

Effect of blast furnace slag on the hydration properties in natural hydraulic lime

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Natural hydraulic lime (NHL) has gained a great deal of attention as an eco-friendly construction material, but its application has remained very limited due to its insufficient mechanical properties. The addition of mineral admixture to NHL has been considered as a means of addressing this drawback and improving the mechanical properties for future commercialization. The effects of adding a mineral admixture such as blast furnace slag (BFS) or anhydrite (AH) to NHL on the hydration properties were systematically investigated in this study. Local Korean NHL (K-NHL) was synthesized using domestic low-grade limestone. The hydration properties of the NHL products were then investigated as a function of the hydration time and the addition ratio of inorganic additives. Through an investigation of the hydration properties of NHL pastes mixed with BFS and AH, Al-based compounds such as calcium aluminate hydrates (C_4AH_{13}) and ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) were observed at early hydration time. The formation of calcium silicate hydrates (C-S-H) increased with enlargement of the amount of inorganic additives. The compressive strength and setting time were improved due to increased quantities of these hydration products.

Key words: Limestone, Natural hydraulic lime, Blast furnace slag, Anhydrite, Hydration.

Introduction

Lime can be categorized into two types, hydraulic lime (HL) and non-hydraulic lime. Natural hydraulic lime (NHL) is included in hydraulic lime because of its hardening property by the hydraulic reaction of C_3S ($3CaO \cdot SiO_2$) and C_2S ($2CaO \cdot SiO_2$), mineral phases of cement, with water [1, 2]. The NHL has the property of setting and hardening when mixed with water and by reaction with carbon dioxide from the air through long term, and the type of NHL is separated according to compressive strength at 28 days [1, 3, 4]. The properties of NHL are revealed by its porosity, and it shows environment friendly characteristics such as constant temperature and humidity, antifungal properties, and absorbability of toxic materials. The manufacturing techniques of light weight brick, porous concrete, and porous mortar have been available for a long time. However, these products may contain hazardous substances and have a heat insulating property lower than that of NHL [5 6].

NHL has garnered attention as an eco-friendly construction material, but its application has remained very limited due to its insufficient mechanical properties such as compressive strength, flexural strength, and setting time. In order to address these drawbacks and improve the mechanical properties of NHL, the addition of organic and inorganic additives has been considered. As inorganic additives, blast furnace slag (BFS), fly-ash, silica fume, and metakaolin having pozzolanic reactions and latent hydraulic reactions can be used [7]. Hydration products such as calcium silicate hydrate (C-S-H), calcium aluminate hydrates (C-A-H), and ettringite ($3CaO \cdot Al_2O_3 \cdot 2CaSO_4 \cdot 32H_2O$) from these reaction are created, which contribute to development of the strength. Here, H is H_2O , A is Al_2O_3 and C is CaO . BFS, a by-product of the steel industry, has been widely used as a mineral admixture for the type of blast furnace slag cement that is specified as promoting green procurement for global environment [7-9]. It is well known that the massive production of Portland cement consumes a huge amount of energy and is hence a primary source of CO_2 and atmospheric pollution. In this light, the experimental program in this study was designed to assess the hydration behavior of BFS blended NHL. The objectives of this study are to (a) clarify the influences of the addition ratio of BFS, the use of

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anhydrite (AH), and hydration time on the hydration evolution of BFS blended NHL paste; (2) investigate the correlation between the hydration behavior and the pore size distribution; and (3) determine the effects of BFS on the compressive strength behavior of BFS blended NHL mortar.

Experimental Procedure

Materials

Fig. 1 presents the X-ray diffraction (XRD) analysis results of K-NHL utilizing local Korean NHL. The hydraulic phase of K-NHL is composed of $\text{Ca}(\text{OH})_2$, C_2S , C_3S , and un-reacted SiO_2 . Fig. 2 indicates the results of the particle size and the distribution of K-NHL. Pulverization of K-NHL was conducted by utilizing air classified mill (ACM), and the average particle size was $12.25 \mu\text{m}$.

