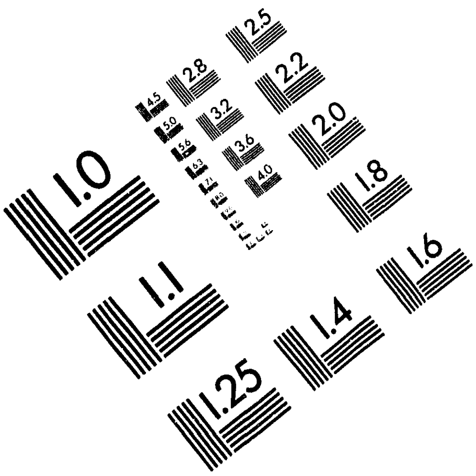

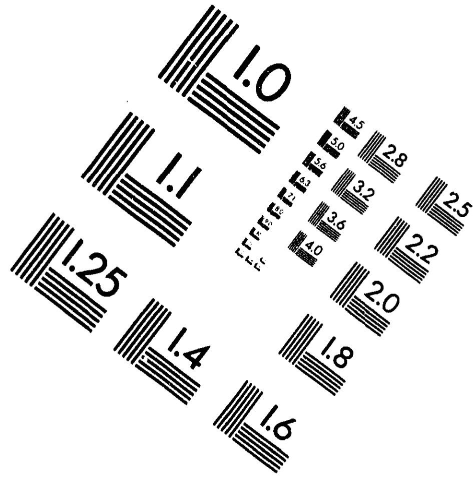

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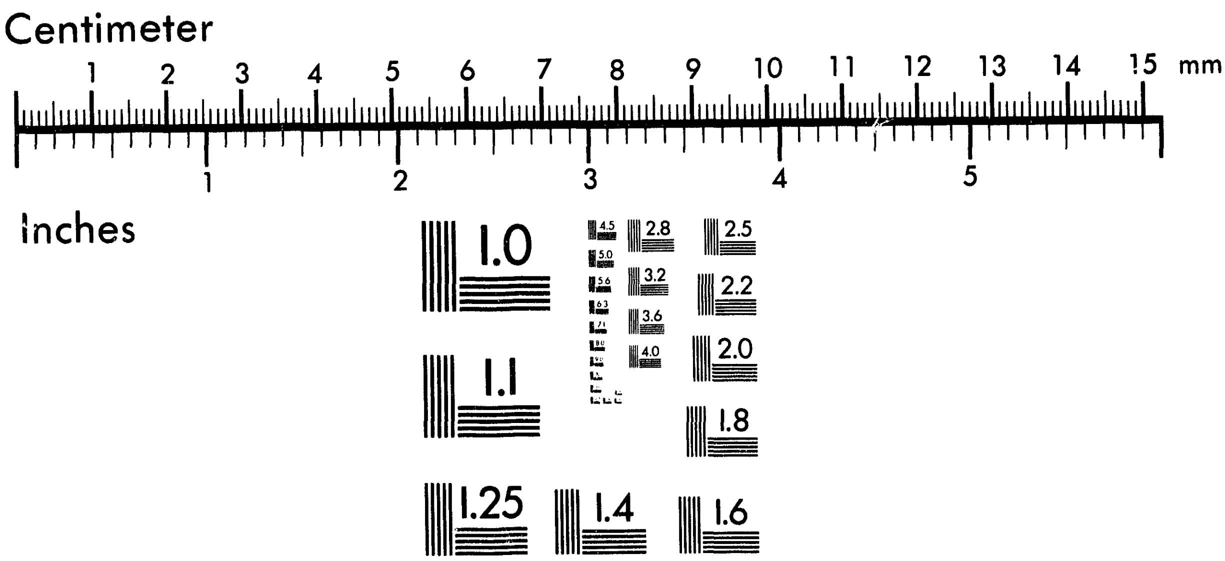

