

CARBONATION MECHANISM OF HIGHLY FLUID CONCRETE CONTAINING SLOWLY COOLED BLAST FURNACE SLAG POWDER

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It is clarified that highly fluid concrete (HFC) containing slowly cooled blast furnace slag powder (CFS) exhibits equivalent strength to HFC containing limestone powder (LSP), and that carbonation proceeds more slowly. The rise in strength of HFC containing CFS during the carbonation process is greater than that of HFC containing LSP and, as a result, the pore volume is lower so the concrete is more rigid and dense. We infer that carbonation is suppressed thereafter. It is also found that carbonation causes melilite and α -CS, which are the main components of the CFS, to react as well.

Keywords: *Slowly cooled blast furnace slag, limestone powder, highly fluid concrete, compressive strength, carbonation, reaction*

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1. INTRODUCTION

Highly fluid concrete (HFC) suitable for constructing durable concrete structures irrespective of the quality of workmanship is obtained by adding, a large amount of granulated blast furnace slag powder or limestone powder (LSP). The additional powder provides resistance to segregation by maintaining the unit weight of powder in The Concrete, while at The same time avoiding excessive strength and controlling the heat of hydration and autogeneous shrinkage associated with cement (binder). Segregation resistance is an important criterion in ensuring that sound concrete structures are obtained. Limestone is the more popular powder, and is heavily utilized in HFC.

Though at first considered simply filler, limestone is now considered a functional material that prevents excessive strength gain and provides resistance to segregation. It will no doubt continue to be utilized in HFC as a functional inorganic powder. However, limestone is a precious natural resource, particularly in Japan.

Consequently, it is important to look for an alternative powder with less environmental Impact. One possibility is slowly cooled blast furnace slag powder, which was once studied as a concrete additive [1] but was dropped as a subject for research when it turned out to contribute nothing to strength development. At present, it is mainly used as a sub-base material [2]. However, since there is now a preference for using recycled aggregate as a sub-base material, there is a need to find a new application for slowly cooled blast furnace slag. The authors have noted the loss of this conventional application of slowly cooled blast furnace, and are studying its application to HFC [3]. They have found that HFC containing slowly cooled blast furnace slag powder has better fluidity retention than concrete containing limestone powder, while exhibiting almost the same strength development, heat of hydration, and autogeneous shrinkage characteristics.

A further significant issue to be considered when discussing the durability of concrete is the process of carbonation. However, until now, there have been no reported investigations of the carbonation of concrete containing slowly cooled blast furnace slag. In this study, in order to collect data to demonstrate the durability of concrete containing slowly cooled blast furnace slag, the carbonation process and its mechanism in HFC containing slowly cooled blast furnace slag powder is investigated in comparison with HFC with the same mix proportion and the same hardened properties containing limestone powder.

2. EXPERIMENTS

2.1 Materials

Figure-1 shows a powder x-ray diffraction analysis pattern of the slowly cooled blast furnace slag used. Also shown is the pattern for granulated blast furnace slag (BFS) that has been rapidly cooled and glassified. It is clear from this figure that slowly cooled blast furnace slag consists mainly of melilite (combined crystalline gehlenite, $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, and akermanite, $2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$).

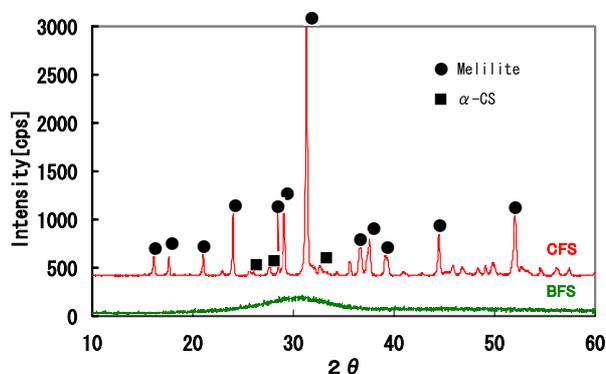


Figure-1 XRD pattern of CFS and BFS

No other compounds are found except for traces of α -CS(α -CaO · SiO₂). The glassification ratio of the slowly cooled blast furnace slag used in this study is 5.7 %, which implies that little glassy phase is present.

