



# Utilization of rice husk–bark ash to improve the corrosion resistance of concrete under 5-year exposure in a marine environment



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## ABSTRACT

Waste rice husk–bark ash was utilized to improve the durability of concrete in a marine environment. The effects of ground rice husk–bark ash (GRBA) on compressive strength, chloride diffusion coefficient, chloride binding capacity, and steel corrosion of concrete exposed to a marine site for 5 years were reported and discussed. The GRBA was used as a pozzolanic material to replace Type I Portland cement at 0%, 15%, 25%, 35%, and 50% by weight of the binder. Concrete cube specimens of 200 mm were cast, and steel bars were embedded in concrete. Concrete specimens were exposed to a tidal zone of seawater in the Gulf of Thailand. After 5-year exposure, the specimens were tested for compressive strength, acid soluble and water soluble chlorides and corrosion of embedded steel bar. The results showed that during 5-year exposure, GRBA concretes gained strength faster than Type I Portland cement concretes and no strength loss was found in GRBA concrete. The findings also indicated that the durability of concrete in terms of chloride diffusion coefficient, chloride binding capacity, and resistance to corrosion of embedded steel could be considerably improved by utilizing GRBA as high as 35%.

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## 1. Introduction

Rice husk–bark ash is a by-product of burning rice husks and eucalyptus bark together as fuel to generate electricity. More than 100,000 tons per year of rice husk–bark ash is produced by a bio-mass power plant in Thailand; moreover, the amount of ash continues to increase annually, while its utilization is minimal [1]. Rice husk–bark ash contains  $\text{SiO}_2$ , as a major chemical component, as high as 70% indicating a high potential for pozzolanic reactivity. Previous studies found that use of ground rice husk–bark ash, with a particle size distribution similar to that of type I Portland cement and as a replacement for Portland cement between 10% and 20%, is a reactive pozzolanic material that has strength activity indices at 28 days up to 110% [2]. Moreover, Sata et al. [3] reported that use of rice husk–bark ash with high fineness (the amount of particles retained on a 45- $\mu\text{m}$  sieve were less than 2%) to replace Portland cement up to 30% by weight of binder could produce high strength concrete.

These studies and other previous research have shown that rice husk–bark ash can be used as a cementitious material in concrete and provides good properties similar to other pozzolans [1–4]. If rice

husk–bark ash can be used in a concrete mixture to improve durability performance, especially in a marine environment, it will reduce the disposal cost and disposal area as well as provide a valuable material in concrete work.

One goal for constructing marine structure concrete is to employ methods and materials that provide for a longer service life. Previous studies reported that the use of pozzolanic material in blended cement paste can reduce pore sizes and average pore diameters, leading to good resistance against chloride ingress and steel corrosion [5–10]. A few studies [11–14] have focused on the utilization of fly ash in concrete to protect reinforced concrete within marine sites in hot and humid climate zones (e.g., the Gulf of Thailand). The results indicated that increasing the fineness of the fly ash and the amount of fly ash replacement of cement in concrete resulted in a significant decrease in the steel corrosion and chloride ingress in concrete. Additionally, where the climate varies greatly from warm summers to cool winters (e.g., Essex, UK marine site), Thomas and Matthews [15] also found that chloride level and steel corrosion were reduced significantly in the fly ash concretes compared to the concrete without fly ash.

The objectives of this research are to study the utilization of rice husk–bark ash to increase corrosion resistance of reinforcing steel bar in concrete in a marine environment and investigate the variables related to compressive strength, chloride diffusion coefficient, chloride binding capacity, and steel corrosion in concrete.

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## 2. Experiment program

### 2.1. Materials

Portland cement type I, graded sand, and crushed limestone with a maximum size of 19 mm were used in this study. Rice husk–bark ash was obtained from a biomass power plant, at which a combination of 65% of rice husk and 35% of eucalyptus bark by weight was used as fuel in a fluidized bed power plant. The received rice husk–bark ash was ground until the particles retained on a 45- $\mu\text{m}$  sieve were less than 3.0% with a mean particle size ( $d_{50}$ ) of 10.8  $\mu\text{m}$  and specific gravity of 2.15. The chemical properties of the binder materials are listed in Table 1.

