C-3.1.1 Low cost desulfurization technology for high S coals

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Abstract

To establish the control technique of SO_2 emission from the combustion of high sulfur coal produced in southwestern region of China, a new low cost flue gas treatment process using a circulating fluidized bed was studied. This method showed higher performance and SO_2 removal efficiency achieved to 85% at Ca/S=1.7. Water steam played a vital role for the desulfurization reaction. Elutriation of fine absorber can be controlled in the range of 50-100%. It means stable operation is possible. Cost of this new process was estimated for a 10 tons/day scale model boiler. Estimated cost was 105,000 Yuan for construction and 1,200 Yuan for daily operation. It means this new process is a competent among other low cost desulfurization processes.

Chemical composition, physical structure after calcination, and reactivity were tested for 7 kinds of Chinese limestone as an absorbent. Generally, purity of CaO was not high as Japanese limestone, and MgO content was rather high. The most important property determining final conversion was the porosity of the absorber particle. There was a good relationship between Mg/Ca molar ratio and porosity. Limestone with higher Mg/Ca showed higher conversion.

Key Words Acid rain, Low cost desulfurization, Limestone

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[1,2]. Moreover, this region is forecast that the energy demand will increase because there are a lot of developing countries and they use cheap but row grade fuels. Especially China is the world-biggest coal consumption country. Southwestern part of China produce high sulfur content coals, and acid rain problem becomes serious due to utilization of this high sulfur coals. In order to reduce SO_2 emission, introducing a flue gas desulfurization equipments may be most effective. However, because of the cost restriction and the maintenance administration, it is difficult to introduce flue gas treatment systems, which are commonly used in advanced countries[3]. From such backgrounds, a simple and cost effective technology for the reduction of SO_2 emission is required in China.

Not only large-scale boilers for power generation but also small and medium-sized scales stoker boilers are operating in China and SO_2 emission from them is estimated as 1/3 of the total SO_2 emission from all stationary sources. It is necessary to apply the desulfurization technology to the small and medium sized coal fired boiler immediately. Although replacement of stoker boilers to the fluidized bed boilers, which allow in-situ desulfurization, may be effective for the long term, a new cost effective technology for existing stoker boilers is required.

Cino-Japan Friendship Center for Environment Protection recently developed a new desulfurization process using a circulating fluidized bed[4]. This new desulfurization process has higher desulfurization efficiency and good operability. In this three years' research program, development of this new desulfurization technology was studied. Study on the characteristics of Chinese limestones as sulfur absorbent was carried to support this new desulfurization process.

2. Research Objectives

To develop a new flue gas desulfurization (FGD) method, following target of developing a new FGD process were set up.

(1) High sulfur retention efficiency more than 75%.

(2) Construction and running costs should be less than 1/3 of flue gas desulfurization process commonly used in advanced countries.

(3) Easy to maintain the plant. No water treatment is required.

In order to achieve above target, fundamental studies were carried out.

3. Flue gas desulfurization process using a circulating fluidized bed

3.1 Principle of new FGD process

Figure 1 shows gas-solid contacting systems with gas velocity. Circulating fluidized bed is the one of the best gas-solid contacting system because of higher slip velocity, higher mass and heat transfer rates. At first, coarse particle are recirculating. Then flue gas, containing SO_2, introduced to the bottom of circulating fluidized bed, whose temperature is kept near 380 K, and fine absorber particles and steam are fed into the bed. High sulfur retention is achieved due to good contact between flue gas and absorber, usage of fine absorber and recirculation of absorber[5]. Generally, fine particles are easily elutriated, and can not be recirculated. However, fine particles are not elutriated when co-flu-

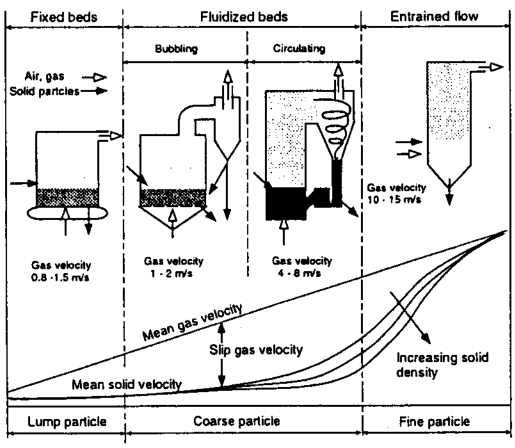

Fig. 1 Gas-solid contacting systems.

