

A Case Study of Desulphurization by Limestone Adsorbent in an Industrial CFBC Boiler

Young Goo Park, Seung Ho Kim and Young Min Jo^{1)*}

*Department of Environmental Engineering, Samcheok National University, Kangwon-do,
South 245-711, Korea*

¹⁾*Department of Environmental Science & Center for Environmental Studies, Kyunghee University,
Kyunggi-do, South 449-701, Korea*

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Abstract

Domestic anthracite contains a large amount of fine particles, which causes to fire the back side of the boiler and to form the clinker deteriorating the combustion efficiency. At this time, the fine limestone adsorbents for a desulphurization agent may be used to facilitate an aggravation of the boiler, so that fine mode of limestone (<0.1 mm) has been used no more than 25% in local power stations of Korea. The present test carried out with an in-situ boiler, however, showed that higher content (up to 50%) of fine limestone particles did not entail any mal-function. In addition, the desulphurization was found to be as good as the old mode of limestone adsorbents.

Key words : Limestone, CFBC, Desulphurization, Coal power station, Ca/S ratio

1. INTRODUCTION

Circulating fluidized bed combustion (CFBC) has been a standard utility in FBC technology since the 1990's due to its advantages in the reduction of SO₂ and NO_x control when burning high-sulfur coals (Grace, 1995).

In the fluidized bed furnace for coal combustion, limestone is a frequently used sulfur capture sorbent (Wang *et al.*, 2002). The fed limestone is calcined to CaO and CO₂ in the furnace, where the CaO reacts with SO₂ and O₂ to form CaSO₄ at about 800~850°C. In general, the molar ratio of Ca to S in the feedstock should be at least 2 in order to achieve

more than 90% efficiency of desulphurization (Leckner *et al.*, 1993). A high ratio of Ca to S in limestone may release a large amount of unreacted limes, ultimately being discharged with the inert fly ash out of the furnace. The Ca/S molar ratio can be reduced by modification of particle size of desulfurizing agents or by recirculation of elutriated lime into the furnace. Fine limestone particles have been known to enhance the desulphurization efficiency, leaving less unreacted residues (Zang *et al.*, 2003). Thus, the fine limestone is more appropriate to the power station, but the elutriation of fine particles may often exacerbate the desulphurization, simultaneously resulting in the increase of solid ash emission. In addition, the fine particles which are largely contained in domestic anthracite cause the high temperature at the rear region of the boiler and facilitate

* Corresponding author. Tel : +82-(0)31-201-2485
Fax : +82-(0)31-203-4589, E-mail : ymjo@khu.ac.kr

the formation of clinkers causing fouling (Jeon *et al.*, 2002). Not only do the coarse clinker lumps stick to the furnace wall, but impede fluidization of the bed. In accordance, the power station has been using an optimum mode of limestone, which occupies only about 25% of fine particles smaller than 0.1 mm, and thereby a large volume of fine limestone has been cast away.

However, the consistent development of collection devices and improvement of circulating processes have enabled to reduce the emission of fine solid particles, it is thereby believed that more addition of fines can be accepted, which could help maintaining the current economic value of limestone produced from domestic open-cut mines. Thus, this work has examined the desulphurization performance using an increased volume of fine limestone to 50% in an in-situ CFBC boiler running at a coal power station.

2. EXPERIMENTALS

Experimental work was carried out with two modes of limestone depending on the content of fine particles (< 0.1 mm); 25% for the currently used limestone sample at Donghae coal power station, symbolized L-I in this work, and about 50% for the new test mode, L-II.

2.1 Materials

Although the limestone of high calcium content is generally favorable for desulphurization, de-SO_x reactivity in the FBC is variable depending on the particle structure and pore size distribution. Thus, in

order to assess the desulphurizing agent accurately, it is best to experiment the test limestone in the real scale boiler. The composition of major elements was similar to both limestone samples as shown in Table 1. The test limestone was received from the same ore which is currently being used in the power station.

