Basic Properties of Non-Sintered Cement Mortar Using Industrial Byproducts as Activators

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Abstract

This paper investigates the basic properties of non-sintered cement (NSC) mortar produced using granulated blast-furnace slag (an industrial byproduct), phosphogypsum (PG) generated in fertilizer production, and slacked lime (SL) as a replacement for cement to reduce environmental load and carbon emissions. The experimental results indicate that NSC mortar using industrial byproducts and waste was initially weaker than mortar using ordinary Portland cement (OPC) but that there was a reversal in their long-term strength and durability. These results indicate that the use of NSC mortar can overcome various limitations of OPC structures and that further NSC research can facilitate the development and use of various alternatives to cement, which is one of the major causes of global warming.

Keywords: non-sintered cement mortar; Industrial byproduct; activator; phosphogypsum

1. Introduction

There is growing interest in environment-friendly products and processes across the world, indicating an urgent need for using low-carbon technologies to mitigate global warming and devising methods to process industrial byproducts and waste and recycle them. In particular, the cement industry has been identified as an industry that accounts for a large portion of natural resources as well as carbon emissions. In this regard, previous studies have paid close attention to reducing the consumption of natural resources through technological development and to using diverse industrial byproducts and waste materials in cement production to reduce carbon emissions through the development of various production methods for reducing energy consumption.

The United Nations Framework Convention on Climate Change was adopted in 1992 in Rio De Janeiro, Brazil, to prevent global warming, and since then, the issue of global warming has been recognized as a critical task facing mankind and thus prompted many countries to develop strategies to mitigate it. The United Nations Climate Change Conference in 2011 in Durban extended the deadline for the Kyoto Protocol, clarifying the need to engage in a new set of negotiations to oblige all members to reduce carbon emissions by 2015 and an effective new set of negotiations by 2020.

Currently, most construction and civil engineering projects make combined use of Portland cement. The process of manufacturing Portland cement requires limestone as the main material and leads to carbon emissions during the breakdown of limestone. It is known that the manufacturing of every one ton of cement discharges approximately 0.9 ton of carbon dioxide.

Therefore, reducing environmental load in the cement industry requires the increased use of industrial byproducts such as slag, which is likely to have a considerable influence on carbon emissions. In this regard, the present paper develops non-sintered inorganic bonding materials that are environmentally friendly by using industrial byproducts and waste as an alternative to cement. In addition, the paper provides a better understanding of the process underlying the manufacture of non-sintered cement (NSC) mortar through the use of a combination of non-sintered inorganic materials.

2. Experiment

2.1 Materials

The fine aggregate used in this paper was Jumunjin standard sand (0.25 - 0.6mm), and for cement, Class 1 ordinary Portland cement (OPC) from a Korean company based on KS L 5201 was used. Table 1 shows the chemical composition and physical properties of these materials. For the production of NSC mortar, granulated blast-furnace slag (GBFS), an industrial byproduct, was obtained from K-Steel Corp. and used as a sulphate activator to induce a hydration reaction with phosphogypsum (PG), which is discharged as waste in fertilizer production and industrial slaked lime (SL) is used as an alkali activator. PG was neutralized...
Table 1. Chemical Composition of OPC

| SiO₂ | Al₂O₃ | CaO | MgO | SO₃ | Fe₂O₃ | LOI | lg. loss |
|------|-------|-----|-----|-----|-------|-----|---------|
| 21.7 | 5.7   | 63.1| 2.8 | 2.2 | 3.2   | 1.3 |         |

