Influence of Lime/Limestone Addition on the SO₂ and NO Formation during the Combustion of Coke Pellet

Man-Seung LEE and Sang-Chul SHIM¹⁾

Department of Advanced Materials Science & Engineering, Mokpo National University, Chonnam 534-729, Korea.

1) Technical Research Laboratories, Steelmaking Research Group, POSCO, Gyeongbuk 790-785, Korea.

(Received on July 22, 2003; accepted in final form on October 15, 2003)

Isothermal combustion experiments of coke pellet mixed with lime/limestone had been performed to investigate the effect of lime/limestone addition on the reduction of NO and SO₂ emission. The coke pellets were combusted between 700°C and 1300°C under pure oxygen atmosphere. Combustion kinetics and conversion data of SO₂ and NO were obtained from the thermogravimetry of coke pellet and gas analysis data. Adsorption of NO by lime mixed with coke was not occurred in the experimental ranges. It was possible to reduce most of SO₂ emission below 900°C by adding lime/limestone to coke. However, the reduction efficiency of SO₂ by the addition of lime/limestone decreased with increasing temperature due to the decomposition reaction of CaSO₄. The variation of the conversion to NO and SO₂ with the combustion conditions during the combustion of coke pellet was compared with the results of thermodynamic calculation.

KEY WORDS: coke pellet; lime/limestone; combustion; thermodynamics; NO and SO₂.

1. Introduction

In sinter plant at steel works, 3.5–4 wt% of coke are added to the raw materials for the sinter as a heat source. About 130–160 ppm of NO and SO₂ are emitted from the sinter plant due to the nitrogen and sulfur in coke. In order to suppress the conversion of nitrogen to NO, the combustion condition is maintained fuel-rich long enough for N₂-forming reaction to proceed. Since the combustion condition cannot be easily changed in the sinter plant, it is difficult to apply the above method to the reduction technology of NO emission in the sinter plant. The technological and economic feasibility of an SO₂ removal process depends on the type and quantity of gases that must be cleaned.

There are two methods for reducing the amounts of NO and SO₂ emitted from sinter plant. One method is the treatment of waste gas. Since gas volume is large and the absolute levels of gas contents are relatively low, it is difficult to apply this method to the sinter plant. The other method is the reduction technology in the sinter bed. There has been a significant amount of effort on the development of process in both categories.

Numerous studies have been performed on the combustion reaction of coke and the adsorption reaction of NO and SO₂ by lime.^{1–8)} It was reported that the reduction efficiency of NO and SO₂ during the combustion of coke pellet mixed with lime/limestone depended on the distribution of lime/limestone in the pellet and combustion kinetics of coke pellet had a great effect on the quality of the sinter.⁶⁾ It was also reported that the adsorption reaction of NO by lime did not occur above 700°C and the degree of reducing the amounts of SO₂ by lime decreased with increasing tem-

perature.¹⁾

In order to develop a technology for reducing the amounts of NO and SO₂ emission from the sinter plant at steel works, the combustion kinetics of coke pellet mixed with lime/limestone and the conversion to NO and SO₂ were investigated by measuring the thermogravimetry of coke pellet and gas concentration. The variation of the conversion to NO and SO₂ with reaction temperature during the combustion of coke pellet mixed with lime was compared with the results obtained from thermodynamic calculation.

2. Experimental

The powders of coke, lime and limestone were prepared by grounding the granules below 20 μm with a vibrating mill. After adding the predetermined amounts of lime/limestone to coke, the powders were mixed thoroughly for 24 h by using ball mill. Approximately 0.3 g of the mixed powder was pressed into a disk (0.9 cm in diameter) at the pressure of 100 atm with press. The results of the analysis of the chemicals used in this study are shown from **Tables 1 to 4**.

