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

Quantitative study and variation of free lime content in BOF slag using Leduc method

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KEYWORDS

BOF slag
Volumetric instability
Free lime
Free lime quantification
Leduc method

ABSTRACT

The main issue hindering the widespread use of steel slag as a construction material is its volumetric instability. This instability is mainly caused by the hydration of free lime and magnesium oxide. Particularly, free lime is the primary contributor to the volume instability in converter slags. Therefore, quantifying the lime content in the slag is essential for assessing its stability. The determination of free lime content is challenging due to its various forms and distribution within the slag. This study employs the Leduc method complemented by TGA and XRD to quantify free lime in selected BOF slags and investigates its distribution. Results show varying free lime content in different slags. Analysis of aggregates indicates higher free lime in cores than periphery. For fine materials, free lime content increases with decreasing particle size, with the smallest fraction (0/0.04 mm) providing the most representative value. These findings contribute to understanding BOF slag properties and improving methods for assessing its stability for construction use.

1. Introduction

The main issue hindering the widespread use of steel slag as a construction material is its volumetric instability [1-6]. The potential volumetric change of steel slag is attributed to the presence of minerals that are prone to hydration-induced expansion, primarily free lime (CaO) and magnesium oxide (MgO) [7].

Lime is present in BOF slag in the following forms [8]: 1) Calcium oxide combined in silicates, alumino-ferrites, and calcium ferrites. 2) Uncombined calcium oxide, or free lime (CaO). 3) Free calcium hydroxide, resulting partly from the hydration of free CaO and partly from the hydrolysis of dicalcium silicate (C_2S) and tricalcium silicate (C_3S) and 4) Calcium carbonate ($CaCO_3$), formed by the carbonation of $Ca(OH)_2$ or even directly from CaO. This compound is very slightly soluble and practically inert. However, the direct carbonation of free lime is also an expansive reaction.

Free lime is responsible for the volumetric instability of converter slags. Therefore, quantifying the lime content in the slag is essential to assess its stability. Several methods exist to determine the free lime content, but the results are often uncertain due to the various forms in which lime can be present. Two main issues arise [8]:

- Quicklime (free CaO), which is the only form relevant to expansion risks-is often measured together with other lime forms such as $Ca(OH)_2$ (slaked lime). Accurately determining the free CaO content is not always straightforward and often requires the implementation of complementary methods to obtain a precise assessment.

- Free CaO can exist either as grains of 10–30 μm dispersed throughout the material, or as micro-inclusions trapped within C_3S and C_2S crystals. The latter are less accessible and more difficult to dissolve during chemical extractions (e.g., using glycol). As a result, the determination of free CaO is often somewhat skewed.

In the literature, several methods for determining free lime content have been reported, including the following [7]:

- Glycol and Sugar Water Extraction (Leduc method): These methods solubilize both free lime and calcium hydroxide ($Ca(OH)_2$), and require additional thermogravimetric analysis to isolate free CaO.

- Complexometric and Acidimetric Titration: These methods use specific reagents to measure calcium content, allowing for the quantification of free lime and $Ca(OH)_2$.

- Thermogravimetric Analysis: TGA helps identify and quantify free CaO, $Ca(OH)_2$, and $CaCO_3$ by measuring mass loss at specific temperatures, thus providing a comprehensive assessment of lime content.

- XRD and Image Analysis: These methods are useful for characterizing crystalline phases in the slag but require specialized equipment and are less accessible for routine analysis.

- Free Lime Estimation by Calculation: This method estimates free lime content based on elemental chemical analysis and furnace input data but has limited applicability due to varying operating conditions across different plants.

Each method has its limitations, with some methods overestimating free CaO content or lacking representativeness. The issue of rapid and reliable determination of free lime remains unresolved, although it is emphasized that free lime is not always the sole cause of expansion-related instabilities.

