# $CO_2$ Utilization in the Ironmaking and Steelmaking Process

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**Abstract:** A overview on application of $CO_2$ in the ironmaking and steelmaking process is presented. Study on resource utilization of $CO_2$ is significant for the reduction of $CO_2$ emissions and the coping with global warming. The paper introduces the research progress of $CO_2$ utilization in the sintering, Blast Furnace, Converter, secondary refining, Continuous Casting and smelting process of stainless steel in recent years in China. According to the foreign and domestic research and application status, the paper analyzes the feasibility and metallurgical effects of the $CO_2$ utilization in the ferrous metallurgy process. The paper mainly introduces such new techniques as 1) flue gas circulating sintering, 2) blowing $CO_2$ through Blast Furnace tuyere and $CO_2$ as a pulverized coal carrier gas, 3) top and bottom blowing $CO_2$ in the converter, 4) Ladle Furnace and Electric Arc Furnace bottom blowing $CO_2$, 5) $CO_2$ as Continuous Casting shielding gas, 6) $CO_2$ for stainless steel smelting, and 7) $CO_2$ circulation combustion. $CO_2$ has a very wide application prospect in ferrous metallurgy process and the quantity of $CO_2$ utilization is expected to be 100kg per ton of steel. It will effectively facilitate the progress of metallurgical technology and strongly promote the energy conservation of metallurgical industry.

**Key words:** Carbon dioxide; Injection; Blast Furnace; Converter; Combustion

## 1 Introduction

Large amounts of carbon dioxide ($CO_2$) was exhausted in the ferrous industry because of its energy-intensive feature [1]. Carbon dioxide utilization has started to attract attention worldwide because it can turn waste $CO_2$ emissions into valuable products [2-6]. Study on resource utilization of $CO_2$ in the ferrous metallurgy process is significant for the reduction of $CO_2$ emissions and the coping with global warming. So far, there are three main ways to the emission reduction and utilization of $CO_2$. The first is to develop new technology and energy and to reduce the use of fossil energy. The second is to develop $CO_2$ storage technology. And the last is to use $CO_2$ as a recycling resource. At present, $CO_2$ emission reduction in metallurgical process mainly relies on the first way, i.e., energy saving and waste heat utilization.

Carbon dioxide is a linear three atom molecule. It is weak acid gas and is colorless and tasteless at room temperature. Its isobaric heat capacity is about 1.6 times higher than that of nitrogen, and its infrared radiation ability is strong. According to the above characteristics, it can play a role in stirring in the ferrous metallurgy process. It can also play a role in controlling the temperature of molten bath because of the carbon endothermic reaction, protecting molten steel from being oxidized and diluting oxidant in the combustion. In the realization of the $CO_2$ emission reduction, it is possible to save energy and reduce costs, and at the same time, improve the quality of the steel products.

$CO_2$ is a weaker oxidizing agent compared to $O_2$. It is possible for carbon dioxide oxidizing carbon, iron, silicon and manganese in molten bath at steelmaking temperature and the oxidation reactions are endothermic or slightly exothermic reactions respectively. Therefore, it is possible to control the temperature and atmosphere by adopting $CO_2$ in steelmaking process, hence realizing the aims of 1) reducing the dust generation, 2) purifying the liquid steel, 3) minimizing the loss of valuable metals, 4) saving the energy and 5) reducing the total consumption etc. So far some applications in the ferrous metallurgy process are shown in Fig.1.

