

Technology of free calcium oxide (f-CaO) digestion in steel slag by origin adjusting under the vision of carbon neutralization

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ABSTRACT

The carbon emissions of the steel industry are enormous. In addition, a large amount of solid waste will be generated in the steelmaking industry. Therefore, the efficient utilization of solid waste in the steelmaking industry is significant for energy saving and carbon reduction. Steel slag is a by-product of the steelmaking process, a bulk industrial solid waste. At present, the comprehensive utilization rate of steel slag in China is less than 30%. Excessive f-CaO content in steel slag is one of the main factors limiting its utilization and will lead to the volume expansion of steel slag during the slow hydration process. The traditional f-CaO digestion method cannot improve the performance of the steel slag from the source, and the sensible heat recovery of the steel slag cannot be carried out. Therefore, the origin adjusting technology, which utilizes the sensible heat of steel slag and can modify the steel slag, has gradually attracted attention. This paper takes the steel slag of a steel plant in Shanxi as the research object. After analyzing its steel slag data, a scheme of origin adjusting is proposed, and the relevant influencing factors are analyzed.

Keywords: Energy saving and carbon reduction; Steel slag; f-CaO, Origin adjusting; Sensible heat recovery

NOMENCLATURE

Abbreviations

FA	Fly Ash
BFS	Blast Furnace Slag
WG	Waste-Glass

Symbols

C/S	The molar ratio of CaO to SiO ₂
a	the target value of C/S
x	the mass of modifier to be added, t
Aw(y)	The mass percentage of y substance in the modifier added A
Sw(y)	The mass percentage of y substance in the steel slag

M(y)	the molar mass of y substance, g/mol
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1. INTRODUCTION

In 2021, the global crude steel output is 1.95 billion tons, and China's crude steel output is 1.035 billion tons. The steel slag output is about 12%-15% of the crude steel output^[1]. Based on this, it is estimated that the global steel slag output in 2021 would be about 230-290 million tons. China's steel slag production is about 120-160 million tons. In 2021, China's steel industry carbon emissions accounted for 15% of the country's total carbon emissions, about 1.5 billion tons. According to the statistics, the total utilization rate of steel slag in China is less than 30%, which is far from the 60% utilization rate set by China.

At the same time, a large amount of unused steel slag is mainly piled up the outdoor, but long-term open storage will not only occupy a lot of land resources but also pollute the air, soil, and groundwater resources, posing a threat to the survival of human beings. Therefore, utilizing steel slag with high added value has become an urgent problem to be solved in the current metallurgical industry. The comprehensive utilization of steel slag can not only turn waste into treasure, improve the utilization rate of resources and reduce the operating cost of enterprises, but also effectively alleviate the environmental pollution caused by steel slag, which is of great significance to the high-quality development of the metallurgical industry^[2].

In steelmaking, due to the difference in raw materials, steelmaking methods, and smelting processes, the chemical composition, and content of the steel slag produced are also different. Steel slag is a by-product produced in the steelmaking process at a high temperature of 1500 °C to 1700 °C. It is mainly composed of added smelting flux, oxides, sulfides, slag-forming materials (such as limestone), and furnace lining materials (consisting mainly of CaO and MgO)^[3].

The chemical composition of steel slag is mainly oxides of silicon, aluminum, iron, calcium, magnesium, potassium, and sodium [7]. The mineral composition of steel slag is analyzed by SEM and XRD. The main mineral composition of steel slag is $2\text{CaO}\cdot\text{SiO}_2(\text{C}_2\text{S})$, $3\text{CaO}\cdot\text{SiO}_2(\text{C}_3\text{S})$, RO phase (solid solution of divalent metal oxides such as MgO, FeO, MnO), f-CaO, f-MgO, iron aluminate, mafic olivine, and elemental iron, etc. [4].