The test limestone particles were distributed in size as summarized in Table 2. While the fine particles below 0.1 mm were 24% in the current limestone (L-I), the test limestone (L-II) included 47% of the fine mode. There was a little difference from the experimental intention, which have arisen from the mechanical classification on a large scale. The relative proportion of particles between 0.5 mm to 0.1 mm was 67% for L-I and 45% for L-II. Fuel coal has been received from the local anthracite mines and collected under 6 mm by a coal crusher. Its composition is introduced in Table 1.

2.2 Experimental apparatus and method

The lay-out of the in-situ CFBC boiler of Donghae power station and dust collection device is schematically depicted in Fig. 1. Particulate limestone is continuously injected into the bed of which combustion temperature was 850°C to 890°C. Most of the solid particles entrained by the gas stream are recycled to the furnace as being separated by the cyclone separator (inside diameter: 7 m) and ESP.

Experimental operation parameters were the emission concentration of SO₂, temperature at lower zone of the bed, electricity power generation, and ash recycle condition. An automatic monitor (pulse UV fluorescence method; Sick, GM 31, Germany) installed at 56 m high of the stack analyzed the real-

Table 1. Summary of XRF analysis for coal, limestone and fly ash (w/w %).

Ash of coal*		CaO	MgO	SiO ₂	Al ₂ O ₃	K ₂ O	Fe ₂ O ₃	TiO ₂	SO ₃
		1.72	0.60	48.9	31.3	5.87	5.49	2.16	3.11
L-I**	Limestone	92.4	2.16	2.35	1.56	0.41	0.78	0.11	0.025
	Fly ash	5.15	0.82	52.3	29.1	3.46	3.98	1.27	3.18
L-II**	Limestone	92.3	1.31	2.57	1.73	0.45	1.21	0.13	0.03
	Fly ash	3.75	0.75	52.4	31.0	4.0	4.0	1.38	1.94

*Fuel coal is composed of 57%-fixed carbon, 32%-ash, 7%-VM and 4%-moisture.

**Remainders in L-I and L-II are other trace elements including LOI.

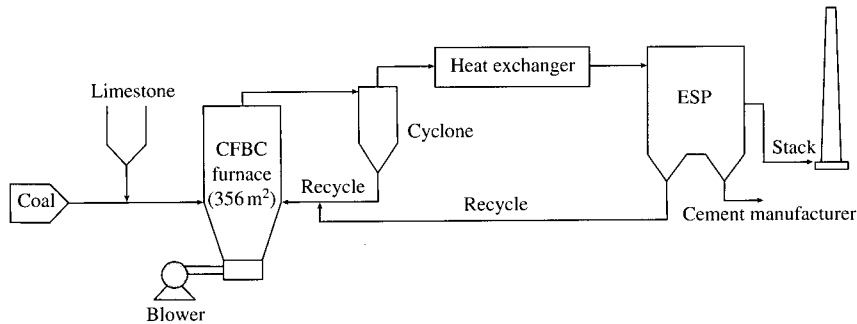


Fig. 1. Schematic diagram of the test CFBC in the power station.

time concentration of the exiting SO_2 of which concentration was from 100 to 130 ppm SO_2 . The test temperature of the furnace bed was 875°C and 880°C . The power generation could be adjusted at 150 MW, 180 MW and 200 MW at 880°C . In order to ascertain the effect by ash circulation, desulphurization was examined for when the recycle circuit was either off or on. The experimental investigation was fulfilled according to the practical operation condition of the in-situ power station. The performance of the test limestone was analyzed based on the molar ratio of Ca to S contained in either limestone or coal respectively. The molar ratio was evaluated by measurement of the required limestone volume to meet 90% desulphurization.