Table 1 and Fig. 3 present the chemical analysis results and the mineral phase analysis results for BFS

and AH. The chemical analysis results of Table 1 show that in the case of BFS, the content of CaO , SiO_2 , and Al_2O_3 was 42.45%, 27.41%, and 14.79%, respectively. The main compounds of AH were CaO and SO_3 , and the content of CaO and SO_3 was 42.2% and 51.0%, respectively. From the mineral phase analysis of Fig. 3, BFS contains amorphous mineral phases and AH contains SiO_2 , CaSO_4 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. As BFS contains a combination of SiO_2 and Al_2O_3 by hydraulic reaction, calcium silicate (C-S-H), calcium aluminate (C-A-H), and ettringite hydrates are generated, and it is assumed they will show excellent properties in compressive strength and condensation [10].

Fig. 4 presents the analysis results on the particle size distribution of BFS and AH. The average particle sizes of admixtures are $12.7 \mu\text{m}$ in the case of BFS and $25.9 \mu\text{m}$ in the case of AH, which is not substantially different from K-NHL.

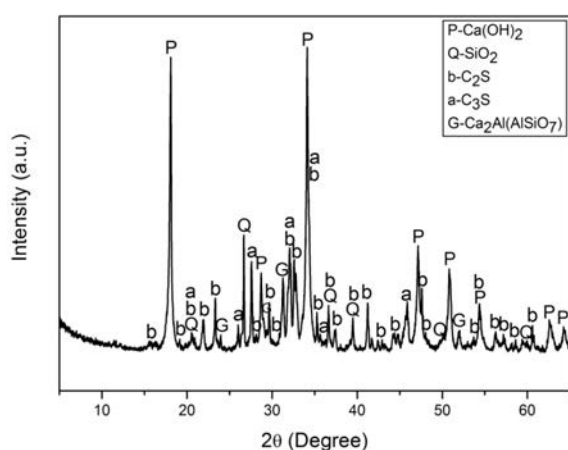


Fig. 1. XRD pattern of K-NHL.

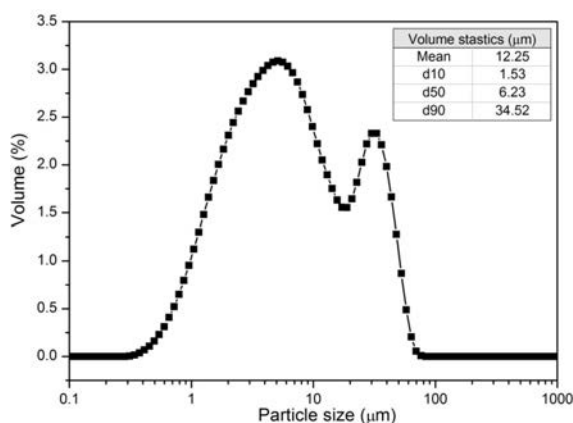


Fig. 2. Particle size distribution curve of K-NHL.

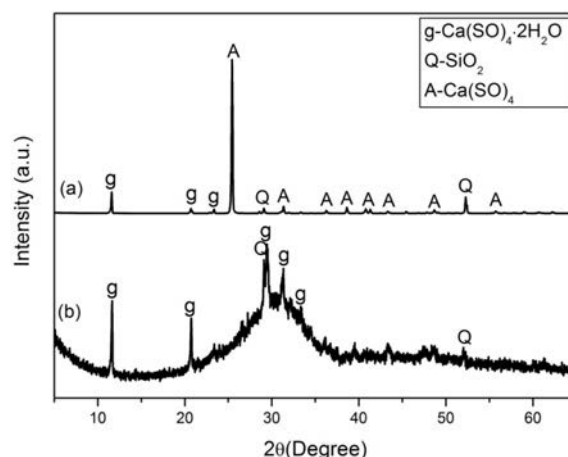


Fig. 3. XRD patterns of (a) AH and (b) BFS.

