

Properties of cementless binders using desulfurization slag as an alkali activator

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The alkali stimulus provided by the Ca(OH)_2 contained in desulfurization slag (DS), a byproduct generated in the preliminary treatment of molten iron and composed of Ca(OH)_2 , CaCO_3 , and $2\text{CaO}\cdot\text{SiO}_2$, is used to cause a cement-free binder to harden by serving as an alkali activator for ground, granulated blast-furnace slag (BFS). The 28-day compressive strength of the BFS-DS binder was found to be about 30% that of ordinary Portland cement (OPC), but the 28-day strength of a binder made from BFS, DS, and anhydrous gypsum (G) was found to be similar to that of OPC. It is confirmed that BFS-DS-G binders have very low hydration heat, which is of use in reducing the heat generated during the curing of mass concrete. The main hydration product of the BFS-DS-G binder is found to be ettringite. Scanning electron microscope images reveal that the needle-shaped ettringite formed in the BFS-DS-G binder is much thicker than that formed in OPC. This thick, needle-shaped ettringite forms a skeletal structure, providing structural stability, and fills the gaps between hydration products such as calcium silicate hydrates and calcium aluminum hydrates, making it highly effective in forming a dense structure. The widespread use of BFS-DS-G binders would result in the value-added utilization of byproducts from the iron & steel making process, and provide an environmentally friendly and more economical construction material, and contribute to a reduction in CO_2 emissions generated by the cement industry.

Key words: Slag cement, Cementless binder, Desulfurization slag, Ettringite.

Introduction

Approximately 800 kg of CO_2 is generated in the manufacture of one ton of ordinary Portland cement (OPC) [1, 2]. On a unit weight basis, the enormous volume of cement produced is responsible for approximately 5% of global anthropogenic CO_2 production [3]. As environmental sustainability becomes a greater priority, solutions are being sought to reduce both the CO_2 emissions and energy burden of cement production without sacrificing its economic viability. As part of efforts to reduce CO_2 emissions generated during cement production, ongoing research has examined the use of industrial byproducts [4-6].

In particular, cementless binders using an alkali activator such as Na (in the form of NaOH , NaCO_3 , Na_2SiO_3 , etc.) have been actively studied [7-11]. These Na-based activators contribute to the effective development of high strengths in the binder by generating a high concentration of hydroxide ions (OH^-) [12, 13]. However, Na-based activators have some disadvantages, such as decreased workability due to quick setting time, high cost, high toxicity (with a pH of 14 or higher), and

expansion characteristics resulting from reactions between alkali-silica and reactive aggregates [14-17].

In response to these disadvantages, the research reported in this paper is focused on finding a new alkali activator. To this end, a Ca-based alkali activator was considered capable of resolving the aforementioned shortcomings of Na-based activators. In particular, from the perspective of the effective utilization of industrial byproducts, attention was paid to iron and steel slag (which both contains calcium) generated in the process of making steel. One such industrial byproduct containing abundant calcium is blast furnace slag (BFS). However, amorphous BFS does not have the characteristics of an alkali activator. Another byproduct generated by the iron and steel making process is desulfurization slag (DS), which is generated in the preliminary treatment process of molten iron. During this process, mechanical stirring is performed after the introduction of an additive such as calcium oxide. As such, DS is abundant in calcium oxide, and once it is cooled by means of water spraying, a considerable amount of this calcium oxide is turned into calcium hydroxide [8, 12, 13].

Coated with a glass-state film, BFS has a low reactivity. However, if BFS is exposed to a high-pH environment, the glass-state film is destroyed, calcium, silicon, and aluminum ions are eluted from within the BFS, and subsequently hydrates such as calcium

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silicate hydrates (C-S-H) and calcium aluminum hydrates (C-A-H) are formed. Hydroxide ions (OH⁻) are required in order to create the high pH environment that serves as a trigger for the chemically stable BFS to become reactive [18-22]. Notably, DS, which contains a large amount of calcium hydroxide, can be used to generate hydroxide ions upon its reaction with water, allowing its application in the hardening of a BFS-based binder, implying that DS can serve that function of an alkali activator. Accordingly, in this research, BFS-based cement-free binders were manufactured utilizing DS as an alkali activator. Analyses of heat evolution, scanning electron microscopy (SEM), X-ray diffraction (XRD), thermal gravity/differential thermal analysis (TG/DTA), and compressive strength tests were performed in order to investigate the chemical and physical properties of the cement-free binder made using BFS and DS.

