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THE EFFECT OF COPPER SLAG ON THE HYDRATION AND MECHANICAL PROPERTIES OF CEMENTITIOUS MIXTURES

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ABSTRACT

The effect of copper slag on the hydration of cement-based materials is studied. Up to 15% by weight of copper slag was used as a portland cement replacement. Hydration reactions were studied through semiquantitative X-ray diffraction and TGA/DTA. Samples of copper slag and hydrated lime (ASTM type S) were used to test the pozzolanic properties of the slag. The porosity was examined using mercury intrusion porosimetry. A decrease in capillary porosity was observed while the gel porosity was increased. A significant increase in the compressive strength for up to 1 year is observed. © *1997 Elsevier Science Ltd*

Introduction

The most common type of slag produced in metallurgical operations is blast furnace slag. Long-term performance records in manufacturing blended cement, lightweight aggregates, and pozzolans for portland cement have demonstrated blast furnace iron and steel slag to be economical and durable (1). Copper slag however is not effectively utilized in the United States, whereas in Canada, approximately 45% is used in base construction, railroad ballast, and engineered fill (2).

Major copper producing regions of the United States are located in the southwestern states, especially in Arizona where large quantities are generated as a by-product of the smelting operation (3,4). The utilization of slag obtained from copper mining operations for applications such as portland cement replacement in concrete and/or as a cement raw material has the benefit of eliminating disposal costs while lowering the cost of concrete. The potential application of copper slag in concrete as a partial substitute for portland cement is studied in the present work.

There are three main objectives for this study. Copper slag is characterized for particle size distribution, Blaine fineness, specific gravity, and chemical and mineralogical compositions. Samples are examined by semiquantitative X-ray diffraction (QXRD) for the potential reaction of copper slag and calcium hydroxide. The hydration process of the slag cement mixtures are studied using QXRD and thermogravimetric analysis (TGA). Finally, the porosity and compressive strength development of mortars with copper slag are studied.

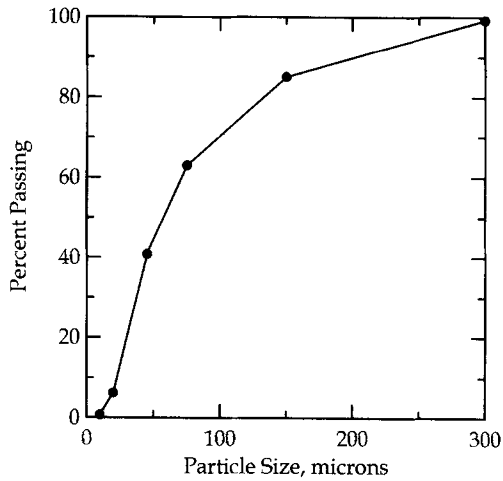

FIG. 1.
Particle size distribution of copper slag.

Characterization of Copper Slag

Physical Properties

The specific gravity as measured by ASTM C128 was 3.5. The size distribution was determined using a sonic sifter. Average particle sizes of 5 replicate samples are reported in Figure 1. The D_{50} is 55–60 μm. The average Blaine fineness of two replicate samples was

TABLE 1
Composition of different copper slags

Reference	Origin	Cu	CuO	SiO_2	Fe_2O_3	MnO	CaO	MgO	Al_2O_3	S	SO_3	LOI
(8)	Copper Queen	1.35		15.9	64.2	0.3	7.0	1.1	10.0	0.2		
	Detroit			24.9	51.9	5.8	7.3	1.7	8.4			
	Prince	1.15		19.1	54.1	0.3	12.3	2.5	10.3	0.2		
	Old Dominion		2.36	17.1	71.5	1.0	3.2	1.6	3.3			
	United Verde	0.12	1.79	24.7	58.2		9.0	0.5	5.7			
	Bisbee	0.25		21.7	50.0		7.0		21.0			
(9)	Quebec	0.4		34.5	49.5	0.1	2.2	1.5	6.6	1.2		−5.2
	Quebec	0.4		36.8	50.0	0.09	1.9	1.5	7.2	1.1		−6.1
	Ontario	1.1		26.5	60.1	0.1	2.1	1.6	3.7	1.3		−5.9
(10)	Spain		0.93	18.4	76.9	0.02	0.32	0.01	3.0		0.50	−5.4
(12)	Poland			43.1	13.4		19.3	5.6	15.8		0.65	0.05
(13)	Taiwan			34.3	53.7		7.9	0.94	3.8		3.78	
Present study	Arizona		0.65	35.2	52.8	0.03	3.3	0.57	5.0		2.46	−4.6

Negative LOI values indicate a gain due to the oxidation of sulfur and iron oxide, FeO.
The present study used a JEOL JXA 8600 electron microprobe.