The pellet was put on the Pt bowl and then this Pt bowl was charged into thermogravimetric analyzer (TGA, SETARAM). The inner diameter of the TGA was 1.8 cm. The temperature was raised at the rate of 10°C/min and N₂ gas was purged to prevent the combustion reaction of coke during the temperature rise. At the reaction temperature, pure oxygen gas was purged at the flow rate of 70 NmL/min. The mass change of the pellet was read through computer. The concentrations of NO and SO₂ were measured by gas analyzer (COSA 6000CD) at the interval of 1 min. In measur-

Table 1. Element analysis of coke (wt%, dry, ash-free basis).

C	H	N	S	O(by diff.)	Total
95.84	0.30	1.56	0.55	1.75	100

Table 2. Ash analysis of coke (wt%).

SiO ₂	Al ₂ O ₃	CaO	TiO ₂	MgO	MnO	T-Fe	Total
59.43	29.17	4.15	1.53	1.08	0.05	4.59	100

Table 3. Chemical composition of lime (wt%).

Al ₂ O ₃	CaO	MgO	TiO ₂	MnO	SiO ₂	T-Fe	Ig-loss
0.66	75.77	4.20	0.034	0.055	1.63	0.27	16.55

Table 4. Chemical composition of limestone (wt%).

Al ₂ O ₃	CaO	MgO	TiO ₂	MnO	SiO ₂	T-Fe	Ig-loss
0.33	48.86	5.38	0.017	0.049	0.73	0.25	43.09

Fig. 1. Schematic diagram of experimental apparatus.

ing gas concentration, most of moisture in the waste gas was removed using moisture absorbing apparatus. **Figure 1** shows the schematic diagram of experimental setup.

The rate of change in the moles of NO and SO₂ was obtained from the analysis data of gas concentration by the following procedure. The rate of change in the mole of NO is related to the concentration of NO by Eq. (1).

$$\frac{dN_{NO}}{dt} = Q \times C_{NO} \times \frac{P}{RT} \dots\dots\dots(1)$$

In Eq. (1), Q represents the flow rate of gas (L/min), C the concentration (ppm), N the number of mole (mol), t time (min), P pressure (atm), T temperature (K) and R gas constant, respectively. In order to obtain the relation between the rate of change in the mole of NO and reaction time, the concentration of NO was plotted against reaction time and this plot was regressed. By integrating the relation obtained from this regression, the number of moles of NO emitted during reaction time t was obtained. And the conversion of nitrogen to NO was calculated by dividing the number of moles of NO emitted during reaction time t by the initial moles of nitrogen in coke.

Fig. 2. Variation of NO conversion with reaction time during the combustion of coke pellet.

Fig. 3. Variation of SO₂ conversion with reaction time during the combustion of coke pellet.

3. Results and Discussion

3.1. Isothermal Combustion Behavior of Coke Pellet

Combustion experiments of the pellet prepared from only coke were conducted first. The variation of the conversion to NO and SO₂ with reaction temperature during the combustion is shown in **Figs. 2** and **3**, respectively. It is seen in **Fig. 2** that the conversion of nitrogen to NO increases with temperature up to 900°C and then decreases greatly with the temperature. At 1300°C, the conversion of nitrogen to NO was very low. However, it is known from **Fig. 3** that the rate of conversion of sulfur to SO₂ increased with the temperature in the experimental ranges. When reaction temperature increased from 700 to 900°C, the conversion of nitrogen to NO increased owing to the increase of gasification

rate of nitrogen. The decrease in the conversion to NO above 900°C was ascribed to the relative gasification kinetics of nitrogen and sulfur in coke by oxygen. From the combustion experiments of coke pellet in the temperature range of 700 to 1300°C, we obtained the following gasification rate constant of nitrogen and sulfur in coke by oxygen.⁹⁾

$$k_{\text{NO}} = 1.81 \times 10^0 \exp\left(-\frac{2450}{RT}\right) \dots\dots\dots(2)$$

$$k_{\text{SO}_2} = 2.23 \times 10^1 \exp\left(-\frac{3460}{RT}\right) \dots\dots\dots(3)$$

