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Effects of recycled copper slag as cementitious material in ordinary Portland cement mortar

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Copper slag is a by-product obtained during the smelting of matte and the refinement of copper. Despite the increasing rates of copper slag reuse, to this date, the tremendously large amount of its annual production lead to its disposal in dumps or stockpiles. One of the potential applications for reusing copper slag is in cement production. The use of copper slag as supplementary cementitious material in ordinary Portland cement mortars is investigated in this study. Various mortar samples were produced with increasing copper slag contents ranging from 0 to 50 wt%. To study the effects of copper slag substitution as a replacement for cement on the properties of cement mortars, specimens were prepared containing different percentages of copper slag with total binder. The physicochemical properties of the cement mortars, i.e., slump, workability, water absorption, and compressive/flexural strength, were investigated aiming towards the replacement of cement. In addition, chemical resistance properties were evaluated by measuring the weight loss during the immersion of cement mortars in 5% sulfuric acid solutions for 28 days.

Key words: Copper slag, Cementitious material, Compressive strength, Chemical resistance.

Introduction

In recent years, concrete has been the most extensively used construction material, and constitutes an essential material for the construction of high-rise buildings, transport networks, and water and energy infrastructures. Construction of green building is a fundamental part of the concept of sustainable development that can be applied to the infrastructure sector. Additionally, the amount of natural resources is declining due to the increased consumption of the produced cement and concrete. However, the fact that the production process of Portland cement requires approximately 4000 MJ/ton of cement especially for the grinding and calcination of raw materials [1-3], thereby causing air pollution due to the discharge of carbon dioxide emission imposes the necessity of use of less costly and environmentally friendly by-products that enhance the performance of the materials. By-products generated by the mining industry can be problematic with regards to the environment, since these materials need large areas for storage, and given the need to protect the environment from the dangers of heavy metals. However, the availability of landfill disposal of slag is not sufficient. Consequently, it would be highly beneficial to exploit these by-products in the cement and concrete production [4-6].

Copper slag (CS), which consists primarily of complex copper, iron sulfides, and traces of other metal sulfides, is a by-product generated during smelting, and is used to extract copper metal from the ore. This process entails pyrometallurgical procedures, i.e., oxidizing the mineral with atmospheric or oxygen-enriched air to eliminate the sulfur in gaseous form such as sulfur dioxide and the iron obtained after mixing an ore-flux with the iron oxide produced in the form of slag [7-9]. The copper slag that is obtained may exhibit pozzolanic activity, and may be used in the manufacturing of addition-containing cements [10-12]. However, its suitability for this particular use may be questioned, owing to the presence of certain heavy metals, even though such pollutants may be trapped in the cement matrix [13, 14]. In this paper the effects of the incorporation of the copper slag in cement are investigated in reference to its workability, slump, water absorption, compressive and flexural strength, and resistance to sulfuric acid.

Experimental

Copper slag (CS) obtained from a metal fabricating company (Seowon Co., Ltd.) at Cheongju in Korea was used. Its chemical composition and physical properties were characterized by wavelength dispersive X-ray fluorescence (WD-XRF), Scanning electron microscope (SEM), particle size analyzer (PSA) and X-ray diffractometer (XRD). The cement used in this study was ordinary Portland cement (OPC) produced by the

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Table 1. Mixing ratio of the cement mortars. (OPC: ordinary Portland cement, CS: copper slag, C: cement, W: mixing water, S: sand, B: C + CS).

Samples	W/B (wt %)	CS ratio (wt %)	Unit weight (kg/m^3)			
			C	W	CS	S
OPC	50	0	480	240	0	1323
CS-10	50	10	432	240	48	1427
CS-30	50	30	336	240	144	1435
CS-50	50	50	240	240	240	1443

Korean company (Ssangyong Cement Industrial Co. Ltd). This cement type is the most extensively used in the construction industry in Korea. Fine sand was aslo used that was extracted from the nearby Nakdong river in the area of Kyoungbuk. These are the aggregates that are typically used in normal concrete mixtures in Korea.

To study the effects of CS substitution as a replacement for cement (C) on the properties of cement mortars, specimens were prepared containing different percentages of CS with total binder (C + CS). The mix design for this study is shown in Table 1. The water-binder ratio of the mortar was fixed at 0.5. All mortars were prepared using the hand-mixed method [15]. The mixtures were compacted using a vibrating table. The slump was measured for all mixtures using the flow table test, according to EN 1015-3 [16], before placing the mortar into the mold. The specimens were demolded after 24 h, cured in water and then tested at room temperature at the required age. Tests to determine specific gravity and water absorption for the cement mortars were carried out in accordance to ASTM C128 [17].

