

Fly ash-Slag-Cement Composite

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The hydration behavior of fly ash and slag on cement paste were investigated. Early stage of hydration reaction was delayed by mixing fly ash and/or slag with cement, but production of C-S-H hydrates by pozzolanic reaction densified the microstructure. The Ca/Si ratio of C-S-H hydrates in OPC and blended cement of fly ash 50%, slag 50%, fly ash+slag 50% were 2.24, 1.80, 1.82 and 1.97, respectively. The C-S-H gel with low Ca/Si ratio showed rather reticulate than needle-like structure.

Key words: Blended cement, Pozzolanic reaction, C-S-H hydrates, Microstructure

I. Introduction

Pozzolanic materials such as slag and fly ash have been used as cement admixtures for many years. The composite matrix is dynamic in that there is continual change in the hydrates and microstructure with time. The addition of fly ash and/or slag to cement has been shown to improve the performance of concrete.¹⁾ The pore structure of cement pastes exerts major control on the ingress of potentially deleterious substances. The pore structure and microstructure constitute major rate-controlling factors for potentially harmful transport processes.^{2,3)}

This study is a part of research which deals with the microstructure and properties of blended cement. This paper describes effects of pozzolanic materials added to OPC on the hydration and microstructure.

II. Experimental Method

The cement used in the study was an ordinary portland cement(OPC). The fly ash was produced at the Boryung power station. Their crystalline mineral, as determined by X-ray diffraction, included quartz, mullite, spinel close to magnetite. The glass contents of fly ash, as determined by QXRD(step scanning method), are about 65%. The blast furnace slag(slag) was obtained from the Pohang Iron and Steel Co., crushed to a fineness similar to that of OPC. Chemical and physical data for the raw materials are given in Table1.

Table 1. Chemical and Physical Composition of Raw Materials

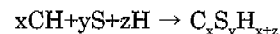
	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	SO ₃	K ₂ O	Density (g/cm ³)	Blaine (cm ² /g)
Fly ash	58.8	22.5	6.1	5.6	1.7	-	0.93	2.3	3900
Slag	33.4	16.6	42.7	0.5	4.6	0.23	1.6	2.8	3800

Pastes were prepared by pre-mixing the required amount of solids(OPC, fly ash and slag) and then mixing solids with de-ionized water(w/s=0.45). The resulting pastes were placed in a polyethylene cylindrical mould(Φ3×5 cm), sealed and cured at room temperature. Hydration was stopped at appropriate times by acetone.

The heat of hydration was measured using a conduction calorimeter at 20°C. The Ca(OH)₂ content of the paste was determined by thermogravimetric analysis in a nitrogen atmosphere and estimated endothermic peak area between 450~500°C. Also ²⁹Si-NMR was performed to characterize C-S-H gel hydrates. The microstructures were examined with a scanning electron microscope(SEM) on gold-coated specimens and MIP(mercury intrusion porosimetry).

III. Results and Discussion

The most important pozzolanic reactions are occurred between reactive silica and calcium hydroxide, resulting in producing calcium silicate hydrates. The reaction can be represented by the following simplified equation.



The reaction products of fly ash-slag-cement mixtures are substantially the same as those found in OPC, i.e., calcium silicate hydrate, calcium hydroxide, calcium aluminate hydrate, AFt, AFm, and hydrogarnet. The amount of calcium hydroxide eventually diminishes with the curing time.

3.1. Influence of fly ash, slag on cement hydration

The addition of fly ash and slag as blending materials causes to different characteristics of the hardened paste due to both chemical reactions and physicochemical effects.

The hydration of cement is an exothermic reaction. The heat evolution curves of OPC, fly ash and/or slag blended cement investigated are shown in Fig. 1. It can be seen that

