Primary Application of the “In-Bed-deNOx” Process Using Ca–Fe Oxides in Iron Ore Sintering Machines

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To decrease NOx emission from iron ore sintering machines inexpensively, a new process removing NOx within the sintering bed, named “In-bed-deNOx”, was studied. This process utilizes the effect of Ca–Fe oxides, named CF, on NOx elimination reaction. This report describes the reaction behavior of NO on mainly the CF liquid surface and the application study of “In-bed-deNOx” to actual sintering process.

The effect of CF on the NO elimination reaction was investigated in the crucible experiments. Reaction gas containing about 400 ppm NO was blown onto the specimen in reaction tube. The NO concentration in outlet was measured in the range of 800°C to 1400°C, and 0.2 to 10⁻¹⁷ mole fraction of oxygen. The CF, including ferrous oxide, shows the higher NOx elimination ratio. The NOx elimination ratio increases with increasing temperature and decreasing oxygen potential.

To verify the “In-bed-deNOx” process, some pot tests and experimental operations in the Kakogawa sintering plant were carried out. Firstly, the sintering pot tests were carried out by means of charging the CF pellets prepared in advance. NOx emission decreases with the increasing CF pellets addition. Secondly a sintering pot test was carried out by means of using limestone powder. NOx emission from the case of using limestone powder is as little as the case of charging CF pellets. An actual plant test was made by means of using fine limestone. Decreased NOx emission was achieved during the test period.

KEY WORDS: iron ore; sintering; air pollution; exhaust gas; NOx; calcium ferrite; iron oxide; limestone; NO.

1. Introduction

The Japanese steel companies have constructed a variety of pollution control equipments for long years. A lot of steel works have built several kinds of dust removal equipments, and plenty of iron ore sintering plants have installed sulfur oxides removal equipment so as to treat the exhaust gas.

Nitrogen oxides related with air pollution problems such as “photo-chemical smog” are often called “NOx”. Although the amount of NOx emitted from sintering plants occupies the majority of total emission in integrated steel works, only a few sintering plants have installed ammonia NOx removal equipment. This equipment has already succeeded in the NOx removal of various combustion plants. But it needs such a huge reaction room to meet the large off gas volume from the sintering plants and such a huge construction investment that the ammonia NOx removal equipment can not be a common device for other sintering plants.

A lot of studies have been done in order to decrease NOx emission from sintering plants inexpensively. Previous studies usually dealt with NOx generation mechanism or phenomena within sintering beds. The results are summarized as that NOx is originated from nitrogen in fuel and that NOx can be reduced by a combustion control. The selective use of the fuel of low nitrogen content is one of the most practical methods for the actual plant at present.

Wu et al. reported the phenomena where the solid Ca–Fe oxides affect NOx elimination reaction. Additionally, using the oxides, abbreviated CF, in the sintering bed, we intend to develop a new process to decrease NOx from the sintering plant. This new process, named “In-bed-deNOx”, is expected to work economically.

Firstly, the behavior of the NOx on the CF was experimentally studied under similar conditions to the sintering bed. Secondly, primary application tests to the sintering process in laboratory and plant scales were carried out.

2. Experimental

2.1. Apparatus

Figure 1 shows a schematic view of the experimental apparatus. It is comprised of the gas supplying part, the reaction tube, and the analyzing part in which the composition of NO, CO and CO₂ in off gas were measured. We used only NO gas because NO is the major gas species in NOx emitted from sintering plants.

The gas supplying part produces the gas mixture from pure gases of CO, CO₂, O₂, and 400 ppm-NO standard gas balancing with N₂, which were regulated by gas flow meters.
and mixing equipment. Ar gas was used for purging purposes.

The reaction tube is made of high-purity alumina. The tubes were enclosed with stainless steel caps on both ends. An alumina crucible is set at the isothermal band in the reaction tube. A pair of thermocouples are placed at the bottom of the crucible to control the experimental temperature. Specimens have been fused in the crucible to make plane surfaces. The reaction gas is blown onto the specimen vertically through an alumina gas nozzle, which is put at 10 mm high over the surface of the specimen. After the reaction gas touches the surface of the specimen, it flows off through the outlet.

During experiments, the total composition of NO and NO2 in off gas was continuously measured by a chemiluminescent NOx analyzer with a NO–NO2 converter. The composition of CO and CO2 was also continuously measured with non-dispersive infrared analyzers.

