Pergamon

A STUDY OF THE BASIC ENGINEERING PROPERTIES OF SLAG CEMENT CONCRETE AND ITS RESISTANCE TO SEAWATER CORROSION

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ABSTRACT

This study uses slag to substitute for up to 50% of cement by weight to make slag-cement concrete. The specimens were subjected to wet-dry cycle accelerated test for more than one year. The compressive strength, permeability, electrical resistance, concentration of chloride ions, corrosion potential, and pore size distribution were measured at various ages. The test results show that the slag concrete with 20–30% substitution has the best corrosion resistance. © *1998 Elsevier Science Ltd*

Introduction

Slag is one of the by-products of steel production. Depending on the production process, there are air-cooled and water-quenched slags. Air-cooled slag is usually used as lightweight aggregate. Because the limited amount of usage, it is usually disposed of in the sea. Water-quenched slag, on the other hand, contains a high percentage of glass material and is a potential binding material. The pozzolanic reaction of slag can form chemicals similar to C-S-H ($3CaO \cdot 2SiO_2 \cdot 3H_2O$). This property of the slag in many instances can replace part of cement (1). To effectively and adequately utilize this resource, the study investigates the basic engineering properties of the slag concrete and its durability against seawater corrosion.

The Research Procedure and Method

In this study, slag was used to partially substitute for cement to make slag-cement concrete specimens. Table 1 shows the chemical composition and physical properties of the slag. The size of the cylindrical specimens is ϕ 10 cm $\times$ 20 cm. The slag substitution percentages by weight relative to cement were 0%, 10%, 20%, 30%, and 50%, and the water/cement ratios were 0.48 and 0.60. The cement used was Portland type I cement. The mix proportions are listed in Table 2. After the specimens were moist cured for 28 days, they were immersed in artificial seawater according to ASTM D1141 (2), and tested under wet-dry cycles. The

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TABLE 1

Chemical analysis and physical properties of slag.

Constituents (%)	Silicone dioxide (SiO_2)	33.46
	Aluminum oxide (Al_2O_3)	15.74
	Ferric oxide (Fe_2O_3)	0.56
	Calcium oxide (CaO)	38.81
	Magnesium oxide (MgO)	7.65
	Sulfur trioxide (SO_3)	1.96
	Loss on ignition	0.10
Physical properties	Specific surface, Blaine (cm^2/g)	3,988
	Specific density	2.88

specimens were immersed for 3 days and kept dry for 4 days to complete one cycle. The control specimens were placed in atmosphere. The compressive strength, permeability, electrical resistance, concentration of chloride ions, corrosion potential and pore volume distribution were then measured.

Results and Discussions

Compressive Strength

Figures 1 and 2 show the compressive strengths of the slag concrete specimens immersed in seawater. The observation is made through a period of one year. It is found that the larger the slag substitution ratio is, the smaller the compressive strength is. Besides, to better understand the improvement of the resistance to seawater corrosion as a result of the slag substitution, the strengths at various ages are expressed in term of the strength ratio, which is the ratio of the strength of the slag concrete immersed in seawater to that of the control group. The control specimens were made of Portland cement without slag and stored in atmosphere. It is seen that the compressive strengths of the slag concrete specimens immersed in seawater are always smaller than those of the control group. This implies that the compressive strength is reduced due to seawater attack, and the older the concrete is, the larger the reduction, as can be seen from the fact that the strength ratio reduces from 0.99 at 7 days to 0.92 at one year with water cement ratio of 0.48, and from 0.96 to 0.92 with water/cement ratio of 0.60. The strength ratio decreases with the time and is always smaller than 1.00. Even though the slag concrete is immersed in seawater, the C-S-H gel may still be

TABLE 2

Mix proportion of concrete.