Table-1 shows the chemical compositions of the materials used in the study. Ordinary portland cement is shown in the table as OPC, and CFS stands for slowly cooled blast furnace slag. Limestone powder (LSP) was also used in the study for comparison purposes. The CSF and LSP were ground to approximately the same fineness.

Table-1 Chemical composition, density and blaine surface area of material used

Material Symbol	Chemical composition (mass%)									Density (g/cm ³)	Blaine (cm ² /g)
	LOI	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	TiO ₂	SO ₃	R ₂ O		
OPC	2.2	20.9	2.9	5.4	64.7	0.9	0.1	1.8	0.5	3.14	3010
CFS	0.4	31.7	1.5	14.8	39.5	7.2	0.7	1.6	0.5	3.00	4500
LSP	43.5	0.1	0.1	0.1	55.3	–	–	–	–	2.71	4500

OPC: Ordinary portland cement, CFS: Slowly cooled blast furnace slag, LSP: Lime-stone powder

2.2 Mix Proportion and Preparation of Concrete

Table-2 shows the mix proportion of the HFC examined in this study. The letter P in the table stands for powder materials and is the sum of the cement and additives. A commonly available poly-carboxylate-based superplasticizer (SP) was used. The aggregate was produced in Himekawa, Niigata prefecture, and the density of the sand and coarse aggregate was 2.62 and 2.64, respectively.

Table-2 Mix proportion of highly fluid concrete

Add. Types	SL flow (mm)	Gmax (mm)	Air (%)	S/a (%)	W/P (%)	Unit weight (kg/m ³)					S.P. (×P)
						W	C	Add.	S	G	
CFS	650±50	25	4.5	48	30	165	350	200	770	840	1.4%
LSP	650±50	25	4.5	48	30	165	350	200	761	831	1.3%

P: Powder(cement+additive), W/P: Water powder ratio, S.P.: Superplasticizer, Gmax: Maximum size of aggregates, s/a: Sand aggregate ratio

Their fineness moduli were 2.82 and 7.43, respectively. Regardless of the powder additive used, the unit weight of the cement and additive was set at 350 kg/m³ and 200 kg/m³, respectively, so as to maintain the total unit weight of powder at 550 kg/m³. The unit weight of water was set at 165 kg/m³ (a water/powder ratio of 30 mass percent), and the concrete was prepared with a sand aggregate ratio of 48%. Therefore, although the concrete mixes had different unit aggregate weights due to differences in the density of the additives, they can be regarded as having the same mix proportion.

The concrete was mixed in a double-axis forced mixer, with the aggregate, cement, and additive initially mixed without water for 10 seconds, followed by 180 seconds of mixing after the addition of water and SP.

2.3 Test Items and Methods

(1) Compressive Strength

To obtain the compressive strength of the concrete, a specimen measuring ϕ 100 mm x 200 mm was made and tested in accordance with JIS A 1108. For the mortar (sampled by wet-screening), a specimen measuring 40 x 40 x 160 mm was made and tested in accordance with JIS R 5201.

(2) Accelerated Carbonation

After curing in water at 20°C for 28 days, the concrete and mortar specimens were subjected to an accelerated carbonation test in an environment controlled to 30°C, 5% CO₂ content, and relative humidity of 60%. The depth of carbonation was confirmed by spraying a solution of 1% phenolphthalein in alcohol onto the cross section of the specimen.

(3) Pore Size Distribution

A paste specimen containing no aggregates was prepared based on the mix proportion given in **Table-2**, and its pore size distribution was measured using a mercury intrusion porosimeter. In order to avoid segregation, the SP dosage was 0.3 mass percent to the powder. The size of the paste specimen was 20 x 20 x 80 mm, and pieces measuring about 5 mm in size were collected for use in measurements.

