41 Year Long-Term Durability of High Volume Blast-Furnace Slag Cement Concrete

Manabu Hashimoto1*, Kazuhide Kurata2, Yusuke Ohtsuka3 and Yasuhiro Dan4

Received 15 September 2020, accepted 15 March 2021 doi:10.3151/jact.19.248

Abstract
In this study, we investigated the durability of high-volume ground granulated blast furnace slag (GGBS) blended cement concrete containing over 70% of GGBS for possible general structural applications. The concrete specimens used were exposed to natural outdoor conditions for 41 years on a building rooftop. The following is found. The exposed top surface of concrete with 88.5% GGBS 4000 replacement, the exposed top surface and the corners of sulfated slag cement showed peel failure of the paste, but the specimens of concrete with 68.5% GGBS 4000 and GGBS 2000 replacement were in sound condition. The compressive strength of all mix proportions did not decrease significantly over 41 years. The carbonation depth of concrete specimens containing 70% GGBS was about 7 to 9 mm, and about 15 mm for specimens containing 90% GGBS. Despite the high volume of GGBS content (70%) in the concrete specimens, traces of Ca(OH)2, which is involved in the chemical reaction of GGBS, were found in parts that remained uncarbonated. Ca(OH)2 increases the alkalinity of the specimen and is thus considered to have a rebar corrosion-inhibiting effect. This paper is the English translation from the authors’ previous work [Hashimoto, M., et al., (2019). “A study on the long-term durability of high-volume blast-furnace slag cement concrete for 41 years.” Concrete Research and Technology, Vol.30, pp.77-84. (in Japanese)].

1. Introduction
Concrete using ground granulated blast furnace slag (GGBS) has been studied for long years (George 2016). GGBS has latent hydraulic property (Harry 1964; Voinovitch et al. 1976; Kondo et al. 1979) by replacing a part of cement with its. The use of GGBS improves the fresh properties of concrete (Suriya et al. 2020) and long-term strength (Shariq et al. 2010; Mohd et al. 2010; Jaehyun et al. 2020) by latent hydraulic properties. It also improves resistance to sulfate deterioration (Higgins et al. 2003; Pawel et al. 2015), chloride attack (Ashish et al. 2016; Ayano et al. 2021) and seawater. In addition, it is effective in suppressing alkali silica reaction (Plusquellec et al. 2018). Recently, the use of GGBS has been attracting attention from the viewpoint of reducing the environmental load (Prasanna et al. 2019). Further effective use of GGBS is required in the future. Researches such as a study on cement and concrete containing high-volume of GGBS (Cao et al. 1997; Higgins et al. 2003; Yuksel et al. 2018; Sanjay et al. 2021), a study on alkali activated slag concrete using GGBS and alkali activators (Li et al. 2010; Xinghua et al. 2000; Hyung-Seok et al. 2011; Lee et al. 2016; Jan et al. 2016; Shahrajabian et al. 2018; Mahya et al. 2019; Li et al. 2019), and a study on geopolymer without using Portland cement as binder (Davidovits et al. 1991; Deb et al. 2014; Ikeda et al. 2015) are actively conducted in each country.

Concrete with high-volume of GGBS shows slower early strength development and faster carbonation. About the low early strength development at a high GGBS replacement rate, many studies such as those on improvements by adding sulfate activator (Xinghua et al. 2000; Hyung-Seok 2011) etc. and using activated slag with different grinding method of GGBS (Sanjay et al. 2008) have been conducted. About the carbonation, the water-cement ratio of concrete using GGBS is smaller than that of concrete using ordinary Portland cement (Chao et al. 2016). In addition, carbonation is improved by extending the wet curing period (Miguel et al. 2018) and carbonation curing (Sean et al. 2010). It has been reported that the progression mechanisms of the carbonation of concrete using GGBS in an accelerating environment and that in a real environment are different (Matsushita et al. 2004), and it has been reported that the carbonation depths of ordinary Portland cement and concrete using GGBS replacement ratio of about 40% in actual structures are comparable (Concrete library 151, Recommendations for design and construction of concrete using ground granulated blast-furnace slag (JSCE 2018)). Since carbonation influences the corrosion of reinforcing bars in concrete, it is necessary to know the progress of carbonation in a real environment. The data which was obtained in this study in a real environment about concrete with high-volume of GGBS is very im-
important in considering durability.

Since 1975, we have continuously implemented exposure tests on concrete block specimens using high-volume of GGBS cement with different specific surface areas and GGBS replacement ratios as well as sulfated slag cement, with a water-binder ratio of about 50% (Nakahara et al. 1976). The purpose of this study is to confirm changes of the hydrates by long-term exposure, assuming the application of concrete with high-volume of GGBS to RC structures. There are many reports on the physical characteristic evaluation of concrete using GGBS including concrete with high-volume of GGBS (Litvan et al. 1986; Bahador et al. 2014; Kangkang et al. 2015; Liu et al. 2014; Richardson 2006; Cabrera et al. 2016). Our findings are part of those studies. In this paper, we report on the basic physical properties such as the appearance, strength, and carbonation depth of concrete over 41 years in the actual environment. It also shows the chemical properties such as the physical properties of hydrated cement paste.

