

Effect of Post-Blowing CO₂ and CO₂-Ar Mixture in BOF Process

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The decarburization and deoxidation by bottom CO₂ or CO₂-Ar mixture post-blow in the BOF process were investigated using the bubble-bath reaction model. When CO₂ is used for the post blow and when the product of $[C][O]$ is 0.0024 in the steel, and a small amount of decarburization was found to occur when $[C]/[O]$ is higher in the steel but the carbon pickup into steel was found to occur when $[C]/[O]$ is lower in the steel. Oxygen will be picked up into steel by blowing CO₂ and the pickup is more significant for lower $[C]/[O]$ the ratio in steel. The product of $[C][O]$ increases by blowing CO₂ and it increases more significantly for higher $[C]/[O]$ in the steel.

The product of $[C][O]$ in steel after the post-blow was observed to increase with higher CO₂ levels in the gas mixture. If the CO₂ concentration exceeded 50%, the post-blow caused a further increase in the product of $[C][O]$ in steel.

Keywords: Bottom blow, CO₂, Post blow, BOF process

1. INTRODUCTION

The steel industry is recognized as an energy-intensive and high-emission sector, generating substantial amounts of carbon dioxide (CO₂) during the production process. A significant portion of this CO₂ is directly released into the atmosphere, making the steel industry one of the major contributors to greenhouse gas emissions.⁽¹⁾ Consequently, the recovery and utilization of CO₂ from steelmaking operations hold significant importance and vast potential. Effective utilization of CO₂ emissions from the steel industry is crucial for mitigating climate change and promoting sustainable development.⁽²⁾

For the modern basic oxygen furnace (BOF) process, the furnace typically has two major gas supply systems: top-blowing and bottom-blowing.⁽³⁾ Among all the blowing technologies, post-bottom blowing (also known as post stirring, end-point bottom blowing) is one of the effective techniques to reduce the carbon and oxygen contents in molten steel, saving alloy consumption and time in the steel refining processes.^(4, 5) Iron loss in the slag may also be reduced since TFe in the final slag is expected to be reduced by decreasing oxygen in the steel.⁽⁶⁾ In the case of blowing argon into a steel bath, produces numerous argon bubbles in the bath. CO pressure in these bubbles is lower than 1atm enabling the reaction of $C + O = CO$ to occur at the gas-steel interface to remove carbon and oxygen from steel into the bubbles as CO.⁽⁷⁾ The reacted bubbles leave the steel bath from

its top surface so that the carbon and oxygen are removed from the bath. In general, argon is preferred for bottom blowing in steelmaking processes when the cost of the inert gas is not a major concern. Nitrogen is often used as a more cost-effective alternative, especially in processes where its potential effects on steel properties are less critical or can be controlled.⁽³⁾

Therefore, to explore the feasibility of CO₂ recycling and reuse in converter bottom blowing technology, it is important to investigate the decarburization and deoxidation phenomena during the post-blow of CO₂ or CO₂-Ar mixture. In addition, the influence on bath quality, such as the product of $[C][O]$, was also analyzed in this work.

2. EXPERIMENTAL METHOD

To understand the mass and heat transport between the bath and the bottom-blown stirring gas, as well as to estimate the effects of the stirring gas on the bath's temperature and composition, and on the temperature, composition, and flow rate of the process off-gas, a model for the stirring gas in the bath was developed in this work.

