Technical Report

UDC 535 . 5 : 662 . 741

Characterization of Gas Generation during Coking Reaction and Continuous Monitoring of COG Using Gas Monitoring System

Masayuki NISHIFUJI* Koji SAITO Makoto UEKI Yuji FUJIOKA Yuji ISHIHARAGUCHI

Abstract

A gas monitoring system applying the infrared absorption method has been developed for continuous monitoring of gas generation during the coking process of coal. The developed system made it possible to continuously monitor coking reactions in a wide temperature range up to 1000 °C, and thus, to follow pyrolysis of the coal in real time. The system was fitted to a commercially operating coke oven to analyze the COG generated during a whole cycle of the coking operation, which yielded information on the details of coking reactions that took place at different stages of the coking cycle. The monitoring results also quantitatively clarified the difference in COG generation of different coal blends.

1. Introduction

Brands of iron ore, coal, and other raw materials for the steel industry have diversified over the last few years. This is mainly because, in view of the depletion of high-quality resources and aiming at reducing production costs, the use of economical materials that were once considered to be of low grade has increased. In addition, techniques to utilize waste plastics^{1, 2)} and other reject materials for steel production together with conventional raw materials have been developed and put into actual practice, and thus, what was once regarded as waste now constitutes an important part of the industry's resources.

To use a wider variety of raw materials effectively, it is essential to understand their characteristics in greater detail and evaluate their behavior and reactions in steelmaking processes. Most past studies into these aspects, however, were insufficient for systematically studying the use of such materials for commercial steel production because available specimens and test conditions were limited, but further similar difficulties will arise as the diversification of raw materials advances.

Before being charged into blast furnaces, coal is turned into coke,

more suitable for ironmaking reactions in ironmaking furnaces. The pretreatment process involves reactions at high temperatures, yielding gases. Therefore, by analyzing the gas generated during the coking reactions, it is possible to understand how these reactions advance and to predict what gas species are generated at different stages. In consideration of this and to monitor process reactions where gas is generated and consumed at high temperatures, the authors developed a system applicable to the actual coking process.

The present paper presents the system developed for monitoring the pyrolysis (carbonization or coking) of coal, and reports the change in gas generation during carbonization of coal in laboratory tests³⁾ and the monitoring results of gas generation from a commercially operated coke oven,⁴⁾ both using the developed system.

2. Monitoring of Gas Generation during the Coking Process

In the cokemaking process, coal is carbonized in coking chambers of a coke oven battery maintained at about 1000° C, during which process the coal softens as its temperature rises, melts, and solidifies again to turn into coke having sufficiently strength high for charging

^{*} Manager, D.Eng., Research Planning Dept., Advanced Technology Research Laboratories 20-1, Shintomi, Futtsu, Chiba

into blast furnaces. The softening behavior of coal and the initial softening temperature in the coking process have been used as indices for evaluating coking coals, and the change in the chemical structure of coal measured by methods such as the conventional viscosity measurement method⁵⁾ and the nuclear magnetic resonance (NMR)⁶⁾ imaging method are also used as such indices. However, in the absence of methods suitable for directly observing the behavior of coal at temperatures above 600° , the information so far available has been insufficient for understanding the whole coking process up to its resolidification.

Some researchers approached the coking process from analysis of the generated gas,^{7,8)} but the brands of coal they used for their studies were limited and the heating temperature of their tests was mostly up to 400-500 $^{\circ}$ C, near the softening and melting point. Thus, there have been no systematic studies on the higher temperature ranges up to the complete resolidification of coal.

Gas chromatography (GC) was commonly used for analyzing gas in those previous studies,⁹⁾ but it is capable only of intermittently measuring average concentrations of gas species during a prescribed period, and for this reason, it is unsuitable for capturing the details of the softening, melting, and resolidification reactions that take place successively during the coking process. Mass spectrometers are often used for gas detection, but the gas generated from coal contains tar and mist, and special treatment is necessary for removing them before analysis. Further, in consideration of gas monitoring of commercially operating ironmaking facilities in rough outdoor conditions, mass spectrometers are unsuitable because they require a vacuum for analysis and their operation is complicated.