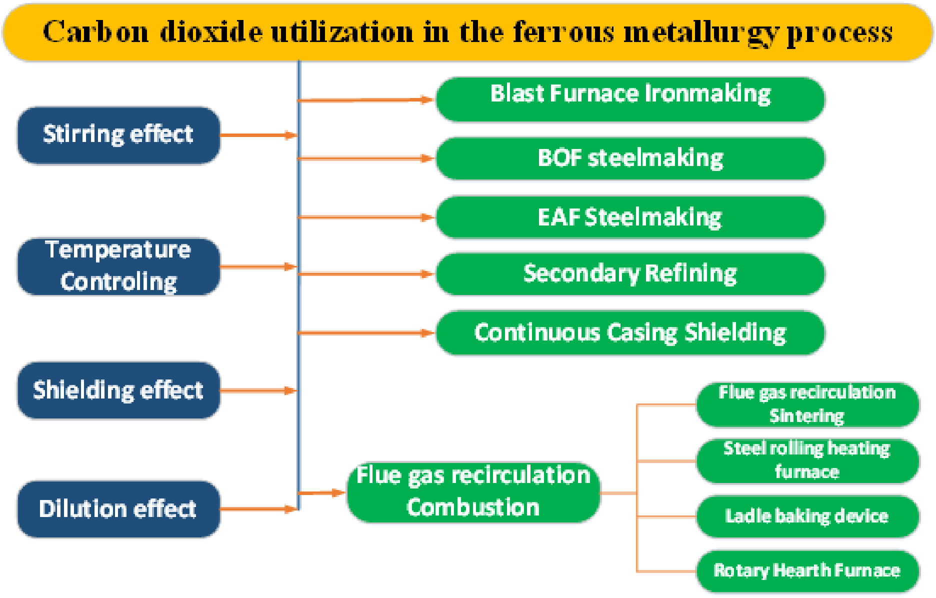


Fig.1 Carbon dioxide utilization in the ferrous metallurgy process

## 2 Application in steelmaking process

### 2.1 Top-blowing carbon dioxide in Converter

As Table 1 shows, compared with pure oxygen, the thermal effect of the reaction is relatively decreased when using $CO_2$ in the steelmaking process as oxidizing agent, due to the endothermic or micro exothermic reaction of $CO_2$ in the molten bath. Therefore, the converter can blow a certain proportion of $CO_2$ from the top to achieve temperature control in the dephosphorization process and create good thermodynamic conditions for the dephosphorization reaction. At the same time, the use of $CO_2$ in reaction can produce more stirring gas, which is conducive to strengthen bath stirring, and create favorable dynamic conditions for dephosphorization reaction.

Since 2004, Zhu Rong et al. [7-14] has committed the basic exploration research and the industrial tests of $CO_2$ utilization in steelmaking. After researching for a decade, they applied $CO_2$ in the top-blowing of Basic Oxygen Furnace (BOF) and researched $CO_2$ injection technology of top-blowing in converter. $CO_2$ was mixed in the oxygen jet and it was used in the bottom blowing of converter. In the Induction Furnace and Converter, top blowing the mixture of $O_2$-$CO_2$ has been realized. The study found that when top-bottom blowing $CO_2$ in the converter, the dust is reduced by 19.13%, total Fe in the dust decreased by 12.98% and the slag iron loss reduced by 3.10%. As the agitation effect and the temperature controlling is improved, the dephosphorization rate is increased by 6.12%, reducing the nitrogen content of the molten steel and improving the quality of the molten steel. In the BOF, not all the $CO_2$ blown into participates in

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chemical reaction. According to some test results, about 80~90% of $CO_2$ participates at 1600℃.

Top-blowing carbon dioxide in the converter is the main breakthroughs obtained in China.

In China, the new technology of top-blowing carbon dioxide in the converter steelmaking has been applied in Shougang Jingtang Company and achieves good results. There is a wide range of $CO_2$ sources in the iron and steel enterprises. It provides a convenient condition for the converter blowing $CO_2$.

**2.2 Bottom-blowing carbon dioxide in BOF**

In 1970s, the scholars began to study bottom-blowing $CO_2$ in the converter steelmaking process and found [9] that $CO_2$ can participate in bath reaction and its bottom-blowing agitation ability is stronger than Ar and $N_2$, unlike that in the top and bottom blowing converter blowing $N_2$/Ar from the bottom which is easy to make [N] increase, and also unlike blowing $O_2/C_xH_y$ from the bottom which is easy to make [H] increase. $CO_2$ is an effective alternatives to high-cost Ar and potentially harmful $N_2$ [15-17].

