JOURNAL OF MATERIALS & CONSTRUCTION

Journal of Materials and Construction
ISSN 2734-9438
Website: www. jomc.vn

Effect of gypsum content on some properties of blast furnace slag cement

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KEYWORDS

Blast furnace slag
Gypsum
Blast furnace slag cement
Content
Properties

ABSTRACT

The objective of the study is to evaluate the influence of gypsum content on certain properties of blast furnace slag cement (with 40% blast furnace slag) at gypsum levels ranging from 2% to 5%. The properties of the cement investigated include water of consistency, initial and final setting times, compressive strength at ages of 1, 3, 7, and 28 days, and heat of hydration of the cement paste within the first 24 hours. Experimental results indicate that increasing the gypsum content has minimal impact on the water of consistency but prolongs the setting time, while still meeting the technical requirements according to TCVN 6260:2020. The optimal gypsum content, in terms of strength, for blast furnace slag cement is 4%, providing compressive strength comparable to the control sample of ordinary Portland cement at 3 and 28 days of age.

1. Introduction

Blast furnce slag (BFS) is a byproduct of the steelmaking industry. It is the liquid slag formed during the iron reduction process in blast furnaces, which is rapidly cooled with water to create granular particles resembling sand [1]. BFS mainly exists in the glassy phase (≥95%). Its major chemical composition includes SiO_2, Al_2O_3, and CaO.

BFS is commonly used in the production of blended Portland cement. When finely ground BFS is mixed with Portland cement, its pozzolanic activity is activated by the calcium hydroxide (CH) produced during the hydration process of Portland cement [2, 3]. BFS can enhance several important properties of cement. It reduces heat of hydration due to its dilution effect [4]. Additionally, it can improve long-term compressive strength and durability by increasing the content of C-S-H gel and densifying the cementitious matrix [4, 5]. However, a significant drawback of BFS is that it may reduce early compressive strength, especially at high replacement levels [4].

The influence of slag on cement properties depends on the characteristics of the slag and the usage level. Douglas et al. reported significant differences in heat of hydration and compressive strength when comparing cement using slag from Canada and the US [6]. Finer slag particles exhibit higher activity and greater cement compressive strength [2, 7, 8]. Increasing the slag content reduces heat of hydration and compressive strength at ages of 1, 3, 7, and 28 days [4].

Gypsum is an essential component of both ordinary Portland cement and blended Portland cement. It prolongs the setting time by reacting with C_3A, forming ettringite on the surface of cement particles, thus slowing down the hydration process of C_3A [9]. Using an appropriate amount of gypsum can enhance early compressive strength due to the hydration reaction that produces ettringite [10, 11]. In cement containing BFS, in addition to its hydration reaction with C_3A in clinker, gypsum also reacts with $Al(OH)^{4+}$ and Ca^{2+} ions released from the slag, resulting in the formation of ettringite. This additional reaction may contribute to improving early strength [12]. However, excessive use of gypsum can lead to reduced strength both in the early and late stages due to the formation of delayed ettringite, which can cause expansion and cracking in the hardened cement matrix structure [10, 11]. Therefore, determining the optimal gypsum content is crucial. Currently, there is no published research in Vietnam specifically addressing this issue related to BFS cement.

Therefore, this study will assess the influence of gypsum content on certain properties of BFS cement at gypsum levels ranging from 2% to 5%. Based on this evaluation, the optimal gypsum content will be determined. The properties of the cement under investigation include water of consistency, setting time, compressive strength at ages of 1, 3, 7, and 28 days, and heat of hydration of the cement paste.

2. Materials and experimental procedure

2.1. Materials

The clinker used in this study is domestically produced industrial clinker, with its chemical and mineral composition presented in Tables 1 and 2. The gypsum used is natural gypsum, and its chemical composition is shown in Table 3. The chemical composition of BFS is given in Table 4.

Table 1. Chemical composition of clinker.