In view of the above, the authors selected the Fourier-transform infrared spectrometer (FT-IR) for the examination of gas generating reactions, because it can analyze gases up to 1000° C (in terms of coal temperature) and is flexible as to working environment, and designed a gas monitoring system with a FT-IR as the core device. 2.1 Configuration of the gas monitoring system

Fig. 1 schematically illustrates the gas monitoring system developed and used for the present test. The system consists of a coal heating section, a gas transfer section, and a gas analysis section, linked together with pipes 1 mm in inner diameter. Specimen coal is heated in a quartz tube at the center of the tubular electric furnace, and the generated gas is transferred with a carrier gas, N₂, to the gas analysis section where its chemical composition is analyzed by the FT-IR every 10 s.

The gas generated from coal contains hydrogen (H_2) , but since FT-IR is insensitive to H₂, a high-sensitivity hydrogen gas sensor using a semi-conductor (SnO₂) is provided downstream of the FT-IR. The details of the monitoring system and the investigation results of the gas generation during coking obtained with the system are presented below.

2.2 Study of gas analysis conditions

2.2.1 Improvement of the IR gas cell

To monitor actual changes in gas generation from the specimen coal, it is necessary to introduce the gas smoothly into the gas analysis section and minimize its term of residence there. Since the developed system has the FT-IR and the hydrogen gas sensor arranged in series, the gas flow in the measuring cell of the FT-IR has a direct influence on measurement by the hydrogen sensor. However, since the measuring cells available on the market and usable for FT-IR are not designed to measure flowing gas, they were inadequate for the monitoring system.

In consideration of this, a new type of measuring cell to minimize the gas flow was designed, wherein the optical path length was set at 20 mm and the gas inlet and outlet ports were arranged symmetrically to minimize disturbance to the gas flow (see Fig. 2). Fig. 3 compares the detection peaks of different gases obtained with a conventional cell having an optical path length of 100 mm and the improved cell. Here, 1 ml each of specimen gases was injected rapidly into the carrier gas using a syringe at a point upstream of the cell; the supply rate of the carrier gas was 60 ml/min. The comparison made it clear that the sensitivity of the FT-IR equipped with the improved cell was sufficiently high for the purpose, though somewhat lowered according to Lambert-Beer's law. The improved cell also proved effective in suppressing tailing of the detection peak and enhancing the time resolution of H₂ measurement by the hydrogen sensor. Based on these results, the improved cell was deemed acceptable for use for all of the present tests.

2.2.2 Carrier gas conditions

The pressure and flow rate of the carrier gas were controllable. To obtain information on the as-generated gas, it is desirable to transfer the specimen gas as quickly as possible to minimize its period of residence in the measuring cell. Through tests, the highest flow rate of the carrier gas of the gas monitoring system illustrated in Fig. 1 proved to be 60 ml/min (at a gas pressure of 0.45 MPa), and the flow controller of the system was set so that this flow rate was kept constant during measurement.

2.3 Coal heating tests

Two brands of coal, Goonyella (Go) and Witbank (Wi) coals, were used as specimens for the present test after crushing them into powder of 100 mesh or finer. These two brands are known to pro-



Fig. 1 Schematic diagram of the gas monitoring system for laboratory use



duce coke with widely different properties; Table 1 shows the chemical compositions of the coals.

These specimen coals were heated, and the change in the chemical composition of the generated gas was measured as the coal temperature rose; Figs. 4 and 5 show the results.

2.3.1 Gas monitoring accuracy

As gas arises from coal under heating in a coke oven, the weight of the coal decreases. In consideration of this, the analysis accuracy of the gas monitoring system was verified from the viewpoint of material balance. Samples of Go and Wi coals were subjected to thermogravimetric analysis (TGA) under heating at a rate of 3°C/ min up to 700° C; Figs. 6 and 7 show the results.

As the coal temperature rose, tar and gas contents volatilized; the proportion of tar in the volatile matter of the Go coal was about 20%, and that of the Wi coal was about 40%; thus, gas generation proved responsible for the major part of the volatility weight loss. On the other hand, judging from the total generation amount and specific gravity, among the component gases of all the gas generated up to 700° C, what had the greatest influence on the volatility weight loss was CH₄. CH₄ generation measured by the monitoring system was compared with the volatility weight loss measured by the TGA, and in consideration of the above, the two agreed well in both of the two coals. This confirmed that gas generation monitored by the developed system correctly reflected the results of thermogravimetric analysis of coal, and the system thus proved usable for the quantitative analysis of coking reactions.