2.2. Specimens

The specimen of the CF was prepared from reagents of CaO, FeO, Fe3O4 and Fe2O3. The reagents were mixed as shown in Table 1. The mixtures of calcia-magnetite, calcia-wustite and calcia-hematite were symbolized as CM, CW and CH, respectively. The mixture was heated to melt in a platinum crucible at 1300°C in N2 atmosphere. When the specimens of different oxidation states such as CH or CW were produced, they were kept in the equilibrum atmosphere of CO and CO2 for about 6 hr. After cooling, the specimen was crushed below 0.25 mm. 10 g of sample were used in each run.

2.3. Procedure and Experimental Conditions

The experimental conditions are listed in Table 2. The reaction gas was prepared by mixing pure gases from cylinders. Especially, 400 ppm-NO standard gas balanced with argon was used in the case of the basic study of NOx elimination reaction, and mixture gas of 400 ppm NO–5%CO–5%CO2–Ar balanced was used to simulate a sintering condition. At the beginning of each run, the reaction tube was sufficiently purged with Ar gas. The specimen was heated to the experimental temperature and then held for 10 minutes before the experiments started.

3. Results

3.1. Definition of NOx Elimination Ratio

The results were expressed in terms of NOx elimination ratio E, which is the mole ratio of the eliminated NO to that supplied:

\[ E = \frac{\text{C}_i - \text{C}_o}{\text{C}_i} \times 100 \] ..........................(1)

Where, E: NOx elimination ratio (%), C: NOx concentration (mol/m3) and i, o: suffix for inlet and outlet gases, respectively.

3.2. NOx Absorption in CF

In order to study the mechanism of the NOx elimination, the amount of nitrogen in the CW specimen after the NOx elimination experiment using 400 ppm-NO standard gas balanced with argon was compared with the original CW specimen. The chemical analyses were carried out by means of two methods based on JIS G 1228. One is the distillation and acid-base titration method expressed as wet method in Table 3, and another is the inert gas transport melting and thermal conductivity detecting method, expressed as dry method. Nitrogen concentration in the specimen after experiment is similar to that in the original specimen. The analysis of off gas showed that the large amount of NO more than 7 \times 10^{-3} mol was eliminated in this experiment. Because the nitrogen in the CW specimen after experiment is much smaller than the amount of the eliminated NO, the nitrogen elements in the eliminated NO likely left the reaction system in another form of molecules. In order to determine the nitrogen compounds in the off gas, a qualitative analysis with a gas chromatography gives a very small amount of N2O and a larger amount of N2. Therefore, almost all of the eliminated NO seems to be changed to N2. This result agrees with thermodynamics considerations.41

The absorption of nitrogen in melting salts and slag is a process to eliminate NOx in off gas. Some researchers stud-
ied several melting salts as absorbents of NOx. Shin et al. reported on the strontium-iron oxide system absorbent\(^5\) and Machida et al. reported on the barium-copper oxide system absorbent\(^6\). Further, some researchers investigating the steel making process reported on the nitrogen solubility in several slags. For example, the calcia-alumina system was reported by Shimoo et al.\(^7\). Maltinez et al. reported that the nitrogen content in calcia-silica slag is over 0.5 mass% in a certain condition. Although the mechanism of the nitrogen absorption has not been clear enough, but the basic component in the systems such as calcia is regarded as an important factor.\(^8\) It can be anticipated from analogy to chemical contents of the materials above mentioned that CF has some solubility or absorptivity of nitrogen and nitrogen oxides. According to the result shown in the Table 3, fixing NO in CF is not the main mechanism of NO elimination, but more examination is necessary for dissolution or absorption and adsorption of NO in CF.

### 3.3. NOx Elimination Ratio for CH, CM and CW

In actual sintering beds, coke combustion produces NOx, CO and CO\(_2\) along with heat, therefore, temperature will increase, oxygen potential will decrease, and ferrous oxide content will increase around coke.\(^9,10\) To study the effects of the oxidation states of the CF, NOx elimination reaction on CH, CM and CW was observed. **Figure 2** shows the change in NOx elimination ratio of the specimens in the standard gas at 1300°C. For all specimens, NOx elimination ratios show descending curves in early 90 sec. The NOx elimination ratio then levels off in each run. The initial period of 90 sec can be regarded as that necessary to exchange gas in the reactor tube. The figure shows that the NOx elimination ratio of CW is the largest. The NOx elimination ratio of CW slightly decreased with increasing reaction time.

