O U R N A L O F

Ceramic Processing Research

Effect of copper slag as a fine aggregate on the properties of concrete

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The effects of using copper slag as a replacement for sand on the physical properties of concrete were investigated. Copper slag was classified into three types depending on particle size distribution. Concrete mixes were prepared with different proportions of copper slag replacing the sand content, ranging from 0 to 100%. The mixes were evaluated for workability, air content, compressive strength, flexural strength and chemical resistance properties. The chemical resistance was evaluated by measuring weight loss throughout the immersion of cement mortars in a 5% sulfuric acid solution for 28 days. The results indicated rapid increases in workability with increases in the copper slag percentage. The use of copper slag as sand replacement yielded a comparable increase in compressive and flexural strength. The optimum percentage of copper slag for mechanical strength and chemical resistance was 60%.

Key words: Concrete, Copper slag, Mechanical strength, Chemical resistance.

Introduction

For many years, the beneficial utilization of some industrial by-products has been recognized in improving the properties of fresh and hardened concrete. Byproducts such as pulverized fuel ash, silica fume and ground granulated blast furnace slag can be added in different proportions to concrete mixes as either a partial substitute for Portland cement or as admixtures [1-3]. Concrete prepared with such materials shows improved in workability and durability compared to normal concrete and is used in the construction of power and chemical plants, as well as under-water structures. The use of certain waste materials is well documented in design specifications. However, new by-products and waste materials are generated by various industries; the dumping or disposal of these materials can causes environmental and human health problems. Therefore, the recycling of waste materials offers great potential in the concrete industry [4-6].

Copper slag is an industrial by-product material produced from the manufacture of copper. Approximately 24.6 million tons of slag are generated from the world copper industry [7]. Although copper slag is widely used in sand-blasting and in manufacturing of abrasive tools, the remainder is disposed of without further reuse or reclamation. Copper slag possesses mechanical and chemical characteristics that qualify it for use in concrete as a partial replacement for Portland cement or as a substitute for aggregates. For example, copper slag possesses excellent soundness characteristics, good abrasion resistance, and good stability all of which favor aggregate use [8-10]. Copper slag also exhibits pozzolanic properties since it contains little CaO and several other oxides such as Al_2O_3 , SiO_2 , and Fe_2O_3 . The use of copper slag in the concrete industry as a replacement for cement and/or fine aggregates has the benefits of reducing disposal costs and assisting environmental protection [11, 12].

Although several studies [1-12] have reported the effects of copper slag replacement on the properties of concrete, further investigations are necessary to obtain the comprehensive understanding for an engineering basis to allow the use of copper slag in concrete. The main objective of this study was to investigate the effects of using copper slag as a partial and/or full replacement for sand in mortars and normal concrete. The effects of copper slag replacement as a fine aggregate on the compressive and tensile strength of concrete cured for different periods were investigated. The durability of concrete made with copper slag was studied by conducting initial surface absorption and total absorption tests.

Experimental Procedure

The cement used in this study, the most widely used cement in the Korean construction industry, was ordinary Portland cement (OPC) produced by the Korean S Company. Fine sand was obtained from the nearby Nackdong River, in the Kyoungbuk Area. This is a typical aggregate used in normal concrete mixtures in Korea. The copper slag used in this work was

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Fig. 1. Gradation of sand and copper slag types of CS-A, CS-B and CS-C.

obtained from Seowon Co., Ltd. The copper slag was ground in the laboratory into a fine powder of the required particle sizes. The ground slag was classified according to the average particle size into three types, as shown in Fig. 1. The gradation tests conducted on the fine sand and copper slag showed that they both met specifications requirements for concrete.

To study the effect of copper slag substitution for fine aggregates on the strength of cement mortars, specimens were prepared with different weight percentages of copper slag comprising the aggregate phase [13]. The mix design for this study is shown in Table 1. The overall mixing time was approximately about 4 min. The mixes were compacted using a vibrating table. The slump of the concrete mixes was determined to ensure that it was within the design value and to study the effect of copper slag replacement on the workability of the mixes [14]. The specimens were demolded after 24 h, cured in water and then tested at room temperature at specified ages.

 Table 1. Mixing ratio of concrete mixtures (OPC: ordinary Portland cement, CS: copper slag, C: cement, W: mixing water, S: sand) and test items.

