Carbonation and strength of self-compacting concrete with coal bottom ash exposed to seawater by wetting-drying cycle

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Abstract. This experimental work presents the carbonation and strength behaviour of self-compacting concrete with coal bottom ash that was exposed to cyclic wetting-drying processes under condition of seawater environment. Six series of mix portions with 0%, 10%, 15%, 20%, 25% and 30% of coal bottom ash replacement to sand were produced. The samples arising from each mixture were exposed to seawater environment with an average of 15 hours of wetting and 9 hours of drying process per day. Thus, the carbonation and compressive strength behaviour at the durations of 28, 60, 90 and 180 days under curing process were observed. The results obtained in this study for seawater exposure has clearly indicated that the incorporation of 10% replacement of coal bottom ash to sand exhibited good result of carbonation and compressive strength.

1. Introduction
Marine environments are very aggressive, since seawater mainly consists of chlorides and sulphates. Both ions can be very harmful to the durability of concrete structures which can affect the long-term durability and may cause a huge economic loss. Furthermore, concretes are exposed to repeated drying–wetting cycles, such as in the marine environment of splash and tidal zone which can accelerate the deterioration of structures [1].

The main attack mechanism in marine environments is external sulphate attack. This occurs when water contaminated with sulphates penetrates into the concrete by means of diffusion or capillary suction. Sulphates are mostly found in the form of sodium sulphate (Na₂SO₄) or magnesium sulphate (MgSO₄). The cation associated with SO₄²⁻ has an influence on the attack mechanism and the consequence of deterioration [2]. Sodium sulphate attack will result in expansive reaction products while magnesium sulphate attack will result in reduction in strength. Al-Amoudi describes the sequence of attack by magnesium sulphate in seawater as follows:

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Ca(OH)_2 + MgSO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + Mg(OH)_2 \\
C-S-H + MgSO_4 + H_2O \rightarrow CaSO_4 \cdot 2H_2O + Mg(OH)_2 + SiO_2 + H_2O \\
4Mg(OH)_2 + SiO_2 \cdot nH_2O \rightarrow MgO \cdot SiO_2 \cdot 8 \cdot 5H_2O + H_2O
\]

The calcium chloroaluminate hydrate or Fridel’s salt is an important phase formed during exposure of concrete to seawater [3]. Generally, chloride and sulphate ion from seawater penetrate into concrete forming Fridels salt and ettringite. However, magnesium sulphate also attacks calcium hydroxide and calcium-silicate-hydrate (C-S-H) phases. According to Leng et al. [4], magnesium sulphate attacks...
calcium hydroxide and C-S-H, reacts with C-H to form secondary gypsum and brucite. Apart from that, Islam et al. [5] found that chloride reacting with C-H of hydrated cement has led to weight loss and weakening the concrete structures. Figure 1 illustrates the mechanism of deterioration act on concrete exposed to seawater.

Figure 1. Concrete exposed to seawater [6].

1.1. Wetting-drying cycle
Wetted and drying cycles can cause constant moisture movement through concrete pores [7,8]. It is well-known that wetting and drying cycles may speed up concrete degradation and durability problems because this has subjected the concrete to the motion and accumulation of destructive elements, such as sulphates, alkalis, acids, and chlorides. According to Hong & Hooton [9], there are several mechanisms governing chloride ingress into concrete such as absorption, diffusion, chloride binding, permeation, wicking and dispersion. Absorption and diffusion are the most significant mechanism of chloride ingress for the structures exposed to cyclic wetting-drying. Chloride-induced corrosion of steel reinforcement is a major cause affecting the service life of reinforced concrete structure exposed to aggressive environments. Chloride ions ingress by pore diffusion is a rare occasion when the concrete structure is exposed to continuous wetting–drying cycles by tidal and splash action [10]. Various model and analysis technology have been proposed including the condition of chloride penetration into sound concrete. Most of analyses were based on the condition of chloride penetration into saturated concrete, however in reality, concrete was often found in an unsaturated condition rather than a saturation condition especially when subjected to cyclic wetting–drying [11].