In the above equation, k represents the rate constant and the unit was cm/min. As shown in Eqs. (2) and (3), the activation energy for the gasification of nitrogen and sulfur were about 2.5 kcal/mol and 3.5 kcal/mol, respectively. However, the intrinsic rate constant of sulfur gasification was about ten times larger than that of nitrogen gasification. Hence, the ratio of gasification rate of sulfur to that of nitrogen increased with reaction temperature. At reaction temperatures above 900°C, the gasification rate of sulfur was far faster than that of nitrogen. In this condition, most oxygen was consumed by the combustion reaction of carbon and sulfur. Therefore, further increase of temperature above 900°C resulted in the decrease of the conversion of nitrogen to NO.

To investigate the effect of adding lime to coke on the amounts of NO and SO₂ emission, 35 wt% of lime were added to coke and combustion experiments were performed with these pellets. The effects of temperature on the conversion to NO and SO₂ are shown in Figs. 4 and 5, respectively. It is known from Fig. 4 that the conversion of nitrogen to NO in the combustion of coke pellet mixed with lime increases with temperature up to 1100°C and then decreases with the temperature. By comparing Fig. 2 with Fig. 4, it is known that the conversion of nitrogen to NO in coke pellet mixed with lime was higher than that of coke pellet at the same reaction time. However, the final conversion of nitrogen to NO was little affected by the addition of lime to coke. This result implied that the gasification rate of nitrogen in coke pellet mixed with lime was faster than that of nitrogen in pure coke pellet. The gasification rate of nitrogen is proportional to the product of rate constant and oxygen concentration. For the same geometry of coke pellet, the amount of combustible components was smaller in the coke pellet mixed with lime than in the pure coke pellet. Hence addition of lime to coke had the same effect as increasing the concentration of oxygen at the constant flow rate of oxygen 70 NmL/min. In this condition, the gasification rate of nitrogen in the coke pellet mixed with lime increased compared to the combustion of pure coke pellet.

It is seen in Fig. 5 that negligible amounts of SO₂ were emitted during combustion of coke pellet at the temperatures of 700°C and 900°C. However, the conversion of sulfur to SO₂ increased with the temperature above 1100°C. The effect of lime addition on reducing SO₂ conversion decreased with temperature above 900°C. The SO₂ conversion of coke pellet mixed with lime was one tenth to that of coke pellet at 1100°C and a quarter at 1300°C. The variation of

Fig. 4. Effect of lime addition to the pellet on the NO conversion during the combustion of the coke pellet.

Fig. 5. Effect of lime addition to the pellet on the SO₂ conversion during the combustion of the coke pellet.

the conversion to NO and SO₂ with temperature in the combustion of coke pellet mixed with lime will be compared later with the results of thermodynamic calculation.

Limestone is more attractive than lime because of its low cost and widespread availability. Therefore, 50 wt% of limestone was added to coke as a source of lime and combustion experiments have been performed with these coke pellets. The experimental conditions were the same as those of coke pellet mixed with lime. Since limestone is decomposed at high temperature, the mass change of coke pellet mixed with limestone includes the mass change due to the decomposition of limestone.

The variation of NO and SO₂ conversion with the temperature during the combustion of coke pellet mixed with limestone are shown in Figs. 6 and 7, respectively. It is seen

Fig. 6. Effect of limestone addition of the NO conversion during the combustion of the coke pellet.