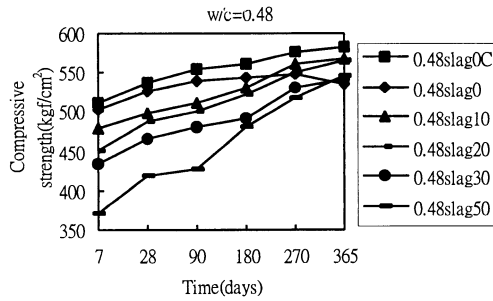| Water cement ratio (w/c)	Water (kg/m^3)	Cement (kg/m^3)	Fine aggregate (kg/m^3)	Coarse aggregate (kg/m^3)
0.48	228	475	594	932
0.60	228	380	670	932

FIG. 1.
Relationship between compressive strength and time.

formed as a result of pozzolanic reaction, which fills in the pores in the material and increases its strength. The best slag substitution rate is 20%. Also, the lower the water/cement ratio is, the smaller the strength reduction is. Note that the strength of ordinary concrete without slag started to decrease after 180 days of accelerated test while the strength for slag concrete continued to increase at the same time.

Diffusion

Figure 3 shows the chloride ion coefficient of diffusion of the slag concrete immersed in seawater. It is seen that the permeability depends on the slag substitution ratio, the age, and the water/cement ratio. Under the same exposure condition, when the slag substitution ratio is 20%, the coefficient is the smallest. This is because that the pozzolanic reaction of slag changes the pore structure of concrete. The large pores are turned into small pores, and the total pore volume is reduced. As a result, the slag concrete can better resist the deterioration due to harmful substance. When the slag substitution ratio is 50%, the permeability is relatively high. This is possibly because that if the slag substitution rate is high, the calcium hydroxide provided by cement is not sufficient for full pozzolanic reaction. The diffusion coefficient of concrete with lower water cement ratio is smaller. The diffusion coefficient decreases with the increase of time due to cement hydration and pozzolanic reaction.
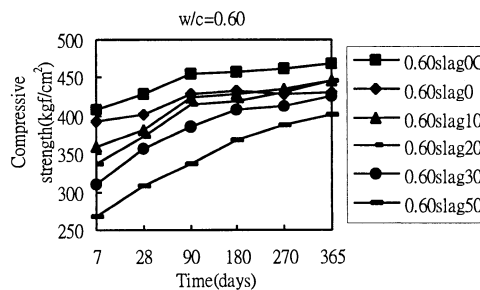

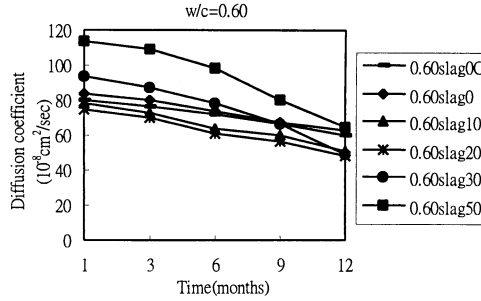FIG. 2.
Relationship between compressive strength and time.

FIG. 3.
Relationship between diffusion coefficient and time.

The relationship between the compressive strength fc (kgf/cm^2) and diffusion coefficient D ($\times 10^{-8}$ cm^2/s) at each stage is shown in Figure 4 and a regression equation (1) is suggested.

$$D = 201.54{-}0.314\,fc \text{ (correlation coefficient } r = -0.92) \tag{1}$$

It is seen from Figure 4 that the diffusion coefficient of concrete decreases with the increase of strength, that is, concrete with higher strength has smaller pore volume and size, so that its diffusion coefficient is smaller and its ability to resist deterioration due to harmful substance is better. On the other hand, for concrete with lower strength, the mixing water used is far more than that needed for cement hydration. The extra water occupies part of the volume and creates pores in concrete. The more water there is, the larger the pore sizes are. However, if the concrete is sufficiently moist-cured so that its strength can be developed before it is immersed in seawater, then even for high slag-substitution-ratio concrete suffi-cient pozzolanic reaction can be promoted and thus its resistance to the attack of salts is improved.
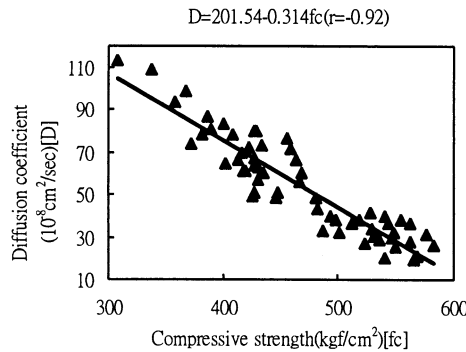