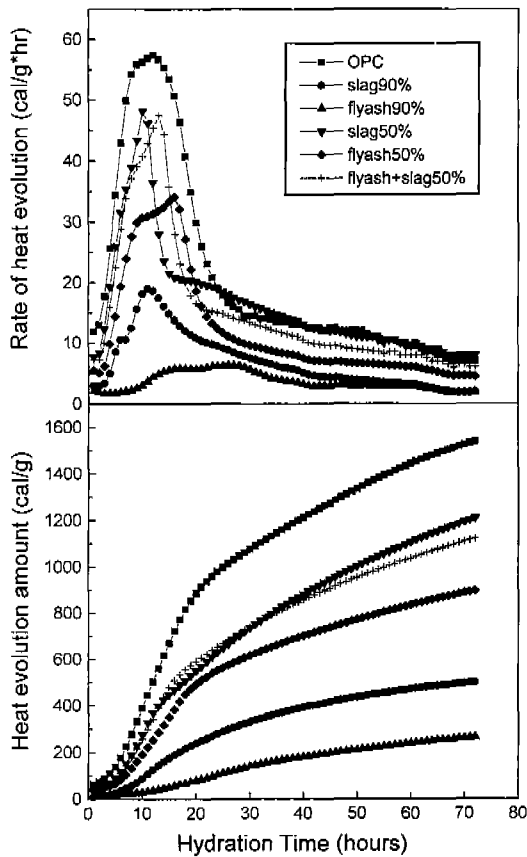


Fig. 1. The calorimetric curves for flyash-slag-cement systems.

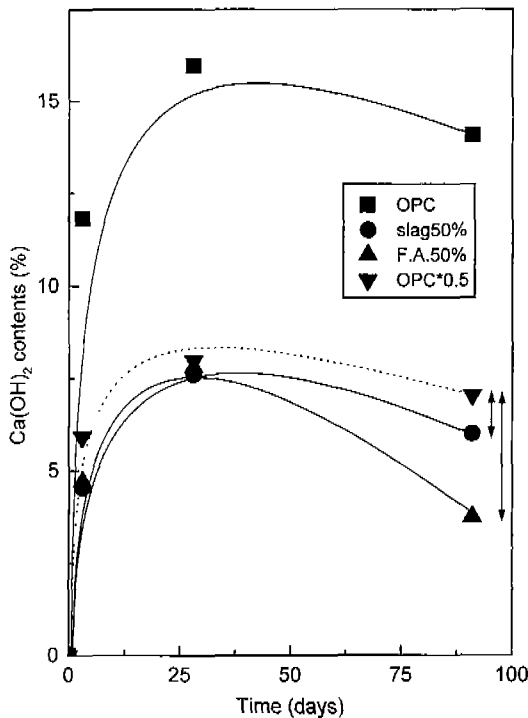


Fig. 2. Changes of calcium hydroxide contents of OPC and several blended cement pastes.

the early hydration of OPC in the presence of fly ash showed retardation of the main(second) heat evolution peak. It is supposed that the retardation was a result of chemisorption of some Ca^{2+} ions on the fly ash particles, which reduced Ca^{2+} concentration and delayed nucleation of calcium hydroxide, and the poisoning effect of soluble silicate and aluminate species on nucleation and crystal growth of calcium hydroxide and C-S-H. But the rate of hydration of slag blended cement was as fast as that of OPC. Chemical composition and the glass content of pozzolanic materials affect the hydraulic reactivity.

Fig. 2 shows change of $Ca(OH)_2$ contents of OPC and blended cement pastes. If there is no consumption of $Ca(OH)_2$ by pozzolanic reaction, blended cement pastes will produce $Ca(OH)_2$ corresponding to the dot line. An arrow indicates $Ca(OH)_2$ content consumed by reacting with fly ash and slag. In the first 28 days, the degree of the fly ash reaction was very slow but pozzolanic reaction increased afterwards. The compressive strength of fly ash blended cement was developed after that time.

The chemical composition of the C-S-H formed in blended cement pastes has been reported to differ from that of portland cement hydration products.⁴⁾

The C/S molar ratio of C-S-H deposited around the fly ash particles in fly ash-slag-cement system is slightly lower than that in fly ash-cement system. Ca/Si ratios of C-S-H hydrate in OPC and blended cement of fly ash50%, fly