Materials and test Methods

The BFS, anhydrous gypsum (G), and OPC materials used in this research had Blaine fineness values of 430 m²/kg, 450 m²/kg, and 340 m²/kg, respectively. The DS used was a non-magnetic slag collected through repeated processes of drying, crushing, and magnetic separation. The Blaine fineness of the DS powder was about 400 m²/kg. The ratio of water:binder was set at 1:2, and the binder, water, and sand were mixed in a ratio of 2:1:6. The BFS-DS binder was mixed in BFS:DS ratios of 95:5, 90:10, 85:15, 80:20, 75:25, and 70:30. Additionally, BFS-DS-G binders were produced by mixing different quantities of gypsum with the = DS samples in BFS:DS:G ratios of 81:10:9, 78:10:12, and 75:10:15. Mixes with 100% OPC (O100) as well as 50% OPC and 50% BFS (O50B50) were also made to provide comparison. Paste specimens for XRD, TG-DTA, and SEM analyses were manufactured with a water:binder ratio of 1:2.

The compressive strength of the resulting mortar was measured in compliance with the procedures of KS L ISO 679 (Korean Standards Association, 2006). A mortar specimen of dimensions 40 × 40 × 160 mm was made using a jolting machine and then water-cured at 20 ± 2 °C. The compressive strength of the specimen was then measured after 3, 7, 28, 56, and 91 days of curing.

The DS powder was subjected to a TG-DTA analysis (Extra 6000, Seiko Instrument Corp.). The temperature was raised from 20 °C to 1100 °C under atmospheric conditions, and the weight loss and exothermic/endothermic calories resulting from the associated thermal decomposition of water and carbon dioxide were evaluated. The hydration heat was measured at 30-s intervals over 7 days using a calorimeter (MMC-511SV6, Tokyo Rico Corp.). Before the test, the binder was placed in the test container for 2 days while the temperature was

maintained at 20 °C. In order to investigate the hydration products, an XRD analysis (D/Max-2500V, Rigaku Corp.) of the paste specimens was performed at 3, 7, and 28 days. Finally, the shape and distribution of hydration products were observed through SEM (S-4300SE, Hitachi Corp.).

Results and Discussion

Material properties

The chemical properties of the test materials can be found in Table 1, which shows their primary components to be calcium oxide, silicon dioxide, aluminum oxide, and iron oxide.

The DS had a significantly lower portion of silicon dioxide and aluminum oxide than the BFS, but contained more calcium oxide and iron oxide. Because the DS is created after the application of a desulfurization additive (calcium oxide) to remove small amounts of sulfur in molten iron, it has high calcium oxide content [23, 24]. Notably, the iron component of DS prior to magnetic selection is approximately 30-40%, which is reduced by recovering the iron through drying, crushing, and magnetic selection, to be reused in the iron and steel making process. However, the composition analysis indicates that a certain amount of iron remained in the DS even though it had already undergone the filtering processes (magnetic separation). Unburned cokes, which are deoxidizers, also exist in molten iron and most of the unburned cokes are mixed with the slag.

Table 1. Chemical compositions of the materials.

	Chemical compositions (%)								
	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	SO ₃	C
OPC	62.2	20.7	6.2	3.10	2.8	0.10	0.8	2.1	–
BFS	43.5	32.8	15.6	0.50	4.41	0.25	0.49	0.04	–
DS	62.2	10.6	1.21	11.	1.5	0.10	–	5.2	4.1
Gypsum	41.6	0.73	0.17	0.16	–	0.02	0.03	55.5	–

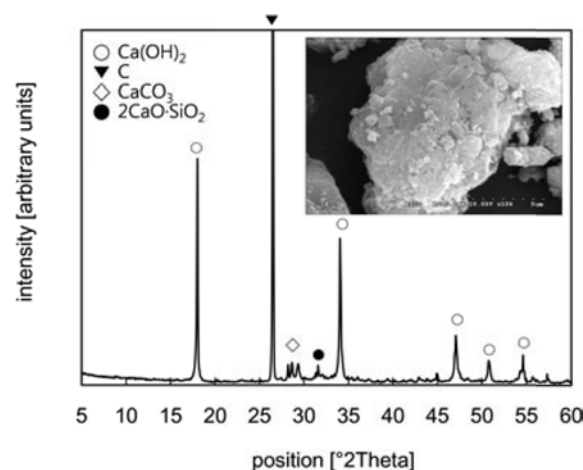


Fig. 1. XRD patterns of DS.

