C-4.1.1 Practical Research on Control Techniques of Acid Rain in Eastern Asia

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Abstract

To establish the control technique of emission of SOx and NOx which cause the acid rain, a sulfur removal process for coal combustion was examined. The usage of coal briquette was investigated for the small and medium size stoker boilers which requires immediate measures. The concept of this method is to replace the fuel from usual caol to coal briquette which containing the sorbent.

At the first step, lab-scale experiments were carried. Results are as follows. The SOx removal efficiency was about 60 to 70 percent when Ca/S = 4. It is, however, difficult to remove the sulfur oxides emitted when the volatile matters burns. Therefore, some measures should be added to the period. When limestone was compared as an absorber with hydrated lime, hydrated lime was effective. A remarkable influence was not seen in the SOx removal efficiency with any condition of molding pressure of molding pressure of coal briquette from 1 to 3 t/cm^2.

As the next step, the coal briquette method was applied to a stoker boiler in China. One of typical stoker boilers in China was selected as a model boiler. The model boiler is operating in the glass machine plant at Shenyang city, the biggest city in the northeastern area of China, for heating in winter season. The SOx and NOx emissions and the operating condition of the boiler were investigated at the situation of no desulfurization process. The SOx emission was about 600 ppm and NOx was about 180 ppm in usual operation. When the coal briquette with 2 of Ca/S molar ratio was used as fuel, the desulfurization efficiency became about 70% and SOx emission lebel became about 140ppm. Operavility in stoker boiler with coal briquette was almost excelent. Therefore, the coal briquette method seems to be a practicable measure to reduce SOx emission in Eastern Asia.

Key Words: Eastern Asia, Acid Rain, Coal Combustion, SOx, Desulfurization, Coal Briquette

1.Introduction

Sulfur oxides (SOx) and nitrogen oxides (NOx) emissions, which cause the acid rain, are increasing in Eastern Asia as well as in Europe and in North America. Moreover, this region is forecast that the energy demand will increase because there are a lot of developing countries and they will use cheap but row grade fuel. Especially China is the world-biggest country in the coal consumption and the low grade and high sulfur content coals, produced in China, should be used. However, because of the cost restriction and the maintenance administration, it is difficult to introduce a flue gas treatment systems which are used in advanced countries. From such backgrounds, A simple and cost effective technology for SOx reduction is required as the acid rain prevention measures.

Not only large-scale boilers for power generation but also small and medium-sized scales stoker boilers are operating in China and it is said that the SOx emission from them is occupy 1/3 of the total SOx emission from all combustors. It is necessary to apply the desulfurization technology to thestoker boiler immediately. This research aims at the practical use of control technology of SOx and NOx emissions from coal combustors which considers the situation of Eastern Asia region, especially China.

2. Research Objective and Contents

For the purpose of establishment of the control technology of SOx and NOx emissions from coal combustors in Eastern Asia region, following researches were executed.

Although it is thought that the replacement from stoker boilers to the circulated fluidized bed combustors which are possible desulfurization in the furnace is effective for the long term, the usage of coal briquette is promising for the stoker boilers which are current operating and need immediate measures. Then, concerning briquette coal, the characteristic of desulfurization and the influence of the kind of chemicals and the molding pressure on desulfurization efficiency were experimentally examined.

Moreover, the proof examination of the desulfurization with the model stoker boiler in Syenyang city decided to be done and the problems for practical use were solved. After the emission of SOx and NOx from the model stoker boiler operating without flue gas treatment system in Shenyang city were investigated, the desulfurization performance of briquette caol was examined. It was proven that the usage of coal briquette is very practicable for the Eastern Asia.

3. Research method and result

3.1 Research by lab-scale

First of all, to examine the desulfurization characteristic of the coal briquette, the samples of coal briquette including absorbents were made. After the coal shown in Table 1 were mixed with the absorbents, briquette were pressurized molded using molasses as a binder. The unsteady-state combustion and the desulfurization characteristic of briquette were investigated. Next, to examine the influence which the kind of the absorbents on the SOx removal efficiency, limestone and hydrated lime were compared. Moreover, the influence of the molding pressure on the SOx removal efficiency was examined.

