A mathematical model for strength prediction of HPC containing copper slag as a cementitious material

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Abstract. High-performance concrete (HPC) encompasses cement, copper slag, sand, coarse aggregate, superplasticizer, and water. The strength of HPC is determined by the specific surface area of supplementary cementitious materials. Hence it is interesting to investigate the effect of copper slag as a cement replacement on the strength of HPC. In this study, three-level of water-to-cement ratios (0.3, 0.4, and 0.5) were chosen. The various concrete mixtures are produced with increasing copper slag contents from 0 to 40 wt.% in steps of 10 wt.% as cement replacement. To obtain two levels of fineness, the copper slag was milled using a ball mill. The result shows that the strength of concrete containing copper slag for all water-to-cement ratio was lower than the control mixture at an early age (7 days). For the longer curing periods (28 days), the compressive strength of concrete was similar or slightly higher compared to the reference mixture at the replacement level up to 20% for two-level of fineness. A new model, according to Abrams Law, which is Abram-RET, is being proposed by the author to predict the compressive strength of high-performance concrete at 28 days, which gives a strong correlation with the experimental results.

1. Introduction
The worldwide demand for copper continues to grow. The production of copper slag, which is a by-product obtained during the smelting and refining of copper matte, also increases. The production of copper slag worldwide is about 35 million tonnes yearly. This number is sufficient to produce 100 million cubic meters of concrete when it is used as a sand replacement, and it can be estimated that more than 300 million cubic meters of concrete can be generated if the slag is utilized as cement replacement [1].

Nevertheless, copper slag is only used for base construction, railroad ballast, and engineered fill, as reported by [2]. Copper slag cannot be used directly as cement replacement since this waste material has to be ground to decrease the size within micron meter as required by ASTM C1709-18. This is the reason why copper slag has not yet been widely used in concrete production especially for cement replacement. Looking into literature reported the use of copper slag as a cement replacement [3, 4]. They found that the highest compressive strength is achieved for 15% copper slag and 1.5% lime at 90 days of curing, which is twice as high compared to the strength at 28 days. The study used the copper slag as a cement replacement up to 60 wt% in steps of 10 wt% [5]. They found that the effect of copper slag on the hydration process was negligible. The previous study reported the potential use of copper slag as a cement replacement in reactive powder concrete (RPC) [6]. They concluded that the reactivity of copper slag could be enhanced by applying heat treatment. Regarding the strength
prediction, a mathematical model to predict the concrete strength using silica fume (SF) was proposed [7]. The study proposes a mathematical model to predict the concrete strength using Silica Fume and Styrene-Butadiene Rubber (SBR) [8].

In the current research, the influence of copper slag on the compressive strength of high-performance concrete (HPC) containing copper slag as the supplementary cementitious material is evaluated. A mathematical model for strength prediction of HPC containing copper slag as the cementitious material is studied.

2. Experimental investigation

2.1. Materials and grinding methods

As cement, an Ordinary Portland Cement (OPC type I) with moderate C_3A was used throughout all experiments. The use of cement with low or medium C_3A for high strength concrete is [9, 10]. They noticed that the cement with a high content of C_3A gives the lower compressive strength of concrete. Besides, the study found that a low influence on viscosity, reducing the demand for water, and a positive effect on compressive strength are the reasons to use cement with low C_3A (less than 3%) for ultra-high-performance concrete [11, 12]. However, since in Indonesia is difficult to find the cement containing 3% of C_3A, so that the author used the cement containing moderate C_3A (6%). The chemical compositions of OPC and copper slag are tabulated in table 1.

| Table 1. Chemical compositions and fineness of OPC and granulated copper slag (%) |
|-------------------------------|---------|---------|
| Constituents  | OPC     | Copper slag |
| SiO_2          | 19.86   | 34.40   |
| Al_2O_3        | 5.33    | 3.31    |
| CaO            | 64.14   | 5.89    |
| Fe_2O_3        | 3.03    | 52.86   |
| MgO            | 2.39    | 1.69    |
| SO_3           | 1.9     | -       |
| C_3S           | 51      | -       |
| C_2S           | 24      | -       |
| C_3A           | 6       | -       |
| C_4AF          | 11      | -       |
| Blaine permeability (cm^2/g) | 3350    | 928 (5 min) and 1798 (1 hours) |

The copper slag used in this study is a by-product obtained during the smelting and refining of copper. In Indonesia, a Smelter Plant operated by Mitsubishi materials corporation generates the copper slag using the wet process to separate the matte and the slag. This process needs a multi-furnace system, which is S-furnace, CL-furnace, and C-furnace [13].