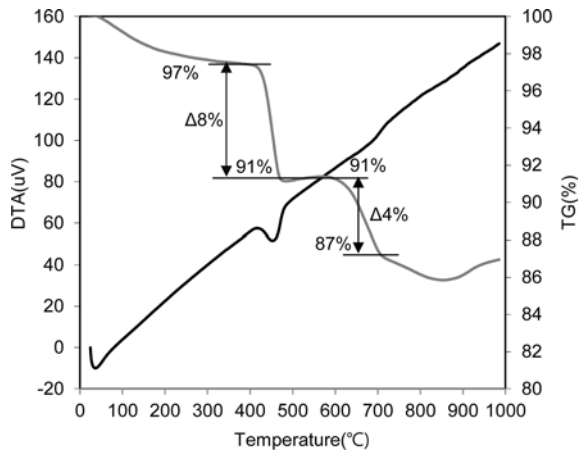


Fig. 2. TG/DTA curves for DS.

Thus DS also contains about 4-5% coke (a carbon component). The most promising attributes of non-magnetic DS are its high calcium oxide content and its feasible use in cement-based materials. Additionally, DS is not only environmentally harmless but also has high calcium oxide content, suggesting that it would be a useful recycled material for producing cement-free binders.

Fig. 1 depicts the XRD patterns of the DS used in this research. Note that calcium oxide was the main component in the DS, but it is turned into calcium hydroxide through its reaction with water. No crystalline peaks of calcium oxide were found in the XRD analysis, but a crystal peak of $2\text{CaO} \cdot \text{SiO}_2$ appeared. It was determined that some of the calcium oxide, added as a deoxidizer, was converted into calcium oxide-silicon dioxide compounds in the reaction, with 10-15% silicon dioxide existing in the slag.

Fig. 2 provides the TG/DTA results for the DS used in this research. The deep dip in the DTA line in the section between 450 and 500 °C indicates that there is an endothermic reaction caused by the decomposition of calcium hydroxide. Additionally, the TG line shows a steep slope in the section between 450 and 500 °C, which indicates weight loss due to the dehydration of calcium hydroxide. Knowing the weight loss rate, it is possible to quantitatively evaluate the content of calcium hydroxide. The weight loss rate can be calculated using the start and end points of the dehydration reaction taken from the TG curve. In order to calculate the amount of calcium hydroxide present in the DG, a conversion factor of 4.11, obtained from the respective molecular weights of calcium hydroxide (74.09 g/mol) and water (18.02 g/mol), was multiplied by the weight loss rate due to dehydration between 450 and 500 °C, as shown by:

$$\text{Calcium hydroxide content} = \text{weight loss rate (6\%)} \times 4.11 = 24.66\% \quad (1)$$

Next, calcium carbonate is decomposed into calcium oxide and carbon dioxide in the 600-800 °C temperature range. The weight loss curve shown in this temperature range is due to the decarbonation of calcium carbonate, so it is also possible to quantitatively evaluate the content of calcium carbonate. In order to obtain the calcium carbonate content, a conversion factor of 2.27, calculated using the respective molecular weights of calcium carbonate (100.09 g/mol) and carbon dioxide (44.01 g/mol), was multiplied by the weight loss rate caused by decarbonation between 600 and 800 °C. The calcium carbonate content in the DS was calculated to be about 9% using Equation (2).

$$\text{Calcium hydroxide content} = \text{weight loss rate (4\%)} \times 2.27 = 9.08\% \quad (2)$$

Analysis of hydration characteristics

Fig. 3 depicts the results of the hydration heat evaluation of the O100, O50B50, and BFS-DS-G binders (proportions B75D10G15, B78D10G12, and B81D10G9).

