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STRENGTH DEVELOPMENT, HYDRATION REACTION AND PORE STRUCTURE OF AUTOCLAVED SLAG CEMENT WITH ADDED SILICA FUME

Y. Xi*, D.D. Siemer and B.E. Scheetz*****
*China Building Materials Academy, Beijing 100024, P. R. China
**LITCO, P.O. Box 4000 Mail Stop 5213, Idaho Falls, ID
***Materials Research Laboratory, The Pennsylvania State University, University Park, PA

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ABSTRACT

Under continuous hydrothermal treatment the strength of portland cement paste decreases with curing time and the pore structure coarsens. It was found in this study that the compressive strength of slag cement paste containing 67.5 wt.% ggbfs also decreases with time after 24 hour hydrothermal processing, but with a small addition of silica fume to the slag cement, the cement strength increases and the pore structure densifies when processed under comparable conditions. Based on observations XRD and SEM, these changes are attributed to: (a), changes in the hydration reactions and products by highly reactive silica fume, such that amorphous products dominate and the strength reducing phase α-C_2SH does not form; (b), slower hydration of slag, partially caused by the decreased pH of the pore solution, favors the formation of a dense pore structure; and (c), the space filling properties of the micro particles of silica fume. *Copyright © 1997 Elsevier Science Ltd*

Introduction

Microsilica has been extensively used for improving the properties of refractory castables (1,2), oil well cement (3), various concretes (4-7) and for making advanced cementitious materials such as DSP material (8).

Under prolonged treatment at an elevated temperature and pressure the strength of plain cement paste decreases with curing time and the pore structure is coarsening (9,10). For quartz cement concrete products, there exist optimum times and temperatures of autoclaving, which, if exceeded, cause a decrease in strength (11,12). The addition of 10% silica fume to concrete of high slag/cement ratio (65% slag + 35% OPC) cured at 23 ± 2°C has no effect on the compressive strength until the age of 91 days and significantly increases the strength at one year (13). Dan et al. (14) found the compressive strength of a steam cured slag cement concrete containing 70% ggbfs of fineness 600 m^2/kg to be higher than that of an OPC concrete. Hooton and Emery (15) reported that the compressive strengths of paste and mortar for pelletized slag cement cured at 185°C for 4 hours was much improved by addition of 20-40% silica flour composed of 93.1 % quartz and of Blaine fineness of 274 m^2/kg.

The objective of this work was to examine the strength development of slag cement with and without silica fume under conditions of continuous hydrothermal processing. This study showed that the strength of slag cement also decreases with prolonged processing, but that with a small addition of silica fume, the cement strength increases and the pore structure is densified. Physico-chemical characterizations were carried out to investigate the reasons for this. The results indicate that the strength development, hydration reactions, hydration products and microstructure of industrial cement products can be controlled by a small addition of microsilica.

Experimental

The raw materials for the study were Ash Grove Type-I portland cement (OPC), Koch Minerals slag (ggbfs), Elkem silica fume (SF) and superplasticizer Mighty-150 from Boremco Specialty Chemicals. Chemical composition and fineness of raw materials are given in Table 1. The OPC-slag cement (OS) and OPC-slag-silica fume cement (OSS) were prepared in advance by sufficient mixing and their formulations are shown in Table 2.

The determination of compressive strength was carried out using 50 mm neat paste cubes. The mixing and molding procedure followed ASTM C 109-92. Cubes of fresh cement were put into a Chandler duplex curing chamber at 125°C or 175°C, which was filled with water and kept at a pressure of 1 ± 0.1 MPa (gauge pressure). The Chandler duplex curing chamber was used here due to availability and the "compressed water" situation in it is not normally practicable in fabricating precast concrete. Under low pressure conditions, however, one may expect to find the broad similarity in strength development and microstructure of the OSS paste between curing in saturated steam and in compressed water.

The cubes were at room conditions for nearly one hour between initial molding and processing. The desired processing temperature was reached in 1.5 hours and was held for various lengths of time. Cooling time was more than 1.5 hours. Fragments of tested cubes were taken for physico-chemical examination. A Quantachrome scanning mercury porosimeter was used for pore structure analysis; the sample particle size was smaller than 6 mm in diameter and the maximum pressure 374 MPa; an ISI-DS 130 dual stage SEM was employed for measurement of the thickness of slag reaction rims, small pieces of freshly crushed hardened cement paste being coated with gold and immediately observed with the secondary electron image under the microscope; a SCINTAG VAX 3100 XRD system with $CuK_{\alpha 1}$ radiation was used for phase identification.

