Protection of Corrosion Attack in Reinforced Concrete Due to Chloride Ion using Calcium Stearate

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Abstract: Concrete is a man-made rock composed of cement, water and aggregates. During the hardening process of concrete, the amount of water not used in the cement hydration reaction, evaporates. The evaporated water leaves the capillary pores in the concrete. Chloride ions as one of the major ions in sea water, can penetrate into the concrete through these capillaries, resulting in corrosion of reinforcing steel bars. This process begins when the chloride ions reach the surface of the reinforcement. A method to control the corrosion process is by the use of the additives. The additives are utilized to improve the microstructure of concrete by reducing the water absorption. Calcium stearate is a compound that can improve these properties. The study investigated the use of calcium stearate in concrete as a concrete additive. The amount used was 0, 1 and 5 kg/m^3 of concrete. Two types of experiments were conducted: the water absorption and accelerated corrosion test. For the water absorption, the test specimen was a cylinder with a diameter of 75 mm and a height of 150 mm while for the accelerated corrosion test the specimen was a beam with a sized about 100×100×200 mm having a plain steel reinforcement bar with a diameter of 12 mm inserted inside. The test results showed that, the addition of calcium stearate in concrete decreased the absorption of 77% and reduced the corrosion by 78%.

Key words: Water absorption, chloride ion, accelerated corrosion, calcium strearate, absorption, leaves

INTRODUCTION

There are many types of the protection system of concrete reinforcement due to corrosion attack mainly infiltration of chloride ions (Maryoto, 2015a, b). Three of them are a coating system, membrane system and integral waterproofing system. A coating system is applied by superimposing the waterproof coating such as epoxy or acrylic styrene on the surface reinforcement or concrete. Membrane system is a system of concrete waterproof by covering the surface of the concrete with a layer of membrane. This membrane serves to protect the infiltration of water contained chloride ions into the concrete. The membranes are impermeable. Both of these concrete protection system have the disadvantages. Once a crack occurs on corrosion protection, they are very difficult to be repaired. This is because the crack location on the concrete extra hard to be detected. Even so, protection by coating or membrane system are able to reduce the corrosive attack on concrete reinforcement (Zacharopoulou *et al.*, 2014). Meanwhile, integral waterproofing system is the corrosion protection system of reinforcement in concrete. The system is to be a unit with the concrete.

The corrosion processes in concrete is mainly affected by chloride ions and oxygen diffusion through the capillaries and pores (Kahyaoglu *et al.*, 2002). During hydration process of cement, network of capillaries is formed. There are two types of capillary which is with a diameter of 10-20 nm and 1-2 nm diameter capillaries (Morin *et al.*, 2002). The corrosion processes starts when the passive layer of the concrete is broken (Broomfield, 1997). Corrosion due to chloride of seawater attacked on the steel bar also occurs in the concrete with fly ash-based geo-polymer (Astutiningsih *et al.*, 2013). The decreasing of carrying capacity in the prestressed concrete structures is faster than the reinforced concrete when the corrosion occurrences. Not only reduction of the pre-stressing strand bonding with concrete but also but also declines the prestressed action. This

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phenomenon does not take place in the reinforced concrete structures. The bonding capacity is weaken when the reinforced concrete attacked by corrosion. The weakening of the bond between reinforcement and concrete influent in loss of solidity between reinforcement and concrete to support the external load (Bilcik and Holly, 2013). The destruction of the reinforcement in the concrete not only happen in the reinforced concrete but also appears in prestressed concrete. Prestressed concrete structures decreased significantly the carrying capacity caused by corrosion attack (Darmawan, 2009).

Some researchers have attempted to resist corrosion attack due to the infiltration of chloride ions and nitrate ions into the concrete with a chemical that is mixed directly in the fresh concrete. The use of silica fume and metakaolin in mortar is able to increase resistance to corrosion attack (Diab *et al.*, 2011). Benzimidazole compound is also applied as an additive for integral waterproofing systems in concrete (Khaled, 2010; Ababneh *et al.*, 2009). The results show that, the use of material is able to reduce corrosion attack on the reinforcement of concrete structures. Not only there, green inhibitors have also been investigated for counteracting corrosion attacks. This material is renewable resources such as alkalis, amino acids and herbs (Rani and Basu, 2011). Nano silica and pozzolanic materil were applied in the concrete and reduced the penetration of chloride ion into concrete (Barmayehvar, 2017).