Fig. 7. Effect of limestone addition of the SO₂ conversion during the combustion of the coke pellet.

in Fig. 6 that the conversion of nitrogen to NO decreases with temperature during the combustion of coke pellet mixed with limestone. In the case of coke pellet mixed with lime, the conversion to NO increased with temperature and then decreased at temperature above 1100°C. The difference in the variation of NO conversion between coke pellet mixed with limestone and coke pellet mixed with lime may be ascribed to CO₂ gas resulted from the calcination reaction of limestone at high temperature. One possibility is that CO₂ gas undergoes solution loss reaction with carbon to yield CO gas. Since NO might be reduced to N₂ by CO, the conversion of nitrogen to NO decreased with increasing temperature. However, conclusive evidence for the decrease of NO conversion with temperature needs further fundamental study on the gasification reaction of coke pellet mixed with limestone. It is known from Fig. 7 that the con-

Table 5. Effect of temperature and the type of coke pellet on the NO and SO₂ conversion.

Temperature(°C)	Coke		Coke+lime(35%)		Coke+limestone(50%)	
	X _{NO}	X _{SO2}	X _{NO}	X _{SO2}	X _{NO}	X _{SO2}
700	0.0062	0.041	0.0044	0	0.011	0
900	0.0052	0.051	0.0058	0	0.0078	0
1100	0.0039	0.058	0.0041	0.0054	0.0029	0.013
1300	0.0004	0.060	0.0007	0.015	0	0.015

version to SO₂ is very low at the temperatures of 700°C and 900°C but the conversion to SO₂ increases with temperature above 1100°C.

Variation of NO and SO₂ conversion with reaction temperature and with the type of the pellet is summarized in Table 5. The conversion values in Table 5 represent the values when the combustion reaction of the coke pellets is completed. In the experimental ranges, the addition of lime/limestone to coke had negligible effect on the conversion of nitrogen to NO. However, the amounts of SO₂ emission during the combustion of coke pellet were greatly reduced by pelletizing coke with lime/limestone.

The efficiency of reducing the amounts of NO and SO₂ by the addition of lime/limestone to coke was investigated in the temperature ranges between 700 and 1300°C. The results of the experiments are represented by the following definition of the reduction efficiency.

$$\text{SO}_2 \text{ reduction efficiency} = \frac{N_{\text{S(Coke)}}^{\text{O}} - N_{\text{SO}_2}}{N_{\text{S(Coke)}}^{\text{O}}} \times 100 \dots (4)$$

In Eq. (4), $N_{\text{S(Coke)}}^{\text{O}}$ represents the number of moles of sulfur initially present in the coke.

It is known from Table 5 that the reduction efficiency of SO₂ was 99% at the temperatures of 700°C and 900°C. Even though the reduction efficiency of SO₂ decreased with temperature above 1100°C, 75% reduction efficiency of SO₂ was achieved even at the temperature of 1300°C.

In the sinter plant at steel works, combustion kinetics of coke has a great effect on the productivity of sinter plant and the strength of sinter. To investigate the effects of lime/limestone addition on the combustion kinetics of various coke pellets, the reaction time of the pellet was divided by the time necessary for the complete combustion of coke pellet. Figure 8 shows the variation of mass conversion of coke (X_M) with this dimensionless time. It is known from Fig. 8 that the addition of lime/limestone to coke and pelletizing these powders has a negligible effect on the combustion kinetics of coke pellet. Therefore, pelletizing coke with lime/limestone could reduce the amount of SO₂ emission without affecting the operation of sinter plant.

3.2. Thermodynamic Analysis

In the sinter plant, coke was combusted in the temperature from 650 to 1350°C. From the results of combustion experiment with coke pellet, it is known that the conversion of nitrogen to NO gas was little affected by adding lime/limestone to coke. However, the amounts of SO₂ emission were greatly reduced by adding lime/limestone to coke and the reduction efficiency of SO₂ emission depended on the

Fig. 8. Effect of lime/limestone addition of the pellet on the combustion kinetics of the various coke pellets.

temperature. Therefore, the effect of temperature on the reduction efficiency of NO and SO₂ was analyzed by thermodynamic calculation. The following chemical reactions were considered in the thermodynamic calculation.