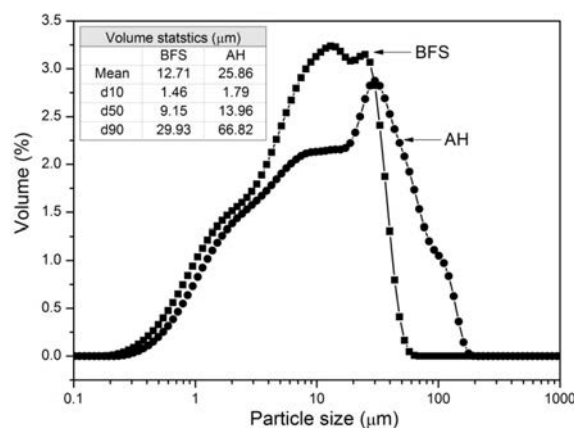


Fig. 4. Particle size distribution curves of BFS and AH.

Table 1. Chemical composition of BFS and AH (%).

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3
BFS	27.41	14.79	0.57	42.45	8.59	0.82	0.26	3.90
AH	1.37	0.61	0.18	42.20	0.31	0.09	0.03	51.0

Table 2. Experimental condition for preparation of NHL pastes.

NHL type	Water ratio (%)	Condition
K-NHL	60	Replacement ratio of BFS (%): 10, 20, 30
		Replacement ratio of AH (%): 0, 3
		Curing condition: 20 °C with 95 % of relative humidity
		Curing age (day): 1, 3, 7, 28

Table 3. Sample designation of NHL mixtures.

Mix proportion (%)			Sample designation
K-NHL	BFS	AH	
90	10	–	S 10-NHL
80	20	–	S 20-NHL
70	30	–	S 30-NHL
87	10	3	S 10-NHL_AH
77	20	3	S 20-NHL_AH
67	30	3	S 30-NHL_AH

NHL paste

To investigate the hydration properties of NHL paste when adding inorganic admixtures in K-NHL, the hydration properties with mixed amounts (10%, 20%, and 30%) of BFS were examined to check the hydrates of K-NHL. AH was only added at a rate of 3% in each mixture. Table 2 presents the water mixing ratio and experimental conditions to prepare the paste. When manufacturing pastes with admixtures, a water ratio of 60% was applied. NHL has setting and hardening properties when mixed with water and by reaction with carbon dioxide from the air. To show these characteristics, fresh NHL paste was placed on a plastic plate with a thickness of (5 ~ 8) mm, and kept at 20 °C and relative humidity of 95% until being analyzed, after 1, 3, 7 and 28 days of aging. The morphology of these hardened pastes was investigated by means of scanning electron microscopy (SEM, Hitach S-4300), and the hydrates that formed were identified, using X-ray diffraction (XRD, Rigaku D/MAX-2500/PC) and differential scanning calorimetry (DSC, Netzsch STA449C Jupiter). The pore structure of the hardened pastes was examined by an automatic mercury porosimeter (AMP, Micromeritics AutoPoreIV 9520). The sample was labeled as S 10-NHL, S 20-NHL, S 30-NHL, S 10-NHL_AH, S 20-NHL_AH and S 30-NHL_AH according to content of K-NHL, BFS, and AH. Details are shown in Table 3.

Compressive strength and setting time test

Mortar preparation and the test method to analyze the compressive strength were carried out according to BS EN 459 - 2 : 2010. When manufacturing mortars in accordance with the water/solid ratio (w/s), it was shown that flow differences were prominent in relation to the sample properties. To verify the compressive

Table 4. Water ratio for setting time test of NHL paste.