### 2.2. Method

The cylindrical concrete specimens (100 mm in diameter and 200 mm in height) of each concrete mix proportion were prepared for the compressive strength test. The 200-mm concrete cube specimens were cast, and the steel bars (12-mm in diameter and 50-mm in length) were embedded at the corners of concrete specimens with covering depths of 20, 50, and 75 mm as shown in Fig. 1a. The embedded steel bars were cut from 12-mm diameter round bar graded SR24 (yield strength of 240 MPa). The ground rice husk–bark ash (GRBA) was used to replace Portland cement type I at 0, 15%, 25%, 35%, and 50% by weight of the binder. The W/B ratios of concrete varied from 0.45 to 0.65. Table 2 shows the mix proportions of the concretes, which followed ACI 211.1 [16]. The water content in the mixtures was adjusted and compensated for the water absorption of aggregates. The superplasticizer (SP) was used to maintain the slumps of fresh concrete within the range of 100–150 mm. The preparation of concrete specimens followed the standard practice for making and curing concrete test specimens in the laboratory [17]. The concrete specimens were removed from the molds 1 day after being cast and then were cured in fresh water for 27 days. Consequently, the concrete specimens were transferred to the tidal zone of the marine site in the Gulf of Thailand (Fig. 1b). The ranges of annual temperature at this site are between 26 and 35 °C, and based on chemical analysis of the seawater, chloride and sulfate compositions range from 16,000 to 18,000 and 2200 to 2600 mg/l, respectively. After being exposed to seawater for 5 years, the concrete specimens were cored to obtain 75-mm diameter cylinders. The core specimens were dry-cut from the surface to obtain a series of 10-mm thick slices, and then were ground into small powdery particles. The powder sample from each slice was selected for acid-soluble chloride testing according to ASTM C 1152 [18], and water-soluble chloride testing according to ASTM C1218 [19], to determine the total and free chloride penetration profiles, respectively. Consequently, the concrete specimen was broken, and then the embedded steel bars

were removed. The corrosion of embedded steel bars was measured in terms of the percentage of rusted area and recorded images. The compressive strengths of concretes at 28 days curing in water and at 5 years exposure in marine environment were also investigated.

## 3. Results and discussions

### 3.1. Compressive strength

The compressive strengths of concretes at 28 days curing in water and at 5 years exposure in marine environment are shown in Table 3. The compressive strength at 28 days decreases as the amount of GRBA replacement increases, and the lowest compressive strength was found in 50%-GRBA concrete (for each W/B ratio). Between 28 days and 5 year-exposure, GRBA concretes continuously gain strength faster than Portland cement type I concretes, especially in concrete containing 15–35% GRBA by weight for the binder. During the 5-year exposure, the seawater did not seem to influence the strength of the concrete containing GRBA; no strength loss was found in GRBA concrete. It was possibly due to the pozzolanic reaction that reduced the amount of  $\text{Ca}(\text{OH})_2$  which is used to react with sulfate solution in seawater resulting in a lesser adverse effect on compressive strength. The pozzolanic reaction would also produce C–S–H product leading to a higher compressive strength of GRBA concretes in the longer exposure period [20–22].

The loss of compressive strength in type I Portland cement concrete during 5 years exposed to marine environment may have resulted from the physical environment, which strongly weakened the surface layers of concrete especially in concrete with high W/B ratio [23]. Accordingly, the greater loss of compressive strength was observed in type I Portland cement concrete with W/B ratio of 0.65 than in type I Portland cement concrete with W/B ratio of 0.45. In addition, sulfate content in seawater may have influenced the measured compressive strengths, especially for Portland cement concrete.

### 3.2. Chloride diffusion coefficient ( $D_c$ )

A commonly used approach for calculating the chloride diffusion coefficient,  $D_c$ , from chloride penetration profiles [11,15] is to fit the general solution of Fick's second law (Eq. (1)) [24] on chloride penetration profile from experiment.

$$C_{x,t} = C_o \left[ 1 - \operatorname{erf} \left( \frac{x}{2\sqrt{D_c t}} \right) \right] \quad (1)$$

where  $C_{x,t}$  is the chloride concentration at the depth  $x$  and exposure time  $t$ ;  $C_o$  is the chloride concentration at the concrete surface; and  $D_c$  is the chloride diffusion coefficient. Fig. 2 shows the fitting curve of a general solution of Fick's second law on the free chloride penetration profile of concrete with a W/B ratio of 0.45 after a 5-year exposure. After the chloride concentration at the concrete surface ( $C_o$ ) was obtained, the regression analysis yielded the chloride diffusion coefficient ( $D_c$ ).