3. RESULTS AND DISCUSSION

3.1 Overall examination

The primarily selected limestone ore under 20 mm is pulverized by a hammer crusher, and collected in granules smaller than 1 mm. The pulverization at the mining site produces a large amount of fine granules less than 0.1 mm, which occupies more than 50% of whole limestone products. Half of these fine limestone particles has been used as a desulphurizing agent in the coal power station, and the other half has been dumped without any commercial application. The disposal also costs high not to be ignored. Thus, it is essential to utilize the fine limestone as much as possible.

Table 1 presents an obvious clue that the test limestone (L-II) should not be much different from L-I. Review of the chemical composition of the fly ash generated by combustion showed that despite of a similar initial content of CaO in limestone samples, combustion with L-II produced less CaO. This means that L-II is quite effective in the de- SO_x reaction. For coarse particles, the desulphurization reaction occurs more on the surface of the solid, and CaO in the core perhaps has less chance to contact the reactant gases (Sandra *et al.*, 1993). But, on the other hand, the coarse particles on the average spend a longer time in the bed, which will lead to a positive effect on the reaction (Best *et al.*, 1977). Besides, the behavior of CO_2 generated from the thermal decomposition of the limestone may alter the micro pores on the CaO particle surface, usually diminishing the molar surface area and having a negative effect on the desulphurization (Montagnaro *et al.*, 2002; Anthony *et al.*, 2001). The measured molar volume of the Ca compounds in this work varied from $36.9 \text{ cm}^3/\text{mol}$ for CaCO_3 to $16.64 \text{ cm}^3/\text{mol}$ for CaO, afterwards increased to $45.98 \text{ cm}^3/\text{mol}$ for CaSO_4 again. Thus, variation of the reaction efficiency due to size modification could not be clearly defined in theory at least under the present experimental condition.

Meanwhile, Fujiwara (1994) reported that iron element can enhance the reaction rate, i.e. if iron oxide (Fe_2O_3) exists at a level of more than 1% in limestone, the desulphurization rate will be 1.5 to 1.8 times higher than one containing less than 1%

Table 2. Size distribution of limestone particles by sieving.

Size (mm)	L-I (%)	L-II (%)
1.0~0.7	1	1
0.7~0.5	8	7
0.5~0.1	67	45
<0.1	24	47

(Fujiwara, 1994). However, its effect does not act in a consistent manner, and thus the present study could not quantitatively analyze it with a high accuracy.

A certain amount of fine coal particles would burn at the upper region of the bed or even in the cyclone, so called after combustion. It causes unexpected partial firing and subsequently may generate the unwanted clinkers. In particular, alkali metals such as Na₂O and K₂O present in coal directly promote the formation of clinkers, but the coal used in this power station contains only a little Na₂O (0.113%) and K₂O (5.87%). Thus, it was estimated that clinker formation or growth attributed by alkali metals should not be significant in this CFBC.

3. 2 Effect of size variation

In gas-solid fluidization with desulphurizing agents, sand and coal including ash particles, the optimum fluidization relates closely to the size distribution of the particulate materials. Particularly the limestone fed to the furnace is rapidly heated and experiences instantaneous thermal and chemical reactions, resulting in breakage or partial agglomeration. Therefore, the preparation of desulfurizing agents must be taken into proper account when crushing and sieving.

The molar ratio of Ca/S was evaluated for the different size distribution of limestone. The ratio of Ca/S to maintain the SO₂ emission with 115 ppm was 2.81 and 2.87 for L-I and L-II respectively. The virtual boilers in the coal power station have emitted 110 to 115 ppm of SO₂; average values of each molar ratio were 2.97 for L-I and 3.07 for L-II as summarized in Table 3. Conversely, in order to restrict the SO_x emission to between 100 to 115 ppm, a little more limestone of L-II should be supplied than L-I.

Table 3. Desulphurization according to the operation condition.

