EFFECTS OF STEEL SLAG SUBSTITUTION IN GEOPOLYMER CONCRETE ON COMPRESSIVE STRENGTH AND CORROSION RATE OF STEEL REINFORCEMENT IN SEAWATER AND AN ACID RAIN ENVIRONMENT

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ABSTRACT

The effect of steel slag substitution as coarse aggregate on compressive strength in fly ash based-geopolymer concrete was studied. The compressive strength was evaluated by measuring the maximum acceptable load using compression testing equipment. Compressive strength depends on several factors, such as time and temperature of curing and the mixing proportion. The compressive strength of geopolymer concrete with steel slag substitution was higher compared to geopolymer concrete with gravel aggregate. The optimum compressive strength was found on the third day of curing at a temperature of 60°C for both the geopolymer concrete with steel slag substitution and normal geopolymer concrete. Reinforcement corrosion was evaluated by measuring the corrosion current density using a linear polarization potentiostatic scan. The corrosion rate of reinforcing steel in geopolymer concrete with steel slag substitution was found to be higher compared to normal geopolymer concrete without steel slag in seawater medium, whereas in an acid rain environment, steel slag substitution increased corrosion resistance. The corrosion rate of geopolymer concrete with steel slag substitution was found to be lower compared to normal geopolymer concrete. The corrosion rate was found to be very high at an early stage and decreased with time.

Keywords: Compressive strength; Corrosion rate; Geopolymer concrete; Steel slag

1. INTRODUCTION

Geopolymer concrete is concrete formed from geopolymer material as the matrix material and mineral aggregate as reinforcement and filler. Geopolymer concrete was invented by Joseph Davidovits, a French scientist in the late 1970s. Geopolymer has the potential to replace Portland cement, especially in its application as a base for the manufacture of concrete. On the surface of geopolymer concrete, a polycondensation polymerization reaction forms aluminosilicate (Davidovits, 1994).

All industries produce waste, which is the remainder of product processing, and this waste, if not managed properly, will cause adverse effects to the environment. As the need for steel globally increases, waste produced from the steel processing industry will also increase. Hazardous waste from steel processing is produced in the form of physically dense coarse aggregate called steel slag.

The amount of solid steel waste (steel slag) generated by the steel smelting industry (in this paper represented by PT. Krakatau Steel, Banten) is up to 150 tons per day, and so waste reduction is needed to lower the impact to the environment.

In this paper we report on the mechanical properties of concrete, represented by compressive strength, and the corrosion rate of the steel reinforcement in a geopolymer mix, using various types of filler materials, such as aggregates.

2. EXPERIMENTAL
2.1. Material
The material used in this study included fly ash from the Suryalaya power plant and steel from the PT. Krakatau Steel plant, both in Cilegon, Indonesia. The chemical and mineral compositions of these materials are listed in Table 1.

Table 1 Chemical and mineral composition of fly ash and steel slag (wt.%) by XRF analysis