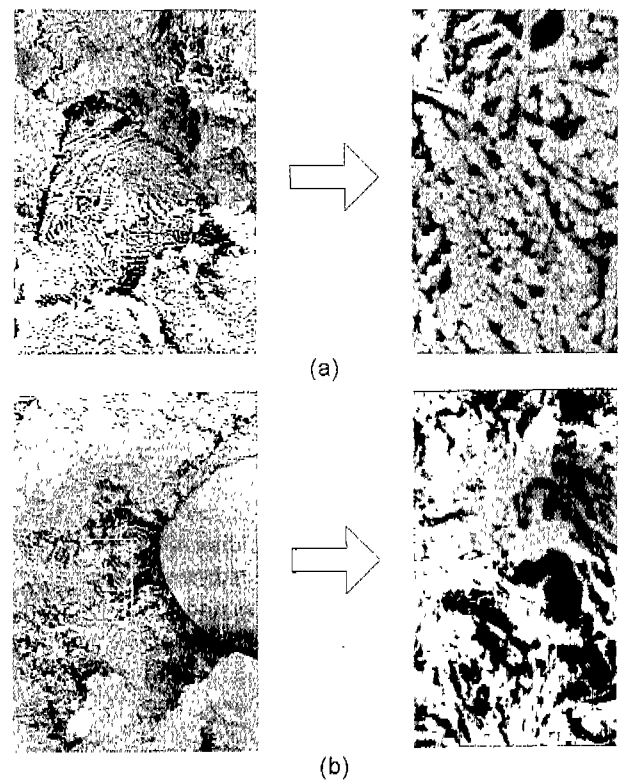


Fig. 3. Split-screen SEM photographs of (a) OPC-slag and (b) OPC-F.A pastes after 91 day. Magnification: left photo, 5000; right photo, 25000.

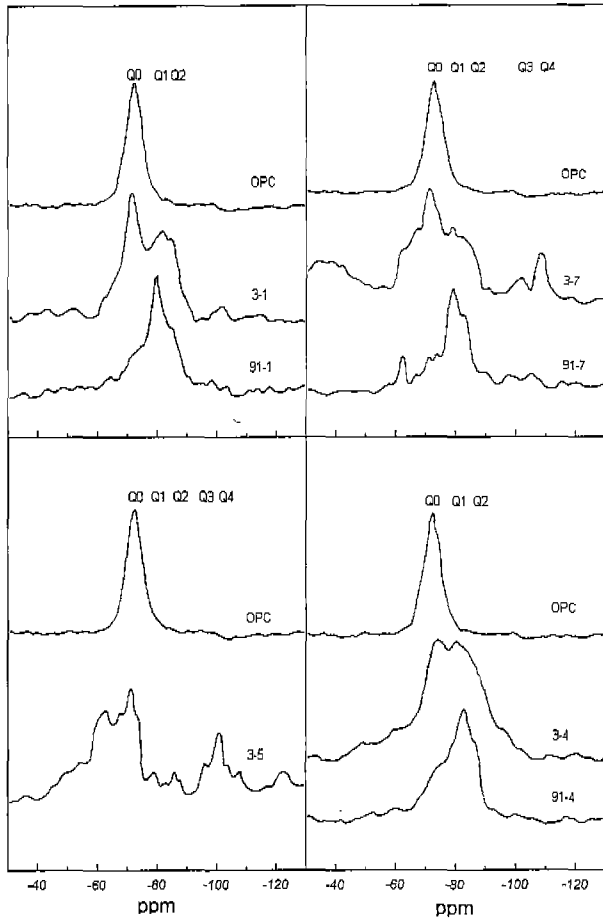


Fig. 4. ^{29}Si -nmr spectra of F.A.-slag-cement systems according to the curing time.

ash+slag50% were about 2.24, 1.80 and 1.72 by EDS analysis. This is referred to that the pozzolanic reaction of slag is competitive with that of fly ash and $\text{Ca}(\text{OH})_2$ is preferentially consumed by the pozzolanic reaction of coexisting slag. C-S-H gel with low Ca/Si ratio showed rather more reticulate than needle-like structure as shown Fig. 3.

Due to the amorphous nature of the C-S-H gel products, it cannot be characterized using X-ray diffraction techniques. The NMR technique relies upon the fact that the silicon nucleus will resonate at slightly different frequencies (chemical shifts) depending on its local environment.⁵⁾ As the silicate anion (SiO_4) becomes increasingly condensed, the chemical shift of the resonance of the ^{29}Si nucleus moves to higher values due to increasing shielding of nucleus.

The hydration of OPC and blended cement paste have been followed using NMR techniques and those spectra are shown in Fig. 4. The broad peak at 71 ppm which corresponds to monosilicate units decreases in intensity as the hydration reaction proceeds and Q1 resonances at ~ 79 ppm followed by Q2 resonances at 84 ppm begin to appear. It was found that the degree of polymerization of the silica in the C-S-H in pastes containing fly ash, slag was higher than OPC pastes.