Oxides	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O+Na_2O
Ratio (%)	22.20	5.36	3.52	66.19	0.64	0.19	0.82

Table 2. Minerals composition of clinker.

Minerals	C_3S	C_2S	C_3A	C_4AF
Ratio (%)	59.4	18.9	8.6	10.1

Table 3. Chemical composition of gypsum.

Component	SO_3	$CaSO_4.2H_2O$	H_2O liên kết	Cặn không tan
Ratio (%)	45.63	90.20	18.88	1.98

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Received 05/06/2024, Revised 10/09/2024, Accepted 16/109/2024
Link DOI: https://doi.org/10.54772/jomc.v14i02.730

Table 4. Chemical composition of BFS.

Oxides	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	MKN	CKT
Ratio (%)	34.22	14.91	2.00	37.43	5.34	-	0.02	0.95

2.2. Experimental procedure

The cement samples were prepared as follows. The clinker and gypsum were separately crushed using a jaw crusher to a size smaller than 5 mm. The reference Portland cement sample (PC) was prepared by weighing the appropriate amounts of clinker and gypsum in a ratio of 95% clinker to 5% gypsum. This mixture was then placed in a laboratory ball mill and ground until it reached a Blaine fineness of (3500 ± 50) cm^2/g (determined according to TCVN 4030:2003 [13]). The BFS cement samples were prepared in two steps as follows:

- Step 1: The original Portland cements with the ratios of clinker and gypsum given in Table 5 were ground to the Blaine fineness of (3500 ± 50) cm^2/g. The slag was separately ground to the Blaine fineness of (5000 ± 50) cm^2/g.
- Step 2: The ground original Portland cements and BFS were mixed in a 60:40 ratio to create BFS cement samples with the gypsum content (based on total cement mass) of 2%, 3%, 4%, and 5%, respectively.

Table 5. Composition of original Porland cements.

No.	Clinker (%)	Gypsum (%)
1	96.67	3.33
2	95.00	5.00
3	93.33	6.67
4	91.67	8.33

The water of consistency and setting time of the cement samples were determined according to TCVN 6017:2011 [14]. The compressive strength of the cement mortar samples is determined following TCVN 6016:2011 [15].

The heat of hydration was determined as follows. 250g of each cement sample was mixed with its water of consistency in a mixer for 2.5 minutes (at the slow speed). The cement pastes were filled into cylindrical plastic cups (with dimensions of Ø5 cm x 4 cm). The cups were put into insulated foam boxes and temperature probes were inserted into the center of the cement pastes. The temperature recording process was automated, with measurements taken every 30 seconds over a 24-hour period.

3. Results and discussion

3.1. Water of consistency

The experimental results for determining the water of constency of the cement samples are shown in Figures 1.

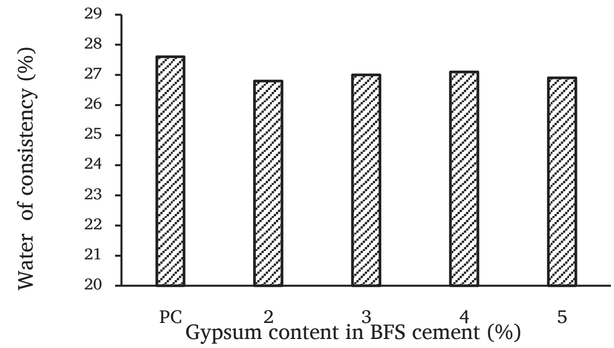


Figure 1. Water of consistency of cement samples.

The results in Figure 1 show that all BFS cement samples have lower values of water of consistency compared to the reference Portland cement sample. The water of consistency of BFS cement samples varies insignificantly, remaining approximately 27% as the gypsum content increases from 2% to 5%. This can be explained by the fact that the majority of water in cement paste is provided for lubricating the surface of cement particles, while a smaller portion is consumed for hydration reactions and lubricating the surface of hydrated products [16]. Although the gypsum content varies, the Blaine fineness of the cement samples remains approximately equivalent, at (4100 ± 50) cm^2/g. Therefore, their water of consistency does not exhibit significant differences.