2. Outline of experiment

2.1 Outline of the exposure tests

Table 1 shows the chemical composition of GGBS 4000 used in the exposure tests, and Table 2 shows the details of the binders tested. Table 3 shows the materials used. The chemical composition of GGBS 2000 is not shown due to the absence of data. Regarding the binder, three types of high-volume ground granulated blast-furnace slag cement with different GGBS types and replacement ratios and a sulfated slag cement (hereafter “BS”) were used. The high-volume ground granulated blast-furnace slag cement used in the test was ordinary Portland cement, 68.5% and 88.5% of which was replaced with GGBS 4000 (with a specific surface area of 3860 cm²/g) and designated as B4-70 and B4-90, respectively. In addition, an ordinary Portland cement, 68.5% of which was replaced with GGBS 2000, was designated as B2-70. As a hardening accelerator, CaCl₂ was added at a rate of 1.5% to all three types. BS consisted of GGBS 4000, gypsum dihydrate, and ordinary Portland cement at a rate of 85%, 13%, and 2%, respectively.
Table 4 Mix proportions and fresh properties of concrete.

| No. | G_{max} (mm) | W/B (%) | s/a (%) | Materials contents (kg/m³) | Slump and Air contents |
|-----|--------------|---------|---------|----------------------------|------------------------|
|     |              |         |         | W  | B* | S  | G  | SL (cm) | Air (%) |
| B4-70 | 25           | 48.8    | 43.0    | 156 | 320 | 868 | 1078 | 8.0    | 2.3     |
| B4-90 |              | 47.5    |         | 152 | 320 | 812 | 1081 | 7.0    | 1.6     |
| B2-70 |              | 50.0    |         | 160 | 320 | 805 | 1072 | 8.0    | 2.1     |
| BS   |              | 50.0    |         | 160 | 320 | 805 | 1072 | 3.0    | 2.0     |

* B: binder (OPC+GGBS)

Table 5 Experimental test items.

| Test item                  | Measuring method          | Notes                       |
|----------------------------|----------------------------|-----------------------------|
| Carbonation depth          | JIS A 1152                | Core with a diameter of 50 mm|
| Compressive strength       | JIS A 1108                | Core with a diameter of 100 mm|
| Static modulus of elasticity| JIS A 1149                | Core with a diameter of 100 mm|
| Vicker’s hardness          |                            | 30 mm from the surface       |
| Pore size distribution     | Mercury intrusion porosimetry|                            |
| Measured amount of Ca(OH)_2| TG-DTA                    | Carbonated portion           |
| Identification of cement hydrate | XRD                      | Uncarbonated portion         |
| Breakdown of C-S-H         | FT-IR                     |                             |
| Observation of texture     | SEM                       |                             |

Table 4 shows the mix proportions and fresh properties of the concrete. The water-binder ratios were determined as about 50%, which had been used in ordinary civil engineering structures; that is, 48.8% for B4-70, 47.5% for B4-90, 50.0% for B2-70, and 50.0% for BS. The target slump was determined as 7.0 cm, and the maximum dimensions of coarse aggregate, the sand percentage, and the unit amount of binder were kept constant at 25 mm, 43.0%, and 320 kg/m³, respectively. The mix proportions were determined by adjusting the water content per unit volume of concrete.

The test specimens were 650 mm in length, 470 mm in width, and 650 mm in height, and exposed to an outdoor environment on the roof of an experiment facility (in Chofu City, Tokyo) for 41 years from July 1975. The roof is exposed to rain and insolation, where carbonation is assumed to be the main degradation factor. Figures 1 shows the condition of the exposed test specimens.

### 2.2 Measurement items and methods

Cores with diameters of 100 mm and 50 mm were obtained at the positions on the test specimen shown in Fig. 2, and the tests were implemented according to the items listed in Table 5. Three core test specimens with a diameter of 50 mm obtained at each exposed top surface were fractured, phenolphthalein solution was sprayed onto the fractured surface in accordance with JIS A 1152, and the carbonation depth was determined based on the uncolored portion. The compressive strength and Vicker’s hardness were tested using cores with a diameter of 100 mm. In the compressive strength test, a por-

---

Fig. 1 Appearance of the exposed test specimens.

Fig. 2 Sample specimen and test locations.
tion 20 mm from the core’s surface was cut away and used. Vicker’s hardness was measured under the conditions of a load of 0.2 HV (1.961 N), a holding time of 5 s, and a measurement interval of 2–3 mm in the direction of the depth from the top surface. For each measurement point, the Vicker’s hardness was calculated as the average measurement value of 10 points.