2.3.2 Presumption of coal pyrolysis reactions from the results of continuous gas monitoring

Based on the gas generation profiles of the two coal specimens shown in Figs. 4 and 5, the coal pyrolysis reactions taking place in different temperature ranges were speculated to be as follows:10) (1) 300 to 600℃

The continuous laboratory gas monitoring made it clear that various gas species arose from coal simultaneously in this temperature range, where coal softened, melted, and resolidified. The Wi coal began to generate gas at lower temperatures than did the Go coal,



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roughly in agreement with their softening and melting temperatures in the fluidity test. On the other hand, although the resolidification

Fig. 6 Comparison of profile between gas monitoring and TGA (Go coal)

Walling South March

600

- 101 -

0.3

0.2

0.1

0

0.15

0.10

0.05

0

300

Abs. Intensity (A.U.)

DTG / mg/min.



500

Coal temperature (°C)

400

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mostly finished roughly at 500° C, gas generation continued as the temperature rose further.

Lower hydrocarbons, or CH_4 and C_2H_6 , that arose at 550°C or below presumably originated mainly from the decomposition of aliphatic chains, and as the temperature rose further, the methyl groups of aromatics decomposed to form CH_4 . Whereas the Go coal exhibited peaks of CH_4 generation up to about 600°C, CH_4 generation of the Wi coal fell drastically at temperatures above 550°C. This difference is presumably because Go coal is rich in methyl groups of aromatics.

On the other hand, CO_2 arose from the Wi coal together with CH_4 , which seems to indicate that, as the ratio between O and C in Table 1 suggests, the Wi coal has a high content of O joining aliphatic side chains, just like those exemplified with the circles in **Fig. 8**, which illustrates the coal structure model proposed by Shinn.¹¹) The combined generation of CO_2 and CH_4 seems to result from the cleavage of such joints. Further, the reason that CO_2 arose instead of CO is presumably that the specimen coal oxidized owing to oxygen that found its way into the quartz tube during heating. (2) 600 to 800°C

The main components of the gas arising in this temperature range, where coal resolidified, were CH_4 , CO_2 , CO, and H_2 . Methane, which arose at temperatures up to 600 °C, continued to arise in this temperature range in gradually decreasing quantities.

It became clear through the laboratory monitoring that the two coals exhibited markedly different behavior of CO₂ generation in this temperature range. While it is natural that the Wi coal generated more CO₂ because of its chemical composition, it exhibited prominent peaks of CO₂ generation in two temperature ranges, one from 400 to 550°C, together with generation of CH₄, and the other at about 700°C. The peak at the higher temperature seems to result from the decomposition of ester and decarboxylation reactions due to decomposition of calcium carbonate in the coal.

Both coals demonstrated peaks of H_2 generation at about 700°C; the hydrogen is likely to have originated from the condensation of aromatic rings during the resolidification process.

2.3.3 Summary of the laboratory coal heating test

In the laboratory heating test, the two coal brands with different properties demonstrated markedly different behavior of gas generation. Thus, the test showed the possibility of clarifying the elementary reactions of gas generation and the chemical structure of coal from the temperature at which different gas species are generated and their respective quantities.

Fig. 8 Shinn's coal model (partial)







3. Gas Monitoring at a Coke Oven

As a result of increased use of economical brands of coal for the production of coke for blast furnaces over the last few years, there have been significant changes in the chemical composition of coke oven gas (COG) and its generation quantity, changes unpredictable from conventional knowledge of the relationship between coal brand and gas generation quantity based on the volatile matter content of coal. To make the situation clearer, it is necessary to establish a method of continuously monitoring COG generation in real coke ovens and to analyze gas generation behavior in actual coking processes in detail.

In the past, some researchers analyzed COG generated from coke ovens using bottles or bags for gas sampling,¹²⁾ and others examined carbonization reactions using reduced-scale test ovens.¹³⁾ However, none of these attempts focused on COG, but focused rather on how to optimize the quality of coke or the efficiency of oven operation, and the details of COG generation have not yet been clarified. Although there have been some reports on how to predict the generation of COG, they have concentrated on analysis of the operation data of a coke oven battery, and no detailed information about individual ovens has been given.¹⁴⁾ This is because no simple method has been available for directly monitoring COG coming continuously from coke ovens in actual operation, at intervals of seconds to minutes.

In consideration of the above, the authors reviewed the application conditions of the developed gas monitoring system, and using the redesigned system, collected COG directly and continuously from a commercially operating coke oven, and analyzed it during the process from coal charging to discharging of red-hot coke.

The following subsections describe the authors' attempts to clarify the reactions taking place in coke ovens based on the results of COG analysis using two different coal blends with markedly different properties.

