SULFUR DIOXIDE REMOVAL WITH SOLID SORBENTS IN A FLUIDIZED BED ABSORBER

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INTRODUCTION

Dry scrubbing flue gas desulfurization (FGD) processes have received considerable attention as lowcost SO2 control technologies over the past several years, and extensive studies on process optimization has been prompted[1]. Higher sorbent utilization, however, is still required for improving the economics of the dry injection method. Recently, water injection and cooling of flue gas has been expected to be another conceivable way to enhance the utilization of dry calcium-based sorbents[2]. It not only activates the sorbent reactivity, but also conditions the flue gas for improved ESP performance by lowering the gas resistivity. The low temperature reaction of dry calcium-based sorbents with SO2 with water injection into a reactor has rarely been studied in a systematic fashion, while earlier investigations[3,4] have primarily focused on the high temperature reaction for the application of the sorbent injection into coal-fired boilers. In addition, to-date water injection techniques are not well developed for fluidized bed reactors, which offer advantages over other gas-solid contacting methods.

A novel desulfurization technology, which combines dry scrubbing using solid sorbents with a circulating fluidized bed absorber (CFBA) reactor, has been developed by Keener et al.[5,6] and Jiang[7]. The main features of the CFBA are high sorbent/gas mixing ratios, excellent heat and mass transfer, and recycle of sorbents and, subsequently, higher SO2 removal efficiencies with high sorbent utilizations than other dry sorbent injection scrubbers. Previous results with a commercial nozzle used for water spraying into a pilot scale CFBA showed a dramatic increase of SO2. The experimental observations from the CFBA operations[8] suggested that a water injection technique during fluidization in a CFBA must be developed for an effective wetting of sorbents to enhance the reaction of lime sorbents with SO2, because the commercial nozzle had physical limitations on the degree of particle wetting in a fluidized bed. Therefore, a novel method injecting water into a CFBA was designed and applied for a bench scale CFBA unit to increase the sorbent wetting and SO2 removal efficiency[9]. The objective of this study is to discuss the results of these efforts on SO2 removal and utilization of lime sorbents under various operating conditions of the CFBA and the development of the water injection technique which can effectively activate sorbent reactivity in a fluidized bed, and its wetting efficiency.

EXPERIMENTAL

Experimental System A bench scale CFBA unit was constructed to study the low temperature SO2 removal, and wetting and attrition effects on utilization of dry lime sorbents. The bench scale CFBA unit, which is similar with the pilot scale unit built earlier by Keener and Jiang[8], consisted of a bed reactor of 0.0762 m in diameter and 3 m in length, two high efficiency cyclones for gas/solid separation, sorbent injection and recycling system, water injection system, gas heating system, and gas flow, concentration, temperature and pressure monitoring system. The scheme of CFBA unit and lime fluidization in it are shown in Figure 1 and 2.

As shown in Figure 1, the bed reactor was built with 1.83 m of steel pipe and 1.22 m of pyrex glass, which allows for visible observation of the solid mixing during the fluidization. A woven stainless steel mesh (mesh # 70) at the base of the bed serves to distribute gas flow and support sorbent materials not to be fluidized. The sorbent injection and recycling systems were also designed to be checked visibly for maintaining constant feeding and recycling rate for the case of continuous operation. The sorbent injection system consists of a pneumatically operated L-valve that is controlled by air flow. The coarse sorbents entrained from bed is captured by two cyclones. Two high efficiency cyclones collect fine solids elutriated from a bed. The sorbents collected by the first cyclone are recirculated to the base of reactor through another L-valve. Gas heater provides the simulated flue gas ranging from 150 °C to 250 °C through the heater located at the bottom of a reactor. For sulfation tests, 3000 ppm of S02 is injected to simulate the flue gas emitted from the combustion of high sulfur coal available in Ohio. Sampling ports to measure S02 concentration are positioned at both top and bottom of reactor, and pressure taps and thermocouples for the measurement of bed pressure drop and temperature are installed at equal distance throughout the height of the fluidized bed. The S02 concentrations of gas is determined with Horiba S02 analyzer (Model 2000) which employs the monodispersive infrared technique. All the gas concentrations, temperatures, and pressures measured at selected locations along the bed are monitored and recorded by a data acquisition system continuously. Sorbent samples can be taken from both bed and two cyclones to measure the total sulfur, weight and size changes of sorbents .