To determine the unconfined compressive strength, a cube (50 × 50 × 50 mm) was cast for each mixture, and three constructed samples were tested after 7, 14, and 28 days of curing [18]. Moreover, to determine the flexural strength for each mixture, three 40 × 40 × 160 mm prisms were cast and tested after 7, 14, and 28 days of curing [19]. The resistance of the CS that substituted the cement mortars was evaluated in a sulfuric acid environment by measuring the weight decrease during the immersion of the cement mortar cubes (50 × 50 × 50 mm) in 5% (by weight of water) sulfuric acid solution (pH = 1.0). The pH of the solution was checked periodically using a portable pH meter. If the pH of the solution decreased, additional concentrated sulfuric acid was added to restore it to the required pH value.

Results and Discussion

The results on the chemical analysis of the CS are presented in Table 2. The CS consisted primarily of Fe, Cu, and Zn. These are metals that remain after the refinement process of copper alloy, in addition to small amounts of other metals. It can be seen from Table 2 that the CS has a very low calcium (Ca) content of approximately 4.43 wt %, whereas the calcium content of OPC originated from free or combined limes that contribute to approximately 60% of its content. This indicates that copper slag is not chemically a very reactive material to be used as a cementitious material since sufficient quality of lime must be available in order to reach the required rate of hydration and to achieve the required early-age strength. However, CS contains has high concentrations of Si and Fe from SiO_2 and Fe_2O_3, respectively, compared to OPC. Therefore, CS is expected to have potential to produce quality pozzolans.

Table 2. Chemical compositions of the copper slag (CS) measured by WD-XRF.

Elements	Fe	Cu	Si	Al	Mg	Zn	Ca	O
wt%	12.18	13.24	5.52	7.35	4.15	2.38	4.43	40.5

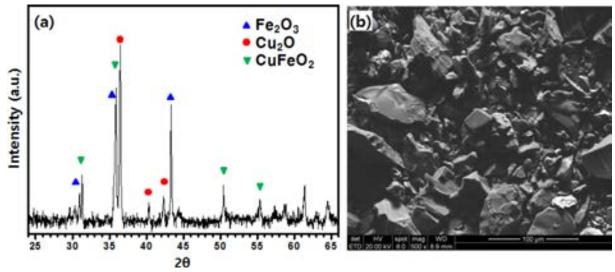

Fig. 1. Crystal phases (a), and particle morphology (b) of the copper slag (CS).

Fig. 1 shows the crystal phases of the CS analyzed by XRD and particle morphology observed by SEM. As shown in Fig. 1(a), CS comprised of metal oxides, i.e., Fe_2O_3, Cu_2O, and $CuFeO_2$ synthesized with the primary metals of the CS. The CS particles were angular, black, glassy, and shiny, with sharp edges, as observed in Fig. 1(b). The average particle size (D50) measured by PSA was 120 mm.

Table 3 shows the physical properties of the CS-blended cement mortars. The workability of cement mortars was assessed based on the measured slump of the cement mortars. The measured water absorption values for the cement mortars (CS samples) using CS was higher than that of the OPC sample. This suggests that CS would demand more water than that required by OPC. Therefore, it is expected that the free water content in the cement mortars will decrease as the CS content increases, which will consequently lead to a decrease in the workability of the cement mortars.

It is clear from Table 3 that the workability of the cement mortars decreases with the increase of CS content. For the control mixture (OPC sample), the measured slump was 135 mm, whereas for the CS-50 sample, containing a 50% replacement of CS, the measured slump was 126 mm. This considerable decrease in the workability with the increase of the CS quantity is attributed to the high water absorption that is a

Table 3. Physical properties of the cement mortars for different proportions of CS.