In 1990s, Angang researchers [18] studied the bottom blowing $CO_2$ in the top and bottom blowing converter and found that $CO_2$ can be used in the bottom blowing of top-bottom blowing converter. Some oxygen was mixed in the bottom blowing gas to prevent the strong cooling effect of the bottom blowing $CO_2$ gas from making the nozzle clog. Unfortunately, it was stopped using due to the problem of the blowing brick's life.

Recent studies have found that by bottom blowing $CO_2$, the converter iron loss of slag can be reduced, the bath stirring can be strengthened, and the dephosphorization rate can be improved. In 2009, bottom-blowing $CO_2$ industrial experiment on the 30t converter was conducted in China. The results show that the converter of bottom blowing $CO_2$ is feasible, with no obvious erosion of the hearth [19].

**2.3 Bottom-blowing stirring of Ladle Furnace**

Previously the bottom blowing of $CO_2$ in a ladle had been studied instead of Ar for stirring to avoid the re-oxidation and the hydrogen and nitrogen absorption when molten steel was heating in the LF. We [20] studied the stirring mechanism of bottom blowing $CO_2$ during LF refining process. Exploratory industrial experiment was conducted and different proportions of $CO_2$ and Ar gas mixtures were bottom blown in a 75t LF. The results showed that stirring was reinforced when blowing $CO_2$ and the desulfurization rate was increased from 49.7 to 65.1% and the average slag (FeO) content is less than 0.5%, which can meet the oxidizing slag requirements. Changes were small for the type and the morphology and the composition of the inclusions in molten steel. Besides, the inclusion equivalent density was decreased and the cleanliness of liquid steel was improved. The tests showed that LF furnace can use $CO_2$ gas for refining.

**2.4 Bottom-blowing stirring in Electric Arc Furnace**

Since the emergence of Electric Arc Furnace (EAF) bottom blowing technology in the 1980s, scholars studied many problems about EAF bottom blowing optimization and found that the EAF bottom blowing technology can improve the bath agitation ability, promote the inter-slag reaction and uniform bath temperature and composition, and improve the alloy yield. It is of great significance to improve the conditions of the furnace dynamics.

Industrial experiments [20] of bottom-blowing $CO_2$ in a 65t Consteel EAF verified that bottom-blowing $CO_2$ instead of Ar is feasible. The studies have shown that compared with the conventional bottom-blown

Ar process, bottom-blowing $CO_2$ increases the end [C] content and oxidizes a small amount of [Cr], but the content of [Mn], [Mo], [O] and [N] is not influenced. This method can also enhance the bath stirring, raise the basicity, and reduce the slag (FeO) content. It provided a good kinetic and thermodynamic condition for EAF desulfurization, with desulfurization degree increasing by 7%, a good bath stirring for dephosphorization.

### 2.5 Shielding gas in continuous casting process

In 1989, reference [21] introduced that a US company applied $CO_2$, instead of Ar, to protect the injection flow when casting special steel rod. $CO_2$ will fall in parallel with the injection flow through the upper portion of the upper casing or spiral holes, maintaining the positive pressure of the stream around to prevent air suction. It shows great effect in cutting off the liquid steel from the air and preventing the oxidation of the molten steel.

To solve continuous casting problems of using Ar with a high cost and using $CO_2$ with specific process issues, our team conducted experiments in a steel plant and found that when using $CO_2$, instead of Ar, in submerged nozzle seal protection, the [N] content is increased. When bottom blowing Ar for 40Cr steel and 45 steel, the [N] content is increased by 10.4% and 53.6%, respectively. While bottom blowing $CO_2$ for 40Cr steel and 45 steel, the [N] content is increased by 17.6% and 54.4%, respectively. Both were basically the same. When observing $CO_2$-protected steel, [O] content is shown to be decreased. $CO_2$ can play a protective role in casting. Analyzing steel gas composition before and after protective casting, we found that using $CO_2$, instead of Ar, in the protective continuous casting can reduce the secondary oxidation.

