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Journal of the AIR & WASTE Management Association

JANUARY 1992

VOLUME 42 NUMBER 1

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**Current Status of ADVACATE Process
for
Flue Gas Desulfurization**

by

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ABSTRACT

Current Status of ADVACATE Process for Flue Gas Desulfurization, Brent W. Hall, Carl Singer, Wojciech Jozewicz, Acurex Corporation, P.O. Box 13109, Research Triangle Park, NC 27709, Charles B. Sedman and Michael A. Maxwell, U.S. EPA, AEERL, Research Triangle Park, NC 27711. The following report discusses current bench- and pilot-plant advances in preparation of ADVANCED silicate (ADVACATE) calcium silicate sorbents for flue gas desulfurization. It also discusses current bench- and pilot-plant advances in sorbent preparation. Fly ash was ground in a laboratory scale grinder prior to slurring in order to decrease the slurring time needed for the sorbent to be reactive with SO_2 . Reactivity of ADVACATE sorbents with SO_2 in the bench-scale reactor correlated with their surface area.

ADVACATE sorbents produced with ground fly ash were evaluated in the 50 cfm ($85 \text{ m}^3/\text{h}$) pilot plant providing 2 s duct residence time. ADVACATE sorbent was produced by slurring ground fly ash (median particle size of $4.3 \mu\text{m}$) with $\text{Ca}(\text{OH})_2$ at the weight ratio of 3:1 at 90°C (194°F) for 3 h to yield solids with 30 weight percent of initial free moisture. When this sorbent was injected into the duct with 1500 ppm SO_2 and at 11°C (20°F) approach to saturation, the measured SO_2 removal was approximately 60 percent at a Ca/S stoichiometric ratio of 2. Previously, when ADVACATE sorbent was produced at 90°C (194°F) and at the same fly-ash-to- $\text{Ca}(\text{OH})_2$ weight ratio using unground fly ash, removal under the same conditions in the duct was approximately 50 percent following 12 h slurring. The report presents the results of pilot-scale recycle tests at the recycle ratio of 2. Finally, the report discusses future U.S. Environmental Protection Agency's plans for commercialization of ADVACATE.

INTRODUCTION

Under U.S. Environmental Protection Agency (EPA) sponsorship, Jozewicz and Rochelle¹ studied the reaction of fly ash with calcium hydroxide $[\text{Ca}(\text{OH})_2]$ for the production of reactive sorbents for use in flue gas desulfurization (FGD) processes. They found that solids produced by slurrying fly ash and $\text{Ca}(\text{OH})_2$ were significantly more reactive than $\text{Ca}(\text{OH})_2$ alone. This work demonstrated that silica was the most reactive compound of fly ash and that reactivity increased with slurrying time/temperature. It also postulated that the rate limiting step of the reaction of fly ash with $\text{Ca}(\text{OH})_2$ was dissolution of silica from fly ash. Three different approaches were tested that could increase the dissolution rate of silica: additives (sodium hydroxide, ammonium phosphate, phosphoric acid), more reactive form of silica (diatomaceous earth, bentonitic clays), and an increased slurrying temperature (pressure hydration).^{2,3} The use of additives, or more reactive form of silica significantly increased the cost of sorbent preparation. High capital cost of pressure hydration and decreased conversion of $\text{Ca}(\text{OH})_2$ above 150 °C likely due to formation of crystalline calcium silicates indicated that the commercial competitiveness of calcium silicate sorbents could be increased by the elimination/modification of this hydration step. Another means to increase the rate of formation of calcium silicates is to increase the availability of silica by fly ash grinding. To test this approach, fly ash was ground in an attritor prior to slurrying with $\text{Ca}(\text{OH})_2$ throughout the work described here.

Current bench- and pilot-plant research has been directed toward optimal sorbent preparation. Fly ash grinding before slurrying was investigated on the bench scale to decrease the slurrying time needed for the sorbent to be reactive with sulfur dioxide (SO_2). Results indicate that the slurrying time can be decreased by a factor of 4, from 12 to 3 h, and will yield the same or better reactivity results than with unground fly ash. The reactivity of these sorbents with SO_2 can be correlated with their surface area, which is also a function of the particle size of the ground fly ash. High reactivities measured can be attributed to the large surface area of the calcium silicate as well as with its water-retaining capability. Time and temperature studies were also conducted to determine the optimum temperature for slurrying the ground fly ash and $\text{Ca}(\text{OH})_2$. Results suggest that 90 °C (194 °F) is optimum.