**Figure 3** shows the NOx elimination ratio at 1300°C in the reaction gas containing CO and CO\(_2\). NOx elimination ratio for CW was again the largest of the specimens. The value was even larger than that obtained using the standard gas. Although CH and CM shows lower NOx elimination ratios than CW, in the early stage, they start to increase toward the level of CW. The mole ratio of CO/CO\(_2\) or oxygen potential is so low that iron oxides in CH and CM may reduce to be the similar state of CW.

### 3.4. Effect of NO Concentration in Reaction Gas

**Figure 4** shows the results using two standard gases containing different NO concentration at 1300°C. The results showed very similar curves with time in NOx elimination ratio. As results, the rate of eliminated NO seems to be proportional to the NOx concentration in input gas.

### 3.5. Temperature Dependency

**Figure 5** shows the temperature dependency of the NOx elimination ratio for CW. When using the standard gas, NOx elimination ratio increases from 800°C to 100°C linearly. It gradually leveled off with increasing the temperature over 1100°C. The NOx elimination ratio was 75% even at 800°C, when using gas containing CO and CO\(_2\). The specimen of CW in the gas containing CO and CO\(_2\) showed larger NOx elimination ratio than in the standard gas at all the experimental temperatures. The CW was at a
liquid state over 1200°C. The observation of the surface of CW specimen showed that the surface of CW specimen did not change its macro shape in every run, because the reaction gas seems to flow weak enough to keep the shape. The interfacial area between reaction gas and CW seems to be almost constant whenever CW is in liquid state or solid state in macro view. Change in NOx elimination ratio with temperature seems to be caused mainly by the dependency of NO elimination reaction on temperature.

3.6 Effect of Oxygen Potential

As mentioned above, when the iron oxide state in the CF does not correspond to the oxygen potential of the reaction gas in terms of chemical reaction equilibrium, NOx elimination ratio changes with time. The relationship between the oxygen potential in reaction gas and NOx elimination ratio was studied. The specimen was held in the atmosphere of the fixed oxygen potential for more than 6 hr. The equilibrium was attained by flow rate control of O2 gas over 0.001 mole fraction oxygen potential, and flow rate control of CO and CO2 gas under 0.001 mole fraction, being based on the Eqs. (2) and (3).11)

\[
CO + \frac{1}{2} O_2 = CO_2 \quad \text{(2)}
\]

\[
G^\circ = -282420 + 86.65 T \quad \text{(J/mol)} \quad \text{(3)}
\]

Figure 6 shows the experimental results after 300 sec from starting the experiments. The NOx elimination ratio in each run, kept a constant value after 120 sec from the start. The values after 300 sec are adapted to study effect of oxygen potential on NO elimination. The NOx elimination ratio in each temperature, increases to maximum levels with decreasing ambient oxygen potential. The maximum level of NOx elimination ratio at 1300°C is larger than that at 900°C. The oxygen potential where NOx elimination ratio reaches the maximum level is about under 10^{-15} mole fraction at 1300°C and 10^{-11} mole fraction at 900°C. The oxygen potential where NOx elimination ratio becomes larger than 1% or conceivable is under 10^{-6} mole fraction at 1300°C and under 10^{-11} mole fraction at 900°C.

3.7 Effect of Amount of Iron Oxides

In the actual sintering process, the sintering bed is not homogeneous. The chemical composition of CF may change during the sintering reaction. Figure 7 shows the relationship between the NOx elimination ratio and the content of iron oxides in the CaO–FeO system at 1300°C. The high NOx elimination ratio was observed from 0.34 to 1.3 of mole ratio with Ca/Fe.

4 Application to Actual Sintering Process

We tried to apply the in-bed-deNOx process using CF to the sintering process in two steps. Firstly, sintering pot tests were carried out to compare different in-bed-deNOx methods. Secondly, sintering plant tests were also made.