A schematic of an oxygen steelmaking furnace is shown on the left side of Figure 1. To enhance mass and heat transport in the bath, stirring gas is usually introduced from the bottom of the furnace. The schematic representation of the mass and heat transports between the stirring gas bubble and bath are shown on the right side of Figure 1. When stirring, gas bubbles travel in the

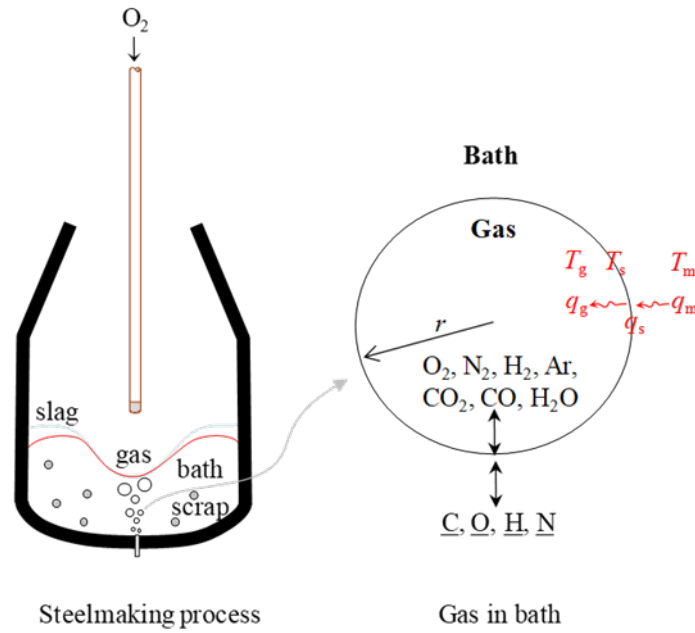
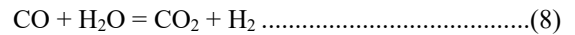
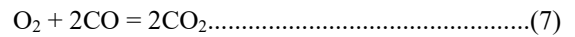
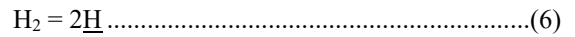
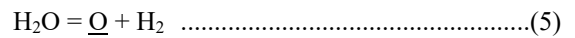
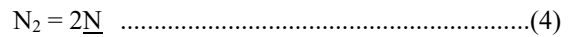
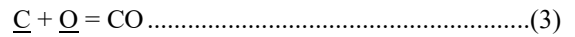
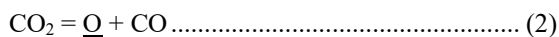
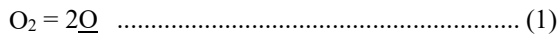


Fig.1. Schematic diagram of the steelmaking process, left, and stirring bubble in bath, right.

bath, the bubbles react and exchange heat with the surrounding metal until they reach the surface of the bath. After being released from the bath surface, the stirring gas bubbles merged with the gases discharged from the hot spot zone and slag-metal reaction. These gases become process off gas and leave the furnace. During stirring gas bubbles travel towards the bath surface, and the bubbles' size changes due to the changes in pressure, number of moles, and temperature of the bubbles. The pressure on the bubbles changes with ambient, hydrostatic, and Laplace pressures. The number of moles and the composition of the bubbles are changed by the reactions at the gas-metal interface and those in the bubbles. The temperature of the bubbles changes due to the thermal effects of these reactions and the heat exchange between the bubbles and the surrounding metal.

The rising velocity of the bubbles is the Stokesian velocity in addition to the velocity of the circulation flow in the bath. Stokesian velocity changes with the bubble size.

When stirring gas contains O₂, CO₂, CO, Ar, N₂, H₂O, and/or H₂ and the metal in a bath contains C, O, N, and/or H, reactions (1)-(6) may occur at the gas-metal interface and reactions (7) and (8) may occur in the gas. The underlined symbols in reactions (1) to (7) represent the element that is melted in the metal bath.



The following process conditions were used in the modeling investigations. Steel temperature is 1660°C and steel composition is 0.04 mass% C, 0.06 mass% O, 0.0001 mass% Si, 0.1 mass% Mn, 0.02 mass% P, 0.005 mass% S, 0.002 mass% N and 0.001 mass% H. CO₂ or CO₂-Ar mixture of 25°C is injected into a 250-ton steel bath from the bath bottom. The depth of the bath is 2 meters. The pressure at the bath top surface is 1 atm. The velocity of metal flow induced by bottom injection in the upward direction is 1 m/s. The injected CO₂ or CO₂-Ar mixture is dispersed into initial bubbles with a diameter of 0.01m at the bottom of the bath, with a gas flow rate of 1000 Nm³/hr. Additionally, the post-blow duration is 5 minutes.