Fig. 3 shows the effect of GRBA and W/B ratio on  $D_c$ . In both concretes with W/B of 0.45 and 0.65, the chloride diffusion coefficient of concrete decreased with GRBA replacement levels up to 35%; however, it increased when the replacement level of GRBA reached 50%. In concrete containing GRBA of 50%,  $D_c$  was close to that of cement with type I concrete with the same W/B ratio. It is noted that the replacement of cement by a high volume of GRBA in concrete does not effectively improve the durability of concrete against chloride attack. Use of high volume GRBA in concrete will result in lower cement content in the concrete mixture. Accordingly,

**Table 1**  
Chemical composition of Portland cement type I and ground rice husk–bark ash (GRBA).

Chemical composition (%)	Sample	
	Cement type I	Ground rice husk bark ash (GRBA)
Silicon dioxide, $\text{SiO}_2$	20.80	87.0
Aluminum oxide, $\text{Al}_2\text{O}_3$	5.50	1.08
Iron oxide, $\text{Fe}_2\text{O}_3$	3.16	2.58
Calcium oxide, $\text{CaO}$	64.97	1.25
Magnesium oxide, $\text{MgO}$	1.06	0.5
Sodium oxide, $\text{Na}_2\text{O}_3$	0.08	0.08
Potassium oxide, $\text{K}_2\text{O}$	0.55	1.0
Sulfur trioxide, $\text{SO}_3$	2.96	0.09
Loss On Ignition, LOI	2.89	5.71

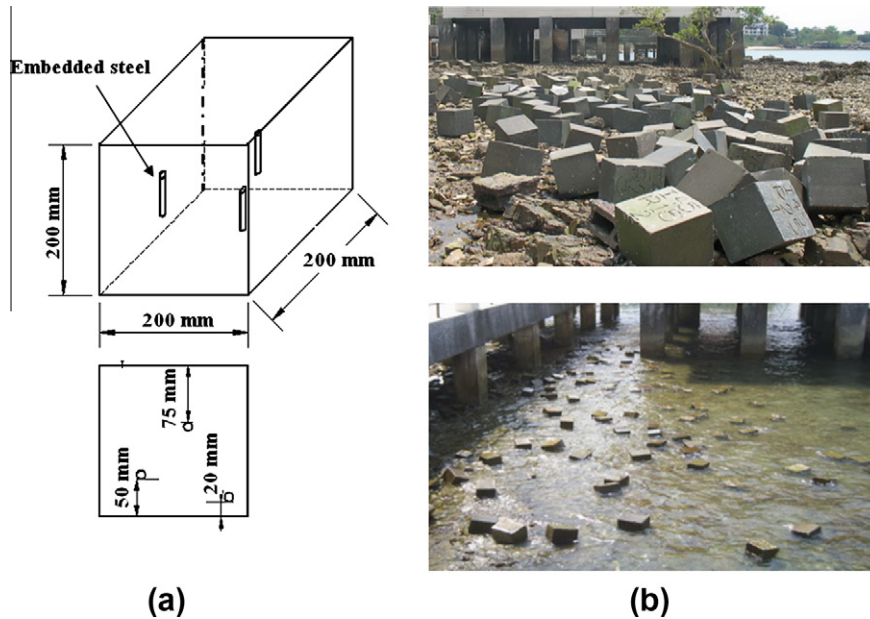


Fig. 1. (a) Details of embedded steel bars in concrete, (b) concrete specimens at the tidal zone of sea water.

**Table 2**  
Mixture proportions of concrete.

Sample	Mix proportion of concrete (kg/m <sup>3</sup> )						W/B ratio
	Cement type I	GRBA	Coarse aggregate	Fine aggregate	Water	SP	
I45	424	–	979	767	190	–	0.45
I65	295	–	1.039	814	192	–	0.65
I45GRBA15	360	64	957	767	190	0.85	0.45
I45GRBA25	318	106	938	767	190	1.70	0.45
I45GRBA35	276	148	925	767	190	2.54	0.45
I45GRBA50	212	212	952	767	190	3.82	0.45
I65GRBA15	251	44	1.023	814	192	–	0.65
I65GRBA25	221	74	1.012	814	192	–	0.65
I65GRBA35	192	103	1.000	814	192	0.30	0.65
I65GRBA50	148	148	982	814	192	0.30	0.65

