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## Effect of Copper-Oxide-Nanoparticles'-Modified Paints to Properties of Cement-Based Mortar Exposed to Seawaters

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Concrete fouling is the accumulation of unwanted material on solid surfaces caused by seawater exposure. Copper oxide (CuO) nanoparticles can be added to protect concrete layer. This study analyse the performance of paint mixed with various amounts of copper oxide nanoparticles and copper-based film applied to cement-based mortar immersed in seawater. The mortar is then soaked in seawater for 7 and 28 days. To measure the effectiveness of the protective layer, compressive test and scanning electron microscopy characterization are conducted to selected samples. The compressive results show that seawater decreases the compressive strength of the sample. Mortar with 7.5% -CuO-nanoparticles' protective layer shows the compressive strength during 28 days increased than one during 7 days. SEM images show that there are more unreacted calcium hydroxide (CH) in sample without protection compared to mortar with CuO-nanoparticles' protective layer; at the same time, more calcium silicate hydrate (CSH) can be examined.

Забруднення бетону — це накопичення небажаного матеріалу на твердих поверхнях, спричинене впливом морської води. Для захисту бетонного шару можна додавати наночастинки оксиду Купруму (CuO). У цьому дослідженні аналізується ефективність фарби, змішаної з різною кількістю наночастинок оксиду Купруму, та плівки на основі міді, нанесених на цементний розчин, занурений у морську воду. Потім розчин замочували в морській воді впродовж 7 і 28 днів. Для міряння ефективності захисного шару було проведено випробування на стиск і характеристизацію за допомогою сканувального електронного мікроскопа (SEM) на вибраних зразках. Результати випробувань на стиск показують, що морська вода знижує міцність зразка на стиск. Розчин із захисним шаром з 7,5% наночастинок CuO демонструє, що міцність на стиск че-

рез 28 днів була більшою, ніж через 7 днів. СЕМ-зображення показують, що у зразку без захисту більше непрореагованого гідроксиду Кальцію порівняно з розчином із захисним шаром з наночастинок  $\text{CuO}$ ; водночас може бути діагностовано більше гідрату силікату Кальцію.

**Key words:** concrete, coating, copper oxide nanoparticles, compressive strength, fouling, ettringite.

**Ключові слова:** бетон, покриття, наночастинки оксиду Купруму, міцність на стиск, обростання черепашками та водоростями (підводної частини судна), етtringіт.

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## 1. INTRODUCTION

Indonesia is the largest archipelagic country in the world consisting of 17.508 islands with a coastline of 81.000 km. To expedite the wheels of economy, many transportation infrastructures are built in the form of full concrete or concrete/steel composite bridges between one island and another. Seaports and docks are also currently being built, which are currently experiencing a lot of damages, if not protected properly, thus, requiring routine maintenance. Degradation of concrete and corrosion of steel-based components in the marine environment, apart from being caused by atmospheric factors or physical and chemical properties of seawater, can also be caused by the attachment of marine biota [1–3]. Some biotas, which live in the sea, have developed their way of life by attaching themselves to objects, which are submerged in seawater, either temporarily or permanently [4–6]. For example, concrete supporting bridges or roads can be attached by barnacles or sessile organisms in biological terms. Concrete that is plastered with barnacles will become more brittle than original concrete [7]. This is caused by the formation of an acidic environment around the concrete due to the metabolic process of barnacles, as it is known that an acidic environment will weaken the bond of cement and water, causing the material to become brittle [8–10]. This condition will be further exacerbated by the diffusivity of seawater, followed by concrete abrasion caused by seawater currents, making the rate of chloride-ions' penetration into the concrete becomes faster, that, if it reaches the steel, results in corrosion of the reinforcement. One of the most widely used countermeasures at this time is to use antifouling paint, namely, paint containing biocidal compounds, which usually consist of cupric oxide compounds, which are antimicrobial [11, 12]. This type of paint is generally applied to ships and will be activated, when the ship is moving, that was called dynamic surface anti-

fouling type [13–15]. This type will not work effectively, when applied to the static structure such as bridge; so, it is necessary to find an antifouling paint formula that can work effectively on static structures and is environmentally friendly.