The Leduc method is selected for determining free lime content due to its simplicity, reliability, and effectiveness in quantifying both free lime (CaO) and slaked lime ($Ca(OH)_2$) in slag materials. One of the primary advantages of the Leduc method is its straightforward

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Received 06/05/2025, Revised 26/05/2025, Accepted 27/05/2025
Link DOI: https://doi.org/10.54772/jomc.v15i01.959

procedure, which does not require complex or costly equipment, making it accessible for routine laboratory analyses. This method is highly efficient in providing a rapid estimation of the total lime content, which is essential for evaluating the reactivity and stability of the material. In comparison to more intricate techniques, such as X-ray diffraction (XRD) or thermogravimetric analysis (TGA), which demand specialized equipment and technical expertise, the Leduc method offers a cost-effective alternative without sacrificing accuracy. Furthermore, it allows for the simultaneous quantification of both free lime and slaked lime, which is critical for understanding materials that may undergo carbonation or hydration over time. The Leduc method's compatibility with thermogravimetric analysis ensures precise isolation and quantification of free CaO content. Given its reliability, efficiency, and accessibility, the Leduc method is an appropriate choice for analyzing free lime content across various industrial and research contexts.

2. Materials and Methods

2.1. Materials

Four BOF slags were investigated in this study, three of which originated from recent steelmaking operations. One sample (BS1) represents a blend of slags from multiple steel productions, reflecting a common industrial practice. The other two (BS2 and BS3) each derive from a single specific production and differ notably in their free CaO content-BS2 being rich and BS3 poor in free lime. An additional sample (BSO), obtained from a previous campaign involving several steel casts, was also examined. At the time of sampling, this slag had undergone approximately three years of natural aging. Following pit cooling, recovery, and subsequent screening and crushing, the BOF slags presented as 0/60 aggregates. The constituent grains exhibited diverse morphologies, ranging from dense and compact to porous and cavernous textures.

2.2. Free Lime Quantification Methods

There is currently no universally accepted method for quantifying the various forms of free lime present in BOF slags [7]. In this study, the sugar water extraction method, commonly referred to as the Leduc method, was selected due to its ability to provide a rapid and reliable estimation of the combined content of CaO and $Ca(OH)_2$ without the need for sophisticated instrumentation. These two forms of lime do not exhibit the same volumetric behavior, and it is therefore important, in principle, to differentiate between them. However, in freshly produced slags, thermogravimetric analyses [9] have shown that the calcium hydroxide ($Ca(OH)_2$) content is relatively low compared to that of CaO. Consequently, it is generally accepted-at least as a first approximation-that the Leduc method provides a reliable estimation of the CaO content in freshly produced slags or in older materials, with the exception of finely ground products.

To isolate and accurately determine the free CaO content, this method Leduc is complemented by thermogravimetric analysis (TGA).

This method enables the determination of free lime content in a BOF slag (LAC) sample. The quantification process is based on the complexation of calcium ions (Ca^{2+}) by sucrose ($C_{12}H_{22}O_{11}$). Concurrently, hydroxide ions (OH^-), released into the solution through the dissolution of calcium hydroxide [$Ca(OH)_2$], are titrated using a 0.1N hydrochloric acid solution until the phenolphthalein indicator is fully decolorized. The procedure for the Leduc method is illustrated in Figure 1, detailed as below:

A representative sample of BOF slag (LAC), composed exclusively of coarse particles, is first quartered, then ground and sieved to a particle size of 80 µm, and subsequently dried at 105°C. One gram of the resulting powder is introduced into a sugar solution prepared by dissolving 30 grams of sucrose in 200 mL of distilled water. The mixture is stirred continuously for 30 minutes and then filtered using a Büchner funnel. A [25-50] mL aliquot of the filtrate is collected and titrated with 0.1N hydrochloric acid using phenolphthalein as a pH indicator. The endpoint of the titration is indicated by a distinct color change of the solution from pink to colorless.

The free calcium oxide content (W_{CaO}), expressed as a percentage of the dry material mass, is defined as follows:

$$W_{(\%)} = \frac{28.V_{HCl}.[HCl]}{v_{aliquot}.m_{slag}}.100 \qquad (1)$$

where:

- V_{HCL} : Volume of hydrochloric acid (in liters)
- [HCl]: concentration of hydrochloric acid (in mol/L)
- m_{slag}: mass of the slag sample (in grams)
- $v_{aliquot}$: volume of the test aliquot (in liters)

An illustrated overview of the method is provided in Figure 1 and an illustration of the experimental steps involved in the Leduc method is presented in Figure 2.