Samples	Slump (mm)	Water absorption (%)	Specific gravity (ton/m^3)
OPC	135	9.5	2.01
CS-10	134	9.8	1.99
CS-30	130	10.4	1.96
CS-50	126	10.7	1.95

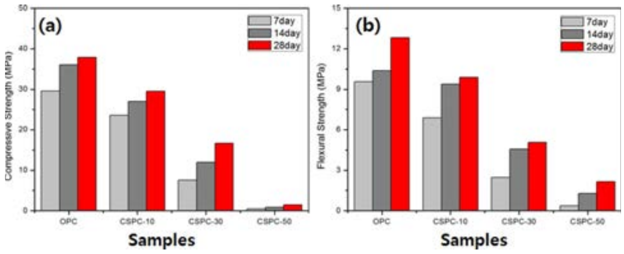

Fig. 2. Average compressive and flexural strengths of the CS replaced cement mortars at 7, 14, and 28 days of curing.

characteristic of CS.

CS has a specific gravity of 3.56 which is higher than that of sand (2.75) and OPC (3.10), and may result in production of cement mortars with higher density when used for the substitution of cement. However, Table 3 shows that there is minor decrease in the density of cement mortars with the increase of the CS quantity. This is mainly due to the higher water absorption compared to the control mixture (OPC sample), which can cause the surplus quantity of free water to remain after the absorption and hydration process have been completed.

The compressive and flexural strengths of cement mortars for different proportions of CS at 7, 14 and 28-days are shown in Fig. 2. Fig. 2(a) shows that the compressive strength of cement mortar is slightly decreased as the CS quantity increases up to 50%. The compressive strength was reduced significantly owing to the significant increase in the free water that remained in the mixture in excess of that required for the hydration of cement mortar and for proper compaction. The excessive free water content in the mixtures with a high CS content causes the particles of the constituents to separate leaving pores in the hardened mortar, which consequently cause a reduction in the compressive strength. Three prisms (beams) were also tested for flexural strength under third point loading conditions. The average modulus of flexural strength was determined using the following expression [18]:

$$F_{Fl} = PL/bd^2 \tag{1}$$

where F_{Fl} is the flexural strength, b is the average width of the specimen, and d is the average depth of the specimen. Fig. 2(b) indicate that the flexural strength results elicited from all tested mixtures showed a similar behavior to the compressive strength results.

The negative effect of CS cementitious material on the mortar strength presented in this study was dissimilar with the CS used in the case of De Schepper et al. [5], especially for 20 wt% CS. In De Schepper's study [5], the strength development of mixtures with slag was faster at early ages but elicited a slower response at 7 days of curing compared to reference mixtures. Moura et al. [12] found a positive effect in the use of CS on compressive strength. The CS used in their study had fineness comparable to cement. This was not the case for the CS used in this study. The lower strength observed in this study could be attributed to the retardation of cement hydration due to the presence of heavy metals in CS, as shown in Table 2. The lower strength could also be due to the fact that the very fine particles of the slag supplied a large amount of surface area per unit volume for coating with cement [19]. This might have effectively reduced the amount of cement available for binding the fine and coarse aggregate required to provide adequate strength [14].

The photographs of the cube specimens of the control mixture (OPC), and the CS-incorporated cement mortars (CS samples) exposed to 5% sulfuric acid solution (pH = 1.0) for 28 days are presented in Fig. 3. The fine aggregate of the OPC specimens were completely exposed after 28 days compared to the CS specimens. The CS-10 specimen showed expansion due to extensive formation of gypsum in regions close to the surface [20], which in turn reflected an increase in the weight of the CS-10 specimen as depicted in Fig. 4. However, with the higher replacement of cement by CS, the gains in weights diminished. Additionally, as time progressed, weight losses were recorded. The CS-50 specimen displayed complete rupture of the surface with the exposure of the fine aggregates.

Fig. 4 presents the weight reduction of cement mortar with immersion time at different proportion of CS. The main reaction products formed in OPC are portlandite [$Ca(OH)_2$] and calcum silicate hydrate (C-S-H) which are vulnerable to chemical degradation [21]. On complete hydration, the OPC paste consists of 50- 60% of C-S-H and a Ca/Si ratio of of calcium sulfoaluminates of 15-20% by volume, while CS pastes consist mainly of C-S-H with a Ca/Si ratio of approximately 1.0, without any formation of $Ca(OH)_2$ [22]. In OPC, the portlandite [$Ca(OH)_2$] tends to decompose at pH values below 12, while the calcium sulfoaluminates decompose at pH values below 11 [21, 22]. Fig. 4 also indicates that all the cement mortars undergo progressive weight loss with time after immersion in sulfuric acid solutions. The cement mortars with CS (CS samples) exhibited better resistance as compared to the OPC samples, a fact that may be attributed to the properties and structure of binders. It is well known that the resistance