Table 1, Analysis value of coal used

	Messina Coal	Miike Coal
Moisture	4.70 %	2.56 %
Ash	17.60 % (dry)	23.84 % (dry)
Volatile	9.60 % (dry)	34.90 % (dry)
Fixrd carbon	72.80 % (dry)	41.26 % (dry)
Carbon	73.50 % (dry)	61.60 % (dry)
Hydrogen	2.70 % (dry)	4.71 % (dry)
Nitrogen	1.80 % (dry)	1.03 % (dry)
Oxygen	3.70 % (dry)	7.69 % (dry)
Sulfur	1.00 % (dry)	1.63 % (dry)
Calorific value	6540 kcal/kg	6200 kcal/kg

Figure 1 shows the schematic diagram of the experimental system. The combustion tube is the perpendicular drop-furnace which is made from the quartz tube of 35mm in the inside diameter and has the sintering quartz plate of 5mm in thickness in the center. The temperature was controlled by an electric heater of a cylinder type outside of the combustion tube. The experiment method is as follows. The sample briquette dropped from the folder to the combustion tube after putting briquette in the folder kept a room temperature and setting the combustion tube at 850 degree C throwing the mixed gas (O_2:21%,N_2:79%). The flue gas from the combustion tube was measured online with gas analyzer of the sulfur oxides meter etc. and the data was taken into the personal-computer in two seconds through the data logger. O_2, CO_2,

CO, NO, N_2O, and SO_2 were measured

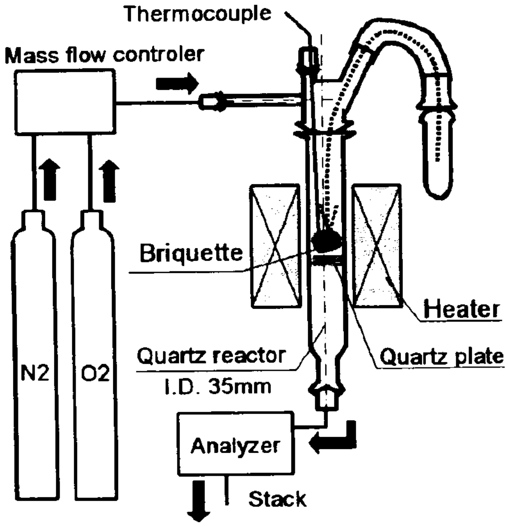

Fig.1 The schematic diagram of the experimental system

Figure 2 shows one example of data measured. This figure is a combustion result of briquette that uses the Messina coal as fuel and contain absorbents at 1 of Ca/S. The briquette dropped when 100 seconds later from beginning. The oxygen concentration decreases rapidly after dropping and increases afterwards. The point that the inclination of increase O_2 concentration becomes more gradual was considered to be the point which changed from a predominant area of the volatile matters combustion (Vola) to an predominant area of the char combustion (Char). The amount of SO_2 emission from the coal 1kg is shown in the lower of Figure 3 separately for Vola and Char and the SOx removal efficiency calculated based on the state without the absorbents is shown in the upper of Figure 3. It is understood from this figure that the amount of the SO_2 emission decreases as Ca/S increases. The SO_2 when the char burns is mainly removed. The reason for SO_2 emission when the volatile matters burns does not decrease so much is that limestone are not calcinated into CaO which effective in desulfuration. It is thought that effective desulfurization when the volatile matters burn becomes important to improve the SOx removal efficiency further.

