

Effects of high SiO₂ coal ash and silica fume on the strength, permeability and leachate of a very early strength cementitious composite

Cheolwoo Park^a and Kyungnam Kim^{b,*}

^aDept. of Civil Engineering, Kangwon National University Samcheok 245-711, Korea

^bDept. of Advanced Materials Engineering, Kangwon National University Samcheok 245-711 Korea

This study aims to enhance the practical applications of coal ash and silica fume as a very early strength cementitious composite material. Both coal ash and silica fume are an industrial by-product from power plants and making silicon metal or alloy. This study considered high SiO₂ coal ash and silica fume simultaneously. Various replacement ratios of coal ash and silica fume were evaluated to come across an optimized mix proportions. Compressive strength was a key monitoring factor in determining the mix proportions and durability characteristics was investigated through the permeability. Both coal ash and silica fume are not quality controlled during their productions and in the consideration of their primary applications in the field, their potential contamination was evaluated by investigating the leachate. The compressive strength development satisfied the required specifications. Potential hazardous contamination was evaluated to be very low. Permeability was high but by adding silica fume it can be greatly reduced. Therefore, coal ash from an electric power plant can be successfully applied to the very early age cementitious composite by replacing the cement. However, the replacement ratio is recommended not to exceed 15% and simultaneous addition of silica fume is necessary.

Key words: Coal ash, silica fume, recycling, very early strength, permeability, contamination.

Introduction

Researchers have placed a great effort to enhance the use of supplementary cementitious materials such as coal ash, silica fume, metakaolin and blast furnace slag, whether natural or as by-products, in the production of cementitious composites because of ecological, economical, and diversified product quality reasons [1]. Recently public attention is being given to the global environment and the supply of industrial supplementary by-product materials. Coal ash is a by-product from coal-fired thermoelectric power plants and the annual production is about 5.5 million tons in S. Korea. Coal ash can react with calcium hydroxide formed during cement hydration, and hence increase the portion of calcium silicate hydrate which enhances strength and impermeability of the hardened cementitious composite [2]. Depending largely on the source of coal and the post-process of coal ash, its chemical composition and physical properties vary significantly. In particular, the amount of silica, SiO₂, and lime, CaO, may have a considerable influence on the pozzolanic reactivity. In addition, the shape of particles influences the workability of a cementitious composite before hardening. Since 1930s, the coal ash has been used as an additive material in cementitious composites and there is plenty of technical and economical benefit, such as reducing the hydration heat evolution and long term

strength and impermeability. A lower reaction rate of coal ash is one of the shortcomings in using the coal ash in cementitious composites. Silica fume is also a by-product in the manufacture of silicon metal and alloys. Its pozzolanic reaction mechanism is similar but its reactivity is much faster than coal ash because of the high content of silica, SiO₂.

As application techniques for cementitious materials advance and a social paradigm varies, more rapid setting of cementitious composite is highly needed and the related market becomes larger. Shotcrete is one of the examples of a rapid setting cementitious composite [3-6]. The technology to use such by-products, as coal ash and silica fume, has been widely sought for increased consumption and technical benefits but studies on the effects of adding coal ash and silica fume on the very early strength have rarely been reported.

This study aims to provide information on the effect of high SiO₂ coal ash and silica fume on the very early strength cementitious composites. Optimized addition proportions were evaluated through compressive strength tests, and long term durability was also investigated through permeability tests. Both coal ash and silica fume are not quality controlled during their production and in the consideration of their primary applications in the field, their potential contamination was evaluated by investigating the content of environmentally hazardous heavy metal in the leachate.