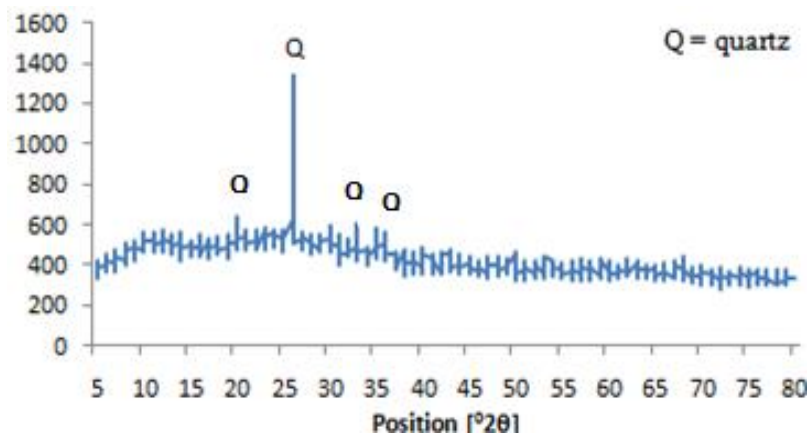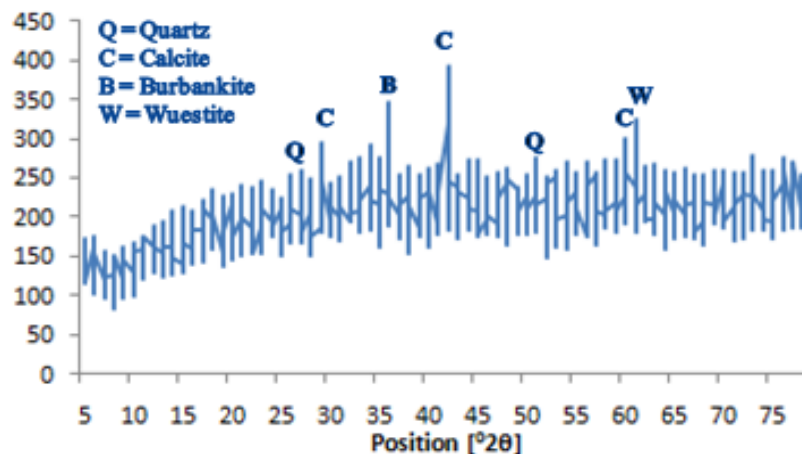| Oxides	SiO$_2$	Fe$_2$O$_3$	CaO	Al$_2$O$_3$	MgO	SO$_3$	Na$_2$O	K$_2$O	TiO$_2$	P$_2$O$_5$
Fly ash	36.57	19.26	16.55	16.08	4.78	1.50	1.28	1.27	1.16	0.50
Steel slag	13.12	26.96	30.74	16.84	8.32	0.12	0.50	0.02	0.50	2.01

Figure 1 Diffraction pattern of fly ash

Figure 2 Diffraction pattern of steel slag

Figures 1 and 2 show the diffraction patterns of the fly ash and steel slag, both of which have an amorphous semi-crystalline composition. Sodium silicate solution or waterglass (composition 9.80 wt.% Na and 16.60 wt.% Si) and sodium hydroxide were used as reagents for fly ash activation.

2.2. Specimen Preparation

We made a number of concrete specimens consisting of either geopolymer concrete with steel slag substitution as the coarse aggregate or geopolymer concrete with gravel as the coarse aggregate. Cylindrical molds of 15 cm diameter and 30 cm height were used for compressive strength test specimens. Plastic lining was placed inside the concrete molds to prevent the geopolymer mixture attaching to the mold and to facilitate extraction. Materials were well prepared before casting, and all aggregates were required to have a saturated surface dry condition. The chemical composition of the geopolymer paste used in the preparation of the concrete specimen and the geopolymer concrete mix ratio are given in Tables 2 and 3, respectively.

Corrosion test specimens were formed in cylindrical molds of 10 cm diameter and 20 cm height. The concrete blocks contained steel bar, which was used as working electrodes. The top and bottom of the mild steel electrode was coated with a resin mounting, leaving an exposed surface area of 8.8 cm^2. Figure 3 shows a corrosion rate test specimen.

Table 2 Composition of geopolymer paste

Material	Function	wt.%
Fly ash	Precursor	68.5
NaOH		6.5
Water glass	Activator	10
Water		15

Table 3 Mix ratio of geopolymer concrete (wt.%)

Fly Ash	Alkali Solution[a]	Water (s/a = 0.46)[b]	Sand	Coarse Aggregate	
				Steel Slag	Gravel
15.95	3.85	3.50	39.72		36.97
15.95	3.85	3.50	23.85	52.83	

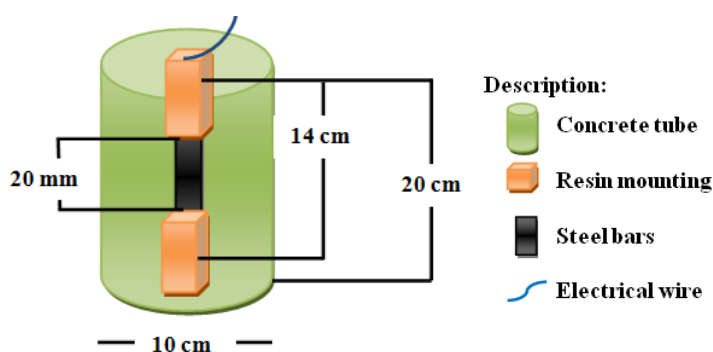Notes: [a] Waterglass + NaOH; [b] Solution/ash

