The Use of Granulated Copper Slag as Cement Replacement in High-Performance Concrete

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Abstract: This research studies the use of waste copper slag as a cement replacement in high-performance concrete (HPC). To obtain two level of fineness, the copper slag was milled using a ball mill. A mixture was prepared with different percentages of copper slag ranging from 0% to 40% in steps of 10%. To obtain the desired workability, a superplasticizer was used for the mixture using water to cement ratio of 0.3. Specific surface area (SSA) of the copper slag was assessed using the Blaine permeability test. The results obtained, showed that the strength of concretes with different copper slag proportions was comparable to or even better than the reference mixture at 56 days. The heavy metal content of copper slag can be solidified/stabilized in concrete, since they did not exceed the Indonesian Environmentally Regulation on the Management of the Waste of Hazardous.

Key words: Copper slag, heavy metal, high-performance concrete, TCLP.

1. Introduction

Currently, concrete has become a popular material for construction projects. The production of concrete annually is more than ten billion tons all over the world [1] and [2]. In Indonesia, over ten million tons of concrete precast are being produced annually. The production of cement dramatically increases to supply the demand for construction project. However, the amount of raw material needed in cement production is decreasing due to the large exploration by cement industry while at the same time the waste materials generated by mining companies are increasing steadily. The impact of these problems will cause environmental degradations and heavy metal pollution. The economic cost needed to recovery of such damage is significant. An alternative way with lower cost to solve these problems is to utilize the waste copper slag in concrete production. Copper slag is one of the by-product materials from the copper smelting. In Indonesia, around 400,000 tons of copper slag are produced per year by Freeport Company and Newmont Company [3]. This number is a motivation for the researchers to study the copper slag as aggregate or cement replacement in concrete. Several previous researchers have reported the potential use of copper slag as cement replacement in mortar and concrete. Moura *et al*. [4] found that the compressive strength of concrete containing copper slag increased gradually for all water-to-binder ratios in comparison to that of reference mixture at 28 days of curing. Another researcher reported that the strength of concrete containing 5% copper slag + 95% OPC was comparable to the reference mixture as reported by Al-Jabri *et al.* [5]. Arino *et al*. [6] and Tixier *et al*. [7] used copper slag combined with lime as an activator to speed up the hydration degree of binders. They found that the highest compressive strength is achieved for 15% copper slag and 1.5% lime at 90 days of curing, Edwin *et al*. [8] investigated the use of secondary copper slag in reactive powder concrete (RPC). They found that the use of secondary copper slag combined with vacuum mixing and heat treatment has a significant effect on the compressive strength of RPC at early days of curing (7 days) [8]. However, this achievement was not the case for longer curing ages since the strength of concrete at 28 and 56 days was only similar to the control mix for all treatments [8].

In this current study, the compressive strength of high-strength concrete (HPC) using two level of fineness the copper slag and the leachability of heavy metals in concrete are investigated.

2. Material and Experimental Procedure

2.1. Material

The copper slag used in this research was a granulated copper slag from an Indonesian Smelter Plant operated by Mitsubishi materials corporation. The concentrates obtained by the separation process with the tailings using the flotation method are smelted in this plant. In this process needs a multi-furnace system which are S-furnace, CL-furnace, and C-furnace [9]**.** After passing the S-furnace (oxidation process), the mixed feed containing copper concentrate, coal and silica sand is injected into the CL-furnace to separate the matte and the slag. At the end of CL-furnace, the slag is discharged, and the remaining matte is flowed to the C-furnace to generate blister copper. The granulated copper slag contains pozzolanic components due to the oxidation process at the stage of S-furnace.

The cement used in this research was Ordinary Portland Cement (OPC type I) from Indonesian Company (PT. Indocement Tunggal Prakarsa). 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	-
Blaine permeability (cm^2/g)	3350	928 (5 min) and 1798 (1 hours)

In Indonesia, both fine aggregate and coarse aggregate used in concrete production are natural aggregates and artificial aggregate. Generally, the natural aggregate can be found in the river basin which has roundness texture and smooth surface. Furthermore, artificial aggregate is a granite rock which is ground using a stone crusher to obtain the desired gradation. 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 (Structuro 335) with long lateral chains which 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. Grinding of Granulated Copper Slag

Before grinding, the granulated copper slag was dried using the oven at a temperature of 100 ^{o}C for 24 hours. Afterwards, this copper slag was intensively ground using a ball mill. To obtain two level of fineness, a short duration (5 minutes) and long duration (1 hours) 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.

