Key Factors for Steady Removal of Sulfur Dioxide
from Flue Gas with Limestone Slurry

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Abstract

The degenerated limestone slurry from a scrubber, i. e., a perforated plate column without downcomer, was returned to a slurry holding tank where the loaded absorbent was regenerated before recycled to the column.

The pH values of the slurry in the tank, the fractional removal of SO_2 and the coversion of limestone were experimentally determined as a function of process time, to obtain the condition under which the degenerated liquor is to be regenerated enough to maintain steady desulfurization with a closed-loop recycling of limestone slurry.

As a result, it was found that the pH values of the liquor in the tank should be equal to or greather than those of 5.8 to 6.1 with fresh feeds of limestone into it to accomplish continual steady desulfurization. The optimal initial concentrations of limestone were found to be 3 to 5 wt%.

Introduction

The removal of sulfur dioxide (SO_2) from waste gases is increasingly important for air pollution control as the combution of the low grade fuels such as high-sulfur coal and residual oil is prevailing. Among many types of processes having been developed for removing SO_2, the limestone slurry scrubbing is considered to be advantageous to a large scale desulfurization as in power plants due to relative simplicity, lower investment and freedom of marketing a by-product (gypsum) etc.

A few practical works have been published on the limestone slurry scrubbing process to remove SO_2 from flue gasses, for example, the reports on the role of a holding tank in a closed-loop limestone scrubbing[1], on the effects of additives to maintain or increase an effecive alkalinity[2], on both an analysis and a prediction of the SO_2 removal data obtained with a turbulent contacting absorber (TCA) and a spray column[3] and so on. Recently, a new type of scrubber called jet bubbling reactor has been developed to improve stability of desulfurization as well as to obtain higher quality of gypsum[4]. By the way, which type of scrubber is suitable for SO_2 removal, was discussed by comparing the performances of spray column, TCA and perforated plate column without downcomer for the desulfurization with red mud slurry obtained as a waste from Bayer process[5,6].

The key for a steady removal of SO_2 using these alkali slurries is that no solid products such as calcium sulfite ($CaSO_3$) and gypsum ($CaSO_4$) produced during absorption of SO_2 into limestone slurry will result in scaling to cause plugging of hole and piping and result in coating on the surface of a limestone particle to cause inactivation of the particle which occurs when the pH value of the slurry is extremely low. In other words, the degenerated

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limestone slurry leaving a scrubber should be regenerated in the holding tank before recycled to the absorber. In spite of the previous works[1~6] mentioned above, the requirements for the key have not yet been suggested clearly. It may be difficult due to complexity of the phenomena to obtain the requirements by analyzing the relevant elementary steps in details. In the present work, therefore, the requirements were investigated in a direct and overall way by following the progressive change of the process properties such as the pH values of the slurry, the SO_2 removal, and the fractional conversion of the limestone etc.in a small scale closed-loop limestone slurry SO_2 scrubbing system which is considered to simulate a practical desulfurization process.

Thus, the purpose of this work is to examine the dynamic behavior of limestone slurry SO_2 scrubbing process using a small scale perforated plate column without downcomer characteristic of the low pressure drop and suitability for slurry absorbent, and then to obtain guidelines for a steady and highly efficient desulfurization.

1 . Experimental

Fig. 1 shows a schematic diagram of the experimental apparatus. In the central part of the figure is shown a scrubber, that is, a perforated plate column without downcomer. The column has a certain number of perforated plates, through which both gas and liquid pass countercurrently, to make the corresponding number of contacting stages where a stable gas-liquid dispersion is formed. In the present experiment, the limestone slurry was fed from the top of the column, and the air containing a small amount of SO_2 was supplied at the bottom of the column. This type of column is suitable for slurry absorbent like limestone slurry due to a relatively large diameter of holes resulting in no plugging, and for large
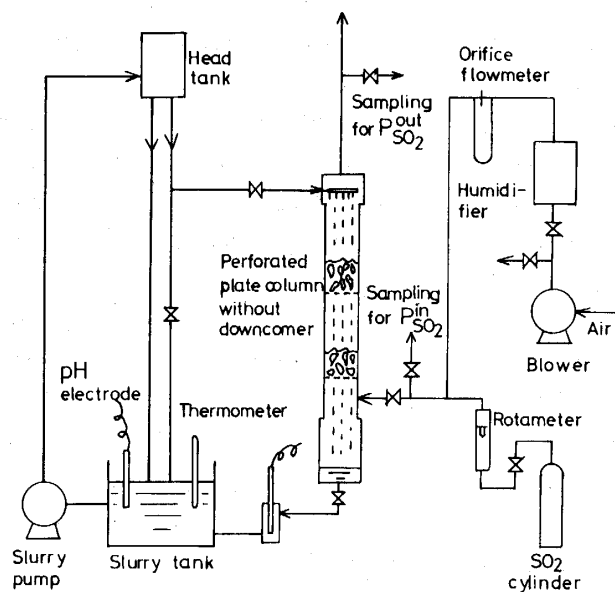

Fig. 1   Experimental apparatus (Column diameter $D_T =$
5 cm, Perforation ratio Fc = 0.473, Stage number N = 2)

volumes of waste gases due to a smaller pressure drop.

