

Application of Coke Oven Gas to MIDREX[®] Process

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The MIDREX[®] process runs without coke, emits less CO₂ and thus is gathering attention as an alternative process for blast furnace ironmaking. To expand business opportunities, a study has been conducted on the use of coke oven gas (COG) so as to diversify the MIDREX process. The study has resolved most of the technical issues for commercialization, as reported in this paper.

Introduction

Midrex Technologies, Inc. (hereinafter referred to as "Midrex Inc."), a wholly-owned US subsidiary of Kobe Steel, possesses the MIDREX[®] process using natural gas as a source gas for reducing iron ore. The MIDREX process runs without coke, emits less CO₂ and thus is considered to be an alternative to the blast furnace ironmaking process.

With the shale gas revolution in recent years, the MIDREX process is gathering attention as a process for producing direct reduced iron (DRI) using natural gas. To further promote the business opportunities, Kobe Steel has been carrying out studies on the diversification of the reductant gas used for the MIDREX process. The company has resolved most of the technical issues in commercializing a MIDREX process that uses coke oven gas (hereinafter referred to as "COG") as its reductant gas. This paper gives an outline of the study.

1. MIDREX process

The flow of the MIDREX process is shown in Fig. 1. Natural gas is reformed by a reformer and is

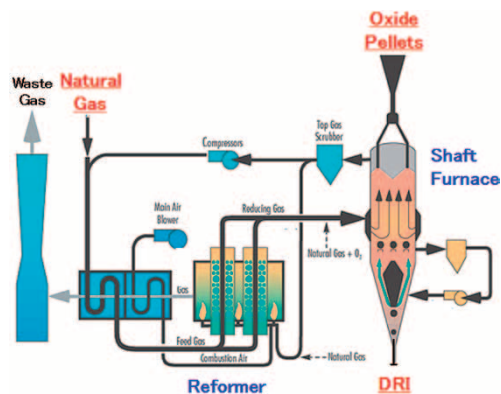
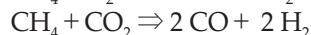
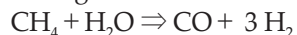
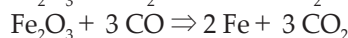


Fig. 1 Flow of MIDREX process

fed into a shaft furnace as reductant gas containing CO and H₂. The reforming reactions of natural gas, the reactions taking place in this reformer, consist of the following steam reforming reaction and CO₂ reforming reaction:



Meanwhile, the raw material iron oxide (i.e., lump ore or fired pellets) is reduced by CO and H₂ in the shaft furnace, and DRI is discharged from the bottom of the furnace. The reduction reactions that occur in the shaft furnace are described as follows:



2. MIDREX plant

In 1967, a pilot plant was built for the MIDREX process. Two years later, in 1969, the first commercial plant was inaugurated in the state of Oregon, U.S. This paved the way for approximately seventy plants currently in operation around the world.¹⁾ Fig. 2 shows the locations of the MIDREX plants actually built. These plants are producing approximately 60% of the DRI produced in the world. In 2012, they produced 45 million tonnes of DRI out of the world's total DRI production of 74 million tonnes.²⁾

This share of 60% is mainly supported by the dramatic increase in the production capacity per plant, while keeping a high annual operation ratio for each. Around 1983, when Kobe Steel purchased Midrex Inc., the maximum annual capacity per plant was 0.6 million tonnes. The technological innovations since then have more than tripled the annual capacity, to 2 million tonnes per year.

3. Diversification of reductant gas for MIDREX process

The MIDREX plants account for approximately 60% of the world's DRI production. They are limited to natural gas producing regions such as the Middle East and Northern South America, because they use natural gas as the source for their reductant gas (Fig. 2).

Against this background, Kobe Steel has been carrying out studies on the diversification of the reductant gas to promote the business opportunities

note) MIDREX is a registered trademark of Kobe Steel.