Figure 3 Corrosion rate test specimen

2.3. Test Procedures

2.3.1. Compressive strength

An alkaline activator solution was prepared by mixing sodium silicate, sodium hydroxide, and water. Sodium hydroxide was diluted with water and then mixed into the sodium silicate. A reaction was characterized by an increase in temperature. Fly ash was manually mixed with the alkaline activator solution to form a homogeneous geopolymer paste. Fine and coarse aggregate that had been passed through a proper sieve were mixed with the geopolymer paste. The concrete was then poured into the plastic-coated mold and was compacted by vibration. The concrete was cured in an oven at 60°C in order to accelerate the hardening reaction of the concrete. A longer time for curing and a higher curing temperature results in higher compressive strength of the geopolymer concrete (Hardjito et al., 2004).

Samples placed in the mold were left for 60 minutes at room conditions before being placed in the oven. The curing process varied between 1 and 6 days in order to determine the effect of heating time on the compressive strength of the geopolymer. Once the material was heated for a few hours and allowed to cool at room temperature for one day, the specimen was removed from the mold.

2.3.2. Corrosion rate

Each sample was subjected to a potentiostatic scan after 1, 3, and 7 days of exposure to determine the corrosion current density (i_{corr}) at a specified time. The sample was immersed in seawater and in simulated acid rain without destroying the sample. Further anodic potentials would force the sample to corrode (i.e., destructive testing). The test parameters were the following:

1. Initial E: the starting point for the potential sweep in volts. The initial potential E was − 0.25 V vs. EOC.

2. Final E: the ending point for the potential sweep in volts. The final potential E was +0.25 V vs. EOC. This scan range (EOC ± 0.25 V) enabled the estimation of i_{corr}.

3. Scan Rate: the speed of the potential sweep during data acquisition in mV/sec. Very high scan rates lead to unreliable data; however, very low scan rates lengthen the test period. The applied scan rate was 0.5 mV/sec. No change in the shape of the curve was noticed when using slower scan rates.

4. Density: the density of the metal tested in g/cm^3.This parameter was used for the corrosion rate calculation. The density of carbon steel is 7.86 g/cm^3.

5. Equivalent Weight: the theoretical mass of metal that will be lost from the sample after one Faraday of anodic charge has been passed. This parameter was used in corrosion rate calculations. The equivalent weight of carbon steel is 27.925 g/mol.

6. Initial Delay: this option was used to allow the open circuit potential of the sample to stabilize prior to the potential scan. The delay time is the time that the sample will be held at its open circuit potential EOC prior to the scan. The delay may stop.

7. Electrode used in the potentiostatic scan:
    a) Reference electrode was Ag/AgCl
    b) Counter electrode was graphite
    c) Working electrode was mild carbon steel.

The potentiostatic scan used CMS 100 (Corrosion Measurement System) software to determine i_{corr} and corrosion rate, using data obtained from cathodic and anodic polarization measurements. The data obtained is i_{corr} and directly results in corrosion rate data. According to Faraday's law, the corrosion rate (CR) is a function of corrosion current density i_{corr} and can be calculated by using Equation 1:

$$CR = 0.129 \cdot \frac{A_r \cdot i_{corr}}{n \cdot D} \tag{1}$$

3.   RESULTS
3.1.   Visual Observations

Geopolymer concrete with a steel slag aggregate has a light brown color, while geopolymer with a gravel aggregate has a darker color. Curing time affects the color, brightness, and porosity of the geopolymer concrete, with a longer curing time causing a brighter geopolymer concrete and a greater concrete porosity (Llyod et al., 2009).

Less curing time of the polymer affects the strength and durability of the concrete. A shorter curing process was intended to accelerate the polymerization reaction of the polymer and also to achieve a high-strength concrete in a short time (Swanepoel & Strydom, 2002). However, with a short curing time, the hardening process did not finish, and therefore, the expected compressive strength was low. Visual observations of the geopolymer concrete samples on day 1 showed that the geopolymer structure was still in a wet or humid condition.

3.2.   Compressive Strength

The compressive strength test used two types of geopolymer concrete specimens, steel slag aggregate and gravel aggregate. Testing was applied after day 1 of curing for 6 days at 60°C by using two cylinders for each test. The data obtained from the tests indicate the maximum load (F max) prior to specimen failure. Compressive strength data are listed in Table 4.

