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Massive Injection of Auxiliary Reducing Agent at Blast Furnace for the Sustainable Development

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Laboratory of Energy Media
Hokkaido University
2016
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   3. 3 Modeling of flow behavior of plastic particles in the lower part of blast furnace
   3. 4 Effect of initial plastic size on the operation of actual blast furnace
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Acknowledgement.
Chapter 1 General Introduction

1.1 Current status of global warming and the roles to be performed by steel making industries

Considerable effort has been made to cope with global warming problem all over the world. The 2015 United Nations Climate Change Conference, COP 21 was held in Paris in late 2015. Several countermeasures were agreed among representatives of the 196 parties who participated in the conference. For example, goal of limiting global warming was set to less than 2 degrees Celsius and they pursue efforts to limit the temperature increase to 1.5 degrees Celsius. In addition, zero net anthropogenic greenhouse gas (GHG) emissions was mentioned as a long-term challenge\(^1\).

Fig. 1-1 shows total annual anthropogenic GHG emissions by gases in 2010\(^2\). Although there are several GHG such as carbon dioxide, methane, nitrous oxide and fluorinated gases, carbon dioxide occupies the majority of them. Therefore, it is considered that significance of carbon dioxide mitigation is extremely great.

As shown in Fig. 1-2, total amount of carbon dioxide emission in Japan was 1.27 Gt-CO\(_2\) in 2014, and share of iron and steel making industry accounts for 15\(^%\)\(^3\). This value is the largest among the industry sector.

The Japan Iron and Steel Federation announced “Report of Commitment to a Low Carbon Society” in January 2015\(^4\). It consists of improvement of coke oven efficiency, more efficient electricity generation, more energy conservation, use of used plastics and development and use revolutionary technologies (Table 1-1). Used plastics contain large amount of hydrogen compared to coke. Use of used plastics as auxiliary reducing agent at blast furnace may reduce carbon dioxide
emissions because of promotion of hydrogen reduction.

Coke is main reducing agent at blast furnace, however, it contains a few hydrogen. Pulverized coal, heavy oil and natural gas has been used as auxiliary reducing agent conventionally\(^5,6\). These materials contain more hydrogen compared to coke as well as plastics. Therefore, massive auxiliary reducing agent injection at blast furnace could be reduce carbon dioxide emissions from iron and steel industries, and it is considered to be contribute to the global warming problem.
R. Murai, “Massive Injection of Auxiliary Reducing Agent at Blast Furnace for the Sustainable Development.”

Fig. 1-2 Japan GHG emissions data (CO$_2$ emissions by sector) in 2014$^3$.

Table 1-1 CO$_2$ reduction targets by the Japan Iron and Steel Federation$^4$. 

<table>
<thead>
<tr>
<th>Actions</th>
<th>Phase II 2030</th>
<th>Phase I 2020</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Improve coke oven efficiency</td>
<td>About 1.3mn tons of CO$_2$</td>
<td>About 0.9mn tons of CO$_2$</td>
</tr>
<tr>
<td>(2) More efficient electricity generation</td>
<td>About 1.6mn tons of CO$_2$</td>
<td>About 1.1mn tons of CO$_2$</td>
</tr>
<tr>
<td>(3) More energy conservation</td>
<td>About 1.5mn tons of CO$_2$</td>
<td>About 1.0mn tons of CO$_2$</td>
</tr>
<tr>
<td>(4) Waste plastics$^2$</td>
<td>2.0mn tons of CO$_2$</td>
<td>2.0mn tons of CO$_2$</td>
</tr>
<tr>
<td>(5) Develop and use revolutionary technologies$^3$</td>
<td>About 2.6mn tons of CO$_2$</td>
<td>—</td>
</tr>
</tbody>
</table>

Total 9mn tons of CO$_2$ 5mn tons of CO$_2$

* These reductions do not include the effect of changes in the electric power emissions coefficient.
1. 2 Review on resent technologies of auxiliary reducing agent injection to blast furnace

1. 2. 1 Liquid auxiliary reducing agent injection

By the concern over tightening supply and demand or the steep rise in prices of coking coal, injection of liquid auxiliary reducing agent injection into blast furnaces had been studied in the 1960s. For example, heavy oil\(^7,8\), coal tar\(^9,10\), naphtha\(^11\), coal slurry\(^12\) and coal oil mixture\(^{13,15}\) was used as liquid phase reducing agent. Heavy oil injection operation at blast furnace in Japan was started in 1961. Since liquid auxiliary reducing agent injection could contribute to achieve a low reducing agent operation, steel making company installed the facility rapidly and all of 42 blast furnaces were operated with heavy oil injection in 1964.

However, after so called oil crisis in 1973 and 1979, injection operation of liquid reducing agent tended to decline rapidly because of loss of price competitiveness. Finally, all of blast furnace in Japan had stopped injecting liquid reducing agent by 1982.

1. 2. 2 Solid auxiliary reducing agent injection

After oil crisis, pulverized coal injection operation began to adopt widely instead of liquid reducing agent injection\(^{16,17}\). This method capable of using the inexpensive steam coal (slightly or non caking coal) is attractive for the steel making industry. Pulverized coal injection operation at blast furnace in Japan was started in 1981 and all of blast furnaces were installed the coal injection facility by 1998.
With the spread of pulverized coal injection operation, researches on the coal combustion have also been conducted. They include studies on effect of kind of coal, combustion behavior of single coal particle, combustion experiments using experimental furnace, development of injection lances, analysis of change in in-furnace situation and numerical simulations. As a result, massive injection of pulverized coal technology has been established to some extent.

Used (or waste) plastics are also attractive as a reducing agent. Use of used plastics as reducing agent of blast furnace is so effective from the viewpoint of construction of a circulation type society. Moreover, as mentioned before, amount of fossil fuel such as coal and coke can be reduced by using used plastics, so used plastics injection into blast furnace can be considered to be a mitigation technology of carbon dioxide emissions.

According to the statistics in 2011, total amount of used plastics (sum of municipal and industrial) was about 9.5 million ton. They were buried or directly incinerated in the past. However, after establishment of “Containers and Packaging Recycling Law” in 1995, ratio of effective use such as thermal recycling or material recycling increased rapidly.

Used plastics injection into blast furnace was started in Germany at first in 1995. Only a one year later in 1996, used plastics injection operation at blast furnace was started in Japan. To maintain a stable operation under the plastics injection, several researches have been conducted so far. They include studies on gasification behavior of single plastic particle, gasification experiments using experimental furnace, analysis of change in in-furnace situation and theoretical studies. Plastics have an elasto-plasticity and are difficult to pulverize. Therefore rather coarse (about 2 to 10mm in diameter)
plastics were used conventionally. However, rate of gasification reaction of solid particle depends on its particle diameter (specific surface area) generally \(^{74}\), so simple and inexpensive pulverizing method has been desired. Asanuma \(^{75}\) et al. developed APR process (Advanced Plastics Recycling, or fine plastic particle production process) that contributes to stable plastic injection operation.

1. 2. 3 Gas auxiliary reducing agent injection

Injection of gas phase auxiliary reducing agent such as natural gas \(^{76-79}\), coke oven gas \(^{80-82}\), and basic oxygen furnace gas \(^{83}\) was adopted from the past because handling of them was easy compared with solid reducing agent. Moreover, because ignition of gas phase auxiliary reducing agent is so fast, they can be used to promote the gasifying or combustion of solid auxiliary reducing agent \(^{84-86}\).

To suppress the soot generation originated from unburnt fraction of gas phase auxiliary reducing agent, it has been pointed out that mixing of gas and hot blast is important. Therefore, several injection methods have been proposed \(^{87}\).

1. 3 Roles of oxygen on the auxiliary reducing agent reaction and conventional oxygen production methods

1. 3. 1 Reaction of auxiliary reducing agent and oxygen

For simplicity, the case that auxiliary reducing agent is pulverized coal is considered. Although the fact that high oxygen content may enhance combustion efficiency can be understood by sensation, Ariyama et al. explained this phenomenon based on the observation result\(^{23}\). Fig. 1-3 shows combustion
behavior of single pulverized coal particle in laminar flow furnace (drop tube furnace). Volatile matter of coal is 33.3 wt%, and furnace temperature set at 1200 degree Celsius. Oxygen content was changed from 7 to 25 vol%. They paid attention to the size of combustion flame. In the case of high oxygen content, flame size is relatively small. The mechanism of this phenomenon can be describe as shown in Fig. 1-4. Combustion and consumption of volatile matter evolved from coal particle may be promoted in the case of high oxygen concentration. So, flame is located in the very vicinity of the particle. As a result, heat exchange between coal particle and combustion flame may also be promoted. With such a synergistic effect, combustion efficiency may increase in the case of high oxygen content. Therefore, to increase in injection rate of auxiliary reducing agent, oxygen may play important role. It can be said that development of a novel, economically viable oxygen production process is urgent need.
Fig. 1-3 Observation of burning behavior of coal particle under different oxygen content conditions.\textsuperscript{23}
Fig. 1-4 Schematic representation of combustion mechanism of a single coal particle.23)

1.3.2 Conventional oxygen production method

Currently, cryogenic air separation is most popular oxygen production method. In this process, oxygen, nitrogen, and argon are separated by the difference of their boiling points. Boiling points of oxygen, nitrogen, and argon are 90, 77, and 87 K respectively.

In typical cryogenic air separation, air is compressed from atmospheric pressure to 450 kPa·G and is cooled to around 73 K by the adiabatic expansion. Oxygen content of air is only a 20.9 vol%. It means that air with 5 times by volume
of oxygen must be compressed. Therefore, the problem of cryogenic air separation is use of large amount of electrical power per unit oxygen. For example, specific power consumption is around 0.36 kWh/Nm³-O₂ at large scale cryogenic air separation with a capacity of 60,000 Nm³/h class[^88].

Pressure Swing Adsorption (PSA) is another route to separate oxygen from the air. Each gas may be adsorbed on the surface of solid (adsorbents) under the higher pressure. When the pressure is decreased, gas may be released. Affinity between each gas and adsorbents (or equilibrium adsorption quantity) is different. By choosing adsorbent and pressure swing width appropriately, oxygen and nitrogen can be separated from air. Table 1-2 shows classification of PSA process[^89]. Each process is sorted by the product gas, operating pressure, adsorbent, and product gas. Regarding oxygen separation process, nitrogen gas is adsorbed and released. So, purity is at most 95 vol% because argon gas in the air can not be removed by this process. Moreover, nitrogen gas occupies majority of 79.1 vol% in the air. So it is suggested that direct separation of oxygen may decrease cost of oxygen production. Table 1-3 shows PSA cost comparison of each gas production[^90]. Specific power consumption of oxygen production is the range from 0.31 to 0.34 kWh/Nm³-O₂.
Table 1-2 Classification of pressure swing adsorption process \(^{89}\).

<table>
<thead>
<tr>
<th>Product Gas</th>
<th>Operating Pressure</th>
<th>Adsorption Pressure</th>
<th>Adsorbent</th>
<th>Product Gas</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.5~1 MPaG</td>
<td>1 atm</td>
<td>PSA</td>
<td>Alumina, ZMS</td>
<td>H₂O &lt; 100 ppm Dryer, Instrument Air</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Non-Adsorption Gas</td>
</tr>
<tr>
<td>N₂</td>
<td>0.5~1 MPaG</td>
<td>1 atm</td>
<td>PSA</td>
<td>MSC</td>
<td>Max.0.9999% Heating Treatment Sealing</td>
</tr>
<tr>
<td>O₂</td>
<td>0.2~0.4 MPaG</td>
<td>1 atm</td>
<td>PSA</td>
<td>ZMS</td>
<td>Max.0.95% Non-Adsorption Gas Mini-Mill, Incinerator, Ozonizer, Glass Making, Medical Use</td>
</tr>
<tr>
<td></td>
<td>1 atm</td>
<td>Vacuum</td>
<td>VSA</td>
<td>ZMS</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.01~0.05 MPaG</td>
<td>Vacuum</td>
<td>VPSA</td>
<td>ZM</td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>over 0.5 MPaG</td>
<td>1 atm</td>
<td>PSA</td>
<td>Activated Carbon, MSC, ZMS</td>
<td>Max.0.9999% Non-Adsorption Gas Semiconductor Manufacturing, Fuel Cell, Glass Making, Heat Treatment</td>
</tr>
<tr>
<td>CO₂</td>
<td>1 atm</td>
<td>Vacuum</td>
<td>VSA</td>
<td>MSC, ZMS</td>
<td>Max.0.98% Adsorption Gas Food Additives, Dry Ice, Welding</td>
</tr>
<tr>
<td>CO</td>
<td>1 atm</td>
<td>Vacuum</td>
<td>VSA</td>
<td>Complex</td>
<td>Max.0.98% Adsorption Gas Chemicals</td>
</tr>
<tr>
<td>Ar</td>
<td>1 atm</td>
<td>Vacuum</td>
<td>VSA</td>
<td>ZMS</td>
<td>Max.0.98% Non-Adsorption Gas Steel Making, Silicon Wafer Manufacturing</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.2~1 MPaG</td>
<td>Vacuum</td>
<td>PSA</td>
<td>MSC</td>
<td>Max.0.98% Non-Adsorption Gas Fuel</td>
</tr>
<tr>
<td></td>
<td>0.01~0.05 MPaG</td>
<td>Vacuum</td>
<td>PVS A</td>
<td>MSC</td>
<td></td>
</tr>
</tbody>
</table>

Table 1-3 PSA cost comparison of each gas production \(^{90}\).

<table>
<thead>
<tr>
<th>Product Gas Purity</th>
<th>O₂ PSA/O₂ PVSA Production</th>
<th>Ni PSA/O₂ PVSA Production</th>
<th>Simultaneous O₂/N₂ Production</th>
<th>O₂ Recovery from Desorption Gas of Ni PSA</th>
<th>O₂ PSVA</th>
<th>N₂ PSA</th>
<th>O₂ PSVA</th>
<th>N₂ PSA</th>
<th>Compressor</th>
</tr>
</thead>
<tbody>
<tr>
<td>90% O₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>95% N₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂ &lt; 1 PPM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DP: -60°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Product Gas Flow Rate</td>
<td>340Nm³/h</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific Power</td>
<td>0.34kW/Nm³</td>
<td>0.24kW/Nm³</td>
<td>equivalent to 0.21kW/Nm³</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Gas Cost</th>
<th>Fixed Cost</th>
<th>6.4 Yen/Nm³</th>
<th>1.8 Yen/Nm³</th>
<th>6.0 Yen/Nm³</th>
<th>1.8 Yen/Nm³</th>
<th>6.4 Yen/Nm³</th>
<th>0.9 Yen/Nm³</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Variable Cost</td>
<td>3.4 Yen/Nm³</td>
<td>2.4 Yen/Nm³</td>
<td>3.1 Yen/Nm³</td>
<td>2.4 Yen/Nm³</td>
<td>3.4 Yen/Nm³</td>
<td>1.7 Yen/Nm³</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>9.8 Yen/Nm³</td>
<td>4.2 Yen/Nm³</td>
<td>9.1 Yen/Nm³</td>
<td>4.2 Yen/Nm³</td>
<td>9.8 Yen/Nm³</td>
<td>2.6 Yen/Nm³</td>
</tr>
<tr>
<td></td>
<td>Annual Cost</td>
<td>25,056,000 Yen</td>
<td>4,536,000 Yen</td>
<td>22,558,000 Yen</td>
<td>4,536,000 Yen</td>
<td>20,656,000 Yen</td>
<td>2,808,000 Yen</td>
</tr>
<tr>
<td></td>
<td>Annual Saving</td>
<td>4,086,000 Yen</td>
<td>3,226,000 Yen</td>
<td>4,086,000 Yen</td>
<td>3,226,000 Yen</td>
<td>4,086,000 Yen</td>
<td>3,226,000 Yen</td>
</tr>
</tbody>
</table>
1. **Needs of furnace wall protection under massive injection of auxiliary reducing agent**

1. 4. **Accumulation of fine in a blast furnace and gas flow segregation toward wall side**

The residential time of coke in blast furnace is prolonged in the case of high rate injection of auxiliary reducing agent\(^9\). So degradation of coke may be promoted and amount of coke fine is increased. Generated coke fine may accumulate to deadman region and the phenomenon leads to decrease in permeability and gas flow segregation to wall side. Therefore, heat load to wall tends to increase.

Heat load to furnace wall is also increased by the decrease of heat flux ratio. Heat flux ratio is calculated by dividing heat capacity flux of solid by heat capacity flux of gas. Amount of coke consumption at the raceway decreases because injected auxiliary reducing agent is consumed instead. So heat flux ratio decreases with increasing auxiliary reducing agent injection rate. It is thought that decrease in heat flux ratio lead to increase in temperature of solid (burden). According to the direct measurement of temperature distributions in actual blast furnace by vertical probe, increase in temperature at shaft part is confirmed and heat load to the wall increases\(^{16}\).

Furthermore, it is pointed out that the highest temperature region (combustion focus) in raceway comes closer to wall side at a higher injection rate of auxiliary reducing agent\(^9\). Wall temperature tends to increase as point of combustion focus approaches to the wall according to study results of experimental furnace\(^9\).
Formation of raceway shell (or bird’s nest) is another noteworthy phenomenon to describe increase in the heat load to wall\(^{27,94}\). Raceway shell is low permeability layer formed at the end of raceway consisting of coke fine and low viscosity ash which comes from solid auxiliary reducing agent. Once the raceway shell is formed, gas permeability towards the inside of the furnace decreases. As a result of this phenomenon, peripheral gas flow is intensified and heat load to wall increases.

1.4.2 Overview of conventional cooling system of blast furnace

As mentioned in previous section, because of increase in heat load to wall, furnace wall protection or enhancement of cooling capability is definitely important. Therefore, cooling system of blast furnace is reviewed in this section.

Cooling plate system was widely used before 1969 in Japanese blast furnaces\(^95\). The system is cooling method by inserting cooling plate into furnace wall brick. Cooling capability is rather low and leakage of in-furnace gas is occurred because thermal expansion ratio is different between cooling plate, wall brick, and furnace steel shell.

To solve such problem, cooling stave (CS) was adopted\(^{95,96}\). Shaft part of the blast furnace can be cooled from wide plane, so the cooling capability increases considerably. To prolong CS campaign life, CS has been improved over the years. For example, water feed system, arrangement of water cooling pipe, design of CS body structure, and materials were improved\(^{97-99}\).

As for material, low chromium cast iron was used at first. Next, ductile cast iron was used to prevent cracks. Thermal conductivity of copper is considerably high compared with cast iron\(^{100,101}\). So excellent cooling capability can be expected
by use of copper CS. Development of cast copper CS is discussed in chapter 5.

1.5 Purpose and contents of this thesis

The purpose of this thesis is to increase injection rate of auxiliary reducing agent by solving above mentioned problems. It is considered that it makes mitigation of carbon dioxide emissions from blast furnace possible because hydrogen content of auxiliary reducing agent is rather high compared with coke. The thesis includes seven chapters.

Chapter 1 presents a general introduction.