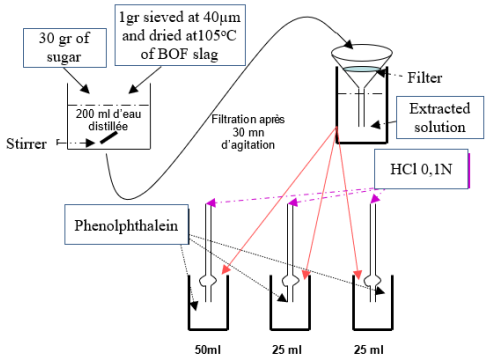

Fig 1. Schematic of Leduc method.

Fig 2. Leduc experimental procedure.

3. Resultats and Discussions

3.1. Free lime content of 3 BOF slags

A substantial number of measurements were conducted on the various products; however, only a limited subset could be deemed representative, owing to frequently inconsistent or suboptimal experimental conditions, such as variations in the particle size of the analyzed fraction, the age of the samples, and their storage conditions. Table 1 illustrates the calculation of free lime content for BS3 slag as determined by the Leduc method, for two distinct particle size fractions: (i) the 16/20 mm fraction, ground to a particle size of 40 μm, and (ii) the fine fraction, consisting of particles passing through a 0.08 mm sieve and subsequently ground to 80 μm.

For the three BOF slags, the average free lime contents retained, derived from a compilation of results obtained across multiple representative samples with varying particle size distributions and morphological characteristics, are summarized in Table 2. These values correspond specifically to measurements performed on the <40 μm fraction, produced by grinding coarse particles and analyzed immediately following the grinding process.

Table 1. Experimental calculation of free lime content in BS3 using the Leduc method.

BOF slag "BS3"											
16/20 → 40 μm						Fines → 80 μm					
Sample	m_{sugar}	30,006			$W_{CaO.avg}$ (%)	Essais	m_{sugar}	30,006			$W_{CaO.avg}$ (%)
	m_{slag}	1,006					m_{slag}	1,006			
N°1	v_{HCl}	9.95	w_{CaO} =	11,08		N°1	v_{HCl}	8,2	w_{CaO} =	9,18	
	$v_{aliquot}$	50					$v_{aliquot}$	50			
	m_{slag}	30,006					m_{slag}	30,006			
	v_{HCl}	1,006					v_{HCl}	1,006			
N°2	$v_{aliquot}$	4.95	w_{CaO} =	11,03	11,08	N°2	$v_{aliquot}$	8.1	w_{CaO} =	9,07	
	m_{slag}	25					m_{slag}	50			
	m_{slag}	30,006					v_{HCl}	30,006			
	v_{HCl}	1,006					$v_{aliquot}$	1,006			9,18
N°3	$v_{aliquot}$	5	w_{CaO} =	11,14		N°3	m_{slag}	4.15	w_{CaO} =	9,29	
	m_{slag}	25					v_{HCl}	25			

Table 2. Free lime content of 03 BOF Slags determined by the Leduc method.

Samples	BS1	BS2	BS3
Free lime content Leduc (%)	7.5 - 8.2	6.7	10.2

It is observed that BS3 contains a higher free lime content than BS2. It is worth noting that both of these materials originate from a single specific casting with an assumed constant lime content. In contrast, BS1-derived from multiple castings-shows a variable free lime content, positioned between that of BS2 and BS3.

To verify whether the extraction of lime was complete, X-ray diffraction (XRD) patterns of the slag with the highest lime content, BS3, were recorded before and after extraction. These patterns are presented in Figure 2, where only the most intense and characteristic peaks of the various calcium phases are indicated.

The peaks corresponding to free lime (CaO) and slaked lime ($Ca(OH)_2$) disappear in the powder after extraction, indicating effective dissolution of these lime phases. However, calcite remains present in the powder.

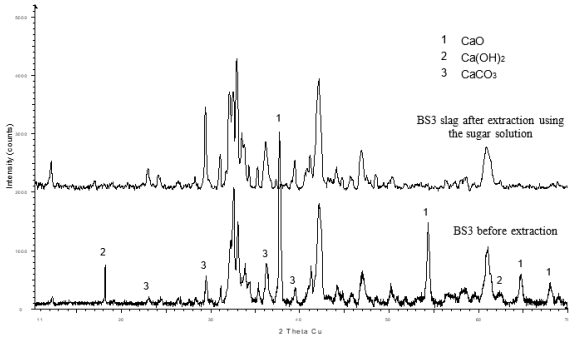

Fig 3. X-ray Diffraction Patterns of the Powder Before and After Extraction.