TABLE 1

Chemical Composition and Fineness of Raw Materials

	CaO	Al_2O_3	Fe_2O_3	SiO_2	MgO	MnO	BaO	K_2O	Na_2O	SO_3	LOI	BF[@]
SF[#]	<0.6	<0.6	<0.4	>93	<0.7			<0.7	<0.4		<1.5	
OPC*	65	4.22	2.69	20.2	1.99	0.05	0.03	1.11	0.17	3.15	1.11	~400
Slag*	41	7.31	0.34	38.8	10.3	0.69	0.06	0.47	0.36		0.18	~600

[@] Blaine fineness (m^2/kg) taken from the product specification;

[#] Chemical composition of silica fume according to the product specification;

*Chemical composition of OPC and slag were determined by DC-plasma emission spectrometry and atomic absorption spectrometry using a graphite furnace. Sulfide in slag was not determined

TABLE 2

Formulations of OS and OSS Neat Cement Paste and Their Compressive Strength

No	PC-I	Slag	S.F.	W/C	M-150	Compressive strength in MPa					
						125°C			175°C		
						24 h	168 h	336 h	24 h	168 h	336 h
OPC	100	0	0	0.32	1.5	77.3					
OS	32.5	67.5	0	0.32	1.5				83.6	44.3	32.5
OSS	32.5	60.5	7.0	0.32	1.5	76.8	83.2	114.1	88.3	89.0	94.1

To assess the pH change of the liquid phase in hardened cement paste (hcp), the broken cube portions after the test for compressive strength were crushed to pass a 0.6 mm sieve and immersed in deionized water (water: hardened paste = 0.75) for three days. The pH of the leachate was measured, which is not the real pH of the pore solution in hcp due to dilution, dissolution and hydration reaction, but related to it (16), giving some information about the alkalinity of pore liquid. The remaining portions of the broken cubes were stored in plastic bags at room temperature for six months and used for estimating the pH again in the same way.

Results and Discussion

pH of Liquid Phase, Hydration Reaction and Products. The pH values of the leachate from the paste is given in Table 3. The pH of the leachate from the OSS paste decreases from 12.3 at 24 h to 11.3 at 336 h, i.e. by one unit while that from the OS paste keeps constant at ~ 12.8, showing that the addition of silica fume causes the hydroxyl ion concentration of pore solution in the slag cement paste to decrease significantly with increased hydrothermal time and that the slag-silica fume cement is a good potential matrix for glass fibre reinforced cement products. Table 3 also indicates that the pH of the leachate from the OSS paste after 6 month storage at room temperature increases to ~ 12.4 as silica fume is exhausted in the hydration reactions and the hydration of the unreacted minerals in the OSS paste continues, and that the pH of the leachate from the OS paste decreases a little probably due to carbonation. The XRD patterns in Fig.1 show that α-C_2SH (JCPDS 29-373) form in OS cement but not in OSS cement where the amorphous C-S-H or semi-crystalline C-S-H(I) dominates. A peak at approximately 12° 2θ (7.4 Å) was also shown by the OS paste, which could not assigned with certainty, it was possibly due to gismondine (CAS_2H_4, JCPDS 39-1373). Therefore the main hydration reaction in OS and OSS cements follows:

TABLE 3

pH of Leachate of Hardened OS and OSS Cement Paste Cured at 175°C

	24 h HT*	6 mon.RT#	168 h HT*	6 mon. RT#	336 h HT*	6 mon.RT#
OSS	12.25	12.20	11.62	12.40	11.29	12.47
OS	12.73	12.36	12.84	12.25	12.76	12.24

*Hydrothermal cured cement paste;

#After hydrothermal treatment, the sample was put in a sealed plastic bag at room temperature for 6 months

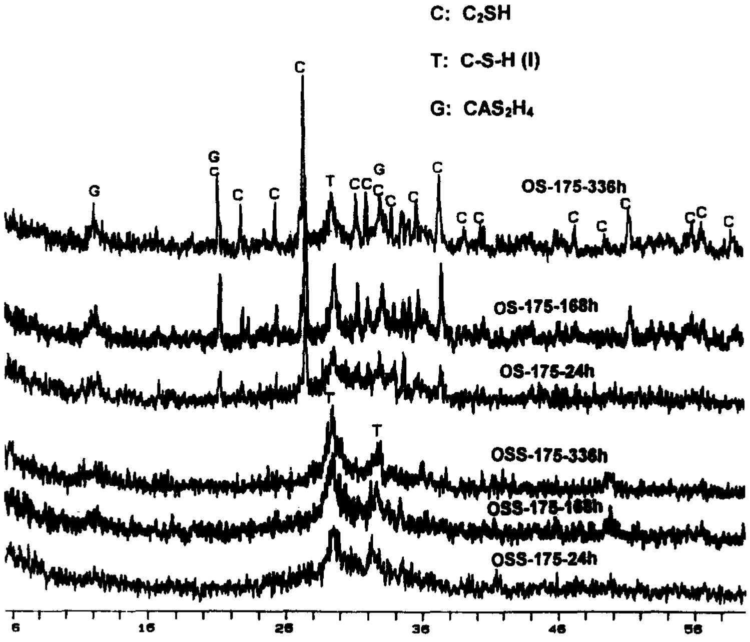

FIG. 1.
X-ray patterns for PC-slag cement (OS) and PC-slag-S.F. cement (OSS) hydrated at 175°C.

