Durability and Engineering Performance Evaluation of CaO Content and Ratio of Binary Blended Concrete Containing Ground Granulated Blast-Furnace Slag

Jaehyun Lee and Taegyu Lee *

Technology Research & Development Institute, Daelim Industrial, Jongno-Gu, Seoul 03152, Korea; archi0528@daum.net
* Correspondence: ninga777@naver.com; Tel.: +82-10-3433-8213

Received: 17 March 2020; Accepted: 1 April 2020; Published: 5 April 2020

Abstract: This study aimed to evaluate the durability and engineering performance of concrete mixed with locally produced ground granulated blast-furnace slag (GGBS) based on CaO content and ratio, and to derive the optimal CaO content range that can secure durability. Hence, tests were conducted by increasing the GGBS replacement ratio by 10% from 0% to 70%, while the unit binder weight was fixed at 330 kg/m³. The results indicated that the compressive strength exhibited a tendency to increase when the CaO content and basicity increased within 28 d of age, although similar compressive strength characteristics were observed at 56 d of age, irrespective of the CaO content and basicity. Additionally, four test items (i.e., carbonation depth, chloride penetration depth, relative dynamic elastic modulus, and weight reducing ratio) were measured to evaluate durability. The optimal CaO content satisfying all four parameters was observed as ranging between 53% and 56% (GGBS replacement ratio: 27.5%–47.1%). The results of the study can provide guidelines on the mixing proportions of GGBS concrete with excellent durability that can be applied to local construction sites and can be used as basic data to set chemical composition criteria for the development of binders to improve durability.

Keywords: durability performance; engineering performance; CaO content and ratio; ordinary Portland cement; ground granulated blast-furnace slag

1. Introduction

Ground granulated blast-furnace slag (GGBS) is an industrial byproduct that is widely used as a substitute for ordinary Portland cement (OPC), and several extant studies focused on the same [1]. Specifically, GGBS are mainly used as supplementary cementitious materials (SCMs) and alkali-activated materials (AAMs). When GGBS is used as a SCM, it improves durability, long-term strength, and constructability [2,3]. Given the high demand for natural resources to satisfy demands for infrastructure, there are significant opportunities to apply SCMs in the construction of carbon-saving infrastructure [4,5]. Furthermore, studies on AAMs have attracted considerable attention in the construction industry over the last few decades because it provides effective alternatives to OPC [6,7]. However, AAMs are not actually applied to the field due to high cost, short initial setting time, and high shrinkage. Therefore, in-depth research on SCMs is necessary to improve field applicability.

Specifically, GGBS is a byproduct that is generated during the production of pig iron. It becomes fine, granular, and amorphous after quenching and crushing. Additionally, GGBS is mainly composed of four chemical elements, namely SiO₂, Al₂O₃, CaO, and MgO. Thus, GGBS can be referred to as aluminosilicate with CaO and MgO as base chemical elements [8,9]. Furthermore, GGBS exhibits a hydration reaction when it is in contact with water, sulfate, or alkali starter, etc. The reaction rate
increases when the pH value increases [3,10]. For example, when GGBS is placed in a saturated aqueous solution of calcium hydroxide (Ca(OH)\(_2\)) corresponding to or exceeding pH 12, hydration begins when the chain structure of aluminosilicate is cut. Nevertheless, the reaction stops when the supply of Ca(OH)\(_2\) is interrupted and the amount of alkali decreases below a certain concentration or the reaction products shielding effect [11]. Additionally, impermeable acid film is generated on the particle surface when GGBS is in contact with water. In this case, the reaction can be resumed when the film is destroyed by the strong alkali stimulation of NaOH, KOH, and Ca(OH)\(_2\) + CaSO\(_4\). Hardening begins when insoluble matter precipitates in the solution following the occurrence of the dissolution reaction on the GGBS surface via the aforementioned type of stimulation [12].

Furthermore, the durability of concrete composed of OPC 100% can be improved by adding GGBS as SCMs [13]. The durability of concrete mixed with GGBS is improved by the latent hydraulic reaction that occurs during the hydration process of the cement [14,15]. Calcium hydroxide (CH) and calcium silicate hydrate (C–S–H) gels are formed during the better hydration of Portland clinker. Moreover, CH is the most soluble hydration product and becomes a fragile linkage by cement. When concrete is in contact with water, porosity increases due to the dissolution of CH, and concrete becomes more sensitive for further leaching and chemical intrusion [16]. Subsequently, the GGBS added to concrete reinforces and fills pores and improves durability to prevent the intrusion of water and other chemicals [17,18].

Huang [19] reported that finer GGBS (specific surface area: 5000 cm\(^2\)/g or 6000 cm\(^2\)/g) increased the fracture toughness of concrete. Ganesh [20] inferred that the compressive strength of ultrahigh performance concrete (UHPC) with a high volume fraction of GGBS improved when the replacement ratio ranged from 40% to 60% based on the temperature condition. It was also verified that UHPC with a higher volume fraction of GGBS exhibited denser microstructure by analyzing the microstructure characteristics by using a scanning electron microscope (SEM). Additionally, Reddy Suda [21] suggested the economic ratio of ternary blended concrete for securing strength at 28 d of age as corresponding to silica:GGBS:OPC = 10:30:60. Cheng [22] reported that the partial replacement of cement with GGBS affected the total charge passed, permeability, and corrosion rate and flexural stiffness of the beam.

