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Abstract. There are many concrete constructions in marine environments. Due to its salinity content, seawater is aggressive, both towards concrete and reinforcement. Concrete interacts with seawater which causes deterioration. The chemical attack occurs at least through 3 common mechanisms: sulfate-attack, carbonation, and chloride-induced corrosion of reinforcement. The chemical resistance of concrete is determined by the porosity and chemical composition of the concrete. Partly subsitution of cement with supplementary cementitious materials (SCM) known as an effective way to create the less permeable concrete. Concrete with fly ash as SCM has excellent potential to be applied to marine construction in Indonesia because the abundant availability of fly ash in Indonesia and the presence of aluminum species in fly ash provide an opportunity to increase binding capacity to chloride.

1. Introduction

Concrete is a material that is widely used in marine construction, for examples are docks, piers, breakwaters, LNG terminals, offshore windmills, and many other structures. The durability of a structural concrete in a specified marine environment likely to depend upon the structural factor (geometries, crack) and material factors (mixture components and its composition, curing, etc). Degradation of reinforced concrete can be classified into: physical (freeze-thaw cycles, fire); mechanical (erosion, abrasion); chemical; biological (biogen attack); structural (overloading). The main chemical damage mechanisms of reinforced concrete are caused by sulfate attack, carbonation, calcium leaching and chloride-induced corrosion.

The hardened cement paste always has capillary pores which decrease in volume as the water to cement ratio (w/c) drops and the degree of hydration increases. The same is true of concrete, but in concrete tends to be more porous as the presence of the aggregates. The existence of these capillary pores creates permeability in concrete. At high porosity, the interconnected pore system connects the concrete surface to the bulk of concrete. Permeability increases sharply if the porosity exceeds 25%, which is obtained from the w / c 0.45 and 75% degree of hydration [1].

Concrete permeability causes ions in seawater to enter the structure or vice versa leaching the constituent components of the concrete to sea water. Four basic mechanisms of the passage of fluid

and ions through concrete are: capillary suction, due to capillary action inside capillaries of cement paste, permeation, due to pressure gradients, diffusion, due to concentration gradients, and migration, due to electrical potential gradients [1]. The transport rate of ions or fluid depend on mechanism, concrete porosity, and the binding of transported substances by the hydrated cement paste as well as on the environmental conditions.

Many studies have been carried out to improve the impermeable properties of concrete, for example by adding clay brick powder [2], regulating water to cement ratio [3], fly ash substitution [4–6] and blast furnace slag subtisusion [7].

Concrete exposed to seawater is deteriorated due to chemical and physical interactions. The chemical failures are majorly caused by sulfate attack, carbonation and chloride-induced corrosion. While mechanical action and the growth of marine biota affect concrete degradation, however, this paper is focused on the durability against chemical attack. The main objective of this paper is to study the chemical breakdown mechanism of concrete and the critical properties of concrete that affect its resistance. Further research needs to be identified to produce concrete that is resistant to seawater attacks by taking into account the availability of materials in Indonesia.

2. Sulfate Attack

The aggressiveness of seawater to concrete is influenced by several factors, including the composition of seawater, climate, waves, and marine zones (immersion, tidal, splash or spray zones). The main ions present in seawater are Na^+, Mg^{2+}, Cl^- and SO_4^{2-}, together with the small quantities of K^+, Ca^{2+}, HCO_3^- and Br^- [8]. The salinity of seawater varies widely, but it can be assumed that an average of 3.5% (35 g / L dissolved salt) [9]. The permeability of the concrete and the compositions of the hydrated phases of the cement are the main factors of concrete materials governing the sulfate reaction. The hydration products of the tricalcium aluminate (C_3A) are known as the susceptible phase to sulfate attack [10].