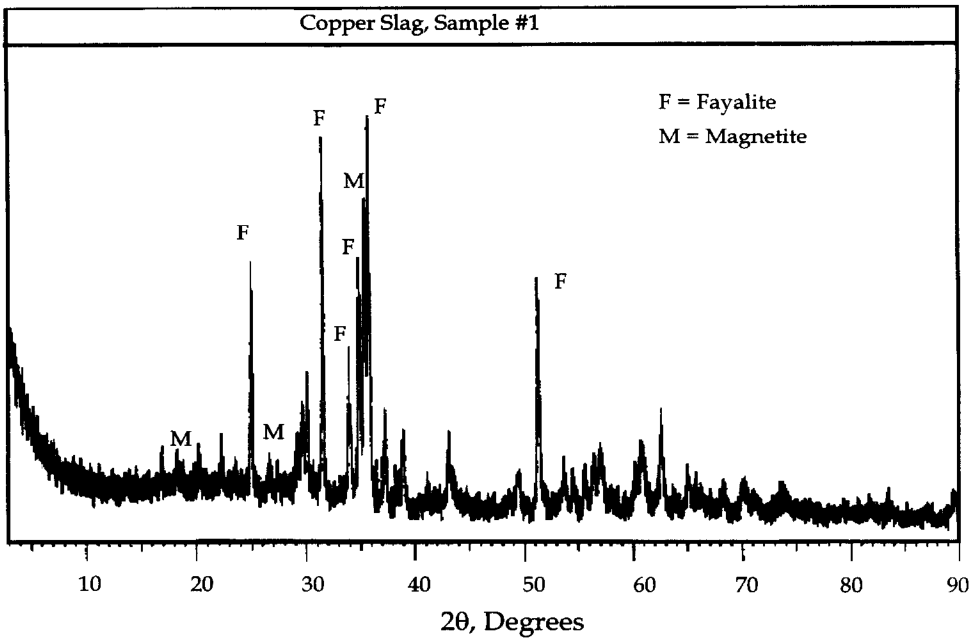

FIG. 2.
XRD pattern of a sample of as-received copper slag.

2,700 cm^2/g. This methodology corresponds to ASTM C 204 (the "b" constant was equal to 0.903). In order to compare the fineness of the slag to that of portland cement, the area of the grains per unit of volume (intrinsic value) instead of the area per unit of weight (whose value depends on the specific gravity) must be calculated. One would obtain a specific surface area of 9,450 cm^2/cm^3 for the slag and 10,900 cm^2/cm^3 for a typical Type I Portland Cement (Blaine fineness: 3,460 cm^2/g); indicating that copper slag is as fine as a Type I Portland Cement.

Chemical Composition

In the early days of copper mining, high-grade oxidized ores were smelted directly in blast furnaces (5). The copper content of the slag was quite high whereas the produced copper was impure and required considerable refining (6). Eventually, the practice of smelting in blast furnaces was abandoned. Currently, the high-grade oxide ores are mixed with sulfide ores and smelted to matte. Low-grade oxide ores are treated by leaching (4,7).

Chemical analysis of various copper slags, including the one used in the present study, are shown in Table 1. Copper content is limited to 1–2% of the production of the smelter and may be present in the form of metallic copper, delafossite, and mostly in the form of cuprite (copper silicate). In addition to iron oxides, other oxides of silicon, aluminum, calcium, and magnesium constitute 95% or more of the total oxides (8–12).