Additive materials added to prevent ingress of corrosive ions into the concrete has been widely circulated in Indonesia. Material prices are still much more expensive when compared with the price of concrete to be made more resistant to corrosion attack. The test is generally used to determine the ability of concrete to resist corrosion attack is the absorption and penetration testing based SKSNI, 1990. Although, this test can be known how much and deeply the infiltration of water into the concrete structure, a direct influence of corrosion on the reinforcement can not be measured in practice.

Another method is applied by adding calcium stearate directly into the fresh concrete. This type of testing was conducted in the macro-cell and half-cell potential. The results showed that the use of calcium stearate in concrete is able to reduce the tendency of the flow of current macro-cell. Also, based on the data half-cell potential can be concluded that the use of calcium stearate can reduce the occurrence of corrosion potentiality in concrete reinforcement (Maryoto, 2015a, b). The process of corrosion in concrete reinforcement can be triggered by the presence of corrosive ions such as chloride and sulfate ions. These chloride ions seep into the concrete along the water. Even though it cannot be determined directly that the use of calcium stearate in concrete can reduce the penetration of corrosive ions. Unfortunately, its influence on corrosion in concrete reinforcement has not been investigated yet (Maryoto, 2015a, b; 2017).

The o bjective of this study is to determine the effect of calcium stearate in the concrete related to water absorption and accelerated corrosion. Corrosion parameters are very important to verify how the effect of calcium stearate to protect concrete against corrosion by the chloride ions attack. Its ability to improve the corrosion resistance can be analysed in the real corrosion.

MATERIALS AND METHODS

Experimental work: This study uses the following tools: manual and digital scales, a set of sieve, ovens, concrete mixer, concrete mould, cone "Abrams", soldering tools and direct current power supply with a maximum capacity of 15 V. The raw materials used are as follows: calcium stearate, coarse aggregate, fine aggregate, cement, water, 3% sodium chloride solution, plain steel bar diameter of 12 mm, copper plates, wires, duct tape and a solution of ammonium citrate. Calcium stearate and direct current power supply can be confirmed as Fig. 1 and 2.

Calcium stearate is a hydrophobic material. It means that this material cannot be mixed with water without being dissolved prior to the other solution media. Superior properties owned by these materials when used in concrete is not toxic or poisonous and do not contain elements that can damage the concrete such as chloride ions and sulphate ions. Characteristics of the calcium stearate can be seen in Table 1 (Maryoto, 2015a, b).

Specimens: Concrete specimen for testing water absorption is a cylinder with a diameter of 75 mm and a height of 150 mm while for the accelerated corrosion test specimen is a beam with a height of 100 mm, width 100 mm and a length of 200 mm. Quality concrete in this study was set at 30 MPa. The type of testing for each code concrete mix can be seen in Table 2. The corrosion test specimen with a plain steel bar diameter 12 mm and length 100 mm inserted inside in concrete is shown in Fig. 3.

In the table the symbols A is to represent additive of calcium stearate and the numbers behind A that is 0, 1 and 5 show the calcium stearate content in kilograms per cubic meter of concrete.