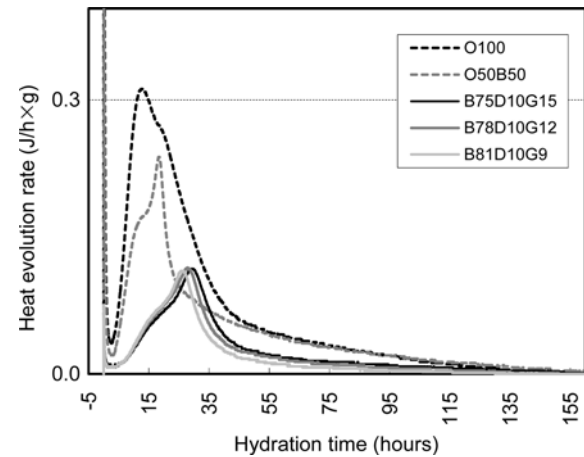


Fig. 3. Heat evolution.

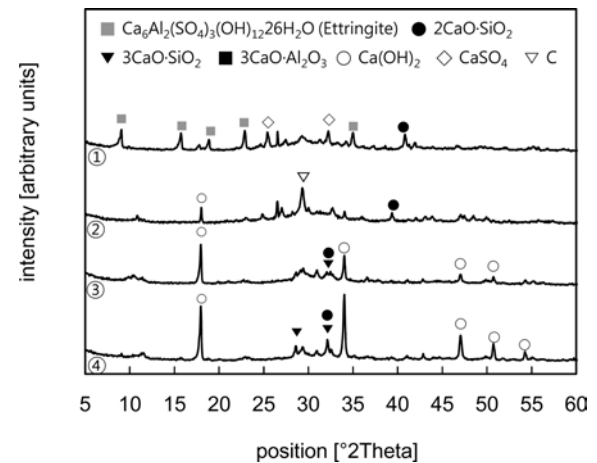
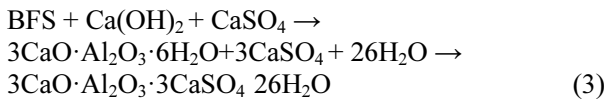


Fig. 4. XRD spectra of ① B75D10G15, ② B80G20, ③ O50B50 and ④ O100.

exothermic reaction resulting from the reaction of water with CaO or $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ [25, 26]. The second heat peak represents the heat of reaction in the C-S-H gel generation process during the reaction of $3\text{CaO} \cdot \text{SiO}_2$ and $2\text{CaO} \cdot \text{SiO}_2$ with water. These hydration heat peaks appeared between 13 and 14 h in O100, and between 18 and 19 h in O50B50. However, the hydration peaks appeared between 26 and 30 h in BFS-DS-G, indicating significantly delayed hydration. Overall, the magnitude of the hydration heat peak was very low in BFS-DS-G when compared with O100 and O50B50. The cumulative heat releases of O100, O50B50, B75D10G15, B78D10G12, and B81D10G9 were 301.4 J/g (100%), 211.7 J/g (70.2%), 109.4 J/g (36.3%), 97.9 J/g (32.5%), and 82.3 J/g (27.3%), respectively. From the facts described above, it is confirmed that BFS-DS-G binders exhibit a very low hydration heat, which is potentially useful in reducing the excessive hydration heat generated during the curing of mass concrete.

Fig. 4 presents the XRD analysis results for the B75D10G15, B80G20, O50B50, and O100 pastes after 28 days of curing. The main hydrates found in the O100 and O50B50 pastes were $\text{Ca}(\text{OH})_2$, $2\text{CaO} \cdot \text{SiO}_2$, and $3\text{CaO} \cdot \text{SiO}_2$. In O50B50, the $\text{Ca}(\text{OH})_2$ peaks appearing near 18° , 34° , 47° , 51° and 54° were lower than those of O100. This may be because the amount of $\text{Ca}(\text{OH})_2$ generated by the OPC was decreasing through a pozzolanic reaction with the BFS. The XRD pattern of B80D20 indicates the presence of calcium hydroxide, graphite, C2S, and low-crystalline C-S-H. This observation was expected, as it can be attributed to the DS acting as an alkali activator, with the formation of hydration products due to its subsequent reaction with the BFS.