**Table 3**  
Compressive strength of concretes after 28 days and 5 years of exposure in a marine environment.

Mix	Compressive strength (MPa)		
	28-day curing	5-year exposure	5-year/28-day (%)
I45	45.1	44.5	98.7
I45GRBA15	42.9	46.3	107.9
I45GRBA25	40.8	44.1	108.1
I45GRBA35	39.4	43.2	109.6
I45GRBA50	39.3	40.5	103.1
I65	30.9	29.5	95.5
I65GRBA15	33.8	35.4	104.6
I65GRBA25	32.9	34.7	105.4
I65GRBA35	31.1	34.1	109.5
I65GRBA50	28.6	29.1	101.7

the amount of  $\text{Ca(OH)}_2$  from hydration reaction between Portland cement and water was not high enough to react with active silica of GRBA in pozzolanic reaction to produce more C–S–H product in concrete. However, concretes containing 15–50% GRBA as a cement replacement produce better chloride resistance than concrete without GRBA. This is due to the packing effect and pozzolanic reaction of finely ground GRBA, which provides a better resistance to chloride penetration [25,26]. For

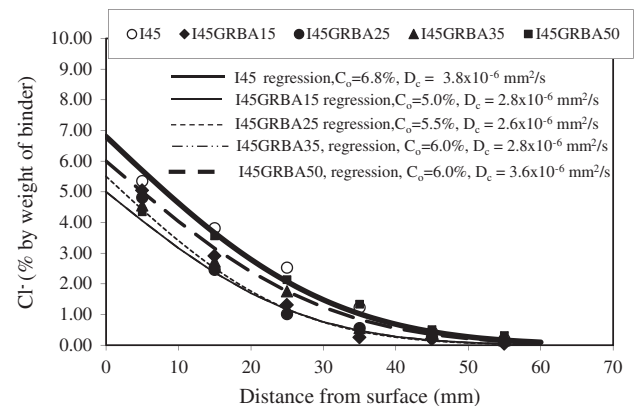


Fig. 2. The fitting curve of a general solution of Fick's second law to the free chloride penetration profile of GRBA concretes with a W/B ratio of 0.45 after 5 years of exposure.

instance, 0%, 15%, 25%, 35% and 50% of GRBA concrete with W/B of 0.45 had  $D_c$  of  $3.8 \times 10^{-6}$ ,  $2.8 \times 10^{-6}$ ,  $2.6 \times 10^{-6}$ ,  $2.8 \times 10^{-6}$  and  $3.6 \times 10^{-6} \text{ mm}^2/\text{s}$ , respectively.

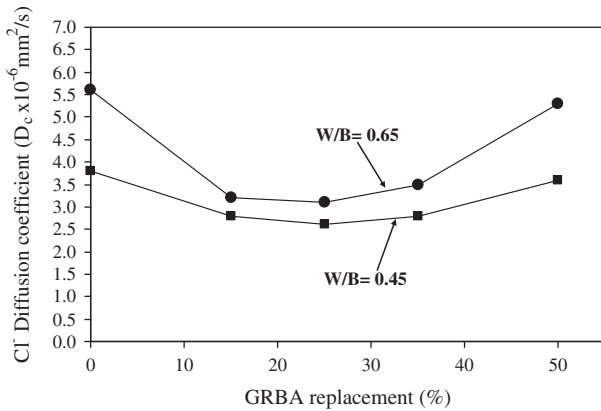


Fig. 3. Effect of GRBA and W/B ratios on the free chloride diffusion coefficient ( $D_c$ ) of concretes after 5 years of exposure to seawater.

### 3.3. Chloride binding capacity

In this study, the chloride binding capacity was calculated in terms of percentage of chloride binding capacity compared to the total chloride content ( $P_b$ ), which is a method similar to that described by Cheewaket et al. [27] and can be calculated from the following equation:

$$P_b = \frac{(C_t - C_f) \times 100}{C_t} \quad (2)$$

where  $C_f$  and  $C_t$  represent the free and total chloride contents, respectively. In Fig. 4, regression analyses were performed to obtain the relationship between the free chloride ( $C_f$ ) and total chloride ( $C_t$ ) of concrete containing GRBA after 5 years of exposure. For instance, concrete I45GRBA15 has the following relationship:  $C_f = (0.8054)C_t$ . By substituting  $C_f$  in terms of  $C_t$  [ $C_f = (0.8054)C_t$ ] in Eq. (1), the percentage of chloride binding capacity ( $P_b$ ) of I45GRBA15 concrete after 5 years exposure is 19.4%.