The locations covered in the pore size distribution analysis and the chemical composition analysis were determined in such a way that the range from the surface to 5 mm of the core test specimen with a diameter of 100 mm was assumed as the carbonated portion, and the range from 220 to 240 mm as the uncarbonated portion, respectively, considering that the previous measurement of the carbonation depths had resulted in a minimum depth of 7 mm. The pore size distribution was measured by using a mercury intrusion porosimetry (MIP), and the amount of Ca(OH)₂ was measured by means of thermogravimetry and differential thermal analysis (TG-DTA). The test specimens used in the MIP and TG-DTA measurements were obtained by retrieving the mortar portion, granulating it to 2.5–5.0 mm, soaking in acetone, and vacuum drying. In addition, the test specimens used in TG-DTA were crushed in a mortar and then screened with a 100 μm sieve, after which a specimen not larger than 100 μm was tested. The amount of Ca(OH)₂ was calculated through conversion to a value per amount of paste, using the dehydrated amount measured at 400–500°C by means of TG-DTA as well as the amount of aggregate-derived insoluble residue contained in the specimen.

The specimens for measurement by X-ray diffraction (XRD) and Fourier transform infrared spectrophotometer (FT-IR) were the same as those for TG-DTA. In the backscattered electron image observation of the morphology of hydrates using a scanning electron microscope (SEM), mortar portions with a size of 5.0 × 5.0 × 5.0 mm were obtained from the concrete specimen that had been obtained from both the carbonated portions and the uncarbonated portions, then solvent exchange by acetone and vacuum drying were used to stop the hydration of cement as in the case of MIP, and they were used for the test. The fractured surfaces were observed under the conditions of low-vacuum mode, 50 Pa chamber pressure, 10 kV accelerating voltage, and ×1000 magnification.

3. Results and discussion

3.1 Visual survey

Figures 3 shows the physical appearance of the test specimens. It has been indicated that carbonation is prone to progress in GGBS with a higher replacement ratio, and accordingly, may cause the absanden phenomenon (Manns et al. 1968) accompanied by embrittlement of the surface layers. B4-70 and B2-70 were in sound condition showing no noticeable degradation. On the other hand, the exposed top surface of B4-90 and the exposed top surface, including the corners, of BS showed peel failure of the paste. This tendency was especially significant for BS, some parts of which showed exposed coarse aggregate. Manns et al. reported that the absanden phenomenon did not occur when 10% or more ordinary Portland cement was contained in binders with a high GGBS replacement ratio (Manns et al. 1968; Uomoto et al. 1980). The results of this study could be interpreted in accordance with the amount of ordinary Portland cement contained in the binders. That is, while B4-90 and BS with a replacement ratio of 10% or less showed degradation including peel failure at the top surface, B4-70 and B2-70 with a 30% replacement rate of ordinary Portland cement did not show any degradation at the top surface. Therefore, the degradation at the top surface was considered to be due to the absanden phenomenon.

3.2 Mechanical properties

Figures 4 shows the relationship between the compressive strength and the material age. For all mix proportions, an increasing trend in compressive strength from 91 days to 11 years of material age was shown. After that, B4-70 and BS showed an increase from 21 years to 41 years of material age, and B4-90 and B2-70 showed a slight decrease but retained a comparable compressive
strength. At the material age of 41 years, the compressive strength of B4-90 was lower than that of B4-70, but the increase rate of B4-90 from 91 days to 41 years was higher than that of B4-70. This indicates that the compressive strength of B4-90 increased due to the activation of the latent hydraulic properties of GGBS over a long period of time. At a material age of 41 years, again, the compressive strength of B2-70 was lower than that of B4-70. The reason is thought to be the smaller specific surface area of GGBS 2000 in B2-70 compared to that of GGBS 4000 in B4-70, resulting in a smaller reactive area for the activation of latent hydraulic properties. In addition, the compressive strength of BS was higher than that of the other mix proportions by about 20–30 N/mm². This is discussed later based on the measurement results of the pore size distributions of the uncarbonated portion and generated cement hydrates.

Figures 5 shows the relationship between the compressive strength and the static modulus of elasticity. In the figure, the relational equation of the JSCE “Standard specifications for concrete structures” (Design) (Standard specifications for concrete structures -2017, Materials and construction (JSCE 2017)) is also shown. The relationship between the compressive strength and static modulus of elasticity at the material ages of 11, 21, and 41 years roughly matched the JSCE relational equation, which is the equivalent relationship to that seen in concrete used for general civil engineering structures.