On the other hand, Löfgren [23] conducted a laboratory study on concrete with various dosages and W/B ratio of mineral admixtures exposed to accelerated carbonation at 1% CO\(_2\) concentration at different ages. As a result, it was found that exposure specimen at accelerated carbonation at an early age increased scaling, but the carbonization depth corresponded to a natural exposure of 10 years. It also reported that scaling was significantly reduced by increasing the curing period prior to accelerated carbonation exposure, and that salt frost scaling resistance appeared to be better related to field observation. In addition, Koenig [24] tested performance on UHPC, normal, and high-strength concrete through an acid testing device for 12 weeks by stressing an organic acid mix and a sulfuric acid. As a result, it was reported that very high acid resistance could only be achieved by very low capillary porosity and very low reactivity to acid solutions. In particular, it was proven that the depth of degradation can be minimized by reducing the content of Ca(OH)\(_2\) by using pozzolanic or latent hydraulic GGBS. In addition, it has been demonstrated that the addition of finely ground secondary raw materials (GGBS, silica fume, fly ash) to cement or concrete can increase the resistance to acidic fluids [25].

As previously mentioned, an increase in the GGBS replacement ratio improves durability under the same unit binder weight, although it decreases compressive strength. However, to the best of the authors’ knowledge, extant studies do not suggest guidelines on optimal mixing proportions that can secure compressive strength and durability using locally produced GGBS materials for the framework of actual construction sites. There is also a paucity of basic data on chemical compositions to develop GGBS-based binders with excellent durability.

Therefore, in the study, durability and engineering performance of binary blended concrete with locally produced GGBS were evaluated based on CaO content and ratio to derive optimal CaO content for excellent durability that can be applied to the framework of actual construction sites. Hence, in series
I, particle size distribution, SEM, X-ray fluorescence, X-ray diffraction, and grading distribution were measured for raw material analysis. In series II, slump, air content, water content, and compressive strength were measured for engineering performance analysis. In series III, carbonation depth, chloride penetration depth, relative dynamic elastic modulus, and weight reducing ratio were evaluated for durability performance analysis.

2. Experimental Procedure

2.1. Materials

Table 1 shows the chemical compositions of OPC and GGBS used in the study. Specifically, OPC and GGBS were mainly composed of CaO, SiO$_2$, and Al$_2$O$_3$. However, GGBS exhibited higher SiO$_2$, Al$_2$O$_3$, and MgO content when compared to OPC. Table 2 shows the physical properties of the materials used. Type 1 OPC (KS L 5201) [26] with a 3322 cm$^2$/g specific surface area was used. With respect to GGBS, type 3 (KS F 2563) [27] with a 4592 cm$^2$/g specific surface area was used. A mixture of washed sea sand and crushed sand was used for the fine aggregate. Crushed granitic aggregate was used for the coarse aggregate. The polycarboxylic acid group was used for the chemical admixture.

| Material | Chemical Composition (%) |
|----------|--------------------------|
|          | CaO | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | MgO | K$_2$O | Na$_2$O | SO$_3$ |
| OPC (1)  | 60.20 | 21.60 | 5.15 | 3.30 | 2.30 | 0.99 | 0.53 | 1.50 |
| GGBS (2) | 44.90 | 35.40 | 13.00 | 0.47 | 5.01 | 0.37 | 0.00 | 1.31 |

(1) OPC: ordinary Portland cement; (2) GGBS: ground granulated blast-furnace slag.

Table 2. Physical properties of the materials.

| Material       | Property                                                                 |
|----------------|--------------------------------------------------------------------------|
| OPC            | Type 1 ordinary Portland cement (KS L 5201)                              |
|                | Density: 3.15 g/cm$^3$, specific surface area: 3322 cm$^2$/g             |
| GGBS           | Type 3 Ground Granulated Blast-furnace Slag (KS F 2563)                 |
|                | Density: 2.90 g/cm$^3$, specific surface area: 4592 cm$^2$/g             |
| Fine aggregate | S1, Washed sea sand, FM (1): 2.01, density: 2.60 g/cm$^3$, absorption: 0.79% |
|                | S2, Crushed sand, FM: 3.29, density: 2.57 g/cm$^3$, absorption: 0.87%     |
| Coarse aggregate | Crushed granitic aggregate                                             |
| Chemical admixture | Size: 25 mm, density: 2.60 g/cm$^3$, absorption: 0.76%                  |
|                 | Polycarboxylic acid group, density: 1.05 g/cm$^3$                      |

(1) FM: fineness modulus.