Fig. 5 shows the effect of GRBA content and W/B ratios on the chloride binding capacity of concrete 5 years after being exposed in a marine environment. The percentage of chloride binding capacity compared to the total chloride content increased as the amount of GRBA increased in the concrete. However, the use of high volume GRBA in concrete (50% replacement) results in decreased  $P_b$ . Generally, part of the intruding chloride ions will be retained by the hydration products of the binder in concrete, either through chemical binding or by physical adsorption [28]. For

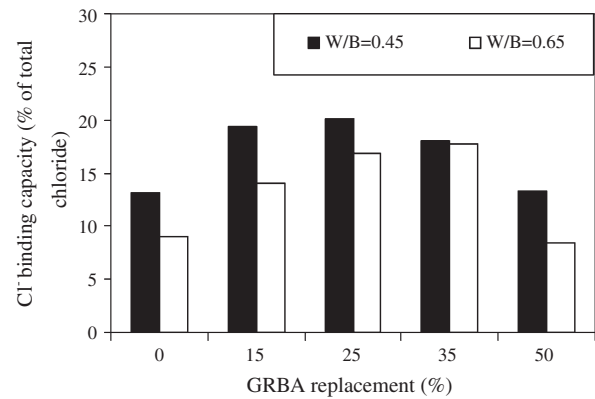


Fig. 5. Effect of GRBA and W/B ratios on the chloride binding capacity of concretes after 5 years of exposure to seawater.

chemical binding, chloride binds more as the  $C_3A$  content in the binder increases. This study found that GRBA has very low alumina contents (1.08%) that are less than those of Portland cement type I. Therefore, increasing the GRBA content in the binder has no effect on the binding of the chloride ion by chemical mechanisms. However, a chloride ion could be captured physically around the surface area of the solid part of the cement gel as C–S–H or C–A–H, for example [29–32]. The results indicate that using less than 35% GRBA replacement in concrete improves the compressive strength after 5 years of exposure, and their strengths were higher than that of Portland cement concrete (Table 3). This result implies that there is much solid cement gel; thus, the physical binding of chloride ion around the surface area of solid cement gel tended to increase. Therefore, the percentage of chloride binding capacity compared to total chloride content ( $P_b$ ) increased as the amount of GRBA increased. Conversely,  $P_b$  tended to decrease when the amount of GRBA exceeded 35%. For instance,  $P_b$  of concretes containing GRBA of 0%, 15%, 25%, 35%, and 50% replacements by weight of binder and W/B ratio of 0.45 were 13.2, 19.4, 20.2, 18.0, and 13.3, respectively.

Considering the effect of W/B ratio on  $P_b$ , it was found that decreasing the W/B ratio caused  $P_b$  to increase, which is probably because the higher compressive strength of the lower W/B ratio concrete may result from a greater amount of calcium silicate hydrate gel. When a large amount of solid cement gel forms, the physical binding of the chloride ion around the surface area of solid cement gel tends to increase as well, and consequently,  $P_b$  increased as W/B decreased.

