

# Microstructure of Non-Sintered Inorganic Binder using Phosphogypsum and Waste Lime as Activator

Kim, Ji-Hoon<sup>1</sup>   An, Yang-Jin<sup>2</sup>   Mun, Kyung-Ju<sup>2</sup>   Hyung, Won-Gil<sup>3\*</sup>  
*School of Engineering, Muroran Institute of Technology, Muroran, Hokkaido, 050-8585, Japan*<sup>1</sup>  
*Technical R&D Center, Construction Materials Doctors Group Inc, Jeonju, 02705, Korea*<sup>2</sup>  
*School of Architectural Engineering, Yeungnam University, Gyeongsan, 38541, Korea*<sup>3</sup>

## Abstract

This study is about the development of a non-sintered binder (NSB) which does not require a sintering process by using the industrial by-products Phosphogypsum (PG), Waste Lime (WL) and Granulated Blast Furnace Slag (GBFS). In this report, through SEM analysis of the NSB paste hardening body, micropore analysis of paste using the mercury press-in method and microstructure observation were executed to consider the influence of the formation of the pore structure and the distribution of pore volume on strength, and the following conclusions were reached. 1) Pore structure of NSB paste of early age is influenced by hydrate generation amount by GBFS and activator. 2) Through observing the internal microstructure of NSB binder paste, it was found that the strength expression at early age due to hydration reaction was achieved with a large amount of ettringite serving as the frame with C-S-H gel generated at the same time. It was confirmed that C-S-H gel wrapped around ettringite, and as time passed, the amount generated continually increased, and C-S-H gel tightly filled the pores of hardened paste, forming a dense network-type web structure. 3) For NSB-type cement, the degree of formation of gel pores below 10 $\mu$ m had a greater influence on strength improvement than simple pore reduction by charging capillary pores, and the pore size that had the greatest effect on strength was micropores with diameter below 10 $\mu$ m.

Keywords : non-sintered binder, microstructure, phosphogypsum, waste lime

## 1. Introduction

The global demand for cement is expected to increase by 2.5~5.8% every year until the early 21<sup>st</sup> century [1]. To comply with the Kyoto Protocol while satisfying this increased cement demand, it is necessary to develop cement with little or almost no carbon dioxide emission.

As a possible approach, studies on the use of inorganic binder made from industrial byproducts

that can replace cement have been underway.

This study is about the production of inorganic binder that does not require a sintering process (Non-Sintered Binder; NSB hereinafter) by using industrial byproducts such as Granulated Blast Furnace Slag (GBFS), Phosphogypsum (PG), Waste Lime (WL) and such. Since it does not use clinker, its use can prevent damage to forest resources due to mining and depletion of mineral resources such as limestone, and it can also save fuel/power consumed in clinker production. In addition, the fugitive dust, vibration, noise and the environmental load caused by limestone mining and transportation can be reduced, as well as the environmental/economic load following the reclamation of industrial waste.

Received : January 10, 2018

Revision received : February 9, 2018

Accepted : March 8, 2018

\* Corresponding author: Hyung, Won-Gil

[Tel: 82-2-1234-5678, E-mail: beda@yu.ac.kr]

©2018 The Korea Institute of Building Construction, All rights reserved.

Not only does the elution of  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$  which are ionic-bonding substances of GBFS take place selectively, but also the silicate hydrates formed with a high degree of polymerization are surrounded by a dense internal hydration layer and spread slowly, so hydration takes place slowly at the beginning. The slow spreading speed of hydrates indicates that the pores (not including the air amount added during mixing) due to the reduced hydrate generation are large. In other words, it indicates that there are large pore volumes with relatively greater diameters, and their quantitative changes have a large influence on various physical properties of NSB. As it ages, however, continued activation reaction of sulfate and strong-alkali activators accelerates the hydration reaction on the granule surface, the degree of polymerization of  $\text{CaO/SiO}_2$  decreases greatly, and the silicate hydrates besieged inside are eluted at a high speed. At this point, not only are the pores generated by bound water and evaporation water tightly charged, but also the coherence among hydrates is greatly improved, so the strength continuously increases. This means that total pores are gradually filled by hydrate formation, so the hydration reaction of NSB can be explained by paste porosity analysis as well.

Accordingly, this study executed a pore analysis of cement paste using the mercury press-in method and microstructure observation through SEM analysis to consider the influence of pore structure formation and pore volume distribution on strength in order to evaluate the relationship between internal pore structure and the properties of NSB hydrates in an integrated manner.