Samples	Water ratio (%)
K-NHL	55
S 10-NHL	54
S 20-NHL	50
S 30-NHL	47
S 10-NHL_AH	53
S 20-NHL_AH	51
S 30-NHL_AH	48

strength properties as per the sample properties when a specific flow was given, mortars were manufactured by fixing the flow at (165 ± 3) mm. Prismatic mortar specimens were made at (40 × 40 × 60) mm in size and housed into two floors and hardened by utilizing a vibrating table. The manufactured specimens were cured at 20 °C and relative humidity of 95%. The compressive strength was tested at 7 and 28 days' and when measuring the compressive strength, the loading speed was set to 144 kN/min. Table 3 presents the w/s ratios of each sample at flow of (165 ± 3) mm, and equation (1) shows the formula to calculate the compressive strength in accordance with adding inorganic admixtures.

$$R_c = \frac{F_c}{1600} \quad (1)$$

Here, F_c represents the maximum load, and

1600 is the cubic area upon which the load is applied.

Paste dough for measuring the setting time was set of its w/s ratio as the distance between the plunger and base plate of (6 ± 2) mm, and put into a mold with a diameter of (75 ± 10) mm and a height of (40 ± 0.2) mm, and after curing at 20 °C and relative humidity of 95% for 30 minutes, the initial setting time was assessed. After the initial setting time was completed, by turning over the mold, the final setting time was assessed utilizing the base of the specimen. Table 4 presents the water ratios of each sample.

Results and Discussion

NHL hydration

Fig. 5 shows the XRD analysis results of NHL pastes with addition of BFS. The main mineral phases were $\text{Ca}(\text{OH})_2$, CaCO_3 , C_2S , un-reacted SiO_2 , gehlenite ($\text{Ca}_2\text{Al}(\text{AlSiO}_7)$) and C_4AH_{13} . In the case of adding BFS 30%, more C-S-H hydrates were formed than in the other samples. CaCO_3 gradually increases as time passes, and after 28 days, it sharply increased. CaCO_3 is created by the reaction of $\text{Ca}(\text{OH})_2$ and CO_2 in the air. The increased formation of CaCO_3 gradually increases the durability of hardened pastes [3, 11, 12]. From hydration of 1 day, C_4AH_{13} formed due to the

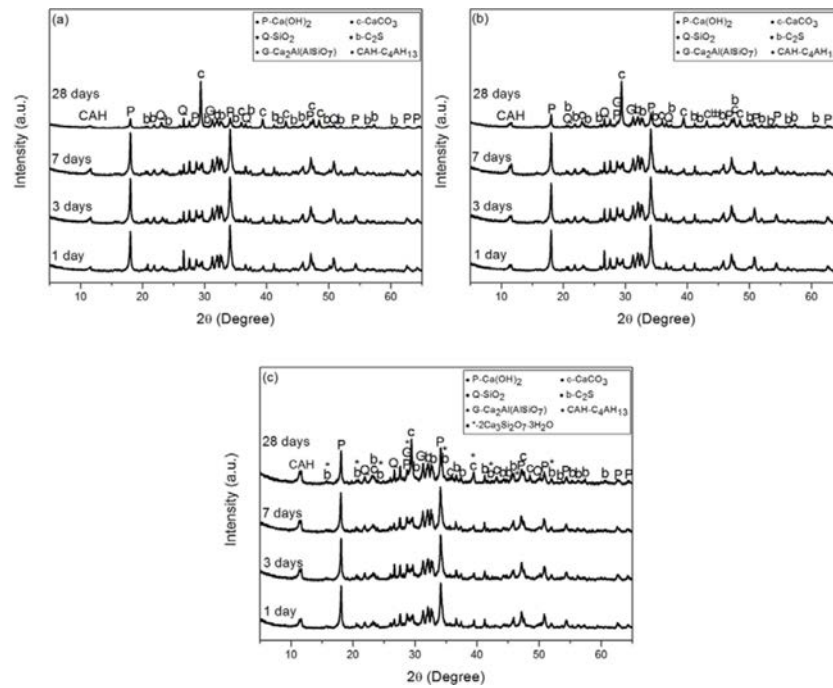


Fig. 5. XRD patterns of the NHL pastes containing BFS; (a) S 10-NHL, (b) S 20-NHL and (c) S 30-NHL.