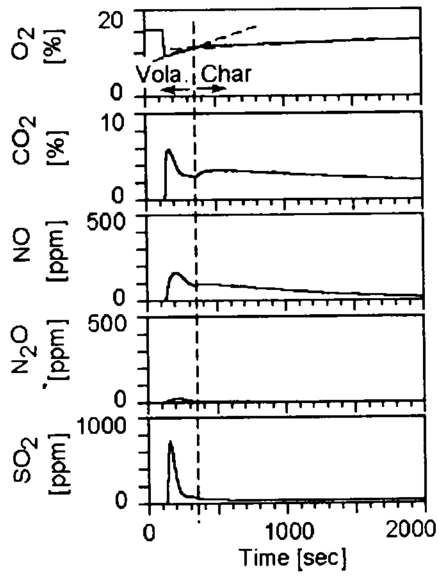

Fig.2 Example of the data measured

Figure 4 shows the influence which the kind of absorbents on the SOx removal efficiency. Miike coal was used as fuel. The horizontal axis is a moler ratio of calcium in the absorbents and sulfur in the coal, and the vertical axis is the SOx removal efficiency calculated based on the state not containing the absorbents. Compared with limestone and hydrated lime as absorbents, hydrated lime was higher than limestone SOx removal efficiencies. It was about 65% in case of hydrated lime while about 50% in case of limestoneat at 4 of Ca/S. Limestone can react with SO_2 after decomposing into calcium oxide (CaO) which react with SOx. On the other hand, hydrated lime can react directly with SOx with decomposing into CaO. Therefore, it is thought that the SOx removal efficiency is better when hydrated lime uses as absorbents because the desulfuration becomes effective from initial step of burning.

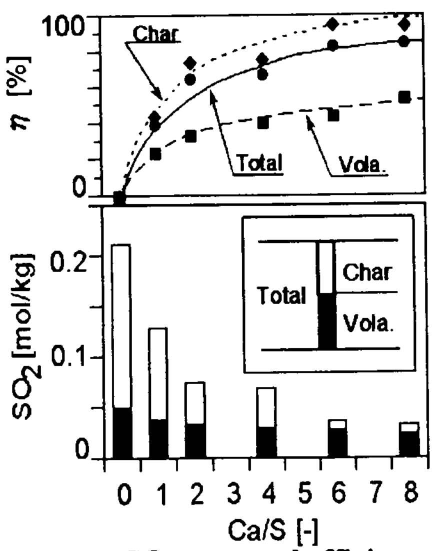

Fig.3 SOx removal efficiency and the amount of SO_2

The coal used are different in Figure 3 and Figure 4. The Messina coal that contain comparatively few volatile matters obtained higher SOx removal efficiency than the Miike coal. Therefore, using coal containing few volatile matters can obtain a higher SOx removal efficiency.

Figure 5 shows the influence on the SOx removal efficiency of the molding pressure. Limestone was used as a absorbents. The molding pressure is taken in the

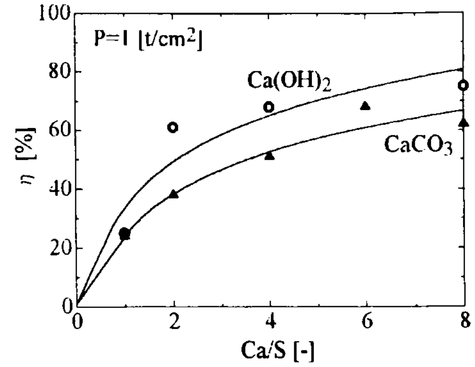

Fig.4 The difference between limesrone and hydrated lime

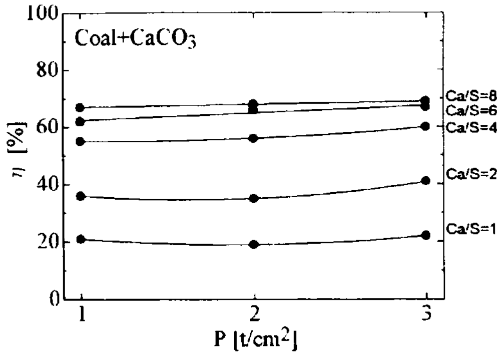

Fig.5 The influence on the SOx removal efficiency of the molding pressure

horizontal axis and the SOx removal efficiency is taken in the vertical axis. A remarkable influence on the SOx removal efficiency was not seen for the molding pressure in the range of 1-3 t/cm^2.