3.3 Changes in carbonation depth

It is reported that high-volume ground granulated blast-furnace slag cement generally shows a faster carbonation rate compared to cases where only ordinary Portland cement is used, and therefore, it is necessary to consider methods for its application to actual structures based on the carbonation rate. Accordingly, the relationship between the carbonation depth, which is calculated using the estimation equation for the carbonation rate (Standard specifications for concrete structures -2017, Materials and construction (JSCE 2017)) in the “Standard specifications for concrete structures” (Design) (hereafter “JSCE equation”), and the actual measurement value was considered. The JSCE equation (Eq. (1)) is calculated based on the carbonation depth when concrete using ordinary Portland cement is exposed to a real environment, and it is estimated the carbonation depth when GGBS is used, by using the material constant $k = 0.7$. Figures 6 shows the carbonation depth at each material age. The carbonation depths calculated using the JSCE equation are also shown in the figure. The conditions for the estimation equation are as follows:

$$X = -3.57 + 9.0W/(C_p + k \cdot A_d)$$  
$$C_p = B \cdot (1 - P_{GGBS})$$  
$$A_d = B \cdot P_{GGBS}$$

where,

- $X$: Carbonation rate coefficient (mm/$\sqrt{\text{year}}$)
- $W$: Mass of water per unit volume (kg/m³) = 160 kg/m³
- $C_p$: Mass of Portland cement per unit volume (kg/m³)
- $k$: Constant determined by the type of admixture (in the case of GGBS, $k = 0.7$)
- $A_d$: Mass of admixture per unit volume (kg/m³)
- $B$: Unit amount of binder (kg/m³) = 320 kg/m³
- $P_{GGBS}$: Replacement ratio of GGBS in binder (set as $P_{GGBS} = 45\%, 70\%, 90\%$)

The estimated carbonation depth of concrete using the binder with 70% GGBS replacement was comparable to the actual measurement value of the carbonation depth of B4-70 at the material ages of 91 days and 21 years, with the exception of 11 years, but it was greater than the actual measurement value by 5 mm at the material age of 41 years. The estimated carbonation depth of concrete using the binder with 90% GGBS replacement was comparable to the actual measurement value of the carbonation depth of B4-90 at the material age of 41 years, but it was less than the actual measurement value by about 3 mm at the material ages of 11 years and 21 years.
years. The actual measurement values of the carbonation depth of B4-70 and B2-70 at the material age of 41 years were less than the estimated carbonation depth of concrete using the binder with 45% GGBS replacement, which is equivalent to blast-furnace slag cement type B. This indicated that the carbonation of concrete using cement with a replacement ratio of 70% progressed relatively slowly in a real environment, as far as this experiment was concerned.

Next, Ca(OH)₂ in concrete was considered. According to previous findings, (Kwak et al. 2005) as the GGBS replacement ratio in the binder increases, the amount of generated Ca(OH)₂ linearly decreases. Ca(OH)₂ has a function to keep the pH of concrete highly alkaline; thus, it is assumed that the carbonation progresses from the part where Ca(OH)₂ is consumed by carbonation. As Fig. 7 shows, a correlation was found between the carbonation depth at a material age of 41 years and the ordinary Portland cement replacement ratio. Therefore, it was presumed that the decrease in the generated Ca(OH)₂ due to the decrease in the ordinary Portland cement ratio in the binder dominated the carbonation progress.

The measured carbonation depth at the material age of 21 years was greater than the estimated value for all mix proportions, but a clear reason has not been found. Studies on this issue should be continued. Specifically, the reason why the carbonation depth of B2-70 was significantly great is not clear. However, considering that B2-70 showed the lowest total pore quantity, it was presumed that the cement hydrate in the area unaffected by carbonation remained in sound condition over a long period of time. Regarding the carbonated region, on the other hand, it was presumed that the Vicker’s hardness decreased as the depth from the top surface decreased because the pore structure of the cement hydrate became loose with carbonation. Only B2-70 showed that the Vicker’s hardness tended to increase as the depth from the top surface decreased. The reason for this is discussed with the following results of both the (2) pore size distribution and (3) backscattered electron images.

(2) Pore size distribution
Figures 9 shows the pore size distributions of the carbonated and uncarbonated portions. It was confirmed that in all mix proportions, the pore quantity for 6–20 mm decreased, that for 20–500 mm increased, and the total pore quantity increased in the carbonated portion compared to the uncarbonated portion. It was presumed that such increase and decrease associated with carbonation occurred because C-S-H became more porous (Ngala et al. 1997) due to carbonation of the blast-furnace slag cement-derived C-S-H with a low Ca/Si ratio. It was also presumed that the decrease in the Vicker’s hardness occurred in the carbonated region because the pore structure became more porous. In addition, considering that the uncarbonated portion of BS showed the lowest total pore quantity, it was presumed that BS showed the highest compressive strength because BS had a denser pore structure compared to that cement associated with carbonation progress

(1) Vicker’s hardness
Figures 8 shows the relationship of the Vicker’s hardness in the direction of the depth from the surface and the carbonation depth. The standard deviation was about 4 HV, and the relative standard deviation was about 15%. Regarding the carbonation region, it was confirmed that the Vicker’s hardness tended to continuously decrease as the depth from the top surface decreased, except in B2-70. Based on the fact that the compressive strength test result for the core test specimen, which was obtained from the uncarbonated portion (central part), showed a stable transition from 11 years to 41 years, it was presumed that the cement hydrate in the area unaffected by carbonation remained in sound condition over a long period of time. Regarding the carbonated region, the reason for this is discussed with the following results of both the (2) pore size distribution and (3) backscattered electron images.