Chapter 2 describes the new injection lance for pulverized coal. To increase the injection amount of pulverized coal, it is so important to improve a combustion efficiency. Enhancement of particle dispersion is one of the measures to increase combustion efficiency by accelerating oxygen-coal particle mixture in blowpipe to tuyere region. To realize this, it is found that convergent – divergent injection lance designed on the basis of the fluid dynamics has superior characteristics. Direct observation results by offline apparatus, hot model experiments, and even in the experiments at actual blast furnace prove that dispersion of pulverized coal particles is enhanced and in-furnace permeability is improved at an actual blast furnace. These results suggest that high combustion efficiency is achieved by using developed injection lance.

Chapter 3 describes flow behavior of waste plastics in the blast furnace. Used plastics injection into blast furnace is considered to contribute to construction of a circulation type society and also mitigation of carbon dioxide emissions. However, research on the flow behavior of plastic particles or unburnt char in the blast furnace is few. Therefore, gasification behavior of plastic particles was determined
quantitatively by hot model experiments and thermogravimetry analysis in condition similar to blast furnace at first. Then flow behavior of plastic particle and unburnt char in a blast furnace was calculated by numerical simulation. As a result of this research, desirable condition of plastic injection was clarified.

Chapter 4 describes novel production process of pure oxygen. Oxygen is indispensable to promote combustion or gasification of auxiliary reducing agent. A major problem of conventional oxygen production process such as cryogenic air separation or nitrogen adsorbing type pressure swing adsorption is high cost of production. Brownmillerite-type Ca$_2$AlMnO$_5$ exhibits remarkable oxygen uptake/release capability, and therefore is a promising material for achieving energy efficient air separation. The optimized conditions for glycine-nitrate-based solution combustion synthesis of Ca$_2$AlMnO$_5$ is investigated.

Chapter 5 describes development of new cooling system. In the case of high rate injection of auxiliary reducing agent, it is confirmed that heat load to furnace wall increases. Therefore, enhancement of cooling capability of furnace wall is necessary to maintain stable operation with high rate injection condition. Design of cast copper cooling stave using finite element method is explained and its application to actual blast furnace and change of in-furnace situation are discussed.

Chapter 6 describes the concept of innovative ironmaking process. Intensive injection of solid/gas reducing agent, oxygen blast, and recycle use of top gas are integrated. As a result, it was evaluated that amount of carbon emission would be reduced by eighty-six percent provided sequestration of carbon dioxide is implemented.

Chapter 7 presents the general conclusions of this study.
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Chapter 2 Enhancement of combustion efficiency to increase injection amount of auxiliary reducing agents to blast furnace

2. 1 Introduction

Pulverized coal injection into blast furnace as an alternative reducing agent has spread widely recently\(^1,2\), because it may reduce coke consumption and decrease carbon dioxide emissions by increase in hydrogen reduction\(^3,4\).

Several studies regarding effect of coke fine generation and accumulation due to the high rate injection of pulverized coal on the permeability of blast furnace have been reported\(^5-8\). To inject large amount of pulverized coal into the blast furnace stably, enhancement of combustion efficiency is important. For example, Sato et al. reported that improvement of combustion efficiency of pulverized coal led to decrease in generation rate of coke fine in the raceway region and improvement of permeability of the blast furnace\(^9\).

To improve combustion efficiency of pulverized coal, several kinds of injection lance have been proposed. They included double lance arrangement\(^10\), eccentric double lance arrangement\(^11\), high turbulence lance with diagonal edge\(^12\), swirl burner\(^13\) for example. Purpose of these injection lance arrangements is enhancement of particle dispersion. In the blowpipe or tuyere region, the momentum of blast is predominant. So dispersion of coal particles in orthogonal direction to the flow is limited. Multi point injection or momentum transportation by turbulent flow to the orthogonal direction is considered to be effective to the particle dispersion. Oxy-coal lance, that is pulverized coal and pure oxygen are injected simultaneously using co-axial lance has been proposed\(^13,14\). Concentration
of oxygen in coal combustion region can be increased directly by using this kind of lance. Therefore, combustion efficiency of pulverized coal is improved greatly. To apply the oxy-coal lance, however, significant amount of pure oxygen is needed. Therefore, there must be some restriction or need for a large amount of investment cost.

In this chapter, convergent - divergent injection lance is proposed. Pulverized coal particles are able to be diffused well in the blow pipe to tuyere region by the combination of effective utilization of particle inertia and control of flow separation phenomenon in the boundary layer. This type of lance can enhance the combustion efficiency by the relatively simple method and it may be combined with existing injection lance arrangement easily.

The Author, at first, designed the lance tip configuration of convergent - divergent injection lance based on the theory of the boundary layer. Then, effect of the lance tip configuration on the particle dispersibility was verified by the direct observation using offline apparatus in the atmospheric condition. Hot model experimental results showed advantages of the lance tip configuration including particle dispersibility in the blowpipe and coke replacement ratio of pulverized coal.

As the convergent - divergent injection lance proved to be valid judging from offline and hot model experiments, the lances were used at actual blast furnace. It was confirmed that permeability of the furnace improved by the use of the lances. The reason of this phenomenon might be decrease in the amount of accumulation of coke fine in the lower part of blast furnace. It was considered that enhancement of coal particle dispersion by the use of convergent – divergent injection lance made combustion efficiency of pulverized coal higher and coke degradation was restrained by enhancement of combustion efficiency of pulverized coal.
2.2 Concept of particle dispersion enhancement by convergent – divergent lance

2.2.1 Flow separation in divergent lance

To enhance combustion efficiency of pulverized coal, it has been pointed out that dispersion of coal particle is important. It is thought that flow control by divergent lance is effective.

Divergent lance, where the stream cross section increases from inlet to outlet, can be generate diffusion flow. Therefore, coal particles carried by the gas can also be dispersed. However, when the divergence angle becomes larger, diffusion is limited by the phenomenon of flow separation. Fig. 2-1 shows schematic diagram of velocity and differential velocity distributions in boundary layer. Here, the direction x is defined as flow direction and y axis is considered as orthogonal to the flow direction (thickness direction). Velocity of flow in boundary layer and boundary layer thickness are defined as \( u(x, y) \) and \( \delta(x) \) respectively.

![Fig. 2-1 Schematic diagram of velocity and differential velocity distributions in boundary layer.](image)

\[
\text{Inflection point}
\]

\[
\begin{align*}
\frac{\partial u}{\partial y} & \\
\frac{\partial^2 u}{\partial y^2} & \\
\end{align*}
\]
At the surface of lance wall (y=0), by the Navier-Stokes equation and Bernoulli’s equation,

\[ \mu \frac{\partial^2 u}{\partial y^2} = -\rho U \frac{dU}{dx} \quad (2-1) \]

where \( \mu \), \( \rho \), and \( U \) denote fluid viscosity, density and velocity of potential flow (= \( u(x, \delta) \)), and because potential flow \( U \) is slowed down along with x direction in the case of divergent lance, so

\[ \frac{\partial^2 u}{\partial y^2} > 0 \quad (2-2) \]

From the boundary conditions at outer edge of boundary layer,

\[ \left( \frac{\partial u}{\partial y} \right)_{y=\delta} = 0, \quad \left( \frac{\partial^2 u}{\partial y^2} \right)_{y=\delta} = 0 \quad (2-3) \]

Considering these conditions, flow velocity in boundary layer u has an inflection point to the orthogonal direction as shown in Fig. 2-1 while u is monotonously increasing function in the case of straight or convergent lance.

As the velocity of flow decreases towards the downstream, velocity gradients \( \partial u/\partial y \) also decreases. When velocity gradients at the surface of lance wall equal to
zero, separation of flow may start as shown in Fig. 2-2.

![Diagram](image)

**Fig. 2-2** Schematic diagram of velocity distribution in boundary layer in the vicinity of inner wall of divergent lance.

Effect of divergence angle on the flow separation phenomenon has been reported by experimentally or using numerical analysis method. According to the results of their studies, maximum allowable angle for preventing flow separation is around 5 to 10 degrees. Therefore, optimum divergence angle was determined experimentally by referring to these reports in this study.

2. 2. 2 Particle flow control by convergent lance

**Figure 2-3** shows a schematic drawing of pulverized coal flow accompanied by carrier gas. In this figure, simple diffuser and convergent – divergent tip is
compared. At the throat area of convergent – divergent tip, solid gas mixed flow is compressed and density of flow lines is increased.

![Diagram of pulverized coal flow with carrier gas](image)

**Fig. 2-3** Schematic diagram of pulverized coal flow accompanied by carrier gas compared with a simple diffuser and convergent – divergent lance tip.

Owing to inertia of the particle, density of particle is increased at the peripheral part of throat. In the divergent part, solid and gas in the center region may flow straight while the solid and gas in the peripheral region may be dispersed. Therefore, it is considered that dispersibility of convergent – divergent lance is better than that of simple diffuser (not having convergent part) lance.
2. 3 Direct observation of flow behavior of pulverized coal particle

2. 3. 1 Experimental apparatus

Fig. 2-4 shows an offline apparatus for the direct observation of pulverized coal particle dispersibility. This apparatus consists of pneumatic transportation device, pulverized coal hopper, table feeder, injection lance, and video camera. Dispersion behavior of pulverized coal into atmosphere can be observed and dispersion angle can be measured by image processing of video image. The inner diameter of the lance was set to 12.7mm and velocity of outlet flow was set at 15.0 m/s as a basic condition. To investigate the effect of flow velocity on the dispersion angle, velocity of outlet flow was also set at 7.5 m/s.

Fig. 2-4 Schematic diagram of offline apparatus for observation of pulverized coal dispersibility.
2. 3. 2 Design of lance tip

Using the offline apparatus mentioned above, the effect of lance tip structure on the dispersion behavior of pulverized coal particle was investigated. Convergent - divergent lance was formed by providing throat part inside a lance tip.

At first, the effect of divergence angle on the diffusion behavior was investigated. Convergence angle was set at constant value of 5 degrees and throat diameter was set at constant value of 8.7 mm at this experiment. Range of divergence angle was determined from zero to 10 degrees considering the study of Gibson\textsuperscript{15). Fig. 2-5 shows the results of the experiments.

<table>
<thead>
<tr>
<th>β</th>
<th>α</th>
<th>Lance tip</th>
<th>Dispersion behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>0°</td>
<td>Flow direction</td>
<td>θ = 0.6°</td>
</tr>
<tr>
<td>5°</td>
<td>3°</td>
<td>Throat diameter</td>
<td>θ = 2.9°</td>
</tr>
<tr>
<td>5°</td>
<td>7°</td>
<td></td>
<td>θ = 7.1°</td>
</tr>
<tr>
<td>5°</td>
<td>10°</td>
<td></td>
<td>θ = 4.6°</td>
</tr>
</tbody>
</table>

Throat diameter = 8.7 mm (constant)
Inner diameter of outlet = 12.7 mm (constant)

Fig. 2-5 Effect of lance tip structure on the dispersion behavior of pulverized coal particle.
As shown in Fig. 2-5, image of dispersion area of pulverized coal is taken by video camera as black pixels. By the image processing, dispersion angle $\theta$ is measured. In the case that divergence angle $\alpha$ is 3 degrees, observed dispersion angle $\theta$ is 2.9 degrees. And in the case that $\alpha$ is 7 degrees, $\theta$ is 7.1 degrees. In these cases, values of $\alpha$ substantially coincide with $\theta$. It means that separation of flow in the divergent lance can be avoided successfully because values of $\alpha$ are relatively small. However, when $\alpha$ is increased further, $\theta$ can not be followed ($\theta$ is only 4.6 degrees to 10 degrees of $\alpha$). It suggests that separation of flow occurs in the higher divergence angle over 7 degrees. Considering these experimental results, optimum divergence angle $\alpha$ was determined at 7 degrees.

Next, the effect of convergence angle $\beta$ on the diffusion behavior was studied using same apparatus. As shown in Fig. 2-6, divergence angle $\alpha$, throat diameter and outlet diameter were set to 7 degrees, 8.7 mm and 12.7 mm as constants respectively.

![Fig. 2-6 Effect of convergence angle on the dispersion behavior of pulverized coal particle.](image-url)
In Fig. 2-6, data of straight tip ($\alpha = \beta = 0$ degree and outlet diameter = throat diameter = 12.7 mm) were also shown for comparison. To clarify the effect of flow rate (Reynolds number: Re), flow rates of 7.5 m/s and 15.0 m/s were chosen and they corresponded to Reynolds numbers of $4.3 \times 10^3$ and $8.6 \times 10^3$ respectively.

Dispersibility could be enhanced even in relatively small angles of 2 to 5 degrees compared with straight tip. However, when $\beta$ is increased further, $\theta$ shows a decrease tendency. It suggests that scatter of particles by colliding with an inner wall of lance tip affects dispersibility of convergent – divergent lance. It seems that effect of Reynolds number is relatively small. If the $\beta$ is small, it takes longer length to form throat shape. So it is decided that optimum $\beta$ value is 5 degrees.

Because optimum divergence angle $\alpha$ and convergence angle $\beta$ were decided, then the optimum height of peak-shaped projection $h$ that forms throat part was investigated. As shown in Fig. 2-7, divergence angle $\alpha$, convergence angle $\beta$ and outlet diameter were set to 7 degrees, 5 degrees and 12.7 mm as constants respectively. Dimensionless function (Throat diameter/Outlet diameter) is also shown on horizontal axis in Fig. 2-7.

Dispersion angle $\theta$ can be enhanced as the $h$ is increased. It seems that effect of Reynolds number is relatively small. Although it is thought that it is better to use higher $h$ for the dispersibility of coal particles, possibility of negative influence such as clogging of lance and increase in pressure loss may be increased. So it was decided that optimum $h$ value was 2 mm. It corresponded to around 0.7 of throat diameter to outlet diameter ratio.
Fig. 2-7 Effect of height of peak–shaped projection on the dispersion behavior of pulverized coal particle.

2. 4 Study on dispersibility and combustion behavior of pulverized coal by hot model experiment

2.4.1 Outline of hot model experimental furnace

In the previous section, pulverized coal was blown to air atmosphere. Considering condition of pulverized coal injection at actual blast furnace, study on dispersion behavior in hot blast is required.

Fig. 2-8 shows a schematic diagram of hot model experimental furnace\textsuperscript{19}. This model comprises a blow pipe, a tuyere, and a coke packed bed. The diameter
of a tuyere is 65mm and the inner diameter of blowpipe is 90 mm. Hot blast of 1473 K at tuyere tip is supplied to blowpipe by combustion of LPG gas. Specific amount of oxygen is added to hot blast to control oxygen concentration at 24 vol% (or 3 vol% enrichment to atmospheric air). Temperature gradient in blowpipe is about $1.4 \times 10^{-1}$ K/mm. Experimental conditions of hot model and properties of pulverized coal used in this study are shown in Table 2-1.

Fig. 2-8 Schematic diagram of hot model experimental furnace.
R. Murai, “Massive Injection of Auxiliary Reducing Agent at Blast Furnace for the Sustainable Development.”

Table 2-1 Conditions of hot model experiment.

<table>
<thead>
<tr>
<th>Experimental conditions of a hot model</th>
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<tbody>
<tr>
<td>Gas volume</td>
</tr>
<tr>
<td>Blast temperature</td>
</tr>
<tr>
<td>Tuyere gas velocity</td>
</tr>
<tr>
<td>Coal injection rate</td>
</tr>
<tr>
<td>Oxygen enrichment</td>
</tr>
<tr>
<td>Pulverized coal rate</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Properties of pulverized coal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size distribution</td>
</tr>
<tr>
<td>Proximate analysis (dry base)</td>
</tr>
<tr>
<td>V.M.</td>
</tr>
<tr>
<td>F.C.</td>
</tr>
<tr>
<td>Ash</td>
</tr>
</tbody>
</table>

(* kg/thm: kg per tons of hot metal)

Two types of blowpipe were used in this study. To observe the behavior of dispersion of pulverized coal, blowpipe A was used. Injection lance could be inserted parallel to the flow direction in this type of blowpipe. So, dispersion behaviors of pulverized coal in ambient atmosphere as mentioned previous section and in hot blast could be compared directly. However, the injection lance used in this type of blowpipe is exposed to high temperature of hot blast. So this type of blowpipe is not suitable to measure the coke replacement ratio of pulverized coal because it takes longer time to collect data required. Therefore, blowpipe B was used to estimate coke replacement ratio by material balance. In this configuration, two injection lances were inserted through the through-holes. Because tips of lance were set at the surface of inner wall of blow pipe, thermal load to the lances were
reduced compared with blowpipe A. Stable and longer injection of pulverized coal was realized using blowpipe B.

2.4.2 Evaluation of particle dispersion

Fig. 2-9 shows observation results of dispersion behavior of pulverized coal in blowpipe of hot model experimental furnace using blowpipe A. Injection lance with straight tip was used in the case of left hand figure while the injection lance with convergent-divergent tip was used in the case of right hand figure. Both figures were taken by video camera through an observation window from a direction orthogonal to two phase flow of gas and coal particles. Dispersion angles \( \theta \) were observed to be 8.7 and 12.4 degrees in the cases of straight tip and convergent-divergent tip respectively. These values were larger than the results obtained by offline apparatus.

![Fig. 2-9 Observation results of dispersion behavior of pulverized coal in blowpipe of hot model.](image-url)
These results suggest that turbulence towards downstream of lance tip generated by the lance itself has a significant influence on the particle dispersion\textsuperscript{12}. However, it is to be emphasized that the dispersion angle $\theta$ of convergent – divergent tip is larger than that of straight tip as in the case of offline experiments. It is confirmed that flow control without flow separation by convergent – divergent lance enhances the dispersibility of pulverized coal particles.

2. 4. 3 Effect of particle dispersibility on coke replacement ratio of pulverized coal in hot model experiment

Using blowpipe B, hot model experiments were conducted to determine the coke replacement ratio of pulverized coal. Because multiple lances can be used in this model, the eccentric double lance arrangement was adopted in this study\textsuperscript{11}. Exchanging only lance tips, two kinds of experiments using straight lance tip and convergent – divergent lance tip could be conducted. The results of combustion experiments were compared.

Coke replacement ratio of pulverized coal is determined as following formula that can be calculated by material balance of hot model experiments.

$$
\text{CRR} = \frac{(W_{C0} - W_{C1}) \times C_C}{W_{PC} \times C_{PC}}
$$

(2-4)

where CRR, $W_{C0}$, $W_{C1}$, $W_{PC}$, $C_C$, and $C_{PC}$ denote coke replacement ratio of pulverized coal (wt%), mass flow rate of coke supply without injecting pulverized coal (kg/h), mass flow rate of coke supply with injecting pulverized coal (kg/h), mass flow rate of pulverized coal (kg/h), content of carbon in coke (wt%) and
content of carbon in pulverized coal (wt%) respectively.

As shown in Fig. 2-10, coke replacement ratio of pulverized coal using convergent – divergent lance tip increased 3 wt% compared with that using straight lance tip. Because more oxygen in the hot blast may be used for combustion of pulverized coal by the effect of dispersion of convergent – divergent lance tip, it is thought that coke consumption rate is decreased and $W_{C1}$ is decreased.