3.1 Direct measurement of COG in an operating coke oven

A coke oven battery generally consists of 100 or so ovens, or coking chambers, and COG generated in each of them goes through an ascension pipe at an end of it, is cleaned of tar and mist with ammonia water spray, collected, and stored in a gas holder. **Table 2** shows the typical chemical composition of COG in a holder.¹⁵⁾

Fig. 9 is a schematic diagram of the modified gas monitoring system applicable to operatings coke oven. It consists of a gas sampling section, a gas diluting section, and a gas analysis section; **Photo 1** shows how they were installed in a coke oven battery. Details of the sections of the system are given below. 3.1.1 Gas sampling section

A sampling probe of a stainless steel pipe 20 mm in inner diameter was inserted horizontally into the ascension pipe at an end of a coking chamber in such a way that its open end came to the center of the ascension pipe, and COG flowing upward in it was sampled continuously at a constant rate through the probe by suction. The probe, about 3 m in length, was connected to another pipe 4 mm in inner diameter, which led the gas to the gas analysis section installed at an end of the battery at a distance of about 20 m. Raw COG coming directly from an oven may contain tar and mist, and when the gas passes through the measuring cell, they may be deposited on the surfaces of the cell windows, adversely affecting its transmittance of infrared rays; in consideration of this, a trap was provided upstream of the measuring cell to remove these impurities.

Table 2 Chemical compositions of typical COG (vol%)

	Gas	Concentration (vol%)				
-	CH ₄	28-32				
	H ₂	42-51				
	C_2H_6	Trace				
	C_2H_4	1-3				
	CO_2	2-5				
	CO	5-8				
	N ₂	3-13				
	O ₂	0.1-0.3				
	H ₂ S	0.75				
	NH ₃	1.1				
	HCN	0.15				



Fig. 9 Schematic diagram of COG monitoring system



sampling probe

sampling gas lin (20m)

Photo 1 COG sampling and monitoring system

3.1.2 Gas diluting section

Of the component gases of COG listed in Table 2, those related to energy control except for hydrogen are measurable with a FT-IR. In relation to this, the upper detection limit of each gas species by the developed system using the reference gas of each of them was checked. As a result, the upper-limit concentration for detection of CO_2 , which has the highest infrared absorptivity of COG components, proved to be about 2%. Since the concentrations of component gases of COG can be as high as several tens of percent, many of them will have concentrations beyond their respective detection limits without dilution. To solve this problem, a diluting section was devised to blend the sampled COG with a prescribed amount of nitrogen gas.

3.1.3 Gas diluting conditions and calibration curves

The conditions for gas dilution with nitrogen were studied using a reference gas simulating COG. The pressure of the reference gas and that of the diluting nitrogen gas were set at 0.1 MPa, the same as that of COG sampling from the ascension pipe by the suction pump, and the dilution ratio was regulated in terms of the readings of the flow meters. As a result, the measurement condition was set so that the infrared transmittance of a reference gas containing 2% CO₂, the COG component having the highest infrared absorptivity (2,362 cm⁻¹), did not fall below 5%. Thus, it became clear that, when the COG was diluted with nitrogen gas at a ratio of 1 to 49 (50-times dilution), it would be possible to detect and measure all the component gases.

Further, to confirm the determination performance of the gas monitoring system after dilution, calibration curves were defined using the same reference gas simulating COG. **Fig. 10** shows the calibration curves for the COG components applicable when the dilution ratio is 30 to 100. The calibration curves for all the component gases exhibited good linearity, and good measurement accuracy with 50-times dilution was thus confirmed; the concentrations of all the COG components mentioned hereinafter were obtained using these calibration curves. The gas detection and measurement conditions for the present test were as follows:

[Gas sampling]

Suction pump: diaphragm-type pump



Sample gas flow rate: 5 ml/min (pressure 0.1 MPa) [Gas detection and measurement]

FT-IR: SPX60 made by JEOL Ltd.

Detector: triglycine sulfate (TGS) Measuring resolution: 4 cm⁻¹ at a scanning speed of 4 mm/s Flow rate of the target gas: 250 ml (5 ml COG +245 ml N_2)/ min, pressure 0.1 MPa

Number of integrations: twice Measuring interval: 60 s

3.2 Analysis of COG generation behavior

3.2.1 Continuous monitoring of COG generation and identification of component gases

Gas generation during a coking process of a commercially operating coke oven was monitored continuously under the conditions



specified above by applying the system shown in Fig. 9 to a coke oven of coke oven battery No. 5 at Yawata Works of Nippon Steel. Two different coal blends were used for the gas monitoring: Blend I with 77% coking coal and Blend II with 60% coking coal.