After 3 days, OPC paste shows short rods of ettringite

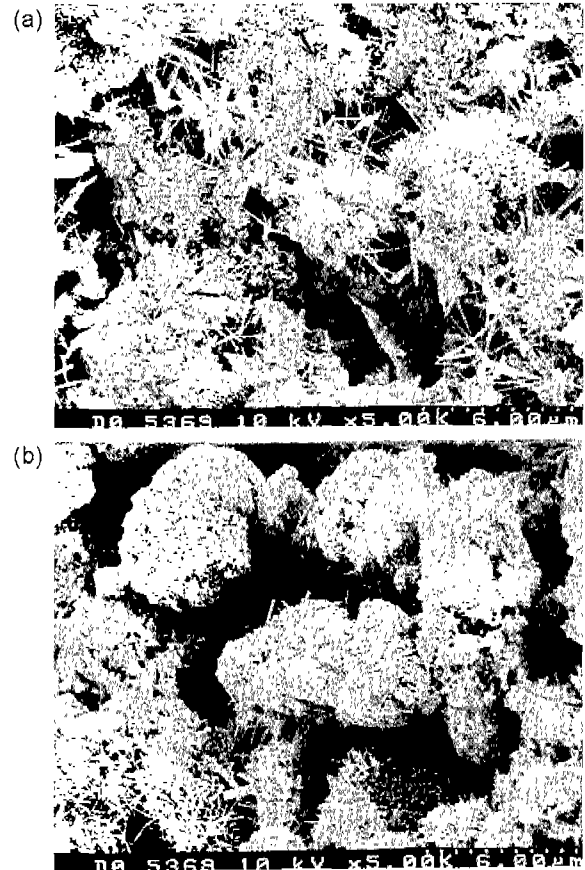


Fig. 5. SEM photographs of (a) OPC and (b) F.A.+slag50% cement after 3 day.

emerging through the outer layers of C-S-H with some crystalline $\text{Ca}(\text{OH})_2$. But blended cement paste reveals retardation of hydration and particles coated with less-developed hydrates are agglomerated as shown Fig. 5.

After 28 days or longer, microstructures of OPC and blended cement pastes are developed but denser in the latter as shown Fig. 6.

Fig. 7 shows an fly ash grain representative of those found in the fly ash blended paste. It is apparent that the erosion caused by reaction at the surface of this fly ash sphere. The glassy phase in the fly ash is dissolving and reacting with the $\text{Ca}(\text{OH})_2$, leaving a clear space around the particles and revealing crystals of mullite on their surface.

3.2. Influence of fly ash, slag on microstructure of hardened cement paste.

The pore structure plays a very important role in the durability of cement-based materials. The durability of concrete is greatly influenced by the permeability of cement paste which, is governed by its pore size distribution.⁶⁾

As curing time of OPC paste increases, the total volume of pores decreases, particularly pores of 0.03 to 0.5 μm . It contributes to the increase in relative volume of the smaller pores, smaller than 0.03 μm . In turn the volume of pores larger than 0.03 μm decreases as the hydrates fill in, or sub-

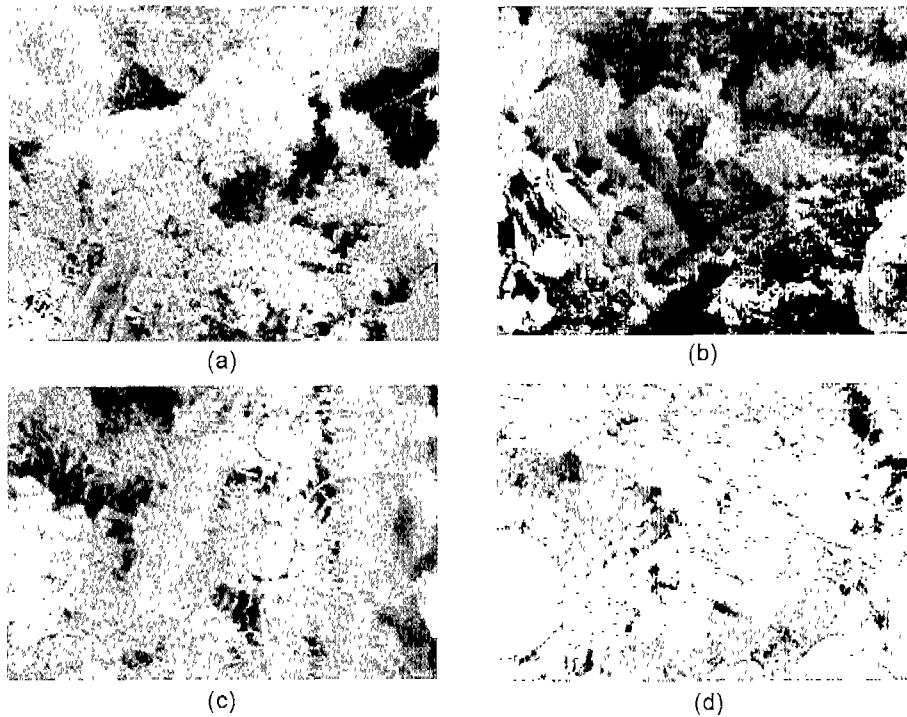


Fig. 6. SEM photographs of (a) OPC, (b) Slag 50%, (c) F.A. 50% and (d) F.A.+slag50% cement pastes after 28 day.