For the enhancement of S02 removals in a CFBA, a toroidal type of pressurized spray nozzle was newly designed and installed at the bottom of bed. Its installation is illustrated in Figure 3, 4 and 5. As shown in Figure 4 and 5, the nozzle reduces wall wetting and thus maximizes the wetting efficiency without disturbance of fluidizing gas stream. The toroidal ring type of nozzle was made of 1/4 inch copper tube and placed just below the sorbent injection point in a bed. It has water injection orifices at an angle, with the horizontal on the upper side. The angle is chosen to optimize the flight of the water drops with respect to the solids and thus to maximize the probability of a drop-solid collision. For this study, it has 2, 3, and 4 holes and 85o angles, based on the droplet evaporation rate and its trajectories in a fluidized bed. The diameter of the holes is 175 μm. Water is injected by means of the high pressure pump to insure good atomization, and a filter is also placed before the pump to prevent the contaminants from clogging the small holes.

Materials and Experimental Procedure. Two discrete ranges of Dravo limes were used as solid sorbents for the S02 removal tests. The sizes of Lime 1 range between 1095 μm (16 meshes) and 2380 μm (8 meshes) in diameter and those of Lime 2 range between 595 μm (30 meshes) and 1095 μm (16 meshes). The measurements of sample size distribution showed that the sizes of lime samples are narrowly distributed. The lime sample is a high calcium quicklime formed by calcining limestone so that CO2 is liberated. Its available lime was measured as about 90 %, and a slaking test confirmed that the lime is very reactive.

The SO2 removal tests under water injection were carried out at a batch mode in the circulating fluidized bed absorber(CFBA) with the narrowly sieved Dravo limes of 903 μm (Lime 1) and 1764 μm (Lime 2) in mass mean diameter (MMD). Gas temperature was about 177 oC and superficial gas velocity was 4 m/s for Lime 1 (903 μm) and 4 - 5 m/s for Lime 2 (1764 μm), respectively. For a sulfation test, 0.5 kg - 0.75 kg of limes were injected so that the initial pressure drop in a bed reactor reaches about 15 - 20 cm H2O. Then water was sprayed into the bed, and SO2 concentrations at inlet and outlet were continuously measured with a Horiba SO2 analyzer. The temperature and pressure drop were also recorded into a data acquisition system. After the CFBA unit was turned off, the bed materials and fines captured by the first and second cyclones were collected, and their total sulfur content and hydration were measured with a LECO sulfur analyzer and a thermogravimetric analyzer (951 TGA, Du Pont Co.), respectively.

RESULTS AND DISCUSSION

A series of experiments was conducted in order to determine SO2 removal efficiency in the CFBA under different wetting conditions. Figure 6 shows the experimental results of the SO2 removal efficiency versus the water injection rate during fluidization of Lime 1 (MMD = 903 μm). For the test, 1 kg of lime was fluidized at the superficial gas velocity of 4 m/s and fines captured by the first cyclone were recirculated into a bed. Water was initially injected at 30 ml/min of flowrate through the 2-hole nozzle, and the water injection rate was gradually increased after the SO2 concentration at the outlet reached at steady state. The results indicate that the SO2 removal efficiency is a strong function of the water injection rate. While the reaction of lime with SO2 did not occur under the dry condition before injecting water, the SO2 removal efficiency dramatically increased with water injection. As shown in Figure 6, the removal efficiency was enhanced from 10 % to 35 % as the water injection rate increased from 30 ml/min to 70 ml/min.

The effect of the number of holes in the nozzle on the SO2 removal was examined in a stationary bed without circulation of the fine solids elutriated from bed and captured by the first cyclone. The results are illustrated in Figure 7. Lime 2 (MMD = 1764 μm) of 0.75 kg in weight was injected at the fluidizing gas velocity of 5 m/s, and the water injection rate through the 2-hole and 4-hole nozzles was 60 ml/min. Figure 7 suggests that more holes may not be significant for the wetting efficiency since it reduces the height of water spray due to the decreased water pressure and thus limits wetting the solids in the upper region of the bed reactor. Under no circulation of solids, the reaction may mainly take place in a dense region because the parent solids only stay in the bed reactor and the attrited fines immediately blow out at high velocity. As a result, when water is sprayed far enough away to reach the dense region, more holes of the nozzle may result in better wetting efficiency and thus higher removal efficiency.