Classification	CS contents (%)	W/C (%)	Unit weight (kg/m)				
			С	W	S	CS	
OPC	0	50	480	240	1423.8	0	
CS-20	20	50	480	240	1139.1	383.3	
CS-40	40	50	480	240	854.3	766.7	
CS-60	60	50	480	240	569.5	1150.0	
CS-80	80	50	480	240	284.8	1533.3	
CS-100	100	50	480	240	0	1916.7	

To determine the unconfined compressive strength, a cube of $50 \times 50 \times 50$ mm in size was cast for each mix. Three samples were tested after 7, 14 and 28 days of curing. To determine the flexural strength for each mix, three $40 \times 40 \times 160$ mm prisms of each mix were cast and tested after 7, 14 and 28 days of curing [15, 16]. The resistance of the copper slag-substituted concrete mixes to sulfuric acid environments was determined by measuring the weight decrease over the course of the immersion of concrete mix cubes ($50 \times 50 \times 50$ mm) in 5% (by weight of water) sulfuric acid solution (pH = 1). The pH of the solution was checked periodically using a portable pH meter. In the case of solution pH increase, concentrated sulfuric acid was added to return the solution to the required pH.

Results and Discussion

The effects of copper slag replacement as a fine aggregate on the workability and density of concrete are presented in Table 2 for different proportions of copper slag of different size types in the aggregate

Table 2. Experimental results for flow, air content, and compressive and flexural strengths with different copper slag types and replacement percentages.

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CS-type	CS contents	Flow (mm)	Air content (%) -	Compressive strength (MPa)		Flexural strength (MPa)	
				7day	28day	7day	28day
-	0	130	4.8	27.3	42.9	5.5	10.8
А	20	120	6.3	17.5	49.9	3.7	12.7
А	40	108	7.5	7.1	39.9	2.5	10.3
А	60	100	25.0	3.7	11.0	1.3	1.9
В	20	156	7.0	22.5	56.3	3.8	14.1
В	40	147	6.4	20.6	53.7	3.6	13.9
В	60	142	6.1	19.6	52.5	3.5	14.0
В	80	138	5.7	5.9	37.4	1.4	8.8
С	20	160	6.4	30.7	55.9	5.9	13.8
С	40	180	7.3	31.3	56.7	6.1	14.2
С	60	205	8.0	36.5	57.5	6.7	14.7
С	80	215	8.5	26.3	47.5	4.8	11.1
С	100	220	9.2	24.9	35.4	3.8	8.5
	CS-type - A A B B B B B C C C C C C	CS-type CS contents - 0 A 20 A 40 A 60 B 20 B 40 B 60 B 80 C 20 C 40 C 60 C 80 C 80 C 100	$\begin{array}{c cccc} CS-type & CS \ contents & Flow \ (mm) \\ \hline & - & 0 & 130 \\ A & 20 & 120 \\ A & 40 & 108 \\ A & 60 & 100 \\ B & 20 & 156 \\ B & 40 & 147 \\ B & 60 & 142 \\ B & 80 & 138 \\ C & 20 & 160 \\ C & 40 & 180 \\ C & 60 & 205 \\ C & 80 & 215 \\ C & 100 & 220 \\ \end{array}$	$\begin{array}{c cccc} CS-type & CS \ contents & Flow \\ (mm) & Air \ content \\ (\%) & (\%) \\ \hline \\ \hline \\ - & 0 & 130 & 4.8 \\ A & 20 & 120 & 6.3 \\ A & 40 & 108 & 7.5 \\ A & 60 & 100 & 25.0 \\ B & 20 & 156 & 7.0 \\ B & 40 & 147 & 6.4 \\ B & 60 & 142 & 6.1 \\ B & 80 & 138 & 5.7 \\ C & 20 & 160 & 6.4 \\ C & 40 & 180 & 7.3 \\ C & 60 & 205 & 8.0 \\ C & 80 & 215 & 8.5 \\ C & 100 & 220 & 9.2 \\ \end{array}$	$\begin{array}{c cccc} CS-type & CS contents & Flow (mm) & Air content (%) & \hline Compress (Mm) & \hline (\%) & \hline (Mm) & \hline (\%) & \hline (\%) & \hline (Mm) & \hline (\%) & $	$ \begin{array}{c cccc} CS-type & CS \ contents & Flow \\ (mm) & Air \ content \\ (\%) & \hline COmpressive \ strength \\ (MPa) & \hline (MPa$	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $

mixtures. The workability of the concrete mixes was assessed based on the measured flow of the fresh concrete. It is clear from Table 2 that the workability of concrete increases significantly with increased copper slag content of the CS-C types.With contents of types CS-A and CS-B, however, the workability of the concrete decreases significantly with the addition of copper slag. For the OPC sample, the measured flow is 130 mm; for CS-C types, containing 100% copper slag and 0% sand, the measured flow is 220 mm. This considerable increase in the workability with the increased copper slag quantity is attributed to the low water absorption and glassy surface of copper slag [17] compared to sand; these cause a surplus quantity of free water to remain after the absorption and hydration processes are completed. This increased workability may have a beneficial effect on the concrete in that concrete mixes with low water-to-cement ratios, for the same amount of sand replaced, may retain good workability, and exhibit greater strength and improved durability compared to conventional concrete. However, it should be noted that the CS-A and CS-B mixes with high copper slag contents did not positively affect concrete performance.