FIG. 4.
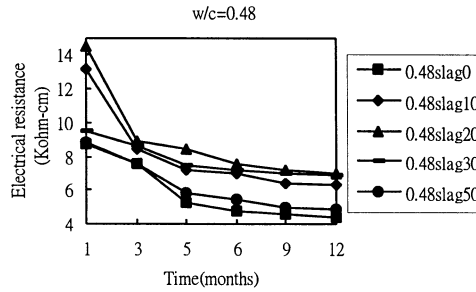Relationship between diffusion coefficient and compressive strength.

FIG. 5.

Relationship between electrical resistance and time.

Electrical Resistance

The degree of corrosion of the steel can be examined indirectly by measuring the electrical resistance of the concrete. In general, the corrosion rate is related to corrosion current and the electrical resistance of the concrete around the steel bar. Hope et al. (3) pointed out that if the electrical resistance of concrete containing chloride was smaller than 6.5 kΩ-cm, corrosion occurred easily. Figure 5 shows the electrical resistance of the slag concrete immersed in seawater. It can be seen that the electrical resistance decreases with the increase of age up to one year. The electrical resistance of concrete with slag substitution ratio 20–30% is higher than those of specimens with other substitution ratios. The electrical resistance of concrete with substitution ratio of 0 and 50% is below 6.5 kΩ-cm, which suggests that corrosion is possible.

Chloride Ion Concentration

The diffusion of chloride ions into concrete follows Fick's law (Eq. 2). It depends on the quality of concrete and external conditions. If the chloride ion concentration in the environment Co is known, and the diffusion coefficient of chloride ion D is measured, then the chloride concentration $C (x,t)$ at depth x and time t can be found from equation (2), where erf is the error function (4)
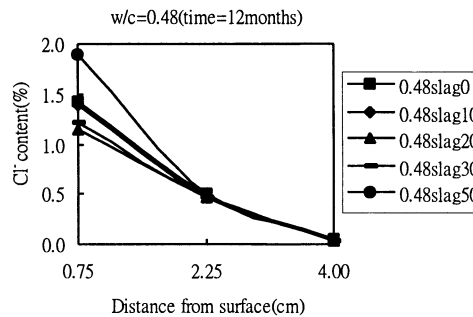

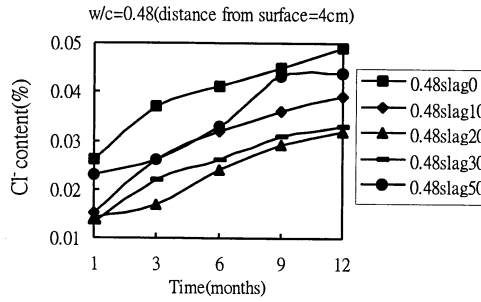
FIG. 6.

Concentration of chloride ions in slag concrete.

FIG. 7.
Relationship between concentration of chloride ions and time.

$$C(x,\ t) = Co\left[1\ -\ erf\left(\frac{x}{2\sqrt{Dt}}\right)\right] \qquad (2)$$

Figures 6-9 show the relations between the chloride ion concentration, time, and depth in concrete specimens immersed in seawater for one year. The chloride ion concentration is expressed in percentage weight of cement. It is seen from the figures that the chloride ion concentrations at a distance 1.5 cm from surface all exceed the chloride corrosion threshold 0.1–0.2% (5–7). At the depth between 1.5–3.0 cm, for the concrete made of water/cement ratio 0.48 the chloride ion concentrations for all specimens are below threshold value, but when the water cement ratio is 0.60, only specimens with slag substitution ratio between 20–30% can have chloride ion concentration below the threshold value. When the depth is between 3.0–5.0 cm, only Portland cement concrete with water cement ratio 0.60 and slag concrete with slag substitution ratio 50% show that the chloride ion concentration is above the threshold value.