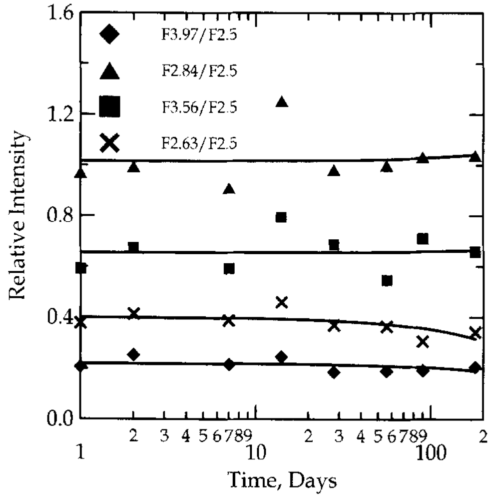

FIG. 3.
Slag/lime mix (without microsilica). Variation of fayalite (*F*) peaks intensity ratios.

Mineralogical Composition

A RIGAKU D/Max-IIB automated powder diffractometer (Cu $K_{\alpha 1}$ radiation) was used for mineralogical characterization. An X-ray diffraction pattern of an as-received sample of copper slag is shown in Figure 2. The observed peaks correlate well with the reference patterns for Fe_3O_4 (magnetite), and Fe_2SiO_4 (fayalite) as the main phases present in the slag. The differences between the observed and tabulated d-spacings for fayalite could be attributed to magnesium substituting for iron atoms, thus changing the size of the unit cell slightly.

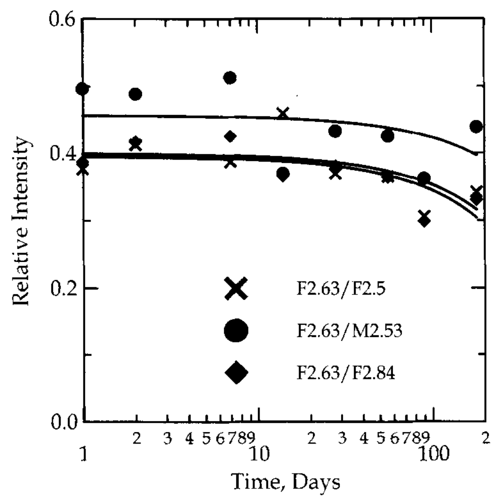

FIG. 4.
Slag/lime mix (without microsilica). Variation of 2.63 fayalite peak intensity ratios. *F*, fayalite; *M*, magnetite.

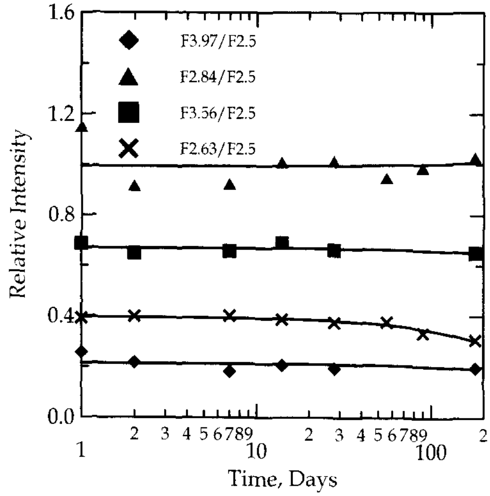

FIG. 5.
Slag/lime mix (with microsilica). Variation of fayalite (*F*) peaks intensity ratios.

Mineralogical observations have indicated that copper slags can contain a large amount of glass (2,11). On the contrary, the slag used in the present study appears to be well crystallized. The X-ray diffraction pattern does not display the usually broad halo of the high glass-content slags.

Hydration of Copper Slag in the Presence of Lime or Cement Paste

Copper Slag-Lime

Two types of paste were studied with and without microsilica. The first type used 95% copper slag and 5% hydrated lime (ASTM type S) pastes with a water/solid ratio of 0.23.