![Fig. 2-10 Effect of lance tip on coke replacement ratio measured by hot model.](image)
2.5 Application of convergent – divergent lance to actual blast furnace

2.5.1 Evaluation of particle dispersibility at actual blast furnace

As the good results on the convergent – divergent lance were obtained in model experiments, effect of this kind of lance was examined at an actual blast furnace in Fukuyama works. Fig. 2-11 shows a schematic diagram of observation equipment. Combustion behavior of pulverized coal was analyzed by image processed method. Pictures were taken by high-speed video camera (frame rate: 13,500 frames in each second) through an observation window installed in the rear side of the tuyere. In the actual blast furnace, eccentric double lance arrangements have been adopted as well as in the hot model experiment.

![Schematic diagram of observation equipment](image)

Fig. 2-11 Schematic diagram of observation equipment for pulverized coal combustion behavior at an actual blast furnace.
The original pictures were processed by image processor as shown in Fig. 2-12. The brightness of pictures was divided into 256 gradations. In this figure, blue area shows low brightness (low temperature) and red region shows high brightness (high temperature). Then four brightness zones of 0-25, 25-50, 50-170, and 170-255 were assumed to be the injection lance, unburnt zone in pulverized coal flow (Zone a in Fig. 2-12), flame zone in pulverized coal flow (Zone b in Fig. 2-12) and background (Zone c in Fig. 2-12). Using these brightness data, ratio of flame zone \[ B/(A+B) \] was determined. Here, A and B represent the area (number of pixels) of zone a and zone b respectively. The calculation results of \[ B/(A+B) \] are shown in Fig. 2-13. The operational conditions of actual blast furnace are shown in Table 2-2.

![Brightness scale](image.png)

**Fig. 2-12 Analysis method of combustibility by the image processing.**
R. Murai, "Massive Injection of Auxiliary Reducing Agent at Blast Furnace for the Sustainable Development."

Fig. 2-13 Combustibility index \( [B/(A+B)] \) measured in actual blast furnace.

<table>
<thead>
<tr>
<th>Table 2-2 Operation conditions of actual blast furnace.</th>
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<tbody>
<tr>
<td></td>
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<td></td>
</tr>
<tr>
<td><strong>Inner volume (m³)</strong></td>
</tr>
<tr>
<td>Blast volume (kg/thm)</td>
</tr>
<tr>
<td>PCR (kg/thm)</td>
</tr>
<tr>
<td>Oxygen enrichment (vol.%)</td>
</tr>
<tr>
<td>T. F. T. (K)</td>
</tr>
<tr>
<td>Coke Strength DI (-)</td>
</tr>
<tr>
<td>( V_{tuy} ) (m/s)</td>
</tr>
</tbody>
</table>

\( T. F. T. \) : Theoretical flame temperature
\( DI \) : Drum Index \( (DI(150/15)) \)
\( V_{tuy} \) : Gas velocity at tuyere
The operational conditions between using straight lance tip and convergent–divergent lance tip were almost same particularly the blast conditions such as blast volume, oxygen enrichment, theoretical flame temperature, and gas velocity at tuyere. It is considered that larger values of \[B/(A+B)\] suggest higher combustibility. According to the Fig. 2-13, \[B/(A+B)\] value of convergent–divergent lance is larger than that of straight lance. Thus, it is proved that convergent–divergent lance has a superior effect of combustion improvement.

2.5.2 Change in permeability and coke replacement ratio at actual blast furnace by use of convergent-divergent injection lance

Effect of convergent–divergent injection lance on the permeability and coke replacement ratio at actual blast furnace was studied by the analysis of operational data.

To evaluate the permeability of blast furnace, \(K_L\) value (lower part permeability resistance index) is often used\(^{20}\). Although blast pressure may be used to calculate this value, enhancement of combustibility, that leads to increase in gas volume in a blowpipe, makes \(K_L\) value higher because blast pressure includes an effect of pressure drop in blowpipe to tuyere region. Fig. 2-14 shows an example of pressure distribution in lower part of actual blast furnace. Where \(P_b\) denotes the blast pressure and \(P_1\) to \(P_4\) denote the in furnace pressures at each level. The values from \(P_1\) to \(P_4\) could be approximated by a straight line. Then virtual pressure \(P_0\) is defined as a pressure of intersection between extrapolated line of pressures \(P_1\) to \(P_4\) and a line of the tuyere level. So, “net” permeability of coke packed bed in the actual blast furnace eliminating the influence of pressure drop inside of blowpipe can be obtained.
Fig. 2-14 Example of pressure distribution in lower part of actual blast furnace.

Then the corrected lower part permeability resistance index $K_L^*$ can be expressed as,

$$K_L^* = \frac{P_0^2 - P_4^2}{V_{bosh}^{1.7}}$$  \hspace{1cm} (2-5)

where $V_{bosh}$ denotes the bosh gas volume.

Fig. 2-15 represents the effect of lance tip on the lower part permeability resistance index of actual blast furnace. Smaller $K_L^*$ value means better furnace permeability. In the general view of this figure, $K_L^*$ value tends to increase as the pulverized coal injection rate increases.
R. Murai, “Massive Injection of Auxiliary Reducing Agent at Blast Furnace for the Sustainable Development.”

**Fig. 2-15 Effect of lance tip on lower part permeability resistance index ($K_L$).**

When the convergent - divergent lance is applied, $K_L$ value (permeability resistance of furnace) shows a tendency to decrease. One of the reasons of this phenomenon is that packed condition in lower part of blast furnace such as accumulation of coke fine might be improved by applying convergent - divergent lance because increase in combustion efficiency of pulverized coal contributed to decrease the coke degradation in the raceway.9)
2. 6 Conclusions

Aiming at enhancing the combustion efficiency of pulverized coal at blast furnace, the convergent – divergent injection lance was proposed. Through the experiments conducted by offline apparatus, hot model and actual blast furnace, the following results were obtained.

(1) Optimum divergence angle where the particle dispersibility is maximized proved to be around 7 degrees by the observation results of offline apparatus. This angle could be explained by the theory of flow separation in the boundary layer.

(2) Optimum convergence angle where the particle dispersibility is maximized proved to be around 5 degrees by the observation results of offline apparatus. Due to the inertia of coal particles, segregation of particle to relatively peripheral region at the throat part in the lance may be occurred. It was thought that this segregation phenomenon played significant role to the good dispersibility of the lance.

(3) The observation results of dispersion behavior by hot model experimental furnace showed that higher dispersibility of convergent - divergent lance could be conserved not only offline ambient atmosphere but even in a high-speed hot blast.

(4) Coke replacement ratio measured by hot model is higher in the case of convergent - divergent injection lance. It is estimated that reason of this result is attributed to increase in combustion efficiency by enhancement of particle dispersion.

(5) Characteristics of the convergent – divergent injection lance including higher particle dispersibility, higher combustibility, and higher coke replacement ratio compared with normal straight injection lance proved in the actual blast furnace.
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Chapter 3 Flow behavior of plastic particle as auxiliary reducing agent in the blast furnace

3.1 Introduction

As an alternative reducing agent, plastics has been injected to blast furnaces aiming at mitigation of carbon dioxide emissions and attainment of sustainable development\(^1\)-\(^3\). Injected plastics may cause high temperature reactions such as gasification in lower part of blast furnace. It is well known that a part of injected plastics generates unburnt char as a result of incomplete gasification. Unburnt char particles, consisting of fixed carbon and ash, are considered to be conveyed with gas flow. And then, they may be consumed completely by the direct reduction at the cohesive zone or they may be accumulated somewhere in coke packed bed.

Several researches concerning pyrolysis of plastic particles have been reported. For example, Ariyama et al.\(^4\) researched gasification and combustion behavior of single plastic particle in the laminar flow furnace. Yamaguchi et al.\(^5\) investigated the behavior of plastic in blow pipe and raceway using vertical tower furnace and hot model. Goto et al.\(^6\) estimated the behavior of plastics in a blast furnace by numerical simulations and the simulation results were verified by the hot model experiments. However, these previous researches focused on the pyrolysis of plastic particles from blowpipe to raceway region, research on the flow behavior of plastic particles and unburnt char in lower part of blast furnace including outer part of raceway is very few. Some plastics has high alumina content of ash, so slag flowability becomes worse. Accumulation of unburnt char in particular part may cause unstable operation of blast furnace because of slag drainage problem\(^7\).
There are various shapes of “used” plastics such as film, grain, lump, sheet, and bar. Processing methods of these plastics to use at blast furnace have been reported. Thin-film shape plastics tend to clog up the injection lines, so they are often agglomerated into granular shape using extruder for instance. In the case of crushing large-size plastics, a part of crushing energy may change into heat, and temperature of plastics increases. As previously reported, “used” plastics are composed of polyethylene, polypropylene, polystyrene, and so on. Pulverizing of plastics is considerably difficult above glass transition temperature of these plastics components. So, large-size plastics have been used to inject after crushing into rather coarse grain in the early stage.

Recently, pulverizing method of plastics has been developed and fine plastics have been injected practically at a particular blast furnace. However, effects of particle size of injected plastics on the operation of blast furnace such as permeability were not clear.

The author, at first, made a model of gasification behavior of plastic particles based on the observation result of plastic injection experiment using experimental furnace which is able to achieve rapid heating condition same as an actual blast furnace. Then, the gasification rate of unburnt char has been quantified by the thermogravimetric analysis. Next, using the results mentioned above, flow and accumulation behavior of plastic particles and unburnt char in lower part of blast furnace was clarified by numerical simulations.

In this chapter, effect of initial size of injected plastics on the blast furnace operation is discussed and verified using operation data at actual blast furnace.
3. 2 Characteristics of plastic gasification

3. 2. 1 Modeling of plastic gasification

To examine the gasification behavior of plastics, plastic injection experiment using hot model\(^{10}\) has been conducted. In the hot model, plastic particle was heated up rapidly as similar condition around blowpipe and tuyere of actual blast furnace. Hot model comprises a blow pipe, a tuyere, and a coke packed bed as shown in Fig. 3-1. Diameter of a tuyere is 65mm. Hot blast of 1473 K at tuyere tip is produced by combustion of propane gas and oxygen content of hot blast is controlled at 24 vol% (or 3 vol% enrichment to atmospheric air) by adding specific amount of oxygen. Temperature gradient in blowpipe is about \(1.4\times10^{-1}\) K/mm. Experimental conditions of hot model are shown in Table 3-1.

Plastic particles used in this experiment have cylindrical shape (φ6mm×10mm).

![Fig. 3-1 Schematic diagram of hot model experimental furnace.](image-url)
R. Murai, "Massive Injection of Auxiliary Reducing Agent at Blast Furnace for the Sustainable Development."

Table 3-1 Experimental conditions of hot model experimental furnace.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas volume</td>
<td>330 Nm³/h</td>
</tr>
<tr>
<td>Blast temperature</td>
<td>1473 K</td>
</tr>
<tr>
<td>Blast composition O₂</td>
<td>24.0 vol%</td>
</tr>
<tr>
<td></td>
<td>N₂</td>
</tr>
<tr>
<td></td>
<td>CO₂</td>
</tr>
<tr>
<td></td>
<td>H₂O</td>
</tr>
<tr>
<td>Gas velocity at tuyere</td>
<td>150 m/sec</td>
</tr>
<tr>
<td>Plastics injection rate</td>
<td>48 kg/h (150 kg/t-pig)</td>
</tr>
<tr>
<td>Fuel equivalence ratio</td>
<td>0.73</td>
</tr>
</tbody>
</table>

They were agglomerated by extruder using thin-film municipal used plastics as raw materials. Typical density of plastic particles ranges from 0.85 to 1.1 g/cm³, although the value varies depending on the components and the properties of the raw materials. As for representative value, 0.975 g/cm³ was adopted. Physical properties and chemical compositions of plastics are shown in Tables 3-2 and 3-3 respectively.

Table 3-2 Physical properties of plastics.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Particle Shape</th>
<th>Particle Size**</th>
<th>Particle Density***</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agglomerated</td>
<td>Cylindrical (Φ6mm x 10mm*)</td>
<td>4</td>
<td>0.85-1.1</td>
</tr>
<tr>
<td>Plastics APR</td>
<td>Granular</td>
<td>0.8</td>
<td>0.9-1.05</td>
</tr>
</tbody>
</table>

* nominal (actually 2 to 10mm)
** Harmonic mean diameter
*** Representative value: 0.975
Plastics were injected through a lance to the blowpipe of the hot model. Injected plastics were heated rapidly by hot blast in the blowpipe of the hot model, then the plastic particles were sampled by water-cooled probe at the just behind the tuyere. Distance between lance tip and probe was set at 800 mm and retention time in high temperature zone is approximately 20 msec. Appearance and change in diameter of the plastics was examined. Fig. 3-2 shows a picture of a plastic particle before and after heating. Plastic particles became smaller to 2 or 3 mm in size when it passed through the furnace. It is interesting that the original plastic material still remain in core region while char is observed in the surface. This means that gasification and combustion of plastic particles are surface reaction. From the observed results, gasification behavior of a plastic particle is estimated as shown in Fig. 3-3 schematically.

Table 3-3 Chemical compositions of plastics.

<table>
<thead>
<tr>
<th>Plastics</th>
<th>Proximate analysis (dry base, wt %)</th>
<th>Ultimate analysis (dry base, wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>VM</td>
<td>FC</td>
</tr>
<tr>
<td>Agglomerated</td>
<td>93.8</td>
<td>3.4</td>
</tr>
<tr>
<td>Plastics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>APR</td>
<td>79.5</td>
<td>10.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Composition of ash (dry base, wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
</tr>
<tr>
<td>------</td>
</tr>
<tr>
<td>Agglomerated Plastics</td>
</tr>
<tr>
<td>APR</td>
</tr>
</tbody>
</table>
Fig. 3-2 Appearance of plastics before heating and cross section of plastics after heating.

Fig. 3-3 Model of gasification behavior of plastics.

At first, volatile matter is evolved at the surface of a plastic particle, then high temperature reaction of evolved volatile matter occurs with surrounding oxygen. Next, diameter of the plastic particle decreases as the plastic particle emits volatile matter. Finally, after completion of volatile matter evolution, unburnt char which consists of fixed carbon and ash remains. Considering the balance of latent heat of
evaporation and heat transfer from surface, change in particle diameter caused by evolution of volatile matter is expressed as:

\[
\frac{dr}{dt} = -\frac{h_p \cdot (T_g - T_p)}{\rho_p \cdot Q} + \frac{E}{\rho_p \cdot Q}
\]  

First term of right side of the formula represents heat convection and second term represents heat radiation. Heat transfer coefficient \( h_p \) is given:

\[
h_p = \frac{\lambda \cdot Nu}{\ell}
\]  

Nusselt number (Nu) is calculated by the Ranz-Marshall correlation\textsuperscript{11).} The equations obtained here are used later (section 3.3) for tracking of plastic particles in blast furnace.

Unburnt char is considered to gasify by the reaction with carbon dioxide, so called solution loss reaction, in the lower part of blast furnace. In the next section, reaction rate of unburnt char with carbon dioxide has been quantified by the thermogravimetric analysis.
3. 2. 2 Reaction rate of char derived from plastics

To obtain unburnt char derived from plastics, plastic particles were heated by electric furnace in inert gas (high purity nitrogen) atmosphere.

Two kinds of plastics were used in this experiment. Agglomerated plastics are same as mentioned previous section. APR\textsuperscript{7} represents fine plastics made by advanced plastic processing method. In this process, Plastics were pulverized using residual stress acts between interfaces of plastics which was provided when different kinds of plastics were cooled to room temperature after melting and mixing. The cost to pulverize plastics is reduced by using residual stress. In this experiment, raw materials to produce agglomerated plastics and raw materials to produce APR were made equal to each other, that is, thin-film municipal used plastics were used as raw materials. Physical properties and chemical composition of APR are shown together with those of agglomerated plastics in Table 3-2 and 3-3 respectively. Typical diameter of APR is 0.8mm while that of agglomerated plastics is 4mm.

Fig. 3-4 shows an experimental apparatus for the carbonization of plastics. Temperature of electric furnace was increased up to 1273 K at a rate of 7 degrees per minute. Specimen was mounted on the quartz boat (75mm in length, 10mm in width and 10mm in height). The amount of specimen was 1g in each case. The boat can be slid from the edge to center of reaction tube. Diameter of reaction tube is 35mm. Nitrogen gas was fed to the reaction tube at the rate of 100 cm\textsuperscript{3}/min. Rapid heating can be carried out by sliding boat from edge to center immediately when center part temperature reaches designated value. And for the gradual heating, boat was fixed at center part throughout the heating process.
Holding the specimen for 10 minutes at 1273K, and cooling it afterwards, char was obtained in each case. There are some studies on the effect of carbonization temperature on the gasification rate of char. Kajitani et al.\textsuperscript{12} reported that gasification rate of coal char carbonized at higher temperature tended to be low because of its higher graphitization degree. To focus on the effect of heating rate, carbonization temperature was fixed at 1273K in this study.

Then, using char obtained by this electric furnace experiment, reaction rates with carbon dioxide were analyzed by the thermogravimeter. 10 mg of char was used for each analysis. Char was mounted on the cylindrical platinum cell with a diameter of 4.4mm and 4.5mm in depth. Char was heated to temperature of 1273, 1373, and 1473 K in the high purity nitrogen atmosphere. When the specimen
heated up to designated temperature, temperature was kept and atmospheric gas was changed to carbon dioxide. Reaction gas comprised carbon dioxide at the concentration of 50 vol% and nitrogen as the rest and flow rate of reaction gas was kept at 1L/min. Rate of gasification reaction by solution loss reaction was able to calculate from weight loss of specimen. The superficial velocity of the reaction gas was a range of 0.31 to 0.35m/s. According to a study of Yagi et al., reaction rate coefficient of carbon solution loss is much smaller than gas-film coefficient of mass transfer in the case of relatively small (under 2 to 3 mm) particles at around 1273 to 1473K\textsuperscript{13)}. Therefore, it was assumed that rate controlling step was chemical reaction in this experiment. In the experiment, it was confirmed that change in gasification rate to gas flow rate variation was small.

**Fig. 3-5** shows a particle size distribution of char derived from plastics obtained by carbonization with electric furnace.
Laser diffraction method was used to analyze particle size distribution. Particle size of char is characterized by 1) existence of fine particles under 10 µm, 2) rather narrow distribution around 60-80 µm and 3) existence of relatively coarse particle over 100 µm. Kinds of plastics and rate of heating do not aﬀect particle size of unburnt char greatly. Sugiyama\textsuperscript{14) reported the condition of powder accumulation in the deadman. He suggested that coke fine which is over 500µm in size caused hold-up in the lower part of blast furnace. It is considered that hold-up of fine in lower part of blast furnace may cause unstable operation. So the condition of accumulation of unburnt char derived from plastics is discussed later.

Fig. 3-6 shows results of char gasiﬁcation experiments with carbon dioxide (Arrhenius plot). Gasiﬁcation rate of char obtained by rapid heating tends to be larger than that of char by gradual heating. On the other hand, gasiﬁcation rate does not depend on the kind of plastics greatly.