The alkalinity of steel slag greatly influences its composition and properties of steel slag. Mason B defines $M=w(\text{CaO})/w(\text{SiO}_2+\text{P}_2\text{O}_5)$ as the alkalinity of steel slag [5], also known as ternary alkalinity, where $w(\text{CaO})$ and $w(\text{SiO}_2+\text{P}_2\text{O}_5)$ respectively represent the mass content of CaO, SiO_2 , and P_2O_5 in the steel slag. Some researchers also classify steel slag by binary alkalinity [6], quaternary alkalinity, or C/S (molar ratio of CaO to SiO_2) [7], and the binary alkalinity and C/S ratio have no difference. Therefore, to better understand the origin adjusting of steel slag, the C/S molar ratio is used to express the alkalinity of steel slag. The alkalinity classification and mineral phase composition of steel slag are shown in Table 1.

Table 1. Alkalinity and mineral phase composition of steel slag

Type of steel slag	Alkalinity $w(\text{CaO})/w(\text{SiO}_2+\text{P}_2\text{O}_5)$		Major mineral phases
	Mason	Other	
Olivine	0.9~1.4	0.9~1.5	Olivine, RO phase, and merwinite
Merwinite	1.4~1.6		
Dicalcium silicate	1.6~2.4	1.5~2.7	C ₂ S and RO phase
Tricalcium silicate	>2.4	>2.7	C ₂ S, C ₃ S, C ₄ AF, C ₂ F, and RO phase

In recent years, steel slag is mainly used as a building material. However, with the slow hydration of some substances in the steel slag, hydration expansion will occur, which will crack the pavement, walls, and other buildings that use the steel slag as a building material, increasing the hidden danger of the use of the steel slag. The main reason for the poor volume stability of the steel slag is the presence of excessive f-CaO in the steel slag.

The f-CaO in the steel slag is different from the f-CaO in other materials. The CaO in the steel slag is calcined at a high temperature of about 1450 °C. The heating rate is slow during calcination and the residence time in the high temperature is long. Although it also underwent rapid cooling, its lattice structure was already tight at this point. It has the following characteristics: the large grain size, complete development, few defects, compact structure, and low activity. These characteristics make the f-CaO in the slag less reactive and take longer for

complete hydration. It is recognized that the main reason for the poor volume stability of steel slag is that the volume of f-CaO increases by 98% during hydration, resulting in local expansion stress and long hydration time [8].

The content of f-CaO in steel slag is also closely related to alkalinity. Xiao [9] et al. aimed to reduce the content of free calcium oxide in the slag and sorted out the flow direction of calcium in the final slag with different alkalinity in theoretical calculations. It is concluded that f-CaO is more likely to be produced in high alkalinity steel slag. The effect of cooling rate on the cooling of steel slag is also studied: increasing the cooling rate can reduce the content of f-CaO in steel slag. The stability of steel slag can be improved by quenching, which is beneficial to the subsequent comprehensive utilization of steel slag.

The traditional f-CaO digestion methods in steel slag include hot splashing, water quenching, disk splashing, air quenching, etc. Still, the f-CaO content of the treated steel slag is unstable, and it is difficult to utilize a large amount of sensible heat of molten steel slag. Therefore, a new process technology is urgently needed to treat the steel slag, which can improve the cementitious activity and stability of the steel slag and utilize a large amount of the sensible heat of the steel slag as much as possible.

The origin adjusting technology, called molten steel slag modification technology, reduces the f-CaO content in the steel slag by adding silicon-rich substances to reduce the C/S in the steel slag. The general principle is to uniformly mix molten steel slag with a certain proportion of a modifier at a high temperature and use the heat of molten steel slag to heat the modified substance and make it react with the substances in the steel slag and f-CaO. While reducing the content of f-CaO in the steel slag, it can generate substances that help to improve the cementitious activity of the steel slag, thereby purposefully changing the chemical composition and mineral composition of the steel slag. This technology can not only make full use of the heat of the steel slag, but also realize the modification of the steel slag to realize the digestion of f-CaO in the steel slag, improve the volume stability and cementitious activity of the steel slag, and improve the utilization rate of the steel slag.