Pilot-plant work investigated using ground fly ash as the basis for calcium silicate formation. ADVANCED siliCATE (ADVACATE) sorbents produced using ground fly ash were evaluated in the 50 cfm (85 m³/h) pilot plant. Fly ash with a median particle size of 16 µm was ground to a median particle size of 4.3 µm and slurried with $\text{Ca}(\text{OH})_2$ for 3 h at a weight ratio of 3:1 and 90 °C (194 °F). The resultant slurry was dried in an oven to form free-flowing solids containing approximately 30 percent free moisture. This sorbent was injected into the duct with 1500 ppm SO_2 and at 11 °C (20 °F) approach to adiabatic saturation temperature (ΔT_s). The measured SO_2 removal was about 60 percent at a stoichiometric ratio of 2.0. Previous tests⁴ using ADVACATE sorbent prepared with unground fly ash, at the same conditions but following 12 h slurrying, yielded approximately 50 percent in-duct SO_2 removal. Pilot-scale recycle tests at a recycle ratio of 2.0 were also conducted using the 50 cfm pilot plant. The results of these tests, through the third pass of recycle, are shown below.

Future plans for developing the ADVACATE process include a 10 MW_e field demonstration at the Shawnee facility of Tennessee Valley Authority. A complete factorial test plan has been developed to evaluate in-duct SO_2 removal along with long-term, steady-state operation.

EXPERIMENTAL

Bench-Scale Facilities

Sorbent reactivity was evaluated in a bench-scale sand-bed reactor designed to simulate baghouse conditions. The reactor was a fixed bed normally using 1 g of sorbent dispersed in 40 g of sand. Each sample was exposed for 1 h to an SO_2 -containing nitrogen stream controlled to the desired conditions of temperature and relative humidity. The experimental apparatus, shown in Figure 1, has been discussed in more detail elsewhere.^{5,6} Experiments were performed at a temperature of 64 °C (147 °F) and at ΔT_s of 10 °C (18 °F) (corresponding to a relative humidity of 60 percent). Flue gas was simulated with 1000 ppm SO_2 in dry nitrogen fed at 280 L/h (10 cfm) at 20 °C (68 °F).

SO₂ removal was determined by integrating the 1-h concentration curve recorded by a Thermoelectron Pulsed Fluorescent SO₂ Analyzer. Conversion has been defined as the moles of SO₂ removed from the flue gas divided by the number of moles of Ca(OH)₂ in the sorbent (0.0034 moles/g at an ash-to-Ca(OH)₂ ratio of 3:1).

Pilot Plant

The pilot-plant facility, shown in Figure 2, consists of humidification to control the gas temperature and humidity. The normal gas flow for the facility is 50 acfm at 177 °C (350 °F), and SO₂ is injected at a rate of 0.4–1.0 lb/h (0.18–0.45 kg/h) to provide an SO₂ concentration of 1000–2500 ppm. Ambient air is drawn through an air filter, heated to 177 °C (350 °F), and then humidified by evaporative cooling to 54 °C (130 °F) in the spray dryer vessel and in the duct. This corresponds to a ΔT_s of 11 °C (20 °F) through the system. The cooled gas stream then flows through an 80-ft (24.5-m) heat-traced and insulated section of duct to a pulse-jet baghouse for collection of solids. The cleaned gas is exhausted into the atmosphere. The calcium silicate sorbents are injected by a screw feeder into the duct downstream of the humidifier. The 5 cm (2 in.) diameter, 24.5 m (80 ft) long duct provides for a flue gas residence time of approximately 2 s. The collected solids are then discharged from the baghouse hopper and stored for later use. A detailed description of the pilot plant is provided elsewhere⁴.

The SO₂ concentrations throughout the system were monitored using a Dupont 411 Photometric Analyzer. Sampling points are at the spray dryer outlet (system inlet), baghouse inlet (duct), and baghouse outlet (total system). The SO₂ concentration was set at the system inlet and held constant by a calibrated rotameter. To ensure no dilution or air leakage, the concentration was checked at the baghouse inlet and outlet before the test. Data were collected every 0.5 h during a 4–8 h test run at fairly constant conditions.