Figure 8 shows the effect of the number of holes on the SO2 removal efficiency with circulation of the elutriated solids. Tests were carried out with lime #2 and nozzles with two and three holes, at the gas velocity of 5 m/s and the water injection rate of 60 ml/min. Circulation of fine solids started at 20 minutes after water was injected. As shown in Figure 9, the nozzle with three holes has higher SO2 removal efficiency than the two-hole nozzle before the circulation of fine solids, but it has lower removal efficiency after circulation begins. This is explained from the fact that the water droplets sprayed through the 3-hole nozzle could not reach the reaction zone which is extended due to the circulation of solids, while water from the 2-holes of nozzle reached the zone, leading to the effective wetting. These results confirm that the height of water spray instead of the number of holes is a more significant factor for the optimization of water injection techniques. Figure 9 shows the effect of the water flow rate and the number of holes on the SO2 removal efficiency under the circulation of lime #2 at the gas velocity of 4 m/s. Water was sprayed at the flowrate of 30 ml/min and 40 ml/min through the two and three hole nozzles. The highest SO2 removal efficiency was obtained with the water injection rate of 40 ml/min through the 2-hole nozzle. It is obvious that higher water spray flow rates can increase the wetting efficiency under the circulation of fine solids, leading to the increased SO2 removal efficiency.

Figure 10 shows the effect of the fluidizing gas velocity on the SO2 removal in a stationary bed. The water injection of 40 ml/min through the two hole nozzle was provided after lime #2 was added into the bed at the fluidizing gas of 4 m/s and 5 m/s. As expected, the SO2 removal efficiency increases slightly with the reduced fluidizing gas velocity since the residence time of SO2 gas stream becomes greater. The effect of gas velocity on the SO2 removal appeared not significant, however.

The SO2 removal efficiency apparently increases with an increase of bed loading as the more sorbent provides a higher Ca/SO2 ratio, which leads to the removal efficiency to increase. Figure 11 indicates the SO2 removal during fluidization with lime #2 of 0.5 kg and 0.75 kg and with a water flowrate of 40 ml/min through the two hole nozzle. At the beginning of water injection the reaction appeared to be independent on the initial loading of bed materials, but the SO2 removal efficiency significantly increased after the hydration and attrition of lime began. This result suggests that an effective wetting allowing the rapid hydration and gradual attrition of lime is required for the enhancement of the SO2 removal efficiency. Such wetting may be obtained by adjusting the droplet size and water pressure.

During fluidization under wet conditions, lime particles are being hydrated and attrited easily. As a result, the removal of the product layer covering the unreacted sorbent by the attrition allows the surrounding SO2 to contact with the fresh sorbent surface continuously, and leads to the increase of sorbent utilization. Figure 12 shows the effect of attrition on the SO2 removal at two different water injection rates. The test was carried out with lime #2 at the gas velocity of 5 m/s. While the parent solid stays in the bed due to their high terminal velocity (10 m/s) during fluidization, the obtruded fines are immediately elutriated and captured by the first cyclone. The weight of fine solids captured by the cyclone was measured at a regular interval. As shown in Figure 11, the highest SO2 removal efficiency and the largest extent of attrition occur at close time. In addition the peak is strongly dependent on the wetting efficiency. An effective wetting to cause the gradual attrition, therefore, is necessary for the increased SO2 removal efficiency as well as sorbent utilization.

CONCLUSIONS

Water injection in dry lime injection FGD processes plays a very important role for the SO2 removal efficiency. The experimental data obtained from circulating fluidized bed absorber (CFBA) operations under water injection through the newly designed toroidal ring nozzle were represented. The results summarized as :

1. The removal efficiency is a strong function of the water injection rate.
2. The height of water spray is more significant in wetting efficiency during fluidization in CFBA instead of the number of holes.
3. The effect of gas velocity appeared not significant, resulting from that the wetting efficiency may increase at higher velocities.
4. The loading of sorbents strongly affects on the SO2 removal as the lime becomes hydrated and attrited, while its effect appears not significant before hydration occurs.
5. As the lime continuously contacts with water droplets, it becomes hydrated and its attrition is significantly taking place. Since the hydration causes the high reactivity and attrition provides the fresh surface of lime, the SO2 removal efficiency closely changes with the extent of attrition.