2.2. Experimental Procedures

Table 3 shows the experimental plan of the study. The binder types corresponded to OPC and GGBS, and tests were conducted by increasing the GGBS replacement ratio by 10% from 0% to 70% while the unit binder content and curing temperature were fixed at 330 kg/m$^3$ and 20 °C, respectively. In series I, the particle size distribution, SEM, X-ray fluorescence, X-ray diffraction, and grading distribution were measured for raw material analysis. In series II, the slump, air content, water content, and compressive strength were measured for engineering performance analysis. In series III, the carbonation depth, chloride penetration depth, relative dynamic elastic modulus, and weight reducing ratio were evaluated for durability performance analysis. Table 4 shows the mixing proportions of the concrete (ready-mixed concrete specification 25-24-180) used in the study.
Table 3. Experimental plan.

| Series | Experimental Factor and Level | Evaluation Item |
|--------|------------------------------|-----------------|
|        | Unit Binder Content (kg/m³) | GGBS Replacement Ratio (%) | Curing Temperature (°C) |
| I. Raw material analysis | 330 | 0 | 20 |
| II. Engineering performance analysis | 30 | 10 | 30 |
| III. Durability performance analysis | 40 | 20 | 50 |
|        | 50 | 30 | 60 |
|        | 60 | 40 | 70 |

- Particle size distribution (%)
- Scanning electron microscope
- X-ray fluorescence
- X-ray diffraction
- Grading distribution (%)
- Slump (mm)
- Air content (%)
- Water content (kg/m³)
- Compressive strength (MPa)
- Carbonation depth (mm)
- Chloride penetration depth (mm)
- Relative dynamic elastic modulus (%)
- Weight reducing ratio (%)

Table 4. Mixing proportions of the concrete.

| Mix No. | W/B (1) | Unit Weight (kg/m³) | AD (5) (B (6) × wt. %) |
|---------|---------|---------------------|-----------------------|
|         | Water | OPC | GGBS | WSS (2) | CS (3) | CGA (4) | |
| Plain   | 0.53  | 175 | 330  | 0  | 351  | 521  | 878  | 0.90 |
| G1      |       |     | 297  | 33 | 351  | 520  | 877  | 0.85 |
| G2      |       |     | 264  | 66 | 350  | 519  | 875  | 0.80 |
| G3      |       |     | 231  | 99 | 350  | 519  | 874  | 0.75 |
| G4      |       |     | 198  | 132| 349  | 518  | 873  | 0.70 |
| G5      |       |     | 165  | 165| 349  | 517  | 872  | 0.65 |
| G6      |       |     | 132  | 198| 348  | 516  | 871  | 0.60 |
| G7      |       |     | 99   | 231| 348  | 516  | 870  | 0.55 |

(1) W/B: water/binder ratio; (2) WSS: washed sea sand; (3) CS: crushed sand; (4) CGA: crushed granitic aggregate; (5) AD: chemical admixture; (6) B: unit binder weight.

2.3. Test Methods

Table 5 shows the test methods with respect to the evaluation item in the study. Tests on the evaluation items in series I (i.e., particle size distribution, scanning electron microscope, X-ray fluorescence, X-ray diffraction, and grading distribution) were conducted based on ASTM C204 [28], ASTM C1723 [29], ASTM C114 [30], ASTM C457 [31], and ASTM C136 [32], respectively. Additionally, for series II, the slump test was conducted based on ASTM C143, and the air content was measured based on ASTM C231 [33]. The compressive strength test was conducted based on ASTM C873 (specimen size: Ø100 mm × 200 mm) [34] and ASTM C39 [35]. The target slump was set to 180 ± 25 mm, and the target air content was set to 4.5 ± 1.5%. For series III, the carbonation depth and chloride penetration depth were measured based on KS F 2584 (specimen size: Ø100 mm×200 mm) [36] and NT Build 492 (specimen size: Ø100 mm × 50 mm) [37]. Tests on the relative dynamic elastic modulus and weight reducing ratio were conducted based on ASTM C666 (specimen size: 100 mm × 100 mm × 400 mm) [38]. For carbonation depth measurement, an accelerated carbonation test was conducted after specimens were fabricated and subjected to standard curing until 28 d of age. The carbonation depth was measured in the fourth and eighth week after the test commenced. To measure the chloride penetration depth, a calcium ion penetration resistance test was conducted based on the potential difference using 0.5 M NaCl solution as the cathode cell solution and saturated Ca(OH)₂ solution as the anode cell solution.
Table 5. Test methods by evaluation items.

| Series                      | Evaluation Item                              | Test Method       |
|-----------------------------|----------------------------------------------|-------------------|
| I. Raw material analysis    | Particle size distribution (%)               | ASTM C204         |
|                             | Scanning electron microscope                 | ASTM C1723        |
|                             | X-ray fluorescence                           | ASTM C114         |
|                             | X-ray diffraction                            | ASTM C457         |
|                             | Grading distribution (%)                     | ASTM C136         |
| II. Engineering performance analysis | Slump (mm)                                 | ASTM C143         |
|                             | Air content (%)                              | ASTM C231         |
|                             | Compressive strength (MPa)                   | ASTM C873         |
|                             |                                               | ASTM C39          |
| III. Durability performance analysis | Carbonation depth (mm)                      | KS F 2584         |
|                             | Chloride penetration depth (mm)               | NT Build 492      |
|                             | Relative dynamic elastic modulus (%)         | ASTM C666         |
|                             | Weight reducing ratio (%)                    |                   |