Procedure of water absorption test: The water absorption test is conducted after specimens are cured, dried and
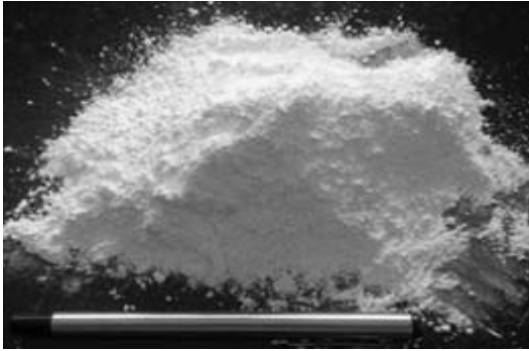
Fig. 1: Calcium stearate
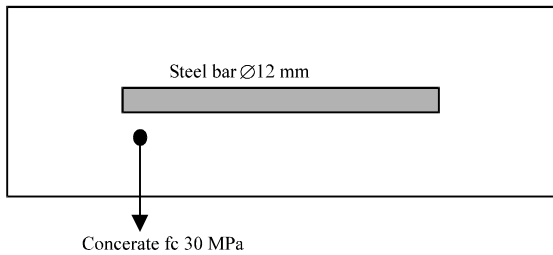

Fig. 2: Direct current power supply

Fig. 3: Specimen for accelerated corrosion

immersed in the water. The specimens are cured by soaking in the water for 28 days as SKSNI S-36-1990-03. Furthermore, the test specimen is dried in an oven with a temperature of 100±5°C for 3×24 h and then removed from the oven and cooling it during 1 day in the room temperature and weigh it in dry condition (a). The next step is immersed the specimens in the water for 10 min.
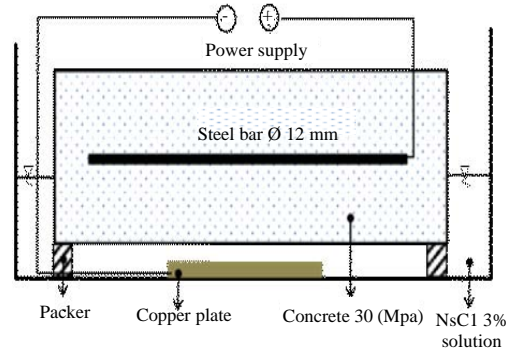

Fig. 4: Scheme of accelerated corrosion (Maryoto, 2017)

Table 1: Characteristic of calcium stearate

Properties	Analysis
Chemical formula	Ca $(C_{18}H_{35}O_2)_2$
Appearance	White fine powder
Melting point	120°C
Free fatty acid	Maximum 0.5%
Loss on drying	Maximum 2%
Metal content	0.65 (ppm)
Specific gravity	0.25

Table 2: Quantity of specimens

Codes	Concrete grade (MPa)	Water absorption (pieces)
A0	Cylinder	3
A1	Cylinder	3
A5	Cylinder	3
A0	Beam	3
A1	Beam	3
A5	Beam	3

Removes and cleans the water on the surface of concrete until in dry condition and weigh it on the saturated surface dry condition (b). Water absorption of the concrete can be calculated using the following formula (Maryoto, 2015b).

$$\text{The water absorption}(\%) = \frac{b-a}{a} \times 100\% \qquad (1)$$

Procedure of corrosion test: The test specimen size of 100×100×200 and 12 mm diameter steel bar inserted in the concrete is cured by covering it with a wet mattress for 28 days. Installation of the cables with the accelerated corrosion is shown as Fig. 4 (Maryoto, 2017). The test specimen is then immersed in a solution containing 3% NaCl as the electrolyte. Direct current electricity is applied to generate the accelerated corrosion process. After the corrosion test completed by the target date, corroded steel bar is taken out by breaking the concrete. Corroded steel reinforcement is cleaned with a wire brush. Steel bar is soaked in a solution of ammonium citrate 10% for 1 day to ensure that the steel bar is free from corrosion product. Percentage of corrosion can be calculated based on the

initial weight of steel bar and the final weight of steel bar after the corrosion product is removed from the steel bar. The ability of the concrete to resist corrosion attack can be shown on the percentage of rust on the steel bar. The smaller the corrosion product formed, the concrete ability to repel corrosion attack is getting better (Anonymous, 1990).

RESULTS AND DISCUSSION

Water absorption: The testing process of water absorption can be seen in Fig. 5a-c. Figure 5a shows the process of weighing the dry specimen shortly after removing from the oven. Figure 5b shows the process of immersion in water for 30 min. Figure 5c is the process of cleaning the surface of the specimen, so that, it becomes Saturated Surface Dry (SSD) and subsequently weighing is done. The results of water absorption tests for the whole specimen can be observed in Fig. 6.