Table 4 Results of compressive strength test data

Sample Day	Steel Slag Bath I		Steel Slag Bath II		Gravel Bath I		Gravel Bath II	
	Weight (kg)	Compressive Strength (MPa)	Weight (kg)	Compressive Strength (MPa)	Weight (kg)	Compressive Strength (MPa)	Weight (kg)	Compressive Strength (MPa)
1	13.871	14.41	13.222	13.01	11.223	7.34	11.017	7.07
2	13.650	18.56	13.279	16.79	11.092	9.21	11.025	8.54
3	13.603	21.89	13.161	20.83	11.375	15.89	11.016	14.93
4	13.598	21.03	13.243	20.40	11.058	14.22	11.023	13.08
5	13.702	13.02	13.304	12.93	10.987	8.56	10.912	7.98
6	13.012	-	13.008	-	10.897	4.53	10.875	3.97

Notes: Curing in oven at 60 °C; (-) sample was not testable

The results of the compressive strength test showed that geopolymer concrete with slag aggregate has a higher compressive strength than that of geopolymer concrete with gravel aggregate (see Table 4). The optimum strength of geopolymer concrete occurred on day 3 at an oven temperature of 60°C. The highest strength of the geopolymer concrete was 21.89 MPa with slag aggregate and was 15.89 MPa with gravel aggregate. The lowest strength for slag aggregate occurred on day 6 at which time the geopolymer concrete was not suitable for testing due to cracks on the surface of the concrete. The lowest strength of geopolymer concrete with gravel aggregate was also recorded on day 6, with the compressive strength being 3.97 MPa.

As shown in Figure 4, the compressive strength of the geopolymer specimen continued to increase until reaching an optimum strength on day 3 of curing. The strength tended to decrease slightly on day 4. Extreme decreases in specimen strength occurred on day 5 and day 6.

The strength of a geopolymer is influenced by composition and curing time (Nevile, 1981), and different types of aggregates and curing times can affect the compressive strength of geopolymer concrete. The test results demonstrate that the use of steel slag as an aggregate has

superior properties compared to gravel. Steel slag can increase the compressive strength of geopolymer concrete because steel slag reduces alkali silica attacks (Lewis, 1982). The essential factors that affect the mechanical strength of geopolymer concrete are time and temperature of curing, the type of alkaline activator, water content, and the relative amount of Si, Al, and Na (Hardjito et al., 2004; Fernandez-Jimenez et al., 2007). In the present study, the amount of fly ash played an important role with regard to the compressive strength of geopolymer concrete.
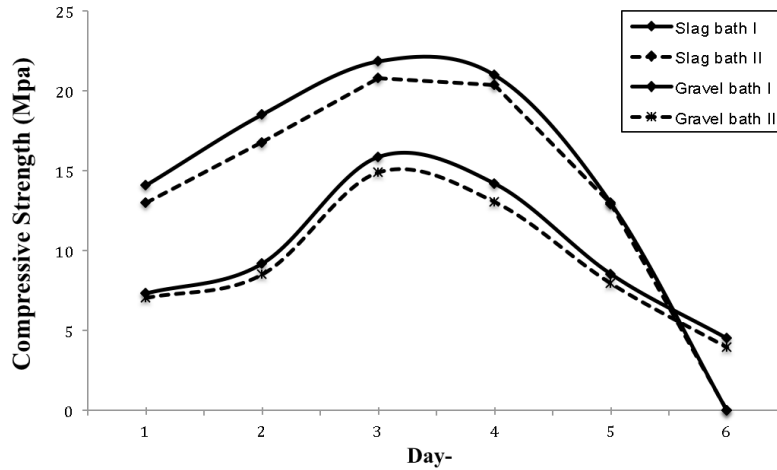