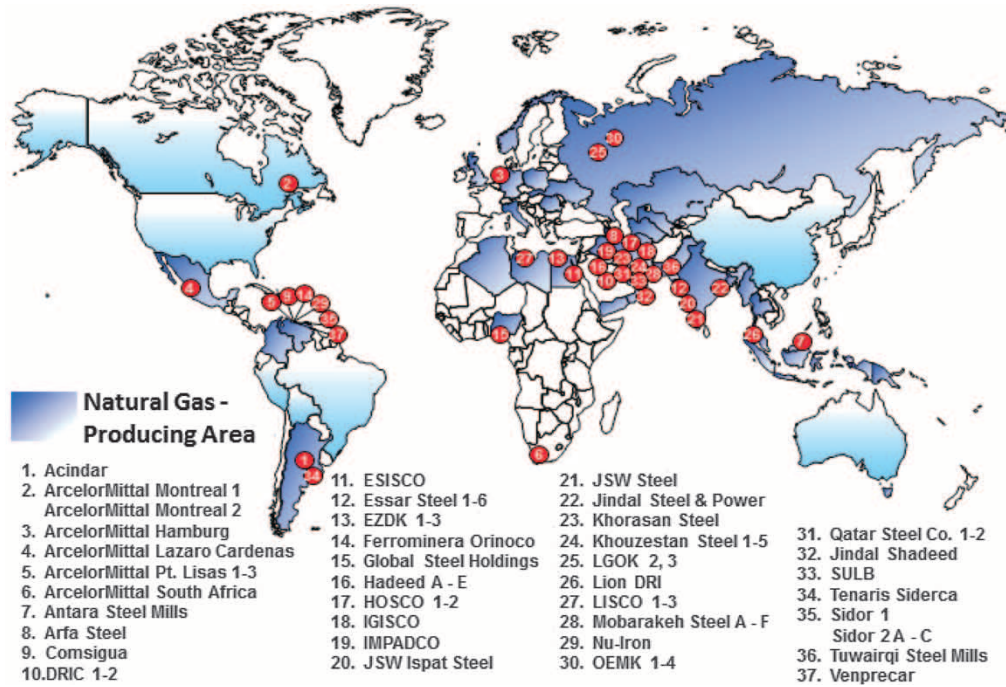


Fig. 2 MIDREX plants actually built

of the MIDREX plants. One commercial example is the use of the off-gas from the COREX process. **Fig. 3** shows the flow of a process combining the COREX process and MIDREX process. The COREX is a process in which ore lumps and/or pellets are reduced in a shaft furnace until their metallization reaches approximately 90%, and the remainder is reduced and melted by a gasifier melter. In 1999, a plant integrating the COREX process and MIDREX process started commercial production at ArcelorMittal South Africa.

Meanwhile, Midrex Inc. has developed a process using reductant gas from coal gasification (**Fig. 4**). A first plant is being built for Jindal Steel and Power Limited (JSPL) in India and is planned to start commercial production in 2014.

In addition, a study was conducted on the application of coke oven gas (COG) as the source for the reductant gas of a MIDREX plant. This study revealed that the then-current technology allowed only a small amount of COG to be used because COG contains tar and unsaturated heavy hydrocarbon. However small the amount may be, COG can still be used to partially substitute for the natural gas. For this reason, a project is ongoing for JSW Steel in India, in which a MIDREX plant currently in operation will be modified so that COG can be utilized. The plant is planned to start commercial production at the end of 2014.

An index for reductant gas, H_2/CO ratio, is greatly affected by the type of the reductant gas source: i.e., natural gas, COREX off-gas and coal gasification gas (**Table 1**). The COREX off-gas with

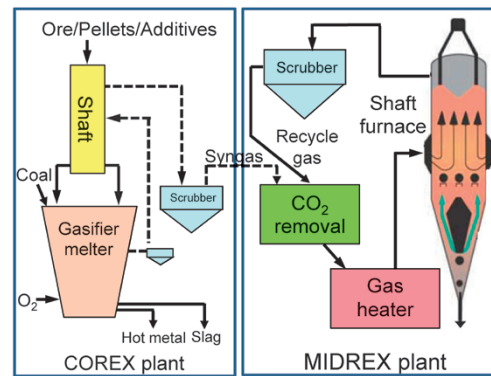


Fig. 3 Combination of COREX plant and MIDREX plant

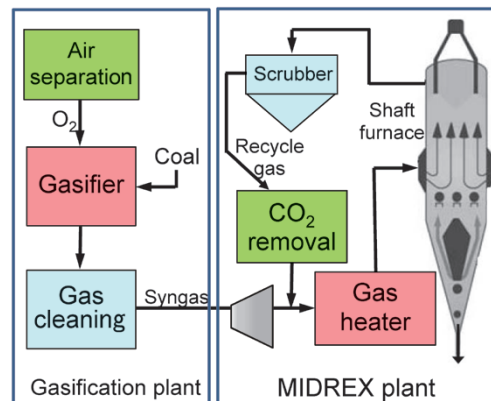


Fig. 4 Combination of coal gasification plant and MIDREX plant

Table 1 H_2/CO ratio due to reformed gas source differences (example)

	Natural gas base	COREX offgas	Coal gasification gas
H_2/CO	1.5~1.7	0.3~0.4	2.0

a low H₂/CO ratio contains a larger amount of CO, which gives rise to CO reduction reaction in the shaft furnace. Unlike endothermic H₂ reduction reaction, the exothermic CO reduction reaction, if its amount is increased, raises the temperature and facilitates the partial melting and clustering of the pellets in the furnace. For this reason, the plant at ArcelorMittal South Africa, using COREX off-gas, must run with the gas temperature at the entrance of the shaft furnace set 100°C to 150°C lower than a regular natural-gas based process.