Sulfate ions from the environment attack the concrete and are known as external sulphate attack (ESA). Sulfate attacks originating from concrete components known as internal sulfate attacks (ISA) or delayed ettringite formation (DEF) are not included in this paper. External sulfate attack includes all chemical reactions from external sulfate sources that cause concrete damage regardless of the type of cation. The sulfate attack mechanisms consists of [8,10]:

2.1. The reaction of sulfates with the constituent components of the cement paste produces gypsum or is known as gypsum attack. The two common reactions are:

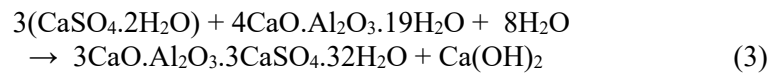*2.1.1. The reaction of sodium sulfate with calcium hydroxide and water result gypsum and sodium hydroxide.*

$$Na_2SO_4 + Ca(OH)_2 + 2H_2O \rightarrow CaSO_4.H_2O + 2NaOH \qquad (1)$$

2.1.2. The reaction of $MgSO_4$ with $Ca(OH)_2$ produce gypsum and magnesium hydroxide.

$$MgSO_4 + Ca(OH)_2 + 2H_2O \rightarrow CaSO_4.2H_2O + Mg(OH)_2 \qquad (2)$$
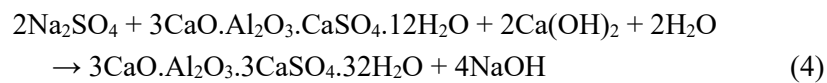
The gypsum produced by those reactions is believed to damage concrete by increases in overall solid volume. In addition, the reduction of $Ca(OH)_2$ lead to depasssivation of reinforcing steel as decreasing the alkalinity of pore solution. Magnesium hydroxide (eq. 2) has very low solubility so it tends to form deposits on the concrete surface. These deposits can protect the next attack if the construction is submerged [8,10].

2.2. Expansion occurs due to the formation of ettringite (called a sulfoaluminate attack), include two reactions:

2.2.1. Gypsum reacts with calcium aluminate hydrate plus water to form ettringite and calcium hydroxide.

$$3(CaSO_4.2H_2O) + 4CaO.Al_2O_3.19H_2O + 8H_2O$$
$$\rightarrow 3CaO.Al_2O_3.3CaSO_4.32H_2O + Ca(OH)_2 \qquad (3)$$

2.2.2. The reaction of sodium sulfate with calcium monosulfoaluminate, calcium hydroxide and water produce ettringite and sodium hydroxide.

$$2Na_2SO_4 + 3CaO.Al_2O_3.CaSO_4.12H_2O + 2Ca(OH)_2 + 2H_2O$$
$$\rightarrow 3CaO.Al_2O_3.3CaSO_4.32H_2O + 4NaOH \qquad (4)$$

The formation of ettringite (eq. 3, 4) causes volume expansion, hence generate the cracks [11–13]. However, interactions with chloride prevent ettringite from forming [8].

2.3. Decomposition of calcium-silicate-hydrate, calcium aluminatehydrate, calcium monosulfoaluminate, resulting in the loss of cementing properties (paste cohesion, paste-to-aggregate bond, strength, and durability
The reaction of $MgSO_4$ with calcium aluminate hydrate

*2.3.1. Forms gypsum, magnesium hydroxide and aluminum-hydroxide.*

$$3MgSO_4 + 3CaO.Al_2O.36H_2O + 6H_2O \rightarrow$$
$$3(CaSO_4.2H_2O) + 3Mg(OH)_2 + 2Al(OH)_3 \qquad (5)$$
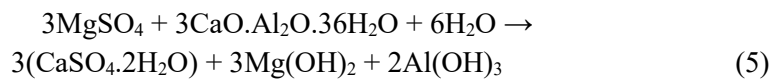
2.3.2. The reaction between magnesium sulfate and calcium monosulfoaluminate hydrate produce gypsum, magnesium hydroxide, and aluminum hydroxide.