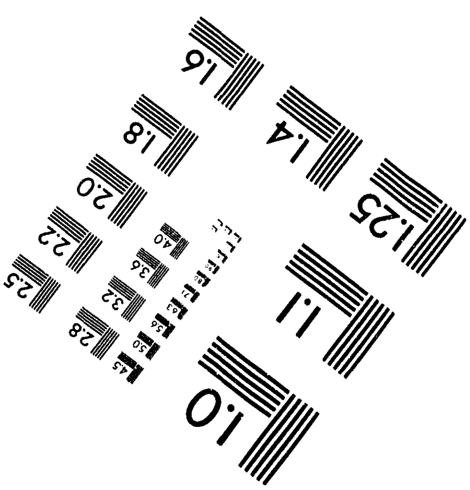

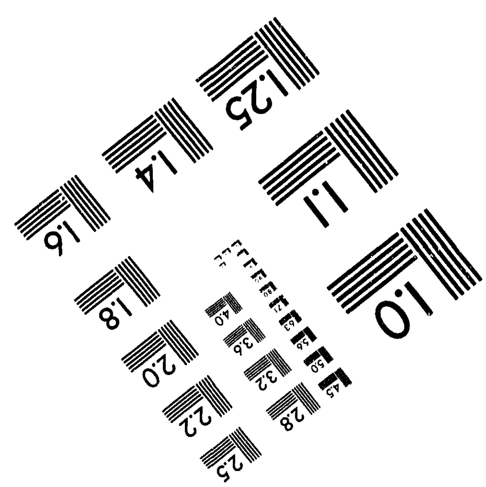

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Quarterly Report

U.S. Department of Energy

Grant No. DE-FG22-91PC91336

Project Title: Low Temperature SO_2 Removal with Solid Sorbents in a Circulating Fluidized Bed Absorber

Period of Performance: May 1 - July 31, 1992

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Abstract

The nozzle installed in CFBA was slightly modified because of a technical difficulty in making the small holes less than 100 μm. The holes was punctured with a very tiny drill bits in diameter of 275 μm, and the number of holes was adjusted. The 951 TGA (Du Pont Co.) was also modified for the kinetic information on the hydration and sulfation of limes under low temperatures. The modified TGA includes a syringe in order to simulate the water sprayings in a CFBA. Water droplets through the needle attached to the syringe are added onto the lime sample in a TGA. Two discrete ranges of Dravo limes were prepared as solid sorbents for sulfation tests. One ranged between 1095 μm (16 mesh) and 2380 μm (8 mesh) in diameter and the other ranged between 595 μm (30 mesh) and 1095 μm (16 mesh). The experimental methods for kinetic studies with TGA and for CFBA operation were established through the pre-operation of CFBA.

I. Work Performed/Results Obtained

Toroidal ring-type nozzle ; As reported previously, a novel method injecting the water in CFBA was designed and installed for the effective wetting because the commercial nozzles had ~~the~~ physical limitations on the degree of particle wetting. However, the nozzle was slightly modified because of a technical difficulty in making the small holes less than 100 μm. The holes ~~was~~ punctured with a very tiny drill bits in diameter of 275 μm, and the number of holes ~~was~~ reduced.

The installed nozzle is shown in Figure 1 and 2. The toroidal ring type nozzle was made of copper tube and placed just below the sorbent injection point in a bed. As illustrated in Figure 2, the ring has water injection orifices on the ring at an angle, α, with the horizontal. 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, the toroidal ring nozzle was made of 1/4 inches of copper tube and has 3-6 holes and 50°- 80° angles based on the evaporation rate and droplet trajectories in a bed. The diameter of hole ~~punctured with the very~~ tiny drill is about 275 μm. Water is injected by a high pressure pump to insure good atomization, and a filter is placed before pump to prevent the contaminants from clogging the small holes.