3.2. Setting time

The experimental results for determining the initial setting time and final setting time of the cement samples are shown in Figures 2.

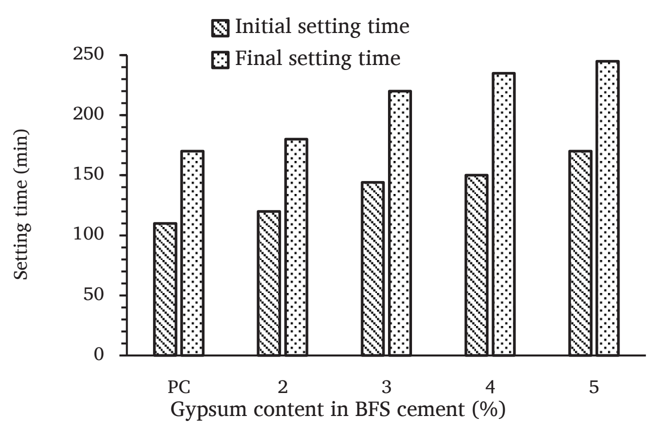


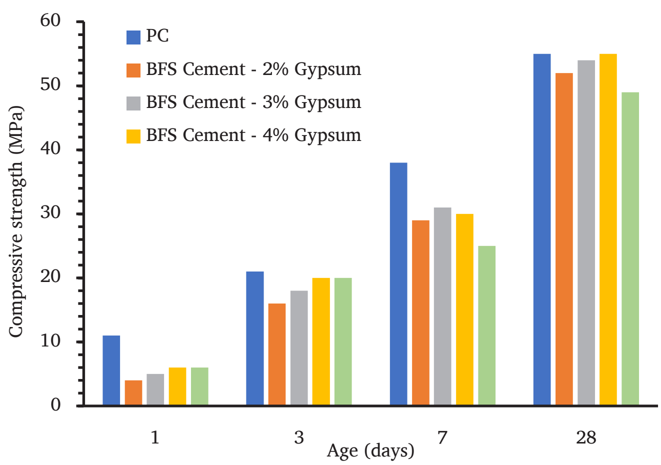
Figure 2. Setting time of cement samples.

Figure 2 reveals that all BFS cement samples exhibit longer setting times than the reference Portland cement sample. Samples with higher gypsum contents have longer initial setting time and final setting time. As the gypsum content increases from 2% to 5%, initial setting time increases from 120 minutes to 170 minutes, while final setting time increases from 180 minutes to 245 minutes. This demonstrates that gypsum contributes to prolonging the setting time of cement. After mixing cement with water, gypsum rapidly reacts with C_3A, producing ettringite. Ettringite crystals adhere to the surface of cement particles, forming a protective layer that reduces water permiablity, thus extending the setting time of cement [9].

Figure 2 also shows that the initial and final setting times of the slag-containing samples comply with TCVN 6260:2020, with initial setting time greater than 45 minutes and final setting time less than 375 minutes [17].

3.3. Compressive strength

The experimental results for determining the compressive strength of the cement samples are shown in Figure 3.



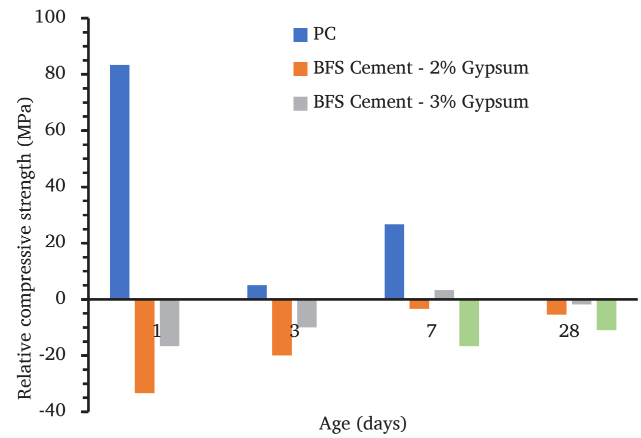
Hình 3. Compressive strength of cement samples.