3.4 Change in physical properties of hardened concrete

Fig. 7 Relationship between carbonation depth and ordinary Portland cement replacement ratio.

Fig. 8 Vicker’s hardness in the direction of the depth from the surface.
of the other mix proportions.

(3) Backscattered electron image

Figures 10 shows the backscattered electron images that were observed by using SEM. In any mix proportion, it was confirmed that the texture of the carbonated portion was looser than that of the uncarbonated portion. Looking at the GGBS particles, the unreacted parts were identified in the central portion and the reactive layer was identified on their surfaces, for both the carbonated and uncarbonated portions.

For the reason why the Vicker’s hardness of B2-70 was greater in the surface layer, as shown in Figs. 9 and 10, while the carbonated portion of B2-70 was as loose as that of other mix proportions, particles of unhydrated slag larger than that of the other mix proportions were identified in B2-70 because coarse ground granulated slag with a small specific surface area was used for B2-70. Since an unhydrated particle is harder than a hydrated part (Chuanlin et al. 2014), B2-70 might show a different tendency in Vicker’s hardness from that of the other levels, and therefore, further detailed study is required.

3.5 Change in cement hydrate associated with carbonation progress

(1) Change in cement hydrate due to carbonation

Figures 11 shows the main cement hydrates identified by XRD. For the uncarbonated portion of all mix proportions, the peak of ettringite was confirmed, but the peak of C-S-H was not confirmed due to its poor crystalline nature. The peak of ettringite was especially high for BS, which might indicate that its composition was unique compared with the other mix proportions. Such generation of ettringite is presumed to be derived from gypsum dihydrate (Ansai et al. 2009), and to contribute to the densification of the pore structure and the increase in the compressive strength at the uncarbonated portion of BS.

Next, for the carbonated portion, the generation of
Calcite was confirmed in all mix proportions, and that of vaterite was confirmed in B4-70, B4-90, and B2-70, but not in BS. Calcite and vaterite are CaCO$_3$ with different crystal structures, and it has been reported that vaterite tends to be generated during the carbonation of C-S-H with a low Ca/Si ratio (Wu et al. 2015). Because the tested cement with a GGBS replacement ratio of 70% or more contained a low proportion of ordinary Portland cement, the amount of Ca(OH)$_2$ generated was small due to hydration. Then its Ca/Si ratio might decrease, and the texture might become more porous due to carbonation. Therefore, to understand the degree of C-S-H carbonation, FT-IR measurements were conducted.

**Figures 12** shows the results of the FT-IR analysis of B4-70. For the uncarbonated portion, a peak caused by C-S-H was confirmed at around 960 cm$^{-1}$, and for the carbonated portion, carbonation reduces the C / S ratio of C-S-H and shifts the peak to greater than 960 cm$^{-1}$. Such tendency of peaks was observed in other mix proportions as well. It has been thought that when C-S-H is completely broken down by carbonation, it becomes silica gel and shows a peak at 1080 cm$^{-1}$ (Wu et al. 2016; Wang et al. 2018). Sagawa et al. (2017) considering the results of FT-IR analysis using an actual concrete structure with blast-furnace slag cement type C that had been exposed to the natural environment for 52 years, where a broad peak at 980–1080 cm$^{-1}$ due to C-S-H was shown, concluded that the C-S-H in the carbonated region had not completely broken down, but C-S-H with a lowered Ca/Si ratio and sound C-S-H were mixed. Because the results of the present study showed a similar tendency to those of Sagawa et al., it was also presumed that C-S-H had not completely broken down and some C-S-H remained in the concrete with a GGBS replacement ratio of 70% and a material age of 41 years.

(2) Residuals of Ca(OH)$_2$

**Table 6** shows the measurement results for the amount of Ca(OH)$_2$. Ca(OH)$_2$ was not detected in the uncarbonated portion of B4-90 and BS. It is presumed that because these binders contained as little as 2% and 10% of Portland cement, Ca(OH)$_2$ generated by the hydration of Portland cement reacted with Si ions, Al ions, etc., which are supplied in association with the hydration reaction of ground granulated blast-furnace slag, and was consumed for the generation of hydrates such as C-S-H, C-A-H, and ettringite. Ca(OH)$_2$ was not detected even in the uncarbonated portion. On the other hand, residuals of 3.2% and 3.1% of Ca(OH)$_2$ were identified in the uncarbonated portion of B4-70 and B2-70, respectively.