The amount of $CO_2$ emission utilization in the BF steelmaking process will be greater than 40kg/ tons of steel.

## 3 Application in sintering and Blast Furnace

### 3.1 Flue gas recirculation (FGR) sintering

The main component flue gas in sintering is $CO_2$. Typical Flue Gas Recirculation (FGR, Fig.2) sintering [22] includes the waste gas regional recirculation process developed by Nippon Steel [26], the Exhaust Gas Recirculation (EGR) sintering technology developed by Hata [23], the Emission Optimized Sintering (EOS) process developed by Corus Ijmuiden in Netherlands [24], the LEEP (Low emission and energy optimized sintering process) developed by HKM and the EPOSINT (Environmental process optimized sintering) process developed by Siemens VAI [25-28].

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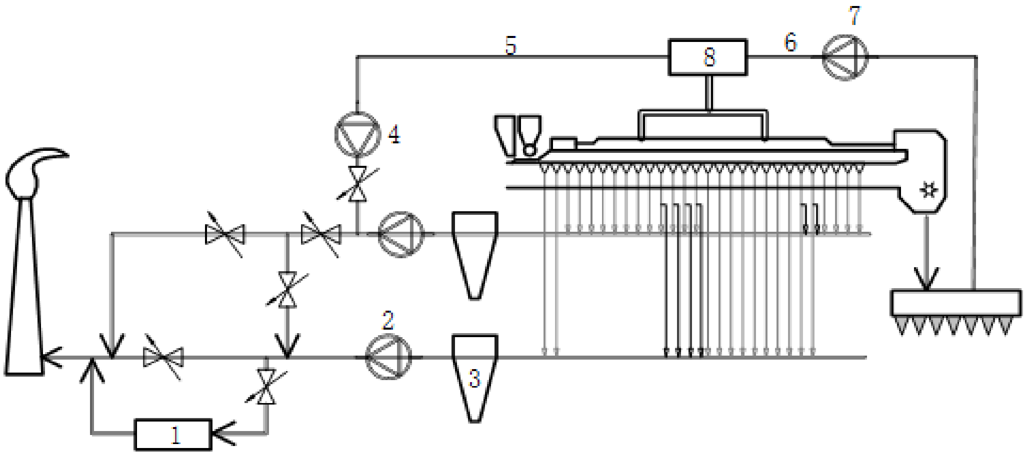


1-Desulfurization system, 2-Main exhaust fan, 3-Dust catcher, 4-Circulating air blower, 5-Large flue circulating flue gas, 6-Air cooling hot exhaust gas, 7-Air cooling heat recovery fan, 8-Flue gas mixing chamber.

**Fig.2 Flow diagram of flue gas circulation sintering process**

The existing recycling technology still has the following disadvantages [22-23]:

1) In the Nippon Steel recycling process, only high oxygen flue gas is circulated. Flue gas emission reduction rate is, relatively low, about 28%. Circulation process is complex and it is difficult for modifying sintering machine. 2) EOS technology has not considered the characteristics of sintering flue gas emission, and the effect of dealing with different components in the flue gas is not the best. 3) In the LEEP technology, the front and rear flue gas for heat transfer, the heat of high temperature flue gas is not fully utilized. The rear part of flue gas is of high content of $SO_2$, which result in that the sintering ore [S] content increases. 4) EPOSINT process only makes high sulfur gas cycle, reduce emission rate is low, 28%~25%. The flue gas is of high content of $SO_2$, which result in that the sintering ore [S] content increases. In addition, the high temperature flue gas is not circulating, the energy saving rate is low, and the rate of dioxin emission reduction is also low.