Sorbents

Clinch River Ash. The fly ash from Appalachian Power Company's Clinch River Plant in Carbo, VA, has been used throughout this work. The Clinch River fly ash (CR) was produced by burning eastern bituminous coal (fly ash CaO content of 5.4 percent). Fly ash morphology was characterized using a Scanning Electron Microscope (SEM). The view of a typical microscope field is presented in Figure 3, where spherical particles with smooth surfaces can be seen. Fly ash density was measured to be 2.1 g/cm³. Mass median particle size was found to be 16.0 µm by sedimentation method (Microtrak). The nitrogen adsorption/desorption Brunauer, Emmett, and Teller (BET) surface area was measured to be 1.8 m²/g, and pore volume was 0.00366 cm³/g.

Ca(OH)₂. Reagent grade Ca(OH)₂ from Fisher (Fisher C-97) was used throughout bench-scale experiments. It was determined by a thermogravimetric analyzer (TGA) to be 93 percent Ca(OH)₂ (the remaining 7 percent was surface water, calcium carbonate, and impurities). Structural properties of a reagent grade Ca(OH)₂ were measured to be: 15 m²/g surface area, 0.100 cm³/g pore volume, and 5.6 µm mass median particle size.

Commercial Mississippi Ca(OH)₂ was used throughout the pilot-scale tests. It was determined by TGA to be 94 percent Ca(OH)₂ and structural properties were: 19 m²/g surface area, 0.100 cm³/g pore volume, and 4.0 µm median particle size.

Bench Scale. Samples of CR were ground in a Union Process laboratory-scale 1-S Batch Attritor. The attritor is a vertically oriented mill with a stationary stainless-steel tank loaded with 0.31-cm (0.125-in.) stainless-steel balls agitated by a rotating internal shaft with arms turning at 300 rpm. Fly ash was ground as a 30 weight percent slurry at room temperature for 1 h, then dried before further use. Fly ash morphology was characterized using SEM. A typical microscope field is presented in Figure 4. Most of the spherical particles (as shown in Figure 3) are broken and of irregular shape. Mass median particle size by Microtrak method of CR fly ash ground by Union Process (UPCR) was found to be 2.93 µm. The BET surface area and porosity have both increased to 5.4 m²/g and 0.017246 cm³/g, respectively.

Samples of CR were also ground in a laboratory ball mill for times ranging from 8 to 56 h. The mill consists of a 23.5 cm (10 in.) dia. horizontal steel cylinder with 1.23 cm (0.5-in.) stainless-steel balls rotating at 50 rpm. CR was loaded dry to half fill the cylinder. Grinding was continuous with pauses only to take periodic grab samples. At the end of 56 h of ball mill grinding, BET surface area of the fly ash ground in the ball mill (BCR) had increased to 3.4 m²/g.

Sorbents were prepared from the above fly ash in a two-step process: hydration and drying. Hydration was performed atmospherically in a beaker placed in a hot water bath controlled at 60 °C (140 °F) to boiling. Reagents were added to hot water (1 part solid:15 parts water) and stirred for the entire hydration time, varied from 1 to 6 h. After hydration, the slurry was vacuum-filtered, and the filter cake was microwaved for 6 min to prevent any further hydration of damp sorbents.

Typical sorbents were made with 3 parts fly ash and 1 part Ca(OH)₂ (fly-ash-to-Ca(OH)₂ weight ratio of 3:1). Several sorbents were characterized by SEM. A typical, well-developed sorbent is presented in Figure 5. The pictured sorbent's BET surface area has increased to 26.3 m²/g from an original fly ash surface area of 3.4 m²/g. The surface area is very irregular with few planes visible.