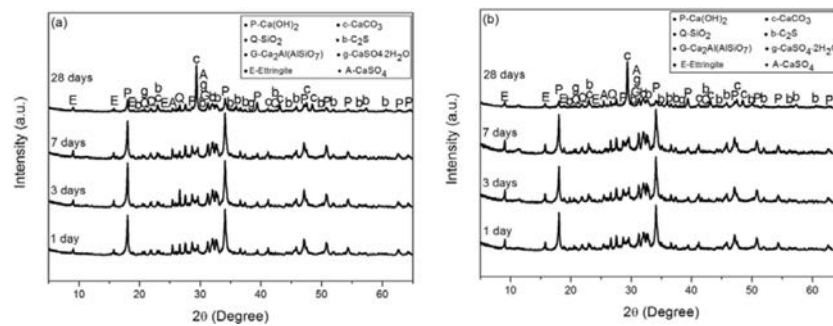


Fig. 6. XRD patterns of the NHL pastes containing BFS and AH; (a) S 10-NHL_AH and (b) S 30-NHL_AH.

latent hydraulic reaction between the Al source in BFS, and $\text{Ca}(\text{OH})_2$ was detected at around 10° . C_4AH_{13} is an Al-based hydration product formed in the absence of a SO_3 source in the mixture, and it affects the early strength of the hardened product [13, 14]. In the case of S 10-NHL and S 20-NHL, the peaks of C-S-H hydrate were not identified because the formation ratio of C-S-H phase is very low, while the C-S-H peak of the S 30-NHL sample was identified at around 30° . Because the C-S-H phase directly affects the strength of hardened NHL, as the BFS replacement rate in NHL increased, it was determined that the strength values of the NHL mortar increased.

The XRD patterns of the NHL paste with addition of BFS and AH are presented in Fig. 6. The main mineral phases were $\text{Ca}(\text{OH})_2$, CaCO_3 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, C_2S , unreacted SiO_2 , and ettringite. Ettringite hydrates due to the addition of AH were detected at around 9° , and decreased with hydration time. If SO_4^{2-} ions in the hardened paste continue to be supplied, the ettringite is maintained. However, when SO_4^{2-} ions are not sufficiently supplied,

the ettringite is converted into monosulfate hydrates [15, 16]. In addition, it was observed that as the BFS replacement rate increases, the ettringite content increases in comparison to S 10-NHL_AH paste. This is a result of the increased latent hydraulic reaction ratio to form ettringite with an increase of the BFS replacement rate.

The results of the DSC analysis conducted simultaneously for BFS and AH replaced NHL pastes after 1 day, 3 days, 7 days and 28 days are presented in Fig. 7. Since dehydration of capillary water occurs at about 100°C and endothermic effects take place at a ($100 \sim 400$) $^\circ\text{C}$ temperature range, dehydration developed in hydration products such as the C-S-H gel, ettringite, and C_4AH_{13} in the hardened NHL pastes. Also, dehydroxylation of $\text{Ca}(\text{OH})_2$ was observed in a temperature range of ($420 \sim 475$) $^\circ\text{C}$. The endothermic peaks by the thermal decomposition of CaCO_3 were detected at about 800°C . The endothermic peaks by dehydration of hydrates and decarbonation of CaCO_3 were increased by the latent hydraulic reaction and the carbonation reaction of $\text{Ca}(\text{OH})_2$ as time passes. Meanwhile, the dehydroxylation of $\text{Ca}(\text{OH})_2$ decreased