	L-I			L-II		
	115	100	Ave.	115	100	Ave
SO ₂ emission (ppm)	115	100	Ave.	115	100	Ave
Molar ratio (Ca/S)	2.81	3.12	2.97	2.87	3.26	3.07
Power output	181	177	179	179	179	179
Temperature lower bed (°C)	880	880	880	880	881	881
Temperature upper bed (°C)	871	870	871	871	871	871
Total air (kg/s)	162	158	160	163	164	164

On the whole, fine mode of limestone is pretty useful for the desulphurization in coal combustion, generating only a little unreacted residues (Pisupati *et al.*, 1996). The molar ratio of calcium to sulfur can be reduced by more use of finer particles. Since high ratio of Ca/S may leave a large amount of unreacted limes, which being released with inert fly ash, the power station generally prefers fine mode of limestone. The elutriation of fine particles rather deteriorates the desulphurization and causes the tremendous generation of fly ash. Thus, the power station decided to utilize only 25% of fine mode (<0.1 mm). However, developing the advanced circulating system of residual ash particles can confine the elutriation of fine solids. Therefore, it is believed that more input of the fine mode limestone does not matter for the desulphurization reaction in the CFBC.

Limestone is composed mainly of CaCO₃, and produces sulphates by the reaction with sulphur elements. Open pores formed while sintering provide potential space and surface where the chemical reactions occur. However, calcium sulphate is apt to close the pore channels even before the sufficient reaction. Thus the limestone must be pulverized to the proper size which can enlarge the pores to the maximum (Wang *et al.*, 2002). It has been known, in general, that the optimum pore size is 0.2 to 0.3 μm. Although MgCO₃ present in limestone does not involve the desulphurization reaction, it plays a role to increase the number of pores through the conversion to MgO in the combustion bed (Kim *et al.*, 2004). The reaction of limestone with sulfuric oxides is rather slow and depends greatly on the retention

time along the whole combustion process. The conversion rate into CaSO_4 will be the larger, the longer the solids stay in the bed. Consequently, since the fine particulate limestone would leave relatively fewer unreacted pores after sulfurization reaction, it is more beneficial for overall desulphurization efficiency.

A set of experiments reported that the optimum limestone powder for CFBC was 0.1 mm to 0.3 mm (Ha, 1998). While a large proportion of the fine limestone under 0.1 mm would be discharged with fly ash without sufficient reaction, coarse particles over 0.4 mm may not provide enough surface for an efficient reaction. Nevertheless, it was predicted to be more economic to utilize the fine limestone with low cost. In order to confirm that the finer the sorbent, the higher its reactivity is, a lab scale experimental work was carried out with practically used limestone. As can be seen in Fig. 2, it is more evident as the reaction proceeds. Even if the limestone particles can not stay in the actual furnace for a sufficiently long time, the excellence of fine particles has been emphasized in de- SO_x process since long time ago (Arsic *et al.*, 1991).

3.3 Desulphurization depending on emission concentration of SO_x

The molar ratio of Ca/S with the emission concentration was investigated for the combustion at

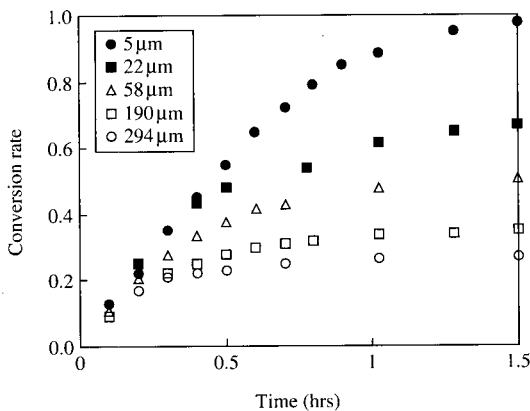


Fig. 2. Desulphurization conversion rate according to limestone size.

880°C. Test concentrations were 100 ppm, 115 ppm and 130 ppm.