3.2. Evolution of free lime content with particle size and within aggregates

Specific measurements were carried out with two main objectives. The first was to determine the variation in free lime content within individual aggregate particles. To this end, the slag aggregates were ground and separated into two distinct parts: the core and the peripheral

layer of the grains. The second objective was to investigate the evolution of free lime content as a function of particle size. The aggregates were therefore classified into different size fractions: 0/4 mm, 4/8 mm, 8/20 mm, 12.5/16 mm, 20/25 mm, and 25/31.5 mm. The collected samples were ground into powder immediately prior to analysis.

It should be noted that these investigations were conducted exclusively on sample BS1, a slag derived from a blend of multiple steel heats, which may limit the generalizability of the results. Moreover, the analytical protocol used in this section differed from that described above- specifically, a lower amount of sugar and a higher slag mass were used. Given the high alkalinity of the materials, these conditions are likely to result in an underestimation of the actual CaO content. Nevertheless, the comparative values obtained provide trends that can be considered reliable.

Grains in the 12.5/16 mm, 20/25 mm, 25/31.5 mm and 31,5/40 mm fractions were subjected to peripheral grinding. The resulting peripheral powders, along with the remaining grain cores, were ground and sieved to 80 µm prior to analysis. The results of these measurements are presented in Table 3 and in Figure 4.

Table 3. Evolution of free CaO content within aggregate.

Position within aggregate	Periphery				Core			
Fraction (mm)	12.5/16	20/25	25/31.5	31.5/40	12.5/16	20/25	25/31.5	31.5/40
W_{CaO} (%)	4.55	5.06	4.27	1.930	4.64	6.29	5.95	3.547
$W_{CaO\cdot avg}$(%)	4.62				5.63			

Table 4. Evolution of free CaO content as a function of particle size BS1.

Fraction (mm)	0/4	3,15/4	4/8	8/20	12,5/16	20/25	25/31,5
W_{CaO} (%)	5.12	5.93	4.97	4.99	4.35	5.68	5.11
$W_{CaOaverage}$ (%)	5.16						

Table 5. Evolution of free CaO content with particle size BS2&BS3.

Sample types	BS2			BS3		
Fraction (mm)	0/0.04	0.04/0.08	0.08/0.125	0/0.04	0.04/0.08	0.08/0.125
W_{CaO} (%)	7.37	5.49	5.12	9.41	7.57	7.48

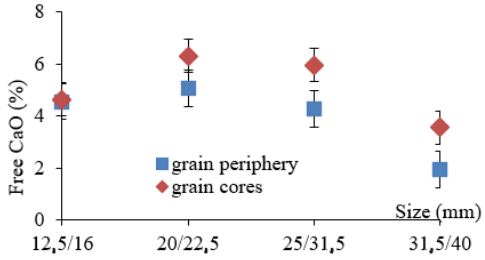

Fig 4. Evolution of free CaO content within aggregate BS1.

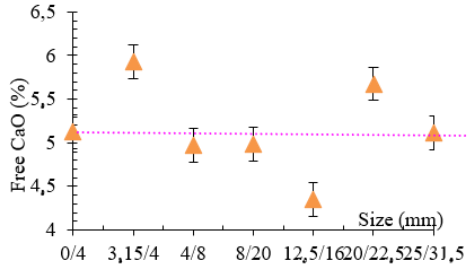

Fig 5. Evolution of free CaO content with particle size BS1.

The measured free lime content presented in Figure 5 and Table 4 varies only slightly or in a non-systematic manner with particle size, suggesting that lime is relatively uniformly distributed throughout the material.

Finally, to assess the influence of powder size on the analytical results, free lime quantification was performed on different granulometric fractions smaller than 125 µm for BS2 and BS3. The following size ranges were considered: 0-0.04 mm, 0.04-0.08 mm, and 0.08–0.125 mm. The corresponding results are presented in Table 5 and Figure 6. It is observed that the amount of detectable free lime increases as the particle size decreases. The 0/0.04 mm fraction exhibits greater water accessibility compared to the other fractions; therefore, the free lime content measured in this fraction is considered to be more representative of the actual amount of free lime present in the materials.