It is considered that gasiﬁcation rate of char is inﬂuenced by speciﬁc surface area. Therefore surfaces of various char are observed with scanning electron microscope. The results are shown in Fig. 3-7. Several micro pores are observed on the surface of rapid heating char, while surface of char heated gradually seems to be rather smooth. As the rate of volatile matter evolution is fast in the case of rapid heating char, pores are formed on the surface. As a result, it is estimated that specific surface area is increased and gasiﬁcation rate is also increased. These results agree very well with the study on the gasiﬁcation rate of the char derived from coal by Luo et al\textsuperscript{15).}

There are various models describing the kinetics of a gas-solid reaction, such as the volume-reaction model, the shrinking-core model, and the random-pore model\textsuperscript{16-19).}
Fig. 3-6 Gasification rates of plastics char with carbon dioxide.

Fig. 3-7 Examples of SEM image of char derived from plastics.
Although random-pore model is able to precisely estimate the gasification rate at an early stage of reaction particularly for the rapid heating char, but the deviation between model and actual data tends to increase in the latter part of experiment. Therefore, volume-reaction model was adopted in this research as a method with small error within wide conversion range, that is

\[
\frac{dX}{dt} = k \cdot (1-X) \cdot P_{CO2}
\]

\[ (3.3) \]

Where \( k \) and \( X \) are rate constant and a fractional char conversion respectively, 
\( k \) is obtained from Fig. 3-6 by the equation of

\[
k = A \cdot \exp(- \frac{E_a}{RT})
\]

\[ (3.4) \]

and \( X \) is expressed as follows:

\[
X = \frac{(W_0 - W)}{(W_0 - W_{ash})}
\]

\[ (3.5) \]

### 3.3 Modeling of flow behavior of plastic particles in the lower part of blast furnace

To analyze flow behavior of plastic particles injected into blast furnace, equation of motion of solid particle in the gas stream is solved.
\[ \frac{d\mathbf{u}_p}{dt} = -g \frac{(\rho_p - \rho_g)}{\rho_p} + \frac{3 \cdot C_d \cdot \rho_g}{4 \cdot \rho_p \cdot d_p} \left| \mathbf{u}_g - \mathbf{u}_p \right| (\mathbf{u}_g - \mathbf{u}_p) \]  

(3-6)

where \( C_d \) is the drag coefficient that is expressed as a function of Reynolds number.
Although many empirical or semiempirical equations have been proposed\(^{20-22} \), following equations were adopted in this calculation,

\[
C_d = \begin{cases} 
24/Re & (Re \leq 2) \\
10/\sqrt{Re} & (2 < Re \leq 500) \\
0.44 & (500 < Re)
\end{cases} 
\]  

(3-7)

To solve equation (3-6), three sub models are coupled as shown in Fig. 3-8. Those are i) 2-dimensional mathematical model of gas flow in lower part of blast furnace\(^{23} \), ii) Model of particle motion in coke packed bed\(^{24-26} \), and iii) Model of plastics gasification.

Here gas flow rate \( u_g \), temperature, and gas composition distribution in blast furnace are given by first model and mean free path of particles in coke packed bed are given by second model. As the particle size of plastics and char is decreased by gasification, change in particle size is calculated by the third model mentioned in former section (equation (3-1) for plastics and equation (3-3) for char).
Fig. 3-8 Three sub-models coupled to simulate flow behavior of plastic particles in lower part of blast furnace.

Outline of 2-dimensional mathematical model (model i)) is as follows. Computational area of the model i) consists of two rectangle regions that correspond to blowpipe and coke packed bed including raceway. Cartesian coordinates system is adopted in this model to enable the asymmetrical calculation to the center axis. Schematic diagram of the model i) is shown in Fig. 3-9. Distributions of void fraction and coke diameter in the coke packed bed are also shown in Fig.3-9. These distributions were determined by referring to the results of deadman probe measurements\(^{27}\) and literatures\(^{28-29}\). Basic equations used in the model i) are shown in Table 3-4. Basic equations comprise mass conservation of mixed gas and component gases, equation of motion, energy balance, and equation of state. Although equation of motion corresponding to laminar flow was used for simplicity, effect of turbulence was considered by introducing effective viscosity \(\mu_e\) (constant \((k_1)\)×molecular viscosity \(\mu_m\)).
R. Murai, “Massive Injection of Auxiliary Reducing Agent at Blast Furnace for the Sustainable Development.”

Fig. 3-9 Outline of 2-dimensional mathematical model in lower part of blast furnace.

Table 3-4 Basic equations used in 2-dimensional model.

\[
\frac{\partial (\rho U_y \phi)}{\partial x} + \frac{\partial (\rho V_y \phi)}{\partial y} = \frac{\partial [I(\partial U_y / \partial x)]}{\partial x} + \frac{\partial [I(\partial U_y / \partial y)]}{\partial y} + \Xi
\]

<table>
<thead>
<tr>
<th>( \phi )</th>
<th>( \Gamma )</th>
<th>( \rho )</th>
<th>( \Xi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>( \rho_g )</td>
<td>( \sum_{i=1}^n (S_{yi} + S_{yi}) )</td>
</tr>
<tr>
<td>( \omega )</td>
<td>( \rho_g D_{ej} )</td>
<td>( \rho_g )</td>
<td>( S_{yi} + S_{ri} )</td>
</tr>
<tr>
<td>( U_y )</td>
<td>( \mu_e )</td>
<td>( \rho_g )</td>
<td>- ( \frac{\partial P}{\partial y} - [f_1 + f_2(U_y^2 + V_y^2)^{0.5}] V_y - \rho_g g )</td>
</tr>
<tr>
<td>( V_y )</td>
<td>( \lambda_g )</td>
<td>( \rho_g C_{pg} )</td>
<td>( \Phi )</td>
</tr>
</tbody>
</table>

\[
\mu_e = k_1 \mu_m, \quad \epsilon \leq 0.8
\]

\[
D_{ej} = k_2 D_{jm}, \quad f_1 = 150(1-\epsilon)^2 \mu_e / [\epsilon^3 (\phi_d c_d)^2]
\]

\[
P = 10^3(\rho_g / M_m)RT_g, \quad f_2 = 1.75(1-\epsilon) \rho_g / [\epsilon^3 (\phi_d c_d)]
\]

\[
\sum_{i=1}^n \omega_i = 1, \quad \epsilon > 0.8
\]

\[
f_1 = 0, \quad f_2 = (3/4) C_{dc} \rho_g (1-\epsilon) / (\phi_d c_d)
\]
Effective diffusion coefficient $D_{ejm}$ in mass conservation equation of component gas was also introduced. Pressure drop in a coke packed bed was considered in equation of motion. To solve these equations, SIMPLER method was adopted\textsuperscript{30}. In order to obtain the gas flow rate, temperature, and gas composition distribution in blast furnace, calculations were made considering actual blast furnace conditions, such as blast rate was 7500Nm$^3$/min, blast temperature was 1473 K, oxygen enrichment was 3.0 vol%, blast moisture was $24\times10^{-3}$kg/Nm$^3$ and pulverized coal rate was 150kg/thm. Calculation results using this 2-dimentional mathematical model, such as contours of temperature distribution, gas velocity in Y-direction and distribution of CO$_2$ are shown in Fig. 3-10. Based on these calculation results, trajectories, change in diameter and rate of gasification of plastics and char particles are estimated.
Fig. 3-11 shows a schematic diagram of fine particle motion in the coke packed bed, considered in model ii). When the fine particles collide with coke, the velocity of fine is assumed to become zero. Then the particles are accelerated by gas flow again.

![Schematic diagram of fine particle motion in the coke packed bed.](image)

Mean free path of the fine particles in a coke packed bed $L$ is represented by

$$L = \alpha \cdot d_c$$

(3-8)

Kusakabe et al.\textsuperscript{24} obtained the value of $\alpha$ as follows,

$$\alpha = \frac{2}{3}$$

(3-9)
In order to express the phenomena of fine particle accumulation, condition of fine particles descent was determined considering balance of ‘drag force’ and ‘friction force between a particle and coke’ as shown in Fig. 3-12. When the velocity of Y direction derived from equation (3-6) became negative value (downward direction), fine particle descended continuously according to equations from (3-6) through (3-9).

![Fig. 3-12 Balance of drag force and the friction force between a particle and coke.](image)

So, following condition was added. That is, when the fine particle landed on the coke particle, it was assumed that descent of fine particles was occurred only if the drag force in X direction $F_{d,x}$ is greater than friction force $F_f$, otherwise velocity of particle in Y direction is assumed to be zero. $F_{d,x}$ and $F_f$ is expressed as follows
\[ F_{d,x} = C_d \frac{\pi d_p^2}{4} \frac{\rho_s u_{g,x}^2}{2} \]  

(3-10)

\[ F_f = \mu_f \left( \frac{\rho_p \cdot \pi \cdot d_p^3 \cdot g}{6} + C_d \frac{\pi d_p^2}{4} \frac{\rho_s u_{g,y}^2}{2} \right) \]  

(3-11)

Terashita et al. reported that internal friction factor of various kinds of fine coal and fly ash were within the range of 0.37 to 0.58\(^{31}\). And considering a study on the particle motions in blast furnace by Yuu et al.\(^ {32}\), friction coefficient between fine particle and coke particle \( \mu_f \) is adopted 0.45 in this study.

Coupling of these three models, tracking of plastic particle in blast furnace was carried out. Computation procedure is shown in Fig. 3-13. Injected plastic particles are accelerated by gas drag force. As the distance traveled can be calculated by equation of motion considering mean free path, so coordinates of particles can be tracked after small time step \( \Delta t \). Reduction in diameter of a plastic particle can be calculated by the heat transfer in \( \Delta t \). After emitting all of volatile matter, reduction in diameter is caused by gasification of fixed carbon or char. As gasification rate is affected heating rate, gasification rate in the case of rapid heating condition (similar to blast furnace) was adopted in this calculation. Thus, coordinates and particle diameter of injected plastic can be calculated.
R. Murai, “Massive Injection of Auxiliary Reducing Agent at Blast Furnace for the Sustainable Development.”

Fig. 3-13 Flow chart of model calculation.
Fig. 3-14 shows an example of simulation result. Particle trajectories are shown in diagram of gas flow vector obtained 2-dimensional mathematical model (model i). In this case, diameter of unburnt char is set to 60µm considering results of carbonization experiments mentioned in chapter 3.2. Trajectories of particle differ depending on the initial diameter. Although trajectories of relatively coarse plastics tend to shift towards center of blast furnace, finally particles move upward along with gas flow. As the concentration of carbon dioxide in the lower part of blast furnace is extremely low except raceway, residual char reached to the cohesive zone and then most of it may gasify by the direct reduction with iron ore.

![Graph showing particle trajectories](image)

**Fig. 3-14** Trajectories of plastic particles injected into blast furnace (char diameter: under 60µm).
Fig. 3-15 shows another example of calculated particle trajectories of plastics. In this case, diameter of unburnt char is set to 350µm. In the case of small plastics (initial diameter of 800µm, corresponding to APR), particles tend to move upward same as in the case of smaller unburnt char. However, it is found that trajectories of coarse plastic particles shift towards center of blast furnace, and unburnt char derived from them are accumulated around the deadman.

Fig. 3-15 Trajectories of plastic particles injected into blast furnace (char diameter: under 350µm).
Char accumulated in the deadman will be consumed by the reaction with FeO or carburization, and then only ash will be left. As shown in Table 3-3, alumina content of ash derived from plastics is very high. Its value is almost twice as large as the ordinary blast furnace slag (alumina content is around 15 wt%). Viscosity of slag with high alumina concentration is high\(^{33}\). This means that accumulation of unburnt char in a particular part of blast furnace lead to the segregation of high viscosity ash. This phenomenon may cause inhibition of gas and liquid permeability of blast furnace. Therefore, it is desirable to avoid accumulation of char in the deadman for the stable operation of blast furnace.

### 3. 4 Effect of initial plastic size on the operation of actual blast furnace

**Fig. 3-16** shows relation between APR ratio in injected plastics and lower K value \((K_l)\) at actual blast furnace. APR (fine plastics: harmonic mean diameter = 0.8mm) along with agglomerated plastics (coarse plastics: approximately φ6×10mm, harmonic mean diameter = 4mm) have been used simultaneously in this blast furnace (inner volume: 5,000m\(^3\)). Data of the same PCR level and same productivity level were used to compare only the difference of plastic injection condition. \(K_l\) is often used to evaluate the furnace permeability\(^{34}\). That is expressed as follows:

\[
K_l = \frac{(P_b^2 - P_4^2)}{V_{bosh}^{1.7}}
\]

(3-12)

Where \(P_b\) and \(P_4\) mean the pressure at the blast pressure and pressure measured at a lower shaft (4\(^{th}\) level) respectively and \(V_{bosh}\) means the average velocity of bosh gas. Smaller K value means better furnace permeability.
R.Murai, “Massive Injection of Auxiliary Reducing Agent at Blast Furnace for the Sustainable Development.”

**Fig. 3-16 Relation between APR ratio in injected plastics and lower K value ($K_L$) (actual blast furnace data).**

APR ratio in injected plastics can be calculated by dividing the injection rate of APR by the total injection rate of plastics (sum of APR and agglomerated plastics). As shown in Fig. 3-16, permeability of lower part of blast furnace is seemed to be improved as the APR ratio increases. This phenomenon corresponds to the assumption mentioned before that accumulation of unburnt char decreases in the case of APR injection.
3. 5 Conclusions

Aiming at clarifying the behavior of plastic particles injected into blast furnace, evolution behavior of volatile matter of plastic was studied by hot model experimental furnace and gasification behavior of unburnt char was quantified by thermogravimetric analysis.

By using the results obtained here in the developed mathematical model, the effect of initial size of plastic particles on the trajectory in the blast furnace was evaluated.

1) According to the observation results of heated plastic samples obtained by the hot model experiment, it was presumed that volatile matter of plastics was evolved at surface of the particle.

2) Several kinds of char carbonized in different heat rates were made by electric furnace and gasification rates of the char were analyzed by thermogravimetric analysis. It was found that gasification rate of unburnt char depended on the heating rate. Gasification rate in the case of rapid heating condition tends to increase.

3) According to the observation results from scanning electron microscope, several micro pores were observed on the surface of rapid heating char. It was suggested that gasification rate was affected by the surface properties.

4) Trajectories of plastic particles injected into blast furnace were calculated by mathematical model considering decrease in particle size by gasification. When relatively small plastic was injected or diameter of unburnt char was small, it was presumed that unburnt char went upward along with gas flow and most of it was consumed at the cohesive zone by the direct reduction with iron ore. On the other hand, when relatively coarse plastics was injected and diameter of unburnt char...
was relatively coarse, it was suggested that unburnt char accumulated around the deadman.

5) Alumina content of unburnt char derived from plastics is rather high in general, therefore viscosity of produced slag is rather high. It is considered that accumulation of unburnt char causes decrease in gas and liquid permeability. Thus it is suggested that fine plastics injection is desirable for the stable operation of blast furnace.
Nomenclature:

\( C_p \) \( \text{specific heat at constant pressure, J/kg} \cdot \text{K} \)

\( C_d \) \( \text{drag coefficient, -} \)

\( D \) \( \text{diffusion coefficient, m}^2/\text{s} \)

\( d_p \) \( \text{diameter of plastic particle, m} \)

\( d_c \) \( \text{diameter of coke particle, m} \)

\( E \) \( \text{radiation energy, W/m}^2 \)

\( E_a \) \( \text{activation energy, J/mol} \)

\( F_d \) \( \text{drag force, N} \)

\( F_f \) \( \text{friction force, N} \)

\( g \) \( \text{gravitational acceleration, m/sec}^2 \)

\( h_p \) \( \text{heat transfer coefficient, W/(m} \cdot \text{K)} \)

\( k \) \( \text{rate constant, 1/s} \)

\( L \) \( \text{mean free path, m} \)

\( \ell \) \( \text{characteristic length, m} \)

\( M \) \( \text{molecular weight, g/mol} \)

\( Nu \) \( \text{Nusselt number, -} \)

\( P \) \( \text{pressure, kPa} \)

\( P_{CO_2} \) \( \text{partial pressure of CO}_2, \text{mol/mol} \)

\( P_4 \) \( \text{pressure at shaft 4}^{\text{th}} \text{ level, kPa} \)

\( Q \) \( \text{latent heat of plastics, kJ/kg} \)

\( R \) \( \text{gas constant, J/mol} \cdot \text{K} \)

\( r \) \( \text{particle radius, m} \)

\( S \) \( \text{rate of generation or consumption, kg/m}^3/\text{s} \)

\( T \) \( \text{temperature, K} \)
\( t \)  time, sec

\( u \)  velocity, m/sec

\( V_{\text{bosh}} \)  average velocity of bosh gas, Nm3/min

\( X \)  fractional char conversion, -

\( W \)  weight of char, g

\( W_{\text{ash}} \)  weight of ash in char, g

**Greek letters:**

\( \alpha \)  constant (calculation for mean free path), -

\( \Phi \)  energy dissipation term, W/m\(^3\)

\( \lambda \)  thermal conductivity, W/(m \cdot K)

\( \mu_e, \mu_m \)  coefficient of viscosity, Pa \cdot s

\( \mu_f \)  friction coefficient, -

\( \rho \)  density, kg/m\(^3\)

\( \omega_j \)  mass fraction of component j, -

**Subscripts:**

\( b \)  blast

\( g \)  gas

\( p \)  particle

\( x \)  x directional component

\( y \)  y directional component

\( 0 \)  value at initial condition
References


R.Murai, “Massive Injection of Auxiliary Reducing Agent at Blast Furnace for the Sustainable Development.”

50(2010), 962.

33) M. Hoshi and T. Kawaguchi: CAMP-ISIJ, 12(1999), 710.

Chapter 4 Solution combustion synthesis of \( \text{Ca}_2\text{AlMnO}_5 \) as an oxygen storage material

4.1 Introduction

Establishing an energy-saving air separation process has the possibility of contributing to the solution of energy problems and global warming. Because oxygen is the element most widely used in a variety of chemical reactions\(^1\), large amounts of high purity oxygen are required for various industries. Oxygen is indispensable element for accelerating the combustion reactions of auxiliary reducing agent also in the blast furnace. Cryogenic distillation, which exploits the difference in the relative volatilities of oxygen and nitrogen, is the most common air separation process. However, it is well known that cryogenic distillation requires a large amount of energy to liquefy air\(^2\). Therefore, development of a more energy-efficient air separation is urgently needed.

As alternative air-separation technologies pressure swing adsorption (PSA) and temperature swing adsorption (TSA) using solid sorbents have attracted increased attention for air separation. In these processes, \( \text{O}_2 \) or \( \text{N}_2 \) in air are adsorbed in a solid and then released by changing the pressure or temperature of the sorbent. Zeolite\(^3\) and carbon molecular sieves\(^5\) have been used extensively as sorbents. However, their selectivities for oxygen or nitrogen as well as their gas storage capacities are insufficient for energy efficient air separation.