$$3MgSO_4 + 3CaO.Al_2O_3.CaSO_4.12H_2O + 2H_2O \rightarrow$$
$$4(CaSO_4.2H_2O) + 3Mg(OH)_2 + Al_2O_3.3H_2O \qquad (6)$$
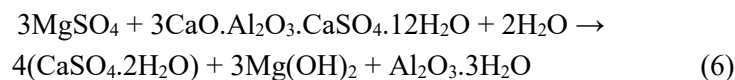
2.3.3. The reaction of magnesium sulfate and calcium silicate hydrate result gypsum, magnesium hydroxide and silica gel.

$$3MgSO_4 + 3CaO.2SiO_2.nH_2O + zH_2O \rightarrow$$
$$3(CaSO_4.2H_2O) + 3Mg(OH)_2 + 2SiO_2.xH_2O \qquad (7)$$
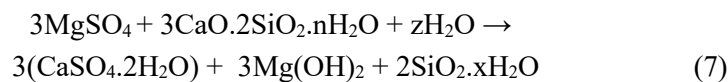
2.3.4. Magnesium sulfate reacts with calcium silicate hydrate and calcium hydroxide to form magnesium silicate and gypsum.

$$4MgSO_4 + CaO.SiO_2.H_2O + (4 - x)\,Ca(OH)_2.nH_2O \rightarrow$$
$$4MgO.SiO_2.8H_2O + 4CaSO_4.2H_2O \qquad (8)$$
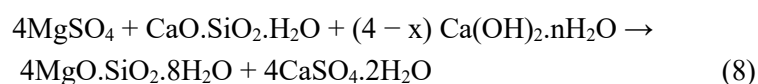
2.4. Thaumasite sulfate attack, namely sulfate attacks together with carbonate to produce thaumasite
Thaumasite is a pulpy soft mass and has no binding ability. This attack often occurs at low temperatures (<10ºC)

$$3Ca^{2+} + SiO_2^{3-} + CO_3^{2-} + SO_4^{2-} + 15H_2O \rightarrow$$

$$3CaO \cdot SiO_2 . CO_2 \cdot SO_3 \cdot 15H_2O \tag{9}$$
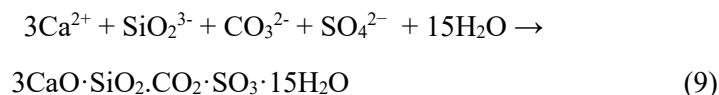
2.5. Salt recrystallization
The ions present in the environment have penetrated the concrete and then react with various possibilities as mentioned above. When the ions, generally sodium and sulfate, reach the surface then recrystallization occurs. This recrystallization often happens when the concrete experiences changes in temperature and humidity, for example in areas that subjected to drying-wetting cycles or tidal zones. Some authors classify it as a physical attack, however, disallowed by the other since the process involves chemical reactions [8].

3. Chloride-Induced Corrosion of Concrete Reinforcement

Chloride-induced corrosion is assumed as the foremost origin of reinforced concrete damage. Many studies have been carried out to determine the values for critical chloride content (C_{crit}) in reinforced concrete, i.e. the chloride concentration value on the surface of reinforcing steel which causes corrosion initiation. According to European standards, EN 206-1, C_{crit} value is 0.2 or 0.4% by weight of cement, depending on the type of cement [14]. In contrast, some experiment state the higher value, for example Kwon [15] reported C_{crit} of 2.5%. The C_{crit} value is the most decisive input parameter in the service life probability modelling.

Chloride from the environment, which is absorbed on the concrete surface enters the deeper zone by diffusion. The diffusion coefficient is the main parameter to describe the diffusion process that occurs.

The mechanism of chloride attack on reinforcing steel occurs in the following steps [1].
(i) Chloride ion penetrates the oxide film on the steel surface at the defect site. The penetration of chloride ion is stronger than other ions, therefore termed as the aggressive ion.
(ii) Chloride ion is adsorbed on the metal surface. At the same time, dissolved oxygen and hydroxyl ion are adsorbed on the metal surface;
(iii) The ferrous-cation formed from corrosion reacts with chloride ions to form a soluble complex of iron chloride. This compound leaving the metal surface attacks the protective layer of $Fe(OH)_2$ so that corrosion continues.