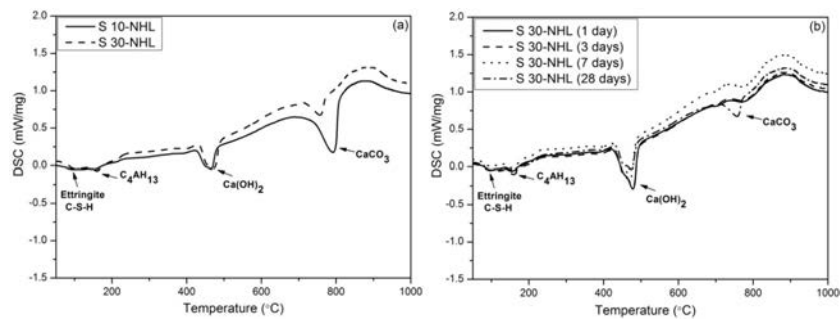


Fig. 7. DSC curves of NHL paste mixed with BFS; (a) S 10-NHL and S 30-NHL after 28 days and (b) S 30-NHL with different hydration time.

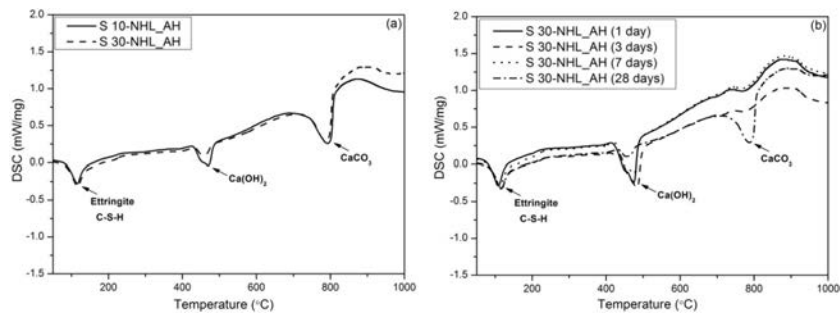


Fig. 8. DSC curves of NHL pastes mixed with BFS and AH; (a) S 10-NHL_AH and S 30-NHL_AH after 28 days and (b) S 30-NHL_AH with hydration time.

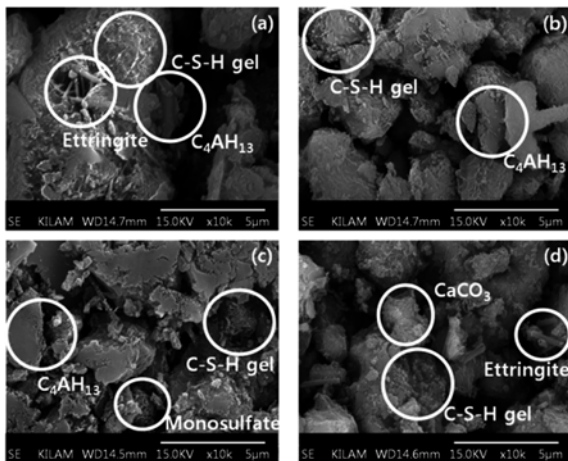


Fig. 9. SEM images of the NHL paste (S 30-NHL) with different hydration time; (a) 1 day, (b) 3 days, (c) 7 days and (d) 28 days.

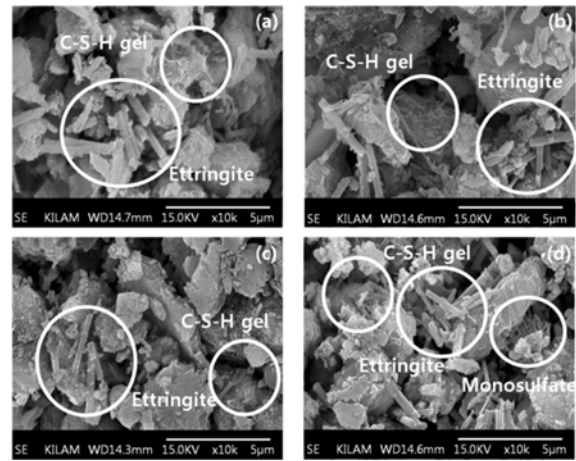


Fig. 10. SEM images of the NHL paste (S 30-NHL_AH) with different hydration time; (a) 1 day, (b) 3 days, (c) 7 days and (d) 28 days.

with an increase of hydration time. This indicates that the results obtained from the thermal analyses are in line with the findings obtained from the XRD analysis.