Fig. 11 shows an example of the infrared absorption spectra of COG; from the positions of the absorption peaks, the component gases that caused them were identified as CH_4 , C_2H_6 , CO, CO_2 , and C_2H_4 . Hydrocarbon gases with more C = 3 were not detected owing to their relatively small amounts. As seen with the spectra, there were absorption peaks due to H_2O in the bands of 3,000 and 1,500 cm⁻¹, but they may have resulted from the water trap to remove tar, and the moisture content of COG could not be defined numerically. For this reason, water was excluded from the analysis targets.

3.2.2 Results of COG monitoring of operating coke oven

Figs. 12 and 13 show the results of continuous monitoring of the generated gas using Blends I and II, respectively, from charging into the oven to coke pushing from it. With both of the two coal blends, steam (water) arose immediately after charging, other components being virtually nil. As water ceased to evaporate, the other component gases began to arise, and a stable coking stage presumably began about 30 min after charging. The graphs indicate that the composition of COG changed significantly about 15 h after charging; this was found to roughly coincide with what is commonly called the end of the coking period. The difference in COG composition due to the difference of coal blend clearly shows in the generation patterns of the component gases. The generation behavior of each component gas can be characterized as follows:

- CH_4 : The concentration of CH_4 decreases gradually during the initial 3 h of the coking period, and stays within a certain range thereafter. At the final stage of the coking period, CH_4 emission increases rapidly with Blend I after 14 h of coking to hit a peak, and then rapidly decreases to a finishing point. In contrast, with Blend II, this increase in the final coking stage is not seen. This seems to reflect the characteristic gas generation behaviors of coking and non-coking coals.
- C_2H_4 : The concentration of C_2H_4 decreases gradually after the coking process enters a stable stage. This agrees with what Yoshino et al. reported based on heating tests up to 1,100°C



Fig. 12 Result of continuous gas monitoring of the coke oven (Coal Blend I)



Fig. 13 Result of continuous gas monitoring of the coke oven (Coal Blend II)

in a 120 kg laboratory oven;¹³⁾ they attributed this to the secondary pyrolysis of some gas species. The result of the present test seems to indicate that identical coking reactions take place in the same manner in ovens of different sizes.

 C_2H_6 : Although C_2H_6 accounts for only about 0.5% of the total COG generation on average, the present monitoring made it clear that its concentration was as high as 3% in the initial period of the stable coking stage. Its concentration decreases gradually thereafter, like those of the other component gases, and the decreasing curve becomes steeper towards the end of the coking period. This is presumably due to the following: since C_2H_6 is more prone to pyrolysis than C_2H_4 is,¹⁵, C_2H_6 origi-



Fig. 14 Comparison of H_2 measurement by a hydrogen sensor with the balance of the total of other gases measured by FT-IR subtracted from 100%

nating from coal near the oven center is decomposed into more stable gases such as CH_4 and C_2H_4 , and, partially, into carbon deposited on the oven walls through secondary pyrolysis during its passage through the coke cake.

- CO: After a rapid increase at the beginning of the coking period, its concentration falls and then remains at a low level thereafter until the end of coking. The initial fluctuation of its concentration is presumably due to combustion of coal by air brought into the oven together with the charged coal.
- CO₂: Its concentration increases temporarily at the beginning of the coking period, as in the case of CO, owing to combustion of coal due to air. The concentration decreases as the coking process advances, probably because it turns into CO as the atmosphere inside the oven becomes a reducing atmosphere.
- H.,: Since the FT-IR used as the gas detector is insensitive to hydrogen, the system was unable to detect it directly. To solve this problem, raw COG before dilution was sampled using a syringe every 10 min and fed to an off-line hydrogen sensor for quantitative determination. Fig. 14 shows the results of the hydrogen determination together with the values obtained by subtracting the percentage amounts of all the other gas species from 100%. Because the two agreed considerably well within an average deviation of 5%, it became clear that monitoring of all the component gases excluding hydrogen was sufficient for estimating the generation pattern of hydrogen without having to rely on direct monitoring by a hydrogen sensor. This also served as a cross examination of the accuracy of the developed monitoring system vis-à-vis the hydrogen sensor, a device working according to a different principle, quantitatively evidencing high monitoring accuracy of the developed system.