2. MATERIAL AND METHODS

It can be seen from Table 2 that the f-CaO content of steel slag is generally higher than the 4% required in GB/T 20491-2017 “Steel Slag Powder for Cement and Concrete”, the national standard in China.

$$a = \frac{\frac{x \cdot Aw(\text{CaO}) + 17 \cdot [\text{Sw}(\text{CaO}) + \text{Sw}(\text{f-CaO})]}{M(\text{CaO})} + \frac{17 \cdot \text{Sw}(\text{Ca}(\text{OH})_2)}{M(\text{Ca}(\text{OH})_2)}}{\frac{17 \cdot \text{Sw}(\text{SiO}_2) + x \cdot Aw(\text{SiO}_2)}{M(\text{SiO}_2)}} \quad (1)$$

The formula (2) is obtained by changing formula (1):

$$x = 17 \cdot \frac{\frac{[\text{Sw}(\text{CaO}) + \text{Sw}(\text{f-CaO})]}{M(\text{CaO})} + \frac{\text{Sw}(\text{Ca}(\text{OH})_2)}{M(\text{Ca}(\text{OH})_2)} - a \cdot \frac{\text{Sw}(\text{SiO}_2)}{M(\text{SiO}_2)}}{a \cdot \frac{Aw(\text{SiO}_2)}{M(\text{SiO}_2)} - \frac{Aw(\text{CaO})}{M(\text{CaO})}} \quad (2)$$

The maximum value of the content of f-CaO is extremely high. Therefore, in order to utilize this kind of steel slag as a resource in the field of building materials, f-CaO must be digested. In this paper, the composition of the steel slag exported from the converter of a steel plant in Shanxi is analyzed, and the chemical composition is shown in Table 2.

Table 2. Major chemical composition (mass fraction/%) and related content of steel slag.

Composition	Content	average
SiO ₂	9.8~15.0	11.6
CaO	33.8~42.7	39.2
MgO	8.1~11.9	10.2
Al ₂ O ₃	0.9~2.1	1.3
f-CaO	0.6~12.5	4.7
TFe	16.4~27.0	21.1

The relationship between the content of f-CaO in the steel slag and the C/S (molar ratio of CaO to SiO₂) in the slag was analyzed, as shown in Figure 1.

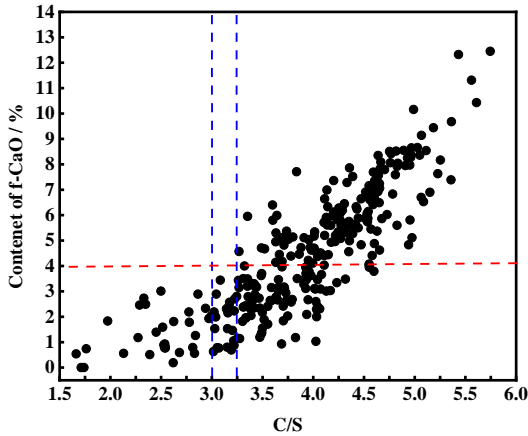


Figure 1. Relation between f-CaO content and C/S in steel slag.

It can be seen from Figure 1 that when the C/S in the steel slag is less than 3 or 3.25, the f-CaO content is basically less than 4%. From the perspective of origin adjusting, the C/S in molten steel slag can be reduced by adding silicon-rich substances to uniformly mix them in the steel slag, thereby reducing the f-CaO content in the steel slag from the source.

At present, there are relatively cheap silicon-rich substances such as Fly Ash (FA), Blast Furnace Slag (BFS) and Waste Glass (WG) on the market, whose chemical

compositions are shown in Table 3. The above substances also belong to industrial solid waste. If they are used for the origin adjusting of steel slag, which can achieve the purpose of ‘using waste to treat waste’.

Table 3. Chemical composition and content (mass fraction/%) of silicon-rich materials.

Name	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Other	C/S
FA	49.9	25.7	7.6	6.8	0.6	9.4	0.2
BFS	34.9	11.3	1.4	36.7	11.3	4.4	1.1
WG	70.2	3.3	-	10.2	1.6	16.3	0.2

3. COMPUTING AND DATA ANALYSIS

The above-mentioned FA, BFS, and WG are used as the modifiers, assuming that the mass capacity of a slag tank is 17 tons and the required modifier quality is calculated. The calculation formulas are as above formula (1) and formula (2).