(4) Reaction Ratios of Slowly Cooled Blast Furnace Slag Constituents

As shown in **Figure-1**, the main component of CFS is melilite and there is also a trace amount of α -CS. It has been confirmed that there is very little of the glassy phase. In this study, hardened paste specimens are used to carry out a study of the reaction rate of the main constituents of CFS, comparing cases subjected to carbonation with those not subjected to carbonation. The reaction ratios of the two main compounds were calculated by quantifying the unreacted amount of melilite and α -CS using the internal standard method of powder x-ray diffraction [4].

(5) Absorption of Carbon Dioxide

The amount of absorbed carbon dioxide in fully carbonated specimens of hardened paste was examined (after 12 weeks of carbonation). This is based on the assumption that, prior to carbonation, hardened paste contains no absorbed carbon dioxide. The amount of absorbed carbon dioxide was obtained by quantifying the total carbon in the hardened paste using a total carbon analyzer (for inorganic carbon), and converting this into a quantity of carbon dioxide.

It is expressed as a mass ratio (mass %) to the amount of unreacted powder (powder before hydration). This method is chosen because the amount of combined water in the hydrated hardened paste varies with the type and age of the additive, thus making quantitative comparison difficult.

However, for the paste containing LSP, the amount of carbon dioxide contained in the LSP was adjusted. For the paste containing CFS, the mass of the unreacted portion of powder in the hardened paste after carbonation was obtained by measuring the loss on ignition (LOI), whereas for the paste containing LSP the CO₂ content of the LSP was added to the LOI.

The total mass of the hardened paste was considered to be the sum of the masses of the unreacted powders and the absorbed carbon dioxide. The relationship between LOI, combined water, and carbon dioxide is expressed by Equation (1).

$$\text{LOI} = \text{combined water} + \text{carbon dioxide} \quad (1)$$

Of the quantity of carbon dioxide appearing in Equation (1), the amount originally contained in the LSP can be back-calculated from the mix proportion. Therefore, the amount of absorbed carbon dioxide is calculated from the LOI, and the total carbon dioxide is then obtained from the total carbon analysis.

3. RESULTS AND DISCUSSION

3.1 Compressive Strength

Figure-2 shows the compressive strength of the various types of highly fluid concrete (HFC) [3]. The HFCs containing CFS and LSP both exhibit a strength of approximately 60 N/mm² at the age of 28 days, and 65 N/mm² at the age of 56 days, so the rate of strength development is approximately the same. LSP acts as a nucleus for hydration, and promotes reaction of the alite contained in the cement [5]. It also reacts with the aluminate phase.

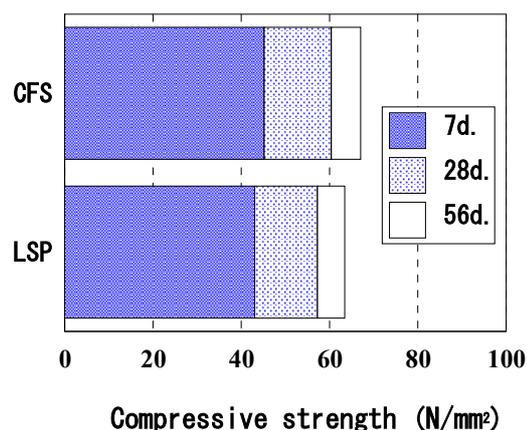


Figure-2 Compressive strength of highly fluid concrete

However, the reaction rate is low, so it can be regarded as an inert inorganic powder from the viewpoint of long-term strength development. This similar strength development exhibited by concretes containing LSP and CFS indicates that CFS can be regarded as an inert inorganic powder similar to LSP [6]. It has previously been reported that adiabatic temperature rise and autogenous shrinkage behavior are similar, and these closely relate to compressive strength development [3].