This research is conducted to synthesize protective compound consisted of paint and CuO nanoparticles (NPs) with various percentage. The mixture was applied to cement-based mortar then immersed into seawater. The density and compressive strength were measured in 7 and 28 days. Selected samples were then analysed for its morphological features by using SEM characterization to measure the effectiveness of protective compound.

## 2. EXPERIMENTAL

### 2.1. Materials

The Portland Cement Composite (PCC) and sand for light aggregate were obtained from local building store in Cimahi, West Java, Indonesia. The water used for reacting PCC and sand was the tap water from West Java, Indonesia. The paint used for protection of mortars was commercially available acrylic copolymer emulsion type. CuO-NPs' powder was prepared from electrolysis of copper scrap in Cimahi, West Java, Indonesia. The copper thin films were obtained from local supplier from Jakarta, Indonesia. The materials were dried and collected, resulting in black powder. Copper thin film was obtained from Cikarang, West Java, Indonesia too. Seawater for immersion of mortars was collected from West Java, Indonesia.

### 2.2. Methods

The mix design of mortars with protective coating is listed in Table. The ratio of PCC:sand was kept as 1:2.75, and w/c of 0.5. It was then mixed and moulded using 50 mm×50 mm×50 mm cubes according to ASTM C109: Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens).

After one day, the hardened mortar was unloaded from the mold and immersed in seawater. It was then tested for its density and strength at 7 and 28 days. The compressive strength of resulting mortars was measured using Universal Testing Machine confirmed to ASTM C-39. Debris from the test was collected for characterization purposes. SEM measurement was performed with HITACHI SU3500. Since the mortars are not conductive, it was coated with carbon with Ion Sputtering Method. The characterization was con-

**TABLE.** Mix design of mortars with CuO-nanoparticles' protective coating.

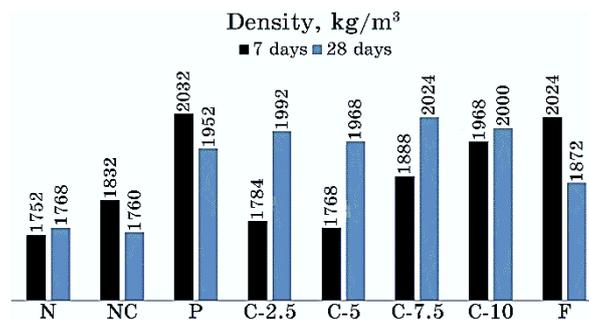
Code	CuO nanoparticles, %	Immersion method
N	—	Tap water
NC	—	Seawater
P	—	Seawater
C-2.5	2.5	Seawater
C-5	5	Seawater
C-7.5	7.5	Seawater
C-10	10	Seawater
F	—	Seawater

ducted at the BPU Politeknik Manufaktur Bandung, Indonesia.

### 3. RESULTS AND DISCUSSION

#### 3.1. Density Test Result

The density of mortars immersed in seawater is presented in Fig. 1. The samples with code NC, P, and F have lower density at 28 days compared to 7 days after immersion in seawater. In contrast, the densities of N, C-2.5, C-5, C-7.5, and C-10 were increased the more time immersed in seawater. The sample immersed in normal water (N) had its density increased. This is due to water for hydration, which was available all the time. When the mortars were not protected (NC) or using paint only (P), the densities at 28 days were decreased. This is due to the presence of organic compound such as glucose, which disrupts the hydration of mortars and can induce low consistency [16–18]. There are also leaching product from the



**Fig. 1.** Density results for mortars with various protection method and immersion media.

mortars because Ca has high atomic size. The same decrease phenomenon in density can be also seen in mortar protected with copper thin film (F). This is because the pores are sealed, so, the cement only relies on the starting water, when mixing, hence, the hydration reaction was not perfect. All the mortars covered with CuO-nanoparticles'-infused paint has the density increased at 28 days. The CuO act as antibiotic to negate the penetration from organic compound, and the water will help the hydration of cement. The visual image of NC, P, C-2.5, and F were presented in Fig. 2. The N and F samples has gray-like colour; this is because N is immersed in normal water, while F has protective film to prevent the penetration of seawater. The P sample has white-like colour from the paint. The C-2.5 sample has slightly blue colour, which indicates the formation of copper sulphate ( $\text{CuSO}_4$ ).