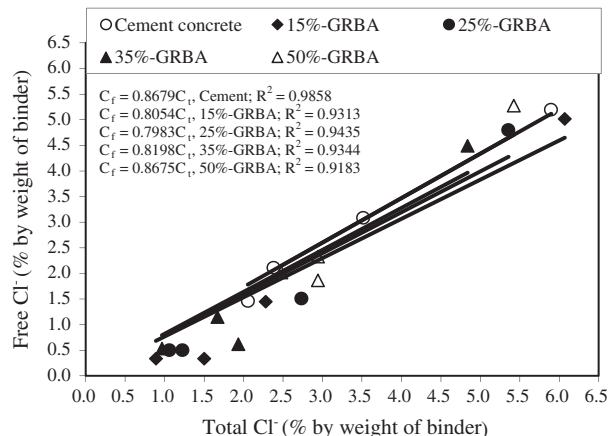
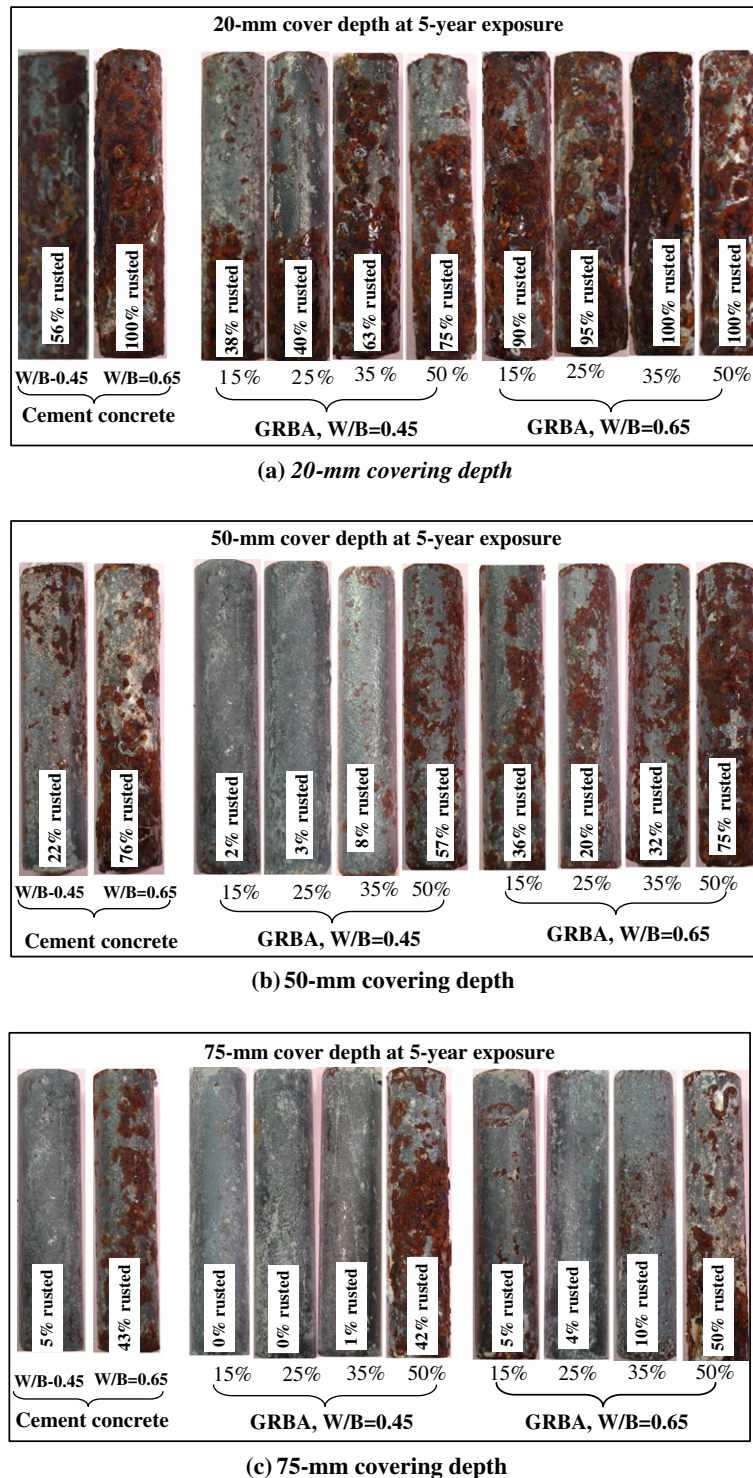


Fig. 4. Relationship between the free and total chloride contents of concrete with a W/B ratio of 0.45 after 5 years of exposure in a marine environment.

### 3.4. Corrosion of embedded steel bars

Fig. 6 shows the effect of GRBA and W/B ratios on the corrosion of embedded steel bars in concretes. The embedded steel at 20-mm covering depth was extremely rusted in almost all of the specimens and the effect of GRBA on the corrosion of embedded steel bars, especially in the concrete with W/B ratio of 0.65, could not be recognized. At the deeper cover depth (50 and 75 mm), for every W/B ratio, the use of 15–35% GRBA replacement is clearly found to reduce the corrosion of embedded steel bars; however, it was found to increase the corrosion of embedded steel bars when the replacement of GRBA reached 50%. For instance, concretes containing GRBA 0%, 15%, 25%, 35%, and 50% by weight of binder with a W/B ratio of 0.45 had percentages of rusted area at 50-mm and 75-mm covering depths of 22%, 2%, 3%, 8%, 57%, and 5%, 0%, 0%, 1%, 42%, respectively. A similar trend was also found in concrete with a W/B ratio of 0.65. Moreover, the steel corrosion was significantly increased as W/B ratio increased.