idization of coarse and fine particles is achieved, because fine particles and coarse particles make clusters. This new FGD process is semi-dry low temperature desulfurization process. No water treatment system is needed. Comparing with other FGD method, this process has following advantages. Investment and operation cost are lower; utilization of absorber (e.g. CaO) is higher; desulfurization efficiency is higher; ; no big space is needed so that retrofit to existing boilers is easy.

3.2 Experimental

Figure 2 shows a schematic diagram of experimental apparatus. A small circulating fluidized bed (CFB) reactor, a stainless steel tube of 90mm I.D. and 5.0m height, is heated by electric heaters. There are two cyclones on the top of the CFB reactor in series. A bag house is installed at the front of induced fan. Flue gas, generated by a small gate stoker coal furnace, was injected into the CFB reactor by a blower. The pure SO_2 gas from a gas cylinder was also added to adjust SO_2 concentration. Outlet SO_2 concentration was monitored by a continuous SO_2 analyzer. Flow rate, depends on residence time, was measured by an orifice type flow meter. Absorbent, $Ca(OH)_2$, was made of lime and it was classified just before experiment and only small size range (D_p<100mm) was used. Feed rate of absorbent was adjusted by a dish-type feeder and sucked into a pneumatic venturi nozzle, and injected at the bottom of the CFB reactor through a nozzle. Steam, generated by two steam generators, was injected to the bottom of the CFB reactor and humidity of flue gas was measured by the weight change of drying materials ($CaCl_2$) by passing through the flue gas.

The experimental procedure is as follow: A certain amount of sand (particle size: D_p=300~500mm) (as coarse particle, bed material) is filled into the down-comer of the CFB reactor. It is circulated when the flue gas passes through the CFB reactor at a fixed flow rate and the recirculating rate is determined by sampling of bed materials in short time. Reaction temperature is adjusted by four electric heaters. When temperature and inlet SO_2 concentration in flue gas reaches steady states condition, steam content is fixed at certain level too. Finally absorbent is fed into the CFB reactor. Fine particles can be elutriated from the CFB reactor with the flue gas and it can be collected by secondary cyclone and bag-house.

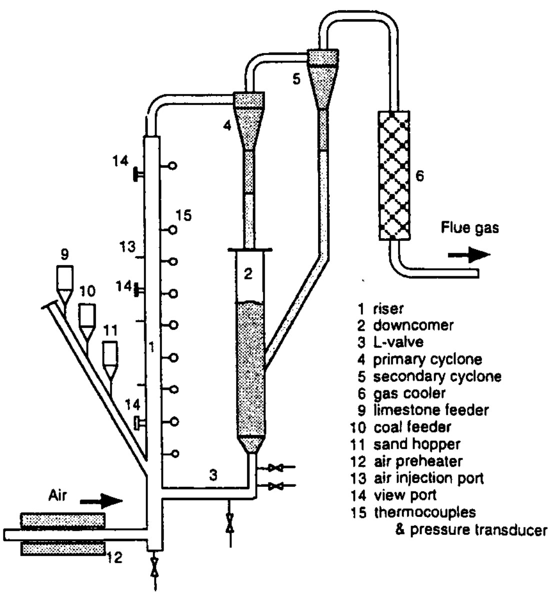

Fig. 2 Circulating fluidized bed reactor for FGD.

Effect of Ca/S ratio, steam content and reaction temperature on SO_2 removal efficiency were tested. Elutriation rate of fine particles varied with changes in flue gas velocity, quantity of fine particles fed and recirculating rate of the bed mate-

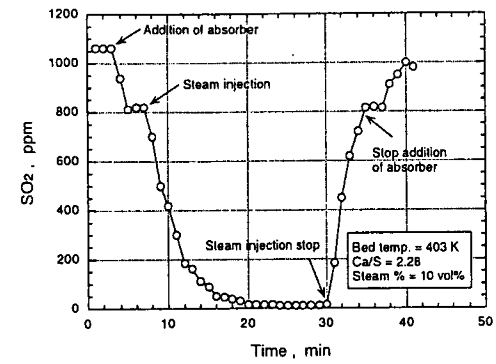

Fig. 3 SO_2 concentration change during experiment.