Based on the test results in Fig. 6 shows that, the water absorption of the concrete specimen with the addition of calcium stearate 0 kg/m^3 of fresh concrete is 2.00%. The water absorption of concrete with the addition of calcium stearate by 1 and 5 kg/m^3 is 0.94 and 0.45%, respectively. The water absorption of concrete with calcium stearate 1 and 5 kg is reduced around 53 and 77%. The tendency of water absorption decreasing is similar with investigation of Maryoto (2015a, b, 2017). This trend is caused by a reaction between calcium stearate and cement to produce something that makes concrete compound becomes hydrophobic. Due to the hydrophobic nature of this improvement, the concrete is more difficult to absorb water and water is also difficult to infiltrate or penetrate into the concrete.

Other effects caused due to the hydrophobic concrete is the increased cohesion properties of water. The cohesion of the water and the concrete is greater than the adhesion. The attraction between water ions cause water hardness to seep into the concrete because the contact angle between the water and concrete is greater than contact angle between water ions.

Accelerated corrosion: Naturally corrosion caused by chloride ions to the concrete reinforcement could take place but the process takes 10-20 years. Testing of the contribution of material to corrosive attack can be done by creating artificial corrosion in the form of accelerated corrosion. The contribution of calcium stearate to protect concrete due corrosion attack is conducted on a laboratory scale. The processes of accelerated corrosion can be seen in Fig. 5. The test object is connected with electric power to generate artificial accelerated
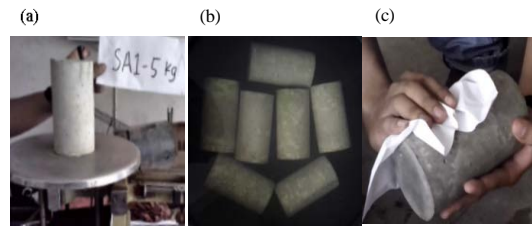

Fig. 5: a) Weight in dry condition; b) Immersing in the water and c) Wiping the water on the surface
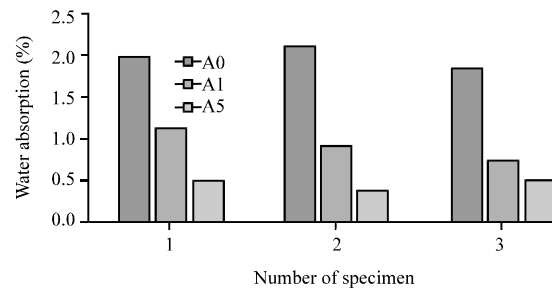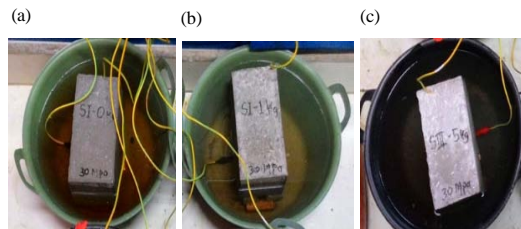

Fig. 6: Result of water absorption

Fig. 7: Color of NaCl solution after performing accelerated corrosion of specimen: a) A0; b) A1 and c) A5

corrosion. A power source is stopped on day 14 after all specimens give signs of corrosion. The visual signs can be visually described as a 3% solution of sodium chloride has a dark red colour because of the impact of corrosion product.

