

Utilizing mineral sequestration technology for enhanced performance of concrete containing basic oxygen furnace slag

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Abstract. Basic oxygen furnace slag (BOFS) is a widely available by-product of the steel-making industry that poses high interest for scientists in various fields. The carbon capture potential of BOFS is proven to be high. However, its further uses are actively investigated. BOFS is particularly attractive as a construction material due to its hydraulic reactivity and good strength, making it suitable for use as binding material and aggregate in concrete. However, it has a major drawback - unstable compounds that lead to material deterioration caused by volumetric expansion. Most of the research in the field focuses on the processing of BOFS in laboratory or industrial settings to eliminate the expensive products inside the slag and make it more durable. The suitability of using mineral sequestration technology instead of artificially accelerated carbonation has not yet been studied well. This research aimed to identify the main properties of the mortar mixes containing BOFS that underwent mineral sequestration over a long period to assess the technology's feasibility. The correlation with quantitative data from thermogravimetric analysis (TGA) was also identified. Based on test results, the correlation between aging conditions and CO₂ uptake was established, indicating that stockpiled and wet/dry cycle conditions were the most optimal aging methods for BOFS to achieve the highest carbonation (4.15-5.15%), hence the maximum stabilization degree of aggregates.

1 Introduction

With a growing demand for steel, a corresponding increase in the production volumes of this material is observed. Over the past 60 years, global steel production has grown dramatically from slightly below 500 million tonnes in 1967 to 1600 million tonnes in 2015 [1]. As waste generation is intrinsic to any industrial process, the steel-making sector produces substantial by-products, such as blast furnace slag, sludge, mill scale, flue dust, ladle slag, and basic oxygen furnace slag (BOFS) [2]. BOFS is a by-product of pig iron processing in a basic oxygen furnace (BOF). The BOF is a converter where an oxygen lance is introduced to initiate oxidation reactions that decrease the carbon content of molten iron. To eliminate

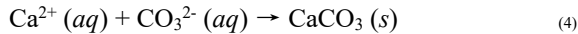
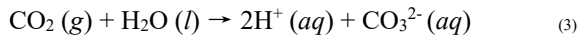
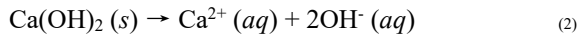
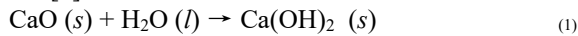
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unwanted chemical elements of the melt, fluxing agents, such as lime (CaO) or dolomite ($\text{MgCa}(\text{CO}_3)_2$), are added to the furnace, leading to the formation of slag [3]. The chemical composition of BOFS is highly determined by the chemical reactions occurring during this process and varies significantly.

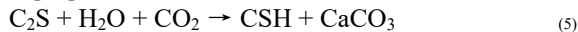
Globally, BOF slag constitutes a major environmental challenge. The steel-making industry contributes to the release of CO_2 , the generation of substantial quantities of waste, and the consumption of energy. Steel production accounts for 5-7% of total anthropogenic CO_2 emissions worldwide [4]. Moreover, based on the raw material, 100-200 kg of BOFS is generated per ton of steel produced [5]. While BOFS finds applications in agriculture and road construction, it is not widely used due to its inherent expansion characteristics. As a result, it is often disposed of in landfills without being utilized [6].

The presence of such unstable compounds as free lime (f-CaO) and free magnesia (f-MgO), which are expansive when undergoing hydration, limits the utilization of BOFS and causes slag disintegration, loss of mechanical properties, crack propagation in concrete, and instability [7, 8]. Furthermore, although the presence of tricalcium silicate (C_3S) and dicalcium silicate (C_2S) in BOFS material could potentially provide cementitious properties to the slag, during the solidification process of BOFS, C_3S is transformed into $\text{C}_2\text{S}+\text{CaO}$ and a crystalline structure is formed [8]. Consequently, BOFS exhibits lower reactivity than ordinary Portland cement (OPC) and becomes more susceptible to expansion.