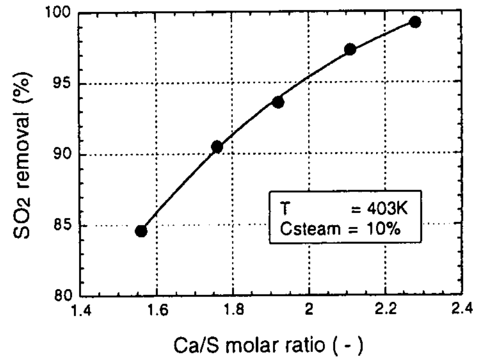

Fig. 4 Effect of Ca/S molar ratio on sulfur removal.

rial was measured.

3.3 Results and discussion

At first, fundamental behaviors were checked. Figure 3 shows a typical SO_2 concentration change in the outlet of the reactor with time. When absorbent was fed into the bed, a slight reduction in SO_2 concentration was observed. After steam injection was started, SO_2 concentration was decreased rapidly and became less than 10 ppm. This time, sulfur removal efficiency reached 99%. Existence of steam with the SO_2 gas and absorbent was a key factor as shown in Fig. 3. Sulfur retention reaction is proceeds as follows,

$$Ca(OH)_2(s) + SO_2(g) + H_2O(g) = CaSO_3 \cdot 2H_2O \quad (1)$$

Effect of the feed rate of absorbent on the sulfur removal efficiency is shown as a function of Ca/S molar ratio with typical reaction temperature and steam concentration. Sulfur removal efficiency of 75% was achieved when Ca/S molar ratio was unity, and 95% was achieved at Ca/S =2. These efficiencies are high enough for semi-dry FGD process. Higher efficiency was achieved due to recirculation of fine absorbent particle which would be elutriated when coarse particles did not exist in the reactor.

In order to get design parameters, effects of the operating conditions were examined. Figure 5 shows the effect of the steam concentration in the riser on SO_2 removal. SO_2 removal efficiency increased with increase in steam concentration below 10 vol%. As shown in Fig. 5, 10 vol% of steam concentration is required to achieve higher SO_2 removal efficiency than 90%. Steam concentration in flue gas is not high enough in actual coal fired boilers, steam should be generated by steam generator and injected

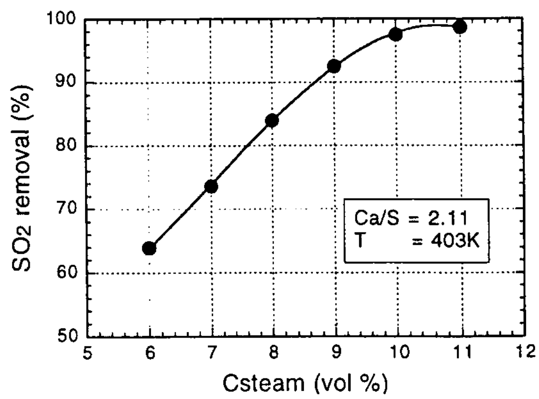

Fig. 5 Effect of steam concentration on SO_2 removal.

into the reactor. If flue gas temperature is high enough, injection of water is available. Effect of the reaction temperature on SO_2 removal efficiency was shown in Fig. 6. In lower reaction temperature, higher SO_2 removal efficiency was observed. Reaction temperature slightly higher than dew point should be the optimum operating temperature of this FGD process.

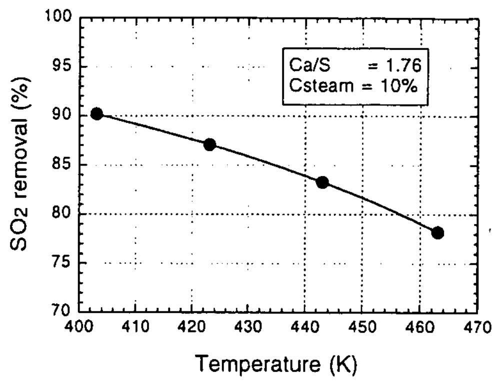

Fig. 6 Effect of reaction temperature on SO_2 removal efficiency.