3.2 SOx・NOx emission investigation in Shenyang city.

Not only large-scale boilers for power generation but also small and medium-sized scales boilers are operating in China and it is said that the SOx emission from them is occupy 1/3 of the total SOx emission from all combustors. There are various types of coal boilers. The stoker boiler is one of the most difficult coal fired boilers to add the SO_2 prevention methods. Because, the scale is in general small. In Japan, such stoker boilers almost have been replaced to oil and gas boilers. However, the stoker boiler should be still a main type in small-scale coal boilers in China. Chinese government is recognize that SO_2 measures in such small boilers are difficult and have a plan to stop the productio of stoker boilers near future. In China, the dependency of coal to the gross energy demand in future a few decades will not vary and almost equal (about 70%) to the the current state. It is thought that the replacement from the stoker boilers to the circulating fluidized bed combustors which are possible desulfurization in the furnace is effective for the long term. However, counter measures to reduce SOx emission for the present stoker boilers are needed urgenty. The use of coal briquette described in the foregoing section of this paper is promising for that. In this research, the investigation and proof tests in China were done concurrently to the basic research of the briquette.

Fig.6 A whole photograph of the boiler

Table 2 Specification of the boiler

Size of Boiler	
Height	4558 mm
Length	5468 mm
Breadth	5050 mm
Size of Furnace	
Diameter	1624 mm
Length	3040 mm
Capacity	1.4 MW
Inner pressure	0.69 atm
Temp. of outlet water	80 degC
Temp. of inlet water	60 -70 degC
(Steam)	(2 t/hr)
Forced fan	
Air flow rate	9030 m^3/hr
Pressure	1850 Pa
Induced fan	
Air flow rate	4870 m^3/hr
Pressure	-2240 Pa
Stack	
Height	25 m

A typical heavy industries city 'Shenyang' in the northeastern area of China was selected as a proposed place of investigation. Shenyang is the largest heavy industries city in the northeastern area. One typical stoker boiler operating at glass machine plant in Shenyang city was selected as a model boiler in cooperation with the Northeastern University. A whole of this boiler photograph is shown in Figure 6 and the specification is listed in Table 2 and a schematic diagram is shown in Figure 7. This stoker boiler works for heating in the glass machine plant in winter season only. This boiler is running only in the morning and the evening in November and March and is continuous operated in whole day in December, January, and February of the severe winter period.

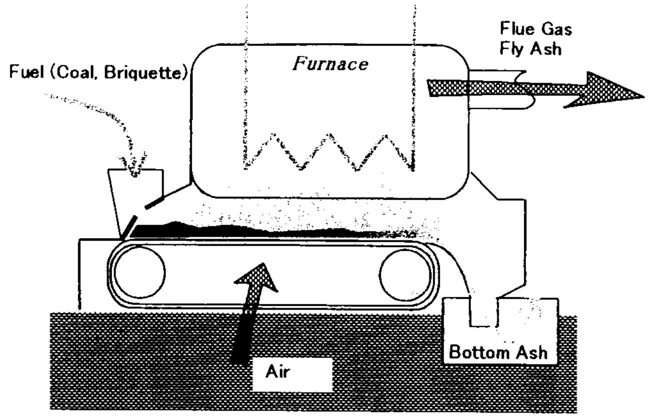

Fig.7 A schematic diagram of the boiler

Table 3 Analysis of coal, flyash, and bottom ash

	Coal	Flyash	Bottom Ash
Moisture	1.46 wt%		
Ash	37.43 wt% (dry)		
Volatile	22.80 wt% (dry)		
Fixed carbon	39.77 wt% (dry)		
Carbon	49.38 wt% (dry)		
Hydrogen	3.07 wt% (dry)		
Nytrogen	0.66 wt% (dry)		
Oxtgen	8.98 wt% (dry)		
Sulfur	0.74 wt% (dry)		
Calorific value	4890 kcal/kg		
SO3		1.29 wt%	0.83 wt%
Ignition loss		30.92 wt%	25.54 wt%