Perovskite and perovskite-like oxides are the most promising solid sorbents for air separation by PSA or TSA, because they can selectively adsorb a considerable quantity of oxygen\(^6\). Yang and Lin have reported on the oxygen storage/release performance of \( \text{La}_{0.1}\text{Sr}_{0.9}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3.6} \) and \( \text{La}_{0.1}\text{Sr}_{0.9}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3.6} \) by
thermogravimetric analysis at 773 and 873 K under oxygen pressures ranging from $1.3 \times 10^{-4}$ to 1 atm. These oxides exhibit high selectivity, large oxygen storage capacity, and fast adsorption/desorption kinetics\(^9\). These authors also have reported the effect of dopant addition on the oxygen storage capacity of $La_{0.1}Sr_{0.9}Co_{0.5}Fe_{0.1}O_{3-\delta}$. Karppinen, Motohashi, and Kadota et al.\(^7\) have reported on the oxygen storage/release properties of $RBaCO_4O_{7+\delta}$ ($R=Y$, Dy, Ho, Er, Tm, Yb, and Lu) and have discovered that the materials can store and release a large amount of oxygen in the temperature range of 473-873 K. He et al. investigated $Sr_{1+x}Co_{0.8}Fe_{0.2}O_3$ ($-0.2 \leq x \leq 0.1$) and discovered that $Sr_{0.9}Co_{0.8}Fe_{0.2}O_3$ has a large oxygen storage capacity and excellent stability after 1120 cycles of oxygen charging and discharging\(^10\).

Although various oxides have been investigated as oxygen storage materials, $Ca_2AlMnO_5$, which consists only of rock forming materials\(^1\), is very promising based on its large oxygen storage capacity. $Ca_2AlMnO_5$ is classified as a Brownmillerite, which is an oxygen-deficient B-site ordered perovskite with a general formula of $A_2B_2O_5$\(^1\). Motohashi et al.\(^1\) first reported that $Ca_2AlMnO_5$ can be applied in oxygen enrichment. They reported that this material can store/release about 3.0 wt% oxygen topotactically in response to variations in temperature and the surrounding atmosphere in a highly reversible manner\(^1\). Palmer et al. reported on the basis of a crystal structure study that $Ca_2AlMnO_5$ absorbs excess oxygen at 873 K under 30 MPa oxygen pressure to form $Ca_2AlMnO_{5.5}$, consistent with the oxidation of $Mn^{3+}$ to $Mn^{4+}$\(^12\). This result indicates that $Ca_2AlMnO_5$ has the potential to store/release 3.3 wt% of oxygen, which is greater than that of other perovskite-structured materials. In addition, it has been reported that it is possible to change oxygen storage/release performance by changing A-site or B-site components\(^1\).
Solid state reaction and coprecipitation are established methods of producing Ca₂AlMnO₅. However, both methods require a heat-treatment period, the former needing 48 h at 1523 K \(^{13}\) and the latter needing 36 h at 1523 K \(^{11}\) and also producing an impurity. In addition, there has been no comprehensive study of the optimal conditions for Ca₂AlMnO₅ production, even though it is a promising material for energy efficient air separation.

Solution combustion synthesis (SCS) is a promising alternative for producing perovskite-like oxides. The process involves a highly exothermic, self-sustaining reaction generated by heating a solution mixture of aqueous metal salts and fuels. The method is reported to enable the uniform (homogeneous) doping of trace quantities of various elements within a solid matrix\(^{14}\). The purpose of this study is to establish optimized conditions for glycine nitrate-based SCS (first proposed by Chick et al. \(^{15}\)) of single-phase Ca₂AlMnO₅. The effect of the amount of glycine and period of heat-treatment on the morphology, crystallinity, and oxygen uptake/release performance of the products are discussed.

4.2 Experiment

4.2.1 Sample preparation

Ca₂AlMnO₅ was prepared by the combination of SCS and heat treatment (firing and annealing). Samples of Ca₂AlMnO₅ were prepared from commercially available Ca(NO₃)₂ 4H₂O (Alfa Aesar, 99 %), Al(NO₃)₃ 9H₂O (High Purity Chemical Co. Ltd., 98.0 %), 50% w/w aqueous Mn(NO₃)₂ (Alfa Aesar), and glycine (C₂H₅O₂N) (Kanto Chemical Co. Ltd., 99.0 %). Glycine was used as the combustion fuel. The SCS of Ca₂AlMnO₅ can be expressed by the following overall exothermic
reaction (4-1):

$$2\text{Ca(NO}_3\text{)}_2\cdot 4\text{H}_2\text{O} + \text{Al(NO}_3\text{)}_3\cdot 9\text{H}_2\text{O} + \text{Mn(NO}_3\text{)}_2 + n\text{C}_2\text{H}_5\text{O}_2\text{N} + \text{XO}_2 \rightarrow \text{Ca}_2\text{AlMnO}_5 + \text{Gases} \quad (4-1)$$

Here, $n$ is a mol number of glycine. An index denoting the relative quantity of glycine used in the synthesis is the fuel ratio, $\phi$, which is defined by the following equation taken from reference\textsuperscript{16}.

$$\phi = \left| \frac{\text{total valency of fuel}}{\text{total valency of oxidizer}} \right|$$

$$= \left| \frac{n[2 \times 4_{(\text{O})} + 5 \times 1_{(\text{N})} + 0_{(\text{O})} - 2 \times 2_{(\text{O})}]}{2 \times [2_{(\text{Ca})} + 2 \times (0_{(\text{N})} - 3 \times 2_{(\text{O})})] + [3_{(\text{Al})} + 3 \times (0_{(\text{N})} - 3 \times 2_{(\text{O})})] + [2_{(\text{Mn})} + 2 \times (0_{(\text{N})} - 3 \times 2_{(\text{O})})]} \right| \quad (4-2)$$

Here, $\phi = 1$ indicates a stoichiometric mixture, $\phi < 1$ indicates an insufficient fuel condition, and $\phi > 1$ means an excess fuel condition\textsuperscript{17}. In this study, $\phi = n/5$.

The starting materials were stoichiometrically mixed with distilled water using the different $\phi$ of glycine. Subsequently, the resulting solutions were evaporated to sol-gels at 368 K, which were transferred to a laboratory made apparatus for SCS as described in our previous study\textsuperscript{14,17-19}. The reactor consisted
of a stainless steel bin with a long vertical stainless steel mesh chimney, which permitted the safe removal of large amounts of gases during combustion. A K-type thermocouple was placed in the center of the sol-gel reactants to measure the combustion temperature. The reactor was transferred to a heater, which was pre-heated and maintained at 673 K. The viscous sol-gel mixtures self-ignited under heating to produce voluminous ashes and the emission of a large quantities of gas. The ashes of the reactants remaining in the reactor were collected.

To obtain $\text{Ca}_2\text{AlMnO}_5$ the precursors from the SCS procedure were fired at 1523 K in air (optionally) and then annealed at 1523 K in flowing $\text{N}_2$ gas (99.99% purity) to minimize the amount of excess oxygen in the $\text{Ca}_2\text{AlMnO}_{5+\delta}$ phase. Table 4-1 lists the experimental conditions used to synthesize $\text{Ca}_2\text{AlMnO}_5$ in this study. The effect of $\phi$, the temperature of firing/annealing, and the period of firing/annealing on the phase compositions, morphology, crystallinity, and oxygen uptake/release performance of the products was investigated.

4.2.2 Material characterization

Powder X-ray diffraction (XRD, Rigaku Miniflex, Cu Ka) was used to characterize the phase compositions of the obtained materials. Scanning electron microscopy (SEM, JEOL, JSM-7001) was used to observe morphology and structure. The decomposition behaviors of the precursors from SCS were studied by use of a combined thermogravimetric and differential scanning calorimetry (TG/DSC1) analyzer (METTLER TOLEDO TG-DSC1). Samples were heated at a rate of 10 K/min in air. The oxygen uptake/release characteristics were investigated by use of a TG analyzer (METTLER TOLEDO TG-DSC1). Isothermal TG data were measured to estimate the equilibrium oxygen content of each
product. Oxygen uptake measurements were carried out on 30 mg specimens after switching the gas flow (200 mL/min) from N₂ to O₂ at 573 K, release measurements were performed after switching the gas flow from O₂ to N₂ at 773 K. The temperature scan was also performed up to 1173 K with heating/cooling rates of ± 2 K/min.

### Table 4-1 Conditions for synthesis of Ca₂AlMnO₅.

<table>
<thead>
<tr>
<th>No.</th>
<th>Fuel ratio, ( \Phi ) [-]</th>
<th>Conditions for firing</th>
<th>Conditions for annealing</th>
<th>Apparatus</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>10</td>
<td>1523</td>
<td>1440</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>10</td>
<td>1523</td>
<td>1440</td>
</tr>
<tr>
<td>3</td>
<td>1.5</td>
<td>10</td>
<td>1523</td>
<td>1440</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>0.5</td>
<td>10</td>
<td>1523</td>
<td>720</td>
</tr>
<tr>
<td>9</td>
<td>0.5</td>
<td>10</td>
<td>1523</td>
<td>3600</td>
</tr>
</tbody>
</table>

TF: Tubular furnace, MF: Muffle furnace, TAI: Thermal analysis instrument
4. 3 Results and Discussion

4. 3. 1 Effect of $\phi$ on the structure, morphology, and oxygen uptake and release

Fig. 4-1 shows the TG curve of the precursors from the SCS procedure, which were obtained at different $\phi$ (0.5, 1.0, and 1.5). The measurements were performed in air at a heating rate of 20 K/min. The total weight loss were found to be about 31 %, 16 %, and 26 % for the precursors obtained at $\phi = 0.5$, 1.0, and 1.5 respectively. The sample at $\phi = 1.0$ showed the lowest weight loss and a remarkable weight loss peak indicating an efficient combustion reaction between the glycine fuel and nitrate oxidizers at near stoichiometric conditions. The weight loss at 923 – 1073 K could be caused by the decomposition of CaCO$_3$, formed during SCS. Because CaO is generated by decomposition of Ca(NO$_3$)$_2$ during SCS, it would easily react with CO$_2$ from the oxidation of glycine to form the carbonate. It was expected that the SCS-derived precursors would show greater weight changes at $\phi = 0.5$ and 1.5, because insufficient combustion reactions at the fuel-poor or rich conditions might leave a large amount of unreacted glycine or nitrate residues. Although different $\phi$ values produced different trends and total amounts of weight loss, all weight changes were completed by about 1013 K for all samples. Therefore, we concluded that the heat treatment temperature needed to form a stable product should be higher than 1013 K.
Fig. 4-1 TG curve of the precursor, from SCS synthesized at $\phi = 0.5$, 1.0, and 1.5 obtained under air at a heating rate of 20 K/min.

Fig. 4-2 shows the XRD patterns of the products at different $\phi$ values. Each sample was fired at 1523 K in air for 24 h and annealed in N$_2$ for 720 min. This heat treatment condition is same as that reported by Motohashi et al. $^{11}$, wherein Ca$_2$AlMnO$_5$ is synthesized almost completely by the coprecipitation method. The peaks of all samples are independent of $\phi$ and are completely in accord with the XRD patterns of the Ca$_2$AlMnO$_5$, confirming the successful synthesis of this compound by SCS and subsequent heat treatments.
Fig. 4-2 XRD patterns of the samples obtained from SCS at different $\phi$. Each sample was fired at 1523 K in air for 1440 min and annealed in N$_2$ for 720 min.

Fig. 4-3 shows the SEM images of the precursor samples from SCS at different values of $\phi$ and the products obtained from the same heat treatment (firing at 1523 K for 1440 min and annealing at 1523 K for 720 min). Porous structures were observed for each precursor, with the higher $\phi$ samples displaying a more porous configuration. On the other hand, the structures of the heat-treated products were similar regardless of $\phi$ and had grain boundaries in the range of 1 to 10 $\mu$m but no porous configuration. This occurred because the heat-treatment
temperature of 1523 K was sufficient to sinter and grow crystal grains, but too high to retain a porous structure. However, a heat-treatment temperature of 1523 K is needed to synthesize single phase Ca$_2$AlMnO$_5$.

![Figure 4-3 SEM images of precursor samples from SCS at different $\phi$, and after firing at 1523 K for 1440 min in air and annealing at 1523 K for 720 min in N$_2$.](image)

As shown in **Fig. 4-4**, porous configurations are retained for products heat-treated in the range of 1173 – 1373 K. These products displayed small, broad peaks corresponding to Ca$_2$AlMnO$_5$ by XRD as shown in **Fig. 4-5**. In addition, they showed smaller oxygen storage and release capacities (see **Fig. 4-6**).
Fig. 4-4 SEM images of the samples prepared by SCS at $\phi = 1$ and heat-treated at different temperatures in comparison to that of the SCS precursor.
R. Murai, “Massive Injection of Auxiliary Reducing Agent at Blast Furnace for the Sustainable Development.”

**Fig. 4-5** XRD patterns of samples prepared by SCS at $\phi = 1$ and heat-treated at different temperatures in comparison to those of the SCS precursor. ($T_f$: Firing temperature, $T_a$: Annealing temperature).
R. Murai, “Massive Injection of Auxiliary Reducing Agent at Blast Furnace for the Sustainable Development.”

Fig. 4-6 TG curves up to 1073 K for the samples prepared by SCS at $\phi = 1$ and heat-treated at different temperatures. Data were measured in a flowing O2 atmosphere with a scan rate of $\pm 2$ K/min.
Fig. 4-7 shows TG curves up to 1073 K for the products obtained at different values of $\phi$ and the same heat treatment conditions (firing at 1523 K for 1440 min and annealing at 1523 K for 720 min). The data were measured in a flowing $O_2$ (Purity: 99.5 %) atmosphere at a scan rate of $\pm 2$ K/min. Looking at the product for which $\phi = 1.0$, the weight of the sample increased rapidly during the heating process by about 3 wt%, around 573 K, then gradually decreased over a 623 K interval, and decreased suddenly around 923 K. In the cooling process, the weight of the sample increased rapidly at about 873 K, and then gradually continued to increase up to about 3 wt %.

Fig. 4-7 TG curves up to 1073 K for the samples obtained by SCS at different $\phi$, fired at 1523 K for 1440 min in air, and annealed at 1523 K for 720 min in $N_2$. The data were measured in a flowing $O_2$ atmosphere with a scan rate of $\pm 2$ K/min.
All products exhibited a similar pattern of oxygen-storage and release. The reversible oxygen storage/release behavior of Ca$_2$AlMnO$_5$ is in good agreement with the report of Motohashi et al.\textsuperscript{11}, in which Ca$_2$AlMnO$_5$ is synthesized almost completely by a coprecipitation method. Our results show that SCS is an effective new route to the synthesis of Ca$_2$AlMnO$_5$.

### 4.3.2 Effect of periods of heat-treatment

Fig. 4-8 shows the XRD patterns of the samples prepared by SCS at $\phi=0.5$, and heat-treated for different lengths of time (1 – 4320 min) at 1523 K. All samples showed clear evidence of Ca$_2$AlMnO$_5$. Interestingly, the sample with only 1 min annealing (without firing) also showed a distinct Ca$_2$AlMnO$_5$ phase. This is a much shorter heat-treatment period for Ca$_2$AlMnO$_5$ synthesis than that of other methods such as coprecipitation and solid state reaction. Motohashi et al. synthesized Ca$_2$AlMnO$_5$ by coprecipitation from nitrate salts and employed a heat-treatment period of 36 h at 1523 K\textsuperscript{11}. Wright et al. and Palmer et al. synthesized Ca$_2$AlMnO$_5$ from carbonate and oxide powders by solid state reaction at 1523 K for 48 h\textsuperscript{12,13}. Therefore, the SCS affords the energy saving advantage of rapid synthesis of high-purity Ca$_2$AlMnO$_5$. The formation of Ca$_2$AlMnO$_5$ by annealing without firing showed that the precursors from SCS consisted of CaO, Al$_2$O$_3$, Mn$_2$O$_3$ and that Ca$_2$AlMnO$_5$ was synthesized by the following reaction:

$$2\text{CaO} + 1/2 \text{Al}_2\text{O}_3 + 1/2 \text{Mn}_2\text{O}_3 \rightarrow \text{Ca}_2\text{AlMnO}_5$$

(4-3)
Fig. 4-8 XRD patterns of the samples prepared by SCS at $\phi = 0.5$ and heat-treated for different lengths of time (1-4320 min) at 1523 K.
Fig. 4-9 shows the crystallite sizes of the samples prepared by SCS at $\phi=0.5$, and heat-treated for different periods (1 – 4320 min) at 1523 K. The crystallite sizes, $t$ were calculated by use of Scherer’s equation:

$$t = \frac{K\lambda}{B \cos \theta}$$  \hspace{1cm} (4-4)

Fig. 4-9 Crystallite sizes of the samples prepared by SCS with $\phi = 0.5$ and heat-treated for different intervals (1-4320 min) at 1523 K.
where $K$ is the shape factor ($K = 0.848$ in study), $\lambda$ is the X-ray wavelength, $B$ is the linewidth (measured in radians) at half the maximum intensity, and $\theta$ is the Bragg angle. The most intense peak at $2\theta = 33.7$ was used for the calculation. The crystallite sizes calculated were $39.2$, $40.1$, $41.1$, $46.3$, $50.7$, and $51.6$ nm for samples heat-treated at $1523$ K for $1$, $5$, $30$, $60$, $1440$, and $4320$ min. Crystallite size increased with increasing length of heat treatment; a notable jump in size occurred in the interval between $30$ and $60$ min.

**Fig. 4-10** shows SEM images of the samples prepared by SCS with $\phi = 0.5$, which were then heat-treated for different length of time ($1 - 4320$ min) at $1523$ K.
Each sample including the one heat treated for 1 min exhibited a clear grain boundary. Grain sizes increased with an increase in the duration of heat treatment. The grain sizes after 1, 5, and 30 min were about 30, 200 and 600 nm respectively, and those after 1440 and 4320 min were over 1 μm. This trend agrees with the results of XRD diffractions and with the crystallinity calculated from Scherer’s equation.

**Fig. 4-11** shows isothermal TG curves for a) oxygen uptake mode at 573 K in an O₂ atmosphere, and b) oxygen release at 773 K in N₂ (99.999%) atmosphere for samples prepared by SCS with φ = 0.5, which were then heat treated for different lengths of time (1-4320 min) at 1523 K. The oxygen storage capacities increase with longer heat treatment. Those of samples heat-treated for 1, 5, 30, 60, 720, and 3600 min were 2.0, 2.2, 2.5, 2.7, 3.0, and 3.0 wt%, respectively. This result suggests that the oxygen storage capacities are strongly related to the crystallinity of Ca₂AlMnO₅ as shown in Fig. 4-9 with samples of greater crystallite size having the larger oxygen storage capacity. Ca₂AlMnO₅ samples obtained by heat treating for 1 and 5 min had low oxygen storage and release rates are affected by crystallinity. On the other hand products prepared by a heat-treatment period of 30 min showed higher rates of oxygen storage and release. This indicates a grain size effect on the rate of oxygen storage and release. A smaller grain size sample possesses a larger proportion of grain boundaries, which would provide a path for oxygen migration on the surface. Therefore, 30-60 min interval at 1523 K represents an optimum condition for the heat-treatment of precursors synthesized by SCS.
Fig. 4-11 Isothermal TG curves for: a) the oxygen uptake mode at 573 K in an O\textsubscript{2} atmosphere, and b) oxygen release at 773 K in N\textsubscript{2} (99.999%) atmosphere for samples prepared by SCS with \( \phi = 0.5 \), which were then heat treated for different lengths of time (1-4320 min) at 1523 K.
4.4 Conclusions

In summary, the high capacity oxygen storage material, Ca$_2$AlMnO$_5$, which has applications in air-separation technology, was synthesized by glycine-nitrate-based solution combustion synthesis. The effects of glycine content and length of heat treatment on the structure, morphology, and oxygen storage/release properties of the products were investigated to find optimized production conditions. Single phase Ca$_2$AlMnO$_5$, whose maximum reversible oxygen uptake and release amounts to about 3.0 wt%, was successfully synthesized with various glycine contents. Single phase Ca$_2$AlMnO$_5$ can be synthesized by combination of SCS and just 1 min of heat treatment at 1523 K. Products prepared with longer periods of heat-treatment exhibited greater crystallinity and larger reversible oxygen storage capacities. The present results indicate that the glycine-nitrate SCS process is an attractive method for the fabrication of Brownmillerite-type Ca$_2$AlMnO$_5$. 
References


Chapter 5 Development of new cooling system to increase injection amount of auxiliary reducing agent to blast furnace

5.1 Introduction

Life time prolongation of blast furnace has been one of the most important issues to avoid considerable investment cost in the iron making process. Life time of a blast furnace is usually determined by the deformation or damage of cooling staves (CS) as well as wear of bottom brick because they are difficult to repair during campaign. Injection of auxiliary reducing agent such as pulverized coal and used plastics has been expanding year by year. However, it has been pointed out that strengthen of peripheral gas flow leads to increase in the heat load to wall of furnace due to the change in the permeability of lower part of blast furnace. Considering the need for increase in the injection amount of auxiliary reducing agent, development of new long life CS is so important to cope with change of the in-furnace situations.