The relationship among the chloride ion concentration, time, and the thickness of the reinforcement cover can be obtained through a regression analysis. If the thickness of the reinforcement cover is known, then the time needed for the steel bar to be corroded (the chloride threshold is 0.20% with respect to the weight of cement) can be estimated. For Portland cement concrete, and slag concrete with substitution ratio 10%, 20%, 30%, and 50%, and water cement ratio of 0.48, the estimated time for the chloride ion to diffuse into
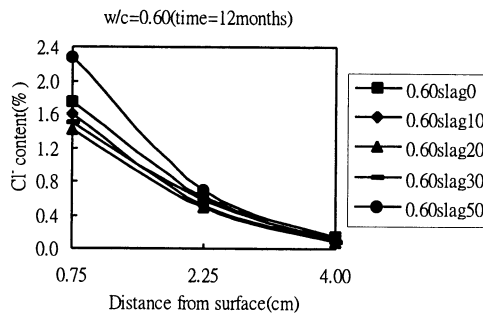

FIG. 8.
Concentration of chloride ions in slag concrete.
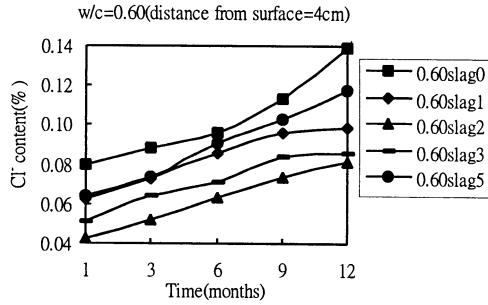
w/c=0.60(distance from surface=4cm)

FIG. 9.

Relationship between concentration of chloride ions and time.

5 cm depth of the concrete and to reach a concentration of 0.20% is about 15.7 years, 16.3 years, 28.6 years, 38.6 years, and 22.9 years, respectively.

For most concrete specimens of age up to 1 year as observed in this study, the chloride ion concentrations at the depth more than 3.0 cm are all below the threshold value. The depths at which the $[Cl^-]$ reaches the threshold value at 1 year for 0% slag concrete of water cement ratios 0.48 and 0.6 are 3.3 cm and 5.8 cm, respectively. The figures also reveal that the best slag substitution ratio is 20% to minimize the chloride ion diffusion.

Corrosion Potential

The corrosion of steel is usually detected by indirect methods, such as measuring the corrosion potential of steel bar, which is done with saturated calomel electrodes in accordance with ASTM C876 (8). As suggested by Stratfull (9), if the potential E is less than -270 mV, there is more than 90% probability that the reinforcing steel corrosion is occurring. For the potential E between -220 mV and -270 mV, the corrosion activity of the reinforcing steel is uncertain. For the potential E greater than -220 mV, there is more than 90% probability that no corrosion is occurring.

Figure 10 shows the corrosion potentials of the slag concrete specimens immersed in
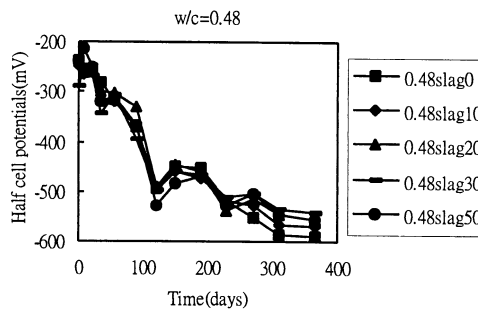
w/c=0.48

FIG. 10.

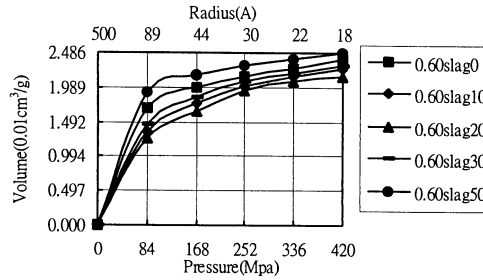Potentials of rebars in slag concrete.

FIG. 11.

Pore size distribution in slag concrete (w/c = 0.60; time: 3 months).

seawater. It is seen that the corrosion potentials of the steel bars in slag concrete with slag substitution ratio 10–30% are relatively high, that is, it has better resistance to corrosion. The control groups labeled 0.48Slag0C and 0.60Slag0C were placed in the air. As a result, their corrosion potentials were highest. The values were −34 mV and −118 mV respectively as observed at the end of 1 year.