3.2 Accelerated Carbonation

Figure-3 shows the depth of carbonation resulting from the accelerated carbonation test. HFC containing CFS is apparently more resistant to carbonation than similar concrete containing LSP. In general, it is known that concrete carbonation, regardless of cement type and mix proportion, is ordered by compressive strength at the start of carbonation [7]. However, as shown in Table-2, HFC containing CFS and that containing LSP exhibited approximately the same strength development despite significantly different degrees of carbonation.

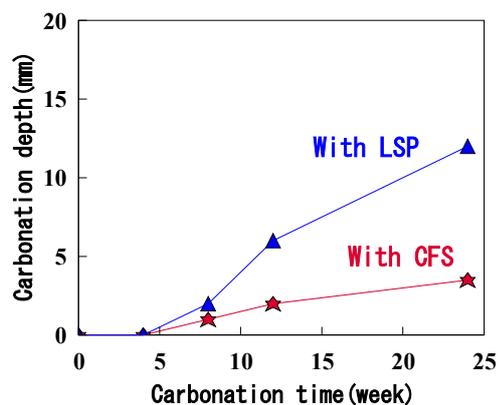


Figure-3 Carbonation depth of highly fluid concrete

Given that these two concrete mixes had the same unit cement weight, the same unit water content, and the same amount of powder additive, it can be inferred that the type of additive had a significant influence on the carbonation process. In order to clarify the reason for this, the development of strength as carbonation takes place was investigated. The authors have previously shown that the degree of carbonation expressed as a ratio of carbonated area to total sectional area of a specimen correlates with compressive strength [8]. Here, using mortar obtained by wet-screening various HFC mixes, the relationship between strength development and degree of carbonation during the carbonation process is examined.

Figure-4 shows this relationship between degree of carbonation and compressive strength. In order to evaluate the effect of carbonation only, it is necessary to eliminate the contribution of time to compressive strength development. In the figure,

the strength level of the specimen cured for the same maturity as the carbonation period of 24 weeks.

The figure indicates good correlation between the degree of carbonation and compressive strength, with compressive strength increasing as the carbonation proceeds. However, looking at the effect of additive type, mortar with added CFS has greater compressive strength at a given degree of carbonation than mortar containing LSP. This contrasts with the specimens not subjected to carbonation and cured for the same period, where the two strengths are not significantly different. This demonstrates clearly that the strength increase caused by carbonation is significant in the system with CFS. Referring back to **Figure-3**, it is inferred that the reason for the system containing CFS being more resistant to carbonation is the greater strength development promoted by carbonation, which in turn leads to further carbonation being hindered.

3.3 Pore Size Distribution

Figure-5 shows the relationship between total pore volume and pore size for pastes containing the two powder additives. **Figure-5(a)** shows the results for specimens continuously cured in water and not carbonated, while **Figure-5(b)** represents samples after 12 weeks of accelerated carbonation. At this age, paste specimens containing both CFS and LSP, and measuring 20 x 20 x 80 mm in size, were fully carbonated. The water-cured specimens were immersed in water for the same period in order to eliminate the effect of elapsed time. These figures demonstrate that there is no difference in the relationship between total pore volume and pore size for the two hardened pastes when cured in water. This coincides with the compressive strength results shown in **Figure-2**. On the other hand, in the case of the completely carbonated hardened pastes, the paste containing CFS has a smaller total pore volume than the paste containing LSP. This backs up the above inference that the microstructure of the system containing CFS is denser than the LSP system after carbonation begins, and that this denser structure hinders further carbonation.