4.1 Pot Test

The pot tests were carried out using a stainless steel pot of 110 mm diameter and 300 mm height. Iron ore and fluxes are sieved and mixed with water in the same manner for each run, in order to keep the sintering profile constant. The pellets of CH shown in Table 1 which were less than 3 mm diameter were supplied as substitutive replacement of limestone and iron ore to keep the chemical compositions of the product sinter constant. Sintering conditions such as suction of air and ignition were also kept for all the run. Figure 8 shows the amount of formed NO+NO2 in the pot tests.
the constant composition of CaO and SiO₂. The results replaced by fine lime stone. This test was carried out under Kakogawa sintering plants when normal size limestone was 4.2. Plant Test NO elimination when using limestone powder.

sintering bed, NOx is generated in combustion zone and moves to bottom of sintering bed by suction air. CF can physically meet with NO only in or below combustion zone. As is reported in the preceding articles, ambient condition of high temperature and low oxygen potential is necessary for effective NOx elimination on CF. In heat pattern during sintering process, it will be better to decrease starting temperature of CF actual formation in sintering bed. Several researchers reported that the starting temperature of assimilation of CaO with Fe₂O₃ decrease with decreasing limestone size. The result of LC run suggests that the formation of CF is fast enough to meet the conditions for NO elimination when using limestone powder.

4.2. Plant Test

Figure 9 shows the NOx conversion ratio at the Kakogawa sintering plants when normal size limestone was replaced by fine lime stone. This test was carried out under the constant composition of CaO and SiO₂. The results were expressed in terms NOx conversion ratio Y, which is the mole ratio of the converted NOx from the supplied nitrogen in fuel, based on the fuel NOx mechanism in sintering plant: $E = \frac{(C_{NOx} \times V)}{(C_N \times F)} \times 100 \quad (4)$

Where, E: NOx conversion ratio (%), $V$: Off gas volume (m³/min), $C_{NOx}$: NOx concentration (mol/m³), $C_N$: Nitrogen concentration in fuel (mol/kg) and $F$: Fuel rate (kg/min).

The use of fine limestone also decreases the NOx conversion ratio even in the actual sintering machine with high productivity. The ratio of the decreased NOx conversion ratio is smaller than that of pot test. It seems to be caused by that the fine limestone used in actual plant was coarser than the limestone powder of pot test and that the replacement ratio of fine limestone was less than 50%.

5. Discussion

5.1. NOx Elimination Mechanism

Wu et al. proposed a hypothesis for the mechanism of NO elimination reaction with iron oxides. It summarized in the following steps:

Step 1: Ferrous oxides reacts with nitrogen monoxide to form ferric oxide.

Step 2: Nitrogen elements in nitrogen monoxide molecules become nitrogen molecules, $N_2$, or nitrous oxides, $N_2O$.

Step 3: When there is some reductant such as CO, ferrous oxide is reproduced from ferric oxide.

The hypothesis also agrees with these experimental results. For example, the specimens of CW in Fig. 2 that initially contains ferrous oxides are effective even when no reductant gas coexists. The chemical analysis of CF after experiments will support the hypothesis of formation of $N_2$ or $N_2O$.

The hypothesis also gives a good qualitative explanation about the experimental result of CH in Fig. 3. The specimen of CH initially contained no ferrous oxides, but CO and CO₂ concentration in off gas analysis suggested that CH was being reduced to form ferrous oxide during the experiment. NOx elimination ratio increased with increasing experiment time, or presumably with increasing ferrous oxide. It, however, seems to be difficult to clarify the relationship between NO elimination and fraction of ferrous oxide in CF during NO elimination where the elimination of NO and the oxidation or reduction of iron oxide proceed simultaneously, because the information of kinetics and transport phenomena of each reactions are not clear enough to estimate the change in the fraction of ferrous oxide in CF.

For a simple discussion, the data in Fig. 6 seem to be suitable, because the iron oxides seem to be stable under the equilibrium of $CO$, $CO_2$ and iron oxides. The data were compared with the equilibrium data reported by several researchers.

The NOx elimination ratio is less than 1% over $10^{-10}$ mole fraction oxygen potential at 900°C. NO elimination seems to be inactive even where there is some CO gas.