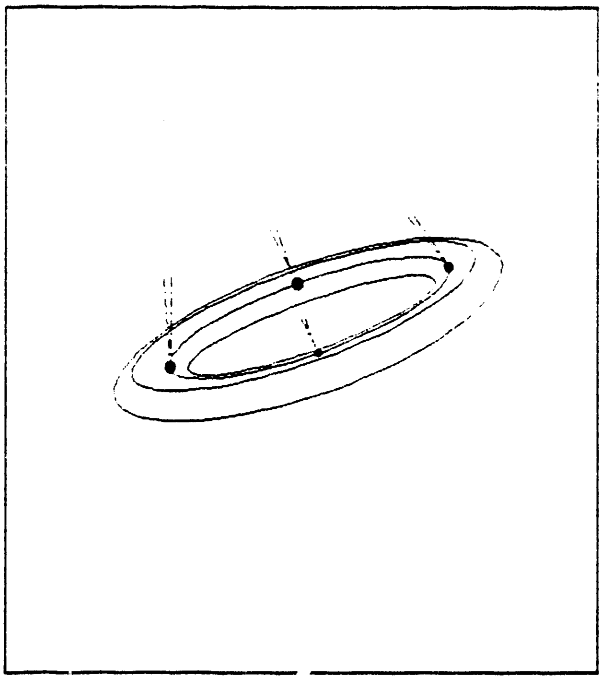

Figure 1. Illustration of nozzle

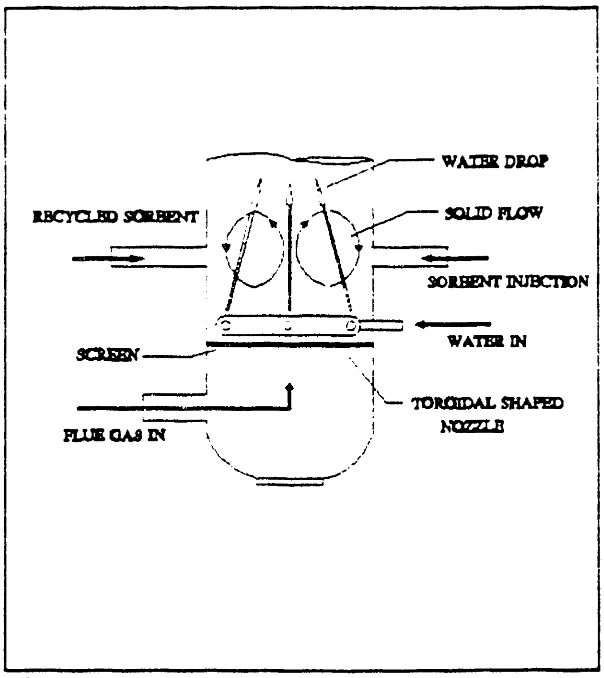

Figure 2. Installation of nozzle

TGA apparatus ; TGA (Thermogravimetric Analyzer) is an instrument that can continuously measure the amount and rate of weight change of material, either as a function of increasing temperature, or isothermally as a function of time, in a varied but controlled atmosphere. A constant intensity lamp built in a TGA is focused through an aperture slit to strike the equal amount of light to two vertically mounted photodiodes. As the sample weight is lost or gained, however, the beam becomes unbalanced and causes more light to strike one photodiode than the other. The voltage output from the photodiode produces a restoring current flow, and the magnitude of the current is directly proportional to the sample weight lost or gained. The sample temperature is obtained from the thermocouple located close to the sample. The heating rate and temperature of furnace are set by the control thermocouple in furnace.

The 951 TGA (Du Pont Co.) is shown in Figure 3, and it was modified for the kinetic information on the hydration and sulfation of limes as illustrated in Figure 4. The modified TGA includes a syringe in order to simulate the water sprayings in a CFBA. Water droplets through the needle attached to the syringe are added onto the lime sample in a TGA.

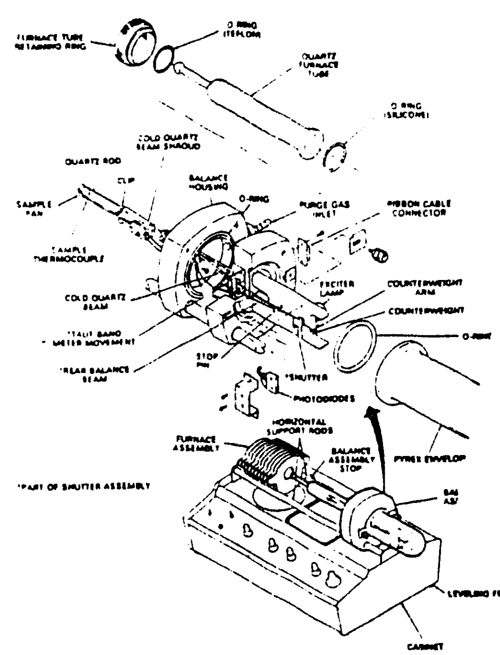

Figure 3. Scheme of 951 TGA (Du Pont Co.)