4. Toward use of COG for MIDREX process

In order to effectively exploit COG as the source of reductant gas, the development of technologies to reform COG has been pursued for many years in various countries. Examples include the development of reforming catalyst by a catalyst manufacturer and non-catalytic partial oxidation by steaming.³⁾⁻⁷⁾ Hardly any catalyst, however, has been commercialized, due to the decline of catalytic activity caused by sulfur content as low as several hundred ppm and also due to the issues of carbon precipitation caused by unsaturated heavy hydrocarbon. Non-catalytic partial oxidation, on the other hand, requires large reactor vessels for commercialization, which tends to make the mixing of steam and COG gas inhomogeneous.⁸⁾ For that reason, this method also has rarely been implemented at a commercial level.

As described above, Kobe Steel in the meantime has applied a small amount of COG to the MIDREX process for JSW Steel in India. As a next step, the company has started collaborating with Midrex Inc. to utilize a larger amount of COG as a source for reductant gas. The target geographical regions include some parts of India and China where natural gas is unavailable but there is a surplus of COG.

Table 2 shows the composition of the COG studied for the above described project in India. As shown in this table, the COG contains at least 60%

Table 2 Gas composition of COG

	Vol%
H ₂	55
CO	7
CO ₂	3
H ₂ O	4
CH ₄	25
C _n H _m	5
Tar	1
H ₂ S	300ppm

of reductant such as H₂ and CO, however, it also contains 25% of CH₄ and 5% of C_nH_m, which makes it difficult to substitute for general reformed gas (containing 1% to 4% of residual CH₄ and almost 0% of residual C_nH_m.)

Tar, contained in the amount of 1%, consists mainly of monocyclic aromatic hydrocarbon (e.g., benzene and toluene) and polycyclic aromatic hydrocarbon (e.g., naphthalene). Including trace constituents, the tar is reported to contain dozens of compounds. This makes the decomposition, or the oxidation reaction, of tar extremely complex, rendering it difficult to decompose all the tar content.

It was against this background that Kobe Steel searched for various newly developed technologies and came to the conclusion that a method using an oxygen burner, the method being developed by Praxair Inc., appeared to be the most promising. Kobe Steel then started joint development involving Praxair Inc.

5. Reforming of COG using oxygen burner

Fig. 5 schematically illustrates an oxygen burner from Praxair Inc. This burner is designed such that the linear velocity of the combustion gas at the burner exit becomes as high as 900m/s. This causes the COG, fed from the side at the burner exit, to be caught by the strong propulsive force of the combustion gas, which facilitates the mixing of the combustion gas and COG.⁹⁾ Meanwhile, the combustion gas at the burner exit has a temperature exceeding 2,000°C, as well as a high concentration of water vapor. This promotes the efficient decomposition of the tar in COG. In addition, the residual oxygen contained in the combustion gas causes partial oxidation of the CH₄ and H₂ contained in the COG at a high temperature (equation (1) below). This enables the production of a greater amount of reformed gas consisting of CO and H₂.

It should be noted, however, that when the combustion gas and COG are insufficiently mixed and the oxygen concentration becomes distributed, the combustion reactions (equations (2) to (6)) are promoted in the oxygen rich region, causing increased amounts of water and carbon dioxide to be

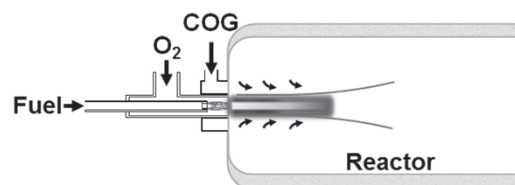
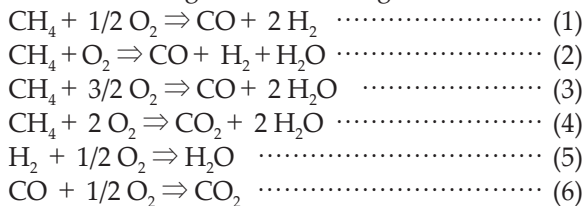


Fig. 5 Conceptual diagram of Praxair's oxygen burner

generated.

Thus, the most important technical issue for a commercial plant with a large-sized burner is to promote the mixing of combustion gas and COG.



Therefore, a lab-scale test was conducted using an oxygen burner from Praxair Inc. The results confirmed that the tar is decomposed while the CH₄ in the COG is reformed, producing usable reformed gas.

Next, an attempt was made to scale-up the laboratory processing capacity of several Nm³/h of COG, while confirming whether or not the same reforming effect is reproducible on a larger scale. A pilot test, with a processing capacity of several tens Nm³/h of COG, was performed at Praxair Inc. Tests conducted under various combustion gas temperatures confirmed that the tar contained in the COG (in the test, benzene was used as a substitute) can be decomposed under certain conditions. More specifically, the states of reformed gas were checked under various oxygen/fuel ratios, while the amount of soot, which can build up and cause problems in the latter process, was also checked.