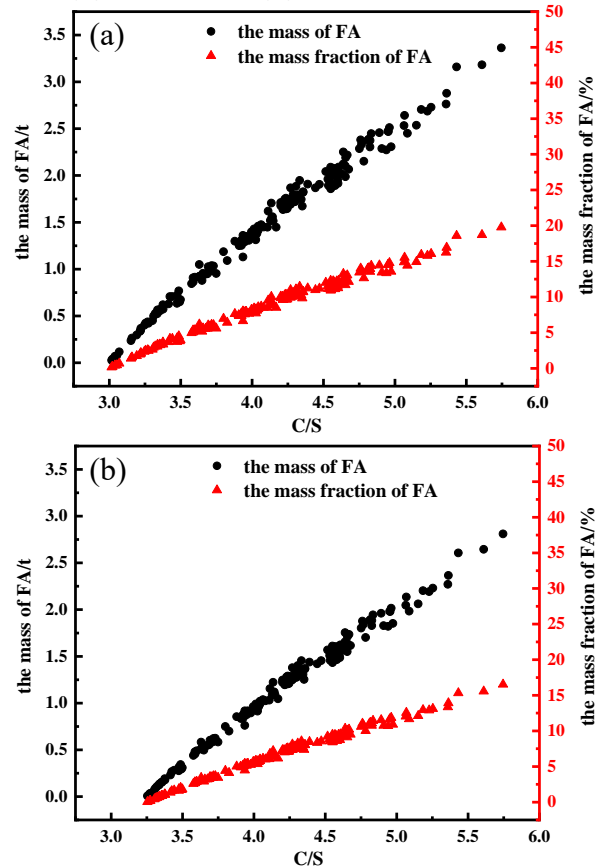


Figure 2. The mass and mass percentage of required FA to reach the C/S target value; (a) C/S=3, (b) C/S=3.25.

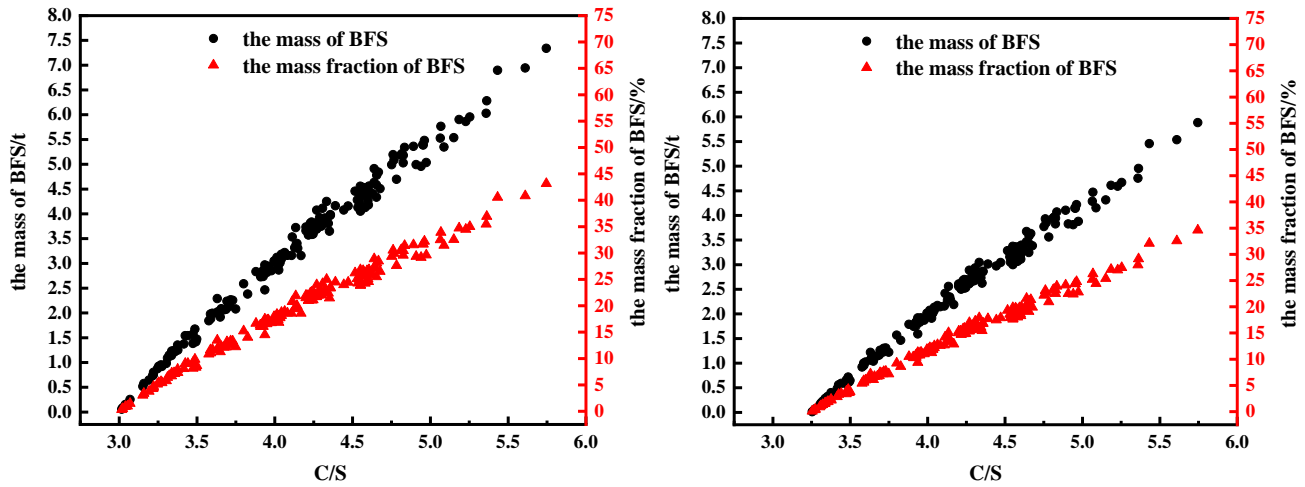


Figure 3. The mass and mass percentage of required BFS to reach the C/S target value; (a) C/S=3, (b) C/S=3.25.