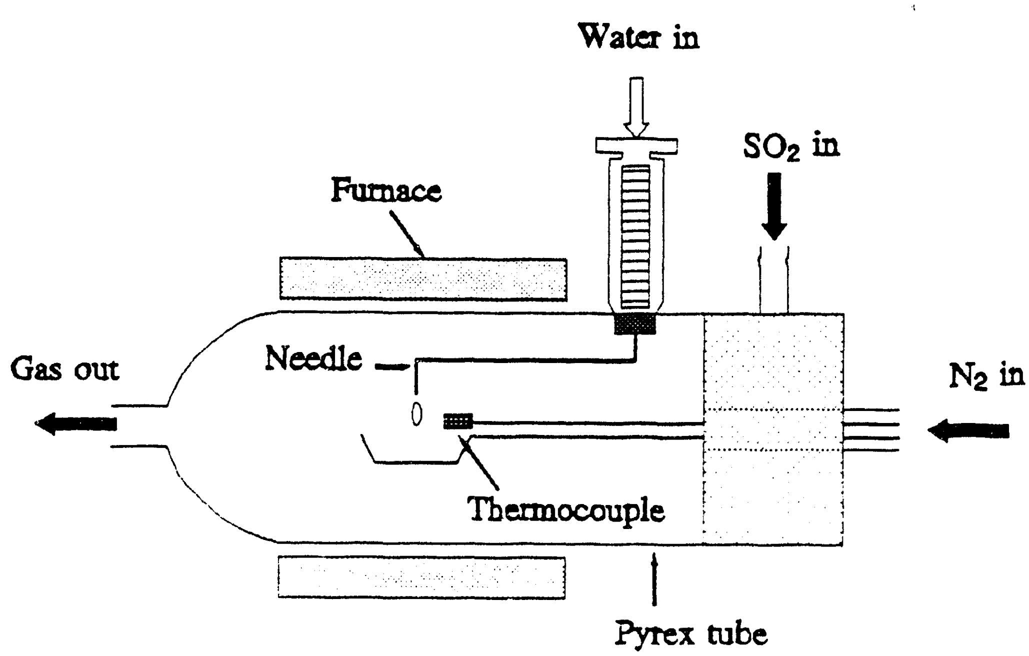

Figure IV-4. The Modified Thermogravimetric Analyzer (TGA)

<u>Preparation of lime samples</u> : Two discrete ranges of Dravo limes were prepared as solid sorbents for sulfation tests. One ranged between 1095 μm (16 mesh) and 2380 μm (8 mesh) in diameter and the other ranged between 595 μm (30 mesh) and 1095 μm (16 mesh). For a sulfation test, very fine sizes of sand is added to the limes for the prevention of the sticky and fine limes from deposition in the transport line. The sand is inert with SO_2 and pneumatically transported to the top of bed, captured by the first cyclone, and recirculated continuously into the bed with the fine lime particles. The fractional size distribution curves of lime samples and sand are shown in Figure 5 and 6.

The lime sample is a high-calcium quicklime formed by calcining limestone so that CO_2 is liberated. The chemical and physical properties of lime samples are summarized in Table 1 and 2, respectively.

Table 1. **Physical properties of lime samples**

SAMPLE NUMBER	MASS MEAN DIAMETER (MICRONS)	SURFACE MEAN DIAMETER (MICRONS)	SPECIFIC BET SURFACE AREA (M^2/G)	BULK DENSITY (G/M^3)
Lime 1	1764	1682	1.27	1.45
Lime 2	903	820	1.36	1.28
Sand	187	160	—	—

Table 2. *Chemical properties of lime samples

CHEMICAL COMPONENTS	WEIGHT %
Total C_aO	93
Available C_aO	87.5-88.5 (95)**
M_gO	2.65-2.75
Sulfur	0.045-0.050
CO_2	1.1-1.2
H_2O	0.4
S_iO_2	1.95-2.05

* The chemical analysis data from Dravo Lime Co. ** Measurement at U.C.