Table 2. Chemical Composition of Each Material for the Manufacture of NSC Mortar

| Item   | SiO₂ | Al₂O₃ | CaO | MgO | Na₂O | K₂O | P₂O₅ | TiO₂ | SO₃ | LOI | Blaine (g/cm²) | Specific Gravity |
|--------|------|-------|-----|-----|------|-----|------|------|-----|-----|----------------|-----------------|
| GBFS   | 34.76| 14.50 | 41.71| 0.48| 6.87 | 0.14| 0.03 | 0.62 | 0.13| 0.23| 4,600          | 2.91            |
| APG    | 1.34 | 0.12  | 40.97| 0.04| -    | 0.06| 0.05 | 5.94 | 0.81| 4,300| 2.88           |                 |
| DPG    | 1.08 | 0.07  | 32.28| 0.21| 0.05 | -   | 0.58 | 0.04 | 43.29| 22.37| 4,100          | 2.36            |
| SL     | 0.19 | 65.88 | 0.12| 1.03| -    | -   | 0.03 | 1.13 | 31.51| 5,400| 2.27            |                 |

Table 3. Combination Table for the Manufacture of NSC-A and D Specimens

| Type   | Mix Proportion of NSC (wt%) | OPC | GBFS | APG | DPG | SL |
|--------|----------------------------|-----|------|-----|-----|----|
| OPC    | 100                        | -   | -    | -   | -   |    |
| NSC1-A | 92                         | 7   | -    | 1   | -   |    |
| NSC1-A2| 89                         | 10  | -    | 1   | -   |    |
| NSC1-A3| 87                         | 12  | -    | 1   | -   |    |
| NSC1-A4| 84                         | 15  | -    | 1   | -   |    |
| NSC1-D1| 92                         | 7   | -    | 1   | -   |    |
| NSC1-D2| 89                         | 10  | -    | 1   | -   |    |
| NSC1-D3| 87                         | 12  | -    | 1   | -   |    |
| NSC1-D4| 84                         | 15  | -    | 1   | -   |    |
| NSC2-A1| 92                         | 7   | -    | 1.5 | -   |    |
| NSC2-A2| 89                         | 10  | -    | 1.5 | -   |    |
| NSC2-A3| 87                         | 12  | -    | 1.5 | -   |    |
| NSC2-A4| 84                         | 15  | -    | 1.5 | -   |    |
| NSC2-D1| 92                         | 7   | -    | 1.5 | -   |    |
| NSC2-D2| 89                         | 10  | -    | 1.5 | -   |    |
| NSC2-D3| 87                         | 12  | -    | 1.5 | -   |    |
| NSC2-D4| 84                         | 15  | -    | 1.5 | -   |    |

NSC mixed using 1% SL.
NSC mixed using 1.5% SL.
Mixed anhydrite gypsum as the activator.
Mixed dihydrate gypsum as the activator.

in the process; spread to the state of type II anhydrite phosphogypsum (APG) calcined at 450°C and the state of dihydrate phosphogypsum (DPG) dried at 80°C; and used in fine grinding. Table 2. shows the physical and chemical properties of these materials.

2.2 Combination and Production of Specimens

NSC mortar was produced under various conditions combining material, which were selected through a preliminary experiment, and for an evaluation of the effectiveness of APG and DPG as activator, separate experiments were conducted using APG and DPG. As shown in Table 3, for an evaluation of its effectiveness based on SL content, several SL mixture ratios were considered (1.0% and 1.5%). Specimens were mixed using the dry-mix method to ensure that the raw materials were fully mixed according to the specified combinations in Table 3. under KS L ISO 679 (a method for testing cement strength), and then water was added to the mixture. Mortar was produced by mixing it using a mortar mixer at a low speed for 30 seconds and at a high speed for 1 minute. Specimens were produced using a 4 x 4 x 16 cm mold. The mixture was cured under a standard condition (20°C; RH = 50%) for 1 day and then cured in water at 20°C ±2 for 27 days for the final specimen.

2.3 Flexural and Compressive Strength

The flexural strength of NSC mortar was measured on days 3, 7, and 28 based on KS L ISO 679, and NCS mortar was executed on days 3 and 7 to determine its initial strength.

2.4 SEM

For the SEM analysis, NCS mortar which was measured on days 3, 7, and 28 was crushed using UTM. The fractured appearance of the inside was immersed in an acetocarmine for a day and used as a sample in the analysis.