Basic performance of new FGD process using a circulating fluidized bed was confirmed. Basically, this process shows excellent performance. For practical use, however, engineering data, such as control technique of solid particle elutriation, are needed to achieve long term operation. Separation of reacted fine absorbent particle from the binary particle mixture is important for this system. How to take out the products from the system is becoming the key technology of the FGD using binary particles. Carry-overed fine particles should be affected by superficial gas velocity and soil recirculation rate. Figure 7 shows the relationship between carry-overed fine sorbent and solid recirculation

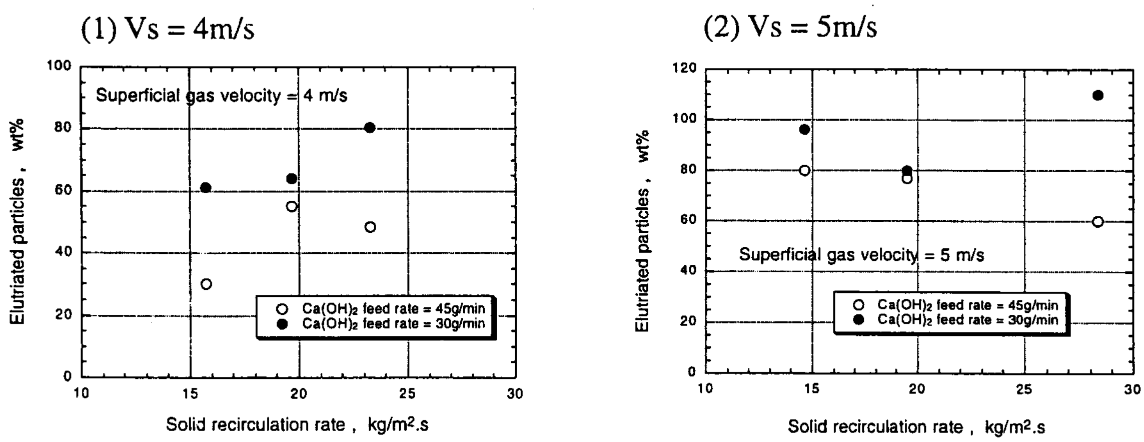

Fig. 7 Relationship between fine particle carry-overed and solid recirculation rates.

rates. At 4 m/s of superficial gas velocity, carry-overed fine particle increased with solid recirculation rates. On the contrary, carry-over decreased with solid recirculation rate when superficial gas velocity is 5 m/s. Above results suggests that amount of elutriated fine particles can be controlled by changing superficial gas velocity and solid recirculation rate. Further research work concerning with how to take out the products is required.

3.4 Cost estimation

Investment, running and maintenance cost are estimated by using basic data obtained above for the 10 tons/day scale conventional coal fired boiler. Estimated costs are shown in Table 1 in

Table 1 Cost estimation of FGD process using a circulating fluidized bed.
Capacity: 10 tons-coal/day; SO_2 concentration = 1000 ppm.

Investiment cost		
Main reactor	Material and process coat	28,000 Yuan
	Insulator	10,000 Yuan
Blowers	Forced draft fan: 30,000 m3/hr	15,000 Yuan
	Induced fan: 30,000 m3/hr	15,000 Yuan
Compressors	Pressure: 0.7MPa	10,000 Yuan
Sorbent feeder	Feed rate: 200 kg/hr	20,000 Yuan
Steam generator	Steam flow rate: 1,500 ~ 3,500 m3/hr	5,000 Yuan
Total		103,000 Yuan
Running cost		
Absorbent	Daily consumption: 4.32 tons/day	500 Yuan/day
Personnel expense	Operators: 5 person	200 Yuan/day
Maintenance fee	10% of construction cost	35 Yuan/day
Utilities	Steam: 24,000 m3/day	240 Yuan/day
	Electricity: 500 kW	200 Yuan/day
Total		1,175 Yuan/day

Chinese currency. Construction cost was estimated as 103,000 Yuan, and daily fee was estimated as 1,175 Yuan. These costs can be acceptable for the conventional coal fired boilers. Among the semi-dry or dry FGD processes, estimated costs are lower. It means this new FGD process is a competent among other low cost desulfurization processes.