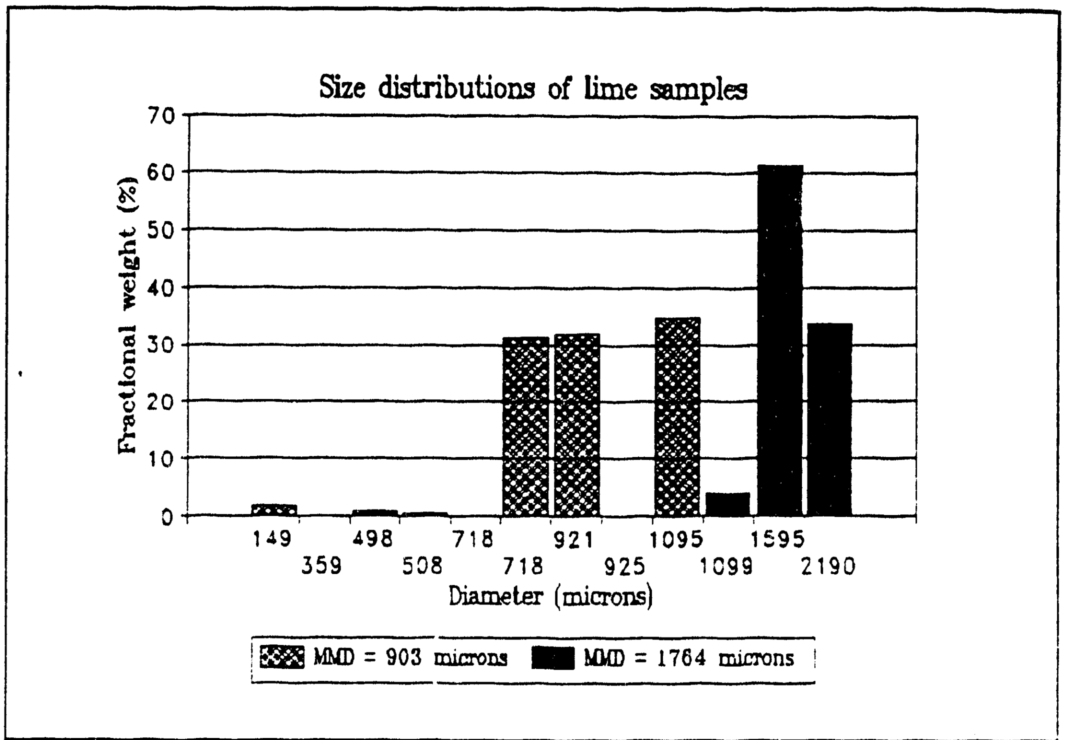

Figure 5. Size distributions of lime samples

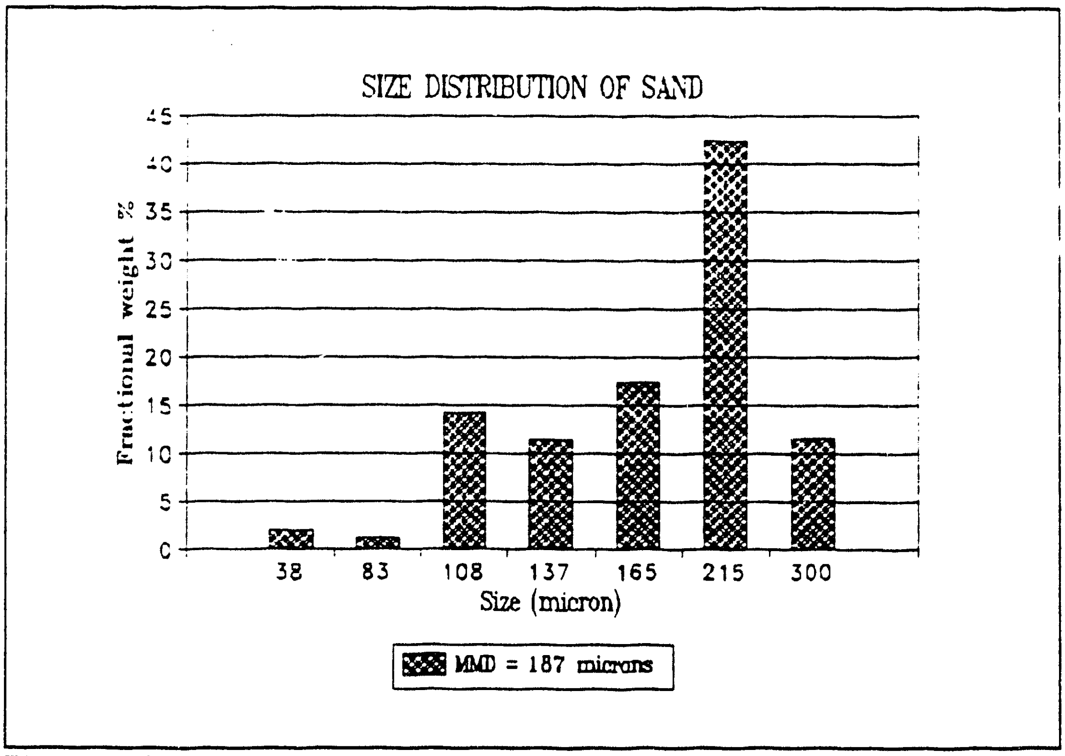

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Figure 6. Size distribution of sand