## 2. Experiment Overview

### 2.1 Used Material

In this study, for the production of NSB, GBFS was taken as the base, and PG which is discharged as

waste from phosphate production was used as a sulfate activator for inducing hydration reaction, and WL which is discharged as waste from  $\text{Na}_2\text{CO}_3$  production process and Slaked Lime (SL) were used as alkali activator. PG was cleaned for 5 minutes at  $20^\circ\text{C}$  in 0.5% limewater, and here the ratio of PG in limewater was 14% by weight. Once cleaned and neutralized, the PG was transferred to type-II anhydrite ( $\text{II CaSO}_4$ , APG) state calcined at  $450^\circ\text{C}$  and to dihydrate gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , DPG) state only dried at  $80^\circ\text{C}$ , and was granulated and used. WL in discharged state was granulated and used after 1 day of drying at  $90^\circ\text{C}$ [2,3]. To compare the physical properties with NSB, a commercial product was used for Ordinary Portland Cement (OPC), and Blast-furnace Slag Cement (BSC) mixing OPC and GBFS at 50:50 was produced and used. The physical/chemical properties of the materials used in this experiment are specified in Table 1. Three types of NSB mix used in this experiment were selected based on a previous study[1].

Table 1. Chemical properties of raw materials

	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{CaO}$	$\text{Fe}_2\text{O}_3$	$\text{MgO}$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{SO}_3$	LOI
GBFS	34.8	14.5	41.7	0.5	6.9	0.1	0.4	0.1	0.2
APG	1.3	0.1	41.0	0.04	-	0.1	-	54.9	0.8
DPG	1.1	0.1	32.3	0.2	0.1	-	-	43.3	22.4
SL	-	0.2	65.9	0.1	1.0	-	-	1.1	31.5
WL	4.9	1.6	42.1	1.4	6.9	0.1	1.9	3.1	33.2
OPC	20.9	5.4	64.7	2.4	1.5	0.3	0.2	1.7	2.0

\* GBFS: Granulated Blast Furnace Slag, APG: anhydrite gypsum, DPG: dehydrate gypsum, SL: Slaked Lime; WL: Waste Lime, OPC: Ordinary Portland cement

Table 2. Mix proportions of binder (%)

	OPC	GBFS	APG	DPG	SL	WL
BSC	50	50	-	-	-	-
NSB1	-	87	12	-	1	-
NSB2	-	82	-	17	1	-
NSB3	-	81	11	-	-	8

\*BSC: Blast-furnace Slag Cement, NSB: Non Sintered Binder

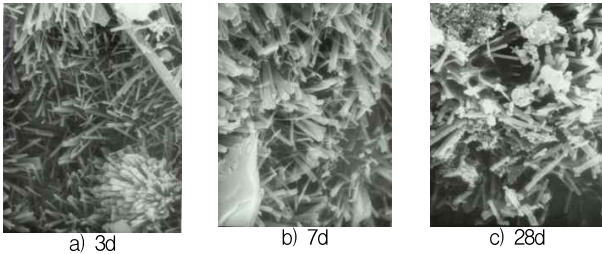


Figure 1. SEM images of NSB1 paste with curing age ( $\times 5,000$ )

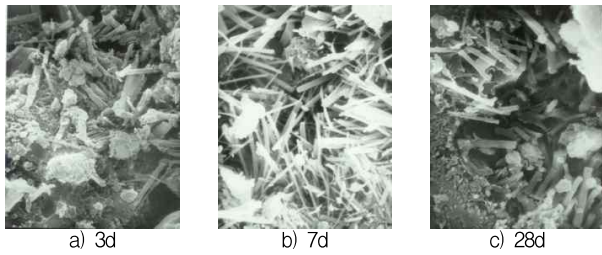


Figure 2. SEM images of NSB2 paste with curing age ( $\times 5,000$ )

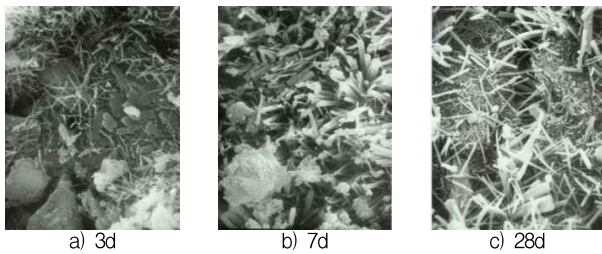


Figure 3. SEM images of NSB3 paste with curing age ( $\times 5,000$ )