### 3.2. Vickers Microhardness Analysis

The compressive strength of mortars immersed in seawater is presented in Fig. 3. The samples with code NC, P, and F have lower

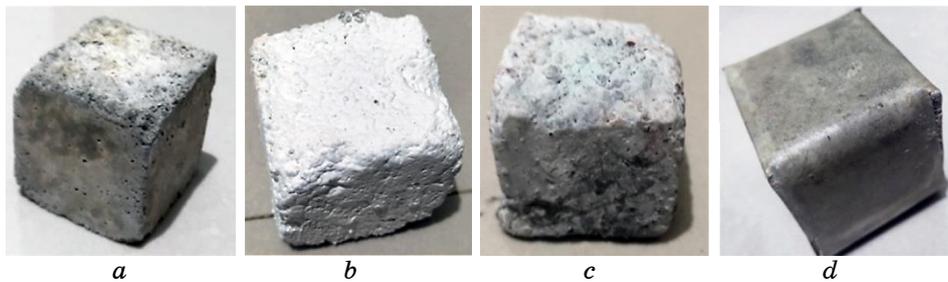


Fig. 2. The visual image of (a) NC, (b) P, (c) C-2.5, and (d) F.

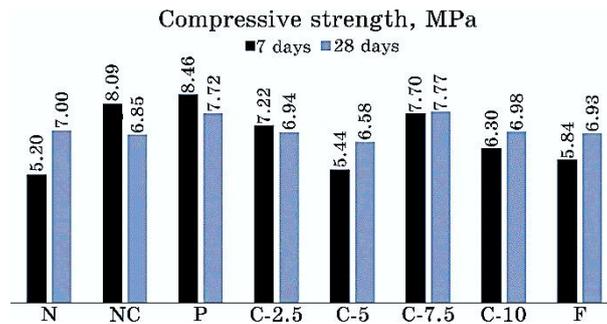


Fig. 3. Compressive strength of mortars with various protection method and immersion.

density at 28 days compared to 7 days after immersion in seawater. In contrast, the densities of N, C-2.5, C-5, C-7.5, and C-10 are increased the more time immersed in seawater. Mortars without coating and paint only have negative effect on seawater immersion. CuO-nanoparticles' addition on paint has mixed effect on compressive strength of mortar exposed to seawater. Small amount (2.5%) has no significant effect on the protection from seawater, as the compressive strength still decreased. Addition of 5–10% CuO nanoparticles protects the mortars from seawater. This is proven by the compressive strength development where as normal as mortar was immersed in normal water. Copper thin film also protects the mortar from seawater, since the film covers almost all the surfaces. Concrete acts like a protective layer, which provides excellent protection to reinforcing steel. In addition, a mixture of Portland cement with water will produce calcium silicate hydrate and calcium hydroxide, which are alkaline with a pH ranging from 13–13.5. This alkaline condition of the concrete will make the reinforcing steel in a passive condition and not corrode [19]. The entry of dissolved oxygen will trigger a series of electrochemical cells, which cause corrosion.