The measured carbonation depth of B4-70 and B2-70 at the material age of 41 years was 10 mm or less, which was less than the estimated carbonation depth of blast-furnace slag cement type B. It is presumed that when the proportion of Portland cement was 30%, the carbonation progress started with the residual of Ca(OH)$_2$, and when the proportion of Portland cement was 2% or 10%, the carbonation progress started without the residual of Ca(OH)$_2$. Within the scope of the present study, the measured carbonation depth of B4-70 and B2-70 was less than the estimated carbonation
depth of blast-furnace slag cement type B, which may indicate that the mechanism of carbonation progress differed depending on the existence or nonexistence of Ca(OH)$_2$ residual, and as a result, deviation occurred between the measurement and the estimation. In terms of corrosion prevention of rebars in the concrete, Ca(OH)$_2$ plays an important role in maintaining the pH in concrete. In other words, when Ca(OH)$_2$ remains, the pH is supposed to be stable. It was presumed that the residual Ca(OH)$_2$ contributed to the corrosion prevention of rebars, and the potential application to actual structures was indicated. Based on the results of the present study, it was presumed that concrete containing a high volume of GGBS is sufficiently applicable to actual structures.

### 4. Conclusions

Using concrete containing a high volume of GGBS, which had been exposed to an outdoor environment for 41 years, a study of the fundamental physical properties including appearance, strength, and carbonation depth as well as an analysis of the physical properties of hardened cement and cement hydrate were implemented, and the following findings were obtained.

1. Exposure test specimens of concrete with 68.5% GGBS 4000 and GGBS 2000 replacement were in sound condition, showing no noticeable degradation including the absanden phenomenon accompanied by embrittlement of the surface layers. On the other hand, the exposed top surface of concrete with 88.5% GGBS 4000 replacement, the exposed top surface and the corners of sulfated slag cement showed peel failure of the paste.

2. For all mix proportions, the compressive strength increased from 91 days to 11 years of material age. It was confirmed that no significant decrease in compressive strength was seen, and the condition was sound from 11 years to 41 years of material age.

3. A correlation was found between the carbonation depth at the material age of 41 years and the proportion of each binder accounted for by ordinary Portland cement. It was presumed that the decrease in generated Ca(OH)$_2$ due to the decrease in the ordinary Portland cement ratio in the binder dominated the carbonation progress.

4. For the concrete using blast-furnace slag cement with 70% GGBS replacement at the material age of 41 years, it was confirmed that when the water-binder ratio was 50%, the carbonation depth was 10 mm or less, and residuals of Ca(OH)$_2$ were identified in the uncarbonated portion.

### Reference

Anzai, T., Nishikawa, M., Ikeo, Y. and Sakai, E., (2009). “Hydration reaction analysis of cement having high blast-furnace slag.” *Cement Science and Concrete Technology*, 63, 22-27. (in Japanese)

Ashish, D. K., Singh, B. and Verma, S. K., (2016). “The effect of attack of chloride and sulphate on ground granulated blast furnace slag concrete.” *Advances in concrete construction*, 4(2), 107-121.

Ayano, T. and Fujii, T., (2021). “Improvement of concrete properties using granulated blast furnace slag sand.” *Journal of Advanced Concrete Technology*, 19(2), 118-132.

Bahador, S. D., Tze, Y. D. L. and Susanto, T., (2014). “Durability Properties and microstructure of ground granulated blast furnace slag cement concrete.” *International Journal of Concrete Structures and Materials*, 8, 157-164.

Cabrera, J. A., Escalante, J. I. and Castro, P., (2016). “Compression resistance of concretes with blast furnace slag. Re-visited state-of-the-art.” *Revista ALCONPAT*, 6(1), 64-83.

Cao, H. T., Bucea, L., Ray, A. and Yozghatliam, S., (1997). “The effect of cement composition and pH of environment on sulfate resistance of Portland cements and blended cements.” *Cement and Concrete Composites*, 19(2), 161-171.

Chao, Q. L., Ravindra, K. D. and Gurmel, S. G., (2016). “Carbonation resistance of GGBS concrete.” *Magazine of Concrete Research*, 68(18), 936-969.

Chuanlin, H., Zongjin, L., Yueyi, G., Yunhe, H. and Yamei, Z., (2014). “Investigation on microstructures of cementitious composites incorporating slag.” *Advances in Cement Research*, 26(4), 222-232.

Davidovits, J., (1991). “Geopolymers.” *Journal of thermal analysis*, 37, 1633-1656.

Deb, P. S., Nath, P. and Sarker, P. K., (2014). “The effects of ground granulated blast-furnace slag blending with fly ash and activator content on the workability and strength properties of geopolymer concrete cured at ambient temperature.” *Materials & Design*, 62, 32-39.

Fu, X., Hou, W., Yang, C., Li, D. and Wu, X., (2000). “Studies on Portland cement with large amount of slag.” *Cement and Concrete Research*, 30, 645-649.

Gerohe, W., (2016). “The utilization of slag in civil infrastructure construction.” Woodhead Publishing Series in Civil and Structural Engineering, Number 68, Woodhead Publishing.

Hashimoto, M., Kurata, K., Otsuka, Y. and Dan, Y., (2019). “A study on the long-term durability of high-volume blast-furnace slag cement for 41 years.” *Concrete Research and Technology*, 30, 77-84. (in Japanese)

Higgins, D. D. and Crammond, N. J., (2003). “Resistance of concrete containing ggb to the thaumasite form of sulfate attack.” *Cement and Concrete Composites*, 25(8), 921-929.