On the other hand, the hydration products of BFS-DS-G were considerably different from those of O100 and O50B50, in that the hydrates mainly consisted of ettringite. When the DS and gypsum are added to the BFS, the following reaction occurs [27-29]:



In other words, Ca^{2+} and Al^{3+} eluted from the BFS by the alkaline stimuli of hydroxide ions from the DS ($\text{Ca}(\text{OH})_2$) form C-A-H hydrates ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$), after which ettringite hydrates are formed by the reaction of the C-A-H hydrates and gypsum (CaSO_4).

Compressive strength with binder types

When water is added to a mixture of BFS and DS, hydroxide ions leach from the calcium hydroxide contained in the DS. The glass-state film coating the BFS particles are then destroyed by the alkali stimulation of the eluted ions (OH^- along with Ca^{2+} , Si^{4+} , and Al^{3+}). These ions react with each other,

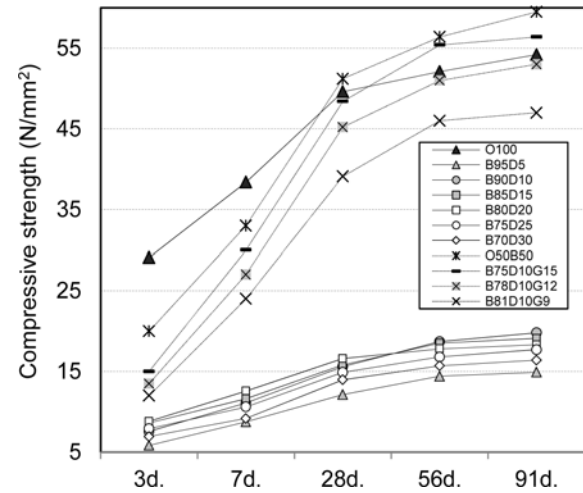


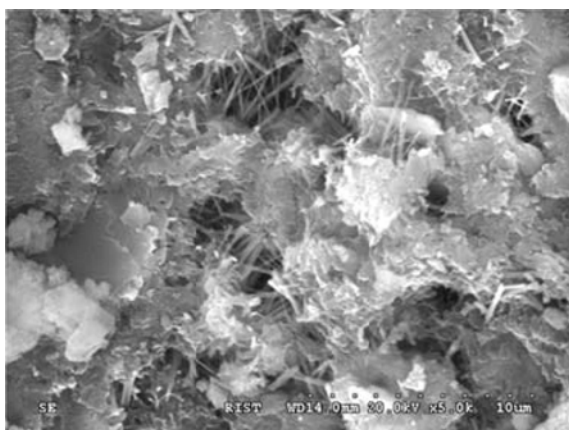
Fig. 5. Compressive strength with binder types.

generating hydration products. Fig. 5 compares the compressive strengths of the mortars made with the BFS-DS-G binder to those of the OPC and the BFS-DS binder without gypsum.

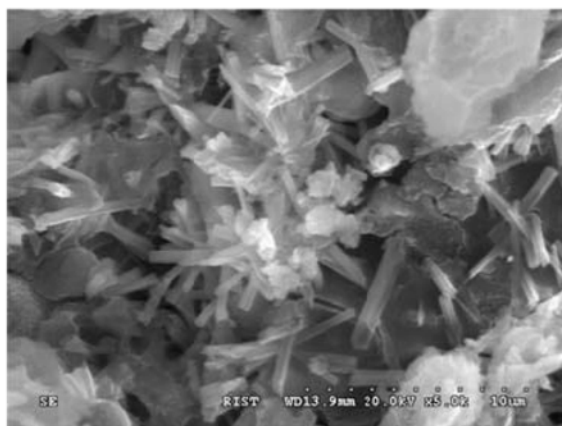
The 28-day strength of the BFS-DS binder with 5%, 10%, 15%, 20%, 25%, and 30% KRS was measured to be 12.1 MPa, 15.6 MPa, 15.8 MPa, 16.6 MPa, 14.9 MPa, and 14.0 MPa, respectively. The 28-day strength of the OPC was determined to be 49.6 MPa, confirming that the compressive strength of the BFS-DS binder mixed with only the DS is much lower than that of O100.