Ye et al. [12] have conducted an experiment on chloride penetration process in concrete exposed to a cyclic drying-wetting and carbonation environment. Based on the findings, the chloride penetration profile in concrete was produced by multiple interactive deteriorating mechanisms, and was dependent on the properties and stress status of the concrete itself. Their study also claimed that the incorporation of supplementary cementitious materials have made concrete more vulnerable to chloride attack under a combined deterioration of cyclic drying-wetting and carbonation, since the deficiency of portlandite dominates the positive effects such as pore refinement.
1.2. Coal bottom ash self-compacting concrete

In the phase of coal-fired power generation, there are three types of coal combustion products that can be obtained such as fly ash, coal bottom ash and boiler slags. The utilization of these products in construction industry is an imperative concern such as reduction in technical and economic problems of plants, the reduction of the amount of solid wastes, greenhouse gas emissions and preserving current natural resources. Some researchers have testified the use of coal bottom ash in concrete as partial replacement of portland cement [13,14] or as a partial replacement of fine aggregates [15,16].

Coal bottom ash usually has particles size range from fine sand to fine gravel. The particles appear similar to natural river sand. As the natural resource of river sand is depleted gradually, the properties of coal bottom ash have attracted many researchers to study its potential as fine aggregate in concrete production. Previously, several investigations on the properties of concrete incorporating coal bottom ash as the sand replacement have been conducted. The incorporation of coal bottom ash as sand replacement material was found to help self-compacting concrete in designing mix proportion which contains extra fine particles content and fewer amounts of coarse aggregates [17]. On the other hand, self-compacting concrete was developed to respond to the need for a self-compacting concrete with improved durability.

The current study aims to investigate the carbonation and strength behaviour of self-compacting concrete with coal bottom ash that was exposed to cyclic wetting-drying processes under condition of seawater environment.

2. Experimental work

Six (6) series of mix portions with 0%, 10%, 15%, 20%, 25% and 30% CBA were casted including the control samples for testing for fresh and hardened properties respectively. The interval percentages of coal bottom ash are reliable suggested by Bilir [18] study which based on arithmetic average for representation of the corresponding group.

2.1. Material

In this study, the materials that were used underwent the similar process of the conventional concrete production. Silica-rich coal fly ash and Portland fly ash cements complied with MS EN 197-1:2007 standard which were widely used during the concrete making process within the main binder. The fine aggregation included both coal bottom ash and river sand where the coal bottom ash was collected from one of coal-fired power plant in Selangor, Malaysia that had a fine classified for the fine aggregations the sizing were in the range of 5 mm. The chemical composition of the cement and coal bottom ash is listed in Table 1. Polymer-based superplasticizer with specific gravity of 1.09 and pH value of 5.29 was used to magnify the workability of fresh concrete.

| Compounds | Composition of Portland fly ash cement (%) | Composition of coal bottom ash (%) |
|-----------|------------------------------------------|----------------------------------|
| SiO₂      | 22.00                                    | 68.90                            |
| Al₂O₃     | 8.35                                     | 18.67                            |
| Fe₂O₃     | 3.92                                     | 6.50                             |
| CaO       | 58.93                                    | 1.61                             |
| K₂O       | 1.01                                     | 1.52                             |
| TiO₂      | 0.72                                     | 1.33                             |
| MgO       | 0.52                                     | 0.53                             |
| Na₂O      | 0.26                                     | 0.24                             |
| CO₂       | 0.10                                     | 0.10                             |
| MnO       | 0.15                                     | -                                |
| Loss on ignition | 1.72                      | 1.72                             |
The proportion of concrete mixtures was adopted from the proposed report by Jawahar [19]. The key proportions of the compositions are presented in Table 2. The water/binder ratio of 0.40 was considered for all six batches, namely SCC-BA0, SCC-BA10, SCC-BA15, SCC-BA20, SCC-BA25 and SCC-BA30. Based on the experimental work, coal bottom ash was partly substituted with sand gradually at the ratings of 10%, 15%, 20%, 25% and 30%. The coarse aggregations and fine aggregations were well-maintained at 28% of concrete volume and 45% of mortar volume, respectively. During the experiment, the air content was assumed to be at 2% for all mixtures.

### Table 2. Mix proportions in kg/m³.

| Mix     | Cement | Coarse Agg. | Fine Agg. | Coal Bottom Ash | Water   | Sp (%) |
|---------|--------|-------------|-----------|-----------------|---------|--------|
| SCC-0BA | 518    | 715.5       | 874.50    | 0.00            | 207.20  | 0.16   |
| SCC-10BA| 518    | 715.5       | 787.50    | 87.45           | 207.20  | 0.20   |
| SCC-15BA| 518    | 715.5       | 743.33    | 131.18          | 207.20  | 0.26   |
| SCC-20BA| 518    | 715.5       | 699.60    | 174.90          | 207.20  | 0.32   |
| SCC-25BA| 518    | 715.5       | 655.88    | 218.63          | 207.20  | 0.16   |
| SCC-30BA| 518    | 715.5       | 612.15    | 262.35          | 207.20  | 0.20   |

