is responsible for expansion and cracking of concrete. To produce concrete with improved sulfate resistance, the amount of calcium hydroxide and calcium aluminate hydrate must be kept to a minimum. It is well known that GGBFS produces the low permeability concrete due to pozzolanic reaction as well as the small amount calcium hydroxide concrete by its replacement of cement.[1] Especially it is generally accepted that the resistance to sulfate ions diffusion into concrete intends to be improved, if used GGBFS as cement replacement materials, owing to a refined pore structure, and, therefore, reducing the diffusion rate of sulfate ions originated sulfate environments.

In the present paper, two series on sulfate tests were carried out to investigate the sulfate resistance of mortar or concrete with and without GGBFS for the purpose of industrial wastes recycling. One (series I) is the continuous immersion test of mortars with ground granulated blast-furnace slag in 5% sodium sulfate solution. The other

(series II) is consisted of diffusion test of concretes using potential difference based on Nernst-Einstein equation.

The durable properties of mortar and concrete with GGBFS were proved through immersion and diffusion tests.

## 2. Process of diffusion and deterioration by sulfate ions

Sulfate attack was generally accepted as an aggressive process originated by the reaction of the sulfate ions from the environments with the calcium aluminates hydrate present in the cement matrix. This reaction produces ettringite, which occupies more space because of the adsorption of water and results in an expansion process that causes disruption of the material. The deterioration by sulfate attack, in general, contains following three stages.

1. permeation and diffusion of sulfate ions into cement matrix
2. reaction of sulfate ions with hydrate products to form ettringite and gypsum
3. deterioration of cement matrix causing to strength loss, expansion and softening

To control the sulfate attack, two major approaches are considered. Namely, restrict of sulfate ions and modification of the components of cement. The use of GGBFS is generally considered beneficial in respect with sulfate resistance, because the calcium hydroxide concentration in the surface zones of concrete is reduced with the addition of GGBFS. Dissolution of calcium

hydroxide and the composition of the hydrated silicates and aluminates is the major source of OH<sup>-</sup> and Ca<sup>2+</sup> ions required for sulfate reaction. Therefore, a reduction in this source provides the higher sulfate resistance.

In addition, there are several reasons that GGBFS can result in significant decrease in sulfate ions diffusion coefficient.

First, GGBFS can improve the distribution of pore size and characteristics of concrete. The pore structure of slag concrete is of a much more discontinuous and tortuous nature due to the ongoing pozzolanic reaction within existing pores.

Second, more C-S-H gel may be formed when GGBFS hydrate, which may block diffusing paths.

Third, the number of total ions of Ca<sup>2+</sup>, Al<sup>3+</sup>, AlOH<sup>2+</sup> and Si<sup>4+</sup> in GGBFS concrete is more than that in portland cement concrete and ions concentration is also high. Therefore, the ions have lower diffusing ability and can restrict the movement of sulfate ions.

### 3. Materials and sample preparation

#### 3.1 Mortar specimens for series I tests

The mortar samples were produced at three different cements, ordinary portland cement [OPC], sulfate resistance portland cement [SRC], ordinary portland cement + 50 % GGBFS [SG50], and the aggregate-binder ratio and water-binder ratio of the mortar specimens were 2.45 and 0.485 respectively. The chemical and mineralogical composition of the binders is presented in Table 1 and the physical properties in Table 2. The 5% sodium sulfate solution was adopted for immersion of pastes and mortars.

After the age of a day, the mortar specimens were demoulded and placed in a curing chamber (20 °C and 95% RH) for pre-curing period, which develops the compressive strength 20 MPa. Mortar samples for compressive strength and length change measurement were prepared according to ASTM C 109 and ASTM C 1012 using cubic moulds 50 × 50 × 50 mm and prism moulds 25 × 25 × 285 mm.