Assuming CF is equilibrated with ambient CO and CO₂, the CF over $10^{-10}$ mole fraction oxygen potential is presumably occupied mainly with phase of CaO–Fe₂O₃ at 900°C. Ferrous oxide seems not to exist sufficiently where NO elimination is inactive. The same manner, NOx elimination ratio is less than 1% over the oxygen potential of $10^{-3}$ mole fraction at 130°C. According to Yazawa’s report about FeO–Fe₂O₃–CaO system liquid, the fraction of ferrous oxide is about 10% where NO elimination is inactive. Therefore, the NO elimination is presumably inactive even where there is some CO gas and some ferrous oxide. Equilibrium concentration of NO increases with increasing ambient temperature and increasing ambient oxygen potential. NO elimination on CF seems to be inactivate when the equilibrium concentration of NO is similar to ambient NO concentration. For example, the equilibrium con-
centration of NO with 78% N₂ and 10⁻⁵ mole fraction oxygen potential is about 40 ppm at 1300°C, and that with 10⁻¹⁰ mole fraction oxygen potential at 900°C is about 1.2×10⁻⁸ mole fraction NO. This comparison showed that the hypothesis by Wu et al. needs more investigation to explain the mechanism of NO elimination.

Figure 7 shows that there is a proper range of CaO content in the CF for NO elimination. Additionally, the surface of the specimens containing more than 60% CaO were covered with small particles of calcia after experiment. EPMA analysis suggested that the particles are made with crystallization reaction from CF specimen. The range of high NO elimination ratio is similar to the range of homogeneous liquid of CaO–FeO–Fe₂O₃ system. Therefore, homogeneous liquid CF seems to be more effective on NO elimination than heterogeneous liquid CF which contains solid calcia or solid ferrous oxide partially, because the solid materials decrease the surface area of the liquid to touch NO gas. But, the essential reason why the addition of calcia to ferrous oxide increases NO elimination remains unclear.

The kinetics of NOx elimination reaction on the CF were not investigated enough to compare precisely with other materials such as absorbents or catalysts. Additionally, few reports have provided the detailed information recently. In spite of these difficult conditions, a simple evaluation was carried out. The apparent elimination rate on the CW at 1300°C was calculated by the data shown in Fig. 3 about 4.1×10⁻⁷ (mole-NO/s m²). Assuming that the reaction interfacial area is the surface area of the CW liquid in the crucible, the elimination rate can be estimated as 1.3×10⁻¹¹ (mole-NO/s m²). Hightower’s summary presents data of several catalysts. The NO elimination rate of the CW is as large as that of a Pt catalyst.

5.2. Application of In-bed-deNOx

Some application tests of the in-bed-deNOx process such as charging CF pellet or using of fine limestone, showed the following problems to be solved.

The amounts of the decreased NOx in the pot test of charging CF pellet is slightly smaller than that in the particle tests conducted by Wu et al. Although all the limestone was replaced by CH pellets, 20% of the NOx decreased comparing to the base condition. One of the reasons is presumably owe to the existing state of CF. The effect of CF does not work in high oxygen potential atmosphere, but oxygen concentration in off gas from sintering plants or sintering pots was more than 10% on average. The proper condition for NOx elimination reaction with the CF is located only near the coke particles. The ineffectiveness in the pot tests may be caused with charging CH pellets randomly into the sinter mix. Most of the charged pellets were far from coke particle and did not work for NOx elimination. The existing state of CF is important for NOx elimination and needs further development to arrange CF near coke particle effectively.

A variety of equipment such as a pan pelletizer is necessary for the production of the CH pellets. The random fine limestone charging is one of the simplest methods for realizing the In-bed-deNOx process, but it has various problems in the production of sinter. For example, fine feed materials are apt to decrease sinter mix permeability and productivity. In addition, an extensive supply of the fine limestone is usually expensive.

Further study is necessary to solve the problems in actual application.

6. Conclusion

The effect of the calcia-iron oxide on NO elimination reaction was experimentally examined. The new process “In-bed-deNOx” using the calcia-iron oxides (CF) was studied by plant tests. The results are summarized as follows:

(1) The CF play a role on nitrogen monoxide elimination reaction.

(2) The effect increases with increasing reaction temperature and decreasing atmospheric oxygen potential, even when the CF is in liquid state.

(3) The effect depends on the oxidation states of iron oxide, the CF, and ferrous oxide is most effective.

(4) The application tests of the new process “In-bed-deNOx process” to the iron ore sintering process were successful in the pot tests and the actual sintering plant.

(5) NOx emission decreases with increasing the charged CF pellets in sintering bed and with increasing supplied fine limestone instead of coarse limestone.

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