3. Results and Discussion

3.1. Effects on Engineering Performance

3.1.1. Raw Material Analysis

Figure 1 shows the particle size distribution of OPC and GGBS used in the study. Specifically, OPC exhibited a mean size of 19.46 µm and a fineness modulus of 1.18, and GGBS exhibited a mean size of 22.47 µm and a fineness modulus of 1.08. The mean size of OPC was lower than that of GGBS although the fineness modulus of OPC exceeded that of GGBS. To observe the detailed grain shapes of OPC and GGBS, SEM analysis was performed via Genesis-2020 (Emcrafts, Gwangju-si, Korea), as shown in Figure 2. The SEM analysis results indicated that OPC and GGBS appeared similar and corresponded to ellipsoidal polyhedrons for particles exceeding 10 µm and atypical crystals for particles lower than 10 µm. Additionally, sieve analysis (ASTM C136) was conducted to analyze the grading of the mixed fine aggregate and crushed coarse aggregate used in the study. The results satisfied all the passing criteria for fine and coarse aggregates based on the sieve opening size as shown in Figure 3, and the fineness modulus was analyzed as 2.84 and 6.94, respectively. Figure 4 shows the results of analyzing the X-ray diffraction (XRD, X’pert Powder PW 3050, Malvern Panalytical, Seongnam-si, Korea) patterns to identify the types of crystalline materials in the OPC and GGBS particles. The results indicated that OPC was mainly composed of C3S(3CaO·SiO₂), C2S(2CaO·SiO₂), C3A(3CaO·Al₂O₃), and C4AF(4CaO·Al₂O₃·Fe₂O₃) minerals while GGBS was composed of gehlenite, akermanite, and a very high X-ray amorphous content.

![Figure 1](image-url)  
Figure 1. Particle size distribution of ordinary Portland cement (OPC) and ground granulated blast-furnace slag (GGBS).
Figure 2. Scanning electron microscopy images of (a) OPC and (b) GGBS.

Figure 3. Gradation sieve analysis curves of aggregates used: (a) coarse aggregates and (b) fine aggregates.

Figure 4. X-ray diffraction patterns of OPC and GGBS.
3.1.2. Engineering Property Analysis

Figure 5 shows the slump and air content measurement results based on the GGBS replacement ratio. The slump satisfied the target range corresponding to 180 ± 25 mm, and the air content also satisfied the target range corresponding to 4.5 ± 1.5 mm. In the study, to secure data with high field applicability, the content of the chemical admixture was fixed and the unit water content required to secure the target slump was measured based on the GGBS replacement ratio. The results indicate that the unit water content exhibited a tendency to decrease by approximately 2.75 kg when the GGBS replacement ratio was increased by 10% as shown in Figure 6. When the GGBS replacement ratio was 70%, the unit water content to secure the same workability decreased to 90.7% when compared to that when the replacement ratio corresponded to 0%. This result was similar to the previous studies [22,39], and the surface of GGBS was denser than OPC and had the characteristics of particle shape, which is advantageous for increased fluidity. Therefore, it is known to have an effect of reducing friction between the paste and the aggregate interface. This indicated that the substitution of GGBS in the field under the same total binder weight condition is helpful in improving the workability of concrete.

![Figure 5](image_url)
**Figure 5.** Result of slump and air contents with respect to replacement ratio.

![Figure 6](image_url)
**Figure 6.** Result of unit water content with respect to replacement ratio.

Figure 7 shows the compressive strength with respect to age for each GGBS replacement ratio. At 3, 7, 28, and 56 d of age, the minimum–maximum values of compressive strength were observed as 5.0–12.0, 15.1–24.9, 30.4–37.3, and 35.0–40.0 MPa, respectively. Figure 8a shows the compressive strengths based on the GGBS replacement ratio. At 3, 7, and 28 d, the compressive strength tended to decrease by 1.0, 1.4, and 0.9 MPa, respectively, when the GGBS replacement ratio increased by 10%.
Conversely, the compressive strength at 56 d remained similar even though the GGBS replacement ratio increased. When the ratio of the compressive strength at 56 d to that at 28 d was analyzed, the results indicate that the ratio exhibits a tendency to increase when the GGBS replacement ratio increases, as shown in Figure 8b. The ratio ranged from 101.3% to 101.6% when the GGBS replacement ratio ranged from 0% to 10%, thereby indicating an insignificant increase in compressive strength. However, the ratio increased to 106.4%–123.3% when the GGBS replacement ratio exceeded 20%. This confirmed that the long-term strength after 28 d of age improved when the GGBS replacement ratio increased. These results and reasons can also be found in a previous study [23]. The development of the compressive strength of GGBS based concrete depends on the GGBS replacement ratio and concrete curing age. GGBS’s glassy compounds react slowly with water, and it takes time to obtain hydroxyl ions to break the glassy slag parcels from the hydration products of OPC at an early age. However, GGBS concrete had a property where the compressive strength was higher than that of OPC after the GGBS hydration and pozzolanic reactions were almost completed.