Experiments

Portland cement used in the study was ordinary Type I complying with ASTM C 150 with a specific surface area

*Corresponding author:
Tel : +82-33-570-6565
Fax : +82-33-570-6557
E-mail: knkim@kangwon.ac.kr

of 3,200 cm²/g. The coal ash used was collected using a bag-house filtering system and post-processed for quality consistency. Silica fume was to enhance the strength development since the coal ash may hinder the strength gain rate at an early age. The used silica fume was commercially available from the market. Table 1 shows the chemical compositions of the cementitious materials used and Fig. 1 represents the shape of coal ash used. The fine aggregate (F.A.) used and coarse aggregate (C.A.) met the requirements specified in ASTM C 33 with specific gravities of 2.61 and 2.75 and fineness moduli of 2.46 and 6.63, respectively. The maximum size of the coarse aggregate was determined to be 10 mm through preliminary tests and following ASTM C 1436. Experimental variables include the replacement ratio of coal ash and silica fume. Silica fume replaced 7% of the cement weight and the coal ash additions were 5% and 10%. Additional coal ash replacement ratios were considered in order to investigate the upper limit of replacement as 12, 15, 17 and 20%. For these additional coal ash replacement ratios, no silica fume was added into the composite mixes. The target slump of the composite mixture was 100 mm and an air content was 5 ± 1%. For the very early strength development, a rapid setting cement hydration accelerator was used and it was a powder-type cement-based mineral accelerator. Workability of the mixtures was obtained by addition of a high range water reducing agent, super-plasticizer (S/P). Table 2 describes the mix proportions of cementitious composite for each variable. From the mixtures, 10 cm diameter and 20 cm height cylindrical specimens were fabricated for a comparison of the compressive strength. The specimens were cured under water at 20 ± 2 °C and

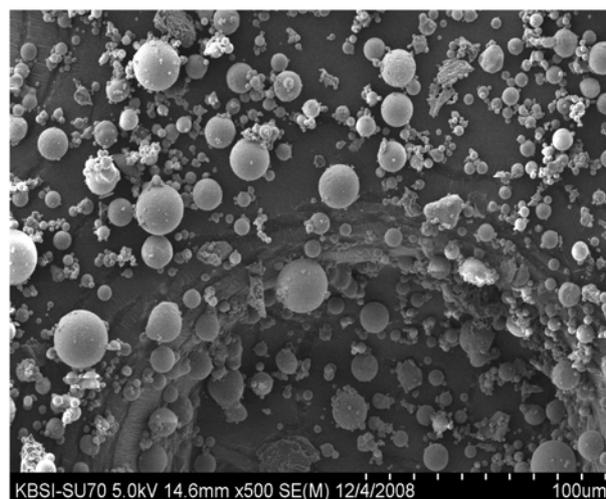


Fig. 1. Detailed view of the coal ash used.

the compressive strength was measured at the ages of 1, 3 and 28 days.

Permeability of the composites was obtained through the rapid chloride penetration test following ASTM C 1202 at the ages of 7 and 28 days. The cylindrical specimens were cut into slices with a thickness of about 50 mm. The slices were coated on the sides with a rapid setting epoxy and put into voltage cells to measure the electric charge passed. The positive terminal, cathode, was connected to a 3.0% sodium chloride solution and the negative side, anode, to a 0.3 M sodium hydroxide solution. A 60 V DC electric potential difference was maintained between the two cut faces in the testing set-up. The voltage between

Table 1. Chemical compositions of cement, coal ash and silica fume (wt %)

Composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	TiO ₂	MnO	K ₂ O	Na ₂ O	P ₂ O ₆	LOI
Cement	20.8	6.3	3.2	61.2	3.3	2.3	-	-	-	-	-	1.0
Coal ash	57.2	16.0	8.3	2.0	2.5	-	0.9	0.4	3.0	0.5	-	8.8
Silica fume	57.2	16.0	8.3	2.0	2.5	-	0.9	0.4	3.0	0.5	-	8.8

Table 2. Mix proportions of very early strength rapid setting cementitious composites