The column used was 5cm in diameter and made of transparent acrylic resin. For convenience, the two contacting stages were employed. The perforated plate made of the same resin as above, was 5mm thick, 0.473 in free area and 13mm in hole diameter. Both the hydraulic[7] and mass transfer[8] characteristics had been found to be determined primarily by the gas and liquid velocities through holes independent of the column diameters, the hole diameters, the free areas, and the stage spacings etc. Thus, the small scale column mentioned above was used because of simplicity and convenience of the experiment. The limestone slurry tank was 20l in volume.

The limestone slurry fed to the scrubber returned to the tank after absorbing SO_2. In the tank, the degenerated slurry was regenerated, and then recycled to the scrubber. To accomplish a steady removal of SO_2, the rate of regeneration of the slurry in the tank should be equal to or greater than that of degeneration in the scrubber. To find out the requirement for this experimentally, the removal of SO_2, $E = 1 - (p^{out}_{SO2}/p^{in}_{SO2})$ caluculated from the SO_2 partial pressures at the inlet and outlet of the absorber, p^{in}_{SO2} and p^{out}_{SO2}, the fraction of limestone unconverted X, and the pH valules of the slurry at both inlet (i. e., in the tank) and outlet of the column, were followed after the start-up of desulfurization. The SO_2 partial pressure was determined with the JIS waste gas analysis. The remaining limestone was also analyzed with titration.

Limestone used is from Yamaguchi prefecture, and prepared by Nihon Sekkai Kogyōsho Co., Ltd. The experiment was carried out at 20℃. The initial limestone slurry concentration C^{0}_{s} ranged from 0.2 to 10 wt%. The initial mean diameter of limestone particles dp was 11.8 μ m. The inlet SO_2 partial pressure p^{in}_{SO2} was varied from 1,000 to 11,000 ppm by volume. The gas flow rate F_G was 280 l/min, and the limestone slurry flow rate F_L 1 l/min, these corresponding to the pressure drop of 15 to 20 mmH_2O. The gas and slurry flow rates employed here are in the range of stable operation[7] where a stable gas-liquid dispersion is established on the stage.

2. Results and Discussion

2.1. Time course of desulfurization process

Fig. 2 shows the progressive change of the SO_2 removal E, the fraction of limestone uncovered X and the pH values of the slurry at the inlet and outlet of the scrubber. It is seen from the figure that the SO_2 removal E is kept almost a constant value corresponding to the initial SO_2 removal E_0 until the pH values of the slurry at inlet of the column decrease to about 6. This region is considered to be the range of the steady desulfurization, characterized by the critical pH value pH_c which was defined as the intersection of the two broken lines shown in Fig. 2. The reason why the SO_2 removal rapidly decreases as the pH values of the slurry at the inlet of the column become less than the critical pH value pH_c, may be that the ammount of the remaining limestone is not enough to neutralize the liquor acidified by absorption of SO_2. Thus, in the case of the pH values greater than pH_c, the concentration of the dissolved SO_2, namely, the eqilibrium SO_2 partial pressure p^{*}_{SO2}, is assumed to be zero. In the case of the pH value less than pH_c, on the other hand, the values of p^{*}_{SO2} is considered to increase progressively, and the overall driving force for absorption $(p_{SO2} - p^{*}_{SO2})$ to decrease correspondingly.
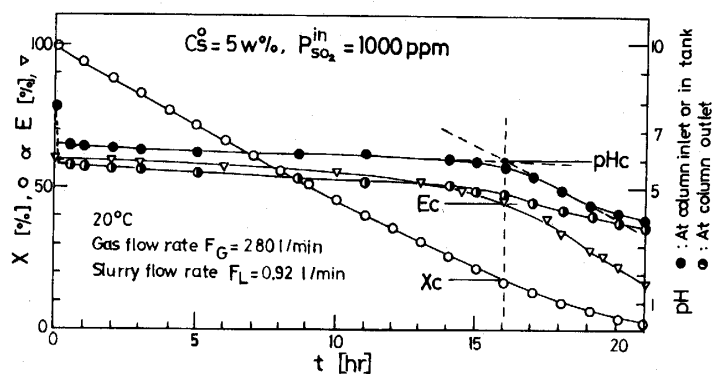
Fig. 2   Progressive change of fraction of limestone unconverted
X, fractional SO_2 removal E and pH of limstone slurry