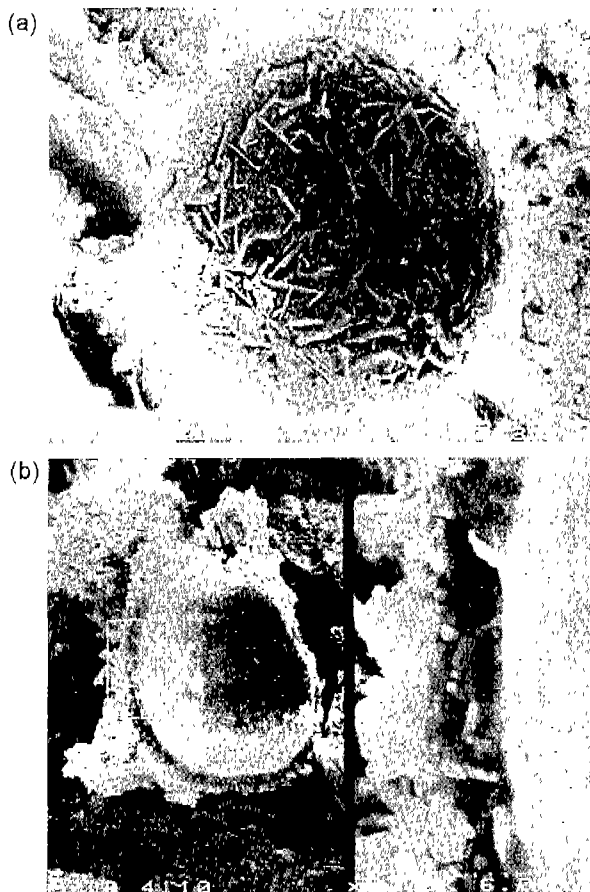


Fig. 7. SEM photographs of F.A.+OPC paste after 91 day. (a) Exposed crystalline and (b) Reacted layer.

divide, the large pore space. In blended cement pastes, the slow pozzolanic reaction reflects at early ages (Fig. 8) the volume of pores in the 0.3 to $0.5\mu\text{m}$ increase which has been related to gaps around pozzolanic materials and pore inside particles. This gaps can be known from a result as shown Fig. 3. A gap of the order of $0.3\sim 0.5\mu\text{m}$ has opened up between the surrounding paste and the residual surface, presumably through reaction and dissolution of the outer layer of the fly ash particle. It was suggested by Takemoto and Uchikawa⁷ that it was due to the existence of a higher alkali content at the surface of fly ash particle which prevented the precipitation of the hydrates thus leaving a vacant space.

The effect of adding fly ash and/or slag is the considerable reduction in the relative volume of pores larger than $0.03\mu\text{m}$, and the increase for pores of smaller than $0.003\mu\text{m}$, as the pozzolanic reaction takes place. Pore size distribution curves in sample containing fly ash and/or slag gradually shift toward finer sizes with increasing the curing time. The C-S-H formed by pozzolanic reaction fills up the pores in hardened cement paste, thus making the structure denser. Fig. 9 shows the pore volume of 0.003 to $0.005\mu\text{m}$ sharply increase in blended cement pastes. It has been pointed out that open channels in hardened cement paste are blocked by pozzolanic reaction and hydration products, leading to changes of pore structure such as the formation of finer and discontinuous pores. In the blended cement pastes, the volume of pores larger than $0.03\mu\text{m}$ decreases sharply at the same time as the $\text{Ca}(\text{OH})_2$ contents start to fall. This is accompanied by a marked increase in compressive strength.