Mineral sequestration of BOFS is an effective technique for mitigating its expansion behavior and reducing the carbon footprint of the steel-making industry. The primary process involved in mineral sequestration is a series of reactions that convert lime and similar reactive substances into calcium carbonate (CaCO_3), which is a stabilized form that does not contribute to expansion. The reactions describing the carbonation of the BOFS in aqueous medium are as follows [9]:



While f-CaO and f-MgO are considered the main carbonation reactants, other calcium-bearing compounds like calcium silicates also contribute to it, as illustrated by the following unbalanced reactions [10]:



Therefore, BOFS's limitations could be addressed by implementing mineral sequestration technology, allowing them to be utilized as aggregates in concrete production without expansion. Most research in this area concentrates on the accelerated carbonation of BOFS in laboratory or industrial settings, often disregarding the CO_2 sequestration potential by natural carbonation. Hence, there is a growing need to evaluate the CO_2 uptake capacity of BOFS subjected to the natural carbonation process (mineral sequestration technology) and its performance in concrete. The primary objective of this study was to assess the compressive strength and expansion of concrete with BOFS cured with various methods and determine the most optimal curing technique for maximum stabilization degree of the aggregates and mitigation of their expansion behavior in concrete. In addition, the link between thermogravimetric analysis (TGA) of BOFS and concrete properties was established.

2 Experimental Program

2.1 Materials and Mixture Proportion

OPC was used as a binding material to cast mortar specimens for compressive strength and water expansion tests. Siliceous river sand (RS) was used as a reference, and fresh BOFS (f-BOFS) and stockpiled BOFS (s-BOFS) were used as aggregate components. BOFS used in this research was supplied by ArcelorMittal company, located near Temirtau city, Kazakhstan. f-BOFS and s-BOFS are about three months and two years old, respectively. Moreover, f-BOFS were exposed to a natural mineral sequestration process under different conditions: fully submersed water (BOFS W sub) and a wet and dry cycle (BOFS W&D) for six months. While the specific gravity values of RS, f-BOFS, s-BOFS, BOFS W sub, and BOFS W&D are 2.68, 3.47, 3.11, 3.42, and 3.31, respectively, the absorption capacity values of those aggregate are 2.87, 3.24, 3.17, 4.82, and 5.17, respectively. Chemical compositions of OPC, sand, f-BOFS, and s-BOFS are presented in Table 1.

A total of 5 mortar mixtures were developed for this study. A plain reference mortar mixture had RS, but the other four mixtures contained BOFS aggregates under different aging conditions. Table 2 summarizes the mortar mix design.

Table 1. Chemical compositions of cement, sand, fresh and stockpiled BOFS in % by weight

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	SO ₃	MgO	TiO ₂	Na ₂ O	K ₂ O	MnO	ZnO
Cement	17.42	4.36	2.96	69.19	2.61	2.05	0.20	-	0.93	0.12	-
RS	64.46	11.38	4.26	12.01	0.20	1.51	0.37	1.78	3.19	0.45	-
f-BOFS	8.73	1.66	24.82	47.95	1.65	11.26	0.38	0	0.11	1.88	0.82
s-BOFS	7.72	1.69	34.44	47.76	0.30	1.31	0.69	0	0.05	2.82	0.19

Table 2. Mixture proportions of mortar mixtures (kg/m³)

Mixture	Cement	Water	River Sand	f-BOFS	s-BOFS	BOFS-W Sub	BOFS W&D
Plain	615.0	289.1	1378.3	-	-	-	-
f-BOFS	615.0	289.1	-	1785.3	-	-	-
s-BOFS	615.0	289.1	-	-	1604.5	-	-
BOFS W Sub	615.0	289.1	-	-	-	1759.2	-
BOFS W&D	615.0	289.1	-	-	-	-	1712.7

Note: While BOFS W Sub indicates water-submersed BOFS, BOFS W&D indicates BOFS exposed to a wet and dry cycle.

2.2 Test Methods

Testing methods included compressive strength (ASTM C109), water expansion (ASTM C1260), and Thermogravimetry (TG)/differential scanning calorimetry (DSC) analysis to identify carbon dioxide (CO₂) uptake. For TG/DSC test, two different BOFS aggregate size groups were evaluated: the average of all sizes of BOFS (38 mm, 19.0 mm, 12.5 mm, 4.75 mm, 2.36 mm, 1.18 mm, 0.6 mm, 0.15 mm, and 0.075 mm) and the average of small sizes (4.75 mm, 2.36 mm, 1.18 mm, 0.6 mm, and 0.15 mm). Mortar cubes (50 × 50 × 50 mm) prepared for the compressive strength test were cured in water containers up to testing day [11]. In contrast, the mortar bars (25 × 25 × 285 mm) for the expansion analysis were put into water containers and placed in the oven maintained at 80 °C [12].