It has been reported that CS made with copper instead of conventional cast iron has been used to enhance the durability of the bosh part. Basically, many of them are only a study of general evaluation to the operational conditions at particular blast furnace, and there are few reports regarding thermal and mechanical characteristics and mechanism of wearing of copper CS considering above mentioned in-furnace situation such as high rate injection of pulverized coal.

Rolled copper has been used as material of copper CS. However, cast copper has excellent features such as good workability (castability) and lower production cost to make CS. In this chapter, characteristics of CS made with cast iron, rolled copper, and cast copper are evaluated by the numerical simulation of heat transfer
and thermal stress using finite-element method (FEM) at first. Then, result of application of developed cast copper CS to the actual blast furnace is discussed.

5.2 Effect of operational condition of blast furnace on heat load to furnace wall

Gas and liquid permeability in the deadman is affected greatly by injection of auxiliary reducing agent as mentioned before. Fig. 5-1 shows a schematic drawing of lower part situation at high rate injection of solid auxiliary reducing agent such as pulverized coal or plastics. Formation of poor permeability layer at the end of raceway and increase in accumulation of coke fine into deadman by injection of auxiliary reducing agent prevent gas and heat supply to the deadman region. And maximum temperature position in the raceway approaches to the tuyere (wall) side by the combustion of auxiliary reducing agent.

For the above reasons, heat load to the furnace wall is increased by peripheral gas flow with high temperature at the lower part of blast furnace.

To clarify the effect of operation conditions of blast furnace on the heat load to the furnace wall, gas flow and heat transfer analysis using two-dimensional numerical simulations are conducted. Table 5-1 shows a calculation condition of the simulation. Case-1 represents base condition. Case-2 represents operation condition with higher reducing agent and higher productivity. Case-3 represents operation condition with high auxiliary reducing agent (pulverized coal) injection.
Fig. 5·1 Schematic drawing of lower part of blast furnace at high rate injection of solid auxiliary reducing agent such as pulverized coal or plastics.
Table 5-1 Calculation conditions of 2-dimensional model for lower part of blast furnace.

<table>
<thead>
<tr>
<th></th>
<th>Case - 1</th>
<th>Case - 2</th>
<th>Case - 3</th>
</tr>
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<tbody>
<tr>
<td>Productivity (t/d·m³)</td>
<td>1.80</td>
<td><strong>2.20</strong></td>
<td>1.80</td>
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<tr>
<td>RAR (kg/thm)</td>
<td>500</td>
<td><strong>550</strong></td>
<td>500</td>
</tr>
<tr>
<td>PCR (kg/thm)</td>
<td>100</td>
<td>100</td>
<td><strong>200</strong></td>
</tr>
</tbody>
</table>

RAR: Reducing Agent Rate  
PCR: Pulverized Coal injection Rate

**Fig. 5-2** shows a simulation result of gas velocity and gas temperature at bosh part (1 meter above the tuyere level). It is clear that gas velocity at 1m above tuyere level is increased by increase in bosh gas volume in the Case-2. In the Case-3, maximum temperature point is approached to the wall and peripheral gas temperature is increased along with increase in the bosh gas volume. According to the simulation results, it is suggested that heat load at the bosh part is increased due to the increase in gas velocity in the case of higher reducing agent operation and high productivity (large amount of bosh gas) operation. Moreover, in the case of high rate injection of auxiliary reducing agent, heat load to the bosh may increase compared with the conventional operation due to the increase in gas velocity and gas temperature at the same time.
Fig. 5-2 Gas temperature and gas velocity at 1 meter height from tuyere axis calculated by 2-dimensional model.

It is considered that increase in heat load accelerates the breakage of CS. Injection of auxiliary reducing agent, however, may spread widely considering its advantage. Therefore, development of high-durability CS that can resist heat load plays important role.
5. Development of cast copper CS

5.1 Concept of enhancing durability of CS

To avoid the breakage of CS by thermal deformation, it is important to keep temperature of CS body low. And wearing of CS is prevented by the formation of slag accretion layer to the surface of CS. To achieve these concepts, copper is considered to be desirable as a material of CS instead of conventional cast iron because of its high thermal conductivity.

Table 5-2 shows physical and mechanical properties of material for CS.

<table>
<thead>
<tr>
<th></th>
<th>Cast iron</th>
<th>Cast copper</th>
<th>Rolled copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda ) (W/m·K)</td>
<td>30-40</td>
<td>190-230</td>
<td>325-350</td>
</tr>
<tr>
<td>Melting point (K)</td>
<td>1453</td>
<td>1353</td>
<td>1353</td>
</tr>
<tr>
<td>Density (kg/m(^3))</td>
<td>7200</td>
<td>8900</td>
<td>8900</td>
</tr>
<tr>
<td>Linear expansion (1/K)</td>
<td>1.1 \times 10^{-5}</td>
<td>1.6 \times 10^{-5}</td>
<td>1.7 \times 10^{-5}</td>
</tr>
</tbody>
</table>

(\( \lambda \): Thermal conductivity)
Copper has higher thermal conductivity compared with cast iron, so cooling ability is also high. Cast copper has been used successfully as material of tuyere and cooling box and it has flexibility in shape. However, cast copper has small amount of additives to prevent occurrence of internal defects. So, thermal conductivity of cast copper is slightly low compared with rolled copper because of its impurities\textsuperscript{12}.

5. 3. 2 Analysis of heat transfer and thermal stress of CS

In this section, characteristics of CS made with cast iron or cast copper are evaluated by the numerical simulation of heat transfer and thermal stress using finite-element method. Difference of thermal conductivity between cast copper and rolled copper is small, so it is possible to deduce the calculation result of rolled copper CS by that of cast copper CS.

Fig. 5-3 shows calculation conditions and outline drawing of the CS.

<table>
<thead>
<tr>
<th>Boundary conditions</th>
<th>Calculation model</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Materials</strong></td>
<td><img src="image" alt="Calculation model" /></td>
</tr>
<tr>
<td>- Stave : Cast Iron, Cast Copper</td>
<td></td>
</tr>
<tr>
<td><strong>Heat transfer coefficient (W/m$^2$ K)</strong></td>
<td></td>
</tr>
<tr>
<td>- On shell outside   : 4.44</td>
<td></td>
</tr>
<tr>
<td>- On stave hot face  : 97.6</td>
<td></td>
</tr>
<tr>
<td>- On cooling pipe inside : 9630</td>
<td></td>
</tr>
<tr>
<td><strong>Boundary temperature(K)</strong></td>
<td></td>
</tr>
<tr>
<td>- Atmosphere : 298</td>
<td></td>
</tr>
<tr>
<td>- Process gas : 1,773</td>
<td></td>
</tr>
<tr>
<td>- Cooling water : 303</td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 5-3 Calculation conditions of the FEM analysis.**
To discuss only effect of material, shape of CS and boundary conditions are exactly same. Although there may be slag accretion layer formed by the solidification of molten slag dropping on the surface of CS when the CS is applied in the actual blast furnace, the effect of accretion layer is excluded from the calculations.

**Fig. 5-4** shows temperature distributions of cast copper CS and cast iron CS, and **Fig. 5-5** shows thermal stress distributions of cast copper CS and cast iron CS. Thermal stress is estimated by Mises’s equivalent stress. Gas temperature of inside of furnace is set at 1773 K. Temperature difference about 500 to 600 K between surface and back face is observed in the case of cast iron CS according to Fig. 5-4. Although there are temperature difference between surface and back face in the case of cast copper CS, the difference is so small. Consequently, thermal stress of cast copper CS is small as a whole as shown in Fig. 5-5.

![Fig. 5-4 Calculated temperature distribution by FEM analysis.](image)
Fig. 5-5 Calculated stress distribution by FEM analysis.

Fig. 5-6 shows comparison of maximum temperature, maximum thermal stress, and heat flux in each CS. Maximum temperature of cast copper CS is 498 K, it is much smaller than that of cast iron CS reflecting its high cooling ability. Value of thermal stress caused by temperature gradient estimated to be small.

On the basis of these basic studies, cast copper CS was newly developed and experiments at actual blast furnace were conducted.
Fig. 5-6 Comparison of FEM results of maximum temperature, maximum stress, and heat flux (Without accretion layer on the surface of CS).

5.4 Long-term wear resistance evaluation of CS at actual blast furnace

It is expected that life time of copper CS is prolonged because its thermal deformation is smaller than that of cast iron staves according to the numerical simulations. Then, wear resistance properties of copper CS was investigated.

A cast copper CS for wear test was installed in December 1983 at the lower shaft part of Fukuyama No. 2 blast furnace and it was removed after ten years and ten months for the investigation. Fig. 5-7 shows a set position of cast copper CS and appearance of removed CS. The cast copper CS was set in front of cast iron CS.
In the case of cast iron CS, a lot of cracks are observed at the surface of CS. On the contrary, there are few damages observed in the case of cast copper CS. Actual wear amount is only two millimeters. That is corresponded to 0.17mm/year. It is reported that mechanical strength of cast iron is decreased rapidly in the high temperature. On the other hand, decrease in the mechanical strength of copper is rather gentle to increase in temperature up to around $573\ K^{14-16}$. Therefore, cast copper CS shows excellent wear resistance property because CS body temperature
is kept low due to its good cooling capability and decrease in mechanical strength is suppressed. On the contrary, in the case of cast iron CS, it is considered that wear and deformation is progressed because CS body temperature is rather high and thermal stress is high.

5. 5 Comparative examination of copper CS and cast iron CS at actual blast furnace

5. 5. 1 Method of the examination

Comparative examination of copper and cast iron CS regarding change in heat flux and thermal deformation had been conducted at the Keihin No.1 blast furnace. Fig. 5-8 shows location of examined CSs at the furnace.

![Diagram](image)

**Fig. 5-8 Location of experimental CS at Keihin No. 1 blast furnace.**
Cast copper CS, rolled copper CS, and cast iron CS were arranged adjacently each other to evaluate difference of materials. Shape and size of CS are made equal to each other.

5. 5. 2 Trends of CS body temperature

Fig. 5-9 shows trends of CS body temperature measured by the thermocouples embedded in the 10 millimeter depth from the furnace inner side. CS body temperatures made of cast copper and rolled copper changed stably low. Although the temperatures increased slightly, the temperatures are around 330 K at most. The difference between cast copper and rolled copper is not clear.

Fig. 5-9 Trends of CS body temperature.
In the early stage, the body temperature of cast iron stave showed a stable state. However, it started upward trend and reached maximum temperature more than 773K only one month after its installation. And it seemed that fluctuation of temperature was large.

5.5.3 Evaluation of heat removal amount of CS

Fig. 5-10 shows a comparison of heat flux (or heat removal amount) calculated by one dimensional heat transfer analysis based on the measured temperature difference between couple of thermocouples installed in the CS body.
Heat flux $q_i$ was calculated by the following equation:

$$q_i = \frac{\lambda_i}{d_i} \cdot \Delta T_i$$  \hspace{1cm} (5-1)

The difference of heat flux based on the measured value is so small and it can be regarded practically equal.

On the other hand, heat flux of cast copper CS simulated by FEM was estimated 1.5 times higher than that of cast iron CS as shown in Fig. 5-6. It is considered that this contradiction is caused by accretion of slag to the surface of CS. Because surface temperature of cast copper CS is decreased by strong cooling condition, slag accretion layer may be formed as a heat insulating layer on the surface of CS. Then, heat flux at actual blast furnace seems to decrease.

Next, thickness of slag accretion layer was estimated by the measurement result of temperature difference in CS. One dimensional heat transfer model with three layer structure was considered as shown in Fig. 5-11. Surface, intermediate and back layer was determined as slag accretion layer, CS body and stain adhering to the surface of cooling pipe as thermal resistance layer respectively. Thermal conductivity of stain adhering layer was estimated by the offline experiment.
Fig. 5.11 One dimensional heat transfer model for estimation of slag accretion layer thickness.

Then heat flux can be explained by

\[
q_i = \frac{T_g - T_w}{\frac{1}{h_g} + \frac{\delta_{1,i}}{\lambda_{1,i}} + \frac{\delta_{2,i}}{\lambda_{2,i}} + \frac{\delta_{3,i}}{\lambda_{3,i}} + \frac{1}{h_w}}
\]  

(5.2)
Using several assumptions such as in-furnace gas temperature and thermal conductivity of slag accretion layer, thickness of slag accretion layer was calculated by measured value of heat flux.

**Fig. 5-12** shows estimation result of slag accretion layer thickness. Slag accretion layer thickness on the surface of cast iron CS was estimated to be 3 mm. On the other hand, that of cast copper CS was estimated to be 10 mm because surface temperature of copper CS was decreased by its high thermal conductivity. The difference between cast copper CS and rolled copper CS could not be recognized in this data.

**Fig. 5-13** shows a short-term variation of body temperature of cast copper CS and cast iron CS. CS body temperature made of cast copper seemed to change stably low, while the CS body temperature made of cast iron may go up suddenly.

---

**Fig. 5-12** Estimated thickness of slag accretion layer formed on the surface of CS.
Fig. 5-13 Trends of CS body temperature in a short period.
Such rapid increase in temperature observed in the case of cast iron CS is attributed to the detachment of slag layer on the surface of CS, gradual decrease in temperature after that may be caused by reforming of slag accretion layer. In the case of cast copper CS, thick slag layer may be formed on its surface because body temperature is maintained rather low. Therefore, heat flux of cast copper CS was suppressed to almost same value of cast iron CS.

There seems to be no difference between cast copper and rolled copper practically, although thermal conductivity of cast copper is smaller than that of rolled copper slightly.

5. 6 Comparison of CS deformation behavior

Fig. 5-14 shows a comparison of transformation ratio of cooling pipe measured after three years from installation.
Transformation ratio represents a value of displacement of expansion joint divided by initial length. Displacement of cast iron CS is about 15%, while those of cast copper and rolled copper are small value around 5%. These phenomena suggest that deformation of CS body is small in the case of copper CS, because of its good cooling capability and retention of mechanical strength compared to cast iron CS.

5. 7 Effect of copper CS on the operation of actual blast furnace

Having good results as mentioned above, fifty-six cast copper CS were installed at second level of whole circumference of bosh part of Fukuyama No.4 blast furnace.

Fig.5-15 shows an operational trend of Fukuyama No.4 blast furnace. As the iron and steel demand increases in this period, productivity went up gradually. Under such condition, high rate injection of pulverized coal and low silicon content operation could be attained stably after installation of cast copper CS. It might be caused by decrease of heat level variation of blast furnace because stable descent of burden could be attained by forming firm slag accretion layer on the surface of CS in addition to decrease in erosion trouble of CS. Wear rate of cast copper CS is so small compared with that of cast iron CS and deformation is small because of low thermal stress to the CS body. Therefore, initial performance may be maintained for a long period of time without receiving aged deterioration in the case of cast copper CS, and it may contribute to stable operation of blast furnace.
5.8 Conclusions

To prolong blast furnace campaign life under the condition of high rate injection of auxiliary reducing agent, cooling staves made by cast copper have been newly developed. Mathematical analysis by using the finite element method and application to actual blast furnace were conducted. Obtained results are as follows:

(1) Simulations using the finite element method probed that maximum temperature and maximum thermal stress of cast copper CS are one third and one
sixth level compared with conventional cast iron CS respectively because of its high thermal conductivity, or high cooling capacity.

(2) Slag accretion layer seems to be formed on the surface of CS of cast copper staves judging from the measurement results of CS body temperature at actual blast furnace. Therefore, heat flux of cast copper stave is estimated as same level as that of conventional cast iron CS. Deformation and wear rate of cast copper CS is so small.

(3) Although thermal conductivity of cast copper CS is slightly inferior to that of rolled copper CS, application result at actual blast furnace showed that cooling capabilities of both CS were approximately same. Considering the flexibility and processability of cast copper, cast copper may be superior to rolled copper as a raw material of CS.

(4) Operation of actual blast furnace turned stably by the decrease in erosion trouble of CS after using cast copper CS to whole circumference of bosh part. Decrease in fluctuation of heat level may contribute to maintain of low silicon operation owing to formation of stable, thick slag accretion layer on the surface of CS.

(5) It is considered that cast copper CS is so effective to prolong blast furnace campaign life operating with injection of massive auxiliary reducing agent such as pulverized coal because of its enough cooling capacity to cope with increase in the heat load to the lower part of blast furnace.
Nomenclature

$q$: heat flux (W/m$^2$)

$\lambda$: thermal conductivity (W/m $\cdot$ K)

$\delta$: depth difference of thermocouples (m)

$T$: Temperature (K)

$\Delta T$: temperature difference of thermocouples (K)

$\delta$: thickness (m)

$h$: heat transfer coefficient (W/m$^2$ $\cdot$ K),

subscripts

i: cast iron, cast copper, rolled copper

1: slag

2: CS

3: stain adhering layer on the surface of cooling pipe
References

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12) H. Ueno: *Chuuzou Kougaku*, 73(2001),469
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Chapter 6 Mitigation of carbon dioxide emission by integrating intensive injection of auxiliary reducing agent and low reducing agent rate operation at blast furnace.

6.1 Introduction

Minimizing of carbon dioxide emissions is considered to be an important subject in steel industry from the viewpoint of green-house problem. Japan Iron and Steel Federation has issued “Report of Commitment to a Low Carbon Society” in January 2015 as a part of voluntary action program to cope with global warming problem\(^1\). Target value of carbon dioxide reduction in 2030 was set at 9 million tons per year. In the reduction of CO\(_2\) emissions, lowering of reducing agent ratio in ironmaking process is a key technology. Recently, several operation results with low reducing agent in blast furnace have been reported\(^2,3\). However, further developments are expected to decrease carbon dioxide emission to attain its target.