The operation method of this boiler is as follows. Because there is always seed fire in the combustion chamber, combustion starts by only starting the air blower and exhaust fan and adding coal. The operation is stopped by stopping the blower and exhaust fan. In usual operation, the coal feed rate is adjusted manually within the range of 300-500kg/hr. The air feed rate is adjusted by the opening of the dumper manually. The temperature and level of the water in drum are watched when operating. The flue gas has not been analyzed. The combution condition is entrusted to the administration by the experience of the boiler operator. The temperature of the water supplied to the boiler is the index of the combustion load adjustment. the boiler operation adjusts the outlet temperature of water usually. The temperature of the warm water which circulates to the boiler lowers when the heating demand grows. Therefore, it is necessary to increase the combustion load. It is said that about 2,000 boilers of this type were operating in the Syenyang city.

The current state without desulfurization was investigated in the first phase and the proof examination with the briquette coal was done in the second phase. The result of investigation of the first phase is as follows. The coal used with this boiler is mixed coal of Fuxin coal and Datong coal. The analytical value is additionally shown the analysis result of flyash and bottom ash in Table 3. The calorific value is a little low though it is a typical bituminous coal. The main reason to use the mixed coal is that the cost is cheap. The Datong coal is comparatively good quality coal and the sulfur content is comparatively low. However, because of the good quality and hight transportation cost, the price is high. On the other hand, because the quality is a little poor and the coal mineed in a place near Shenyang, the price of Fuxin coal is low. By mixing these, fuel expenses were suppressed low during winter.

The flue gas analysis was done as follows. The metal tube for the gas sampling was inserted into the boiler flue, the sample gas was sucked by air pump. SO_2, NOx, O_2, and CO measurment was done in online. Gas analyzers used are as follows. SO_2 and CO were measured by HORIBA VIA510 (NDIR analyzer), NO and O_2 were measured by SIMAZU NOA-500 (chemiluminescence and zirconia type). The standard gases for calibration were brought from

Japan. Measurment was done as almost same in Japan, so that measuring results should have high rerliability. The output signals of these gas analyzers were taken into a small computer after A/D convertion by a data logger (ETODENKI, Thermodac E) and were recorded as time series data. Moreover, the temperature of the boiler was measured with thermo-couple (JIS-K).

Figure 8 shows the measurement result of SO_2. The solid line is a measurement value and the short dashes line is predicted value of the sulfur oxides calculated from the ultimate analysis of coal and the oxygen concentration in the flue gas. The measured values almost agreed with the predicted value. This means measurement is high reliable. The operation of the boiler in this trial is as follows. The blower and exhaust fan were started at 300 seconds and the combution began. The coal feed rate was increased from 350kg/hr to 430kg/hr at 1,020 seconds and to 780kg/hr at 2,640 seconds. The coal feed rate was decreased again to 350kg/hr at 3,360 seconds. The blower and exhaust fan were stopped at 4,080 seconds. Figure 9 shows the result of NOx, CO, and the O_2 measured at the same trial. In usual operation, the SOx emission from the model stoker boiler was about 600ppm and NOx was about 180ppm. The combustion efficiency of this boiler is estimated as 80% from the ignition loss of flyash and the bottom ash. This value is considerably bad. It is judged from these data that they operate in a comparatively high air ratio to maintain a good combution condition, though it is suggested that the operation in a lower air ratio is preferable. Although operation highly depends on the experience of the boiler operator, a good operation was achieved.

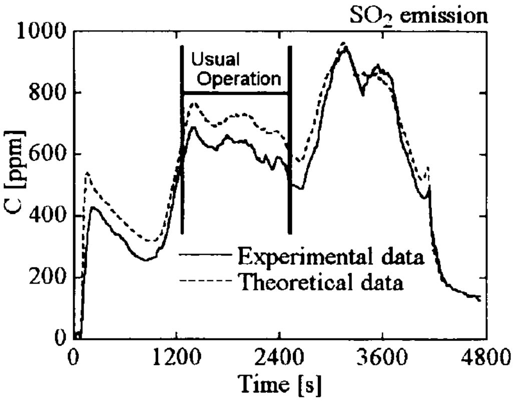

Fig.8 SO_2 emission without desulfurization process.