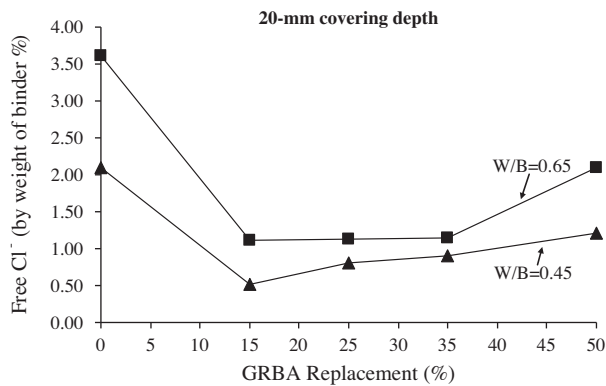




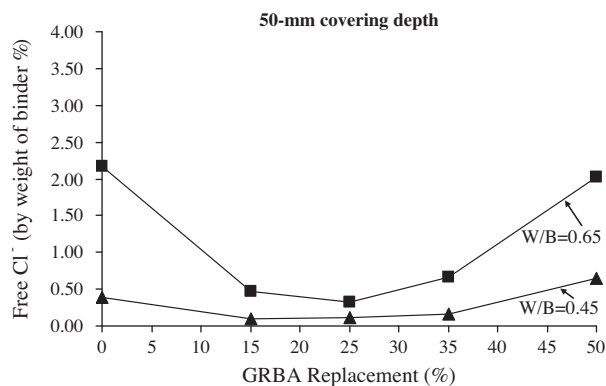
**Fig. 6.** Effect of GRBA and W/B ratios on the corrosion of embedded steel bars in concrete after 5 years of exposure to seawater.

In this study, the corrosion resistance of embedded steel bars was significantly enhanced by using GRBA to replace cement from 15% to 35% by weight of binder while the use of a high volume GRBA in concrete (50% replacement) resulted in low resistance to steel corrosion. This finding indicated that the pozzolanic reaction of GRBA in concrete can improve the physical characteristics of paste (low permeability), which enhances the corrosion resistance as well [1,4,33]. Previous researches had reported that the alkalinity ( $\text{OH}^-$  concentration) in pore structure of blended concrete with

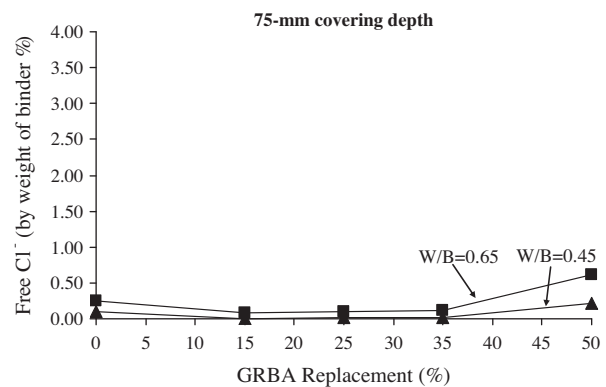
pozzolan materials significantly decreased when compared with normal concrete [29]. That should result in fast initial corrosion rate of embedded steel bars in GRBA concrete. However, the finding found that the use of 15–35% GRBA in concrete enhanced chloride binding capacity and could lower free chloride content in the pore solution which resulted in lower the  $\text{Cl}^-/\text{OH}^-$  ratio and consequently higher steel corrosion resistance. In addition, the pozzolanic reaction of GRBA concrete would also greatly decrease the permeability in concrete which leads to higher chemical resistance