3 Test Results and Discussions

3.1 Thermogravimetric Analysis (TGA)

TGA was used to identify the mineralogical changes in the composition of BOFS, namely the amount of CO₂ uptake (Table 3). Percent weight loss during the decomposition of carbonates in the 550-900 °C range was used to assess the uptake amount. The results of TGA showed that wet/dry curing is the most effective method with a percent of CO₂ sequestered: 4.15% for all sizes and 5.15% for smaller sizes. Conversely, the least effective curing condition is full submersion in water, achieving only 1.81% of CO₂ for all sizes and 2.22% for smaller ones. Fully dry conditions yielded intermediate results with 2.90% and 3.50% for all sizes and smaller sizes, respectively.

Table 3. TGA results of different BOFS aging conditions (Wt %)

Sieve size	Condition	H ₂ O	Ca(OH) ₂	CO ₂	Max. CO ₂ uptake
Average of all sizes	Fully immersed	1.40	1.08	1.81	
	Fully dry	3.07	2.11	2.90	
	Wet/dry	1.68	1.86	4.15	X
Average of small sizes (#4-#100)	Fully immersed	1.69	1.18	2.22	
	Fully dry	3.44	2.44	3.50	
	Wet/dry	1.73	1.69	5.15	X

Low carbon uptake in fully submerged samples is due to the low solubility of CO₂ in water, which prevents the carbonation reaction as it is a necessary component for mineral sequestration. Without the external pressurized supply of CO₂, full submersion aging of BOFS hinders the mineral sequestration process and results in high instability of BOFS due to the lack of consumption of f-CaO in BOFS. Wet-dry cycles are the best in terms of CO₂ uptake amount due to a moderate supply of H₂O and CO₂ that keep moisture content and access to CO₂ on an appropriate level for noticeable carbonation. Results from similar studies, such as that of Chetri et al., showed that a liquid-to-solid ratio of 0.1-0.2 improves slag carbonation [13], which supports this finding. The in-air aging of BOFS only utilizes moisture from the air, which slows down the reaction, but a higher CO₂ concentration than in water gives moderate results.

3.2 Compressive Strength

A compressive strength test was conducted at 7 and 28 days, and the average strength of 3 specimens under each curing condition was demonstrated in Fig. 1. Mortar mixture with s-BOFS achieved the highest average compressive strength on both testing days, which is 33.32 MPa at 7 days and 39.5 MPa at 28 days. These aggregates were subjected to a natural weathering process of mineralization similar to wet and dry cycles curing in the lab. As demonstrated in Table 3, wet and dry aging was the most optimal method, resulting in the highest amount of CO₂ sequestered. The increased CO₂ uptake is expected to enhance the strength of the mixture as the carbonation reaction mitigates the expansion behavior of BOFS aggregates, thereby reducing their contribution to crack propagation in the mortar mixture matrix. It should be noted that s-BOFS aggregates were exposed to filed wet and dry cycles for at least two years.

Despite that, the mortar mixture with BOFS aged by wet and dry cycles at the laboratory displayed lower 28-day compressive strength than the mixture with f-BOFS, which is 35.42 MPa and 39.21 MPa, respectively. Although the expansion tendency of wet/dry BOFS was alleviated by the formation of CaCO₃ during the carbonation process, the mixture with f-BOFS that had a lower degree of carbonation achieved higher strength by 10.7%. However, the standard deviation for the mixture containing BOFS W&D is also high, indicating that other uncontrolled factors might have influenced the result.

Moreover, the higher compressive strength in the mixture with f-BOFS compared to that containing BOFS W&D might be attributed to the lower porosity of BOFS aggregate and the strong interfacial transition zone (ITZ) that determines the compressive strength of the mixture. Generally, BOFS aggregates are considered dense material. However, their porosity is dependent on the steel-making processing method. The porosity of f-BOFS seems to be lower than that of BOFS W&D. It should be noted that the absorption capacity of f-BOFS (3.24%) is lower than that of BOFS W&D (5.17%), as stated earlier. The f-BOFS with dense and rough surface texture can increase the bond between cement paste and aggregates, leading to a stiffer ITZ and, hence, higher compressive strength of the mixture.