## 2.2 Mix and Specimen Production

NSB mix is as specified Table 2. All proportions were determined through preliminary experiments. As for the specimen for pore size measurement and SEM analysis, raw materials measured according to the mix conditions were dry-mixed for sufficient blending, and water (W/C 40%) was added and then it was mixed for 1 minute 30 seconds with mortar mixer to produce the paste. The produced specimen underwent sealed curing to be of specified age under curing conditions of 20°C, 50%RH. Specimen for compression strength measurement was produced with B:S=1:2.45, W/B= 50% for mortar. It was placed in the 5×5×5 cm mold for compression strength measurement, and underwent sealed curing for 24 hours under the curing conditions of 20°C, 50%RH, and then was cured underwater at 20±2°C.

## 2.3 Experiment Items

### 2.3.1 SEM Analysis

To observe the degree of hydrate generation according to NSB mix conditions, SEM (Scanning Electron Microscope) analysis was executed. Fracture plane of paste was collected per age which was then deposited with acetone, and then measurement was executed using the dry-processed specimen.

### 2.3.2 Pore Size Measurement

To evaluate the internal pore size of NSB, mercury press-in porosimeter (Micromeritics, Autopore III) was used to measure pore size distribution. By age, specimen of grain size 2mm was taken from paste, deposited in acetone, and then the dry-processed specimen was used to take measurements. Through mercury press-in, the pore size distribution curve was found based on the relationship of the pressure and mercury press-in amount.

### 2.3.3 Compression Strength Measurement

The compression strength was measured by age according to KS L 5105.

## 3. Experiment Result and Considerations

### 3.1 SEM Analysis Result

To observe the degree of hydrate generation according to NSB mix conditions, SEM Figure analysis result is as shown in Figure 1~3.

Figure 1 shows the internal microstructure of NSB1 with APG mix of 12% according to age, and ettringite at the age of initial three days shows a thin and long needle-shape but is in a large amount with a very dense form, and through continued hydration reaction, at the age of seven days, it was formed in the thick needle structure shape. At the age of 28 days, sealed form of hydrates appearing to be C-S-H gel beside ettringite were observed in a large amount.