Ikeda, K. and Li, Z., (2015). “Development of paper sludge ash-based geopolymer and application to the solidification of nuclear waste water.” In: Proc. *14th ICSCC*, Beijing, Session 6, Alternative binders, 36, 1-14.

Jaehyun, L. and Taegyu, L., (2020). “Durability and...
engineering performance evaluation of CaO content and ratio of binary blended concrete containing ground granulated blast-furnace slag.” *Applied Sciences*, 10(7), 2504.

Jan, P., Patrycja, M. and Beata, L. P., (2016). “Influence of hardening accelerating admixtures on properties of cement with ground granulated blast furnace slag.” *Procedia Engineering*, 161, 1070-1075.

JSCE, (2017). “Standard specifications for concrete structures -2017: Materials and construction.” Japan Society of Civil Engineers, (in Japanese)

JSCE, (2018). “Recommendations for design and construction of concrete using ground granulated blast-furnace slag (Concrete Library 151).” Japan Society of Civil Engineers, 140-141. (in Japanese)

Kim, H., Park, J., An, Y., Bae, J. and Han, C., (2011). “Activation of ground granulated blast furnace slag cement by calcined alunite.” *Materials Transactions*, 52(2), 210-218.

Koga, H., Shinmi, T., Nakamura, A. and Kato, H., (2014). “Influence of specific surface area and calcium sulfate of blast-furnace slag on slag the effect of calcium hydroxide powder to the cement containing blast furnace slag.” *Cement Science and Concrete Technology*, 68(1), 233-238. (in Japanese)

Kondo, R., Chong, T., Goto, S. and Daimon, M., (1979). “The latent hydraulic property of granulated blast furnace slag by various activators.” *Tetsu-to-Hagane (Iron and Steel)*, 65(13), 1825-1829. (in Japanese)

Kangkang, T., Steve, M. and Greg, B., (2015). “Technical and economical feasibility of using GGBS in long-span concrete structures.” *Advances in Concrete Construction*, 3(1), 1-14.

Kumar, S., Kumar, R., Bandopadhyay, A., Alex, T. C., Ravi Kumar, B., Das, S. K. and Mehrotra, S. P., (2008). “Mechanical activation of granulated blast furnace slag and its effect on the properties and structure of portland slag cement.” *Cement & Concrete Composites*, 30(8), 679-685.

Kwak, D., Kokubu, K. and Uji, K., (2005). “A study on carbonation rate of mortar using ground granulated blast-furnace slag.” *Doboku Gakkai Ronbunshu*, 802, 49-59. (in Japanese)

Lee, B., Kim, G., Nam, J., Cho, B., Hama, Y. and Kim, R., (2016). “Compressive strength, resistance to chloride-ion penetration and freezing/thawing of slag-replaced concrete and cementless slag concrete containing desulfurization slag activator.” *Construction and Building Materials*, 128, 341-348.

Li, D., Wu, X., Shen, J. and Wang, Y., (2000). “The influence of compound admixtures on the properties of high-content slag cement.” *Cement and Concrete Research*, 30, 45-50.

Li, Z., Thomas, R. J. and Peethamparan, S., (2019). “Alkali-silica reactivity of alkali-activated concrete subjected to ASTM C 1293 and 1567 alkali-silica reactivity tests.” *Cement and Concrete Research*, 123, 105796.

Litvan, G. G. and Meyer, A., (1986). “Carbonation of granulated blast furnace slag cement concrete during twenty years of field exposure.”, In: *Proceeding of the 2nd International Conference of Fly, Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete*, Madrid Spain 1986. ACI SP 91-71, 91(2), 1445-1462.

Liu, S., Wang, Z. and Li, X., (2014) “Long-term properties of concrete containing ground granulated blast furnace slag and steel slag.” *Magazine of Concrete Research*, 66(21), 1095-1103.

Manns, W. and Wesche, K., (1968). “Variation in strength of mortars made of different cements due to carbonation.” In: *Proceedings of 5th International Symposium on Cement Chemistry*, Tokyo: The Cement Association of Japan, III, 385-393.

Matsushita, F., Aono, Y. and Shibata, S., (2004). “Microstructure changes in autoclaved aerated concrete during carbonation under working and accelerated conditions.” *Journal of Advanced Concrete Technology*, 2(1), 121-129.

Mahya, A., Zhong, T., Bijan, S., Georgi, A. and Richard, S., (2019). “Mix composition and characterisation of one-part geopolymers with different activators.” *Construction and Building Materials*, 225, 526-537.

Miguel, A. S., Esteban, E., Cristina, A. and Daniel, D. B., (2018). “Effect of curing time on granulated blast-furnace slag cement mortars carbonation.” *Cement and Concrete Composites*, 90, 257-265.

Mohd, S., Jagdish, P. and Amjad, M., (2010). “Effect of GGBFS on time dependent compressive strength of concrete.” *Construction and Building Materials*, 24(8), 1469-1478.