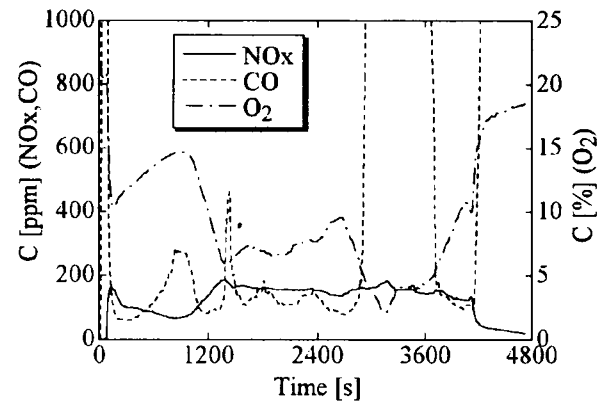

Fig.9 NOx, CO, and O_2 emission without desulfurization process.

Next, in the second phase, the proof examination of the simple sulfur removal process with the briquette coal which contain the absorbent was done. The measurement system is the same as the first phase. The coal used to manufacture the briquette is Japanese domestic coal which contain sulfur at 0.87%(dry). Hydrated lime was used as an absorbent. The biomass used is a mixture of the chip dust and the peat. This works as a binder of briquette and as the combustion subsidiary material. After mixing three kinds of raw materials at 2 of Ca/S molar ratio, briquette was pressurized and molded at setting value 175 kg/cm^2 of molding machine. The analysis value of briquette after manufacturing is listed in Table 4. From this analysis value, the predicted SO_2 emisson is 520 ppm at the 6%

Table 4 Analysis value of briquette which manufactures

	Briquette
Moisture	4.18 %
Ash	28.82 % (dry)
Volatile	40.29 % (dry)
Fixed Carbon	30.89 % (dry)
Carbon	50.90 % (dry)
Hydrogen	4.48 % (dry)
Nytrogen	1.10 % (dry)
Oxygen	14.64 % (dry)
Sulfur	0.53 % (dry)
Calorific Value	5050 kcal/kg

of the oxygen concentration in the flue gas if absorbent does not work.

Figure 10 shows the measured SO_2 concentration in the stoker boiler. 0-15 minutes are the pre-combustion stage and the blower and exhaust fan are started at 15 minutes. As understood from the experimental results in the lab scale, when the volatile matters burnt, the concentration of SOx had a peak value and indicated the value of about 270ppm. At 30 minutes, when the volatile matters combustion was finished and char combustion were predominant, the concentration of SOx almost became constant and showed the value of 140ppm. It was proven to obtain the SOx removal efficiency of about 70% by this technique because predicted SOx was 520ppm. Figure 11 shows the NOx concentration measured at the same trial. When usual operation, it was about 180ppm. This was the almost same level as in the previous year's measurement. The operability with briquette was excellent because ignitability was high and the calorific value was higher than that of the coal used in there. After experiments, the boiler operators said that applying the coal briquette is very reasonable to a stoker boiler. The ash is powderly and the generation of the clinker is a little. However, the problem of storing occurred. Although strength is comparatively high when briquette coal are dry, strength of briquette decrease and crush easily with moisture absorption. Therefore, it is necessary to set up the indoor coal storing yard.

In the boiler operation, it was understood that briquette was excellent and accepted in goodwill.

Even the reference shows the calculation result of applying this technology in Figure 12. The total annual SO_2 emission from this boiler is calculated 12t/year. There are a similar 2,000 boilers in Shenyang city, so total annual SO_2 emission from stoker boilers in Shenyang becomes about 24,000t/year. It can be expected when this technology is applied, 70% of total annual SO_2 emission can be reduced. So, the annual SO_2 emission is expected to decrease to 7,200t.