As seen from the experiment (see Fig. 3), the molar ratio of Ca/S must be high in order to maintain the low concentration of SO_x in the flue gas stream. As for the currently applied limestone, L-I, the ratio of Ca/S was 2.12, 2.81 and 3.12 to meet 130 ppm, 115 ppm and 100 ppm of the SO_x emitted respectively. It was slightly higher for the test limestone, L-II, 2.21, 2.87 and 3.26 for the respective concentration. Limestone is ubiquitous throughout the country with low mining cost, so it has been widely used as a plausible desulphurization agent. However, the conversion rate is not highly efficient, well below 100%. As previously stated, this is possibly due to pore clogging occurred by a larger molar mass of a consecutive product, CaSO_4 , than CaCO_3 . In other words, preceding the desulphurization reaction, the CaSO_4 fills up the intrinsic pores as well as the newly formed pores while firing. The open pores close up prohibiting the reactant gases from contacting with calcium oxides and finally terminating the reaction earlier. The surface pores of limestone particles are rapidly clogged from the initial stage of the reaction. Thus, although there are calcium pores inside the particles, it is difficult for the reactant gases to penetrate into the unreacted core pores due to the closed surface layer (Krammer *et al.*, 1997). Since the gaseous reactant diffuses very slowly through the solid layer, the reaction rate becomes far lower than the prediction. As a conse-

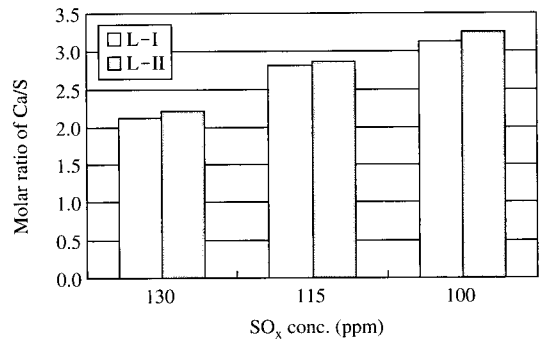


Fig. 3. Molar ratio of Ca/S with emission concentration of SO_x .

quence, due to such a complicated mechanism it is reasonable to compare the desulphurization efficiency by evaluating the volume of the feed limestone for a fixed emission concentration of sulfur dioxide.

3.4 Operation condition

According to the theoretical review, the desulphurization reaction generally initiates at 700°C (Jung *et al.*, 2003), and satisfactory desulphurization occurs at 840~870°C. In this work, two combustion temperatures widely applied to the industry; 875°C and 880°C, were chosen with focusing on 115 ppm SO₂ emission. The molar ratio of Ca/S for L-II was 2.59 and 3.18 for the output 150 MW and 200 MW respectively at 875°C. When the temperature of the fluidized bed was increased to 880°C, the required ratios were 2.71 for 150 MW and 3.25 for 200 MW. It was found that the desulphurization efficiency would be gradually decreased over the temperature of 870°C as reported in else where (Kuni *et al.*, 1969). In particular, the hot gas stream partially dissolves the sulphuric compounds, forming a thin inactive layer on the particle surface. It isolates the active contact between solids and gases, finally leading to the steep drop of reaction rate.

On the other hand, as noticed above, the power generation also relates with the desulphurization efficiency. To examine this, the emission concentration of SO_x was fixed at 115 ppm, and the output power varied from 150 MW to 200 MW. As a result of the test with L-II, the molar ratio of Ca/S required for 150 MW, 180 MW and 200 MW were 2.7, 2.9 and 3.3 respectively. At the same time, the pressure drop across the whole process decreased from 1610 mmH₂O for 150 MW to 1520 mmH₂O for 200 MW. On the contrary, total air consumption was increased from 138 kg/s (150 MW) to 186 kg/s (200 MW). Increase of the combustion air in the furnace according to the high output of electricity power leading to the increase of flow velocity. Thereby, the retention time of the limestone in the furnace would be decreased, and consequently the molar ratio of Ca/S was increased.