2.2.   Requirement for steady removal of SO_2

The SO_2 removal and the fraction of limestone unconverted at the critical pH values pH_c, are designated E_c and X_c, respectively. Table 1 shows the relationship among each critical value pH_c, E_c, or X_c, the initial limestone slurry concentration C^0_s and the inlet SO_2 partial pressure p^{in}_{SO2}. The results in the table suggest that the critical pH values pH_c are almost constant of 5.8 to 6.1 independent of the operating conditions. The requirement for a steady desulfurization is, therefore, considered to be that the pH values of the slurry at the inlet of the column, i. e., in the tank, should be equal to or greater than 5.8 to 6.1. It is assumed to be inherent to any closed-loop limestone slurry SO_2 scrubbing process. Most of the reported pH values for the practical desulfurization[1~3] fall within the above range of the pH values for a steady SO_2 removal.

Table 1   Critical pH values, pHc at various operating conditions

C^0s [wt%]	P_{SO2}^{in} [ppm]	pHc [−]	Ec [%]	Xc [%]
3	2500	6.05	47.0	47.0
5	1000	5.90	45.0	18.0
5	2500	5.85	35.0	18.0
5	6000	5.80	35.0	36.0
5	11000	5.80	30.0	27.5
7.5	2500	5.95	30.0	12.0
10	2500	6.05	25.0	11.0

C^0s   : Initial concentration of limestone
P_{SO2}^{in} : Inlet concentration of SO_2
Ec   : Fractional removal of SO_2 at pHc
Xc   : Fraction of limestone unconverted at pHc

2.3. Effects of initial limestone slurry concentration and inlet SO_2 partial pressure

In Fig. 3 and Fig. 4, the values of the critical SO_2 removal E_c listed in Table 1 are plotted against the initial limestone slurry concentration C^0_s and the inlet SO_2 partial pressure p^{in}_{SO2}, respectively. In both figures are plotted the value of the initial SO_2 removal E_0 for comparison. Fig. 3 shows that the optimal values of C^0_s are 3 to 5 wt% in view of higher SO_2 removal. From Fig. 4, the SO_2 removal is seen to be almost independent of p^{in}_{SO2}.
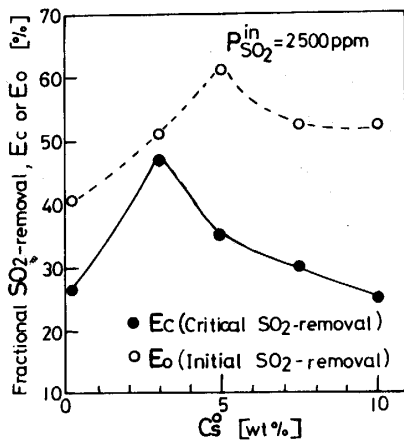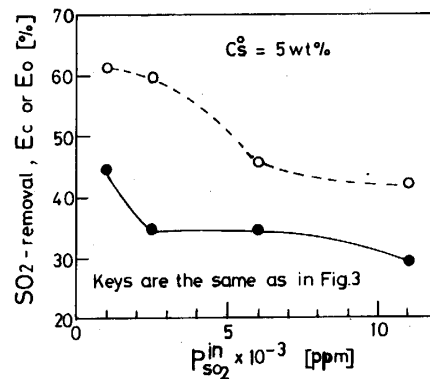
Fig. 3 SO_2 removal vs. C^0s

Fig. 4 SO_2 removal vs. P^{in}_{SO2}

2.4. Progressive change of remaining limestone

Fig. 5 is a correlation of the data on the progressive change of the remaining limestone or the fraction of limestone unconverted X. The data is well correlated with the relationship $(1-X^{2/3})$ vs. t. The relationship is derived on the basis of the well known shrinking core model[9] with the liquid film mass transfer limitation. The assumption employed here is that the hydrogen ion resulting from absorption of SO_2 into the solution diffuses toward the surface of a limestone particle, and is neutralized by the dissolved calcium carbonate
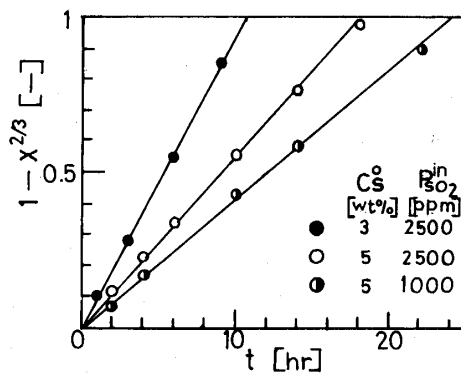
Fig. 5 $(1-X^{2/3})$ vs. t

diffusing from the surface of the particle.