Figure 7. Result of compressive strength with respect to age.

Figure 8. Results of (a) compressive strength and (b) CS (56 d)/CS (28 d) ratio with respect to the replacement ratio.

3.1.3. Chemical Composition Analysis

Figure 9 shows the CaO/SO₃ and SO₃/Al₂O₃ molar ratios based on the GGBS replacement ratio. When the GGBS replacement ratio increased, the CaO/SO₃ and SO₃/Al₂O₃ molar ratios decreased. With respect to the representative chemical components, CaO, Fe₂O₃, and SO₃ exhibited a tendency to decrease, although SiO₂, Al₂O₃, and MgO increased when the GGBS replacement ratio increased. This
is because GGBS exhibited higher SiO₂, Al₂O₃, and MgO content when compared to OPC. Regression analysis on the triangular graph of CaO/SO₃ and SO₃/Al₂O₃ indicated that construction must be managed by considering long-age strength when the GGBS replacement ratio is increased.

Figure 9. CaO/SO₃ and SO₃/Al₂O₃ molar ratios based on the replacement ratio.

Figure 10a shows the compressive strength based on the CaO content. When the CaO content increased, the compressive strength also increased. Under the mixing conditions of the study, the ratio of the maximum strength among the specimens to the minimum strength was observed as 239.7% at 3 d of age, 165.0% at 7 d, and 122.8% at 28 d. Conversely, all the specimens at 56 d exhibited similar compressive strengths irrespective of the CaO content. The result suggested that the long-term compressive strengths measured after 28 d were found to be similar because the total binder weight was fixed at 330 kg/m³. To analyze the compressive strength increase rate after 28 d, the regression curves of the rate of increase in compressive strength with increasing age at the same CaO content level are shown in Figure 10b. The results indicated that the rate of increase in compressive strength after 28 d exhibited a tendency to decrease. Specifically, the compressive strength (C.S., 7 d)/C.S. (3 d) ratio regression curve exhibited the largest reduction rate. This indicated that when the CaO content increased, the rate of increase in compressive strength exhibited a relative decrease when compared with that for low CaO content after 28 d because the compressive strength was rapidly developed at an age lower than 7 d.

Figure 11 shows the compressive strength based on the basicity. The basicity was calculated as the CaO content/SiO₂ content ratio. When the basicity increased, the compressive strength increased.
at all ages with the exception of 56 d. Specifically, when the basicity exceeded 2.3, the compressive strength at 28 d was similar to that at 56 d. The result was similar to the aforementioned CaO content analysis result. This was potentially because GGBS affected the development of long-term strength in specimens with low basicity in the case of long-term strength after 28 d. Figure 12 shows the CaO content and CaO/SiO$_2$ ratio based on the GGBS replacement ratio. The two variables decreased when the replacement ratio increased. The CaO content decreased to approximately 82.2% and the CaO/SiO$_2$ ratio to 56.8% when compared to that of the plain specimen. It is expected that these chemical composition analysis data will be used as basic data for the development of binders for high volume GGBS concrete.

![Figure 11](image1.png)

**Figure 11.** Compressive strength with respect to basicity.

![Figure 12](image2.png)

**Figure 12.** CaO content and CaO/SiO$_2$ ratio with respect to replacement ratio.

3.2. Effects on Durability Performance

Figure 13 shows the carbonation depth measurement results based on the GGBS replacement ratio. In the case of the specimens at four weeks of age, the carbonation depth remained at similar levels until the replacement ratio reached 50%, although it significantly increased when the replacement ratio exceeded 50%. In the case of the G7 specimen, the carbonation depth increased to approximately 266.7% when compared to the lowest value. For specimens at eight weeks of age, the carbonation depth also remained at similar levels until the replacement ratio reached 50%, although it significantly increased when the replacement ratio exceeded 50%. With respect to the G7 specimen, the carbonation depth increased to approximately 161.7% when compared to the lowest value. These results indicate that it is desirable to set the GGBS replacement ratio to 50% or less to minimize the carbonation depth in the field application. This finding is complemented by the existing literature. It has long been known...
that concrete is adversely affected by carbonation when large amounts of GGBS are used [40,41]. Some studies reported that the amount of GGBS that started to be affected by this negative effect was about 30–40% of the total binder content based on field data [42,43].

Figure 13. Carbonation depth ratio with respect to replacement ratio.