3.3 Comparison of the generation behavior of COG from a coke oven with the generation behavior of gas from coal pyrolysis in a laboratory test

To investigate the details of gases generated in real coke ovens, the authors conducted laboratory examination of gas generation of

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Table 3 Analytical results of gas generated from coal (laboratory) (vol%)

Coal	CH_4	C_2H_6	C_2H_4	СО	CO ₂	H ₂
Coal Blend I	26.5	4.5	0.5	5.9	2.8	58.9
Coal Blend II	24.6	6.1	0.7	7.8	3.9	56.0

Table 4 Analytical results of gas generated from coal (coke oven) (vol%)

Coal	CH_4	C_2H_6	C_2H_4	СО	CO ₂	H ₂
Coal Blend I	28.2	0.9	2.7	4.1	1.8	60.0
Coal Blend II	26.9	1.1	2.5	8.2	3.5	57.5

the two coal blends used for the gas monitoring of the operating coke oven. Specimens of the two blends were ground to 150 μ m or finer, and a 50 mg sample of each of them was subjected to monitoring by the laboratory system shown in Fig. 1. The results in **Table 3** show the difference in COG composition due to the difference in the chemistry of the two coal blends.

Based on the COG monitoring results from the real coke oven in Figs. 12 and 13, the authors considered that the coking period ended after 17 h from coal charging, and determined the chemical composition of COG based on the area in the graph between the concentration curve of each component gas and the abscissa up to the end of the coking period. **Table 4** shows the composition of COG from the coke oven thus determined. The results of the laboratory test on Blends I and II shown in Table 3 and the results from the real coke oven shown in Table 4 agree considerably well with respect to their component gases. This leads to the presumption that identical pyrolysis reactions take place in the laboratory and commercial facilities, in spite of their different sizes. It has to be noted in this relation, however, that since C_2H_6 is prone to decomposition at high temperatures, it probably changes secondarily into CH_4 or C_2H_4 inside a coke oven chamber.

3.4 Summary of monitoring of COG generation from operating coke ovens

The following findings were obtained through the study on the conditions for the direct monitoring of COG in a coke oven in actual operation and the monitoring results:

- (1) Direct monitoring of COG in an operating coke oven was made possible by sampling COG at the ascension pipe of a cove oven, transferring the sampled COG using a suction pump over a distance of about 20 m to a FT-IR serving as a gas detector, and providing traps to remove tar and mist from the sampled COG to minimize adverse effects on the detector.
- (2) Since the concentrations of the component gases of COG as sampled from the ascension pipe were too high for determination by a FT-IR, the sample gas was diluted with nitrogen gas at a ratio of 1 to 49, which allowed continuous and reliable analysis of COG.
- (3) The change in the composition of COG during the coking period presumably resulted from gas generation due to pyrolysis of coal and secondary decompositions and reactions of the generated gas species.
- (4) Continuous monitoring of COG generation makes it possible to analyze the details of reactions taking place in coke ovens and to quantitatively study the difference in the gas generation behaviors of different blends of coal.

4. Conclusion

A gas monitoring system has been developed to heat specimen coal in an electric furnace, transfer the gas arising from the coal to a FT-IR and a hydrogen sensor together with a carrier gas, and thus continuously analyze its composition. The developed system made it possible to monitor gas generation due to coal pyrolysis during coking in a wide temperature range from room temperature to 1,000 $^{\circ}C$ and to follow the reaction process in real time. Investigation into the details of gas generation from two coal blends with different properties using the developed system suggested the possibility of clarifying the elementary reactions of gases and the chemical structure of coal based on the generation amounts of the component gases and the coal temperatures at which they arise.

The developed system was then applied to an operating coke oven to continuously monitor the generation of COG. As a result, it became possible to clarify the details of reactions taking place in coke ovens and quantitatively study the change in COG generation due to difference in coal blend.

The new monitoring system will be applicable to various other

processes in a steel works, many of which involve chemical reactions at high temperatures and have not yet been clarified in detail.

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Masayuki NISHIFUJI Manager, D.Eng., Research Planning Dept., Advanced Technology Research Laboratories 20-1, Shintomi, Futtsu, Chiba



Yuji FUJIOKA Chief Researcher, D.Eng., Materials Characterization Research Lab., Advanced Technology Research Laboratories



Koji SAITO General Manager, D.Eng., Ironmaking R&D Div., Environment & Process Technology Center



Yuji ISHIHARAGUCHI Manager, Ironmaking Dept., Yawata Works

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Makoto UEKI Manager, Ironmaking Dept., Yawata Works