2.5 Resistance to Chloride Ion Penetration

Resistance to chloride ion penetration was tested by executing standard curing for 28 days (KS F 2476). Then the specimen was immersed in 10% NaCl for 2 weeks, and its middle part was cut. The cut surface was sprayed with 0.1% of fluorescein sodium, and those portions with no change in color were calculated for the depth of chloride ion penetration.

2.6 Chemical Resistance

For chemistry, an experiment was conducted based on ASTM C 267/579 to assess acid resistance. Any moisture on the surface of the cured specimen was removed, and the weight of the specimen was measured. Then the specimen was dipped in a sulfuric acid solution. For an analysis of acid resistance, the specimen was immersed in the solution for a certain period. Then its surface was wiped in flowing water with a soft brush, and any damaged parts on the surface were removed with a damp cloth. The specimen's weight was measured, and the weight of reduction ratio was calculated as follows:

\[ \text{Weight Reduction Ratio (\%) = } \frac{W_0 - W_n}{W_0} \times 100 \]

where

W₀: Weight of the specimen before soaking.
Wₙ: Weight of the specimen after soaking.

3. Results

3.1 Flexural and Compressive Strength

Fig.1 shows the flexural strength of NSC1-A mortar according to the mixture ratio for APG as the sulphate activator for GBFS. NSC1-A mortar (which used APG)
was initially weaker than OPC mortar, but after 7 days, it was stronger than OPC mortar. After 28 days, it was approximately 1.5 times stronger than OPC mortar. In particular, it achieved its maximum strength under a 12% APG mixture. This indicates that there was non-reaction plaster but that a 12% APG mixture maximized the production of ettringite. Relative to OPC mortar, NSC mortar strengthened faster from day 3 to day 7 than from day 7 to day 28. In mixing APG, the SO$_4^{2-}$ ion was adsorbed as the active component of Al$_2$O$_3$ ion (out of GBFS components), extracted in the air gap together with ettringite, and accelerated the initial hydration reaction. The role of SO$_4^{2-}$ ion and Al$_2$O$_3$ ion is to stimulate the reaction of the hydration of C$_3$S and C$_3$A. However, as the hydration reaction proceeded, there was a steady decrease in the elution of the Al$_2$O$_3$ ion. For this reason, the speed of the hydration reaction decreased steadily, and its strength increased at a slower rate.

Fig.1. Flexural Strength of NSC1-A Mortar

Fig.2. shows the flexural strength of NSC1-D mortar according to the DPG mixture ratio. NSC1-D mortar (with DPG as the activator) showed no strength for 3 days. After 3 days, however, the hydration reaction proceeded gradually, and on day 28, its strength was almost equal to that of OPC mortar. A 7% DPG mixture produced the maximum strength on day 7, followed by 10%, 12%, and 15%, in that order. However, after 28 days, a 12% DPG mixture produced the maximum strength. That is, a DPG mixture above 12% weakened mortar strength. This may be because surplus plaster did not react with GBFS in the state of cohesion between hydration products and thus weakened their combined strength while controlling its ettringite generation. These results indicate that the optimum mixture ratio for flexural strength over time was 1% SL, 87% GBFS, and 12% DPG.

Fig.2. Flexural Strength of NSC1-D Mortar

Fig.3. shows the compressive strength of NSC1-A mortar according to the APG mixture ratio. SL was fixed at 1% as an alkali activator. In terms of compressive strength on day 3, NSC1-A mortar was weaker than OPC mortar, but there was a reversal after 7 days. In particular, a 7% APG mixture maximized compressive strength after 28 days. More specifically, NSC1-A mortar was more than 1.5 times stronger than OPC mortar in terms of compressive strength. This indicates that an impermeable acid membrane first formed on the particle surface of GBFS and then obstructed the hydration reaction but that, over time, ions such as Ca$^{2+}$, Mg$^{2+}$, and Al$^{3+}$ flowed out and facilitated the hydration reaction, increasing mortar strength.