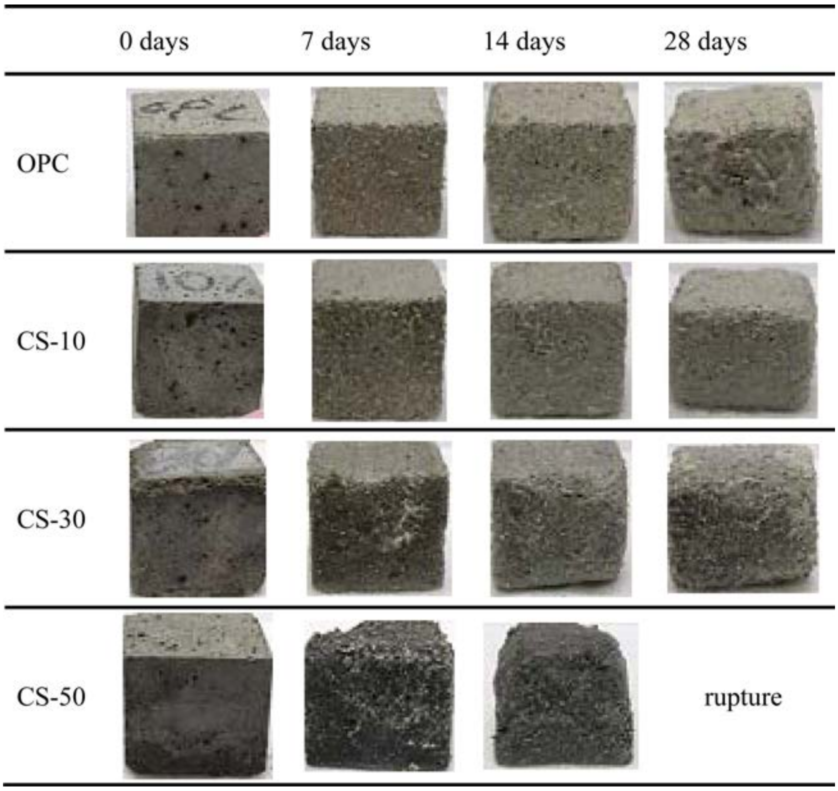

Fig. 3. Images showing the deterioration of cement mortar specimens with CS content after immersion in a sulfuric acid solution (pH = 1.0) for 28 days.

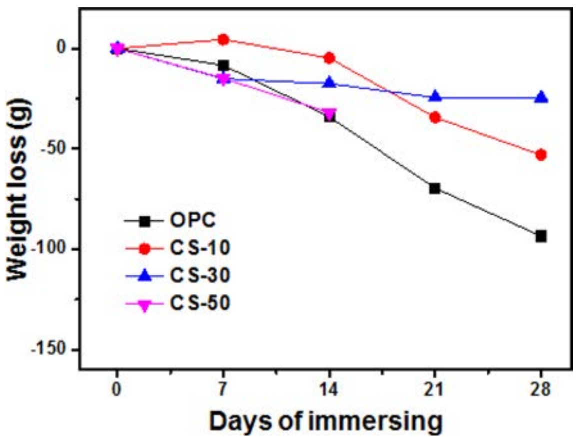

Fig. 4. Weight variation of the cement mortar specimens with CS content after immersion in a sulfuric acid solution (pH = 1.0) for 28 days.

to an acid attack depends on the permeability of the cement mortars [23]. Cement mortars with permeable structures are more vulnerable to the acid attack, and a less permeable microstructure is achieved with the application of CS [20]. This may constitute the reason on for the better resistance that is elicited for the acid attack of the CS-incorporated cement mortars.

Summary

In this study, the use of copper slag (CS) was investigated as supplementary cementitious material in ordinary Portland cement mortars. The workability of the cement mortars decreased with the increase of CS content in cement mortars. This was attributed to the high water absorption characteristics of CS. The compressive and flexural strengths of the CS-incorporated cement mortars (CS samples) were found to be lower than those of ordinary Portland cement (OPC) mortar. Heavy metals present in the CS retarded the initial and final setting of cement due to interference with the normal hydration reactions. The deterioration rate of OPC subjected to a sulfuric acid attack was much higher than that of CS samples and, increased replacement of CS increased the resistance to the sulfuric acid attack.

Acknowledgments

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