Figure 3 shows that when varying the gypsum content from 2% to 5%, the compressive strength of the BFS cement samples with 4% gypsum reaches a maximum value at all investigated ages. This indicates that 4% gypsum content is the optimal level. This BFS cement sample exhibits compressive strengths at 3 and 28 days that are nearly equivalent to those of the reference Portland cement sample.

Figure 4 shows the difference in strength between the BFS cement containing 4% gypsum and the samples with 2%, 3%, 5% gypsum and the reference Portland cement sample.

The compressive strength of BFS cement samples increases as the gypsum content increases up to 4%. The compressive strength at 1 and 3 days is improved at a greater extent than at 7 and 28 days. This phenomenon occurs because gypsum reacts with C_3A from clinker and $Al(OH)^{4+}$ and Ca^{2+} ions leached from the slag, resulting in the formation of ettringite [12].

When increasing the gypsum content from 4% to 5%, the strength of BFS cement remains unchanged at 1 and 3 days but significantly decreases at 7 and 28 days. This indicates that an excessive amount of gypsum negatively affects the strength of BFS cement. According to Leklou et al, the main cause of this phenomenon is the formation of delayed ettringite, a form of sulfate attack with cement [18]. The delayed ettringite crystals increase the volume of the cement paste, leading to stress-induced cracking in the cement matrix structure and resulting in reduced strength of the sample.



Hình 4. Difference in strength between the BFS cement containing 4% gypsum and the samples with 2%, 3%, 5% gypsum and the reference Portland cement sample.

3.4. Hydration heat curves of cement pastes

Figure 5 shows temperature variation of cement pastes during the first 24 hours of hydration.

In BFS cement samples, increasing the gypsum content prolongs the induction period, reduces the slope of the acceleration period, and shifts the position of the highest peak to a later time. This phenomenon occurs because gypsum reacts with C_3A in clinker, forming ettringite and slowing down the hydration process of C_3A. Increasing the gypsum content also delays the moment at which gypsum is exhausted and ettringite transforms to monosulfate. These results align with the findings related to setting time, where higher gypsum content leads to longer setting times.

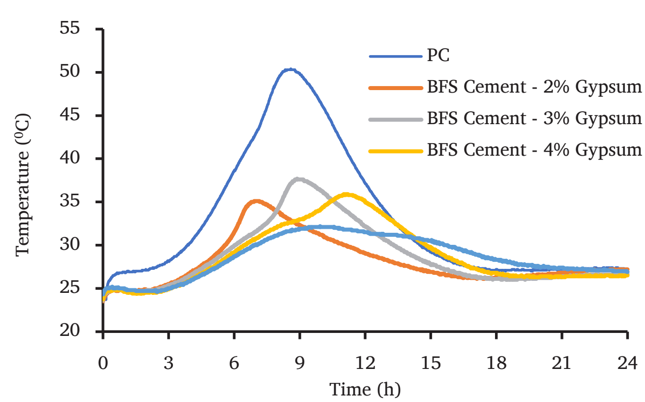


Figure 5. Temperature variation of cement pastes during the first 24 hours of hydration.

4. Conclusion

Based on the research results of the control Portland cement samples and BFS cement samples (with 40% slag) containing varying gypsum content from 2% to 5%, we can draw the following conclusions:

- When increasing the slag content in BFS cement while keeping the Blaine fineness constant, the water of consistency does not significantly change.