Specimen	W/C (%)	S/a (%)	Unit content (kg/m ³)								Slump (cm)	Air (%)
			Water	Binder	C	S/F	C/A	F.A.	C.A.	S/P		
Plain					422	-	-	988	644		10	6.0
PS7					393	30	-	983	640		8.5	5.8
PS7F5					372	30	21	978	637		9.5	4.8
PS7F10					350	30	42	973	634	8.4	8.0	4.8
PF5	45	60	190	422	401	-	21	983	640		10.0	5.8
PF10					380	-	42	978	637		11.5	5.6
PF12					372	-	51	977	636	8.022	10.0	5.0
PF15					359	-	63	974	634	4.222	11.5	4.9
PF17					350	-	72	972	633	3.167	10.0	4.0
PF20					338	-	84	969	631	2.744	10.0	3.5

the cells was recorded every 30 minutes for up to 6 hours. The measured voltage was converted to a current and the total passed charge was calculated using the equation below:

$$Q = 900 \times (I_0 + 2I_{30} + 2I_{60} + \dots + 2I_{30} + I_{360}) \quad (1)$$

where, Q is the total charge which passed the disc specimen and I_n is a current at n minutes after the voltage is applied. Fig. 2 shows the schematic view of the permeability test circuit and testing scene.

The application of very early strength cement composites used to be exposed to underground water. Therefore, this study also investigated potential harmful effects such as heavy metal contamination through the leachate. The hardened composites were broken into small pieces to pass through a 5 mm sieve and shaken in a concussion jar for 6 hours with a 40 mm amplitude at 200 cycles per minute. The leachate was analyzed using inductively coupled plasma emission spectroscopy. The results obtained were compared with the regulations of Waste Management Act, Water Environmental Reserve Act in S. Korea and US Environmental Protection Agency-Toxic Characteristic Leaching Procedure.

Results and Discussions

At each testing age, at least three cylinders were tested and the values were averaged. The measured results are

described in Table 3 and compared in Fig. 3. At every curing age, the strength requirements by various specifications in Table 4 were successfully satisfied for all mixes [7, 8]. At 1 day, when silica fume was added (PS7) the strength was very comparable to the plain cement specimen (Plain). Addition of coal ash alone, however, decreased the 1-day strength especially with 10% of coal ash to some considerable extent. When silica fume was added with coal ash at the same time (PS7F5 and PS7F10) the addition of silica fume did not contribute to the 1-day strength

Table 3. Measured compressive strength (MPa)

Specimen	1 day	3 days	28 days
Plain	16.9	23.4	34.1
PS7	16.6	25.1	33.3
PS7F5	13.5	19.9	29.0
PS7F10	13.0	17.6	29.0
PF5	16.1	22.9	25.4
PF10	13.2	22.1	25.7
PF12	12.9	21.5	31.1
PF15	6.8	19.8	31.0
PF17	5.9	19.6	30.6
PF20	5.6	17.0	29.8

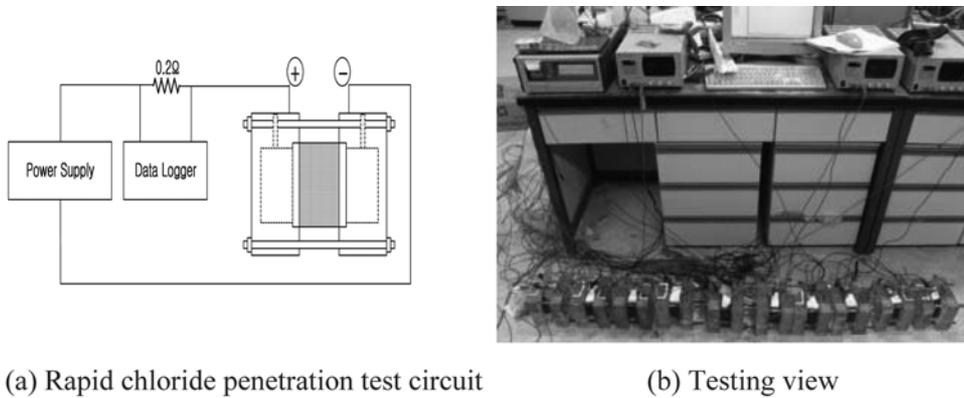


Fig. 2. Rapid chloride penetration testing equipment and view.