Figure 14 shows the chloride penetration depth measurement results based on the GGBS replacement ratio. The chloride penetration depth significantly decreased until the replacement ratio reached 25%, although it remained at similar levels when the replacement ratio ranged from 25% to 70%. In the case of the plain specimen, the chloride penetration depth was approximately 442.1% when compared to the lowest value. Therefore, it is deemed as desirable to secure 25% or higher GGBS replacement ratios during concrete mix design at construction sites where the chloride attack must be considered. According to a previous study [44], laboratory accelerated tests resulted in lower chloride transfer coefficients with higher replacement ratios of GGBS in concrete. Therefore, cement-free slag concrete was found to have the greatest resistance to chloride ion penetration compared to other specimens. In addition, it was similar to the previous studies [24,25] where the depth of degradation can be minimized and resistance to acid fluids can be improved by adding raw materials such as GGBS.

Figure 14. Chloride penetration depth relative to the replacement ratio.

To examine the effect of the GGBS replacement ratio on freeze–thawing or other chemical reactions, the relative dynamic elastic modulus was measured based on the GGBS replacement ratio, as shown in Figure 15a. The relative dynamic elastic modulus exhibited a tendency to increase when the replacement ratio increased. It was as low as 64.6% when the replacement ratio ranged from 0 to 45%, although it increased to 86.8%–94.5% when the replacement ratio exceeded 45%. This indicated that the GGBS replacement ratio must be 45% or higher to secure resistance to freeze–thawing.
When the replacement ratio exceeded 50%, the durability and engineering performance of binary blended concrete with the chloride transfer coefficients with higher replacement ratios of GGBS in the optimal CaO content range for enduring durability performance was secured. 

Figure 15b shows the weight reducing ratio based on the GGBS replacement ratio. The test was conducted to examine the effect of the replacement ratio on the surface degradation of the specimens. When the replacement ratio increased, the weight reducing ratio exhibited a tendency to increase. While the weight reducing ratio of the plain specimen was measured as 96.8%, the weight reducing ratio reached 99.9% or higher when the GGBS replacement ratio exceeded 20%. This indicated that it is necessary to secure 20% or higher GGBS replacement ratios in the field to minimize surface degradation of structures. This result is similar to that of the previous study [44]. The slag replacement concrete had a higher coefficient of durability as the slag replacement ratio was higher. In addition, it was found that the slag replacement concrete was more resistant to freezing/thawing than cement concrete.

All of the aforementioned contents were summarized, and the optimal CaO content range to secure durability performance is shown in Figure 16. For concrete mixed with GGBS to secure durability performance, it is important to minimize the carbonation depth and chloride penetration depth and maximize the relative dynamic elastic modulus and weight reducing ratio in the concrete mix design. The results indicated that the optimal CaO content that can satisfy all four conditions ranged between 53% and 56%. This corresponded to the GGBS replacement ratio ranged from 27.5% to 47.1%. In the study, the ready-mixed concrete specification was set to 25-24-180. When the CaO content ranged from 53% to 56%, the compressive strength at 28 d of age was observed as between 31.3 MPa (130.5%) and 33.0 MPa (137.6%), thereby confirming that the target compressive strength ($f_{ck} = 24$ MPa) was secured.
4. Conclusions

In the study, the durability and engineering performance of binary blended concrete with ground granulated blast-furnace slag (GGBS) were evaluated based on the CaO content and ratio, and the optimal CaO content range to secure durability was derived. The results of the study are summarized as follows.

(1) Regression analysis on the CaO/\(\text{SO}_3\) and \(\text{SO}_3/\text{Al}_2\text{O}_3\) molar ratios in the triangular graph revealed that the molar ratios decreased when the GGBS replacement ratio increased. This indicated that it is necessary to consider long-age strength when the GGBS replacement ratio increased.

(2) While the compressive strength exhibited a tendency to increase when the CaO content increased within 28 d, similar compressive strengths were observed at 56 d, irrespective of the CaO content. The rate of increase in compressive strength after 28 d decreased when the CaO content increased. Additionally, within 28 d, the compressive strength exhibited a tendency to increase when the basicity increased.

(3) When the GGBS replacement ratio ranged from 0 to 50%, the specimens at eight weeks of age exhibited similar carbonation depths. However, when the replacement ratio exceeded 50%, the carbonation depth significantly increased. Conversely, the chloride penetration depth significantly decreased when the GGBS replacement ratio was less than 25%, although it remained at similar levels when the replacement ratio ranged from 25% to 70%.

(4) The relative dynamic elastic modulus remained at similar levels when the GGBS replacement ratio ranged from 0 to 45% although it increased to 86.8%–94.5% when the replacement ratio exceeded 45%. Additionally, the weight reducing ratio reached or exceeded 99.9% when the GGBS replacement ratio exceeded 20%.

(5) The optimal CaO content to satisfy all of the four parameters set in the study to secure durability performance (carbonation depth, chloride penetration depth, relative dynamic elastic modulus, and weight reducing ratio) was observed as between 53% and 56% (GGBS replacement ratio: 27.5%–47.1%).

The durability and engineering performance evaluation data based on the CaO content and ratio and optimal CaO content ranged to secure durability (which were derived in the study) can provide guidelines on mixing proportions when high volume GGBS concrete is applied to local construction sites in the future. They are also expected to be used as basic data to set chemical composition criteria for the development of binders to improve durability.