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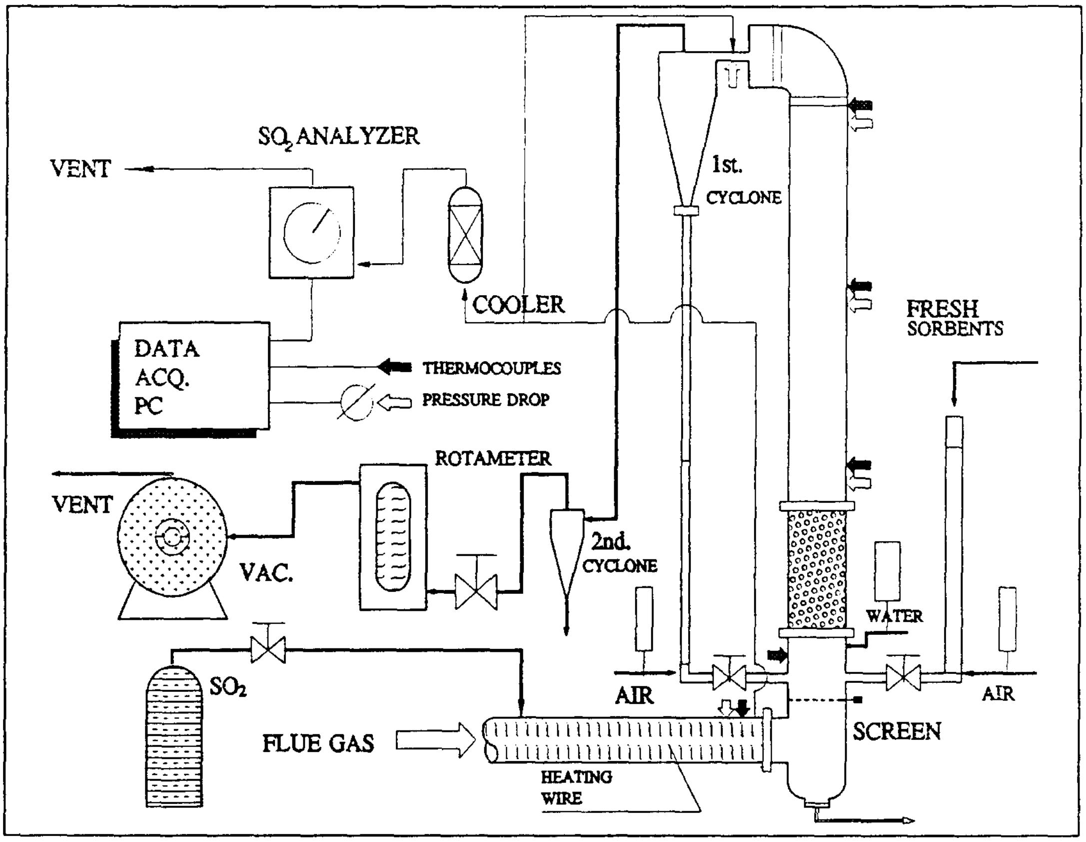

Figure 1. Scheme of bench scale CFBA unit.

Figure 2 Illustration of lime fluidization.

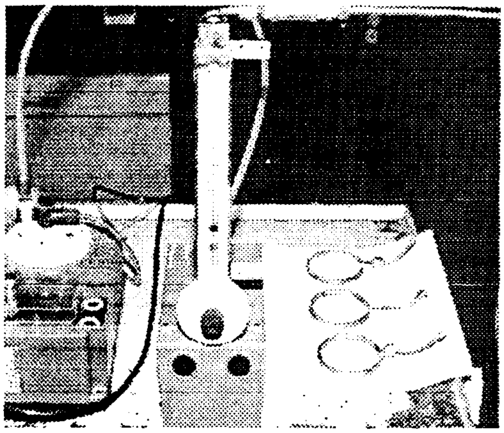

Figure 3 Water pump and nozzles.