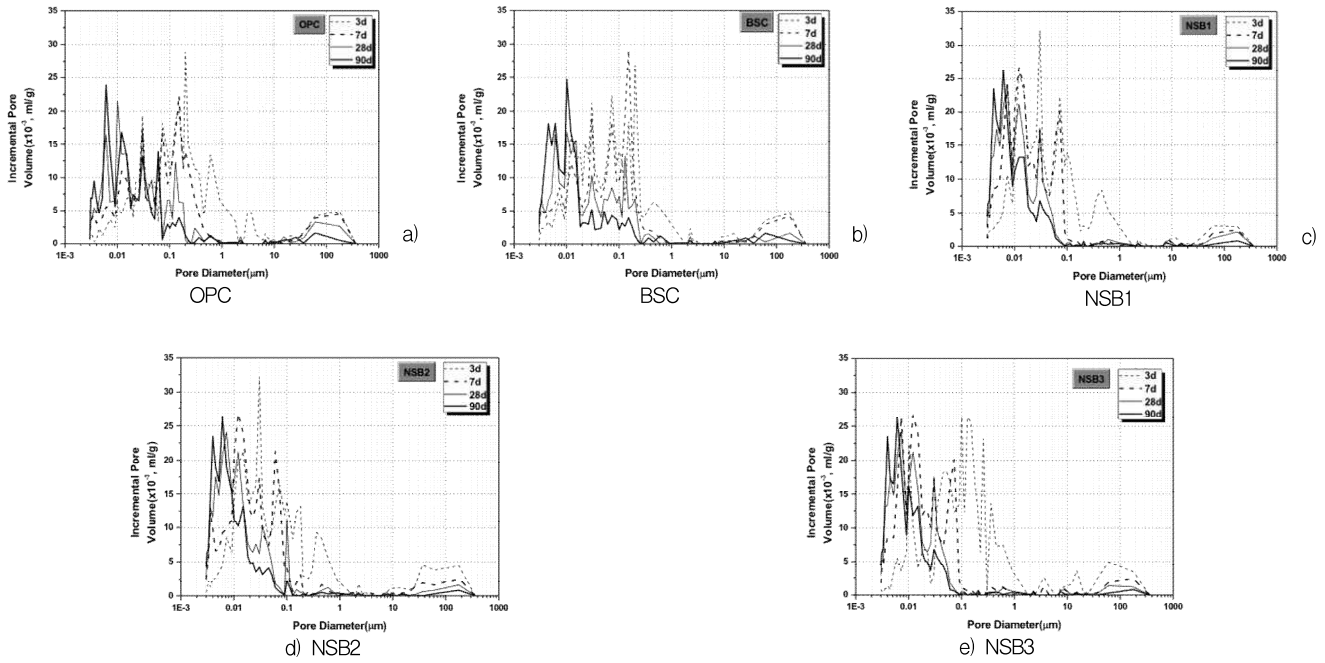


Figure 4. Change of pore size distribution curves of paste with different curing ages (3 days~90 days)

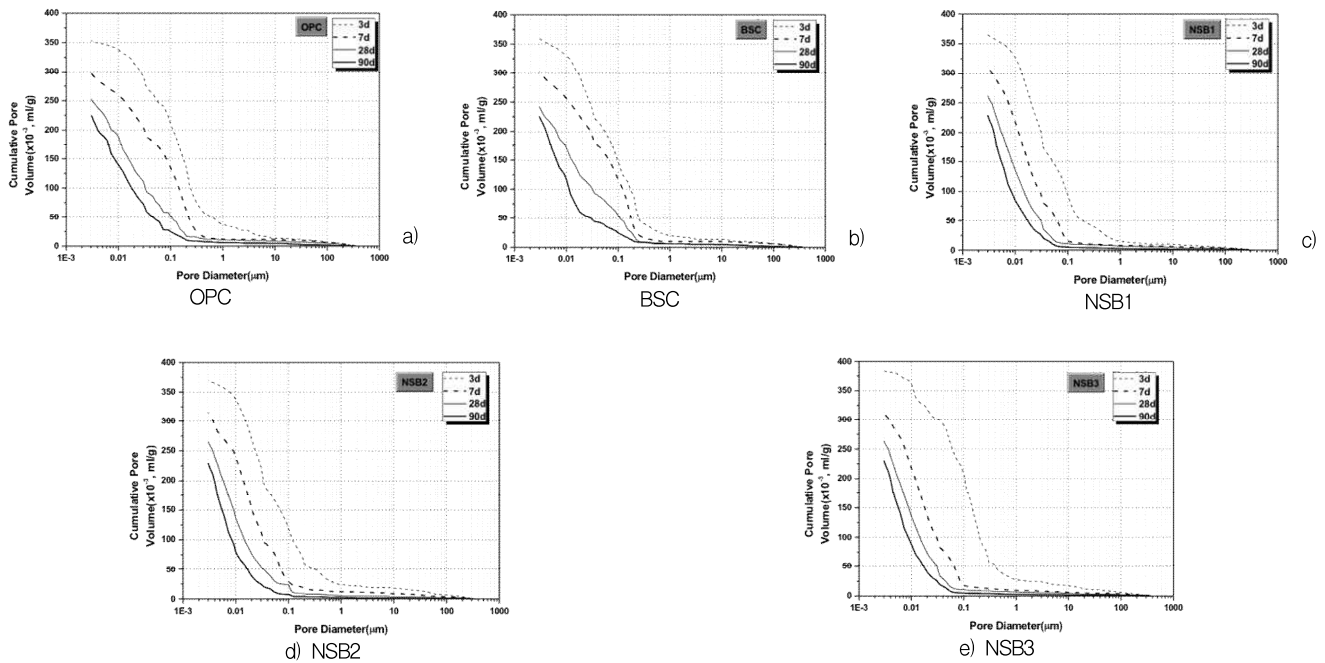


Figure 5. Cumulative pore volume curves of paste with different curing ages (3 days~90 days)

NSB at an early age forms strength with tight-form ettringite as the frame. After it has aged for a while, it is thought to achieve a high level of strength expression as ettringite forms a tight network-type web structure with C-S-H gel as the frame. Figure

2 and Figure 3 show the internal microstructure according to the age of NSB2 and NSB3 using DPG and WL. At the age of 3 days, it can be confirmed that unreacted GBFS and PG exist, around which thin long needle-shaped ettringite exists. At the age of

---

7 days, however, just like NSB1, a large amount of ettringite is generated and is developed into a thick needle shape. At the age of over 28 days, C-S-H gel is well developed and the pores in between are filled with ettringite.