- Increasing the slag content prolongs the setting time of BFS cement. When increasing the slag content from 2% to 5%, the initial setting time increases from 120 minutes to 170 minutes, and the final setting time increases from 180 minutes to 245 minutes, while still meeting the requirements of TCVN 6260:2020.

- The optimal gypsum content added to BFS cement is 4%, resulting in higher compressive strength at all researched ages. At this gypsum level, the BFS cement has compressive strengths at 3 and 28 days approximately equal to those of the reference Portland cement.

References

[1]. Chen W. (2007). Hydration of slag cement: theory, modeling and application. *University of Twente*, The Netherlands.

[2]. Escalantea J. I., Gomez L. Y., Johal K. K., Mendoza G., Mancha H., Mendez J. (2001). Reactivity of blast-furnace slag in Portland cement blends hydrated under different conditions. *Cement and Concrete Research*, Elsevier, 31:1403–1409.

[3]. Darquennes A., Espion B., Staquet S. (2013). How to assess the hydration of slag cement concretes. *Construction and Building Materials*, Elsevier, 40:1012–1020.

[4]. Tao J., Wei X. (2019). Effect of ground granulated blast-furnace slag on the hydration and properties of cement paste. *Advances in Cement Research*, ICE publishing, 31(6):251-260.

[5]. Siddique R., Khan M. I. (2011). *Supplementary Cementing Materials*. Springer.

[6]. Douglas E., Elola A., Malhotra V. M. (1990). Characterisation of ground granulated blast furnace slag and fly ashes and their hydration in Portland cement blends. *Cement Concrete and Aggregates*, CCAGDP, 12(2):38–46.

[7]. Pal S.C., Mukherjee A., Pathak S. R. (2003). Investigation of hydraulic activity of ground granulated blast furnace slag in concrete. *Cement and Concrete Research*, Elsevier, 33:1481–1486.

[8]. Wang P. Z., Trettin R., Rudert V. (2005) Effect of fineness and particle size distribution of granulated blast-furnace slag on the hydraulic reactivity in cement systems. *Advances in Cement Research*, ICE publishing, 17(4):161–166.

[9]. Taylor, H.F.W. (1997). *Cement Chemistry*. Second Edition. Thomas Telford Publishing, London.

[10]. Nguyen D. D., Nguyen H. N. (2021). Nghiên cứu sử dụng thạch cao phế thải công nghiệp gốm sứ làm phụ gia sản xuất xi măng Pooc lăng. *Tạp chí Vật liệu và xây dựng*, Viện vật liệu xây dựng, 3:9-13.

[11]. Mohammed, S., Safiullah, O. (2018). Optimization of the SO_3 content of an Algerian Porland cement, *Construction and Building Materials*, Elsevier, 164: 362-370.

[12]. Odler I. (2000). *Special Inorganic Cements*. E & FN Spon, New York, USA.

[13]. TCVN 4030:2003. *Xi măng – Phương pháp xác định độ mịn*. Bộ Khoa học và Công nghệ, Việt Nam.

[14]. TCVN 6017:2011. *Xi măng – Phương pháp xác định thời gian đông kết và độ ổn định thể tích.* Bộ Khoa học và Công nghệ, Việt Nam.

[15]. TCVN 6016:2011. *Xi măng – Phương pháp thử - Xác định cường độ*. Bộ Khoa học và Công nghệ, Việt Nam.

[16]. Schiller, B., Ellerbrock, H.G. (1992). The grinding and properties of cement with several main constituents, *Zement-Kalk-Gips*, 45(7):325-334.

[17]. TCVN 6260:2020. *Xi măng Poóc lăng hỗn hợp*. Bộ Khoa học và Công nghệ, Việt Nam.

[18]. Leklou, N., Nguyen, V. H., Mounanga, P. (2017). The effect of the partial cement substitution with fly ash on delayed ettringite formation in heat-cured mortars. *KSCE Journal of Civil and Engineering*, Springer, 21:1359–1366.