The average 7- and 28-day compressive strengths for different proportions of copper slag of different sizes are shown in Fig. 2. The results show that the compressive strength of concrete increases slightly as the copper slag quantity is increased to 60% in the CS-C case. For CS-A and CS-B additions, the compressive strength of concrete is slightly increased as the copper slag quantity is increased to 20%. At higher proportion of copper slag, the compressive strength decreases significantly because of the dramatic increase in the free water content remaining in the mix after the hydration of cement paste and the proper compaction of the fresh concrete, reflecting the increased flow shown in Table 2. The excessive free water content in the mixes with high copper slag contents causes the constituent particles to separate, leaving pores in the hardened concrete, which consequently decrease the concrete strength. The highest compressive strength of ~57.5 MPa is achieved in the sample containing 60% CS-C compared to the 42.9 MPa compressive strength of OPC sample. This indicates an increase of almost 34% in the compressive strength compared to that of the OPC sample. However, the mixture with 60% replacement of CS-A type copper slag shows the lowest compressive strength of ~ 11 MPa which is less than 25% of that of the OPC sample.

Three prisms (beams) of each mix 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. 3 indicate that the flexural strength of all mixtures showed similar behaviors to the compressive strength. The results show that the flexural strength of the concrete increases slightly as the copper slag quantity is increased to 60% substituted copper slag in the CS-B and CS-C cases. In the case of CS-A, the compressive strength of the concrete increases as the copper slag quantity is increased to 20%. Beyond these proportion of copper slags, the flexural strengths decrease significantly. The highest flexural strength of $\sim 14.7 \text{ MPa}$ is achieved in the sample containing 60% CS-C compared to the 10.8 MPa flexural strength of the OPC sample. This corresponds to an increase by almost 36% in the flexural strength compared to that of the OPC sample. However, the mixture with 60% CS-



Fig. 2. Average compressive strengths with different proportions of copper slag and size distribution types of (a) CS-A, (b) CS-B and (c) CS-C.



Fig. 3. Average flexural strength with different proportions of copper slag and size distribution types of (a) CS-A, (b) CS-B and (c) CS-C.

erting age

23 day

23 day

21 day

28 day

28 dan

28 day

14 day

14 day

14 day

(a)

OPC

A-20

A-40

A-60

(b)

B-20

8-40

B-60

8-80

(c)

C-20

C-40

C-60

C-50

acid solution for 28 days.

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7 day

7 day

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Fig. 4. Images showing the deterioration of concrete specimens with varying copper slag contents and size distribution type of (a) CS-A, (b) CS-B and (c) CS-C after immersion in pH = 1.0 sulfuric

A copper slag shows the lowest flexural strength of ~ 1.9 MPa, which is less than 18% of the flexural strength of the OPC sample.

Fig. 4 presents images of the concrete specimens after immersion in 5% aqueous sulfuric acid solution for 28 days. The concrete mixes with CS-C type copper slag exhibit better resistance than the OPC mix, or mixes containing CS-A or CS-B type copper slags. The main reaction products formed in OPC are portlandite (Ca(OH)₂) and calcum silicate hydrate (C-

Fig. 5. Weight variation of the concrete specimens with varying copper slag contents and size distribution type of (a) CS-A, (b) CS-B and (c) CS-C after immersion in pH = 1.0 sulfuric acid solution for 28 days.

S-H) which are both vulnerable to chemical degradation [19]. On complete hydration, the OPC paste consists of $50 \sim 60\%$ of C-S-H with the high Ca/Si ratio of $15 \sim 20\%$ calcium sulphoaluminates by volume, while the copper slag-modified pastes consist mainly of C-S-H with a Ca/Si ratio of ~ 1.0 , without any formation of Ca(OH)₂ [20]. In OPC, portlandite (Ca(OH)₂) tends to decompose at a pH below 12.0, while calcium sulphoaluminates decompose at a pH below 11.0 [19, 20].