The second type used 85% copper slag, 10% commercial blend of microsilica (Force 10,000, manufactured by W.R. Grace Construction, Products Division) with gypsum, and 5% hydrated lime pastes with a water/solid ratio of 0.29. Three identical replicates of each series were prepared. After mixing, the samples were cast in small plastic containers and stored in a 23°C temperature and 100% RH atmosphere. The specimens were examined at 1, 2, 7, 14, 28, 56, 90 and 180 days by semiquantitative X-ray diffraction. Relative intensities of the fayalite peaks versus time are considered. One of these peaks corresponds to the major peak of calcium hydroxide, i.e., CH (2.63 Å). Other peaks of CH are either too weak to be detected or are covered by fayalite or magnetite. If the amount of CH decreases, the relative intensity of the 2.63 Å decreases, but the ratios corresponding to the other fayalite peaks should remain constant. The ratio of the fayalite 2.63 Å peak to other fayalite peaks and to magnetite 2.53 Å peak are plotted in Figures 3 through 6. The study of peak ratios shows that the intensity of the 2.63 Å peak decreases as the other ratios remain constant. This is observed for both the paste with and without the microsilica. This reduction in CH is indicative of the pozzolanic properties of slag. Figures 7a and b display typical patterns of slag/lime pastes (without activator) at 1 day and 180 days.

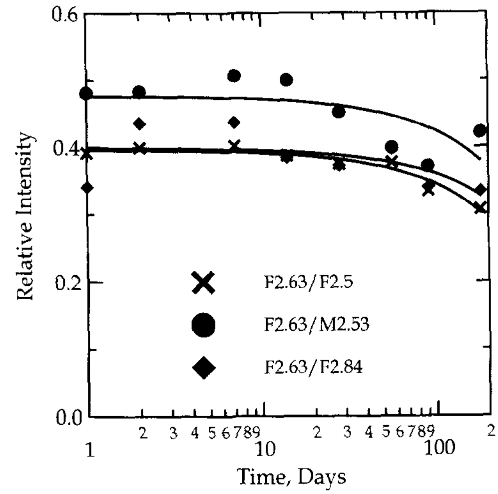

FIG. 6.
Slag/lime mix (with microsilica). Variation of 2.63 fayalite peak intensity ratios. *F*, fayalite; *M*, magnetite.

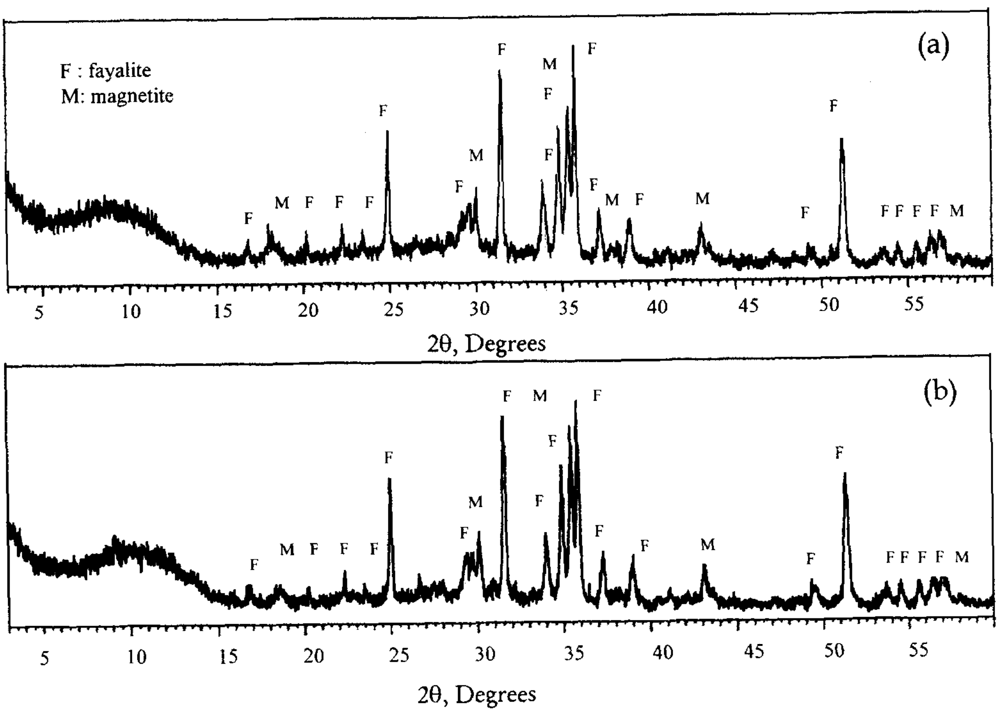

FIG. 7.
Copper slag/lime paste (without microsilica): (*a*) 1 day, (*b*) 180 days.