Table 1. Chemical composition of cements and GGBFS (%)

	OPC	SRC	GGBFS
SiO <sub>2</sub>	20.2	22.6	33.2
Al <sub>2</sub> O <sub>3</sub>	5.8	3.8	15.2
Fe <sub>2</sub> O <sub>3</sub>	3.0	4.3	0.3
CaO	63.3	62.8	43.0
MgO	3.4	2.5	6.4
SO <sub>3</sub>	2.1	2.0	1.0
Ig. loss	1.2	1.2	0.1

Table 2. Physical properties of cement and pre-curing period

		OPC	SRC	SG50
Specific gravity		3.13	3.18	3.01
Specific surface area (m <sup>2</sup> /kg)		312	328	401
Setting time (min.)	Initial set	270	290	285
	Final set	400	460	515
Compressive strength of mortar (MPa)	7 days	25.0	24.0	21.1
	28 days	43.1	42.3	38.6
	91 days	46.1	45.5	47.0
Pre-curing period before 20 MPa (days)		7	6	8

#### 3.2 Concrete specimens for series II tests

4 types of concrete specimens were prepared for sulfate ions diffusion tests. The specimens were made with water-binder ratio 40 and 50 %, demoulded and then cured in water at 20 °C for a scheduled duration (28 and 60 day).

The cements used for diffusion test were same to those of immersion test and GGBFS was replaced 40 and 60 % of OPC weight.

The specific gravity, absorption and fineness modulus of the fine aggregate employed for concrete were 2.59, 0.80 % and 2.80 respectively. The coarse aggregate with maximum size 25 mm was adopted. Additionally, AE reducer was used in concrete mixture.

The mix proportion of concrete for diffusion test is presented in Table 3.

Table 3. Mix proportions of concrete for diffusion test (kg/m<sup>3</sup>)

	Water	Cement	Sand	Gravel	GGFBS
OPC-40	187	468	734	977	-
OPC-50	187	374	668	965	-
SRC-40	187	468	736	979	-
SRC-50	187	374	670	967	-
SG40-40	187	281	730	971	187
SG40-50	187	224	663	958	150
SG60-40	187	187	728	969	281
SG60-50	187	150	661	954	224

### 4. Test methods

#### 4.1 Immersion tests (series I)

The sulfate deterioration of mortar specimens was evaluated by measuring the reduction in compressive strength and length change after pre-curing period to obtain the 20 MPa. Sulfate deterioration factor (SDF) of cubic mortar specimens, 50 × 50 × 50 mm size, related to the reduction in compressive strength was determined using the following equation.

$$SDF = \frac{P_w P_s}{P_w}$$

where,

SDF : sulfate deterioration factor

$P_w$  : the average compressive strength of mortar specimens cured in water (MPa)

$P_s$  : the average compressive strength of mortar specimens cured in sodium sulfate solution (MPa)

Length change measurements of prism mortar specimens,  $25 \times 25 \times 285$  mm size, were performed according to ASTM C 1012 and measured on three mortar specimens withdrawn from test solutions and the average value was adopted.

#### 4.2 Diffusion tests (series II)

The effect of GGBFS were examined through total passed charge and sulfate ions diffusion coefficient of concrete.

A diffusion cell (cathode : 5 %  $\text{Na}_2\text{SO}_4$  solution, anode : saturated  $\text{Ca}(\text{OH})_2$  solution) was used. The concrete for cell was sliced as a length of 50 mm and diameter of 100 mm size and placed between the electrodes, as shown in Fig. 1. The voltage of 30 V was applied to migrate the sulfate ions from cathode part for 12 hours. The passed current was recorded with 30 min. interval as using TDS 601 data logger.

The sulfate ions diffusion coefficient was calculated as following equation.