In the thermodynamic calculation, it was assumed that all the combustible components in the coke pellet mixed with lime were gasified during the combustion in the air atmosphere. The number of chemical species present in the equilibrium state after the combustion reaction is ten (CO, CO₂, NO, N₂, SO₂, O₂, CaO, Ca(NO₃)₂, CaSO₄, CaS). To calculate the number of moles of the chemical species at equilibrium, ten independent equations are needed. These ten equations are obtained from the five chemical equilibria [Eqs. (5)–(9)] and from the following five mass balance equations for Ca, C, N, O and S. In deriving mass balance equations, the oxygen content in the ash was not considered.

$$N_{\text{C,T}} = N_{\text{C(Coke)}} = N_{\text{CO}} + N_{\text{CO}_2} \quad \dots\dots\dots(10)$$

$$N_{\text{N,T}} = N_{\text{N(Coke)}} + 2N_{\text{N}_2, \text{air}} = N_{\text{NO}} + 2N_{\text{N}_2} + 2N_{\text{Ca}(\text{NO}_3)_2} \quad \dots\dots\dots(11)$$

$$N_{\text{S,T}} = N_{\text{S(Coke)}} = N_{\text{SO}_2} + N_{\text{CaSO}_4} + N_{\text{CaS}} \quad \dots\dots\dots(12)$$

$$N_{\text{O,T}} = N_{\text{O(CaO)}} + 2N_{\text{O}_2, \text{air}} = N_{\text{CO}} + 2N_{\text{CO}_2} + N_{\text{NO}} + 2N_{\text{SO}_2} + 2N_{\text{O}_2} + N_{\text{CaO}} + 6N_{\text{Ca}(\text{NO}_3)_2} + 4N_{\text{CaSO}_4} \quad \dots\dots\dots(13)$$

$$N_{\text{Ca,T}} = N_{\text{Ca(CaO)}} = N_{\text{CaO}} + N_{\text{Ca}(\text{NO}_3)_2} + N_{\text{CaSO}_4} + N_{\text{CaS}} \quad \dots\dots\dots(14)$$

In the above equations, N represents the moles and subscript T the total moles.

In the calculation, the ideal gas law was applied to the gas phase and the activities of solid (CaO, Ca(NO₃)₂, CaS,

Table 6. Thermochemical data for various substances.^{9,10)}

	ΔH_{298}° (kcal/mol)	S_{298}° (cal/mol/K)	C_p (cal/mol/K)			Reference
			a	$B \times 10^3$	$c \times 10^{-5}$	
C	0	1.372	5.841	0.104	-7.559	9
Ca(NO ₃) ₂	-223.4	46.02	23.13	43.98	-	10
CaO	-151.6	9.5	11.86	1.08	-1.66	9
CaS	-113.8	13.5	10.8	1.85	-	9
CaSO ₄	-342.76	25.5	16.78	23.60	-	9
CO	-26.42	47.22	6.79	0.98	-0.11	9
CO ₂	-94.05	51.07	10.55	2.16	-2.04	9
N ₂	0	45.77	6.66	1.02	-	9
NO	21.58	50.35	7.03	0.92	-0.14	9
O ₂	0	49	7.16	1.0	-0.4	9
SO ₂	-70.94	59.3	10.38	2.54	-1.42	9

Fig. 9. Effect of temperature on the SO₂ reduction efficiency calculated by thermodynamics.

CaSO₄) were assumed to be equal to the mole fraction of each species. Table 6 shows the thermochemical data necessary in calculating the equilibrium constants of the chemical equilibria.^{10,11)} In calculation, the number of oxygen moles was taken as the value corresponding to 10% excess necessary to complete combustion of carbon to CO₂. In this case, the ratio of number of oxygen moles to that of carbon in coke was 1.1. The above ten nonlinear equations were solved by Newton–Raphson method in case that the weight of coke pellet was 0.3 g.

From the thermodynamic calculation, it was found that the adsorption reaction of NO by lime did not occur in the temperature ranges from 700 to 1300°C. The result of this calculation on the reduction of NO by lime addition agrees well with the experimental results on the variation of the conversion of nitrogen to NO with temperature.