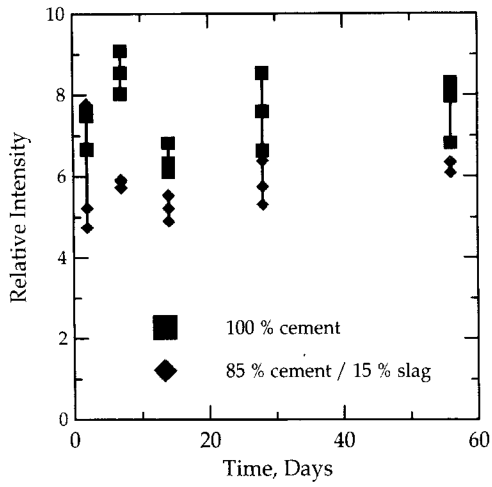

FIG. 8.
Variation of CH in slag/cement pastes.

Cement-Copper Slag

A paste blend consisting of 85% type I Portland cement and 15% copper slag was compared to a blend of 100% Portland cement. A water to cement ratio of 0.29 was used for both mixtures. Three replicates of each mixture were studied at 2, 7, 14, 28, and 56 days of curing. The amount of CH and anhydrous calcium silicates were monitored by semiquantative XRD using the intensity of the 2.63 Å peak for the CH and the alite/belite 2.74 Å peak for the anhydrous calcium silicates. The intensities of the slag/cement pastes were corrected to match the intensities of the 100% cement paste. Figure 8 shows that there is not a significant

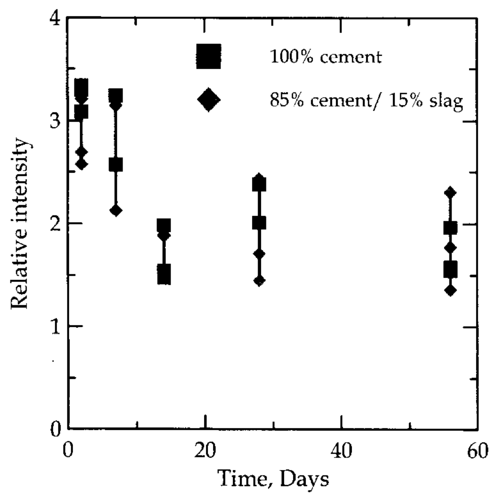

FIG. 9.
Variation of alite/belite in slag/cement pastes.