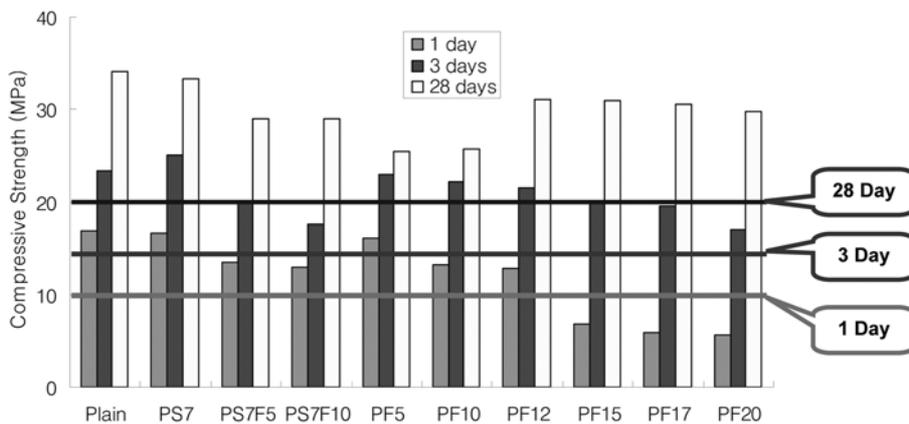


Fig. 3. Comparison of compressive strength of composites.

Table 4. Strength requirements from various institutes and specifications (MPa)

Specifications	1 day	3 day	28 day
S. Korea Concrete Institute	5-10	-	18
Tunnel Design Specification	10	-	18
Standard Specifications of S. Korea Expressway Corporation	10	14	20
Japan Concrete Institute	5-10	-	18

development significantly. When they both were added the strength was lower than when the coal ash alone added. This might be because too much of the Portland cement was replaced with the mineral admixtures. At 3 days into the curing initiation, all the specimen showed greater than 14 MPa strength, which is the required limit from the specifications for shotcrete construction from the S. Korea Expressway Corporation. Here the early strength up to at most 3 days is very important. However the replacement of cement with coal ash reduced the strength development regardless of the addition of silica fume. When the coal ash replacement ratio was greater than 12% the 1 day strength was below that required. Therefore, the addition of coal ash may not replaced greater than 15% of the cement weight in a consideration of early age strength development. 28 day strengths were well above the requirements and somehow the 10% coal ash added specimens (PF10 and PS7F10) showed an even greater strength than those with 5% added. The strength gain rate from 3 days to 28 days were proportional to the added amount of coal ash. This may imply that the addition of silica fume and coal ash activated the pozzolanic reaction to develop additional strength by reacting with calcium hydroxide which was produced from cement hydration. From these results, it is concluded that the shotcrete incorporations coal ash may not have a problem in meeting the specified requirements. In addition as the age of cement composite increases, the strength development is more enhanced by the pozzolanic reaction.

The permeability of the composites was evaluated in accordance with the rapid chloride penetration test and the results are shown in Fig. 4 with respect to the measured

age. At 7 days, all the specimens show a high range of permeability, in other words, a low long term durability. However, the effect of addition of silica fume was very obvious. As the age increased up to 28 days, the permeability became reduced considerably but without silica fume the permeabilities were still in the high and moderate ranges. Only the specimens with silica fume added showed a low range of permeability. When fabricating the specimens, compaction of the mixture into a shape before the hardening initiation was difficult because of the rapid setting agent so that the macrostructure of the specimen may not be as good as in field applications. From the test, it is concluded that the early age permeability of the very early strength cementitious composite with coal ash should be improved and the addition of silica fume can be a solution of the problem.

The test results for hazardous materials are shown in Table 5. Shotcrete involves discrete steel fibers to enhance its crack control and ductility. Therefore, its corrosion

Table 5. Analyzed results for hazardous materials(unit: mg/l)

Regulations	Pb	Cu	As	Hg	Cr	Cd	pH(20)
Waste Management Act S. Korea	≤3.0	≤3.0	≤1.5	≤0.005	≤1.5	≤0.3	5.8-8.6
Water Environmental Reserve Act S. Korea	≤0.2	≤0.5	≤0.1	≤0.0	≤0.1	≤0.02	5.8-8.6
EPA-TCLP*-USA	≤5.0	-	≤1.5	≤0.2	≤5.0	≤1.0	-
Plain	-	0.027	0.018	-	-	-	12.6
PS7	-	0.028	0.009	-	-	-	12.6
PF5	0.03	0.022	0.027	-	-	-	12.5
PF10	-	0.026	0.022	-	-	-	12.5
PS7F5	-	0.023	0.007	-	-	-	12.5
PS7F10	-	0.020	0.012	-	-	-	12.3
PF12	0.04	0.040	0.022	-	-	-	12.5
PF15	0.03	0.029	0.017	-	-	-	12.5
PF17	0.04	0.040	0.018	-	-	-	12.5
PF20	-	0.039	0.039	-	-	-	12.4