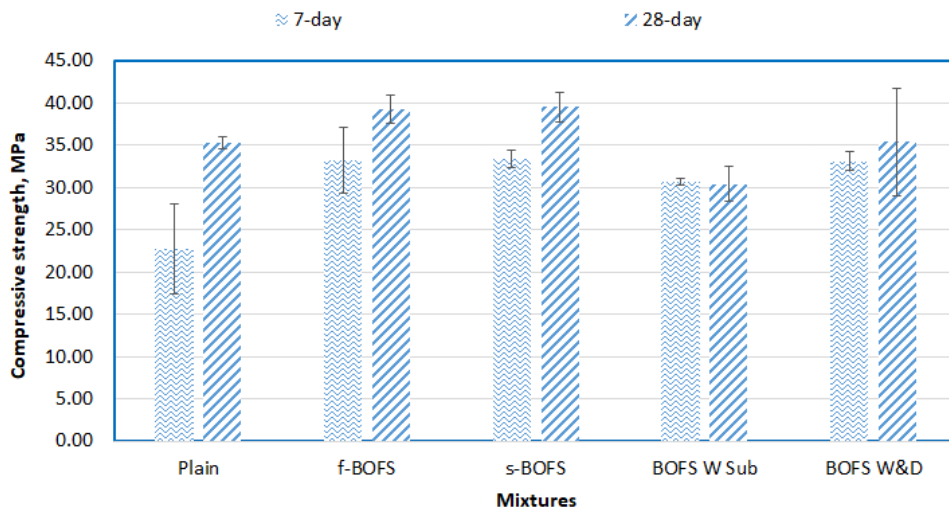


Fig. 1. Compressive strength of concrete containing BOFS

As anticipated, under TGA results, the lowest compressive strength at 28 days was achieved by the mixture with fully water-submerged BOFS (BOFS W sub), which is 30.43 MPa. As evidenced by the data presented in Table 3, a fully water-immersed aging condition was the least effective method for mineral sequestration of BOFS aggregates due to decreased CO₂ concentration in water impeding carbonation reaction. Consequently, BOFS had much f-CaO that, upon reaction with water, led to volumetric instability and interior deterioration of the mortar mixture matrix. This is also supported by the decrease in compressive strength from 30.70 MPa to 30.43 MPa at 7 and 28 days. Compared to f-BOFS, which also has much f-CaO, fully water-submerged BOFS has lost its hydraulic components during the reaction with water, and there is a high possibility of Ca(OH)₂ forming in these conditions. Thus, expansion in the mortar mixture appears again, leading to cracking.

Plain mortar mixture containing RS specimens demonstrated lower 7-day compressive strength (22.67 MPa) compared to mixtures with BOFS aggregates. Because BOFS aggregates contain high Fe₂O₃ and CaO contents regardless of aging conditions, BOFS mixtures exhibit higher early-age strength than the plain mixture. However, at 28 days, the compressive strength of the plain mixture increased to 35.28 MPa, showing the rapid strength gain behavior. This may be attributed to the continuous reaction of C₃S and tricalcium aluminate (C₃A) and the active reaction of C₂S and tetra calcium aluminate ferrite (C₄AF) that occurs at later stages. In contrast, in BOFS, these reactions took place earlier due to additional hydraulic components of BOFS and acceleration of the reaction owing to the more alkaline environment provided by BOFS. However, the standard deviation indicates significant fluctuations, which may have affected this finding.

3.3 Expansion Behaviors

The major issue related to using BOFS as an aggregate component in mortar and concrete is the expansive nature of its constituents, particularly f-Ca and f-Mg oxides. The potential reactivity of all mixtures was evaluated based on the ASTM C 1260, which imposes a limiting value of 0.1% expansion at 14 days for mixtures containing potentially expansive components. This value is used to distinguish aggregates primarily due to the $\text{Ca}(\text{OH})_2$ formation, which induces volumetric strains inside the concrete and leads to matrix cracking.

As depicted by Fig. 2, the expansion of mixtures submerged in water differs drastically depending on the aging conditions of BOFS. For up to 7 days, all mixtures except for the mixture with f-BOFS showed similar expansion behavior to that of the plain mortar mixture. As expected, direct use of f-BOFS was totally unsuitable for the mixture since the mixture reached extreme expansion after 7 days and was broken at 9 days. Wet/dry and stockpiled BOFS mixtures passed this test with approximately 0.05% expansion at 14 days, while fully water-submerged one reached 0.13% at the same age. After 14 days, the fully water-submerged BOFS mixture had noticeably more pronounced growth compared to the other two mixtures and was broken at 24 days.