Based on Fig. 7a-c, it can be seen that the water used to trigger the process of corrosion on the test specimen A0 has darker red markings when compared with water under the test specimen A1 and A5. The darkness red colour is caused by rust product is squeezed out of the concrete and mixed with water. The more products of rust mixed with water, the colour is more intense red. These colour signs can be used to estimate how much corrosion has occurred on the reinforcement in the concrete. The water that is under test specimen A5 is still clear and very little rust products are mixed in water. Hypothesis based on the appearance of the color of water indicates that the
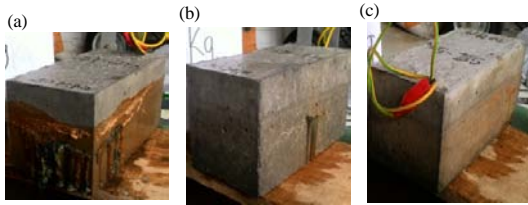
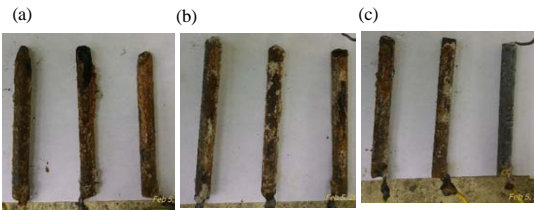Fig. 8: Crack on the surface, specimen: a) A0; b) A1 and c) A5

Fig. 9: Corrosion product on the surface, specimen: a) A0; b) A1 and c) A5

Fig. 10: The reinforcement after soaking in the ammonium: a) A0; b) A1 and c) A5

Fig. 11: Percentage of corrosion (accelerated corrosion)

greater the level of calcium stearate is used in the concrete mixture the less corrosion occurs on the reinforcement. Figure 8 a-c shows the cracks that generate on the surface of the specimen due to the expansion of corrosion products. Specimen A0 in Fig. 8a shows that elongated and widened the crack path almost occurs on the whole sides of the concrete surface. Even the corrosion product still appears, so, clear and stick to the surface of the specimen and the numbers are very much. Although, the visual width of the crack can be seen but the magnitude is still in the range 0.3-0.5 mm.

Rather different conditions can be observed in Fig. 8b. Cracks on the specimen A1 occurs only in part on an elongated path. Only a few of corrosion products still adhere to the concrete surface. The width of the cracks is described by the average width was 0.3 mm. A very striking results can be found in the test specimen A5 in Fig. 8c. Cracks almost did not occur on the surface of the concrete.

The result of the accelerated corrosion that occurs in the surface of the reinforcement can be seen in Fig. 9a-c. Corroded reinforcements are obtained after splitting the concrete specimen. Once the reinforcements are removed from the concrete, some parts of rust products remain adhered to the reinforcement. It can be confirmed clearly that the amount of corrosion product on the specimen A0 is more than the rust on the specimen A1 and A5. In order to analyze the levels of corrosion that occurs, the product adhered to the reinforcement rust are cleaned with a wire brush. A few of corrosion products still stick on the reinforcement after cleaning using a wire brush. Therefore,
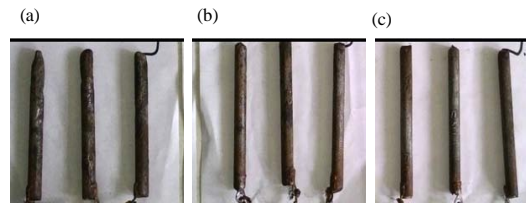
to remove rust perfectly, the reinforcements are soaked with a solution of ammonium citrate for 24 h. When the soaking has finished, the rust does not seem on the reinforcement such as those in Fig. 10. It appears that the entire reinforcement completely clean from the rust. Weight of reinforcement will be reduced after the corrosion process.

Percentage of corrosion of the reinforcement can be observed in Fig. 11. Figure 11 shows that, the percentage of corrosion on the specimen A0 is 11.79%, further corrosion on the specimen A1 and A5 are at 4.18 and 2.54%.

The corrosion rates are reduced when the addition of calcium stearate in the concrete is added. This trend also occurs in the previous analysis that the water absorption in concrete with higher of calcium stearate addition, absorption values begins to decline. The use of calcium stearate can reduce the corrosive attack by chloride ions in the concrete reinforcement.

CONCLUSION

Use of calcium stearate 1 and 5 kg/m^3 in concrete grade 30 MPa reduce the water absorption around 53 and 77% consecutively. Percentage of corrosion on the reinforcement of concrete decline around 64 and 78% when concrete is added 1 and 5 kg of calcium stearate.

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