As a next step, the research work by a full scale plant is needed to get practical engineering data and to estimate costs accurately. However, possibilities of this new FGD process using a circulating fluidized bed were shown in this 3 years research program.

4. Characteristics of Chinese limestones as absorber

4.1 Backgrounds and objectives

Practical flue gas desulfurization process should use natural limestones as sulfur absorbent because limestone is cheep and easily obtained elsewhere. Properties of limestones, however, are much different with production place, and desulfurization reaction characteristics are also different. For example, purity of Japanese limestones are generally very high. On the contrary, China produces many kind of limestones with wide range of purity. Desulfurization reaction characteristics may be different from those of Japanese limestones. Unfortunately, data of Chinese limestone as sulfur absorbent are very few. More data are required to know the reaction characteristics of Chinese limestones.

4.2 Experimental

Name of seven Chinese limestones used and analytical data are listed in Table 2 and 3 respectively. In order to compare their characteristics with those of Japanese limestones, two typical Japanese limestones (Kuzuu and Tsukumi) and scallop shell are used in experiments. As shown in Table 3, Chinese limestones have relatively low purity of $CaCO_3$ comparing with Japanese.

Table 2 List of limestones used.

No.	Name	
A	Chinese	Gui ying Sui ni chang
B		Gui ying Ying guan
C		Gui ying Da wa
D		Beijin Si shan
E		Chong qing
F		De ying
G		De ying
H	Japanese	Kuzuu
I		Tsukumi
J		Scallop

Table 3 Chemical component of lime stone.

No.	Component, wt%		
	$CaCO_3$	$MgCO_3$	Ign. loss
A	91.33	1.48	40.99
B	82.82	12.86	43.18
C	88.33	2.11	40.00
D	91.58	4.00	42.59
E	91.83	2.32	41.67
F	58.05	34.14	45.68
G	91.33	4.85	43.00
H	92.08	1.69	41.53
I	98.09	0.63	43.45
J	94.77	0.46	45.44

Figure 8 shows experimental system to evaluate the characteristics of limestones[6]. Limestone was calcinated (air, 1273K, 10min) and classified to 0.074 ~ 0.125 mm. 100mg of calcined lime particle and 3g of quartz sand were mixed well and set inside the quartz reactor (24mm inside diameter and 600mm in length) forming a 10mm height fixed bed. Reactor tube were heated by a electric heater up to 1123 K, and temperature of fixed bed containing calcined lime particles was monitored by a thermocouple immersed in the fixed bed.

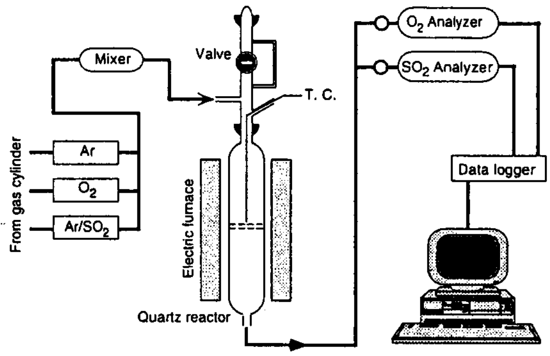

Fig. 8 Schematic diagram of experimental system .

Pure nitrogen gas passed through the fixed bed during heating period. After temperature of fixed bed reached reaction temperature, nitrogen gas was changed to a mixture of $N_2/O_2/SO_2$ and outlet SO_2 concentration was monitored by a SO_2 analyzer. Inlet O_2 and SO_2 concentration were fixed as 10% and 1000 ppm respectively. Sulfur capture reaction occurs at this temperature range is different of the low temperature desulfurization reaction described former section. Fundamental desulfurization characteristics, however, may be same.