$$D = \frac{RT}{nF^2} \frac{it_{\text{SO}_4} l}{\Delta E AC_{\text{SO}_4} Z}$$

where,

$D$  : diffusion coefficient of sulfate ions

$R$  : gas constant

$T$  : absolute temperature

$I$  : total passed current

$t_{\text{SO}_4}$  : transport number of sulfate ions

$l$  : thickness of specimen

$F$  : Faraday constant

$\Delta E$  : potential difference

$A$  : area of specimen

$C_{\text{SO}_4}$  : concentration of sulfate ions

$Z$  : valence of ion

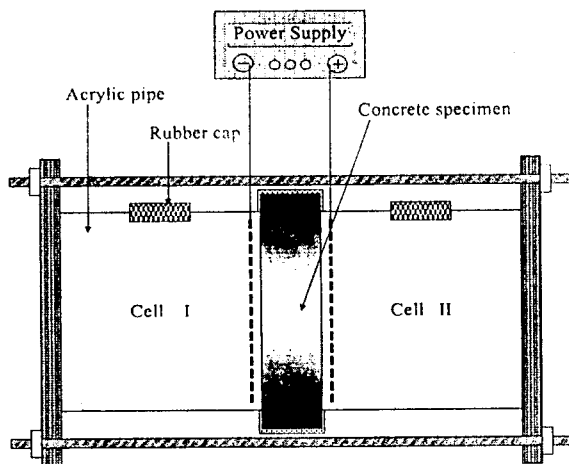


Fig. 1 Detail of cell for sulfate ions diffusion test

## 5. Results and discussion

### 5.1 Sulfate deterioration of mortar by continuous immersion

#### Reduction in compressive strength (SDF)

Reduction in compressive strength, which is expressed as deterioration factor (SDF), of cement mortar specimens made with a w/b ratio of 48.5% is shown in Fig. 2. The SDF in specimens made with OPC ( $C_3S/C_2S=3.31$ ,  $C_3A=10.3\%$ ) immersed in sodium sulfate solution was about 0.76 at 400 days of immersion. The SDF in specimens made with SRC was about 0.36 at the same immersion period. The negative SDF at 56 days of immersion in SRC mortar specimens signifies an increase in compressive strength, which is attributable to the filling up of the pores by the reaction products which densify the mortar matrix in early period of immersion. Similar studies have been reported by Brown[2] and Irassar [3].

This figure also shows the effect of GGBFS on reduction in compressive strength of mortars in sodium sulfate solution. The data on SDF in SG50 mortar specimens indicates deterioration of OPC mortar specimens was more pronounced compared with that of SG50 mortar specimens used as 50% GGBFS partial replacement of OPC in sodium sulfate solution during test period. However, the SDF of SG50 mortar specimens was similar to that of SPC mortar specimens till 300 days of immersion.

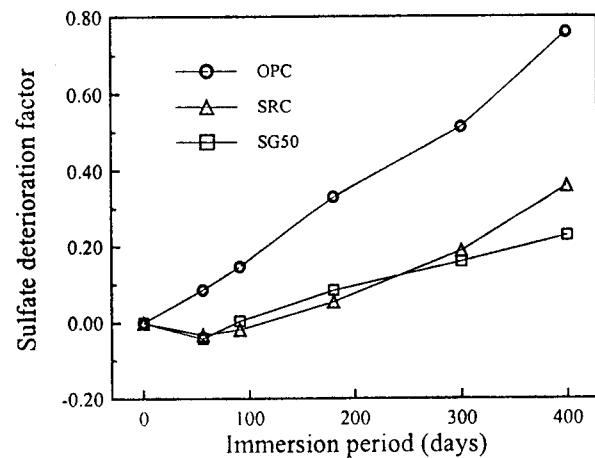


Fig. 2 SDF of mortars immersed in 5 % sodium sulfate solution

#### Length change

Length change was investigated, using a small steel vertical frame that incorporated a dial gauge. Length change of cement mortar specimens immersed in sodium sulfate solution was measured for 800 days of immersion. Fig. 3 shows length change of 3 types of cement mortar specimens. The average length change in OPC mortar specimens immersed in sodium sulfate solution at 180 days recorded the value of 0.416% while at the same immersion period, the data on average length changes of SRC mortar specimens were 0.089%, respectively.

SG50 mortar specimens (GGBFS was used as 50% replacement of OPC) immersed in sodium sulfate solution experienced about 20% (0.08%), at 180 days of immersion, of length change of OPC mortar specimens as shown in Fig. 3.