To reduce carbon dioxide emissions by reducing carbonaceous material, use of hydrogenous reducing agent such as used plastics is so effective. The utilization of used plastics in the blast furnace has been reported in several papers\(^4-6\). However, the massive gasification technology of used plastics under the low oxygen excess ratio is required for lowering reducing agent ratio remarkably. Some studies on low temperature reduction of wustite or lowering carburization temperature of metal have been reported\(^7,8\). These studies are useful with the intention of decrease in reducing agent rate by low temperature operation of blast furnace. Top gas recycling process has been also proposed to decrease reducing agent rate\(^9-12\). Although these are valuable as an individual technology, it is
desirable to propose integrated process as so called “innovative blast furnace” to attain the target of steel industry mentioned above.

In this chapter, simultaneous injection of pulverized coal/plastics or solid/gas reducing agents was discussed as massive injection technology under low oxygen excess ratio. Combustion efficiency of solid reducing agent is optimized by hot model experiments and three-dimensional mathematical simulation. Then, several operational parameters of innovative blast furnace such as effects of hydrogen, control of thermal reserve zone temperature, and top gas recycling are evaluated on the basis of material and heat balance calculation. Finally, possible innovative blast furnace characterized by massive used plastics injection, low temperature reduction and top gas recycling under high productivity is projected. Moreover, integrated ironmaking process with co-generating oxygen production process was proposed.

6. 2 Optimization of solid auxiliary reducing agent combustion

6. 2. 1 Concept of simultaneous injection of pulverized coal and used plastics

As mentioned before, development of intensive injection of plastics under the low oxygen excess ratio is critical technology to realize innovative blast furnace. According to the former studies, optimization of arrangement of injection lances or use of pure oxygen so called oxy-coal lance are so effective to enhance solid fuel combustion like pulverized coal. Effective use of oxygen nearby coal particles is intended in these methods. However, available oxygen is limited in the case of innovative blast furnace with low reducing agent ratio due to decrease in specific blast volume. Under such condition, other promising intensive combustion method
must be developed.

**Fig. 6-1** shows a concept of simultaneous injection method. In this method different size or kind of auxiliary reducing agents are used. Pulverized coal, plastics, and reducing gas are injected simultaneously from the tuyere. Each auxiliary reducing agent has their features such as combustibility and ignition rate. It is important to make use of such features of each fuel as much as possible.
6. 2. 2 Improvement of combustibility by simultaneous injection of pulverized coal/used plastics

Used plastics are one of the ideal reducing agents replacing coke because it contains relatively high hydrogen, so carbon emission can be reduced if massive plastics injection is achieved. Moreover, use of “used” plastics as a reducing agent in ironmaking process contributes to environmental conservation compared with use in conventional incineration process.

One of the important subjects in plastics injection is generation of unburnt char. As mentioned in chapter 3, unburnt char derived from plastics may accumulate in the lower part of blast furnace. It possibly causes the problem of low permeability or increase in coke rate. To avoid these situations, used plastics must be so sufficiently consumed in raceway.

Fig. 6-2 shows an example of an observation result of plastics particle in the blowpipe of the experimental furnace. Agglomerated plastics of approximately 5mm in diameter are injected into hot blast with temperature of 1473 K in this case.
Fig. 6-2 Observation of combustion behavior of plastic in hot blast.

This photograph was taken through the observation hole located at a position of 300 mm from the injection lance tip in the blowpipe. As shown in this figure, such coarse plastics particle could not ignite in the blowpipe. Although APR (Advanced Plastics Recycling method: see chapter 3) was developed recently, the average diameter of APR is 800 μm. That is rather coarse, while the diameter of pulverized coal is about 50 μm, method to improve the reaction of plastic particles in blowpipe to tuyere region must be developed. Fig. 6-3 shows a calculated temperature of pulverized coal and plastics particle in blowpipe. Temperature of particle is calculated considering particle velocity in blowpipe, heat convection through interface of fluid/solid, and heat conduction inside particle. In the case of plastics, temperature of particle is rather low due to specific small surface.

Fig. 6-4 shows the change of particle velocity in the blowpipe after injection.
The particles of plastics are slowly accelerated in comparison with pulverized coal because of its large mass and diameter even in the case of rather fine plastic (APR).

From this result, the author proposed a process to inject both pulverized coal and plastics simultaneously.

Fig. 6-3 Calculated temperature of particles in blowpipe.
Concept of this injection method is shown in Fig. 6-5. Larger particles are inferior in ignition but residence time in combustion zone is longer. Behavior of pulverized coal is opposite. So, combustion efficiency of pulverized coal can be increased when pulverized coal particles adhered on plastics due to the prolongation of its residence time. Then, generated heat by pulverized coal combustion can promote the plastics gasification.
Fig. 6-5 Schematic drawing of effect of simultaneous injection of pulverized coal and plastic.

Fig. 6-6 shows an appearance of normal and pulverized coal adhered plastics. Pulverized coal adhered plastics are made by mixing in atmospheric temperature. As shown in this figure, it is proved that pulverized coal particles easily adhere on plastics particle even in such a simple method. Fig. 6-7 shows the effect of simultaneous injection on the total gasification efficiency of the mixture of plastics and pulverized coal measured by hot model. Gasification efficiency of pulverized coal and agglomerated plastics is greatly enhanced by using this simultaneous injection method.
Fig. 6-6 Appearance of normal agglomerated plastic and pulverized coal adhered plastic.
Fig. 6-7 Effect of simultaneous injection on combustion and gasification efficiency measured by hot model.
6. 2. 3 Improvement of combustibility by simultaneous injection of solid/gas auxiliary reducing agents

Combustion heat of gaseous auxiliary reducing agent is considered to be available to accelerate solid auxiliary reducing agent combustion because ignition of gaseous auxiliary reducing agent is fast. To make sure this concept, combustion behavior of solid and gaseous auxiliary reducing agent is studied using 3-dimensional simulation model. Outline of the model such as arrangement of injection lances and calculation range is described in Fig. 6-8. In this model, solid and gaseous auxiliary reducing agent are injected through the lance into blowpipe and combustion behavior in blowpipe can be examined. Conditions such as blast temperature, blast volume, and oxygen concentration are set as actual blast furnace. Region of calculation is set at 500 mm from injection lance tip. Conservation of mass, conservation of momentum, conservation of energy, and k-epsilon turbulence model are used to solve fluid flow. Interaction between fluid and particle flow based on particle drag force is also considered\textsuperscript{13}.

![Fig. 6-8](image_url) Arrangement of injection lances and calculation range of 3-D simulation model for analysis of simultaneous auxiliary reducing agent injection.
Methane gas used as a gaseous auxiliary reducing agent because methane is major component of liquefied natural gas that can easily obtain and is so effective to reduce coke rate compared with other reducing gases. Fig. 6-9 shows effect of various reducing gases on the coke rate estimated by material and heat balance calculation. Methane, coke oven gas, and hydrogen are compared as practical reducing gases. Temperature of reducing gases are set at 298 K and flame temperature is controlled at 2273 K by adding oxygen properly. Maximum injection rate is determined when oxygen concentration in blast reaches 100%. From this figure, it is clearly confirmed that reduction of coke rate is significant by using methane gas.

**Fig. 6-9 Effect of various reducing gases on the coke rate estimated by material and heat balance calculation.**
**Fig. 6-10** shows calculated results of carbon monoxide distribution. Upper figure shows the result in the case of simultaneous injection of pulverized coal and methane gas, and bottom figure shows the result of pulverized coal injection. Total injection amount is set at 250 kg/thm in each case. In the case of simultaneous injection of methane gas and pulverized coal, carbon monoxide gas generation is faster than that of pulverized coal injection. Carbon monoxide gas is generated as a result of combustion reaction.

\[
C + \frac{1}{2} O_2 = CO \quad (6-1)
\]

\[
CH_4 + \frac{1}{2} O_2 = CO + 2H_2 \quad (6-2)
\]

Therefore, generation of carbon monoxide gas can be an index to estimate combustion rate.

**Fig. 6-10** Calculation result of carbon monoxide concentration by 3-D mathematical simulation model.
Fig. 6-11 represents a calculation result of gas temperature in the blowpipe. In the case of simultaneous injection of methane gas and pulverized coal, rapid increase in temperature can be seen compared with pulverized coal injection. This phenomenon also shows the effectiveness of simultaneous injection of solid/gas injection. Thus, effect of simultaneous injection on combustion efficiency of injected auxiliary reducing agents is verified.

Fig. 6-11 Calculation result of gas temperature by 3-D mathematical simulation model.
6. 3 Relationship of blast furnace operational condition and the CO₂ emission

6. 3. 1 Evaluation of CO₂ emissions by RIST diagram

Besides the intensive combustion of injected auxiliary reducing agents, it is important to determine the operational conditions to ensure the minimum carbon dioxide emission. In this section, effect of several operation parameters on the carbon dioxide emission is estimated by material and heat balance calculation. Calculations are carried out based on modified RIST diagram that can consider top gas recycle\(^ {14,15} \).

At first, oxygen balance in indirect reduction zone of blast furnace was considered as shown in Fig. 6-12. Iron Oxide is charged at \( n_{Fe} \) (mol/s) from upper end of indirect reduction zone (top of furnace) and CO and H₂ gas are supplied at \( n_{g1} \) and \( n_{g2} \) (mol/s) respectively from the lower end of the indirect reduction zone. Lower end of indirect reduction zone is determined as the level where the solution loss reaction occurs below. As auxiliary reducing agent, \( \gamma_{j} \) (mol/molFe) of \((H_{2})_{a}(O)_{b}(C)_{c}\) is injected and moisture of \( e_{w} \) (molH₂O/molFe) is included in the hot blast.

Composition of iron oxide Y is described by:

\[
Y = \frac{O}{Fe} \quad \text{(atomic ratio)} \tag{6-3}
\]

and compositions of CO-CO₂ and H₂-H₂O gas are described by:
\[ X_1 = 1 + \frac{\%CO_2}{\%CO + \%CO_2} \]  

\[ X_2 = 1 + \frac{\%H_2O}{\%H_2 + \%H_2O} \]  

Fig. 6-12 Schematic drawing of oxygen balance in the indirect reduction zone of blast furnace.
and putting \( n_g \) and \( h \) as:

\[
  n_g = n_{g1} + n_{g2} \tag{6-6}
\]

\[
  h = \frac{n_{g2}}{n_g} = \frac{[(\%H_2O)+(%H_2)]}{[(\%CO)+(%CO_2)+(%H_2)+(%H_2O)]} \tag{6-7}
\]

then oxygen balance can be described as:

\[
  n_{Fe}\cdot(Y+dY) + n_{g1}\cdot X_1 + n_{g2}\cdot (X_2\cdot-1)
  = n_{Fe}\cdot Y + n_{g1}\cdot (X_1 + dX_1) + n_{g2}\cdot (X_2\cdot-1 + dX_2) \tag{6-8}
\]

to simplify the formula:

\[
  n_{Fe}\cdot dY = n_{g1}\cdot dX_1 + n_{g2}\cdot X_2 \tag{6-9}
\]

from (6-7), (6-8), and (6-9), we can get:

\[
  n_{Fe}\cdot dY = [(1-h)\cdot dX_1 + h\cdot dX_2] \cdot n_g \tag{6-10}
\]

by putting \( X \) as:

\[
  X = [(1-h)\cdot X_1 + h\cdot X_2] \tag{6-11}
\]
from (6-10) and (6-11):

\[ \frac{dY}{dX} = \frac{n_y}{n_{Fe}} = \mu \]  \hspace{1cm} (6-12)

\( \mu \) represents amount of reducing gas to 1 mol of Fe, or reducing agent rate. By integrating (6-12) from lower end of indirect reducing zone to arbitrary level, the following equation is acquired as:

\[ Y - Y_B = \mu (X-1) \]  \hspace{1cm} (6-13)

Equations (6-4), (6-5), and (6-7) are substituted for (6-11). Then

\[ X = \frac{[(%CO)+2(%CO_2)+(%H_2O)]+[(%H_2)+(%H_2O)]}{[(%CO)+(%CO_2)+(%H_2)+(%H_2O)]} \]

\[ = \frac{O + H_2}{C + H_2} \]  \hspace{1cm} (6-14)

Therefore, equation (6-13) can be drawn by the straight line of an inclination \( \mu \) on the \( X, Y \) orthogonal coordinate as shown in Fig. 6-13. Segment AE is called as “Operating diagram” of the blast furnace.

From the Fig. 6-13, \( Y \) component of segment BE is equal to the \( \mu \). And it corresponds to sum of the CO and \( H_2 \) generated per 1 mol of Fe in blast furnace. They include the CO from direct reduction of iron oxide \( (y_{sl}) \), CO from reduction of oxide impurities \( (y_f) \), CO from combustion of blast \( (y_b) \), CO from moisture in blast \( (e_{yb}) \), CO from auxiliary reducing agent \( (by_j) \), \( H_2 \) from moisture in blast \( (e_{yb}) \), and \( H_2 \) from auxiliary reducing agent \( (ay_j) \). Then, \( \mu \) can be expressed as:
\[ \mu = \{ y_{sl} + y_t + y_b + ay_b + by_t \} \] (6-15)

**Fig. 6-13** Comparison of operation conditions of conventional blast furnace and innovative blast furnace with top gas recycling on operation diagram.

- **TRZ**: temperature of thermal reserving zone
- **HL**: heat loss
- **TGI**: Top gas injection from tuyere
- **PGI**: preheating gas injection
Considering point U on the Fig. 6-13 which satisfies the condition of following equations:

\[ OU = y_i + (a+b) y_j \]  
\[ UE = (1+2e) y_b \]

then the equation (6-13) can be rearranged as:

\[
y = \mu X - [ y_i + (a+b) y_j + (1+2e) y_b ] = [ y_i + (a+b) y_j + (1+2e) y_b ] (X-1) + y_{sl} X
\]  

Equation (6-18) represents oxygen balance in the blast furnace.

Next, heat balance in the blast furnace is considered. From the balance of heat input and heat output in the processing zone of blast furnace, following equation can be given as:

\[
y_b (q_b + q_c) + Y_w q_i = y_{sl} q_{sl} + y_i q_i + f + i + p + e y_b q_e + y_i q_j
\]  

Eliminating \( y_{sl} \) by (6-18) and (6-19), operating diagram which satisfies both heat and material (oxygen) balance can be acquired as:

\[
y_b \left[ \frac{q_b + q_c + (1+2e)q_{sl}eq_e}{q_{sl}} \cdot X - (1+2e) \right] - \left( y_i \{ y_i + (a+b) y_j \} (X-1) + \frac{Q+y_i q_i}{q_{sl}} \cdot X \right) = 0
\]
Here, $Q$ is expressed by:

$$Q = f + i + p + \gamma_i q_i + \gamma q_i - Y_w q_i \tag{6-21}$$

The conditions to hold the identical equation (6-20) are described as:

$$\begin{align*}
\frac{q_b + q_c + (1+2e)q_{sl} - eq_e}{q_{sl}} \cdot X - (1+2e) &= 0 \\
Y - \{y_f + (a+b)y'_f \} & \cdot X = 0 \tag{6-22}
\end{align*}$$

Operating diagram (6-20) is a straight line which passes through the point $P(X_p, Y_p)$ or solution of simultaneous equation (6-22) and point $W(X_w, Y_w)$ in the case of ideal operation of blast furnace. Coordinate of point $P$ is described as:

$$X_p = \frac{(1+2e)q_{sl}}{q_b + q_c + (1+2e)q_{sl} - eq_e} \tag{6-23}$$

$$Y_p = - (y_f + (a+b)y'_f) - \frac{(1+2e)\{Q+y_i q_i - \{y_f + (a+b)y'_f \} q_{sl} \}}{q_b + q_c + (1+2e)q_{sl} - eq_e} \tag{6-24}$$
Coordinate of point W that represents equilibrium gas composition of wustite and metallic Fe depends on the temperature of thermal reserving zone (TRZ). Lower TRZ temperature leads to larger $X_w$ value. That makes reducing agent rate ($\mu$) smaller. For example, in the case of TRZ temperature is 1273K under CO-CO$_2$ equilibrium, coordinate of point W is expressed by W(1.295, 1.05).

Then, we can estimate the reducing agent rate ($\mu$) or carbon emission from blast furnace when auxiliary reducing agent rate ($y_j$), moisture in blast ($e y_b$), and hot metal temperature ($f$) and so on are changed.

Conventional blast furnace and innovative blast furnace with top gas recycling are compared in Fig. 6-13. Blast furnace is divided into two parts at the level of upper end of reduction zone and material and heat balance are calculated in each parts. Reducing gas in top gas is injected to both upper and lower part in the case of innovative blast furnace. It is assumed here that iron oxide is reduced till wustite in upper part and further reduction reaction till metallic Fe occurs in lower part. TRZ temperature is set at 1223 K and 1023 K in conventional blast furnace and innovative blast furnace respectively. Operation diagrams go through P or P’ that are called thermal pinch point and W or W’ as mentioned before. Blast volume is determined by the segment OE or OE’ and flame temperature is calculated by plastics injection rate, top gas recycling rate and blast condition. In the case of innovative blast furnace, preheating gas was injected to control heat flow ratio in upper part. Therefore, gradient from W’ to A’ becomes steeper because of increase in reducing gas volume. Although apparent reducing agent rate (sum of coke rate, plastics injection rate and top gas recycling rate) corresponds to gradient of segment EW’ is increased, amount of coke and plastics can be reduced considerably.
Table 6-1 shows a concept of reducing carbon dioxide emission. Use of hydrogenous reducing agent such as hydrogen, coke oven gas, methane gas, pulverized coal and particularly plastics is effective to reduce carbon emission. Hydrogen content of coke is only about 0.5%, so using these hydrogen rich reducing agent can promote hydrogen reduction, and is so effective to reduce carbon dioxide emission.

In addition, decrease in carbonaceous material by reduction of required energy is basically needed. To decrease required energy, low temperature operation such as lowering hot metal temperature or thermal reserve zone temperature is effective. Moreover, top gas recycling process could be effective. Apparent gas utilization efficiency can be increased to 100% because only reducing gas in top gas is injected from tuyere and only sequestrated carbon dioxide is emitted.

Table 6-1 Concept of reducing carbon dioxide emission.

- **Promotion of H₂ reduction**
  - massive coal and plastics injection

- **Reduction of reducing agent rate**
  - lower thermal reserve zone temperature
  - lower heat loss from furnace shaft
  - lower slag rate
  - lower hot metal temperature
  - use of pre-reduced sinter or scrap

- **Recycling of de-CO₂ blast furnace top gas**
6.3.2 Effect of hydrogenous reducing agent on CO₂ emissions

Fig. 6-14 shows the effect of plastics injection on the carbon emission calculated by material and heat balance calculation for example. Where composition of plastics is assumed to be \( n \cdot (CH_2) \cdot n \), or content of hydrogen is three times as large as coal. Total injection amount of plastics and pulverized coal is set at 250kg/thm and flame temperature and moisture in blast are kept constant by controlling oxygen enrichment. In the figure effect of flame temperature is also shown, however effect of flame temperature on the carbon emission seems to be not important. According to Fig. 6-14, as plastics injection rate (PLR) is increased, amount of exhausted carbon is decreased remarkably. Thus, solid auxiliary reducing agent such as plastics that has high hydrogen content and high calorific value is found to be effective to reduce CO₂ emission.