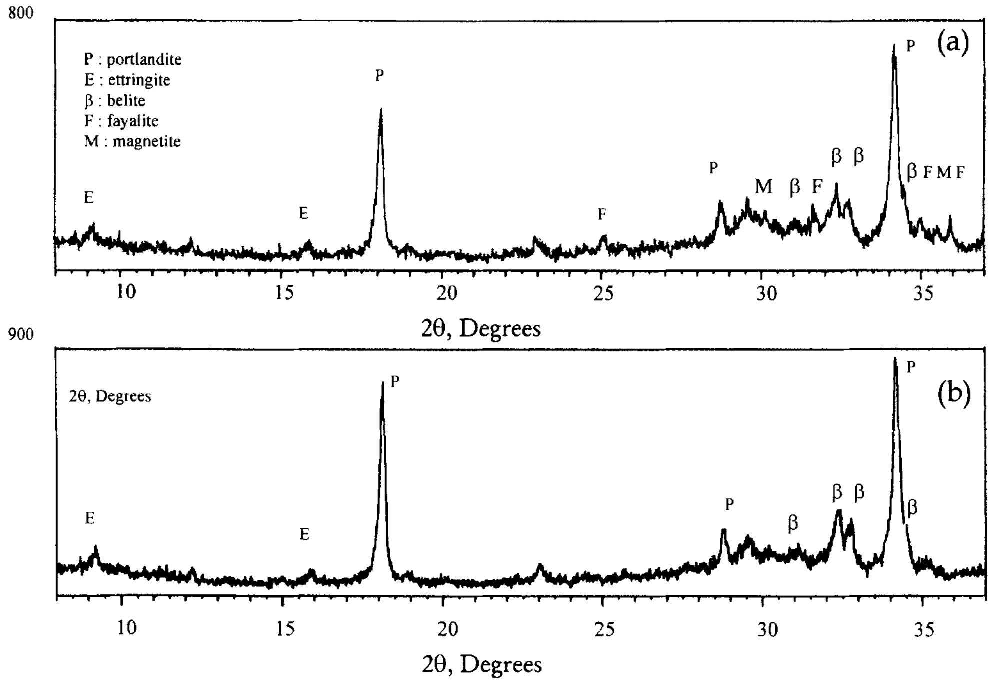

FIG. 10.
XRD pattern after 56 days of hydration: (*a*) copper slag/cement paste, (*b*) Portland cement paste.

difference in the process of CH formation between the two types of paste. In addition, one cannot positively differentiate the two trends of the decrease of the quantity of alite/belite as shown in Figure 9. Figures 10a and b display typical patterns of slag/cement pastes and 100% cement at 56 days.

Thermogravimetric analysis were conducted on a SETARAM TG-DTA 92 model.

Samples were examined for the amount of CH. The weight loss from 105°C to 900°C was used as an indicator of the bound water. The weight loss temperature relationship is plotted in Figure 11. The weight loss magnitudes were normalized based on the weight of raw Portland cement in the reference specimen. A higher amount of hydration product is observed in the copper slag samples than the 100% Portland cement samples for up to 14 days of hydration. The amount of CH related to the initial weight of the sample was estimated by a graphical method (13). Tangents to the TG curve at points corresponding to two temperatures, 425°C and 550°C, were drawn. The weight loss was determined by applying the Mean Value Theorem to the two tangents. The average slope of the two lines was used to estimate the weight loss.

The slag paste samples after 56 days of hydration are observed to have less calcium hydroxide available and less hydration products. These data confirm the conclusions obtained through XRD that the hydration process may continue at a lower rate in the presence of slag. However, the hydration does not seem to be adversely affected by the copper slag (see Table 2).

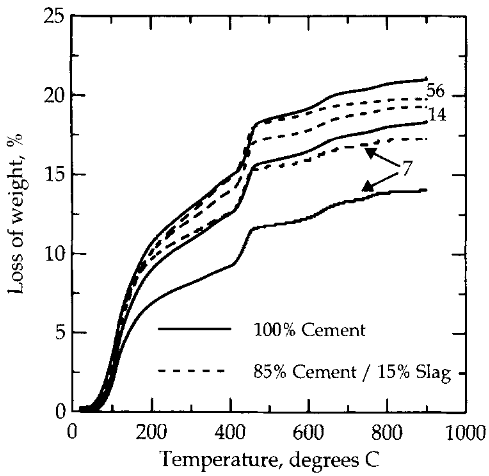

FIG. 11.
Thermogravimetric analysis of cement/slag pastes at 7, 14, and 56 days.

Mercury Intrusion Porosimetry

Mercury intrusion porosimetry was used to compare the pore size distribution of paste containing 10% slag with a control sample. A plot of intruded volume vs. applied pressure for both samples is shown in Figure 12. The total volume of mercury intruded into the control sample is less than that for the 10% slag-cement paste sample, indicating a larger total porosity for the copper slag paste. The capillary porosity is indicated by the porosity in the larger pore sizes, (considered larger than 10 microns in the present study). As shown in Figure 12, the slag-cement paste has higher gel porosity (i.e., pores whose size is smaller than 500 nm were considered as gel pores) as compared to the control paste with more capillary porosity. The reduction in capillary porosity may be attributed to the size of the slag particles and their role in densifying the microstructure.