Combining the results of observation of internal microstructure of NSB paste, the strength expression at early age of hydration reaction is achieved by C-S-H gel generated at the same time with ettringite as the frame. Also, C-S-H gel wraps around ettringite, and as it ages, the generation amount continuously increases and the pores of the hardened paste are tightly filled with C-S-H gel, forming a tight network-type web structure with ettringite.

### 3.2 Pore Volume and Distribution

Figure 4 and Figure 5 show pore size distribution and cumulative pore volume of paste measured at the age of 3–90 days according to binder types. Generally, at the early age, pore structure of the hardening body is greatly influenced not only by the hydrate generation amount, but also by the fineness of the cement. Overall, in terms of the pore size distribution and cumulative pore volume of 3-day-old, NSB has a higher fineness than OPC or BSC, yet there is no significant difference in the degree of pore generation, which leads to the judgment that initial hydrate production is smaller than OPC and BSC. After the age of 7 days, however, the pores over 100  $\mu\text{m}$  with an adverse effect on strength[4,5] significantly decrease while the pore volume below 10  $\mu\text{m}$  significantly increases for NSB compared to OPC and BSC, and this indicates that the hydrate generation amount increases after the age of 7 days for NSB compared to OPC and BSC. That is, the hardening body gets a smaller pore size with hydrates filling up the pores as hydration progresses, and in such a pore structure, it comes to have a pore structure with large tortuosity, and ion spreading is suppressed, but the trend is more

noticeable as it ages for NSB compared to OPC and BSC.

Looking at the changes in the cumulative porosity of each pore size according to the binder type, there was no large difference according to the cement type for the age of 3 days, but at 7 days of age, the cumulative porosity of OPC and BSC significantly increased for over 120~130  $\mu\text{m}$ , while for NSB except NSB2, cumulative porosity tended to increase in the range of about 100  $\mu\text{m}$ . NSB in particular showed a trend of a rapid increase of cumulative porosity in the range below 100  $\mu\text{m}$  at the age of 28 days and 90 days.

It can be seen that NSB2 and NSB3 show a large difference in cumulative porosity at the age of 3 days and 7 days. This is because the activation reaction by DPG and WL usage is weaker than APG and SL at the early age, and this is thought to be because while the hydrate generation amount is significantly smaller at the age of 3 days, the hydration generation rapidly increases at the age of 7 days.

Total pore volume at the age of 3 days appeared to be in the order of OPC < BSC < NSB1 < NSB2 < NSB3. The total pore volume of NSB1~NSB3, whose fineness is not much higher than OPC and BSC, did not show a large difference, but there was a large difference in pore size distribution. In the pore diameter range of 3~100  $\mu\text{m}$ , pore size of NSB1 appears to be greater than that of OPC and BSC, but the pore size of NSB2 and NSB3 which used DPG and WL as activators tends to appear smaller. Generally, pore volume and pore size distribution of the hardening body are determined by matrix charging action of mixed substance and hydration products. This means that NSB2 and NSB3 have great charging actions but their hydrate generation amount is relatively smaller than other binders. Thus, it is thought that NSB1, which uses APG as the main activator, has a higher share of pores with diameter in the range of 3~100  $\mu\text{m}$  among NSB with the same fineness because the grain size of GBFS is smaller

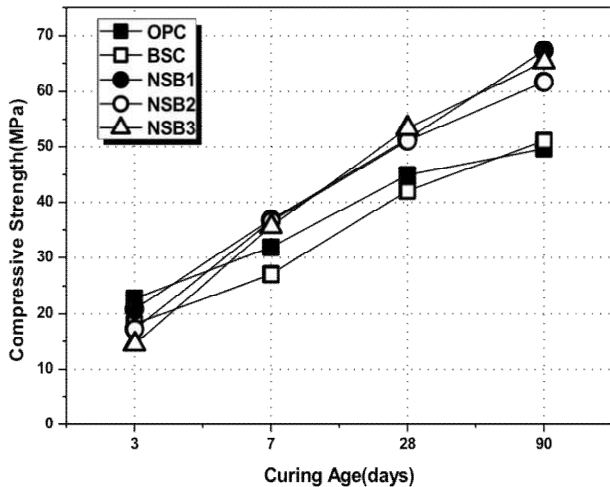


Figure 6. Compressive strength of mortar using various binder elapsed curing age

than that of OPC, which means that charging action is outstanding, hydration reaction speed is faster in comparison and micropore charging is accelerated by hydrate production. It could be confirmed that the pore structure of NSB at early age was greatly influenced by the amount of hydration product generated by a GBFS activator.