$$\begin{array}{l}
\text{silica fume in OSS cement} \\
\downarrow \qquad\qquad 175^\circ\text{C} \\
\text{active } SiO_2 + CaO \longrightarrow \text{C-S-H(I)} \\
\qquad\qquad\qquad 175^\circ\text{C} \\
SiO_2 + CaO \longrightarrow \alpha\text{-}C_2SH + \text{C-S-H(I)} \\
\uparrow \\
\text{OPC, slag in OS cement}
\end{array}$$

The C-S-H formed in slag cement hydrated at 25°C has CaO/SiO_2 of 1.61-1.79 (17).The very fine silica fume contains mainly reactive amorphous silica. Under hydrothermal conditions it consumes CaO rapidly to form C-S-H with a low CaO/SiO_2 ratio and the formation of α-C_2SH is impossible. Unlike silica fume, the silica flour is composed of coarse quartz, much less reactive; it reacts with CaO to form 1.1 nm töbermorite and α-C_2SH (15).

Pore Structure. As seen in Fig. 2, the pore structure of the OS paste coarsens on hydrothermal curing, e.g. for 175°C curing, the total porosity increases from 21.6% at 24 h to 26.4% at 336 h, and the critical pore radius increases from 12 nm at 24 h to 19 nm at 336 h; however the microstructure of the OSS paste with silica fume becomes denser with increased curing time, e.g. for curing at 125°C, the porosity decreases from 20.7 % at 24 h to 14.1 % at 336 h, and the critical radius narrows from 3.7 nm to 2.7 nm over the same period.

The OPC, OS, and OSS pastes cured at 125°C or 175°C for 24 hours all have porosities of around 20% (Fig. 2), but the OS paste has a much smaller critical pore radius than the OPC

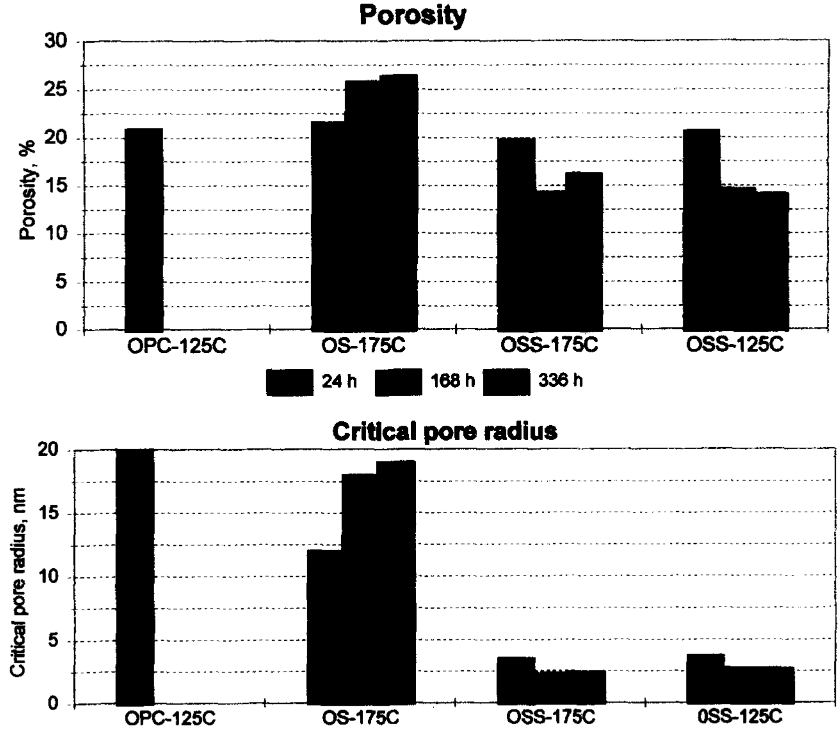

FIG. 2.

Porosity and critical pore radius of different hardened cement pastes after hydrothermal curing.

paste, and the OSS paste has an even smaller pore radius, showing that the addition of slag or silica fume greatly reduces the proportion of large pores.

Hydration Rate. For an OPC-slag cement with 67% slag hydrated at room temperature, only 19-36% of initial weight of slag had reacted at one year (18), indicating that the reaction rate is slow.