### 3.2 $CO_2$ injection through Blast Furnace tuyere

In 2010, Fu Zhengxue [29] et al. developed a method of injecting carbon dioxide into Blast Furnace (BF). Blowing $CO_2$ or the exhaust gas containing $CO_2$ into BF can effectively solve some ironmaking problems such as resources saving, $CO_2$ emissions reduction and environmental pollution elimination. The technical scheme is: firstly, $CO_2$ or the waste gas containing $CO_2$ is blown into BF cooling pipes. After heating the hot blast stove, $CO_2$ is blown or sprayed into the BF tuyere zone by the hot air pipeline. Oxygen reacts with the burning carbon in the tuyere zone and then $CO_2$ generates. $CO_2$ of New generation and $CO_2$ blown into the BF tuyere zone to react with the hot carbon then is all transformed into CO. CO is the smelting reduction agent of BF, thus achieving the purpose of blowing $CO_2$ into BF. However, the technology has not been industrialized application.

### 3.3 Carrier gas of pulverized coal injection

In 2011, China researchers [30] invented a method to use $CO_2$ as the transmission medium of pulverized coal injected into BF (Fig.3). Mixed coal powder is used in BF tuyere to replace coke, providing heat and reduce agent.

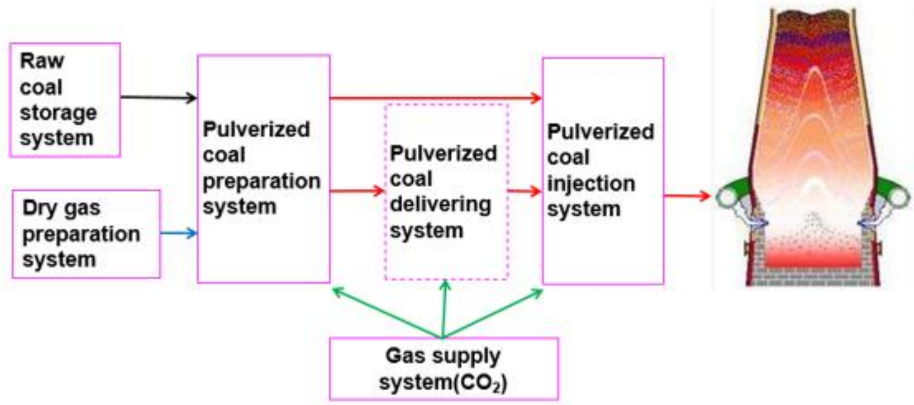


Fig.3 Flow diagram of pulverized coal injection of BF

After $CO_2$ is used as a transmission medium, pulverized coal in the tuyere zone reacts not only with the enriched $CO_2$, but also with the oxygen from hot air. It is necessary to adjust the amount of pulverized coal injection and the oxygen enrichment level to achieve the best ratio and promote complete combustion of the pulverized coal in front of the tuyere. Due to the use of $CO_2$, instead of the compressed air or nitrogen as the transmission medium, the total amount of exhaust gas through BF should be reduced, which will significantly reduce the nitrogen content and increase the amount of $CO_2$ + CO. Therefore, the purity and calorific value of BF gas increase.

So far there is no industrial application being reported for the above two patents. But $CO_2$ injection through Blast Furnace tuyere creates a new route of $CO_2$ utilization, increase $CO_2$ consumption, and pushes $CO_2$ utilization to a new height. The amount of $CO_2$ utilization in the BF process will be greater than 50kg/ tons of iron.

## 4 Application in other ferrous metallurgy process

### 4.1 Application in smelting stainless steel

In 2011, Anshan Iron and Steel Co., Ltd. [31] invented a smelting method of AOD by blowing $CO_2$ to produce stainless steel, which is mainly about injecting $CO_2$ to the molten steel to enhance the decarburization ability of molten steel and be suitable for smelting steel whose carbon content ranges from 0.001% to 0.3%. $CO_2$ injected into the molten steel not only can decarburize, but also enhance the bath stirring. Besides, it can promote oxygen reaction and cool oxygen lance whose life is improved by 20%.

Our team studied the mechanism of Cr retention and decarburization when injecting $CO_2$ to AOD from the aspects of thermodynamics and kinetics. In laboratory, tube furnace experiments found that the Cr retention and decarburization effect of $CO_2$ is very good and the carbon content steel can reach 0.5%, with little chromium oxidation occurring. When $O_2$ proportion of smelting gas is increased, the decarburization effect would be reduced, and large amounts of chromium oxidation occurred. Analyzing the changes in

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materials and the energy balance found that it will meet the requirements of refining temperature when $CO_2$ injection ratio is less than 9.13%. As the proportion of $CO_2$ increases within this range, AOD furnace surplus heat is reduced, and CO proportion of furnace gas is increased.