Though the potential is below −270 mV after 10 days, the specimens were split and the embedded steel bars were examined after 1 year. It is found that for water cement ratio 0.6 specimens, only the steel embedded in ordinary Portland cement concrete and 50% substitution ratio concrete was found to be corroded. This confirms that the critical threshold of the chloride concentration of 0.1–0.2% for corrosion to occur is reasonable as discussed in the previous section. In contrast, the steel bars in other specimens were not corroded.

Pore Volumes

The pore structure of cement mortar is closely related to its engineering properties. The factors determining the pore structure include the amount of mixing water and cement, the degree of cement hydration, and the condition of consolidation. A measurement of the pore structure may be used to investigate the effect of slag to the pore structure in cement mortar. In this study, a mercury intrusion porosimetry method is used to measure the accumulated pore volumes in cement mortar.

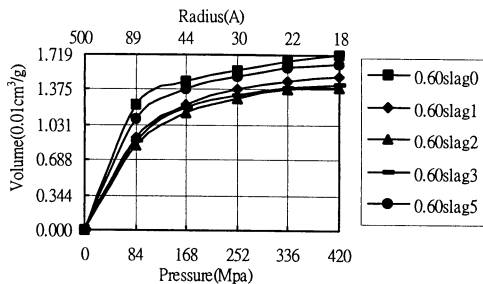Figures 11 and 12 show the accumulated pore volumes in mortar from slag concrete. It is

FIG. 12.

Pore size distribution in slag concrete (w/c = 0.60; time: 1 year).

seen from the figures that the pore volumes decrease with the increase of age, that is, large pores were gradually changed into small pores, and the accumulated pore volumes were reduced. This is because of the growth of the chemical products of cement hydration and pozzolanic reaction, which fill the pores and reduce both their volumes and numbers.

It can be seen from Figure 12 that the pore volumes per gram specimen of mortar from Portland cement concrete and from slag concrete with slag substitution ratio of 10%, 20%, 30%, and 50% are 0.0172 cm^3, 0.0148 cm^3, 0.0138 cm^3, 0.0143 cm^3 and 0.0162 cm^3 respectively. If the pore volume is divided by the volume of hardened mortar (the volume of 1 gram of mortar is about 0.417 cm^3), the porosity (the percentage of pore volume to bulk volume of specimen) can be obtained. The porosity of mortar from Portland cement concrete and from slag concrete with slag substitution ratio of 10%, 20%, 30%, and 50% is 4.1%, 3.5%, 3.3%, 3.4%, and 3.9% respectively, in a sequence roughly corresponding to that of the diffusion coefficient. The pore volume is a minimum when the slag substitution ratio is 20%.

Conclusions

- The compressive strength of slag concrete immersed in seawater increases with time up to one year, while the strength begins to decrease after 90 days for ordinary concrete.
- Slag concrete with slag substitution ratio 20% shows the smallest diffusion coefficient.
- Slag concrete with slag substitution ratio 20–30% has higher electrical resistance and the steel bars in it are better protected.
- At the age of 1 year, for concrete cover depth more than 3.0 cm, Portland cement concrete with water/cement ratio 0.60 and slag concrete with slag substitution ratio 50%, the chloride ion concentrations are above the chloride corrosion threshold, which is further evidenced by the observation of corrosion on the embedded steel.
- The time needed for the steel bars embedded in concrete to corrode can be estimated from the relation between the chloride concentration in concrete and the thickness of the reinforcement cover. For concrete with water/cement ratio 0.48 and 5 cm cover, the time needed for the steel bars to corrode for ordinary Portland cement concrete and slag concrete with slag substitution ratio 10%, 20%, 30%, and 50% is 15.7 years, 16.3 years, 28.6 years, 38.6 years, and 22.9 years respectively.
- At the age of 1 year, slag concrete with slag substitution ratio 10–30% is found to have higher corrosion potential, or higher resistance to corrosion.
- At the age of 1 year, slag concrete with slag substitution ratio 20% has the least pore size. The sequence of pore volumes corresponds to the sequence of coefficient of diffusion.

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