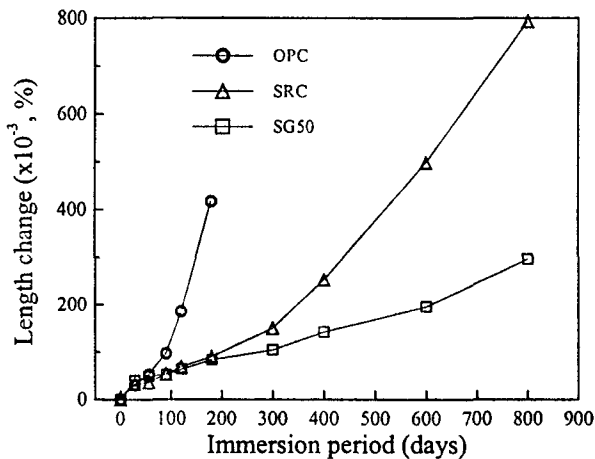


Fig. 3 Length change of mortars in 5 % sodium sulfate solution

#### X-ray diffraction

To explain the sulfate resistance performance behaviors of cement pastes, XRD diffractograms shown in Fig. 4 and 5 have been developed to identify the products formed. Fig. 4 shows the diffractograms to identify the products in powders from OPC pastes after immersion of 400 days in pour water and sodium sulfate solution. It is seen that, whereas ettringite, gypsum and thaumasite as well as portlandite are identified in OPC in sodium sulfate solution, In case of OPC paste in pour water portlandite peaks, which identifies the maximum intensity peak, are mainly identified. It is generally noted that the types of ettringite crystal can be classified on the basis of differences in the structure and length-width ratio of crystals. Thaumasite intensity peaks were also observed in OPC paste immersed in sodium sulfate solution. These products such as ettringite, gypsum and thaumasite can be formed due to the reacting with sulfate ions and portlandite by through-solution mechanism, thereby resulting in reduction of the portlandite content.

Fig 5 shows that the addition of GGBFS results in the consumption of calcium hydroxide due to pozzolanic reaction, and the dilution of the C<sub>3</sub>A phase, and thereby reducing the intensity peaks of portlandite and ettringite. Disappearance of the gypsum peaks in sulfate solution may be explained through poorly crystalline formation of it. And the intensity peaks in the diffractograms as well as the conversion to secondary C-S-H gel due to strong pozzolanic reaction can explain a good agreement with SDF and length change of SG50 mortars.

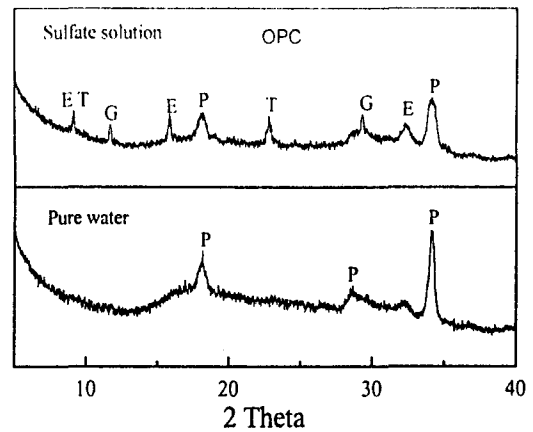


Fig. 4 XRD diffractograms for OPC pastes. (Note : E=ettringite, T=thaumasite, G=gypsum, P=portlandite)

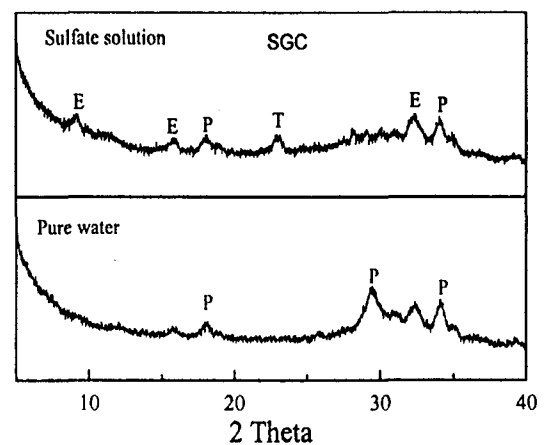


Fig. 5 XRD diffractograms for OPC pastes. (Note : E=ettringite, T=thaumasite, G=gypsum, P=portlandite, Q=quarez)

#### 5.2 Diffusion characteristics of sulfate ions in concrete

##### Total passed charge

Fig. 6 and 7 show the values of total passed charge through the concretes with water-binder ratio 40 and 50 % at the curing ages of 28 and 60 days respectively. It could be observed that the values of total passed charge of concretes increasing water-binder ratio are greater than those of low-w/b concretes.

For portland cement concrete, SRC concrete had a higher value of total passed charge compared with OPC concrete regardless of w/b or curing ages. In case of concrete using GGBFS (SG40 and SG60), it was seen that the denseness of concrete containing GGBFS contributed to the low total passed charge owing to pozzolanic reaction. The advantages shown by concretes containing GGBFS are also explained as micro-pore structures blocking the permeation of sulfate ions into concrete .[4]