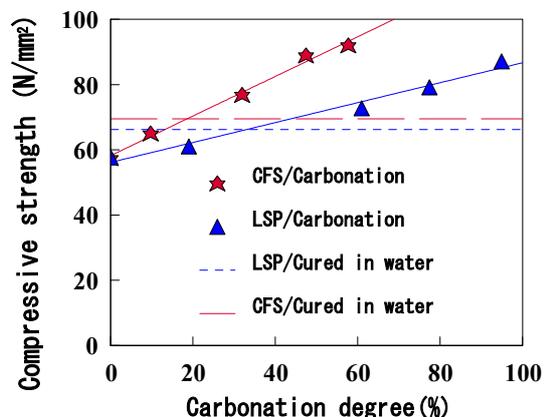


Figure-4 Relationship between carbonation degree and compressive strength

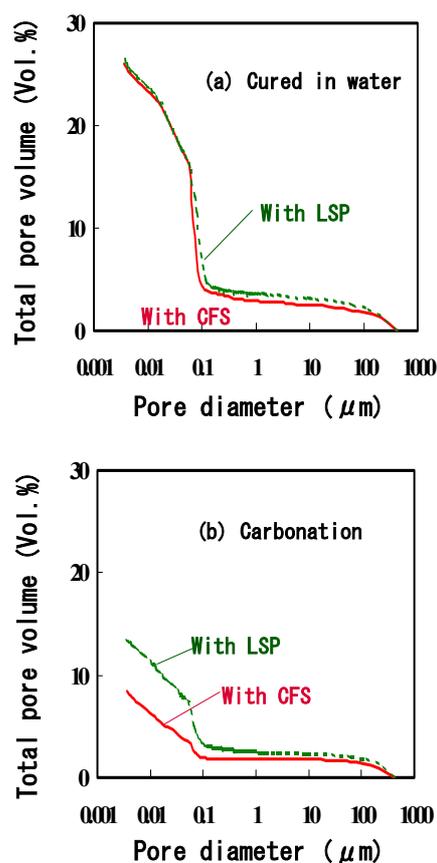


Figure-5 Relationship between total pore volume and pore size

3.4 Reaction Ratios of Slowly Cooled Blast Furnace Slag Constituents

Figure-6 and **Figure-7** show the reaction rates of the melilite and the α -CS, respectively, for carbonated specimens and, for comparison, continuously water-cured specimen. Since the maturation period was the same for both carbonated specimens and non-carbonated specimens, the effect of elapsed time in the hydration process can be ignored. Although the melilite reacted little in the case with no carbonation, about 14% of it took part in the reaction in the carbonated case. For the α -CS, about 26% of it underwent reaction in the non-carbonated case, but the figure was 100% in the case with carbonation. This signifies that melilite and α -CS, the main components of CFS, are reactive under carbonation conditions.

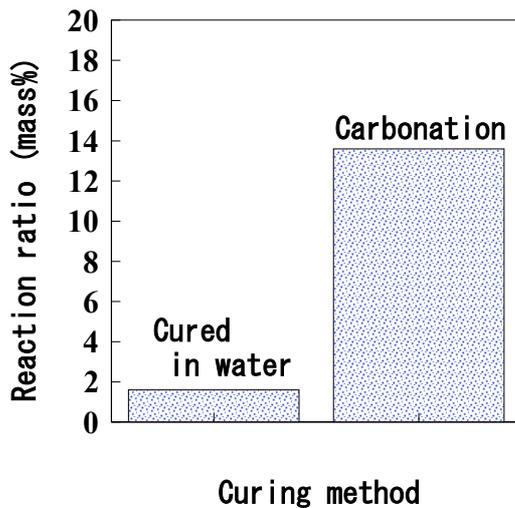


Figure-6 Reaction ratio of melilite

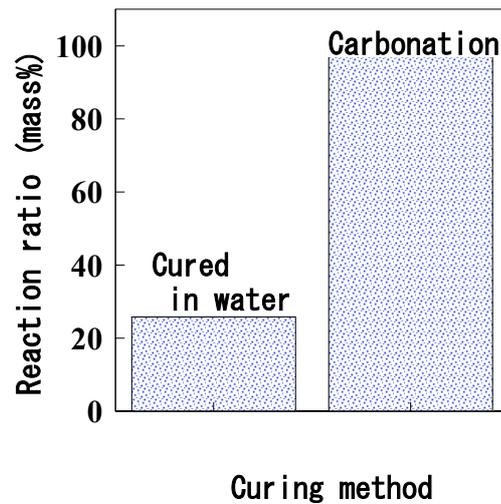


Figure-7 Reaction ratio of α -CS

This provides an explanation as to why HFC containing CFS is not easily carbonated; the main components of the CFS, melilite and α -CS, react under the carbonation condition, causing densification of the microstructure and a strength increase, which in turn hinder further carbonation.