After the excavation process, the raw materials go to the S-furnace for the oxidation process. Afterward, the materials containing copper concentrate are mixed with coal and silica sand in the CL-furnace. In this stage, the copper concentrates are separated into the matte and the slag. The matte is flowed to the C-furnace to generate pure copper, and the remaining slag is discharged and sent to the stockpile. Regarding the cooling process, the slag is flowed out in the CL slag outlet, and water is poured over it. In this quick cooling process, the slag changes from liquid to granulated, which contains pozzolanic components due to the oxidation process at the stage of S-furnace.

The level of fineness determines the reactivity of supplementary cementitious materials. So, in this study, the granulated copper slag is ground intensively using a ball mill. Since the granulated copper slag was in wet condition after the rapid cooling process using water, the slag was dried using the oven at a temperature of 100 °C for 24 hours before the grinding process. To obtain two levels of fineness, a short duration (5 minutes) and a long duration (1 hour) were chosen. The fineness of the granulated
copper slag was evaluated by their specific surface area (SSA) using the Blaine air permeability test, according to ASTM C204. The fineness of copper slag is shown in Table 1. The aggregates used in this study were fine aggregate and coarse aggregate. These aggregates are normally available in the batching plant. The physical properties of aggregates are shown in Table 2.

Table 2. Physical characteristics of aggregates.

| Test                     | Fine aggregate | Coarse aggregate |
|--------------------------|----------------|------------------|
| Specific gravity (oven dry) (g/cm$^3$) | 2.46           | 2.68             |
| Specific gravity (SSD) (g/cm$^3$)        | 2.34           | 2.53             |
| Bulk density (g/cm$^3$)                | 1.29           | 1.54             |
| Fineness modulus           | 3.4            | 7.34             |

The superplasticizer used in this research was carboxylic ether polymer (Structure 335) with long lateral chains that separate and disperses cement particles to obtain a longer slump life. The dosage of superplasticizer used in this research was 1.5% of the total weight of cementitious to obtain the slump of ±100 mm.

2.2. Mix design and mixing procedure
The mix design used in this research was based on Indonesian Standards (SKSNI T-15-1990-03). The water-to-cement ratio (w/c) used in this study was 0.3, 0.4, and 0.5. The concrete was made with copper slag varying between 0 and 40 wt% in steps of 10 wt%. A horizontal, inclined drum was used to mix the materials.

First, the dry materials (cement, copper slag, and aggregates) were mixed in this inclined drum with horizontal rotation for 1 minute. Afterward, the water was added, and finally, the superplasticizer was dosed. The total mixing time needed to obtain a homogeneous mixture was about 4 minutes. This method was applied to the concrete with w/c of 0.3 and 0.4. In the case of concrete with w/c of 0.5, the superplasticizer is not added to the mixture during mixing time since the slump of ±100 mm can be achieved without using the superplasticizer. The procedure of mixing is mentioned in Figure 1.

![Figure 1. Mixing procedure](image)

3. Result and discussion

3.1. Effect of copper slag on compressive strength
Figure 2 describes the effect of copper slag fineness as cement replacement on the strength of HPC with w/c of 0.3, 0.4, and 0.5 at 7 and 28 days. It can be seen that the strength of concrete containing copper slag for all w/c ratio was lower than the control mixture at an early age (7 days). It can be observed that the strength of HPC decreased with rising copper slag substitution in the concrete mixture. In this shorter curing ages, the use of copper slag as cement replacement did not have a positive effect on the strength enhancement of HPC. Besides, the use of copper slag with longer grinding time (1798 cm$^2$/g) does not significantly increase the compressive strength of HPC as seen in Figure 2. This phenomenon might be attributed to the heavy metals content in copper slag which tends to delay the setting time of cement hydration at early days as reported [10, 14].

The effect of copper slag on the strength of HPC at 28 days is also described in Figure 1. The strength of concrete increased at lower replacement levels and decreased at higher replacement levels
for two-level of fineness and all w/c. Nevertheless, it can be observed that the compressive strength of concrete was similar or slightly higher compared to reference mixture at the replacement level up to 20% for two-level of fineness, as shown in Figure 2(c) and 2(d). The highest compressive strength is achieved by 10% copper slag content (fineness of 1798 cm$^2$/g) at 28 days for w/c of 0.3., which is about 76 MPa, as seen in Figure 2(d). From these results presented, the strength of HPC using finer copper slag is higher than the HPC using coarser copper slag. This finding is caused by the finer copper slag which is more reactive than, the coarser ones. Looking into the literature, the study found that the strength of ultra-high performance mortar (UHPM) using the finer secondary copper slag is also higher compared to the strength of UHPM using the coarser secondary copper slag, which corresponds to the results presented [10]. The reaction degree is determined by the level of fineness of supplementary cementitious materials, which can speed up the cement hydration to generates CSH gel as hydration products to fill concrete pores and increases the concrete strength. This is the reason for the higher strength of HPC using the finer copper slag.