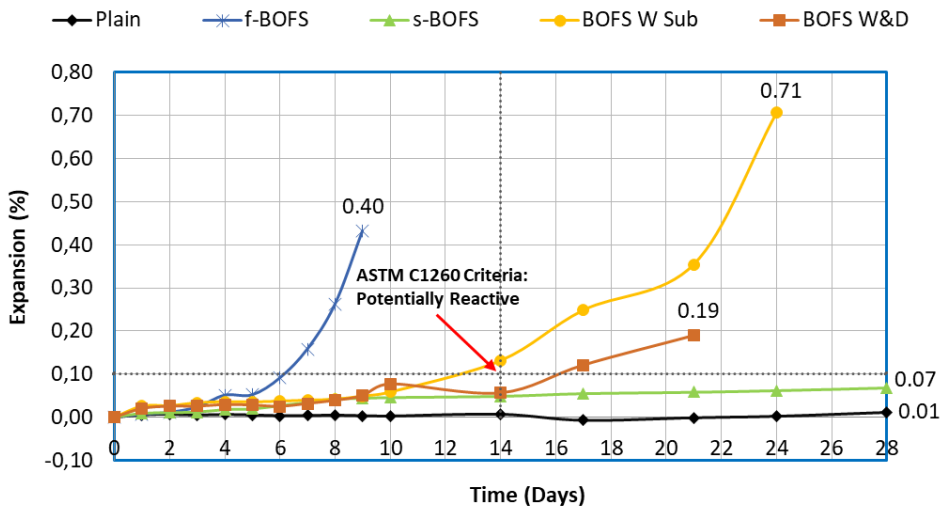


Fig. 2. Expansion behavior of concrete containing BOFS

As expected, the mixture with s-BOFS did not exceed the threshold value of expansion at 28 days. It should be noted that s-BOFS materials were exposed to the field (natural CO_2 sequestration) for two years, which induced the reaction to convert f-CaO to CaCO_3 . As a result, the volumetric expansion was minimized. Interestingly, the mixture containing BOFS W&D showed a very similar trend with the mixture with s-BOFS up to 14 days, but the latter then began to increase steadily and was broken at 21 days, although the expansion of this mixture (0.19%) was lower than that of a fully water-submerged one (0.35%) at the same age. This might be attributed to the localized formation of $\text{Ca}(\text{OH})_2$ at a certain area of the mixture. When the mixture was submerged in water, the remaining f-CaO in BOFS aggregates still made a reaction to form $\text{Ca}(\text{OH})_2$ and caused localized cracks in the mortar mixture matrix. From this result, it can be concluded that carbonation is directly related to the stability of BOFS in mortar mixture, and it is essential to entirely consume f-CaO content in BOFS (a full conversion of f-CaO to $\text{Ca}(\text{OH})_2$).

In correlation with TGA results in the section above, wet/dry conditions show the highest carbonation, which removes most of f-CaO and f-MgO, thereby producing a less expansive

mixture (complying with results from Fig. 2). As projected, a full water-submersion negatively affects the stability of concrete because in these conditions the mineral sequestration is severely hindered, thus leaving a lot of f-Cao and f-MgO. Unreacted BOFS is evidently very unstable due to the absence of any carbonation.

4 Conclusion

The results of the studies can be summarized as follows:

- Stockpiled BOFS had the best performance in terms of compressive strength and soundness in the mortar mixture. It has demonstrated the highest compressive strength at 7 and 28 days and superior stability with the lowest volumetric expansion.
- The mixture with BOFS aged by wet/dry cycles exhibited approximately the same compressive strength as the plain mixture, although in wet/dry BOFS, hydration reactions took place at an early stage due to a more alkaline environment and additional hydraulic components in the aggregates.
- The mixture containing wet/dry BOFS showed a very similar trend to the mixture with s-BOFS up to 14 days, but the latter began to increase steadily and was broken at 21 days due to the localized formation of $\text{Ca}(\text{OH})_2$.
- The mixture with f-BOFS achieved the second-highest compressive strength on both testing days, nearly equivalent to the mixture containing s-BOFS due to the improved bond between cement and aggregates and stiffer ITZ resulting from low porosity and high rough surface texture.
- The direct use of f-BOFS was proven to be unsuitable for the mixture, as it broke at 9 days and exhibited significant expansion.
- The mixture with fully water-submerged BOFS achieved the lowest compressive strength due to the aggregates' low carbonation degree, ultimately leading to volumetric expansion.
- The mixture with fully water-submerged BOFS had the highest expansion because this aging method hinders mineral sequestration and substantial amounts of f-CaO remains.
- The correlation between aging conditions and CO_2 uptake was established, indicating that stockpiled and wet/dry cycle conditions were the most optimal aging methods for BOFS to achieve the highest carbonation, hence the maximum stabilization degree of aggregates.

Regarding the industrial setting of BOFS stabilization, stockpiled aging is the most suitable since it does not require additional resources. However, future studies should identify the optimum duration of aging.

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