Once the fraction of limestone uncovered X at a steady state operation is chosen, the time required to reach the steady state at which a fresh limestone slurry starts to be fed continuously after the start-up, can be predicted using the correlation shown in Fig. 5.

2.5. Prediction of SO_2 removal

Fig. 6 shows a comparison of the observed values of SO_2 removal with the calculated ones obtained from the hydraulic[7] and mass transfer[8] characteristics of the column as well as the correlation of the remaining limestone shown in Fig. 5. Fig. 6 indicates that an accuracy of the prediction is within 20%.

An examination of the enhancement for SO_2 absorption with limestone particles suggested that the particles had almost no contribution to an increase in the liquid phase mass transfer coefficient under the present experimental conditions, and only increased a
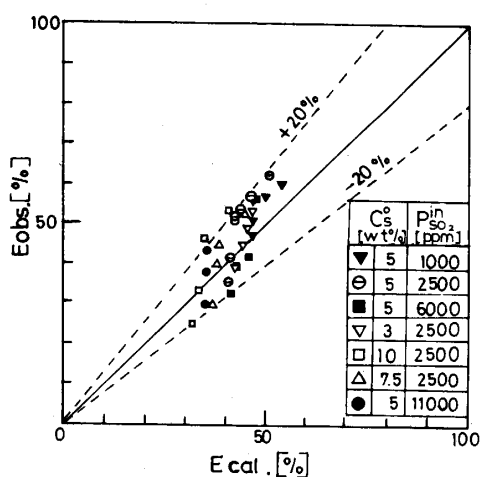

C_s^o [wt%]	$P_{SO_2}^{in}$ [ppm]
▼ 5	1000
⊖ 5	2500
■ 5	6000
▽ 3	2500
▢ 10	2500
△ 7.5	2500
● 5	11000

Fig. 6   Calculated SO_2 removal Ecal. vs. observed one Eobs.

capacity of the absorbent liquor. This is partly the reason why the SO_2 removal was kept almost constant in spite of a decrease in the limestone present.

2.6. Guidelines to improve efficiency of closed-loop limestone slurry SO_2 scrubbing process

The results shown above suggested the following operation to accomplish a steady and highly efficient desulfurization.

A fresh limestone slurry should be fed continuously to the slurry tank in the manner that the pH values of the slurry in the tank are kept equal to or greater than 5.8 to 6.1, and that the equivalent amount of the slurry containing the solid products and remaining limestone, should be withdrawn at the same time. The limestone concentration at the start-up of an operation shoud be 3 to 5 wt% from the viewpoint of the highest possible SO_2 removal. The steady state of the operation should be chosen at the nearest possible point to the critical condition where pH = pH_c, E = E_c, and X = X_c from the viewpoint of the higher utilization of the limestone fed into the process. A newly developed scrubber called jet bubbling reactor[4] employs an extemely low concentration of the remaining limestone (0.1 wt%), and thus is operated at the pH values of 5 to 3, slightly less than the critical pH values

determind in the present work, to keep the utilization of limestone almost 100%.

Conclusion

The dynamic behavior of a closed-loop limestone slurry SO_2 scrubbing process was followed using a small scale system consisting of a holding tank and a perforated plate column without downcomer to simulate a practical limestone/gypsum process. The following results were obtained.

(1) The requirement for a steady operation with almost constant SO_2 removal, was found to be that the pH values of the slurry in the holding tank, that is, those of the slurry at the inlet of the scrubber shoud be equal to or greater than 5.8 to 6.1 regardless of operating conditions. The requirement is considered to be inherent to the present process, and in accordance with the range of the pH values observed for the practical large scale limestone slurry SO_2 scrubbing systems.

(2) The optimal initial concentration of limestone in the slurry was found to be 3 to 5 wt% in view of the highest possible SO_2 removal.

(3) The conversion of limestone particles was shown to be correlated with the well known shrinking core model with the liquid film mass transfer limitation. This enables the time required to reach a steady state operation after the start-up to be predicted.

(4) The SO_2 removal was found to be kept almost a constant value corresponding to its initial value until the pH values of the slurry in the tank decreased to about 6. This allows the SO_2 removal under a steady operation to be predicted in terms of the initial limestone slurry conditions.

Acknowledgement

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