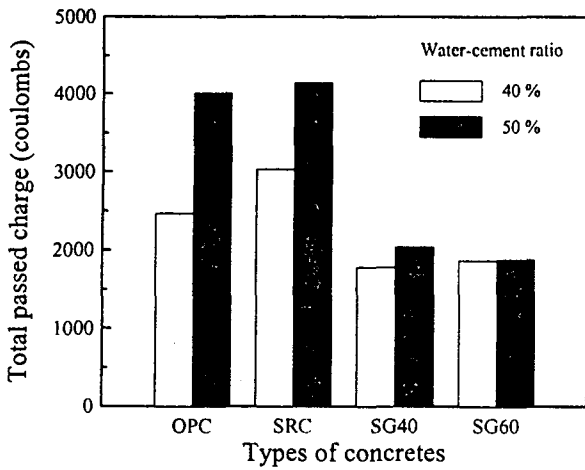


Fig. 6 Total passed charge of concretes (28 days)

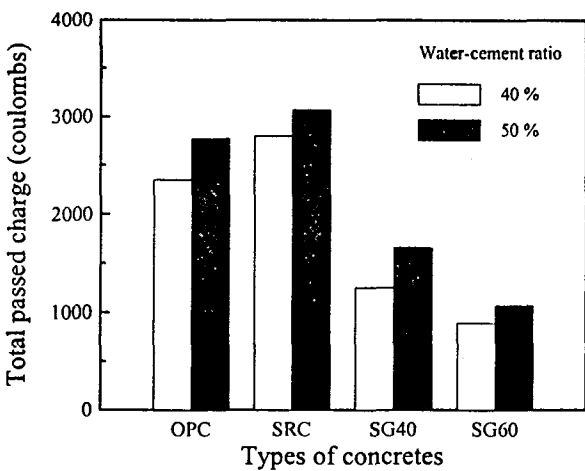


Fig. 7 Total passed charge of concretes (60 days)

#### Diffusion coefficient

Fig. 8 shows sulfate ions diffusion coefficient of concrete tested for series II at the curing ages of 28 and 60 days. This figure explains the concretes of w/b 50% has a higher sulfate ions diffusion coefficient compared with the concretes of w/b of 40% at the both curing ages of 28 days and 60 days. As to sulfate ions diffusion coefficient increasing of OPC concrete with an increase in w/b, the reason is apparent. The diffusing paths of sulfate ions into concrete have three paths : the interconnected pores in cement paste, the interconnected pores in aggregate, and the interconnected pores in the interfaces between paste and aggregate. If the permeability of aggregate is very lower than that of cement and the interface between aggregate and paste has no deficiencies, the volume of capillary pores is determined by w/b. Therefore with an increase in w/b, more pores and diffusing paths may be expected to form, so the sulfate ions diffusion coefficient may increase.

In curing ages of 28 days, diffusion coefficient of OPC concrete with w/b of 50 % was about  $8 \times 10^{-12} \text{ m}^2/\text{s}$ , whereas SG60 concrete with w/b of 50 % recorded about  $4 \times 10^{-12} \text{ m}^2/\text{s}$ . However as to concretes with w/b of 40 %, OPC concrete had a diffusion coefficient value of about  $5$

$\times 10^{-12} \text{ m}^2/\text{s}$  while diffusion coefficient of SG60 concrete was similar irrespective to w/b.

In concrete tested in the present study, SRC concrete had lowest resistance to sulfate ions diffusion during curing ages and the addition of GGBFS contributed to decrease of diffusing ability of sulfate ions into concrete. The previous results(reference) have also reported that the partial replacement of GGBFS to portland cement could improve the sulfate resistance.

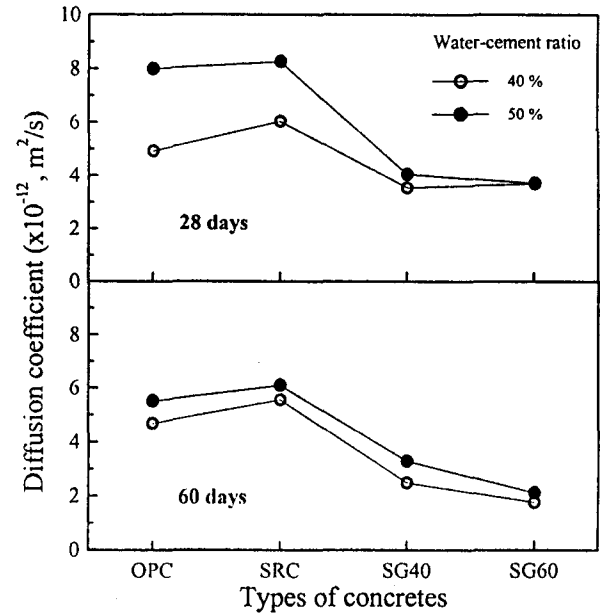


Fig. 8 Diffusion coefficient of sulfate ions in concretes

#### 5.3 Effect of GGBFS for improvement on sulfate resistance

The data on results of series I and II tests summarized in Table 4, indicate that the deterioration of mortar and diffusion characteristics of concrete are significantly affected by the addition of GGBFS.