3. RESULTS AND DISCUSSION

3.1 Post Blow by CO₂

In the calculation of the effect of the $[\text{C}]/[\text{O}]$ ratio in steel on the post-blow of CO₂ in the BOF process, the product of $[\text{C}][\text{O}]$ are kept at 0.0024 and the ratio of

carbon content to oxygen content ($[C]_0/[O]_0$) in steel before post-blow was allowed to vary from 0.167 to 4.167.

Figure 2 shows the effect of $[C]_0/[O]_0$ in steel before the post blow on the carbon and oxygen contents in the steel after 5 min of post blow of CO_2 . Dashed lines are the contents of carbon and oxygen before post-blow and solid lines are the contents of carbon and oxygen after 5 min post-blow. As shown by solid lines, carbon increases, and oxygen decreases in the steel after the post-blow. When $[C]_0/[O]_0 < 1$ in steel before post-blow, carbon content after post-blow ($[C]$ line) is higher than that before post-blow ($[C]_0$ line) indicating the carbon pickup during post-blow. When $[C]_0/[O]_0 > 1$ in steel before post-blow, carbon content after post-blow ($[C]$ line) is lower than that before post-blow ($[C]_0$ line) indicating the removal of carbon from the steel during post-blow. The oxygen content after post-blow ($[O]$ line) is higher than that before post-blow ($[O]_0$ line) indicating the oxygen pickup into the steel during post-blow.

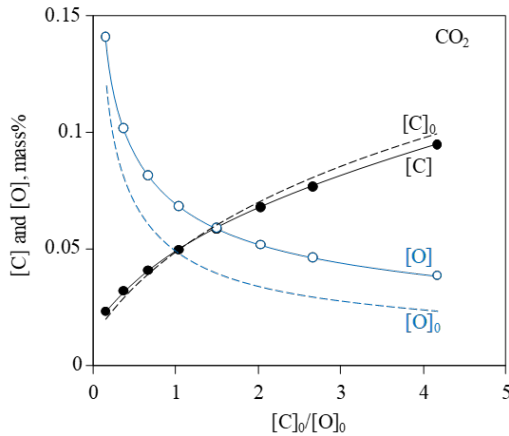


Fig.2. Effect of $[C]_0/[O]_0$ in steel before/after 5 minutes post-blow w on $[C]$ and $[O]$ in steel. Dashed line: contents before post-blow; Solid line: contents after post-blow.

As shown by red circles in Figure 3, the product of $[C][O]$ in steel before post-blow is 0.0024 mass% 2, and it becomes higher after 5 min post-blow of CO_2 , indicating $[C][O]$ increases by the post-blow. The product of $[C][O]$ after the post-blow was also found to increase by the increase of $[C]_0/[O]_0$ ratio in steel. Nitrogen and hydrogen in steel before post-blow are 0.002 mass% and 0.001 mass% respectively. Their contents after 5 minutes post-blow are also shown in Figure 3. $[N]$ is almost not removed by the post-blow but $[H]$ is decreased after 5 minutes post-blow. Hydrogen content after the post-blow is slightly decreased by the increase of $[C]_0/[O]_0$ ratio in steel.

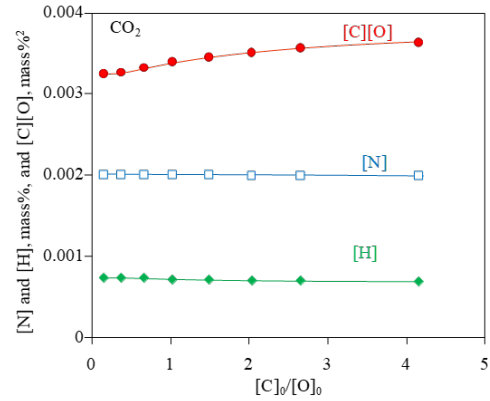


Fig.3. Effect of $[C]_0/[O]_0$ ratio in steel on $[N]$, $[H]$ and product of $[C][O]$ after post-blow.