TABLE 2
Data extracted from the thermogravimetric tests

	Type of paste			
	100% cement		85% cement 15% slag	
Age (days)	Amount of CH (%)	Loss between 105 and 900 deg.C (%)	Amount of CH (%)	Loss between 105 and 900 deg.C (%)
2	1.6	11.7	1.8	13.2
7	2.4	16.1	2.4	14.2
14	2.5	15.4	2.3	15.6
56	2.8	17.1	2.6	16.2

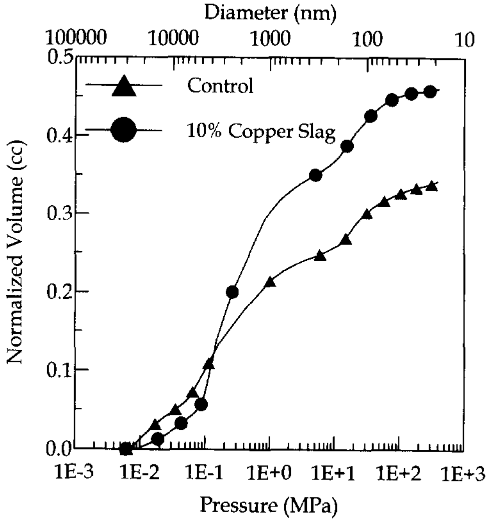

FIG. 12.

The volume vs. pressure for the mercury intrusion porosimetry of copper slag paste compared to a control mixture.

Compressive Strength

Mortar samples were prepared with the ratio of fine aggregates to total cementitious solids of 2:1 and a water to solids ratio of 0.4. Curing was achieved by storage in a constant temperature curing chamber at 90 RH, 21°C until the time of the test. The rate of strength development for three dosages of 5, 10 and 15% copper slag used as Portland cement

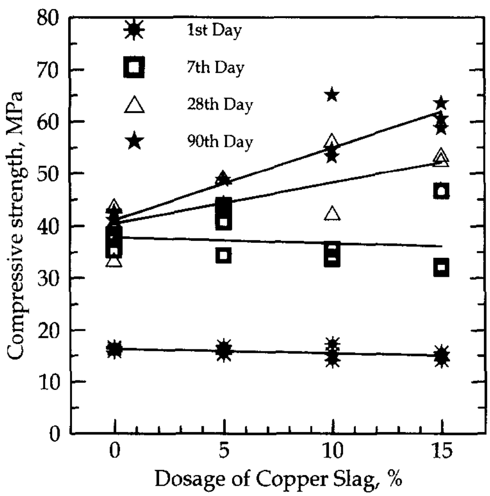

FIG. 13.

Strength development in copper slag mortar specimens as a function of age and dosage of copper slag.

replacement was compared with that for control mixtures. Cubes were tested for compressive strength after 1, 7, 28, and 90 days of curing according to ASTM C109. The trends of the compressive strength of mortar with copper slag are shown in Figure 13. Data points correspond to the mean strength of three replicate samples.

The use of copper slag reduced the early age strength (1 day) while increasing it beyond the 7 days. The compressive strength of the mortar cubes increases up to 90 days for all levels of slag studied. The strength of copper slag mixtures are significantly superior to that of the control specimens. With the addition of lime at the higher percentages of copper slag (15% copper slag and 1.5% lime as activator), the compressive strength increased from 30 MPa at Day 28 to 61 MPa at Day 90, reflecting a 100% increase. Note that a major portion of strength gain took place during the period between Day 28–90. At Day 90, 15% slag mortar exceeds in strength by as much as 45% over the control sample (14). In consideration to the marginally lower amount of hydration products formed in the presence of slag, it is expected that the strength enhancement is due to the densification of the microstructure in the capillary pore region.

Conclusions

This study points out the beneficial aspects of using copper slag as a cement replacement material. Copper slag is shown to significantly increase the compressive strength of concrete mixtures. This added increase is expected to be due to the densification of the microstructure in the capillary pore region. XRD results of slag lime samples indicate a clear decrease in the available CH content. This observation however was not clearly verified in the slag cement mixtures. Analysis of mercury intrusion porosimetry data indicate that the most likely source of the strength increase is due to the reduction in capillary porosity by the copper slag grains. It is also possible that the minor pozzolanic property of the slag as exhibited for slag/lime pastes enhances the performance of slag cement mixtures.

Acknowledgments

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