2.3. Mixing Procedure

The mix design used in this research was based on Indonesian Standards (SKSNI T-15-1990-03). The water to cement ratio used in this study was 0.3. The concrete was made with copper slag contents 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 60 seconds. Afterwards, the water was added, and finally, the superplasticizer was dozed. The total mixing time needed to obtain a homogeneous mixture was about 240 seconds.

2.4. Compressive Strength

After curing in a water bath, the cylinders (100 mm diameter and 200 mm height) were tested in triplicate to evaluate the compressive strength according to ASTM C 39 at the age of 7, 28, and 56 days. A compressive strength machine with the capacity of 1800 kN was used. To obtained the compressive strength of concrete, the load at rupture obtained was divided by the cylinder area.

2.5. Toxicity Characteristic Leaching Procedure (TCLP Test)

The method used for the TCLP test was SW-846 Method 1311 (USEPA Test Method). The method used to determine the concentration of heavy metal ions was an air-acetylene flame (AAS). The concrete specimens were crushed and extracted using this method to calculate the metal released as the similar condition when the copper slag is stored in a landfill.

3. Results and Discussions

3.1. Toxicity Characteristic Leaching Procedure (TCLP Test)

Table 3. The Results of TCLP Test of HPC Containing Copper Slag

Heavy metal compounds	Results of w/c. 0.3 (mg/l)		Methods	Indonesian Regulation on the Management of the Waste of Hazardous [10]	
	10% CS	20% CS		TCLP A	TCLP B
Arsen (As)	-	-	AAS	3.0	0.5
Mercury (Hg)	<0.00001	<0.00001	CV-AAS	0.3	0.05
Cadmium (Cd)	0.008	0.008	AAS	0.9	0.15
Lead (Pb)	0.024	0.033	AAS	3	0.05
Zinc (Zn)	<0.001	<0.001	AAS	300	50

Heavy metal content ≥ TCLP A = landfill category 1 (double geomembrane) ; TCLP A <Heavy metal content ≥ TCLP B = landfill category 2 (single geomembrane) ; Heavy metal content ≤ TCLP B = landfill category 3 (without geomembrane).

Table 3 shows the results of TCLP test on the sample of 10% and 20% copper slag replacement of OPC with the water to cement ratio of 0.3. It is clear that the heavy metal content after solidification/stabilization is lower than the limit value of the TCLP A and TCLP B. This means that according to the Indonesian Waste Management Regulation (PP 101 2014) [10], only a landfill without geomembrane is needed. The decreased of the heavy metal compound in HPC after leaching test (TCLP) is caused by the solubility of these compounds in cement particles during hydration process to generate metal hydroxides.

3.2. Compressive Strength

Fig. 1 describes the effect of copper slag fineness as cement replacement on the strength of HPC with water to cement ratio of 0.3 at 7, 28 and 56 days. In general, the strength of HPC containing copper slag at 7 days was lower than reference mixture. The compressive strength of HPC containing lower replacement level was higher than reference mixture after curing at 28 days. The highest compressive strength (78 MPa) was achieved for 10% copper slag with a fineness of 1798 cm2/g at 56 days of curing, which increased about 18% in comparison to that of the reference mixture. Comparing the result of HPC strength using two level of fineness, it can be observed that the strength of HPC using finer copper slag is higher than the HPC using coarser copper slag as seen in Fig. 1. This achievement was caused by the fact that the finer copper slag was more reactive than the coarser one. The finer copper slag had a specific surface area of 1798 cm2/g, which was double in fineness than the coarser one. When the finer copper slag reacts with the cement, the pozzolanic compounds of this material may play a role to bond the unreacted portlandite ($Ca(OH_2)$) from cement to generate CSH gel. The pozzolanic activity is determined by the summation of three oxide ions, which are SiO_2, Al_2O_3, and Fe_2O_3. The SiO_2 content in copper slag used in this research was 34.4% as seen in Table 1. The amount of CSH gel formed is determined by the amount of SiO_2 available during the hydration process. When the copper slag is added to the mixture, the unreacted portlandite as a hydration product in cement itself reacts with SiO_2 to generate CSH gel as a hydration product cement and copper slag. This CSH gel will fill the concrete pores. This is the reason for increasing the compressive strength of HPC containing lower replacement level of copper slag compared to that of the reference mixture as seen in Fig. 1. This phenomenon also occurred for the HPC containing coarser copper slag for lower replacement level, which is higher in strength compared to the reference. This current finding corresponds with the result obtained by Edwin *et al*. [8]. They concluded that the increase in compressive strength of concrete is determined by CSH gel generated during the hydration process which leads to decrease in the porosity of concrete.