![Fig. 6-14 Effect of plastic injection on carbon emission calculated by material and heat balance calculation.](image)
6.3.3 Effect of low temperature operation on CO$_2$ emissions

Fig. 6-15 shows the effect of thermal reserve zone temperature and heat loss on carbon emission where pulverized coal injection rate, theoretical flame temperature, and moisture in blast are kept constant at 250 kg/thm, 2273 K, and 20 g/Nm$^3$ respectively. As thermal reserve zone temperature decreased, carbon emission can be greatly reduced. Factor contributing this reduction is considered to be the shift of chemical equilibrium of metallic iron and wustite. When the equilibrium temperature decreased, reducing gas utilization ratio is improved. Decrease in thermal reserve zone temperature can be attained by using high reactivity coke. In the case of low temperature operation of blast furnace, decrease in heat loss from blast furnace can be also attained by decrease in thermal reserve zone temperature and decrease in hot metal temperature.
It is clear that effect of decrease in heat loss on carbon emission is considerable from Fig. 6-15.

As shown in this figure, low temperature operation of blast furnace is also effective to reduce carbon emission.

6.3.4 Evaluation of carbon dioxide emissions in various operation conditions

Case study to estimate the amount of carbon emission is carried out. Effect of moisture addition to blast, temperature of thermal reserve zone and hot metal, slag rate, pre-reduced sinter, and top gas recycle on the CO$_2$ emission is quantified by similar calculation. Table 6·2 shows calculation conditions and Fig. 6·16 shows results of calculation.

<table>
<thead>
<tr>
<th>Case No.</th>
<th>$T_b$ (K)</th>
<th>$O_{enr}$ (%)</th>
<th>Moi (g/Nm$^3$)</th>
<th>PCR (kg/t)</th>
<th>PLR (kg/t)</th>
<th>TRZ (K)</th>
<th>Slag.R (kg/t)</th>
<th>TFT (K)</th>
<th>HMT (K)</th>
<th>HL (MJ/t)</th>
<th>DRI (%)</th>
<th>RR (%)</th>
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<td>7</td>
<td>20</td>
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<td>0</td>
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<td>420</td>
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</table>

Ten cases are calculated where blast temperature is maintained at 1473 K and oxygen concentration and moisture in blast are controlled to keep given flame temperature. Exhausted carbon amount is decreased in due order except case II. Case II represents high moisture addition operation intended to promote hydrogen reduction. However, increase in moisture addition results in considerable increase in coke rate due to heat compensation for endothermic reaction of hydrogen reduction of wustite and water gas reaction.

Fig. 6-16 Calculation results of material and heat balance calculation to estimate operation conditions at various cases.
On the contrary, cases using plastics as a source of hydrogen, case III and up show better results. Lowering reserve zone temperature (case IV), use of pre-reduced sinter (case VIII) and top gas recycling (case IX) are effective in particular. In case X, reduction of nearly half amount can be attained.

6. 4 Design of innovative blast furnace process considering top gas recycling

Effect of reducing gas injection from tuyere on combustion efficiency of solid auxiliary reducing agent has been proved, and reducing gas injection is considered to be effective to decrease reducing agent rate in the above discussion. Therefore, combination of top gas recycling and innovative blast furnace is discussed as an optimized case.

Fig. 6-17 shows a schematic drawing of the process.

![Schematic drawing of optimized innovative blast furnace with top gas recycling.](image)

*Fig. 6-17 Schematic drawing of optimized innovative blast furnace with top gas recycling.*
Oxygen concentration in blast must be increased because top gas injection from tuyere results in decrease in flame temperature. This process is basically similar to the oxygen blast furnace proposed by several researchers, however this case is characterized by massive plastics injection, low thermal reserve zone temperature, and low hot metal temperature. Shaft gas injection is also needed to decrease heat flow ratio at upper furnace due to decrease in sensible heat of nitrogen in hot blast. Carbon dioxide and moisture in top gas are removed before recycling.

Several material and heat balance calculations are carried out using an improved RIST diagram that can consider top gas injection from tuyere and shaft. The results are shown in Fig. 6-18.

![Fig. 6-18 Change in carbon emission, RAR, and TFT by top gas injection rate from tuyere.](image)
Change in carbon emission, reducing agent rate, and theoretical flame temperature by top gas injection rate from tuyere are shown in this figure. All these values tend to decrease as increase in top gas injection rate. Considering lower limit of flame temperature, top gas injection rate is set at 400 Nm³/thm. Then, Reducing agent rate can be decreased by 34% compared with ordinary blast furnace. Carbon emission rate can be also decreased by 25%. If the process for sequestration and fixing of carbon dioxide can be developed, 86% of carbon emission will be reduced.

Moreover, productivity of optimized innovative blast furnace is studied. Fig. 6-19 shows flooding diagram.
Stable operation can not be continued upper region of flooding limit line indicated in the figure because droplet of slag and metal is carried over along with gas flow. Although productivity of conventional blast furnace tends to be controlled by flooding limit, however in this process, flooding condition is not critical because oxygen blast decreases amount of bosh gas rate. Productivity of optimized innovative blast furnace may be controlled by fluidizing condition at top instead. Although fluidizing limit depends on the diameter of raw materials, it is estimated that productivity of 3.5 and more is available in this process.

Table 6-3 shows an operational condition of optimized innovative blast furnace compared with conventional one based on above mentioned calculations.

| Table 6-3 Operational conditions of conventional and optimized innovative blast furnace. |
| --- | --- | --- |
| **Inner volume (m³)** | Conventional B.F. (Base) | Optimized innovative B.F. (Compact B.F.) |
| Production (t/d) | 8576 | 15000 |
| Productivity (t/dm³) | 2.0 | 3.5 |
| Blast volume (Nm³/t) | 957 | 207 * O₂ |
| Blast composition (vol%) | 0 | 400 |
| O₂ | 29.0 | 34.1 |
| N₂ | 71.0 | 17.6 |
| CO | 0.0 | 30.0 |
| CO₂ | 0.0 | 0.0 |
| H₂ | 0.0 | 18.3 |
| Blast temperature (K) | 1473 | 298 |
| TFT (K) | 2273 | 2023 |
| PCR (kg/thm) | 250 | 0 |
| PL A (kg/thm) | 0 | 100 |
| Coke rate (kg/thm) | 270 | 245 |
| Carbon emission (kg/thm) | 379 (Excluded CO₂:52(▼86%)) | 286(▼25%) |
| Slag rate (kg/thm) | 300 | 189 |
Increase in productivity is remarkable because blast volume is decreased remarkably by oxygen blast. Upper limit of productivity is determined by not flooding but fluidization condition at top. As mentioned in chapter 4, a large scale and commercially viable oxygen separator must be developed because 207 Nm$^3$/thm of pure oxygen is needed. On the other hand, hot stoves are unnecessary. Exhaust carbon can be reduced by 25% in ordinary case, but 86% will be reduced when sequestration and fixing of carbon dioxide (CCS) will be commercially available.

6. 5 Carbon balance in steelmaking works

Ironmaking process plays an important role as a source of energy in steelmaking plant. In this section, energy supply to down stream as well as carbon emission are estimated. Fig. 6-20 shows relationship between carbon emission from ironmaking process and energy supply to downstream. Calculations are carried out using material and heat balance model as mentioned before under the conditions of conventional blast furnace and innovative blast furnace. As one of the main features of innovative blast furnace, top gas recycling is considered. Amounts of carbon emission in decarbonated top gas recycling and in untreated top gas recycling are estimated separately. Carbon emission from ironmaking process can be estimated by adding carbon emissions from sinter plants, coke ovens, hot stoves, and blast furnaces. Recoverable carbon such as tar from coke oven is subtracted. Energy supply to downstream is also estimated by subtracting total energy of blast furnace gas and coke oven gas from energy consumed in ironmaking process. Generation rate of coke oven gas and carbon emission from sinter machine and coke ovens are properly assumed in this calculation.
As shown in Fig. 6·20, not only carbon emission from ironmaking process but also energy supply to downstream are decreased in the case of innovative blast furnace with top gas recycling even in without carbon dioxide sequestration compared with conventional blast furnace. In the case of innovative blast furnace with carbon dioxide sequestrated top gas recycling, energy supply to downstream goes down to around zero. It is obvious that saving energy at downstream of steelmaking works is required to realize innovative blast furnace aiming at energy half consumption and decrease in carbon emission.

Fig. 6·20 Relationship between carbon emission from ironmaking process and energy supply to downstream.
6. 6 Concept of innovative blast furnace integrated with co-generating oxygen production system

Low temperature operation, massive injection of plastics under low oxygen excess ratio condition, and top gas recycling are the key technologies for the innovative blast furnace. Apart from these, development of commercially viable process for oxygen production and sequestration of carbon dioxide is necessary.

Cryogenic distillation is the most spread air separation method. However, to liquefy the air, a large amount of energy is required. Therefore, the author focused on the oxygen storage material used in PSA or TSA process in chapter 4. In addition to this, oxygen separation by membrane filter is under development\textsuperscript{16,17}. This method can separate oxygen through inorganic membrane. These methods may be able to produce pure oxygen inexpensively compared with cryogenic distillation. Concept of integration of innovative blast furnace and oxygen production system is described in Fig. 6-21. In PSA/TSA air separation process, high temperature of 800-1000K is needed, and in membrane air separation process, oxygen transfer can be enhanced under conditions of high temperature of about 1173 K and high oxygen partial pressure. Therefore, a part of top gas is used in partial combustion chamber to heat up air. Top gas pressure is recovered by turbine to generate power and power is used to compress the air or at other plant such as carbon dioxide sequestration. Oxygen separated in this process can be used at innovative blast furnace. This process can be efficient ironmaking system characterized by integrated blast furnace process with co-generating oxygen production.
Fig. 6-21 Concept of innovative blast furnace integrated with co-generating oxygen production system.

6.7 Conclusions

Concepts to realize innovative blast furnace with minimum CO₂ emission are successively projected. The main technical features making this innovative blast furnace possible are the following:

1) Simultaneous injection of solid/solid auxiliary reducing agents using particle size difference were developed. Combustibility of small particles such as pulverized coal can be improved when they adhered on large particles thanks to
prolongation of their residence time. Then, generated heat by combustion of small particle can promote the gasification and combustion of large particles.

2) Simultaneous injection of solid/gas fuel was developed. Combustion heat of gaseous auxiliary reducing agent was considered to be available to accelerate solid auxiliary reducing agent combustion because ignition of gaseous auxiliary reducing agent is rapid.

3) Use of hydrogen rich reducing agent such as hydrogen, coke oven gas, methane gas, pulverized coal, and particularly plastics and promoting hydrogen reduction is so useful to reduce carbon dioxide emission.

4) Low temperature operation of blast furnace is also favorable to reduce carbon emission for example decrease in thermal reserve zone temperature and heat loss from the blast furnace.

5) Top gas recycling process could be effective. Apparent gas utilization efficiency can be increased to 100% if only reducing gas in top gas is injected from tuyere and only sequestrated carbon dioxide is emitted.

6) To combine with efficient oxygen production process, integration of innovative blast furnace and co-generating oxygen production system was newly proposed.

As a whole, it is expected that 86% of exhaust carbon can be reduced in optimized innovative blast furnace with top gas recycling and sequestration and fixing of carbon dioxide. Productivity can be also enhanced due to relaxation of flooding condition in this process. Productivity of 3.5 and more can be attained in this innovative ironmaking process. This innovative blast furnace enables to solve global warming problem in future.
Nomenclature:

\%
CO \quad \text{composition of CO, vol}\% \\
\%
CO_2 \quad \text{composition of CO}_2, \text{vol}\% \\
\%
H_2 \quad \text{composition of H}_2, \text{vol}\% \\
\%
H_2O \quad \text{composition of H}_2O, \text{vol}\% \\
y_{\text{sl}} \quad \text{CO gas generated per mol Fe from direct reduction, mol/mol Fe} \\
y_t \quad \text{CO gas generated per mol Fe from reduction of oxide impurities, mol/mol Fe} \\
y_b \quad \text{CO gas generated per mol Fe from oxygen in blast, mol/mol Fe} \\
éy_b \quad \text{CO or H}_2 \text{ gas generated per mol Fe from blast moisture, mol/mol Fe} \\
by_j \quad \text{CO gas generated per mol Fe from auxiliary reducing agent, mol/mol Fe} \\
ay_j \quad \text{H}_2 \text{ gas generated per mol Fe from auxiliary reducing agent, mol/mol Fe} \\
q_b \quad \text{sensible heat of blast, kJ/mol O} \\
q_c \quad \text{combustion heat of carbon, kJ/mol O} \\
q_i \quad \text{reaction heat of CO gas reduction of iron oxide, kJ/mol O} \\
q_{\text{sl}} \quad \text{reaction heat of direct reduction of iron oxide, kJ/mol C} \\
q_t \quad \text{reaction heat of reduction of oxide impurities, kJ/mol O} \\
(q_{\text{sl}} = 289 \text{ kJ/mol O}, \ q_{\text{Mn}} = 276 \text{ kJ/mol O}, \ q_b = 305 \text{ kJ/mol O}) \\
\gamma q_f \quad \text{dissolution heat of carbon to hot metal, kJ/mol Fe} \\
f \quad \text{sensible heat of hot metal, kJ/mol Fe} \\
l \quad \text{sensible heat of slag, kJ/mol Fe} \\
p \quad \text{heat loss from the furnace wall, kJ/mol Fe}
\( q_e \) reaction heat of moisture in blast, kJ/mol Fe
\( q_l \) reaction heat of auxiliary reducing agent, kJ/mol Fe
References

8) K. Ohno, T. Nagasaka and M. Hino: Steel Research, 74(2003),5
Chapter 7 General conclusions

Auxiliary reducing agents used in blast furnace such as pulverized coal, used plastics, and natural gas contain a lot of hydrogen compared with coke. It is thought that massive auxiliary reducing agent injection at blast furnace could contribute to mitigation of carbon dioxide emissions. To cope with global warming problem, further research and development of this field will be required. Moreover, construction of a circulation type society by effective use of used plastics is so significant as Japan has to depend on import for most of resources.

Technical problems to increase the injection rate of auxiliary reducing agents and to mitigate carbon dioxide emissions are

1) Enhancement of combustion efficiency of pulverized coal.
2) Clarification of the plastic particle behavior in the blast furnace and optimizing the injection condition of plastics.
3) Development of a novel, economically viable oxygen production process.
4) Development of new cooling system with a high cooling capability for coping with increase in heat load to furnace wall.
5) Integration of various elemental technologies.

Therefore, the purpose of this thesis is to solve the above-mentioned problems for massive injection of auxiliary reducing agent at blast furnace. This chapter summarizes this thesis.

In chapter 1, a general introduction was provided. First, current status of global warming and the role to be performed by steel making industries was
introduced; second, resent technologies of liquid, solid, and gas phase auxiliary reducing agent injection were reviewed; third, conventional oxygen production methods were explained; fourth, needs of furnace wall protection under massive injection of auxiliary reducing agent were described and conventional cooling system was reviewed; and finally, the purpose and contents of this thesis were described.

In chapter 2, new injection lance with convergent – divergent nozzle for pulverized coal injection was developed.

First; as the results of the experimental results performed by offline apparatus, optimum angles of divergence and convergence turned out to be 7 and 5 degrees respectively. Optimum divergence angle could be explained by the theory of flow separation. On the other hand, it is suggested that segregation of particle to relatively peripheral region at the throat part in the lance may be occurred due to the inertia of coal particles in the convergence part. It was thought that this segregation phenomenon played significant role to the good dispersibility of the lance.

Second; after the lance was tested at hot model experimental furnace, convergent-divergent injection lance was installed in the actual blast furnace. As a result, superior characteristics of the lance including higher particle dispersibility, higher combustibility, and higher coke replacement ratio compared with normal straight injection lance proved.

In chapter 3, flow and gasification behavior of injected plastic particle in the blast furnace was clarified.

First; gasification mechanism was estimated by the observation results of
heated plastics with a similar conditions of actual blast furnace. It was presumed that volatile matter of plastics was evolved at the surface of the particle. Then, gasification rates of the char were analyzed by thermogravimetric analysis. It was found that gasification rate of unburnt char depended on the heating rate. Gasification rate in the case of rapid heating condition tends to increase.

Second: Trajectories of plastic particles injected into blast furnace were calculated by mathematical model considering decrease in particle size by gasification. As a result, it is suggested that fine plastics (for example APR) injection is desirable for the stable operation of blast furnace.

In chapter 4, the high capacity oxygen storage material, Ca$_2$AlMnO$_5$, which has applications in air-separation technology, was synthesized by glycine-nitrate-based solution combustion synthesis (SCS).

First: it was found that maximum reversible oxygen uptake and release amounts of single phase Ca$_2$AlMnO$_5$ was about 3.0 wt%. Ca$_2$AlMnO$_5$ was successfully synthesized with various glycine contents.

Second: Condition to synthesize single phase Ca$_2$AlMnO$_5$ was determined. That is SCS and just one minute of heat treatment at 1250 °C. Longer periods of heat-treatment leads to greater crystallinity and larger reversible oxygen storage capacities.

In chapter 5, cooling staves (CS) made by cast copper have been newly developed to cope with increase in heat load to the furnace wall in the case of massive auxiliary reducing agent injection.

First: according to simulations by finite element method, maximum temperature and maximum thermal stress of cast copper CS was one third and
one sixth level compared with conventional cast iron CS respectively.

Second; heat removal amount of cast copper CS was estimated as same level as that of conventional cast iron CS at actual blast furnace. One of the reasons of that slag accretion layer may be formed on the surface of cast copper CS by estimating the measurement results of CS body temperature.

Third; in comparison, thermal conductivity of cast copper CS is slightly inferior to that of rolled copper CS. However, cooling capabilities of both CS were approximately same. Cast copper may be superior to rolled copper as a raw material of CS in terms of the flexibility and processability.

Thus, cast copper CS is so effective to maintain stable operation and prolong blast furnace campaign life at high rate injection of auxiliary reducing agent operation.

In chapter 6: by integrating several elemental technologies, concepts to realize innovative blast furnace with minimum carbon dioxide emission characterized by massive auxiliary reducing agent injection was projected.

First; to enhance gasification or combustion efficiency, simultaneous injection of solid/ solid or solid/ gas was developed. In the case of solid/ solid injection, point is the velocity gaps that is caused by difference of size. Combustibility of small particles such as pulverized coal can be improved when they adhered on large particles by the prolongation effect of their residence time. Then, generated heat by combustion of small particle can promote the gasification of large particles. As a result, reaction both small and large particles may be promoted.

Second; hydrogen, coke oven gas, methane gas (natural gas), pulverized coal, and particularly plastics are confirmed to be so useful to reduce carbon dioxide emission because hydrogen reduction is promoted. Top gas recycling and low
temperature operation for example decrease in thermal reserve zone temperature is also desirable to reduce carbon emissions.

Third: combining efficient oxygen production process as mentioned in chapter 4 and innovative blast furnace is promising process to reduce carbon emissions. It is expected that 86% of exhaust carbon can be reduced in optimized innovative blast furnace with top gas recycling and CCS (carbon capture and storage).
List of Publications related to the dissertation


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