Fig.3. Compressive Strength of NSC1-A Mortar

Fig.4. shows the compressive strength of NSC1-D mortar mixed with DPG, not APG, as the activator for GBFS. The main materials were combined in the same way as above. The compressive strength of NSC2-D mortar showed a pattern similar to that for flexural strength. NSC2-D mortar showed no initial compressive strength on day 3, and even after 7 days, it was still weaker than OPC mortar. However, after 28 days, its compressive strength was almost equal to or even greater than that of OPC mortar, which is consistent with the results for the flexural strength of NSC1-D mortar.

Fig.4. Compressive Strength of NSC1-D Mortar

Fig.5. shows the flexural strength of NSC mortar according to the APG mixture ratio. NSC2-A mortar was weaker than OPC mortar on days 3 and 7, but its flexural strength was almost equal to that of OPC mortar at day 28. The flexural strength of NSC2-A mortar increased by 0.5% for a 1% SL mixture. There
was little difference in flexural strength between NSC2-A and NSC1-A mortar on day 3, but on days 7 and 28, NSC2-A mortar was weaker than NSC1-A mortar. In particular, a 12% APG mixture minimized the flexural strength of NSC2-A mortar, indicating that the acid membrane formed on the surface of the GBFS particle was rapidly destroyed by a strong alkali (pH>12) granted by SL from an early hydration reaction and eluted Si and Al ions within the particle. The hydration of eluted ions proceeded actively at first through the rapid spread of the hydration product, but over time, the spread of eluted ions slowed, and there was a gradual decrease in the reaction speed.

Fig.5. Flexural Strength of NSC2-A Mortar

Fig.6. shows the flexural strength of NSC2-D mortar for DPG, not APG, as the activator for GBFS. On day 3, NSC2-D mortar was weaker than OPC mortar but stronger than NSC1-D mortar under the same conditions for a 1% SL mixture. The flexural strength of NSC2-D mortar was almost equal to that of OPC mortar on day 7 and increased gradually over time. On day 28, NSC2-D mortar was stronger than OPC mortar. In terms of the initial flexural strength on days 3 and 7, NSC2-D mortar was stronger than NSC1-D mortar for a 1% SL mixture.

As discussed earlier, this result may be due to the fact that the obstruction of the hydration of GBFS by the acid film was rapidly destroyed by a strong alkali from the initial hydration reaction.

Fig.6. Flexural Strength of NSC2-D Mortar

Fig.7. Compressive Strength of NSC2-A Mortar

Fig.7. shows the compressive strength of NSC2-A mortar according to the APG mixture rate. In terms of compressive strength, NSC2-A mortar was weaker than OPC mortar on days 3, 7, and 28. In particular, a 15% APG mixture minimized the compressive strength of NSC2-A mortar, followed by 7%, 10%, and 12%, in that order. This indicates that a 0.5% increase in SL allowed for the full maintenance of a strong alkali (pH>12) necessary for the initial hydration reaction of GBFS. However, the solubility of SL was 1.25g/l at 20°C, and there was a surplus of SL. This SL surplus was extracted as a crystal of calcium hydroxide and reduced the interface cohesion strength of the aggregate and cement hydrate, and over time, its strength decreased. On day 7, NSC2-A mortar was stronger than OPC mortar, particularly for a 7% APG mixture, and on day 28, it was 1.5 times stronger.

This indicates that at the start of the hydration reaction of GBFS, GBFS maintained a high pH by the eluted alkali component and that an increase in the alkali activator was not necessary. That is, if the alkali activator is sufficiently supplied such that it induces an initial hydration reaction, then the subsequent reaction leads to the elution of CaO and SiO\(_2\) in GBFS, sustaining the hydration reaction and forming the hydrate of the C-S-H series.