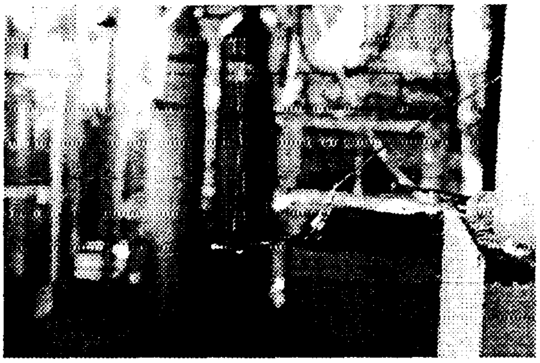

Figure 4 Water injection with 2-hole nozzle.

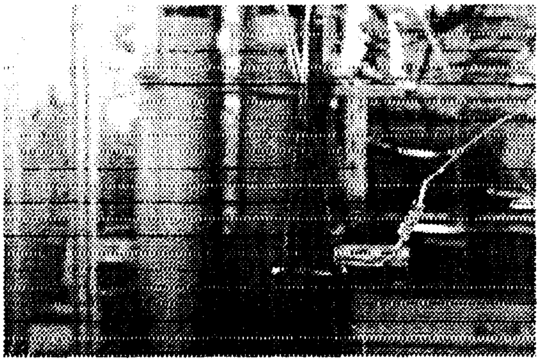

Figure 5 Water injection with 4-hole nozzle.

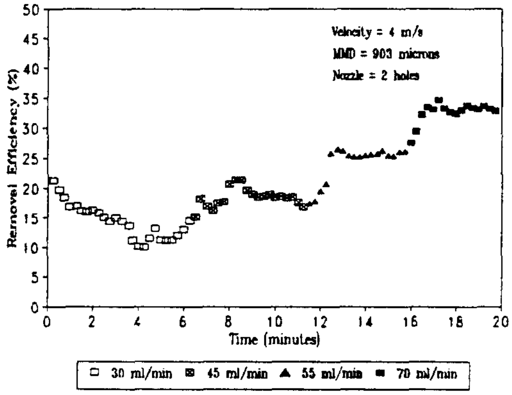

Figure 6. SO_2 removal efficiency versus water injection rate.

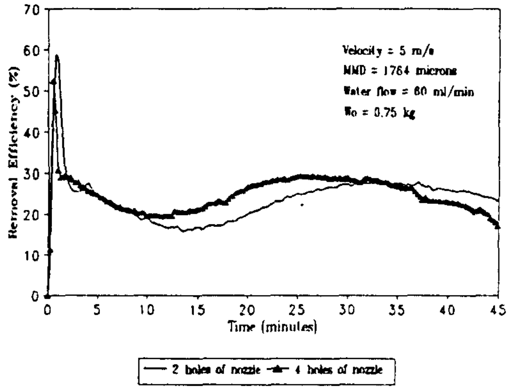

Figure 7. Effect of the number of nozzle holes on SO_2 removal efficiency.

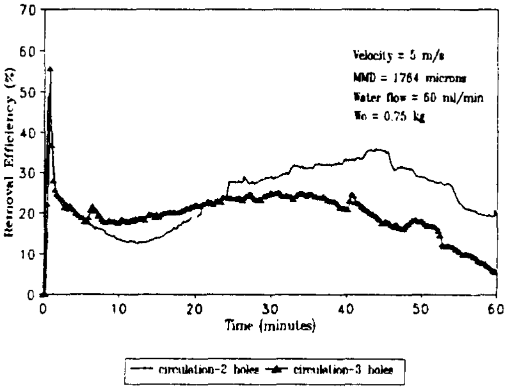

Figure 8. Effect of the number of nozzle holes on SO_2 removal efficiency.

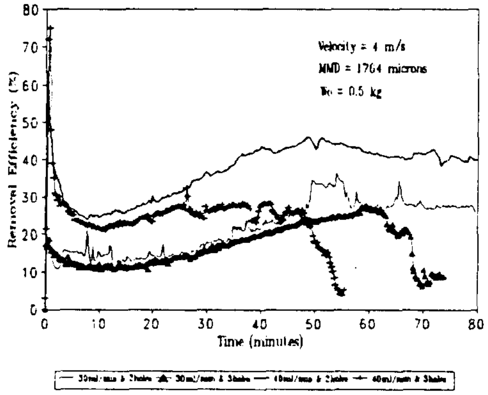

Figure 9. Effect of water injection rate and number of holes on SO_2 removal efficiency.