Figure 9 shows the results of thermodynamic calculation about the effect of temperature on the reduction efficiency of SO₂ in the combustion of coke pellet mixed with lime. It is known from Fig. 9 that the reduction efficiency of SO₂ by CaO decreases with temperature at above 1100°C and decreases more rapidly in the combustion of air atmosphere

Fig. 10. Effect of CaO wt% on the SO₂ reduction efficiency calculated by thermodynamics.

than in the combustion of oxygen atmosphere. The difference in the reduction efficiency of SO₂ between the air and oxygen atmosphere may be explained by using the adsorption reaction, Eq. (4). It is known from Eq. (4) that oxygen is necessary for the adsorption reaction of SO₂ by CaO. Therefore, the reduction efficiency of SO₂ was higher in the oxygen atmosphere than in the air atmosphere. The partial pressure of CO increases greatly with increasing temperature. Therefore, the decomposition reaction of CaSO₄, Eq. (5), occurs as the reaction temperature increase. This explains why the reduction efficiency of SO₂ decreases with increasing temperature. The variation of reduction efficiency of SO₂ with temperature obtained from experiments was in good agreement with that calculated by thermodynamics.

Figure 10 shows the effect of the weight percentage of CaO in coke pellet on the reduction efficiency of SO₂ obtained from thermodynamic calculation. In a similar way to Fig. 9, the reduction efficiency of SO₂ in the combustion of

oxygen atmosphere was higher than that in the combustion of air atmosphere. In order to obtain 80% reduction efficiency of SO₂ during the combustion of coke pellet in the air atmosphere, it is necessary to add CaO above 30 wt% of coke.

4. Conclusions

From the combustion experiments of coke pellet mixed with lime/limestone and the thermogravimetric data of coke pellet and gas concentration, the following conclusions were obtained.

(1) Addition of lime/limestone to coke had a negligible effect on the reduction of NO emission in the temperature ranges between 700 and 1300°C.

(2) Conversion of sulfur to SO₂ was low enough to be neglected at the temperatures of 700 and 900°C. However, the conversion of sulfur to SO₂ increased with increasing temperature above 1100°C due to the decomposition reaction of CaSO₄.

(3) The variation of the conversion of sulfur to SO₂ with the temperature obtained experimentally was in good agreement with those calculated thermodynamically.

(4) The combustion kinetics of coke pellet mixed with lime/limestone was similar to that of pure coke pellet.

REFERENCES

- 1) R. H. Borgwart: *Environ. Sci. Technol.*, **4** (1970), 59.
- 2) N. J. James and R. Hughes: *Environ. Sci. Technol.*, **11** (1977), 1191.
- 3) H. Y. Sohn and K. Rajamani: *Chem. Eng. Sci.*, **32** (1977), 1093.
- 4) K. Rajamani and H. Y. Sohn: *Metall. Trans. B*, **14B** (1983), 175.
- 5) A. M. Paul, D. R. Struan and F. U. John: *Fuel*, **65** (1986), 1546.
- 6) E. Kasai, S. Wu, T. Sugiyama, S. Inaba and Y. Omori: *Tetsu-to-Hagané*, **78** (1992), 1001.
- 7) O. D. S. Mota and J. B. L. M. Campos: *Chem. Eng. Sci.*, **50** (1995), 433.
- 8) M. Matsukata, K. Takeda, T. Miyatani and K. Ueyama: *Chem. Eng. Sci.*, **51** (1996), 2529.
- 9) M. S. Lee: *J. Korean Inst. Met.*, **36** (1998) 1849.
- 10) O. Kubaschewski and C. B. Alcock: *Metallurgical Thermochemistry*, 5th ed., Pergamon Press, NY, (1983).
- 11) I. Barin: *Thermochemical Data of Pure Substances*, VCH, Weinheim, Germany, (1989), 302.