The slag reaction rims in the hardened OSS cement paste are shown on SEM secondary electron micrographs (Fig.3). The average thicknesses of the slag reaction rims, based on multiple measurements, are given in Table 4. The thickness increment of the reaction rim for the OSS paste cured at 125°C is only ~ 0.1 μm from 24 h to 168 h and the same from 168 h to 336 h, showing that the hydration of the slag in the OSS paste is very slow even under hydrothermal conditions. The reasons for that are: (a) The slag hydration needs alkaline activation, but silica fume greatly lowers the pH of liquid phase, causing the slag reaction to slow down; (b) A dense microstructure is established through the "space filling" effect of silica fume (19), also called the "micro particle effect"(20). The average size of silica fume particles is about 150 nm. Such small particles fill pores in cement paste and thereby make them much smaller, which limits the particle size of new formed hydrates, which in turn reduce pore size further. The dense microstructure due to introduction of silica fume limits water supply for deeper hydration and restricts the space for new hydrates.

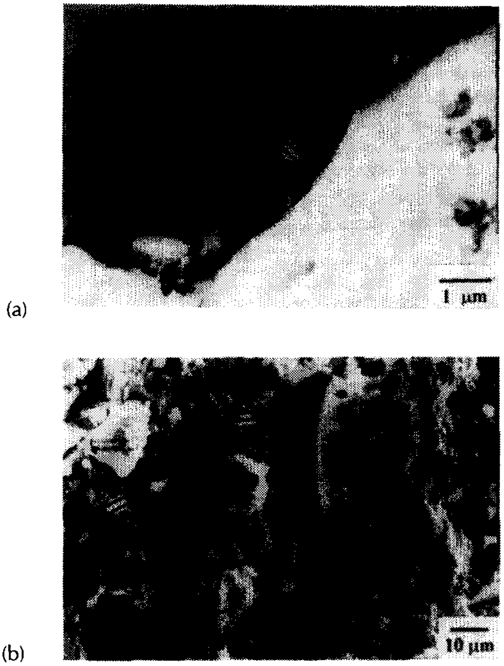

FIG. 3.
SEM secondary electron images of OPC-slag-silica fume cement paste cured at 125°C: (a) 24h; (b) 168 h. Arrows show slag reaction rims.

Trend of Strength Development. Under hydrothermal treatment at 175°C for 24 h, the strength of slag paste (OS) is enhanced by a small addition of silica fume (Table 2), from 83.6 MPa to 88.3 MPa, which confirms the results by Dan et al. (14). The compressive strength of PC-slag cement cured at 175°C drops steeply from 83.6 MPa at 24 h to 44.3 MPa at 168 h, and to 32.5 MPa at 336 h. In contrast that of PC-slag-silica fume paste (OSS) goes up from 88.3 MPa at 24 h to 94.1 MPa at 336 h. The strength of OSS paste cured at 125°C increased more markedly with curing time (76.8 MPa to 114.1 MPa). With 7 wt.% substitution of silica fume for slag, the trend of strength development for slag cement changes completely.

Why does the strength of OPC-slag cement paste go down with hydrothermal curing time but that of OPC-slag-silica fume cement paste go up? The pH range of liquid phase in OS paste is such that α-C_2SH crystallizes. Due to the high density and particle morphology of this phase, the pore structure coarsens, the porosity increases and the strength decreases. With addition of silica fume, the highly reactive SiO_2 takes up much CaO, and α-C_2SH no longer crystallizes. Instead, more C-S-H(I) forms, which does not grow markedly in particle size with continuous hydrothermal processing. The dense and rational microstructure builds

TABLE 4

Average Thickness of Slag Reaction Rims in OPC-slag- silica fume Cement Cued at 125°C

Code	OSS-125-48	OSS-125-168	OSS-125-336
Thickness	~0.2 µm	~0.3 µm	~0.4 µm

gradually as silica fume and new hydrates fill the pores in the paste, and the strength continues to increase.

Conclusions

1. The compressive strength of hydrothermally treated OPC-slag cement decreases with curing time after passing the maximum strength. A few percent addition of silica fume greatly changes the pattern of the strength development and the microstructure. In contrast to OPC and OPC-slag cement, the strength of OPC-slag-silica fume cement continues to grow during prolonged hydrothermal curing.
2. For 175°C hydrothermal curing, the main hydrates of OPC-slag cement are α-C_2SH, C-S-H(I) and probably a little CAS_2H_4. In presence of silica fume, CaO is consumed dramatically, the pH of the pore fluid is reduced, hydration reactions and products are changed and α-C_2SH is not able to form. In addition, silica fume particles fill micro- and submicro-meter level pores in paste and limit the particle size of hydrates (space filling effect). That is the reason for the change in properties.
3. The hydration of slag in OPC-slag-silica fume cement is still slow despite hydrothermal treatment. The pore solution with reduced pH and dense microstructure are responsible for the slow hydration.

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