Nakahara, Y., Kotani, K., Narahara, K. and Hirata, S., (1976). “Study on slag-cement concrete (Part2).” *Annual Report Kajima Technical Research Institute*, 24, 19-24. (in Japanese)

Nakamoto, J., Togawa, K. and Fujii, M., (1997). “A study on the strength development of high blast-furnace slag content concrete.” *Doboku Gakkai Ronbunshu*, 564, 121-131. (in Japanese)

Ngala, V. T. and Page, C. L., (1997). “Effects of carbonation on pore structure and diffusion properties of hydrated cement pastes.” *Cement and Concrete Research*, 27(7), 995-1007.

Nito, N., Hanehara, S. and Koibuchi, K., (2008). “Influence of hydration heat of blast-furnace slag cement by surface area of blast-furnace slag and anhydrite content.” *Cement Science and Concrete Technology*, 62, 101-107. (in Japanese)

Pawel, L. and Ali, S., (2015). “Durability of mortars containing ground granulated blast-furnace slag in acid and sulphate environment.” *Procedia Engineering*, 108, 47-54.

Plusquellec, G., Geiker, M. R., Lindgard, J. and De Weerdt, K., (2018). “Determining the free alkali metal content in concrete – Case study of an ASR-affected dam.” *Cement and Concrete Research*, 105, 111-125.
Prasanna, P. K., Srinivasu, K. and Murthy, A. R., (2019). “Compressive strength assessment using GGBS and randomly distributed fibers in.” *International Journal of Innovative Technology and Exploring Engineering*, 9(2), 1078-1086.

Richardson, D. N., (2006). “Strength and durability characteristics of a 70% ground granulated blast furnace slag (GGBFS) concrete mix.” Organizational Results Research Report, Missouri Department of Transportation.

Sagawa, T., Ueki Y., Matsushita, T., Kanda, T., Yonezawa, T. and Sakai, E., (2017). “Investigation of the durability of 52 year aged RC structures constructed of portland blast-furnace slag cement type-C.” *Concrete Research and Technology*, 28, 47-59. (in Japanese)

Sakai, E., Ansai, T., Atarashi, D. and Ikeo, Y., (2011). “Material design of high volume blast furnace slag cement in consideration of early hydration of cement.” *Cement Science and Concrete Technology*, 65(1), 20-26. (in Japanese)

Sanjay, S., Chetankumar, M. and Uppara, B., (2021). “An experimental study on various industrial wastes in concrete for sustainable construction.” *Journal of Advanced Concrete Technology*, 19(2), 133-148.

Sean, M. and Yixin, S., (2010). “Carbonation curing of slag-cement concrete for binding CO₂ and improving performance.” *Journal of Materials in Civil Engineering*, 22(4).

Shahrajabian, F. and Behfarnia, K., (2018). “The effects of nano particles on freeze and thaw resistance of alkali-activated slag concrete.” *Construction and Building Materials*, 176, 172-178.

Shariq, M., Prasad, J. and Masood, A., (2010). “Effect of GGBFS on time dependent compressive strength of concrete.” *Construction and Building Materials*, 24(8), 1469-1478.

Suriya, M., Anandkumar, M. and Ravichandran, P., (2020). “Study on behaviour of GGBS as partial replacement of cement in concrete with addition of polycarboxylate ether.” In: *AIP Conference Proceedings*, 2240, 060002.

Taylor, H. F. W., (1964). “The Chemistry of Cements.” London, New York: Academic Press, 480.

Uomoto, T., Kobayashi, K. and Hoshino, T., (1980). “Deterioration of slag-gypsum cement concrete.” In: *Proceedings of the Japan Concrete Institute*, (2), 69-72. (in Japanese)

Voinovitch, I. A. and Dron, R., (1976). “Action des différents activants sur l'hydratation du laitier granul.” *Silic. Ind.*, 41(4-5), 209-212.

Wang, K., Ren, L. and Yang, L., (2018). “Excellent carbonation behavior of rankinite prepared by calcining the C-S-H: Potential recycling of waste concrete powders for prefabricated building products.” *Materials*, 11(8).

Wu, B., Ye, G. and Zhang, Y., (2015). “Development of porosity of cement paste blended with supplementary cementitious materials after carbonation.” In: *Proc. of the 14th International Congress of the Chemistry of Cement (ICCC 2015)*, Beijin 13 Oct. 2015. 1-18.

Wu, B. and Ye, G., (2016). “Carbonation mechanism of different kind of C-S-H : rate and products.” *Concrete with Supplementary Cementitious Materials*, 455.

Yonezawa, T., Kamano, H., Kinoshita, M., Koibuchi, K. and Sakai, E., (2010). “Energy-CO₂ minimum (ECM) cement-concrete system.” *Concrete Journal*, 48(9), 69-73. (in Japanese)

Yuksel, I., (2018). “12 - Blast-furnace slag.” *Waste and Supplementary Cementitious Materials in Concrete*, 361-415.