It is clear from the above discussion that copper slag has the potential to be used as cement replacement in high-performance concrete. Besides the fact that the concrete quality can still be maintained, the production of this concrete implies low costs. Therefore, further study is necessary to investigate the effect of copper slag on permeability and shrinkage in HPC.

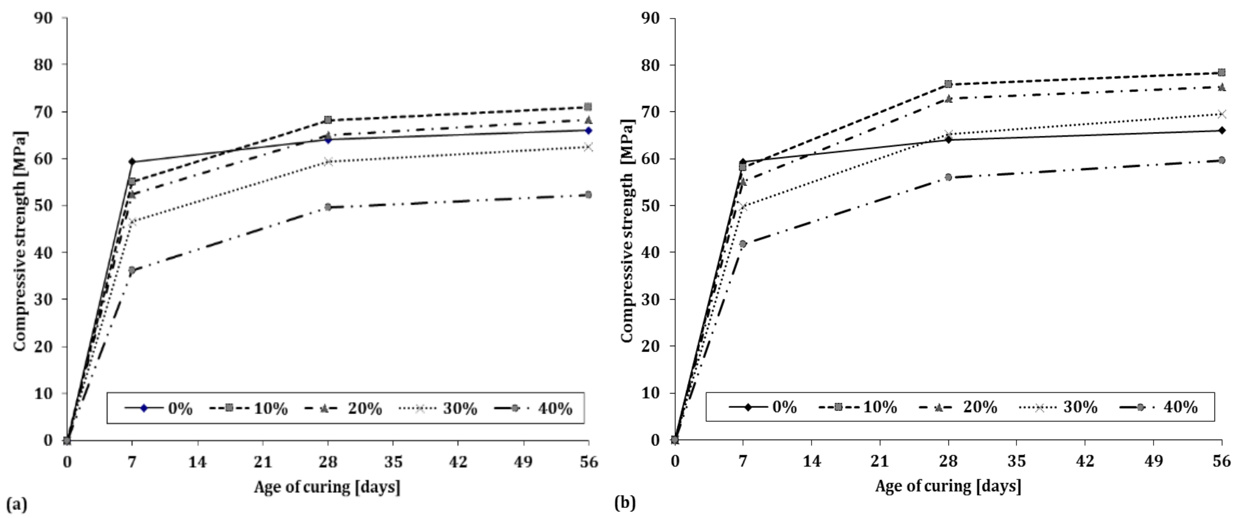

Fig. 1. HPC compressive strength results for: (a). fineness 908 cm^2/g ; (b). fineness 1798 cm^2/g.

4. Conclusion

In this article, the use of copper slag as cement replacement in high-performance concrete was studied. Based on the results obtained in this research, the following conclusions can be made :

1. The highest compressive strength of concrete can be enhanced by 10% copper slag with a fineness of 1798 cm^2/g at 56 days of curing, which is about 78 MPa.
2. The higher compressive strength of concrete can be obtained by using the finer copper slag. This confirms that the reactivity of supplementary cementitious material is determined by the specific surface area.
3. The results of TCLP test show that HPC containing 10% and 20% copper slag indicates low heavy metal content, which only needs a landfill without geomembrane.
4. It is recommended that the use of copper slag as cement replacement up to 30% can obtain HPC with good quality and low cost.

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