The bottom-blown gas before the reaction is pure CO_2 , it changes after traveling through and reacting with the bath. The composition of reacted gas at the beginning of post-blow is shown in Figure 4(a). There is no argon in the reacted gas and CO is the major gas species in the reacted gas. CO is more than 80% and it is increased with increasing $[C]_0/[O]_0$ in the steel. H_2 is about 12% in the reacted gas due to the dehydrogenation of the steel by CO_2 bubbles. H_2 after post-blow was found to be independent of $[C]_0/[O]_0$ ratio in the steel. CO_2 and H_2O in the reacted gas are higher when $[C]_0/[O]_0$ ratio is lower in the steel. They decrease sharply when increasing the $[C]_0/[O]_0$ ratio in the steel. N_2 is very low in the reacted gas indicating the denitrogenization by bottom-blown is slow.

The composition of reacted gas at 5 minutes of post-blow of CO_2 as a function of $[C]_0/[O]_0$ ratio in the steel is shown in Figure 4(b). CO in the reacted gas is about 90% which is higher than that at the beginning of the post-blow. CO in the reacted gas at 5 minutes of post-blow increases with increasing $[C]_0/[O]_0$ ratio in the steel. H_2 is about 7% in the reacted gas at 5 minutes post-blow which is less than H_2 of 12% at the beginning of the post-blow, indicating dehydrogenation of the steel by CO_2 bubbles during post-blow becomes slower. H_2 in the reacted gas at 5 minutes post-blow slightly decreases with increasing $[C]_0/[O]_0$ ratio in the steel. CO_2 in the reacted gas at 5 minutes of post-blow is more than that at the beginning of the post-blow, and it decreases with increasing $[C]_0/[O]_0$ ratio in the steel. H_2O in the reacted gas at 5 minutes of post-blow is less than that at the beginning of the post-blow, and it also decreases with increasing $[C]_0/[O]_0$ ratio in the steel. N_2 is less than 0.01% in the reacted gas at 5 minutes blow.

The volume of injected gas is changed by the reaction with steel during the gas travel through the bath from its bottom to its top. Effect of $[C]_0/[O]_0$ ratio in steel on the volume of reacted gas produced by each

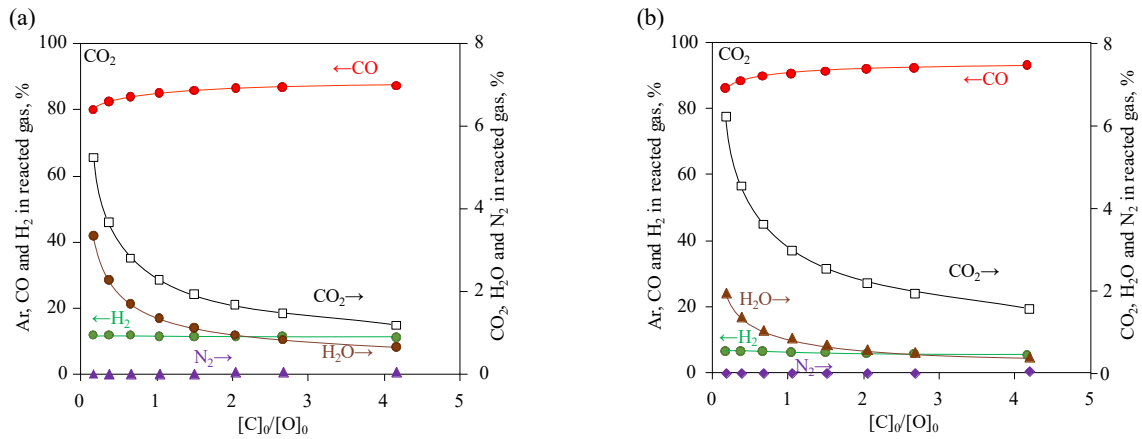


Fig.4. Effect of $[C]_0/[O]_0$ ratio in steel on the composition of reacted gas, (a) before and (b) after 5 minutes post-blow.