Fig. 8 presents the DSC analysis results for the thermal decomposition of NHL paste mixed with BFS and AH. The broad peak in a range of (100 ~ 200) °C is evidence of the existence of colloidal C-S-H gel and ettringite, where are higher than that of NHL paste mixed with only BFS. In the case of BFS and AH blended NHL, ettringite hydrates were formed in large quantities due to the latent hydraulic reaction of BFS and AH. The peak located at about 180 °C due to the decomposition of C₄AH₁₃ hydrated products was not observed because Al element in BFS by the reaction with AH was exhausted [11, 15].

The morphology of the hardened NHL paste in the presence of BFS and AH is presented in Fig. 9 and Fig. 10, respectively. In the absence of AH, needle-like type ettringite, foil-like type C-S-H and hexagonal type C₄AH₁₃ are created by the latent hydraulic reaction from hydration 1 day and these phases are presented in Fig. 9a. At hydration for 28 days, the CaCO₃ phase was formed by the carbonation reaction of Ca(OH)₂ in NHL paste and CO₂ in the air. These phases play a role in filling pores in the hardened NHL paste. In the presence of AH, a large amount of ettringite was formed by the reaction of BFS and AH from early hydration time. The ettringite phase rapidly increases the amount of small capillary pores in the NHL paste. Also, plate-formed monosulfate phases

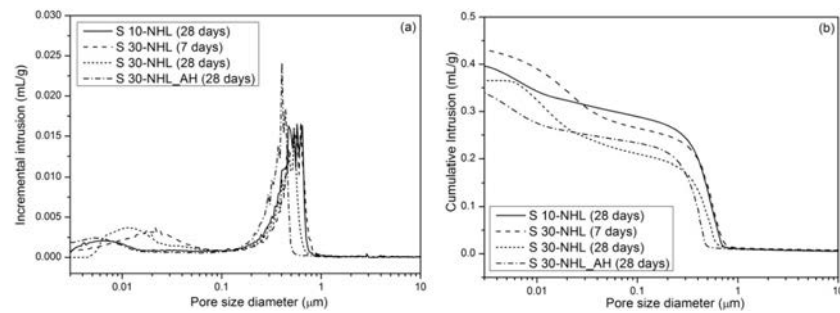


Fig. 11. Pore size distribution curves of NHL pastes mixed with BFS and AH; (a) Incremental intrusion data (b) Cumulative intrusion data.

Table 5. Porosity of NHL pastes.

Samples	Porosity (%)
S 10-NHL (28 days)	48.46
S 30-NHL (7 days)	51.36
S 30-NHL (28 days)	43.62
S 30-NHL_AH (28 days)	46.19

created by the lack of a SO_3 source were observed in the S 30 NHL_AH paste at hydration for 28 days.

Fig. 11 presents the analysis results for the pore size distributions of NHL mixed with BFS and AH. The pore size decreases as the content of BFS increases and the hydration time increases. This is a result of better packing of pores in the hardened paste due to the filling effect of hydrates created by hydraulic and carbonation reactions. In the case of adding AH, the pore size is smaller than it would be without AH. Needle-like type ettringite hydrates are produced by hydraulic reaction of BFS, AH, and $\text{Ca}(\text{OH})_2$ from early hydration time, and they fill the inside large pores of the hardened NHL paste. The porosity of the hardened NHL paste is presented in Table 5. From the porosity analysis results it is obvious that as the content of BFS and the hydration time respectively increase, the porosity is decreased whereas the porosity of the hardened paste with added AH slightly increased, which is attributed to ettringite increasing the amount of small capillary pores.