Figure 2. HPC compressive strength results for : (a). fineness 908 cm$^2$/g 7 days, (b). fineness 1798 cm$^2$/g at 7 days, (c). fineness 908 cm$^2$/g at 28 days, (d). fineness 1798 cm$^2$/g at 28 days.

3.2. Abrams formula
The optimum content of copper slag used in this research was a 10% replacement. Beyond that, the compressive strength decreased with increasing copper slag replacement, as seen in Figure 2. The compressive strength of the reference mixture was comparable or slightly lower than the 20% copper slag replacement at 28 days. Based on these parameters, a model can be proposed as a function of compressive strength and w/c. In this study, the author used the Abrams Law which represents a correlation between compressive strength and workability. The Abrams Law is expressed below:

$$Fcr = \frac{A}{B^{0.7c}}$$  (1)
where $f_{cr}$ stands for the compressive strength of concrete at a designated age, while A and B are the identified constants for a given age, material and curing condition and w/c is w/c ratio by weight. The result of the compressive strength of HPC reference in the function of w/c at 28 days is used to determine the identified constants (A and B). The least-squares method is used to calculate the correlation coefficient between compressive strength and w/c. To obtain the significance of a correlation coefficient of $R^2 = 0.99$, Abrams Law requires a single-size aggregate. However, this is problematic to implement in the construction projects because of the higher cost in concrete production when using a single-size aggregate especially the small size. Based on the linear regression approach, a best fitting curve can be drawn, as shown in Figure 3. Furthermore, a linear regression equation is expressed as follow:

$$Y = -1.551X + 2.2937$$  \hspace{1cm} (2)

The result of the correlation coefficient was less than 0.99 ($R^2=0.8948$) due to the use of two-size aggregates, as shown in Figure 3.

Based on Eqs. 2, the identified constants (A and B) can be calculated as:

$$\log(A) = 2.294$$
$$A = 197$$
$$\log(B) = 1.551$$
$$B = 36$$

Figure 4 shows the compressive strength results of HPC at 28 days using a two-level of fineness of copper slag. Due to the plotted data in this figure confirms a quadratic polynomial, the author proposes a new model with modifying Abrams Law as given in Equations 3:

$$f_{cr} = \frac{A}{B^{n/c}} \left[ 1 + f \left( \alpha \left( \frac{c'}{c} \right)^2 + \beta \left( \frac{c'}{c} \right) \right) \right]$$  \hspace{1cm} (3)

Where: $c'/c$ is copper slag replacement level (%), f is the ratio of copper slag fineness ($f \leq 1$), $\alpha$ & $\beta$ are the identified constants at 28 days.

By using empirical approach, the identified constants can be obtained: $\alpha = -9$ and $\beta = 2.25$.

Thus the author proposes the modified Abrams Law (Abrams-RET) for HPC at 28 days concrete using two-level of fineness as given in Equations 4:

$$f_{cr} = \frac{A}{B^{n/c}} \left[ 1 + f \left( -9 \left( \frac{c'}{c} \right)^2 + 2.25 \left( \frac{c'}{c} \right) \right) \right]$$  \hspace{1cm} (4)

This formula can be used for the fineness of copper slag between 1798 cm$^2$/g and 908 cm$^2$/g and the copper slag replacement level up to 20%. This also considers that there is a significant increase in the compressive strength of HPC at 7 days to 28 days. This Abrams-RET model has a good correlation with the experimental result as shown in figure 2.

![Figure 3. The relationship between water to cement ratio and compressive strength](image-url)
4. Conclusions

Based on the results obtained in this research, the following conclusions can be made:

- The strength of concrete containing copper slag for all w/c was lower than the control mixture at early ages. However, it was slightly higher or comparable than the reference mixture at longer curing ages for the replacement level up to 20%.
- The highest compressive strength of concrete can be enhanced by 10% copper slag with a fineness of 1798 cm/g and the w/c of 0.3 at 28 days of curing, which is about 76 MPa.
- The formulation of Abrams-RET for high strength concrete using copper slag as cementitious materials gives a strong correlation with the experimental results.

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