Fig.8. shows the compressive strength of NSC2-D mortar according to the mixture ratio for DPG, not APG, as the sulphate activator for GBFS under the same mixture conditions. Here the alkali activator SL was fixed at 1.5%. In terms of the initial compressive strength, NSC2-D mortar was weaker than OPC mortar on day 3, but its strength was almost equal to that of OPC mortar on day 7. In addition, it was stronger than OPC mortar on day 28, particularly for a 12% DPG mixture.

In terms of the initial compressive strength, NSC2-D mortar was stronger than NSC1-D mortar. This may be because the amount of SL increased from 1% to 1.5%, facilitating an alkali strong enough to destroy the acid membrane formed on the surface of the GBFS particle.
Fig. 9. SEM Images (×5,000) of OPC Mortar by Age

Fig. 10. SEM Images (×5,000) of NSC1-A Mortar by Age

Fig. 11. SEM Images (×5,000) of NSC2-D Mortar by Age

Fig. 12. SEM Images (×5,000) of SC2-A Mortar by Age

Fig. 13. SEM Images (×5,000, ×10,000) of NSC2-D Mortar by Age
3.2 SEM

Figs. 9.-13. show the results of the SEM analysis for the extent of hydrate generation according to a combination of activators. Portland cement is a hydraulic mineral whose C3S (alite; 3CaO·SiO2) and C2S (belite, 2CaO·SiO2) react with water to generate a low crystallization of C-S-H (3CaO·SiO2·6H2O) and Ca (OH)2. In addition, the aluminate, which is an interstitial phase reacts with plaster and generates ettringite first, and when all the plaster is consumed, the unreacted interstitial phase reacts with ettringite and generates monosulfate hydrate.

Fig. 9. shows the internal structure of OPC mortar on days 3 and 28. Three days after the hydration reaction, ettringite formed (thin but long needle-shaped crystals), and there was a large quantity of monosulfate. In the vicinity of the hydrate, a C-S-H gel was also present. This indicates that this hydrate supported the initial strength of OPC mortar.

Fig. 10. shows the internal structure of NSC1-A mortar on days 3 and 28. Three days after the hydration reaction, ettringite formed (thin but long needle-shaped crystals) but was very compact, indicating that it developed as thick needle-shared crystals until day 28 through a continuous hydrate reaction. A lot of dense hydrate was found as an ettringite and C-S-H gel as well. This indicates that the early hydration reaction of NSC mortar facilitated the formation of web networks with ettringite, which strengthened the mortar.

Fig. 11. shows the internal structure of NSC1-D mortar on days 3 and 28. Three days after the hydration reaction, there was ettringite, but it was thin and not dense. This suggests that the acid film needs to be removed for the initial hydration reaction of GBFS to proceed smoothly but that the lack of a strong alkali activator makes the required condition of strong alkali difficult, the quantity of the hydration product is less than the other NSC. Ettringite was thicker on day 28 than on day 3, and the hydrate in the form of a C-S-H gel was dense.

Fig. 12. shows the internal structure of NSC2-A mortar on days 3 and 28. Three days after the hydration reaction, there was a large amount of ettringite, although it was thinner than that in NSC1-A mortar. In its vicinity, there was a C-S-H gel, and the amount of this gel increased from day 3 to day 28.

Fig. 13. shows the internal structure of NSC2-D mortar on days 3 and 28. Three days after the hydration reaction, among all types of NSC-D mortar, NSC2-D mortar showed the most extensive formation of ettringite. This may be because an increase in the amount of SL (which was not sufficient in NSC1-D mortar) facilitated the initial hydration reaction. On day 28, ettringite was more long and thick than thin and short. In addition, the C-S-H gel was cohesive and formed a tight and strong structure.