*Environmental Protection Agency-Toxic Characteristic Leaching Procedure

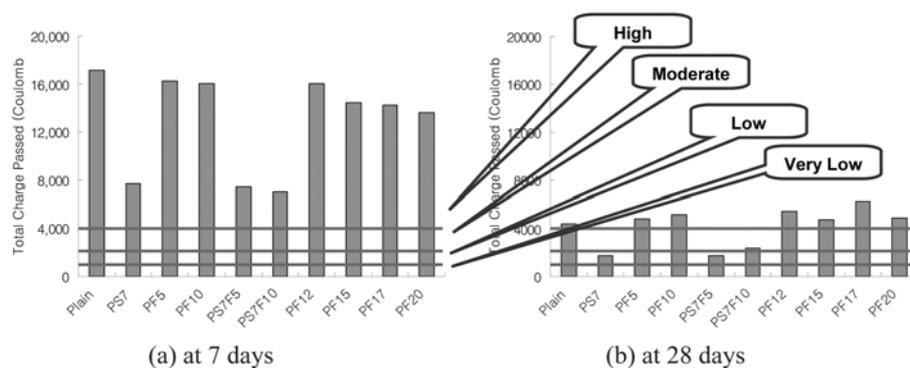


Fig. 4. Comparison of permeability tests (ASTM C 1202).

protection through alkalinity is also important. The measured pH was more than 12 showing a high alkalinity and the shotcrete in this study is expected to provide as good steel protection against corrosion as a normal concrete. The pH values are greater than the considered regulations but they are from the leachate of the crushed pieces of the specimens. In the potential contamination evaluation, the contents of harmful heavy metals, Pb, Cu, As, Hg, Cr, and Cd, in the leachate from shotcrete was measured. Three different environmental regulations considered were Waste Management Act and Water Environmental Reserve Act from S. Korea and Environmental Protection Agency-Toxic Characteristic Leaching Procedure (EPA-TCLP) from USA. As addressed in Table 5 all the mix types provided results within the specified limits satisfying the three different regulations. From the results it is known that the very early strength cementitious composite using coal ash from a power plant does not contain environmentally harmful materials at least in its early age. Even though its long term performance is not yet evaluated as the age of the composite increases its microstructural system will also be further stabilized. From these experimental investigations it is tentatively concluded that the application of coal ash to the cementitious composites can be successfully used as the hazardous material contents are within the allowed limitations in the specifications.

Conclusions

This study investigated the application of coal ash, which is by-product from a coal-fired thermoelectric power plants and has been used for low valued applications, as a construction material. Silica fume was also considered as an additive material for the application. The coal ash replaced a portion of the cement in the very early age strength cementitious composite mixes. The appropriate mix proportions were evaluated through compressive strength measurements. It is concluded that a coal ash incorporated

composite may not have a problem meeting the specified strength requirements. As its age increases the strength development is further improved with the pozzolanic reaction of the coal ash and silica fume. The permeability of the specimens was not satisfactory but the addition of silica fume greatly reduced the permeability. Therefore, the use of silica fume was not just for the early age strength development but rather permeability enhancement. Since the quality control of coal ash and silica fume is difficult by their nature, potential hazardous materials contamination was evaluated using an inductively coupled plasma emission spectroscopy analyzer. The pH was greater than 12 similar to a normal cement composite and the heavy metal content was well below the specifications. Therefore, coal ash from an electric power plant can be successfully applied for a very early age cementitious composite by replacing some of the cement. However, the replacement ratio is recommended not to exceed 15% and simultaneous addition of silica fume is necessary.

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