4.3 Results and discussion

Two important parameters, sulfur capture capacity and reaction rate were examined. Amount of captured sulfur and conversion were calculated as follows;

$$Q(t) = \frac{\frac{F}{v_M}\int_0^t (C_{in} - C_{out})\,dt}{W_0} \tag{2}$$

$$X(t) = \frac{\frac{F}{W_0\, v_M}\int_0^t (C_{in} - C_{out})\,dt}{Q_0} \tag{3}$$

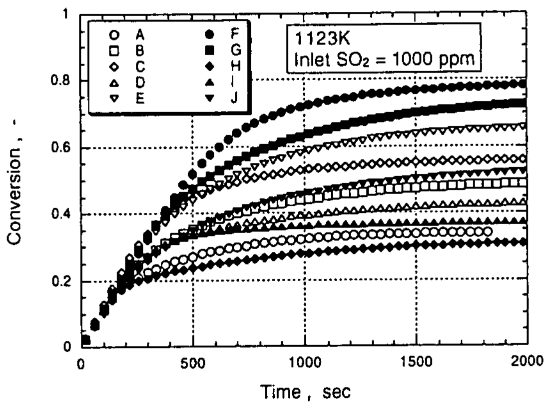

Fig. 9 Conversion of tested limestones as a function of time.

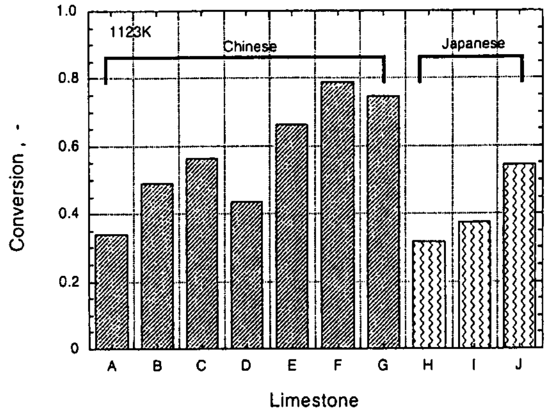

Fig. 10 Maximum conversion of tested limestones.

where $Q(t)$: amount of captured SO_2 (mol-SO_2/g), Q_0: theoretical SO_2 absorb (mol-SO_2/g), W_0: initial charge of calcined lime (g), $X(t)$: conversion (-), F: gas flow rate (cm^3/s), V_M:molar volume (2.24×10^4 cm^3/mol), C_{in}: inlet SO_2 concentration (volume ratio) , C_{out}: outlet SO_2 concentration (volume ratio), t : time (s).

Changes in conversion of limestones with time and final conversions, sulfur capture capacity, are shown in Figs 9 and 10 respectively. As shown in Fig. 9, final conversions were much different. Sulfur capture capacity highly depended on limestone. Generally, Chinese limestones have higher sulfur capture capacity than those of Japanese. Initial reaction rates, dX/dt, were not so much different as shown in Fig. 9. In order to know why sulfur capture capacity highly depended on limestone, physical structure of limestones were measured. Generally speaking, gas-solid reaction depends on the physical structure of solid particle.

Porosity and specific surface area of calcined limestone particles were measured by a mercury porosimeter and BET specific surface meter. Measured specific surface area is shown in Fig. 11. Limestone F, which has the largest sulfur capture capacity, has largest specific surface area. For other limestones, there may be a relationship between specific surface area and final conversion. However, porosity is more important factor to determine the sulfur capture capacity. Final conversion of each limestones and porosity showed good correlation as shown in Fig. 12. Final conversion of limestone increased with porosity of calcined limestone particle. Hence, both specific surface area and porosity are key factor to determine the sulfur capture capacity. Especially, porosity primary determines final conversion. In desurfurization reaction takes place as follow;

$$CaO + SO_2 + 1/2O_2 \rightarrow CaSO_4 \qquad (4)$$

Because molar volume of $CaSO_4$ is larger than CaO, pore should be plugged by the formed

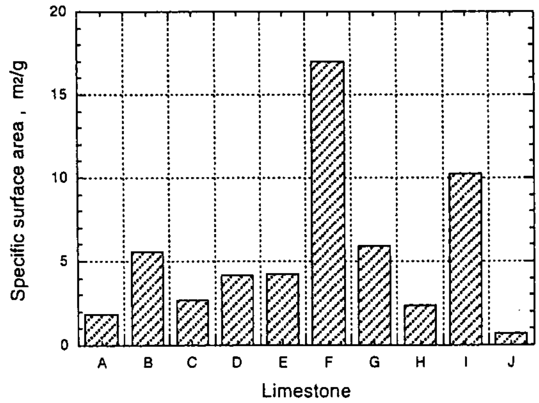

Fig. 11 Specific surface area of limestones.