Physical and mechanical properties of blended NHL

Fig. 12 shows the compressive strength assessment

results of mortar mixed with BFS and AH into K-NHL. As the mixing rate of both admixtures was increased, the compressive strength increased, and higher compressive strength than that of K-NHL was observed in the absence of AH. At hydration of 28 days, BFS in Fig. 12a shows strength of 4.0 MPa when the mixing rate was 20%, and a value of 6.8 MPa at 30%, and it is verified that compressive strength similar to NHL 3.5 or NHL 5 in ES BN 459 was possible. BFS_AH in Fig. 12b shows better compressive strength properties than those of BFS at 4.1 MPa with a 10% mixing rate, and at 8.6 MPa with a 20% mixing rate, reflecting twofold greater twice as much compressive strength properties than BFS. Needle-like type ettringite hydrates produced by the latent hydraulic reaction of BFS and AH, and they fill the interior pores of the hydrates, thereby facilitating the development of compressive strength.

Table 6 presents the setting time measurement results of NHL with the addition of admixture and K-NHL. All samples, except for K-NHL, showed setting properties of an initial setting time between 550 min and

Table 6. Setting time of NHL pastes.

(unit: min)

Sample name	Initial setting time	Final setting time
K-NHL	2640	3960
S 10-NHL	1470	2100
S 20-NHL	630	1170
S 30-NHL	550	870
S 10-NHL_AH	1020	2100
S 30-NHL_AH	690	1080

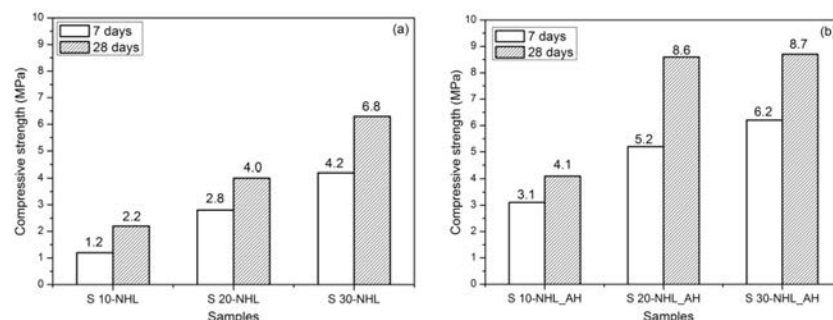


Fig. 12. Compressive strength development of the NHL mortars at 7 and 28 days; (a) Addition of BFS and (b) Addition of BFS and AH.

1470 min and a final setting time within 2100 min, which corresponded to BS EN 459 - 1 : 2010. However, K-NHL showed properties that did not comply with the standards, with an initial setting time of 2640 min and a final setting time of 3960 min. The mixture of BFS and AH showed values that comply with the EU standard due to shortening of more than 2000 min for the initial setting time and more than 3000 min for the final setting time, with records of 550 min for the initial setting time and 870 min for the final setting time of S 30-NHL. In the case of NHL with added AH, there was no significant difference with NHL mixed with BFS.

Conclusions

This paper mainly discussed the influence of inorganic admixture type on the hydration behavior and mechanical and physical properties of K-NHL. Moreover, the relationship between the hydration degree and the microstructure characteristics was also determined. Hydration products such as C-S-H, C-A-H, and ettringite due to the addition of BFS and AH in K-NHL were formed, and the amount of hydrates increased with an increase of the replacement rate of BFS. The pore size and porosity of hardened NHL paste decreased with increases of the amount of BFS and the hydration time. However, the porosity of the hardened paste with added AH increased slightly, which is attributed to the ettringite increasing the amount of small capillary pores. Ettringite hydrates with needle-like morphology were produced by the latent hydraulic reaction of BFS and AH, and they fill the pores of hydrates and thereby facilitate the development of compressive strength. Also, the setting time by these hydration products was significantly improved. This behavior can be attributed to better packing of hydration particles due to the filling effect of the additional hydrates. It is speculated that the results of this study can be practically applicable for construction materials that require loading resistance to compressive strength such as flooring materials and stacking materials.

Acknowledgments

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