(a) 20-mm covering depth



(b) 50-mm covering depth

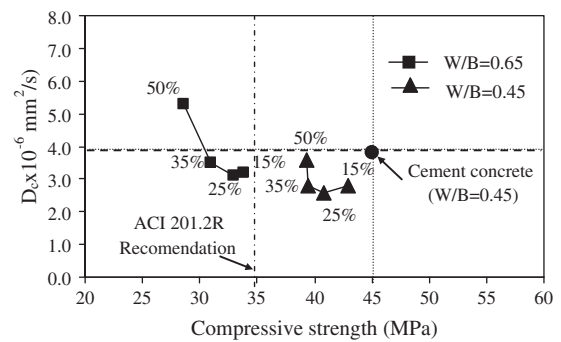


(c) 75-mm covering depth

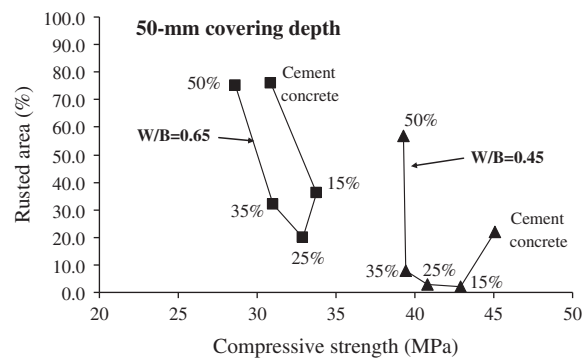
Fig. 7. Effect of GRBA and W/B ratios on the free chloride content at the position of embedded steel bars in concretes after 5 years of exposure to seawater.

with lesser corrosion of embedded steel. In addition, the high corrosion of embedded steel in high-volume GRBA concrete may result from the high permeability of these concretes that allowed chloride ion, water, and oxygen to penetrate into the concretes easily. This result is similar to that reported in other research [4].

The free chloride concentration at the position of embedded steel bar of concrete containing GRBA after 5 years of exposure in a marine environment (Fig. 7) also indicates that as the chloride content in concrete increases, the amount of corrosion of the embedded steel bar increases. The use of 15–35% GRBA in concrete significantly reduces the chloride penetration and increases its durability. For instance, concretes having W/B of 0.45 and GRBA replacement of 0%, 15%, 25%, 35% and 50% by weight of binder were



(a) Compressive strength and chloride diffusion coefficient



(b) Compressive strength and corrosion of embedded steel bar

Fig. 8. Relationship between compressive strength at 28 days and (a) chloride diffusion coefficient and (b) corrosion of embedded steel bar.

found to have chloride contents at 50 mm depth of 0.39%, 0.10%, 0.12%, 0.16% and 0.65%, respectively.

### 3.5. Relationship between compressive strength and durability performance

Generally, compressive strength and durability properties are the two major indicators of good performance of concrete in a chloride-rich environment. Fig. 8a shows the relationship between compressive strength at 28 days and the chloride diffusion coefficient ( $D_c$ ) of GRBA concretes. It is shown that all GRBA concretes with a W/B ratio of 0.45 had lower  $D_c$  than that of Portland cement concrete, although they also had lower compressive strength than that of the Portland cement concrete. According to ACI 201.2R [34], the standard for cement concrete in a marine environment, low permeability is attained by using a low W/B ratio (kept below 0.45). This concrete should have compressive strength no less than 35 MPa at 28 days. In this study, all GRBA concretes with a W/B ratio of 0.45 were found to be equivalent to or better than the concrete recommended by ACI 201.2R (in terms of both compressive strength and  $D_c$  when compared to Portland cement concrete with W/B = 0.45). Also, the relationship between the percentage of rusted area of embedded steel bars in concrete after 5 years of exposure and the compressive strength of concrete at 28 days is presented in Fig. 8b. The result shows that concretes containing 15–35% GRBA as a cement replacement with a W/B ratio of 0.45 produced a good durable concrete with a high compressive strength and little embedded steel corrosion. The findings are consistent with the low  $D_c$  (Fig. 3) and high  $P_b$  (Fig. 5) of these GRBA concretes (15–35% GRBA concretes with W/B ratio of 0.45) resulting in the lesser amount of free chloride ion to initiate the corrosion of reinforcing steel [29,35,36].

#### 4. Conclusions

Based on the experimental results, GRBA is a good pozzolan and can be used as a Portland cement replacement in concrete. The following conclusions are made.

- (1) During 5-year exposure in a marine environment, the concrete containing GRBA gained strength faster than type I Portland cement concretes and no strength loss was found in GRBA concrete.
- (2) The concretes containing 15–35% GRBA as a Portland cement replacement had a lower chloride diffusion coefficient and a little steel corrosion.
- (3) The chloride binding capacity increased as the amount of GRBA in the concrete increased, especially in concrete containing 15–35% GRBA as a cement replacement, and it was found to decrease in the high-volume GRBA concrete (50% replacement).
- (4) The use of 15–35% GRBA in concrete with a W/B ratio of 0.45 can be used to improve corrosion resistance of reinforcing steel in concrete under seawater because it produces good mechanical properties (high compressive strength) together with good durability properties (low chloride ingress into concrete, high chloride binding and low embedded steel corrosion).

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