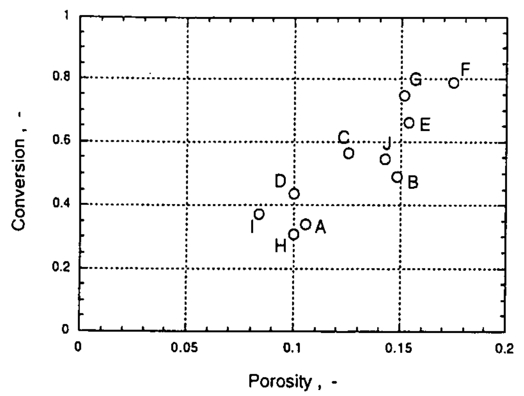

Fig. 12 Conversion of tested limestones as a function of porosity.

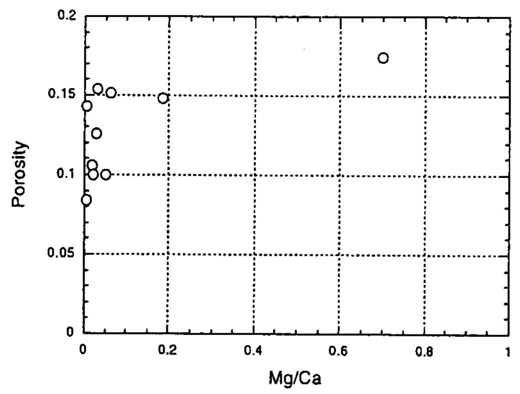

Fig. 13 Relationship between porosity and Mg/Ca molar ratio of tested limestones.

CaO, pore should be plugged by the formed $CaSO_4$ layer inside the lime particle. Limestone having higher porosity and specific surface area should have a number of pores. Possibility of pore plugging may be lower than others having lower porosity and specific surface area.

Although it is clearly shown that sulfur capture capacity depend on pore structure, final conversion can not be estimated. Parameters of pore structure should be measured to predict the reactivity of limestones. This is not convenient for practical use, especially for developing countries. If reactivity of limestones can be predicted by some way, it becomes very easy to select limestone. There is a good correlation between chemical composition and pore structure formed after calcination. Figure 13 shows the relationship between porosity and Mg/Ca molar ratio. Porosity increased with Mg content in limestone. Hence, a limestone having large Mg content becomes a good absorbent.

As shown above, Chinese limestone shows various chemical composition, desulfurization characteristics. To select what kind of limestones should be used for the flue gas desulfurization process, more data about Chinese domestic limestones are needed. Further study on domestic limestones should be continued.

5. Conclusions

During three years cooperative research between Chinese and Japanese research institutes on low cost desurfurization technology, following results are obtained.

(1) A new flue gas treatment process using a circulating fluidized bed was studied and examined fundamental performance.

(2) SO_2 removal efficiency achieved to 85% at Ca/S=1.7.

(3) Water steam played a vital role for the desulfurization reaction.

(4) Elutriation of fine absorber can be controlled in the range of 50-100%. It means stable operation can be possible.

(5) Cost of this new process was estimated for a 10 tons/day scale model boiler. Estimated cost was 105,000 Yuan for construction and 1,200 Yuan for daily operation. It means this new

process is a competent among other low cost desulfurization processes.

(6) Chemical composition, physical structure after calcination, and reactivity were tested for 7 kinds of Chinese limestone as an absorbent. Generally, purity of CaO was not high as Japanese limestone, and MgO content was rather high. The most important property determining final conversion was the porosity of the absorber particle. There was a good relationship between Mg/Ca molar ratio and porosity. Limestone with higher Mg/Ca showed higher conversion

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