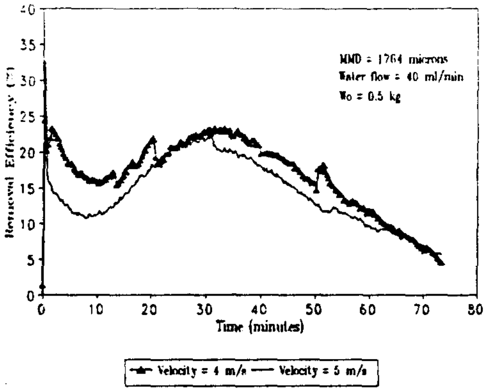

Figure 10. Effect of gas velocity on SO_2 removal efficiency.

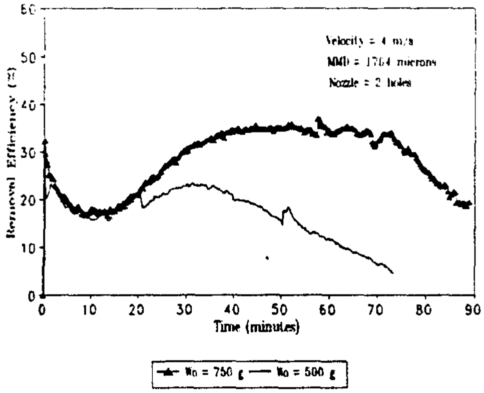

Figure 11. Effect of the initial weight of sorbents on SO_2 removal efficiency.

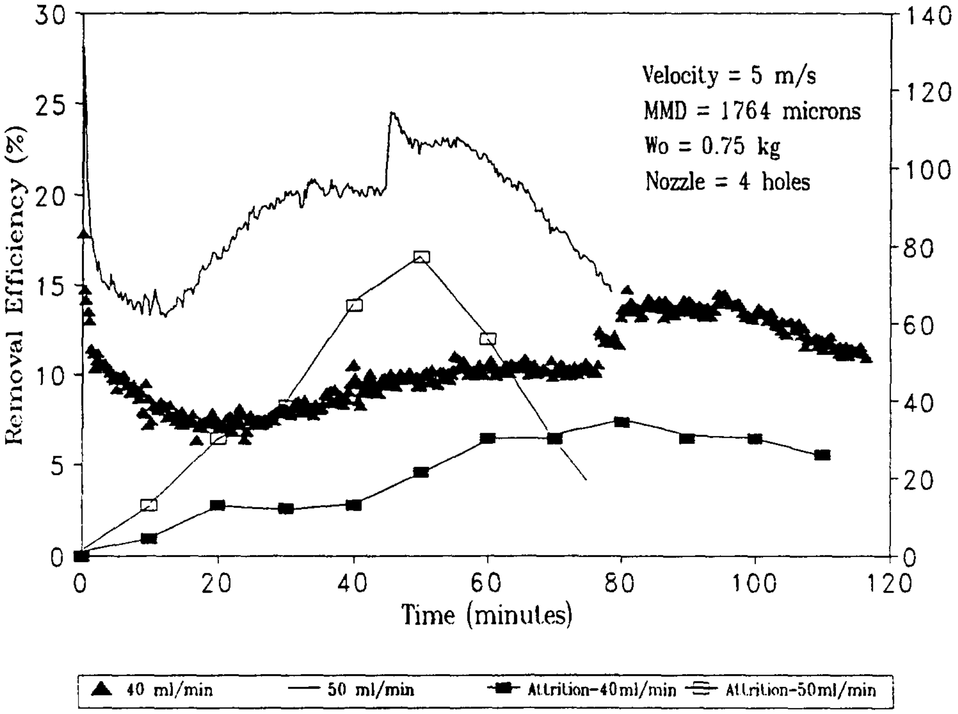

Figure 12. SO_2 removal and attrition at different water injection rate.