Figure 4 Compressive strength-curing time

3.3. Corrosion Rate

The potentiodynamic polarization test conducted by Tafel analysis showed that a geopolymer concrete specimen with different aggregate variations has different potential and current limits that affect the corrosion rate. Potentiodynamic polarization testing for the geopolymer concrete was measured in two different immersion media on three occasions (days 1, 3, and 7). Figure 5 shows the results of the potentiostatic scan of the reinforcing steel on the geopolymer concrete in seawater and acid rain media.
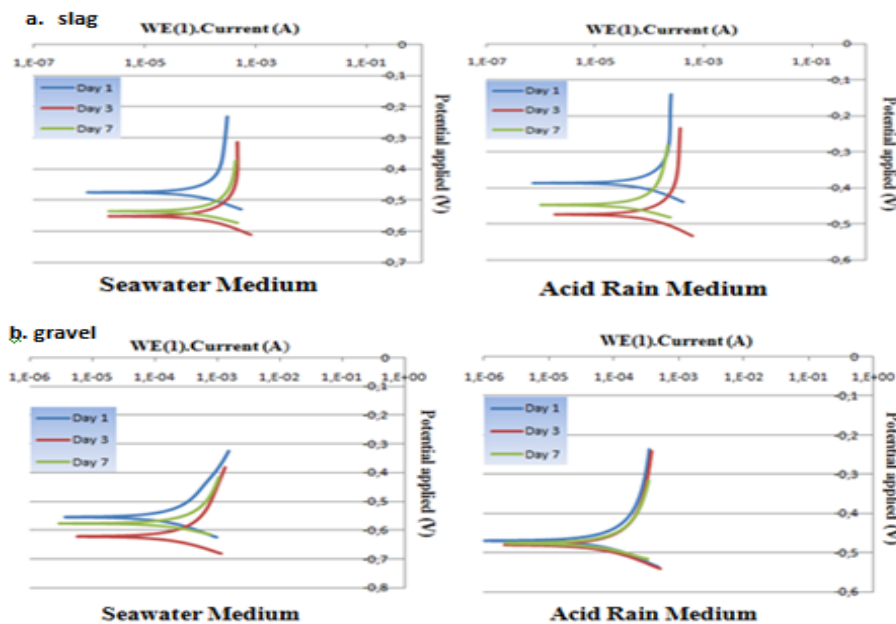

Figure 5 Graphical outputs for the potentiostatic scan test: (a) geopolymer concrete with steel slag substitution; (b) geopolymer concrete with gravel aggregate

All the current density (i_{corr}) results have been determined graphically and are listed in Table 5 along with the calculated corrosion rates.

Table 5 Current density and corrosion rate of reinforcing steel in a geopolymer

Concrete	Immersion Media	Immersion Time (days)	Density (gr/cm^3)	Eq. Weight (gr/mol)	Surface Area (cm^2)	i_{corr} (A/cm^2)	Corrosion Rate mm/year
Steel slag aggregate	Seawater	1				6.2341	0.07241
		3				6.4456	0.07487
		7				6.3900	0.07422
	Acid Rain	1				3.7830	0.04394
		3				4.4990	0.05226
		7	7.86	27.925	8.8	3.4209	0.03974
Gravel aggregate	Seawater	1				5.2310	0.06076
		3				6.2314	0.07238
		7				5.3725	0.06240
	Acid Rain	1				4.6408	0.05390
		3				5.4310	0.06308
		7				4.8374	0.05619

Based on the above figures, the coarse aggregate was shown to have a significant effect on the corrosion rate of geopolymer concrete both in seawater and acid rain environments. The corrosion rates of the gravel aggregate and steel slag were not notably different. Data from the test results show that the corrosion rate of the gravel aggregate was higher in seawater than in an acid rain environment, similar to the steel slag aggregate. Comparisons of the corrosion rate between the gravel aggregate and the steel slag demonstrate that the corrosion rate of gravel in a seawater medium is lower than that of steel slag, indicating that gravel has more corrosion resistance than slag aggregate in seawater. On the other hand, the steel slag specimen showed a lower corrosion rate under acid rain conditions compared to the gravel aggregate specimen.

3.4. Seawater medium

The corrosion rates of reinforcing steel in concrete depend on various factors. The most important are moisture content of the concrete, access to oxygen (permeability of the concrete), and especially the presence of chloride ions. Chloride is aggressive because of its ability to destroy the passive layer of the steel surface due to the formation of the soluble complex of iron chloride with chloride ions, thus accelerating the corrosion rate (Yalcyn & Ergun, 1996).

The corrosion rate of reinforcing steel in geopolymer concrete with gravel aggregate was relatively higher in the seawater environment. Over the curing time period of the experiments, the corrosion rates of the reinforcement in the seawater medium were significantly higher compared to one and two days of curing time. The corrosion rate was equal to 0.07238 mm/year on day 3 and decreased on day 7 to 0.06240 mm/year, which was still above the corrosion rate on the first day.