cubic meter of injected CO_2 is shown in Figure 5. “0 min” line is the volume of reacted gas at the beginning of the post-blow and “5 min” line is that at 5 minutes of post-blow. The volume of reacted gas increases with increasing $[C]_0/[O]_0$ ratio because high carbon in the steel allows more CO_2 to react with carbon through $\text{CO}_2 + \underline{\text{C}} = 2\text{CO}$ which increases the gas volume. The volume of reacted gas at 5 min of post-blow is larger than that at the beginning of the post-blow because oxygen is increased in the steel during the post-blow, which enhances the reaction of $\underline{\text{C}} + \underline{\text{O}} = \text{CO}$ to generate CO into the reacted gas. It is noted that, at the beginning of the post-blow, as shown by the “0 min” line, the volume of reacted gas is smaller than 1 cubic meter when $[C]_0/[O]_0$ ratio is less than 1 in the steel. This means the gas volume is decreased during the gas travel in the bath since the reactions of $\text{CO}_2 = \text{CO} + \underline{\text{O}}$ and $\text{CO} = \underline{\text{C}} + \underline{\text{O}}$ prevail over other degassing reactions. As a result, the gas volume is reduced while the gas bubbles travel in the bath.

3.2 Post Blow by CO_2 -Ar

Figure 6 shows the product of $[C][O]$, nitrogen content and hydrogen content in steel after 5 minutes post-blow. The product of $[C][O]$ is 0.0024 mass%² before post-blow. After the post-blow, the product of $[C][O]$ is increased with increasing CO_2 in the blown gas mixture, and it is lower than 0.0024 when $\text{CO}_2 < 42\%$ in the mixture and it is higher than 0.0024 when $\text{CO}_2 > 42\%$ in the mixture. This indicates there is less decarburization and deoxidation or more carbon pickup and oxygen pickup of steel when CO_2 content is higher in the mixture. $[N]$ is 0.002 mass% before post blow and it is unchanged during post blow. $[H]$ is 0.001 mass% before post blow and $[H]$ after the post blow is 0.0007 mass%. The effect of CO_2 in the mixture on $[H]$ after the post-blow is not observable.

Figure 7 shows the effect of CO_2 content in the

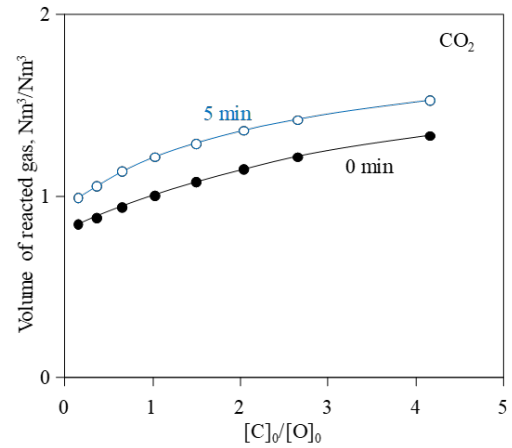


Fig.5. Effect of $[C]_0/[O]_0$ ratio in steel on the volume of reacted gas produced by each cubic meter of injected CO_2 at 0 and 5 minutes of post-blow.