The C_{crit} value is influenced by the pH of the concrete or concentration of hydroxyl ions in the pore solution, steel potential, and the presence of voids on the steel/concrete interface. The concentration of hydroxyl ions depends on the type of cement mixture. The risk of corrosion attack increases when the $[Cl^-]/[OH^-]$ ratio increases to a certain value. However, several authors have shown different critical values [1].

The substitution of cement with SCM has two-fold effects. The first has the effect of reducing porosity, and the second increases the binding capacity of chloride. The binding capacity behaviour for cement paste with metakaolin, silica fume, fly ash, and slag substitution has been studied. The highest binding capacity is found in pastes with metakaolin. This fact can be understood since the formation of Friedel's salt ($FC_3A.CaCl_2.10H_2O$) requires aluminium, while metakaolin is a mineral with a high aluminium content. The use of fly ash with different calcium content did not show a significant

difference. However, apart from the type of mineral, the w/c factor also plays an important role. The increase in binding capacity due to mineral substitution was detected at w/c 0.5, while at w/c 0.3, the binding capacity change was only slightly. It is suspected that an increase in w/c provides the availability of free Al for the formation of Friedel's salt [16].

In another study, concrete with 56 and 58% fly ash was exposed to the marine environment for 24 years. It was found that the cement substitution with fly ash resulted in resistance to chloride ion penetration. However, to get the best results, it is necessary to take synergic steps of SCM substitution, low w/c ratio (not more than 0.4) and sufficient cover depth. [6].

The combination of chloride and magnesium sulfate attack was studied on the three kinds of mortar made of Portland cement, sulfate resisting cement and a blended of 50% OPC -50% slag. Substitution with slag prevents the formation of brucite ($Mg(OH)_2$) hence there are no protective properties on the surface [17].

4. Carbonation

Carbonation take places when carbon dioxide in the environment infiltrates into the concrete to react with calcium hydroxide giving calcium carbonate:

$$CO_2 + Ca(OH)_2 + \rightarrow CaCO_3 + H_2O \qquad\qquad (10)$$
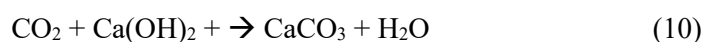
Reduction of $Ca(OH)_2$ causes an increase in porosity and causes a decrease in pH. Under normal conditions, the pH of the concrete pore solution is in the range 13-14 so that the reinforcing steel is in a passive state. In the case of carbonization, the pH can drop close to neutral.

Water to cement ratio (w/c) is the main factor controlling the resistance against carbonation of normal concrete. When chloride ions ingress and carbonation occur at the same time in concrete, chloride ions become soluble due to the deterioration of cement hydrates caused by carbonation. In addition, the chloride bound in the form of calcium chloroaluminate hydrate is released into the pore solution so that it becomes more aggressive [1].

Carbonation is affected by moisture. In both completely dry and wet environments, carbonation does not occur. In marine structures, the splash zone and above water are at risk of carbonation attacks. The condition for the attack is getting worse if there is chloride from both concrete components and the environment [1].

Research to determine the resistance of concrete to gas and water permeability was carried out on high-volume fly ash (HVFA). A 50% fly ash mixture by mass and a water-to-binder ratio of 0.4 is obtained to have water and gas permeability lower than normal concrete, provided that fly ash has a fairly low LOI (loss on ignition), 3.5% and high refinement (19% retained) on a 45 μm sieve [18].

The leaching resistance of concrete is sensitive to w/c and the paste composition. The concrete undergoes leaching due to the presence of portlandite in the paste. Furthermore, the leached concrete is susceptible to sulfate attack. High C3S cement substitution with 30% FA had an increased impact on leaching resistance and sulfate attack. Substitution of cement with 62% GGBS (ground granulated blast-furnace slag) gives the best results [12]. However, different results were found by Ashish [19], the slag substitution of 20% affected increasing durability, but an increase in substitution of 40% or more resulted in a decrease in durability.