The overall pressure drop across the furnace

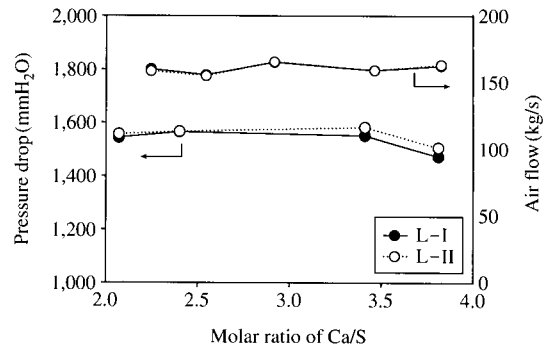


Fig. 4. Overall pressure drop and air flow rate with molar ratio of Ca/S.

varied in a very similar manner between the two limestone modes according to the molar ratio of Ca/S as seen in Fig. 4. Both fell in the range of operating pressure allowed in the practical process; 1500 mmH₂O to 1600 mmH₂O.

Meanwhile, steady state fluidization can be achieved with an optimum volume of the bed. If there are not enough solid particles in the bed, incomplete coal combustion may occur and entail unexpected mal-operation of CFBC. The furnace was designed so that the bed height could be controlled by Disch dampers which were installed at the lower zone of the furnace. When Disch dampers are fully opened, no bed would be formed resulting in low pressure. As the dampers are slowly closed, the pressure should be risen up and the bed volume increases too. Thus, the necessary output power could be adjusted by pressure control; low power (140 MW) needs 1600 mmH₂O and high power (190 MW) could be obtained from the operation at 1500 mmH₂O. The air flow rate was found to be nearly same for both limestone samples throughout the test molar ratios of Ca/S as shown at the right axis in Fig. 4.

In order to examine the effect of fly ash recycle, the molar ratio of Ca/S was estimated with 100 ppm-SO_x emission and 180 MW output. While the molar ratio was 3.38 required when the fly ash was recirculated through the recycle process, it was 3.54 when the circulation system was closed. Total pressure drop along the entire process decreased from

1572 mmH₂O for recirculation-OFF to 1501 mmH₂O for-ON. The total pressure difference in the CFB combustor implies the amount of solid materials in the bed. Retention of more solids means the increase of the total pressure drop. It resulted in the increase of pressure drop at the upper region of the furnace, which could decrease the temperature. The increase of total pressure drop by ash recirculation positively affected desulphurization, ensuring the decrease of molar ratio of Ca/S.

3.5 Cost evaluation

The price of the desulfurizing limestone currently being used at Donghae power station was briefly evaluated on the basic price of 2003. The purchasing price was 30,350 won per ton (US\$ 25.3) for L-I, whilst the new limestone (L-II) is expected 27,412 won/ton (US\$ 22.8). In accordance, total cost for desulphurization per one year was 15.6 billion won (US\$ 13 million) for L-I, but L-II will cost about 14.6 billion won (US\$ 12.1 million). The daily cost of limestone depends on the emission concentration of SO_x. The best economical efficiency had been found at the emission of 110 ppm which was much lower than the national regulation, 150 ppm, so that the power station has kept 110 ppm since 1999. However, to maximize the cost efficiency using L-II, it was found that the emission concentration should be revised to 115 ppm. It then will reduce the additional 54 million won every year (US\$ 45,000).

4. CONCLUSIONS

The purpose of this work was to examine the desulphurization efficiency using a new mode of particulate limestone in order to better utilize the fine limestone in CFBC. The test limestone (L-II) including about 50% of fine grains smaller than 0.1 mm showed a similar desulphurization efficiency to the limestone currently used, which contained about 25% of fine particles. The modern CFBC processes applied in the coal power stations enable to collect the fine fly ash with high efficiency and to re-

inject them into the furnace. In addition, the new mode of limestone was found to be economically advantageous; saving more than 1 billion won every year.

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