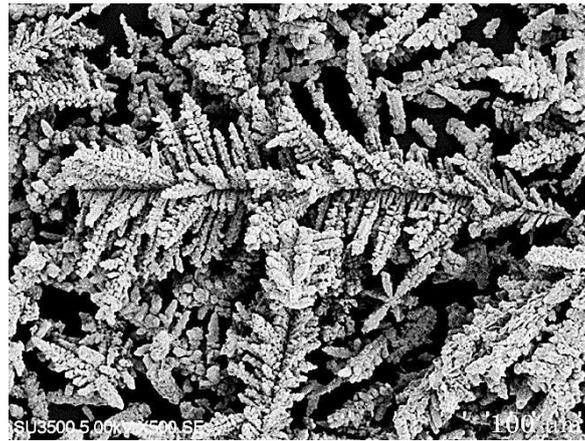
Dissolved chloride ions come from the penetration of seawater. CO<sub>2</sub> gas can also cause corrosion of concrete, but at a slower rate than corrosion caused by chloride penetration. Carbonation in concrete occurs due to the interaction between carbon dioxide gas in the atmosphere and hydroxide compounds in the moist concrete pores. The runoff of this carbonation process causes a decrease in the pH of the concrete and causes a shift in the corrosion potential of reinforcing steel to become actively corroded [20].

### 3.3. SEM Analysis

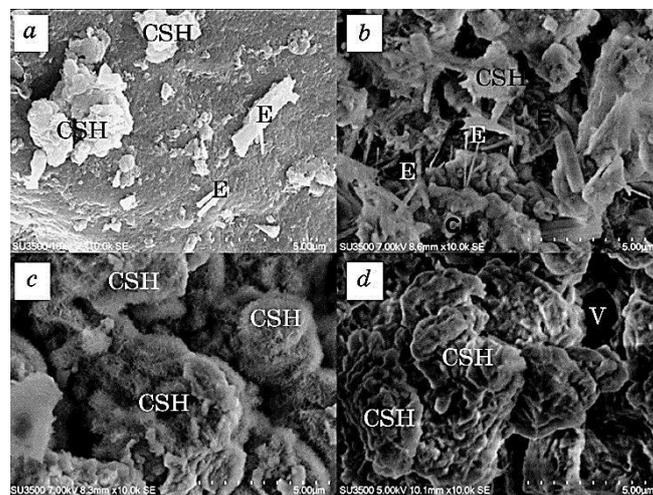
Figure 4 shows that the morphology of CuO-nanoparticles' powder has a dendritic-like structure with average particle size of 74  $\mu\text{m}$ . Finer size means that the specific area is higher, and the contact to surrounding is increased. To observe the performance of CuO after exposure in seawater environment, SEM test was conducted to the mortar immersed in normal water (N), mortar immersed in seawater without protection (NC), mortar with highest compressive strength, which was protected by paint and 7.5% CuO (C-7.5), and mortar with copper film (F). These data are represented in Fig. 5.

Figure 5, *a* shows the calcium silicate hydrate (CSH), which is a trademark compound of hydration and calcium hydroxide (CH) formation on mortar N. Both CH and CSH have a role in the strength of mortars [21].

Figure 5, *b* shows that there is some unreacted CH on mortar NC,



**Fig. 4.** SEM results for CuO nanoparticles magnified by  $\times 1000$  (left) and  $\times 10000$  (right).



**Fig. 5.** SEM images of (a) N, (b) NC, (c) C-7.5, and (d) F.

as well as ettringite (E). Ettringite plays an important role in setting time of mortars. The presence of CH indicates unreacted cement particles that is why the compressive strength of 28 days was lower than 7 days [22]. The presence of organic compounds in seawater delays the hydration of cement.

Figure 5, *c* shows the formation of CSH with the fibre-like structure on mortar C-7.5. This shows that CuO has a role on prevent the organic compound to interfere on hydration. Copper is reported to improve the concrete resistance against sulphate attack, setting

periods, and water tightness.

Figure 5, *d* also shows the presence of CSH mortar F. However, there is an internal pressure inside that makes the voids (V); and since most of the surface was covered, that is why, although the compressive strength development was normal, its strength was not as good as N or C-7.5.

#### 4. CONCLUSION

This study concludes that CuO can prevent the mortar from fouling after immersion in seawater. Mortar immersed in seawater tends to have lower compressive strength at 28 days compared to 7 days. Addition of 2.5 and 5% CuO in paint still cannot negate the strength decreasing effect of seawater. Mortar protected with paint and 7.5% and 10% CuO as well as copper film shows normal strength development. This shows that, when used at right amount, CuO powder can protect mortar from seawater environment.

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