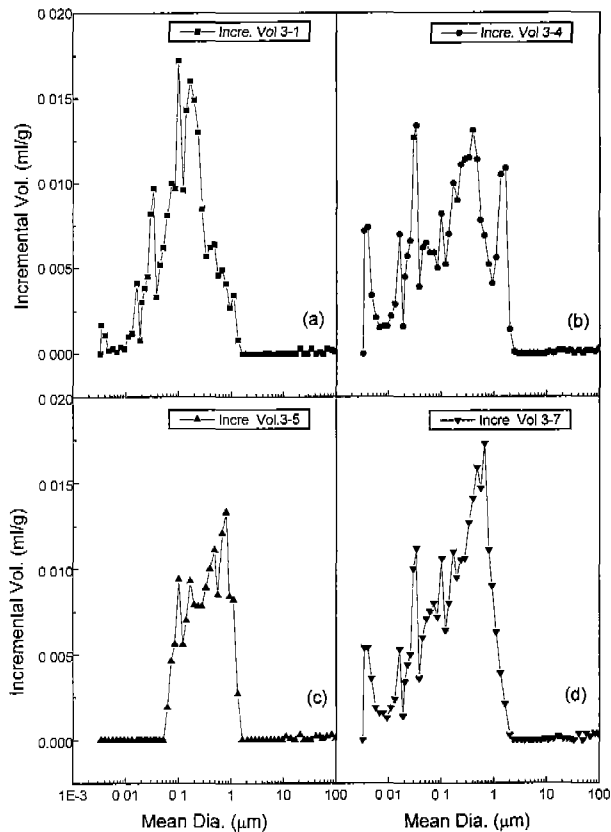


Fig. 8. Pore size distributions of (a) OPC, (b) slag 50%, (c) F.A.50% and (d) slag+F.A.50% cement cured after 3 day.

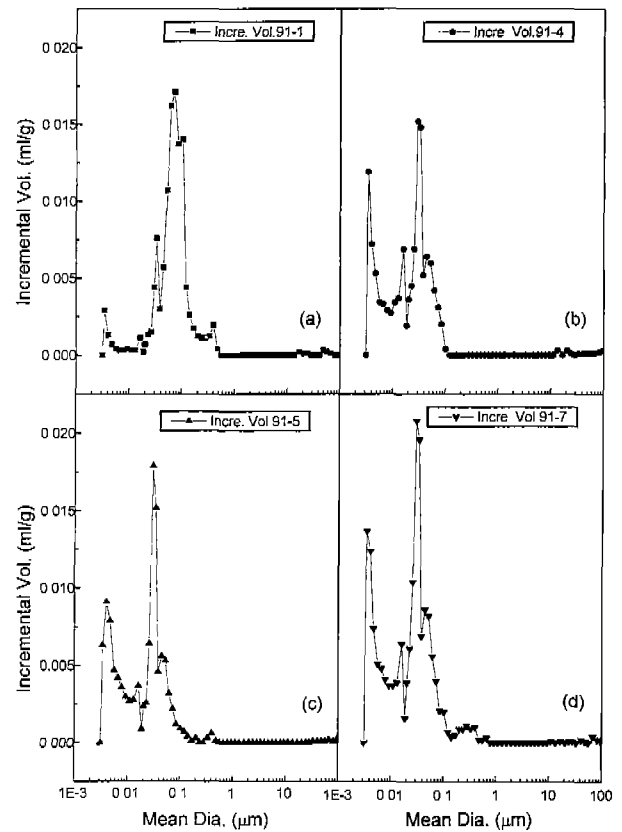


Fig. 9. Pore size distributions of (a) OPC, (b) slag50%, (c) F.A.50% and (d) slag+F.A.50% cement cured after 91 day.

IV. Conclusions

Based on the above results, the following conclusions can be deduced.

1. Compared to OPC, hydrates of fly ash and/or slag blended cement are similar to C-S-H, C-A-H, $\text{Ca}(\text{OH})_2$ but $\text{Ca}(\text{OH})_2$ content decreased due to pozzolanic reaction and C-S-H, C-A-H hydrates increase.

2. If there is no reaction of fly ash or slag, 50% blended cement pastes will produce half of $\text{Ca}(\text{OH})_2$ content in OPC paste. But, $\text{Ca}(\text{OH})_2$ content of blended(50%) cement pastes is lower than calculated value. It is deduced that $\text{Ca}(\text{OH})_2$ is consumed by reaction with fly ash, slag.

3. Pore size distribution curves of fly ash and/or slag blended cement pastes gradually shift toward finer sizes with increasing the curing time due to pore blocking by C-S-H and C-A-H hydrates produced by pozzolanic reaction.

4. ^{29}Si -NMR results of CSH hydrates revealed $(\text{SiO}_4)_n$ polymerization proceeded with increasing curing time. The Ca/Si ratio of CSH hydrate in blended cement pastes was lower than OPC.

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