### 4.2 $CO_2$ circulation combustion

$CO_2$ circulation combustion technology uses recycling flu gas to replace the nitrogen in the air (Fig.4). It can reduce nitric oxide emissions and improve the thermal efficiency of combustion [32]. When it was applied in the vessel pre-heating process, nitric oxide emissions reduced, and thermal efficiency was improved. Its application in steel rolling heating furnace and pit furnace can reduce the fuel consumption, shorten the heating time, and reduce nitrogen oxide emissions.

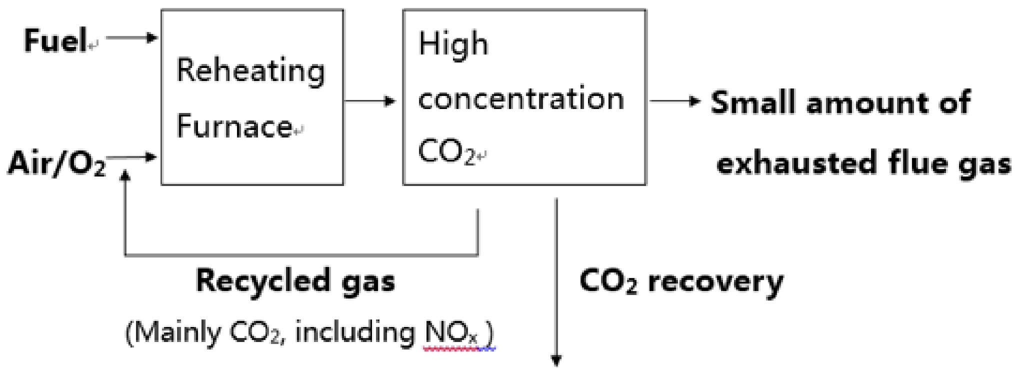


Fig.4 Flow diagram of flue gas circulation combustion technology

In 1920s, Linde Group [33] tried applying flameless combustion for heating in the ferrous industry, reducing fuel consumption and emissions of $NO_x$ and $CO_2$ through the development of special burner to realize the special way of combustion. In addition, the Swedish Hofors works Ovako also used the technology in the heating furnace (Fig.5), finding that the production is increased by 30-50%, the fuel is reduced by 30-45%, with more uniform heating and reduction of $CO_2$ and $NO_x$ emissions.

Fig.5 Flameless oxyfuel burner installation at Outokumpu, Nyby[37]

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## 5 Conclusions

$CO_2$ utilization in the ferrous metallurgy process is listed in many aspects, such as directly being blown in BF and Converter, serving as carrier gas of coal injection in BF, using as shielding gas and mixing gas in refining, continuous casting process and stainless steelmaking, and circulating using in the exhaust gas of steel rolling heating furnace. All of that reflect the special role that $CO_2$ plays in the ferrous metallurgy process.

In China, country policies of $CO_2$ utilization and emission reduction are actively carried out. The historical carbon emissions of carbon emission is being investigated, so as to build a unified nationwide carbon emissions trading system. Meanwhile some Chinese steel plants have carried out the practice of carbon utilization in the production flow. The technology of top and bottom blowing $CO_2$ in the 300t converter has been applied and achieved good results.

With the continuous improvement of application technology and further expansion of application field for $CO_2$ in the ferrous metallurgy process, carbon dioxide usage in the ferrous metallurgy process is expected to be 100~200 kg per ton steel. At present, annual steel output of China is about 800 million tons. Therefore, the annual recycling $CO_2$ utilization is around 80 million tons in metallurgical process, which will effectively facilitate the progress of metallurgical technology, strongly promoting the energy conservation of metallurgical industry. It is in need of the sustainable development of China.

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