In the future, we will proceed with research on ternary blended concrete that has been replaced with high volume industrial by-products. For this, more detailed micro structural analysis is needed.

Author Contributions: Conceptualization, J.L. and T.L.; Investigation, J.L. and T.L.; Resources, J.L.; Writing—original-draft, J.L.; Writing—review and editing, J.L. and T.L. All authors have read and agreed to the published version of the manuscript.

Funding: The study received no external funding.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Crossin, E. The greenhouse gas implications of using ground granulated blast furnace slag as a cement substitute. *J. Clean. Prod.* 2015, 95, 101–108. [CrossRef]

2. Çakır, Ö.; Aköz, F. Effect of curing conditions on the mortars with and without GGBFS. *Constr. Build. Mater.* 2008, 22, 308–314. [CrossRef]

3. Özay, E.; Erdemir, M.; Durmuş, H.I. Utilization and efficiency of ground granulated blast furnace slag on concrete properties—A review. *Constr. Build. Mater.* 2016, 105, 423–434. [CrossRef]

4. Rashad, A.M.; Sadek, D.M. An investigation on Portland cement replaced by high-volume GGBS pastes modified with micro-sized metakaolin subjected to elevated temperatures. *Int. J. Sustain.* 2017, 6, 91–101. [CrossRef]
5. Sojobi, A.O. Evaluation of the performance of eco-friendly lightweight interlocking concrete paving units incorporating sawdust wastes and laterite. *Cogent Eng.* **2016**, *3*, 1255168. [CrossRef]

6. Pacheco-Torgal, F.; Abdollahnejad, Z.; Camões, A.F.; Jamshidi, M.; Ding, Y. Durability of alkali-activated binders: A clear advantage over Portland cement or an unproven issue? *Constr. Build. Mater.* **2012**, *30*, 400–405. [CrossRef]

7. Lee, J.; Lee, T. Effects of high CaO fly ash and sulfate activator as a finer binder for cementless grouting materials. *Material* **2019**, *12*, 3664. [CrossRef]

8. Pal, S.C.; Mukherjee, A.; Pathak, S.R. Effect of curing conditions on the mortars with and without GGBFS. *Cement Concrete Res.* **2003**, *33*, 1481–1486. [CrossRef]

9. Jin, F.; Gu, K.; Al-Tabbaa, A. Strength and hydration properties of reactive MgO-activated ground granulated blastfurnace slag paste. *Cement Concrete Comp.* **2015**, *57*, 8–16. [CrossRef]

10. Yi, Y.; Gu, L.; Liu, S.; Jin, F. Magnesia reactivity on activating efficacy for ground granulated blast furnace slag for soft clay stabilisation. *Appl. Clay Sci.* **2016**, *126*, 57–62. [CrossRef]

11. Lee, J.; Kim, G.; Kim, Y.; Mun, K.; Nam, J. Engineering properties and optimal conditions of cementless grouting materials. *Material* **2019**, *12*, 3059. [CrossRef] [PubMed]

12. Frigione, G. Manufacture and Characteristics of Portland Blast-furnace Slag Cements, in Blended Cements; ASTM International: West Conshohocken, PA, USA, 1986; pp. 15–28.

13. Uysal, M.; Sumer, M. Performance of self-compacting concrete containing different mineral admixtures. *Constr. Build. Mater.* **2011**, *25*, 4112–4120. [CrossRef]

14. Kavitha, S.; Felix Kala, T. Evaluation of strength behavior of self-compacting concrete using alcocofine and GGBS as partial replacement of cement. *Indian J. Sci. Technol.* **2016**, *9*, 1–5. [CrossRef]

15. Lee, J.; Lee, T. Influences of Chemical Composition and Fineness on the Development of Concrete Strength by Curing Conditions. *Material* **2019**, *12*, 4061. [CrossRef] [PubMed]

16. Juradin, S.; Vlajic`, D. Influence of cement type and mineral additions, silica fume and metakaolin, on the properties of fresh and hardened selfcompacting concrete. In *Mechanical and Materials Engineering of Modern Structure and Component Design, Advanced Structured Materials*; Springer International Publishing: Basel, Switzerland, 2015; p. 70.

17. Mohan, A.; Mini, K.M. Strength and durability studies of SCC incorporating silica fume and ultra fine GGBS. *Constr. Build. Mater.* **2018**, *171*, 919–928. [CrossRef]

18. Peng, H.; Yin, J.; Song, W. Mechanical and hydraulic behaviors of eco-friendly pervious concrete incorporating fly ash and blast furnace slag. *Appl. Sci.* **2018**, *8*, 859. [CrossRef]

19. Huang, C.H.; Wu, C.H.; Lin, S.K.; Yen, T. Effect of slag particle size on fracture toughness of concrete. *Appl. Sci.* **2019**, *9*, 805. [CrossRef]

20. Ganesh, P.; Murthy, A.R. Tensile behaviour and durability aspects of sustainable ultra-high performance concrete incorporated with GGBS as cementitious material. *Constr. Build. Mater.* **2019**, *197*, 667–680. [CrossRef]