According to ACI Building Code 318-95, one of the reasons for recommending the replacement of pozzolan materials for increasing sulfate resistance is to remove excessive  $\text{Ca}(\text{OH})_2$  from the hydrated cement paste.

Sulfate deterioration is primarily due to ettringite formation and the lower content of calcium hydroxide produced by the blended cements containing mineral admixture improves the sulfate resistance, since this phase provided the  $\text{Ca}^{2+}$  ions needed to form either ettringite or gypsum.[5]

In addition, the GGBFS hydration has been shown to produce a pore-blocking effect resulting in increased long-term hardening of cement paste. The blocking of pores leads to higher strength and lower permeability, which besides other improved binding and absorptive effects, enhances resistance of GGBFS concrete to sulfate diffusion.

According to Torii[6], the sulfate deterioration of high fly ash content concretes was much less in 10 % sodium sulfate solution during 24 months, compared with that of

OPC concretes regardless of the binder content 300 or 400 kg/m<sup>3</sup>. He also indicated that the effects of fly ashes on the improvement of sulfate resistance of concrete could be explained by the microstructural change associated with the pozzolanic reaction of fly ashes as well as the small content of calcium hydroxide, similar to Wee's study.[7]

Metha[8] has hypothesized that in the absence of Ca(OH)<sub>2</sub>, the ettringite produced is in the form of large crystals which are not expansive. It is only under conditions of high-hydroxyl ions concentration, due to the presence of Ca(OH)<sub>2</sub>, that a microcrystalline ettringite is formed, which is capable of adsorbing large quantity of water on the surface and causing considerable expansion.

But the blended materials effectively convert Ca(OH)<sub>2</sub> into secondary C-S-H phase as confirmed in XRD diffractograms (Fig. 5). Compared with blended cements, as expected, the more enhanced deterioration of parent cements (OPC) was recognized from the result of Table 4.

Table 4. Summary on results obtained in the present study

	Series I test (800 days)		Series II test (28 days) *	
	SDF (%)	Length change (x10 <sup>-3</sup> %)	Total charge (coulombs)	Diffusion coef. (x10 <sup>-12</sup> m <sup>2</sup> /s)
OPC	0.76	0.416*	4,006	8.00
SRC	0.36	0.795	4,150	8.27
SG40	-	-	2,038	4.05
SG50	0.22	0.302	-	-
SG60	-	-	1,875	3.72

\* Water-binder ratio is 0.5

\*\* Value at 180 days

## 6. Conclusions

(1) The SDF in specimens made with OPC and SRC immersed in sodium sulfate solution was about 0.76 and 0.36 at 400 days of immersion respectively, and the SDF of SG50 mortar specimens was similar to that of SPC mortar specimens.

(2) The length change in OPC mortar specimens at 180 days recorded the value of 0.416% while that of SRC mortar specimens were 0.089% at the same immersion period, respectively, and SG50 mortar specimens experienced about 20% (0.08%) of length change of OPC mortar specimens.

(3) In XRD diffractograms, the 50 % partial replacement of GGBFS in OPC results in the consumption of calcium hydroxide due to pozzolanic reaction, and the dilution of the C<sub>3</sub>A phase, and thereby reducing the intensity peaks of portlandite and ettringite.

(4) From results of total passed charge through series II tests, the denseness of concrete containing GGBFS contributed to the low total passed charge owing to pozzolanic reaction.

(5) In 28 days, diffusion coefficient of OPC concrete with w/b of 50 % was about  $8 \times 10^{-12}$  m<sup>2</sup>/s, whereas SG60 concrete recorded about  $4 \times 10^{-12}$  m<sup>2</sup>/s. However as to concretes with w/b of 40 %, OPC concrete had a diffusion coefficient value of about  $5 \times 10^{-12}$  m<sup>2</sup>/s.

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