2.2. Casting
The cube specimens with a dimension of 100×100×100 mm were prepared accordingly to BS EN 12390-1:2012 and BS EN 12350-1:2009 standards. The fresh properties of the mixtures, namely slump flow, slump spread time (T₅₀₀), L-box ratio and segregation resistance were performed before molding process. These tests were important to classify the rating and suitability of the mixtures to maintain a fresh state of self-compacting concrete. All specimens were unmolded after 24 hours and placed in a water tank for curing process for up to 28 days. Thereafter, the cyclic simulation through wetting-drying processes were initiated.

2.3. Laboratory cyclic simulation and compression test
The cyclic simulation technique that was adopted in this study had been successfully applied by other researchers as reported by Ramadhansyah et al. [20]. The specimens were positioned in a square shaped 10 litre plastic container that was filled with seawater. Table 3 presents the analysis of the seawater that was used during the cyclic wetting and drying processes. In the drying cycles, specimens will be placed in an enclosed chamber with temperature ranging from 25-31°C which was considered as a single cycle. In the next cycles, the samples will be placed again in the solutions for 15 hours, followed by 9 hours in enclosed chamber where the specimens will be located for the final drying stage. These processes were repeated until the periods of the cycles were completed as according to Ramadhansyah et al. [20], the time interval of wetting and drying cycles to emulate the Malaysian climate conditions require 15 hours of wetting period, followed by 9 hours of drying per day. The solutions were refreshed every week or as per requirement basis according to the change of pH value. The densities of the concrete were recorded and the compressive strength was tested at the specimen’s age of 28, 60, 90 and 180 days. In the case of compression test, the procedures of the test were conducted according to the technique described by the British Standard.

2.4. Carbonation test
The carbonation test is detailed in BS EN 14630:2006. Carbonation of concrete occurs when the carbon dioxide in the atmosphere with the presence of moisture, will reacts with hydrated cement minerals to produce carbonates. Carbonation penetrates gradually below the exposed surface of concrete.

Carbonation depth was assessed using a solution of 1% phenolphthalein indicator that will be appeared in pink/purple colour when have contact with alkaline concrete with pH values in excess of 9 and colourless at lower levels of pH. The test was carried out at the age of 7, 28, 60, 90 and 180 days using split tensile specimens. The test is conducted by spraying the indicator on freshly exposed surfaces of concrete broken from the structure or on split cores. After 24 hours, carbonation depth was
measure at three different locations. The average values were considered as carbonation depth. Unchanged colour indicated carbonated in the zone at the front head, while colour changed into purple shows non-carbonated zone.

3. Results and discussion

3.1. Compression test

Figure 2 shows the compressive strength of self-compacting concrete with coal bottom ash as fine aggregate replacement subjected to seawater environment. The strength is initially increased during period up to 60 days, and then it started to decrease until the specimens ultimately disintegrated after 180 days. This event could be explained by two mechanisms involve in the influence of strength increment. First, the formation of calcium hydroxide \((\text{Ca(OH)}_2)\) by presence of coal bottom ash, pozzolanic and cementitious materials, hence transformed into calcium silicate hydrate (CSH) gel. This has resulted to an increase in the strength of the concrete. Second, the reactions of sulphate and chloride ions with hydrated cement constituent to form ettringite. This ettringite formation contributes to the increase in concrete strength. Conversely, the decrease in compressive strength observed in this study was due predominantly to two phenomena: (i) disintegration as a result of the reaction of \(\text{MgSO}_4\) with hydrated cement and (ii) the continuous process of crystallization cycles of \(\text{MgSO}_4 \cdot n\text{H}_2\text{O}\) by wetting and drying of hardened pastes thus can produce pores internal stresses leading to formation of cracks.

Ganjian & Pouya [21] explained that concrete or mortars exposed to seawater in cyclic condition can affect the salts crystallization, hence distressing the defensive layer that facilitating the ions ingress. The reaction of specimens subjected to seawater is similar to of the sulphate and chloride solutions; however the effects are diverse due to the attendance of chloride ions. The effect of seawater has been attributed to the reaction of \(\text{MgSO}_4\) with \(\text{Ca(OH)}_2\), forming gypsum and \(\text{Mg(OH)}_2\) [22]. On the other hand, Al-Amoudi [23] stated that the presence of chlorides in seawater reacts with \(\text{Ca(OH)}_2\) as well as \(\text{C}_3\text{A}\) to produce Friedel’s salt. This statement has been supported by Santhanam et al., [24] and claimed that the formation of Friedel’s salts can be one of the factors leading to the compressive strength reduction.