Fig. 5 shows the weight variation of the concrete specimens with copper slag contents and size types of

CS-A, CS-b and CS-C after immersion in sulfuric acid solution with a pH of 1.0 for 28 days. From Fig. 5, all the concrete mixes noticeably experience progressive compressive strength losses with time upon immersion in the sulfuric acid solution. The concrete specimens with copper slag exhibit better resistance than the OPC sample which may be attributed to the properties and structure of the binders [21]. The concrete mixes containing CS-C type copper slag exhibit better resistance than either the OPC mix, or the concrete mixes containing CS-A or CS-B type copper slags. It is well known that the resistance to acid attack depends greatly on the permeability of the concrete [22]. Concrete with a permeable structure is more vulnerable to acid attack; less permeable microstructures are obtained by applying copper slag as a fine aggregate [23], which may contribute to the improved resistance to acid attack of the copper slagincorporating cement mortars.

Summary

In this study, the effects of using copper slag as a replacement for sand on the properties of concrete mixtures were investigated. The workability of concrete increased significantly with the increase of CS-C type copper slag content, which may benefit the concrete in that concrete mixes with lower water-tocement ratios and greater strengths than those of conventional concrete can be produced. The highest compressive strength of ~ 57.5 MPa was achieved in the sample with 60% CS-C copper slag replacing sand, which corresponds to an increase by almost 34% in the compressive strength compared to that of the conventional sample. The flexural strength of all mixtures showed similar behavior to the compressive strength results. The concrete specimens with copper slag exhibited better acid attack resistance than the conventional sample, which is attributed to the properties and structure of binders in the concrete. The concrete containing the copper slag with a particle size most similar to that of sand exhibited better resistance than concrete containing other types of copper slags.

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References

- K.S. Al-Jabri, M. Hisada, S.K. Al-Oraimi and A.H. Al-Saidy, Cem. Concr. Compos. 31 (2009) 483-488.
- 2. T.-Y. Tu, Y.-Y. Chen and C.-L. Hwang, 36 (2006) 943-9508.
- 3. M. Khanzadi and A. Behnood, Const. Build Mater. 23 (2009) 2183-2188.
- 4. B.M. Mithun and M.C. Narasimhan, J. Clean. Prod. 112 (2016) 837-844.
- 5. M.U. Ashwath, Bull. Ass. Cons. Civ. Eng. (Ind) 12(2) (2013) 23-29.
- T. Ayano, O. Kuramoto and K. Sakata, J. Soc. Mater. Sci. Jpn. 49(10) (2000) 1097-1102.
- 7. N. Palankar, A.U. Ravi Shankar and B.M. Mithun, J. Clean. Prod. 129 (2016) 437-448.
- 8. M. Tang, B. Wang and Y. Chen, Concrete 4 (2000) 30-32.
- 9. W. Wu, W. Zhang and G. Ma, Mater. Des. 31 (2010) 2878-2883.
- 10. L. Zong, J. Qingdao Inst. Architect. Eng. 24(2) (2003) 20-22. 11. C.J. Shi, C. Meyer and A. Behnood, Resour. Conserv.
- Recycl. 52(10) (2008) 1115-1120.
- T. Ayano and K. Sakata, Am. Concr. Inst. Spec. Pub. 192 (2000) 141-158.
- 13. BS 1881: Part 125, Testing concrete: methods for mixing and sample fresh concrete in the laboratory. British Standard Institute (BSI), 1986.
- 14. BS EN 12350: Part 2, Testing fresh concrete: slump test. British Standard Institute (BSI), 2000.
- BS EN 12390: Part 3. Testing hardened concrete: compressive strength of test specimens. British Standard Institute (BSI), 2000.
- BS EN 12390: Part 5. Testing hardened concrete: flexural strength of test specimens. British Standard Institute (BSI), 2000.
- K.S. Al-Jabri, A.H. Al-Saidy and R. Taha, Const. Build Mater. 25 (2011) 933-938.
- EN-196-1, Methods of Testing Cement-Part 1: Determination of Strength, CEN, Brussels, Belgium, 2005.
- 19. S.D. Wang and K.L. Scrivener, Cem. Concr. Res. 25(3) (1995) 561-571.
- 20. D.M. Roy and G.M. Idorn, ACI J. Proc. 79(6) (1982) 445-457.
- 21. C.W. Hong, J.-I. Lee and J.H. Ryu, J. Ceram. Process. Res. 17(7) (2016) 768-772.
- P.S Ambily, C. Umarani, K. Ravisankar, P.R. Prem, B.H. Bharatkumar and N.R Iyer, Const. Build Mater. 23 (2009) 2183-2188.
- 23. M. Najimi, J. Sobhani and A.R. Pourkhorshidi, Const. Build Mater. 25 (2011) 1895-1905.