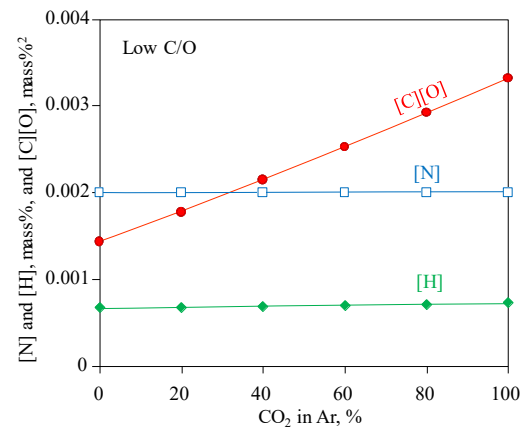


Fig.6. Effect of CO_2 in blown gas on $[N]$, $[H]$ and the product of $[C][O]$ in steel after 5 minutes post-blow.

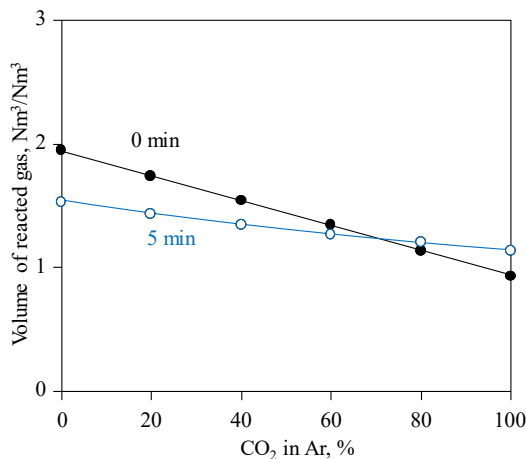


Fig.7. Effect of CO₂ in blown gas on the volume of reacted gas produced by each cubic meter of injected gas at 0 and 5 minutes post-blow.

injected CO₂-Ar mixture on the volume of reacted gas produced by each cubic meter of the mixture at 0 and 5 minutes post-blow.

The volume of reacted gas decreases with increasing CO₂ in the mixture because decarburization and deoxidation are promoted by the increase of argon fraction in the mixture. This indicates the stirring power in the bath by bottom blow is reduced when CO₂ replaces argon in the mixture. If the volume of reacted gas is smaller than 1 cubic meter, for example, when CO₂ in the mixture is close to 100% at the beginning of the post-blow, the volume of reacted gas is less than the gas mixture blown into the bath. This indicates the dissolution of CO₂ into steel through the reactions of $\text{CO}_2 = \text{CO} + \text{O}$ and $\text{CO} = \text{C} + \text{O}$ prevail over other degassing reactions by the bubbles.

4. CONCLUSIONS

The decarburization and deoxidation by bottom CO₂ and CO₂-Ar mixture post-blow in the BOF process were investigated using the bubble-bath reaction model. When CO₂ is used for the post-blow, it was found that:

1. The decarburization occurs when $[\text{C}]/[\text{O}]$ is higher in the steel and the carbon pickup occurs when $[\text{C}]/[\text{O}]$ is lower in the steel.
2. Oxygen is picked up into steel by blowing CO₂.
3. The product of $[\text{C}][\text{O}]$ increases by blowing CO₂ and it increases more significantly when $[\text{C}]/[\text{O}]$ is higher in the steel.

4. The volume of reacted gas in the earlier post-blow period is smaller than that in the final post-blow period and the volume of reacted gas increases with increasing $[\text{C}]/[\text{O}]$ ratio in the steel.

When the gas mixture of CO₂-Ar is used for the post-blow, and the steel contains 0.04 mass% carbon and 0.06 mass% oxygen, it was found that the product of $[\text{C}][\text{O}]$ in steel after the post blow increases with increasing CO₂ in the gas mixture, and if CO₂ is more than 50% in the gas mixture, the product of $[\text{C}][\text{O}]$ in steel was found to increase by the post-blow.

Therefore, when using CO₂ or CO₂-Ar mixture during post-blow in the BOF process, the decarburization and deoxidation reactions will be restricted. However, the proper use of a CO₂-Ar mixture during post-blow can further reduce the product of $[\text{C}][\text{O}]$, thereby improving the quality of the molten steel.

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