5. Discussion

Marine concrete must be resistant to sulfate attack, carbonation, calcium leaching and chloride penetration. Physically, low permeability properties are the main requirement for concrete to have

resistance to chemical attack. However, the chemical composition of concrete is also a determinant besides its permeability.

Permeability is controlled by the w/c ratio and the volume of hydrated cement. The higher the w/c, the larger the pore volume and the increased permeability. Carbonization and calcium leaching are attacks against $Ca(OH)_2$ from hydration. Carbonized and calcium leaching concrete has a higher porosity, making it more sensitive to attack by other chemical species, such as sulfate or chloride. Moreover, calcium leaching causes a higher supply of calcium ions in the pore solution thereby increasing the rate of reaction in chemical attack [20].

Concrete with fly ash or GGBS substitution has better permeability than normal concrete. Mittermayr [21] found that concrete made with CEM IIIB cement (Blast furnace cement), fly ash and calcium carbonate with low w/c have high resistance to sulfate attack. The use of calcium carbonate, together with fly ash provides a synergistic effect in increasing cement hydration. Calcium carbonate chemically reacts with the aluminate in fly ash to form a carboaluminate phase, whereas physically, the calcium carbonate surface provides an additional site for the C-S-H phase deposition. The chemical similarity of calcium carbonate and C-S-H enhance the growth of C-S-H calcium carbonate particles [22,23].

Efforts to reduce pores are also carried out by adding inhibitors based on natural ingredients. Bambusa Arundinacea is reported to have the ability to replace nitrite and amine-based corrosion inhibiting admixtures for durable concrete structures due to its pore-blocking effects [24]. Meanwhile, [25] used silica fume to reduce pores and increase chemical resistance.

The resistance of concrete to chloride attack requires special attention. Sulfate-resistant cement is usually designed to have a low alumina content. This is because the alumina reacts with the sulfate to form an expansive ettringite which increases the risk of cracking. On the other hand, alumina is a species necessary to bind chloride to form Friedel's salt. The binding capacity of a concrete determines its resistance to chloride. And almost the same as the resistance to sulfate, concrete with SCM has better properties than normal concrete. If in general, the w/c is designed to a minimum to produce concrete with small pores, this is not the case with chloride resistant. The value of w/c needed is not too small, generally around 0.4 to ensure the availability of alumina which is ready to bind with chloride ions.

The porosity of the concrete is determined by w/c and the hydrated phases. Several studies have recommended blended cement with GBFS to produce a mixture that is durable in seawater. However, there is a controversy that says the substitution of GBFS is not suitable for environmental conditions containing magnesium sulfate and chloride.

Concrete with cement substitution using fly ash is considered suitable for applications in the marine environment in Indonesia. This is due to the abundant availability of fly ash in Indonesia. In 2020, fly ash and bottom ash from the steam-power plants in Indonesia be around 13.5 million tons, and only 10% have been used. Another reason is that the substitution of fly ash, with any calcium content, is thought to be effective in producing concrete that is able to withstand the attack of seawater, especially chloride. This is because fly ash has an aluminium content for the formation of Friedel's salt so that the chlorine is bound to the concrete.

The drawback of fly ash is its relatively low reactivity so that the substitution of fly ash at a relatively high level has an impact on decreasing compressive strength. Selection of fly ash with high fineness and high morphology [29] provides an opportunity to produce good properties as SCM, as well as adding activator to increase its reactivity [26–28].

6. Conclusion

Marine concrete has a risk of chemical degradation against sulfates, carbonates and chlorides attacks. For reinforced concrete, chloride ion attack is critical since it generates corrosion of the reinforcement.The chemical resistance of concrete is determined by the porosity and the chemical composition of the concrete. The aluminium content is required for concrete to increase the binding capacity against chloride. Concrete with fly ash as SCM has excellent potential to be applied to marine construction in Indonesia because the abundant availability of fly ash in Indonesia and the presence of aluminium species in fly ash provide an opportunity to increase the binding capacity to chloride.

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