It is known that ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$) is a needle-shaped hydrate that fills the gaps between hydration products, resulting in densification of the binder as well as improved strength [30-31]. With this in mind, gypsum was used to improve the strength performance of the cement-free binder made from BFS and DS. The main component of gypsum is calcium sulfate, which dissolves into calcium and sulfate ions (Ca^{2+} and SO_4^{2-}) when reacting with water. Like hydroxide ions, sulfate ions can also act as alkali activators. Additionally, calcium ions contribute to the formation of hydration products [31]. Calcium sulfate can also make a significant contribution to the generation of ettringite over other C-S-H and C-A-H products.

When the mix proportion of DS was set at 10% (considered to cause no decrease in workability), and the mix percentages of gypsum were set at 9%, 12%, and 15%, the 3-day and 7-day strengths of the BFS-DS-G binder were much lower compared to those of mixes O100 and O50B50. On the other hand, the 28-day strengths of two of the BFS-DS-G binders (48.4 MPa and 45.2 MPa for B75D10G15 and B78D10G12, respectively) were similar to those of O100 (49.6 MPa) and O50B50 (51.2 MPa), with the strength of binder B81D10G9 being lower (39.1 MPa). Notably, the addition of gypsum to the BFS-DS binder can be seen in Fig. 5 to result in an approximately three-fold increase in the binder strength.



(a) O100



(b) B75D10G15

Fig. 6. SEM images.

The 28-day strength of B75D10G15 was 97.6% that of the O100 OPC, and its 56-day strength was found to be 104.3% that of O100. On the other hand, the 28-day and 56-day strengths of B78D10G12 were shown to be about 91.1% and 96% that of the O100 OPC, respectively. The 28-day and 56-day strengths of B81D10G9 were found to be significantly lower at 78.8% and 86.6% those of O100, respectively.

These results indicate that the strength of the BFS-DS-G binder can be equivalent to that of pure OPC or slag cements, and it is anticipated that this combination could serve as a cement-free binder to reduce the environmental impact of the cement manufacturing industry.

SEM image of ettringite

Fig. 6 depicts SEM images of O100 and B75D10G15 pastes at 28 days. Compared with the thin needle-shaped ettringite present in O100, the ettringite in the BFS-DS-G binder has a thicker needle shape. Because ettringite makes the binder structure denser by filling

gaps between hydrates, if there is sufficient ettringite with a comparatively thick needle shape, it can form a sort of skeletal structure that contributes to structural stability, resulting in hardened cement with a high strength. Accordingly, the compressive strength of the BFS-DS-G binder was found to be higher than that of OPC. It is believed that this is due to the structural stability and densification effects of the relatively thicker needles of ettringite.

Conclusions

In this research, it was found that a more economical and environmentally friendly cementless binder could be manufactured using desulfurization slag, which is a byproduct of the steel making process. The findings of this research can be summarized as follows:

1) The DS material contains a great deal of calcium oxide and other components such as silicon dioxide, iron oxide, and carbon in the forms of calcium hydroxide, calcium carbonate, and C_2S . It poses no environmental danger and can be utilized as a useful alkali activator in a cementless binder because of its high calcium hydroxide content.

2) It is confirmed that BFS-DS-G binders have a very low hydration heat, and thus could be utilized to reduce the hydration heat generated during the curing of mass concrete. The hydration products of BFS-DS-G are considerably different from those of O100 and O50B50, in that the main hydrates of BFS-DS-G are ettringite.

3) When DS powder was mixed with only BFS, the alkali stimulus of the calcium hydroxide in the DS caused the cementless binder to harden. However, its 28-day compressive strength was only about 30% of that of OPC.

4) For a BFS-DS-G binder, made with the addition of anhydrous gypsum, the 28-day compressive strength developed to a level comparable to that of OPC. The 28-day strength of a binder made with 75% BFS, 10% DS, and 15% G (B75D10G15) was measured to be 48.4 MPa, similar to that of O100 OPC (49.6 MPa). The 56-day and 91-day strengths were found to be even higher than those of O100.

5) The ettringite formed in OPC was observed have a thin needle shape, while the ettringite in the BFS-DS-G binder was observed to consist of comparatively thicker needles. This thick, needle-shaped ettringite present in the BFS-DS-G binder formed a sort of skeletal structure that likely contributes to improved structural stability.

The use of blast furnace slag, in conjunction with desulfurization slag to provide alkali stimulus and gypsum to form ettringite, holds great promise as a cement-free binder, reducing the cost and environmental impact of cement production and the construction industry as a whole.

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