At the early age of NSB2 and NSB3 mixed with DPG and WL, the activator action was not as significant as NSB1, but as time passes, it destroyed the acidic film of GBFS which generated a large amount of hydration products, significantly increasing the number of micropores after the age of 7 days.

### 3.3 Compression Strength

Figure 6 is the compression strength measurement result for mortar age 3~90 days according to binder types. NSB shows an overall smaller strength expression than OPC does at the initial age of 3 days, but beginning on day 7, this trend begins to reverse, showing a large difference, and it can be confirmed that the strength is continuously increasing. Particularly at the age of over 28 days, mortar using OPC shows a tendency of slow strength expression, but NSB shows a steady strength increase trend up

to 90 days, in an almost linear manner. NSB2 is mortar of binder which used DPG instead of APG as the activator, and the expression was about 80% the level of NSB1 at the age of 3 days, but beginning on day 7, it showed almost the same level of strength. This is because APG is a soluble substance whose elution amount is about twice as much as that of DPG, which means that the opportunity to come into contact with acidic film of GBFS grain surface is increased, and also that the hydration heat discharged during elution is greater than that of DPG. If APG is used, the initial strength increases, but such actions gradually diminish as time passes by, so eventually it becomes similar to the case using DPG[3,6].

As for NSB3 mixed with WL, the strength for the first 3 days is about 70% of NSB1, and is expressed as lower than NSB2, and at the age of over 7 days, it shows a strength expression almost similar to NSB1. Alkali activation action of WL is weaker than the case using SL, but continues to maintain a pH over 12 so that it can eventually destroy the acidic film of GBFS. Since hydrates are formed through the hydration reaction of PG and modified ion inside GBFS and calcium carbonate and other inorganic substances existing in WL beside calcium hydroxide provide the charging without interrupting their hydration reactions and behave safely, it is thought that a great degree of strength increase was achieved at an older age. NSB expressed a higher strength at an older age compared to OPC and BSC. This is because GBFS is activated by PG and WL so that ettringite, C-S-H gel and such are consistently generated[7,8,9,10]. The compression strength of a mortar specimen using NSB past 90 days was about 1.3 times higher compared to OPC and BSC.

### 3.4 Correlation of Pore Structure and Compression Strength[4,5,11]

Figure 7 shows the relationship between mortar

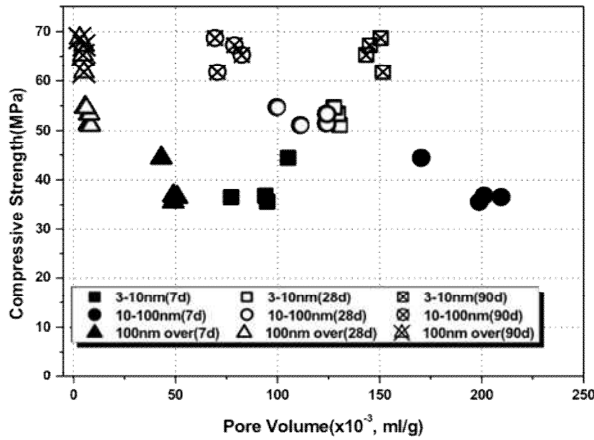


Figure 7. The relationship between pore volume according to pore size and compressive strength of NSB

compression strength and pore volume according to pore size of NSB paste. In order to evaluate the change in the pore structure related to the hydration product, the age of 3 days influenced by GBFS charging action was excluded and only the correlation at the age of over 7 days was shown. This shows a proportional trend where the volume of 3~10  $\mu\text{m}$  pore size increased as it aged, and compression strength increased accordingly, but for the 10~100  $\mu\text{m}$  pore size, it showed a disproportional tendency in which the volume decreased as it aged, and compression strength also decreased. This means that NSB has a pore size influencing strength in a smaller range than OPC. That is, for NSB, the degree of below 10  $\mu\text{m}$  gel pore generation has a greater influence on strength improvement than simple pore reduction by charging the capillary pores, and it can be confirmed that the pores with the greatest influence on strength are micropores with a pore size under 10  $\mu\text{m}$ .