3.3 Resistance to Chloride Ion Penetration

Fig. 14. shows the depth of chloride ion penetration in NSC mortar through a practical spread. The images show the state, which was obtained through the state of the depth of chloride ion penetration in the mortar fracture. The average penetration depth was 9.4 mm for OPC mortar. In terms of NSC mortar, NSC-A and NSC-D mortar showed much stronger resistance to chloride ion penetration than OPC mortar.

As shown in Fig. 14., NSC-A mortar showed stronger resistance to chloride ion penetration than OPC mortar. A 12% APG mixture maximized the resistance of NSC-A mortar to chloride ion penetration (an average penetration depth of 3.5 mm compared to 9.4 mm for OPC mortar). This indicates that the use of NSC mortars can significantly reduce the risk of chloride-induced corrosion in concrete structures.
of 1.8 mm) such that its resistance was 4-5 times that of OPC mortar. For NSC-D mortar, a 12% DPG mixture maximized its resistance (an average of 2.7 mm).

This strong resistance of NSC mortar to chloride ion penetration may be due to the fact that NSC mortar forms more densely than OPC mortar.

3.4 Chemical Resistance

Figs. 16. and 17. show the rate of change in weight based on a test of acid resistance. This test was conducted by immersing NSC mortar (produced by adding APG or DPG to GBFS as an activator) in a sulfuric acid solution. According to the test, NSC mortar showed stronger resistance to $H_2SO_4$ than OPC mortar. In particular, APG facilitated NSC mortar's strong resistance to $H_2SO_4$ until day 28 such that there was no difference in its weight before and after its immersion.

After day 28, there was a gradual decrease in the weight of NSC mortar, but it still showed much stronger resistance to $H_2SO_4$ than OPC mortar. For NSC mortar using DPG as an activator, a 7% DPG mixture reduced its resistance to $H_2SO_4$, but it still showed stronger resistance than OPC mortar. NSC-D3 and NSC-D4 mortar, which are the amounts of mixing over 10% were no different in their weight before and after their immersion until day 56. After 56 days, their weight decreased rapidly, but they still showed stronger resistance to $H_2SO_4$ than OPC mortar.

This suggests that the superiority of NSC mortar over OPC mortar in terms of acid resistance is due to the type of hydration product and its quantity. OPC mortar, unlike NSC mortar, produces a substantial amount of Ca (OH)2 as a hydration product, and this Ca (OH)2 is easily eroded in acid. This indicates that because NSC mortar produces little Ca (OH)2, it is superior to OPC mortar in terms of acid resistance.

4. Conclusion

Given the growing concern over the environment, this study examines the basic properties of NSC mortar produced using GBFS (an industrial byproduct), PG generated in fertilizer production, and SL as a replacement for cement for reducing the environmental load and carbon emissions. The main results can be summarized as follows:

1. NSC mortar was initially weaker than OPC mortar, but there was a reversal on day 28, indicating the potential use of NSC mortar as an alternative to Portland cement.
2. The SEM results for the internal structures of NSC and OPC mortar indicate that OPC mortar initially produced more ettringite and monosulfate in the form of a C-S-H gel but that an NSC mortar hydration product whose initial hydration was thin or not delicate. However, by day 28, NSC mortar's initial hydration product which is made faster than OPC mortar developed rapidly, and was more dense.
3. In terms of the depth of chloride ion penetration upon immersion, the resistance of NSC mortar to chloride ion penetration was 4 times that of OPC mortar, indicating that NSC mortar can be a good alternative for structures exposed to sea water.
4. NSC mortar produced little Ca (OH)2, which can easily erode in $H_2SO_4$, and thus showed strong resistance to $H_2SO_4$, indicating that it can be a good alternative for structures exposed to acids as well as for all types of landfill facilities.

In sum, NSC mortar using industrial byproducts and waste was initially weaker than OPC mortar, but over time, it was superior to OPC mortar in terms of long-term strength and durability. These results indicate that the use of NSC mortar can overcome various limitations of OPC structures and that further NSC research can facilitate the development and use of various alternatives to cement, which is one of the major causes of global warming.

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