21. Suda, V.R.; Rao, P.S. Experimental investigation on optimum usage of Micro silica and GGBS for the strength characteristics of concrete. * Mater. Today Proc.* **2020**, *1–7*. [CrossRef]

22. Cheng, A.; Huang, R.; Wu, J.K.; Chen, C.H. Influence of GGBS on durability and corrosion behavior of reinforced concrete. *Mater. Chem. Phys.* **2005**, *93*, 404–411. [CrossRef]

23. Löfgren, J.; Esping, O.; Lindvall, A. The influence of carbonation and age on salt frost scaling of concrete with mineral additions. In *Proceedings of the Materials, Systems and Structures in Civil Engineering 2016, Lyngby, Denmark, 22–24 August 2016*; pp. 91–100.

24. Koenig, A.; Dehn, F. Acid resistance of ultra high-performance concrete (UHPC). In *Nanotechnology in Construction*; Springer International Publishing: Basel, Switzerland, 2015; pp. 317–323.

25. Koenig, A.; Dehn, F.; Neumann, T.; Rasch, S. Concepts for concrete exposed to acidic fluids. In *Proceedings of the Conference BetonTage “Concrete Solutions”, Neu-Ulm, Germany, 7–9 February 2012*; p. 56.

26. Korean Industrial Standards. *KS I 5201, Portland Cement*; Korean Agency for Technology and Standards: Seoul, Korea, 2006; pp. 1–8.

27. Korean Industrial Standards. *KS F 2563, Ground Granulated Blast-Furnace Slag for Use in Concrete*; Korean Agency for Technology and Standards: Seoul, Korea, 2009.

28. ASTM. ASTM C204. Standard test methods for fineness of hydraulic cement by air-permeability apparatus. In *Annual Book of ASTM*; American Society of Testing and Materials: West Conshohocken, PA, USA, 2007.
29. ASTM C1723-16. Standard guide for examination of hardened concrete using scanning electron microscopy. 

Concr. Aggregat. 2010, 4, 02.

30. ASTM C114-18. Standard Test Methods for Chemical Analysis of Hydraulic Cement; American Society of Testing and Materials: West Conshohocken, PA, USA, 2018.

31. ASTM C457/C457M. Standard Test Method for Microscopical Determination of Parameters of the Air-void System in Hardened Concrete; American Society of Testing and Materials: West Conshohocken, PA, USA, 2016.

32. ASTM C136/C136M-19. Standard Test Method for Sieve Analysis of Fine and Coarse Aggregates; American Society of Testing and Materials: West Conshohocken, PA, USA, 2019.

33. ASTM C231/C231M. Standard Test Method for Air Content of Freshly Mixed Concrete by the Pressure Method; American Society of Testing and Materials: West Conshohocken, PA, USA, 2017.

34. ASTM C873/C873M. Standard Test Method for Compressive Strength of Concrete Cylinders Cast in Place in Cylindrical Molds; American Society of Testing and Materials: West Conshohocken, PA, USA, 2015.

35. ASTM C39/C39M. Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens; American Society of Testing and Materials: West Conshohocken, PA, USA, 2018.

36. Korean Industrial Standards. KS F 2584, Standard Test Method for Accelerated Carbonation of Concrete; Korean Agency for Technology and Standards: Seoul, Korea, 2015.

37. NT Build 492. Chloride Migration Coefficient from Non steady state Migration Experiments; Nordtest: Espoo, Finland, 1999.

38. ASTM C666/C666M. Standard Test Method for Resistance of Concrete to Rapid Freezing and Thawing; American Society of Testing and Materials: West Conshohocken, PA, USA, 2015.

39. Lee, S.S.; Won, C.; Kim, D.S.; Park, S.J. A Study on the Engineering Properties of Concrete Using Blast-furnace Slag Powder. J. Korea Concr. Inst. 2000, 12, 49–58.

40. Utgenannt, P. The influence of ageing on the salt-frost resistance of concrete, Report TVBM-1021. In Division of Building Materials; Lund Institute of Technology: Lund, Sweden, 2004.

41. Stark, J.; Ludwig, H.M. Freeze-thaw and freeze-deicing salt resistance of concretes containing cement rich in granulated blast furnace slag. Mater. J. 1997, 94, 47–55.

42. Hooton, R.D.; Boyd, A. Effect of finishing, forming and curing on de-icer salt scaling resistance of concretes. Frost Res. Concr. 1997, 174–183.

43. Utgenannt, P. Frost resistance of concrete - Experience from three field exposure sites. In Proceedings of the Workshop proc. no. 8: Nordic Exposure Sites - Input to Revision of EN 206-1, Hirtshals, Denmark, 12–14 November 2008.

44. Lee, B.; Kim, G.; Nam, J.; Cho, B.; Hama, Y.; Kim, R. Compressive strength, resistance to chloride-ion penetration and freezing/thawing of slag-replaced concrete and cementless slag concrete containing desulfurization slag activator. Constr. Build. Mater. 2016, 128, 341–348. [CrossRef]