In the meantime, pore sizes above 100  $\mu\text{m}$  showed a general decreasing tendency as time passed by, and the compression strength also decreased.

#### 4. Conclusion

This study executed pore analysis of cement paste

to consider the influence of pore structure formation and pore volume distribution on strength, and the relationship between internal pore structure and NSB hydrate properties was evaluated in an integrated manner, to reach the following conclusion.

- 1) Pore structure of NSB paste of early age is influenced by the amount of hydrate generation by GBFS and activator.
- 2) Early hydration reaction of NSB binder appeared to be slower than for OPC or BFS, but at the age of 7 days, pores over 100  $\mu\text{m}$  which have an adverse effect on strength decreased and micropore volume below 10  $\mu\text{m}$  increased about 1.5~1.8 times compared to OPC and BSC paste. The pore structure of 28-day-old NSB binder paste showed a further increase of the amount of micropores below 10  $\mu\text{m}$ , representing about twice the total pore volume of OPC paste, and pore volume above 100  $\mu\text{m}$  greatly decreased, being in the range of 1/3~1/10 compared to OPC paste. That is, as hydration progressed, hydrates fill up the pores with both pore size and pore amount decreasing.
- 3) Through observing the internal microstructure of NSB binder paste, it was found that the strength expression at early age due to hydration reaction was achieved with a large amount of ettringite serving as the frame with C-S-H gel generated at the same time. It was confirmed that C-S-H gel wrapped around ettringite, and as time passed, the generation amount continually increased, and C-S-H gel tightly filled up the pores of hardened paste, forming a dense network-type web structure.
- 4) For NSB-type cement, the degree of formation of gel pores below 10  $\mu\text{m}$  had a greater influence on strength improvement than simple pore reduction by charging capillary pores, and the pore size that had the greatest effect on strength was micropores with diameter below 10  $\mu\text{m}$ .

## Acknowledgement

Sheffield, UK, Wexham springs slough(UK): Cement Concrete Associate; 1976, p. 2–30.

This research was supported by Basic Science Research Foundation of Korea(NRF) funded by the Ministry of Science, ICT and future Planning (No.2015R1A2A2A01005901)

## References

1. Mun KJ, Hyung WK, Lee CW, So SY, Soh YS, Basic properties of non-sintering cement using phosphogypsum and waste lime as activator. *Construction and building materials*, 2007 Jun; 21(6):1342–50.
2. Bijen J, Niël E, Supersulphated cement from blastfurnace slag and chemical gypsum available in the Netherlands and neighbouring countries, *Cement and concrete research*, 1981 May;11(3):307–22.
3. Erdem E, Olmez H, The mechanical properties of supersulphated cement containing phosphogypsum. *Cement and concrete research*, 1993 Jan;23(1): 115–21.
4. Uchikawa H, Development of new cement and concrete. *Gypsum and Lime*, 1990;229: 497–505.
5. Takemoto K, Uchikawa H, Hydration of pozzolanic cement. *Proceedings of the 7th International Congress on the Chemistry of Cement*; 1980 Jun 30–Jul 4; Paris, France, Paris(France): Editions Septima; 1980. p. 1–29.
6. Gruskovnjak A, Lothenbach B, Winnefeld F, Figi R, Ko SC, Adler M, Mäder U. Hydration mechanisms of super sulphated slag cement. *Cement and concrete research*, 2008 Jul;38(7):983–92.
7. Peiyu Y, Wenyan Y. The cementitious binder derived with fluorogypsum and low quality of fly ash. *Cement and concrete research*, 2000 Feb;30(2):275–80.
8. Midgley HG, Pettifer K, The microstructure of hydrated super sulphated cement. *Cement and concrete research*, 1971 Jan;1(1):101–4.
9. Dan TK, Chatterjee MK, Activation of an indian blast furnace slag by lime and lime-gypsum mixed activator in solution phase. *Indian journal of technology*, 1985;23(9):337–44.
10. Bijen J, Niël E, Supersulphated cement: Improved properties, silic. *Ind.* 1982;47(2):45–53.
11. Diamond S, Cement paste microstructure—an overview at several levels. *Proceedings of a conference on Hydraulic Cement Paste: their structures and properties*; 1976 Apr 8–9; University of