![Figure 2](image_url)

**Figure 2.** Compressive strength of specimens subjected to seawater with wetting-drying cycles.

As shown in Figure 2, self-compacting concrete with 10% replacement coal bottom ash to sand displayed a significant increase in compressive strength and it is more resistant to seawater attack compared with others mixture up to 28 days. However, at the cyclic day of 60 to 180 days, the control specimens display significant improvement in strength value, while SCC-10BA shows slightly lower than control. It can be concluded that the incorporation of 10% replacement of coal bottom ash to sand in concrete exhibited good strength and comparable to of the control mixtures, even when
exposed to seawater environment by cyclic wetting-drying. Kasemchaisiri & Tangtermsirikul [25] have carried out a study on properties of self-compacting concrete containing coal bottom ash as a replacement material of fine aggregate also claimed that 10% as a good performance in terms of strength and durability. Their result indicated that the 10% replacement of coal bottom ash is potential to be used as sand replacement for the construction in marine structures.

3.2. Carbonation test

Figure 3 presents the effect of coal bottom ash replacement in self-compacting concrete exposed to seawater on carbonation depth. It can be seen that the carbonation depth decreased with time in all concrete mixes. According to Kasemchaisiri & Tangtermsirikul [25], the carbonation depth of coal bottom ash self-compacting concrete mixtures was reduced at the long period. This has clarified the reduction of carbonation depth at 180 days. The reduction of carbonation depth was due to the pore refinery effect by pozzolanic reaction of coal bottom ash. The dependable factors of carbonation depth such as cement types and curing condition is usually linked to the reduction of carbonation depth.

The increased of concrete carbonation is initiated by the decrease of calcium hydroxide Ca(OH)$_2$ and calcium silica hydroxide (CSH) compounds which formed by the reaction of coal bottom ash and hydrated cement paste [26]. Consequently, the less amount of Ca(OH)$_2$ decreased the ettringite and gypsum formation. As a result, the carbonation depth increased with the increase of coal bottom ash replacement ratio. Based on the Figure 3, this trend occurred in all coal bottom ash replacement ratio. It also observed that the carbonation depth of specimen exposed to seawater at 10% coal bottom ash replacement was the lowest compared to others. This indicates that the carbonation resistance is very high by incorporating 10% replacement ratio.

3.3. Relationship between compressive strength and carbonation depth

Figure 4 presents the relationship of carbonation test and compressive strength on specimens subjected to seawater through cyclic wetting-drying. The results showed that the lowest compressive strength attained highest measurement of carbonation depth. Based on the correlation, the carbonation depth is the lowest when the compressive strength increases accordingly. This result indicates that coal bottom ash in concrete has a great influence to the strength reduction of specimens in exposed to chloride solution. It shows that the compressive strength of carbonated concretes with high coal bottom ash content is slightly decreases in comparison with controlled. Calcium carbonate that occupies in specimens has a greater volume than calcium hydroxide, hence reduced the exterior porosity of concrete.
Since the carbonation depth decreases with an increase in compressive strength, the indication of carbonation depth and compressive strength are restrained by the pore size and structure is acceptable. Furthermore, the specimens exposed to seawater have experienced strength reduction due to the sulphuric acid attack. Chloride and sulphate ion from seawater penetrate into concrete forming Fridel's salt and ettringite. Both compounds are found in concrete and will make the matrix became weak. The size of specimens will also decreased due to loss of cement paste and subsequently will reduce compressive strength.

![Figure 4. Relationship between carbonation depth and compressive strength (exposed to seawater).](image)

4. Conclusion
In this study, the influences of coal bottom ash as fine aggregates on the carbonation and compressive strength for self-compacting concrete were investigated.

- The results obtained in this study for seawater exposure has clearly indicated that the incorporation of 10% replacement of coal bottom ash to sand in concrete exhibited good compressive strength and comparable to of the control mixtures, even when exposed to seawater environment by cyclic wetting-drying.
- It can be concluded that the addition of coal bottom ash as a sand replacement provides additional improvements in chloride penetration depth to seawater attack via wetting and drying cycles at 10% level replacement. The inclusion of 10% coal bottom ash in self-compacting concrete reduces the content of calcium hydroxide formed due to the pozzolanic reaction during cement hydration; consequently decrease the content of ettringite and gypsum during seawater attack of concrete.

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