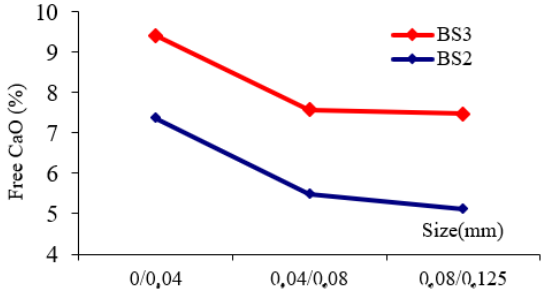

Fig 6. Evolution of free CaO content withe particle size BS2 &BS3.

4. Conclusions

The primary impediment to the widespread utilization of steel slag as a construction material is its inherent volumetric instability. This instability is predominantly linked to hydration-induced expansion, primarily driven by the presence of free lime (CaO) and magnesium oxide (MgO). Specifically, free lime is identified as the key constituent responsible for the volumetric instability observed in converter slags. Consequently, a quantitative assessment of the lime content within the slag is indispensable for evaluating its stability.

However, the determination of free lime content presents challenges, largely due to the various forms in which lime can exist within the slag. A significant issue is that quicklime (free CaO), the form most critical to expansion risks, is often measured concurrently with other forms, such as slaked lime ($Ca(OH)_2$). Furthermore, free CaO can be present either as relatively accessible dispersed grains or as less accessible micro-inclusions trapped within crystalline structures, potentially affecting the accuracy of chemical extraction methods. Accurate quantification of free CaO frequently necessitates the application of complementary analytical techniques.

This study employed the sugar water extraction method, widely recognized as the Leduc method, for determining the free lime content. The Leduc method was chosen for its simplicity, reliability, and efficacy in quantifying both free lime (CaO) and slaked lime ($Ca(OH)_2$). Its principal advantages include a straightforward procedure requiring no complex or costly equipment, making it suitable for routine laboratory analyses. It provides a rapid estimation of total reactive lime. In this research, the Leduc method was complemented by thermogravimetric analysis (TGA) for precise isolation and quantification of free CaO. X-ray diffraction (XRD) was also utilized to verify the effectiveness of the chemical extraction process.

Analysis of three BOF slags (BS1, BS2, BS3) yielded average free lime contents (for the <40 μm fraction) ranging from 7.5 to 8.2 % for BS1, 6.7 % for BS2, and 10.2 % for BS3. It was observed that BS3 exhibited a higher free lime content than BS2. XRD analysis confirmed the effective dissolution of free lime (CaO) and slaked lime ($Ca(OH)_2$) from the slag powder during the sugar solution extraction, although calcite remained present.

Investigations into the spatial distribution of free lime within aggregates of BS1 revealed notable variations. The core of the grains consistently demonstrated a significantly higher free CaO content compared to the peripheral layer, with an average difference of approximately 18 %. This discrepancy is attributed to the faster rate of hydration and carbonation occurring at the aggregate surface following production, which renders the free lime in the core less accessible to ambient water and carbon dioxide.

Regarding the influence of particle size, measurements on BS1 across various larger size fractions (0/4 mm up to 25/31.5 mm) indicated that the measured free lime content varied only slightly or in a non-systematic manner. This finding suggests a relatively uniform distribution of lime throughout the material for these aggregate sizes. However, when examining finer fractions (<125 μm) of BS2 and BS3, the amount of detectable free lime was found to increase as the particle size decreased. The 0/0.04 mm fraction displayed greater accessibility to water compared to the other fine fractions, leading the study to consider the free lime content measured in this smallest fraction as more representative of the actual amount present in the materials.

In conclusion, this study successfully applied the Leduc method, supported by TGA and XRD, to quantify free lime in selected BOF slags and elucidate its distribution patterns. The findings highlight variations in free lime content between different slag types, demonstrate that the core of aggregates contains more free lime than the surface due to differential environmental interactions, and show that for very fine materials, the analysis of the smallest particle size fraction provides the most representative assessment of free lime content.

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