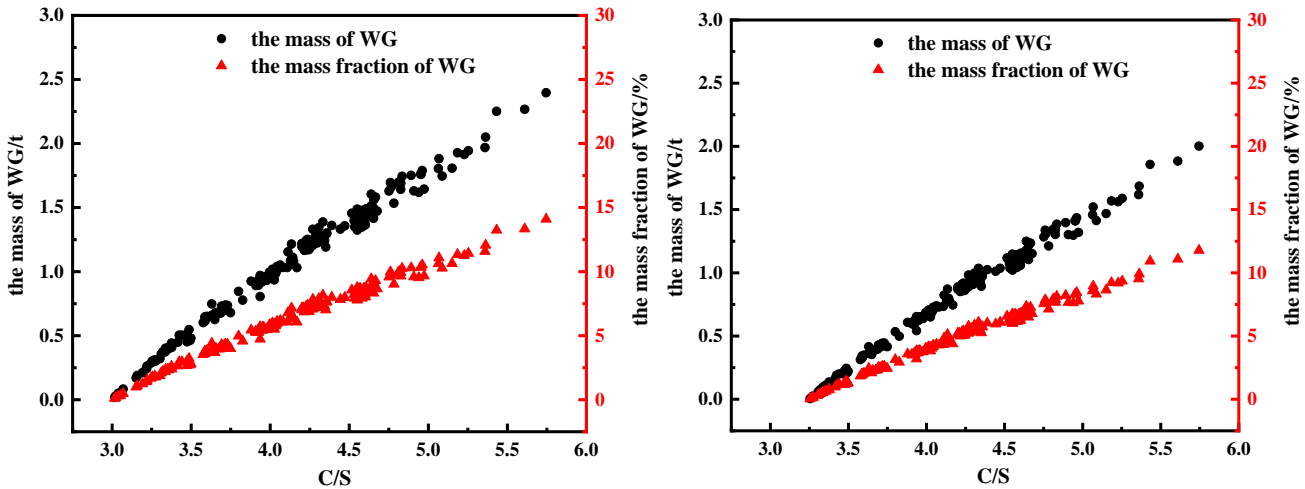


Figure 4. The mass and mass percentage of required WG to reach the C/S target value; (a) C/S=3, (b) C/S=3.25.

FA, BFS and WG were selected as the modifiers of origin adjusting, and C/S=3 and C/S=3.25 were selected as the modification targets, respectively. Calculate the required mass of the corresponding modifier and its mass percentage in the molten steel slag, and the results are shown in Figure 2-4.

From Figure 2 to 4, it can be concluded that different modifiers have different requirements to achieve the same modification target (C/S value) due to different compositions. Since C/S in steel slag is generally higher than 3 or 3.25, it is necessary to add modifiers with C/S lower than 3 or 3.25 to reduce C/S in the steel slag.

To achieve the same C/S modification target, if the C/S of the modifier is larger, then the required additional amount is larger.

In theory, any modifier whose C/S is less than the C/S modification numerical target can be used to modify the steel slag. However, the mass percentage of the modifier added to the original steel slag is an important parameter. If too much modifier is added, not only the mixing of steel slag and modifier will be insufficient, but also the temperature of molten steel slag will drop rapidly. The fluidity of the steel slag will be greatly

reduced, which will further affect the mixing uniformity.

If the preheating of the modified substance is considered, the energy consumption is very high. In addition, it is generally necessary to grind the modifier to reduce its particle size. If a large amount of modifier is added, the energy consumption of mechanical grinding is a huge cost.

4. CONCLUSION

From the above analysis, it is more effective to add modifiers with smaller particle sizes and high silicon content. At the same time, raw material cost, grind ability, mixing adequacy, feeding method (one-time feeding or multiple batches feeding), and heat preservation measures should also be considered. It is further necessary to consider how to realize online modification according to the composition of molten steel slag and control the composition of molten steel slag more accurately.

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