When benzene (C₆H₆) is decomposed under a gas temperature that is not high enough and/or with a low concentration of water vapor, the decomposition proceeds only to C₂ or C₃ species. The general understanding is that these C₂/C₃ species electrically attract each other to form fine particles, and these fine particles repeatedly collide and coalesce to form soot.

This implies that the generation of soot may possibly be suppressed if the conditions of high temperature and high concentration of water vapor are met. However, on the other hand, an attempt to raise the gas temperature may result in the production of a decreased amount of reformed gas and the consumption of an increased amount of oxygen, which decreases the cost effectiveness. Therefore, the key to accomplishing the primary objective of using COG as a source of reformed gas is to find the conditions that will prevent the generation of soot, while avoiding an excessive rise in temperature.

Kobe Steel has explored various measures through the pilot test and, as a result, confirmed that the generation of soot can be prevented under conditions almost equal to those of the laboratory test. In other words, the pilot test has achieved

mixed state approximately equivalent to that achieved on the laboratory scale.

6. Demonstration test of oxygen burner

Judging from the maximum capability of the Praxair's oxygen burner, a commercial plant adopting the oxygen burner will have a COG processing capacity of several tens of thousands Nm³/h per oxygen burner. The apparatus used for the pilot test, on the other hand, is about 1/500 to 1/200 the size of the apparatus for the commercial plant. The risk of scaling-up the pilot test, by a factor of several hundreds, to a commercial level was considered to be too high. Therefore, a demonstration plant on a scale of approximately 1/20 of that of the commercial plant was introduced to the Research and Development Technology Center, Midrex Inc. (Fig. 6)

One persistent problem encountered during this demonstration test was the generation of a large amount of soot, an issue that had been suppressed in the pilot test. The cause was found to be the fact that the demonstration plant is larger than the pilot plant by a factor of several tens, which resulted in an insufficient mixing of the combustion gas with COG. Measures were then devised to facilitate mixing without increasing the temperature of the gas at the exit. The following implementations were confirmed to be effective in improving the mixing state, and no soot was found to be generated under operating conditions almost equal to those of the pilot test.

- i) Optimizing the supply point of COG and the nozzle size of the supply point
- ii) Optimizing the linear velocity of the combustion gas

In this demonstration test, toluene was used as a replacement for tar. This was done because toluene is available in quantities of several tonnes, exhibits the slowest oxidative degradation among the substances contained in tar, and is easiest to handle from the aspect of safety.

It was judged that, if toluene, with the slowest



Fig. 6 Demonstration plant (left) and reactor (right)

rate of oxidative degradation, is almost completely decomposed, the other components of tar would all have been decomposed. It should be noted that the tar contained in the actual COG is approximately 1%, as shown in Table 2, while the demonstration test ascertained that no soot was generated in conditions containing up to 1.9% of toluene.

7. General flow of commercial plant

Fig. 7 shows the outline flow of a commercial plant designed on the basis of the reformed gas composition obtained by the demonstration test. As shown in this figure, the MIDREX process based on reformed COG has been confirmed. The marketing of this system has been implemented in India, China and other countries. The "THERMAL REACTOR SYSTEM®" in the figure represents a COG reforming system including the reactor. Kobe Steel has registered it as a trade mark in the U.S. and other countries.

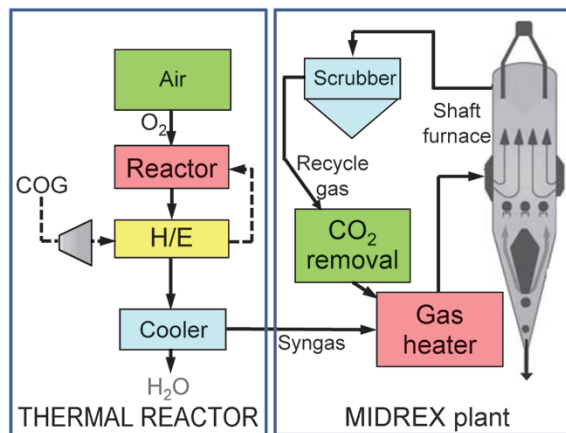


Fig. 7 Supposed general flow in commercial plant

Conclusions

A MIDREX process based on reformed COG has been established as a result of problem solving through collaboration with Midrex Inc. and Praxair Inc. This collaborative project involved laboratory testing, a pilot test and demonstration test.

Recently, the demand for DRI to be used as a substitute for scrap as a clean iron source is expanding even in the advanced countries. An increasing amount of steel is being produced in electric arc furnaces worldwide.¹⁰ Kobe Steel will continue to strive for the diversification of reductant gas and thus contribute to the iron and steel production of the world.

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