During the polycondensation process, a high alkaline solution forms pores in the concrete at pH levels of approximately 11–13 (base conditions) (Davidovits, 1999). This solution forms a thin oxide layer (passive film) that protects the steel reinforcement from corrosion. However, the layers may be broken from a decrease in the pH caused by the decomposition of carbon dioxide

and sulfide from the atmosphere. This condition worsens with the penetration of chloride ions from the environment.

The corrosion rate of reinforcing steel is high because of the broken passive layers caused by the presence of Cl^- ions. The corrosion products have a large volume and so produce tension in the concrete. If the tensile stress of the corroding product is greater than the concrete tension strength, cracks will occur in the concrete. In addition, the carbonization process will cause a decrease in the alkalinity of the specimen, which could change the steel environment from having passive zones to active zones. Therefore, the corrosion rate on day 2 increased primarily due to the broken passive layer and the formation of carbonated compounds.

On the third day, the corrosion rate of the reinforcing steel decreased due to passive layer reformation, which prevented corrosion and reduced the corrosion rate of the steel reinforcement. Chloride ions from the sodium chloride salt are commonly available in seawater and are used in the corrosion rate expressed by Griffins and Henry (1962). The corrosion rate increases proportionally to the increasing concentration of salt until it reaches the maximum limit; the corrosion rate is then reduced even though the concentration of salt has increased. The decrease in the corrosion rate of reinforcing steel is therefore always coupled with reformation of the passive layer.

As in the case with reinforcing steel in the specimen with steel slag aggregate, the corrosion rate is high in seawater environments and is higher for steel slag than for gravel because of the high levels of calcium in the slag. The steel slag reacts with CO_2 to form carbonate compounds, and the presence of carbonate compounds increases the rate of corrosion. However, the specimen with gravel aggregate showed a lower corrosion rate on the third day due to reformation of the passive layer and the concentration of chloride ions reaching the maximum limit.

3.5. Acid rain medium
The corrosion rate of reinforcing steel in geopolymer concrete with gravel aggregate is less in acid rain than in seawater. During the experimental period, the corrosion rates of the reinforcement in acid rain conditions were higher on the first and the third day, with the rate equal to 0.05390 mm/year; however, the rate decreased to 0.05619 mm/year on day 7, which was still notably higher than that of the first day.

As noted previously, a high alkaline pore solution is formed in concrete during the polycondensation process with pH levels of approximately 11–13 (base conditions) (Davidovits, 1999). A thin oxide layer (passive film) covers and protects the steel reinforcement from corrosion. However, the layers may be broken due to a decrease in pH caused by the decomposition of carbon dioxide and sulfide from the atmosphere. The corrosion rate decreased on the seventh day as a result of the reformation of the passive layer and formation of deposits on the surface of the gypsum concrete. In addition, sulfide and nitrate ions will inhibit the diffusion of the constituent acid rain ions, thus reducing the corrosion rate.

The reinforcing steel in steel slag aggregate had a corrosion value on day 1 of 0.04394 mm/year, which increased to 0.05226 mm/year before dropping to 0.03974 mm/year on day 7. Steel slag has a lower corrosion rate compared to that of gravel because the steel slag contains high levels of calcium, which increases the amount of gypsum in geopolymer concrete. Gypsum helps protect concrete from diffusion acid ions and protects the reinforcing steel from acid attack. However, too much calcium oxide has a risk because resistance decreases while gypsum is forming.

4. CONCLUSION

Steel slag substitution as an aggregate in fly ash-based geopolymer concrete increases the compressive strength to a greater extent than gravel aggregate in geopolymer concrete. The optimum compressive strength was found after 3 days of curing at 60°C for both the geopolymer concrete with steel slag substitution and normal geopolymer concrete. The optimum compressive strength of the geopolymer reached 21.86 MPa with steel slag substitution and reached 15.89 MPa with gravel aggregate.

The corrosion rate of reinforcing steel in geopolymer concrete with steel slag substitution was found to be greater (0.07487 mm/year) compared to that of normal geopolymer concrete without steel slag (0.07238 mm/year) in seawater medium, whereas in an acid rain environment, steel slag substitution increased corrosion resistance.

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