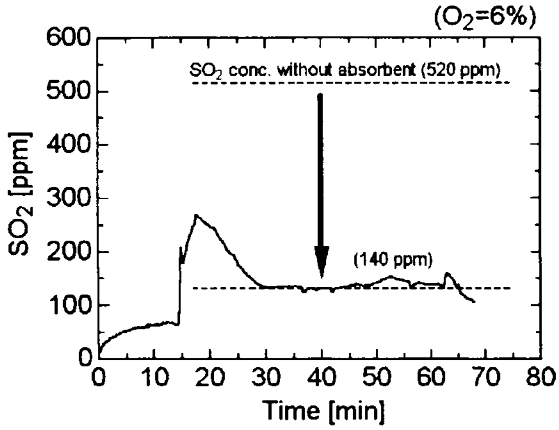

Fig.10 SO_2 emission with the briquette coal method.

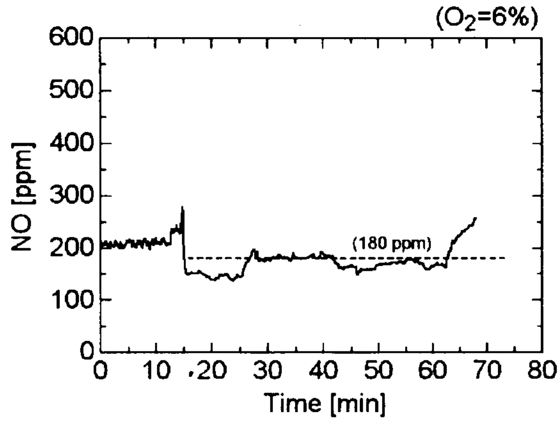

Fig.11 NOx emission with the briquette coal method.

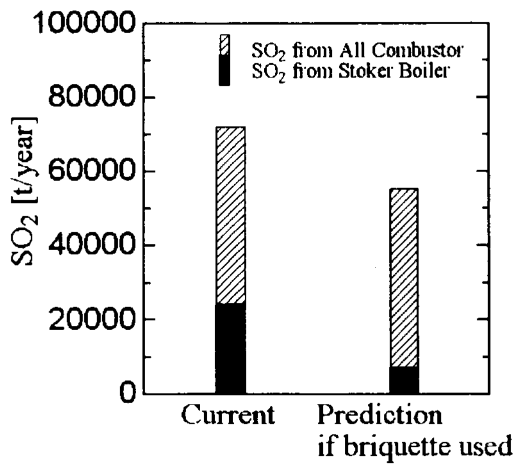

Fig.12 Prediction of SOx emission with the briquette coal method.

4. Conclusion

The control technology of SOx and NOx from coal combution equipment was researched based on the current situation in the Eastern Asia region, especially in China.

The coal briquette method was investigated for the small and medium-sized scale stoker boilers which immediate measures were urged. Moreover, after the SOx・NOx emission investigated, the proof test of coal briquette method was done in China.

Following conclusions were obtained.

1) In the lab scale experiment, the SOx removal efficiency was about 60 to 70 percent at 4 of Ca/S molar ratio.
2) It is difficult to remove the SOx emission when the volatile matters burn even if the amount of the absorbents are increased. It is important to improve the SOx removal efficiency that the sulfur oxides measures are taken when the volatile matters burn.
3) The influence which the kind of tabsorbents on the SOx removal efficiency was examined. It was about 50% for limestone at 4 of Ca/S while about 65% for hydrated lime. It is thought that this relates to the sulfur retention in an area predominant the volatile matters combustion of burning initial.
4) A remarkable influence on the SOx removal efficiency was not seen for the molding pressure in the range of 1-3t/cm^2.
5) One typical stoker boiler operating at glass machine plant in Shenyang city was selected as an model boiler.In usual operation, the SOx emission from the model stoker boiler was about 600ppm and NOx was about 180ppm.
6) It was proven to obtain the SOx removal efficiency of about 70% by the coal briquette method.

Reference

1) Coal technology which aims at the 21st century, KAGAKUKOUGAKKAI, (1995)