Experimental method for wetting efficiency measurement ; The CFBA is one of the dry scrubber processes though it includes a water injection system. It was designed such that the solids entrained from the top of bed become completely dried while water is continuously injected. Thus, it is reasonable to assume that the water sprayed into a bed is either evaporated, or captured by the solid sorbents, or penetrated as a vapor through a bed. Then the penetration can be expressed as the product of rates that the water is not either evaporated or captured by solids as followings ;

$$\rho = (1 - \phi_e)(1 - \eta_w)$$

where ρ is the penetration rate (moles/sec) and ϕ_e, evaporation rate (moles/sec), and η_w, wetting rate (moles/sec), respectively. The penetration rate, ρ can be obtained by measuring the wet-bulb temperature at the outlet. Hence the evaporation rate, φ_e can experimentally be determined by measuring the penetration before the solid injection. If the penetration and evaporation are known the wetting rate, η_w can be obtained as ;

$$\eta_w = 1 - \frac{\rho}{(1 - \phi_e)}$$

Those evaporation and wetting rates obtained experimentally will be compared with the rates determined by heat and mass transfer balance, and collection efficiency as described in the previous section. For the measurement of wetting efficiency the temperature in a bed should be kept steady state, and the wet bulb temperature must be obtained under the steady state because the evaporation rate strongly depends on the temperature. The detailed experimental procedure is explained in the CFBA operation because the measurement is performed as a part of the SO_2 removal tests in CFBA.

Kinetic study method with TGA; The typical run with TGA is carried out as follows;

1. Power up and warm up the TGA.

2. Set the run parameters for isothermal operations.

3. Turn on the SO_2 gas to keep the concentration of 3000 ppm.

4. Put limes in a port, and measure the weight.

4. Inject one or more droplet to limes, and measure the weight change.

CFBA operation for SO_2 removal ; A general experimental procedure for the SO_2 removal in CFBA includes ; 1) heating the bed reactor ; 2) water injection ; 3) SO_2 injection ; 4) injection of mixture of lime and sand. For the blank test, the step (2) is skipped to evaluate the removal efficiency under dry conditions.

The CFBA is heated to the temperature of 350°F in order to simulate the flue gas of the power plant. After the reactor reaches the steady state temperature, the wet bulb temperature is measured for the measurement of humidity of flue gas. Then water is sprayed into the bed, and at the steady state the wet bulb temperature is measured again The measurement of wet bulb temperatures before and after water injection gives the evaporation rate.

The SO_2 gas of 3000 ppm is injected after the wet condition become steady state, and the inlet and outlet SO_2 concentrations are measured. The differences in SO_2 concentration indicate the absorption by the water droplets.

As a final step, the mixture of limes and sand are injected into the bed, and the inlet and outlet SO_2 concentrations are measured for the determination of the removal efficiency, and the wet bulb temperature, for the wetting efficiency. Before the sorbent injection 500g of sand is added to the limes for the prevention of the sticky and fine limes from deposition in the transport line. The sand is fluidized at the very lean phase, and thus pneumatically transported to the top of bed, captured by the first cyclone, and recirculated continuously into the bed with fine lime particles. During fluidization the weight loss of bed materials occurs due to attrition, and hence the recirculation rate is reduced slowly. Therefore, the recirculation of the mixture of lime and sand are kept steady state by adjusting the recirculating L-valve.

The blank test without water injection gives the SO_2 removal efficiency under the dry condition, and the test with only sand allows to determine its effect on the reactivity of limes.

During the experiments SO_2 concentrations are continuously measured with a Horiba SO_2 analyzer, and temperatures and pressure drops as well as the concentrations were automatically recorded into an data acquisition system. In addition, the bed materials and fines captured by the first and second cyclones are collected after the CFBA are turned off. The sulfur content in the waste sorbents and fines are measured by a LECO sulfur analyzer.

II. Unusual Problems/Circumstances

As mentioned previously, there was a technical difficulty in making the small holes less than 100 μm on the nozzle. Alternatively, a little bigger holes were punctured with tiny drill bits and thus, the number of holes were reduced.

III. Tasks/Work to be Performed

Major works to be performed during the following quarter are summarized as ;

. Measurement of wetting efficiency of the nozzle installed in CFBA

. Kinetic tests with TGA

. Development of a kinetic model for the low temperature reaction between SO_2 and dry lime (CaO).

. Measurement of SO_2 removal efficiency in CFBA

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