3.5 Amount of Absorbed Carbon Dioxide

Figure-8 compares the amounts of carbon dioxide absorbed by completely carbonated hardened pastes containing LSP and CFS. The paste containing CFS contains more absorbed carbon dioxide than the paste with LSP. This is further evidence that LSP does not carbonate because its main constituent is calcium carbonate, whereas CSF reacts with carbon dioxide. There are two types of reaction that might be taking place with the CFS. One is where the CFS itself reacts with carbon dioxide, and the other is where CFS exhibits a hydraulic property under carbonation conditions, forming hydration products that then react with the carbon dioxide.

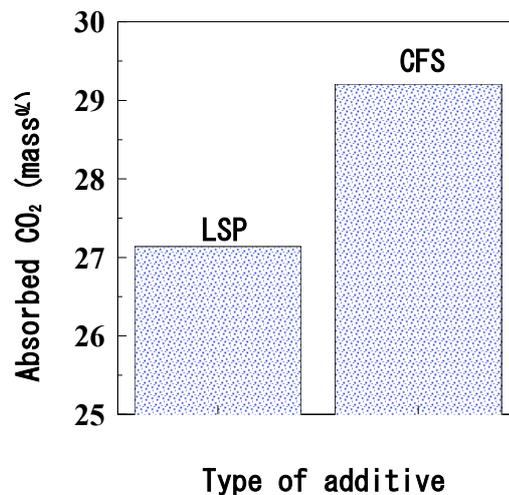


Figure-8 Absorbed CO₂

An example of the former can be found in a report stating that formed γ -C₂S, which does not exhibit a hydraulic property, hardens due to carbonation [9]. As for the latter, it is known that hydration of the belite in low-heat portland cement is accelerated by carbonation curing [10]. To investigate which phenomenon is involved in the chemical reaction of melilite under carbonation conditions, further research will be necessary.

4. CONCLUSIONS

The process of carbonation and its mechanism has been investigated for highly fluid concrete (HFC) containing slowly cooled blast furnace slag powder. The following conclusions have been reached on the basis of the results:

- 1) HFC containing slowly cooled blast furnace slag powder is more resistant to carbonation than HFC of the same mix proportion and similar strength containing limestone powder.
- 2) HFC containing slowly cooled blast furnace slag powder exhibits a greater increase in strength as carbonation proceeds than HFC containing limestone powder with the same mix proportion.
- 3) Melilite and α -CS, which are the main components of the slowly cooled blast furnace slag, react by carbonation to form a denser microstructure that hinders further carbonation. A larger quantity of carbon dioxide is absorbed than by the system containing limestone powder.

These experimental results demonstrate that slowly cooled blast furnace slag acts as an inert inorganic powder similar to limestone powder until carbonation starts. Thereafter, it behaves as a reactive material that might be regarded as an “intelligent” material. Its carbon dioxide absorption capacity turns out to be excellent. Future investigations will look into the effects of various characteristics such as chemical composition, fineness, and glassification ratio.

Meanwhile, the authors have already proposed cement containing a large proportion of slowly cooled blast furnace slag powder [11]. This cement has been designed to have properties equivalent to those of cement containing a large amount of limestone powder. Cement containing limestone is closely related to the globalization of the cement design codes, and the proposed cement is equivalent to cement of strength class 32.5 N/mm². When preparing the mix design for a concrete with low design strength, the unit powder content can be maintained and resistance to segregation added independently by adding limestone.

Further, this can be regarded as low environmental impact cement. However, since limestone is a limited natural resource, it is considered necessary to establish technology for more environmentally friendly cement with equivalent performance obtained using an alternative inorganic powder with lower environmental impact. The authors will continue to study the effective use of slowly cooled blast furnace slag powder, not limiting their purview to highly fluid concrete, but also looking at a broader perspective.

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