Pilot Scale. Baseline tests were performed with unground CR that had been atmospherically hydrated with Ca(OH)₂ at 90 °C (194 °F) and at a fly-ash-to-Ca(OH)₂ ratio of 3:1 for 12 h. This sorbent was termed unground CR ADVACATE (UCA). The resultant slurry, approximately 70 percent water, was then dried in an oven at 65–93 °C (150–200 °F) until the bulk residual moisture of the solids was about 30 percent. Other tests involved using ground CR ash that had been wet ground in a Union Process Model 15-S Attritor. The fly ash was ground in a 15-S Attritor from an initial mass median particle size of 16.0 µm to a final mass median particle size of 4.3 µm. The ground ash was also hydrated with Ca(OH)₂ at a weight ratio of 3:1, at 90 °C (194 °C), but only for 3 h. This sorbent was termed ground CR ADVACATE (GCA). The resultant slurry, for the first pass, was also dried in the oven to approximately 30 percent residual moisture. All other passes of ground material, namely recycle tests, were prepared by backmixing the dry spent silicates collected in the baghouse with the fresh ADVACATE slurry. All solids were then passed through a Vibro-Energy separator to break down all agglomerates to suitable size for feeding. The screen that the solids passed through was 18 mesh, which resulted in moist solids with a free-flowing consistency. The fresh ADVACATE slurry consisted of 2 parts recycle (spent silicates) to 1 part fresh Ca(OH)₂, corresponding to a recycle ratio (RR) of 2.0. It also contained 1.5 parts fresh ground fly ash to 1 part fresh Ca(OH)₂, which simulated the inherent ash in the system from the boiler. All recycle work was performed at a bulk solid moisture content of 35 percent.

RESULTS AND DISCUSSION

Bench Scale

Sorbent made from unground CR hydrated at 90 °C (194 °F) was used as a baseline for bench-scale sorbent reactivity. No significant improvement in conversion was seen by increasing hydration time from 1 to 4 h; however, an increase in conversion was observed from 36 percent at 4 h to 54 percent at a 6 h hydration (see Figure 6). Because hydration time is directly related to hydrator size, which affects capital cost for commercial application, hydration time must be minimized. In order to test the potential for decreased hydration time, sorbent was made from UPCR and Ca(OH)₂ at the weight ratio of 3:1 by hydrating at 90 °C (194 °F) for periods ranging from 1 to 6 h. All UPCR sorbents tested had significantly higher reactivity than similar sorbents made from CR, when exposed to SO₂ in the sand-bed reactor operated at a ΔT_s of 10 °C (18 °F). Shorter hydration time was needed to obtain a given conversion with UPCR than with CR sorbents. For example, only 2 h was needed to give about 50 percent conversion for UPCR sorbent, whereas 6 h was needed for similar conversion with CR sorbent. UPCR sorbent conversion increased with increased hydration time. Conversion increased significantly from 1 to 3 h hydration, but little improvement occurred from 3 to 6 h hydration.

Increased temperature of hydration increases the cost of sorbent. To test the possibility of using lower temperatures, sorbents were prepared by hydrating from 60 to 100 °C (140 to 212 °F). Figure 7 shows reactivity of these

sorbents prepared from CR and UPCR. Reactivity of CR sorbents remained at a conversion of about 0.33 mol SO_2 /mol $\text{Ca}(\text{OH})_2$ over the hydration temperature range of 70 to 100 °C for 3 h hydrations. Sorbents prepared from UPCR decreased in reactivity as hydration temperature decreased from 100 to 60 °C. There seemed to be a step change in conversion for UPCR sorbents hydrated 3 h from about 0.42 mol SO_2 /mol $\text{Ca}(\text{OH})_2$ below 70 °C to 0.80 mol SO_2 /mol $\text{Ca}(\text{OH})_2$ or better above 80 °C. Reactivity for UPCR sorbent prepared at 60 °C increased with hydration time, but not as dramatically as UPCR sorbent prepared at higher temperatures.

As shown in Figures 6 and 7, grinding fly ash before hydration with $\text{Ca}(\text{OH})_2$ to produce ADVACATE sorbents yielded substantial improvement in conversion over similarly prepared sorbents using unground fly ash for conditions tested. However, the amount of grinding needed will influence mill size and power requirements. To test the effect of the amount of fly ash grinding on the sorbents' reactivity, sorbents were made with CR ground in a ball mill (BCR) from 8 to 56 h. The ratio of BCR surface area to CR surface area (normalized surface area) was used to indicate the amount of grinding performed. BCR sorbents were produced at the BCR-to- $\text{Ca}(\text{OH})_2$ weight ratio of 3:1 and at 90 °C (194 °C) for 3 h and were subsequently tested on the sand-bed reactor. Figure 8 shows the effect of grinding on sorbent reactivity. Conversion increased steadily as the normalized surface area of BCR increased from 1 to 2. The data point at a normalized surface area of 3 reflects UPCR sorbent.

For the same hydration conditions, surface area of sorbents increased as the fly ash surface area increased due to grinding. In Figure 9, sorbent surface area is correlated with conversion for sorbents hydrated under different conditions using CR, UPCR, BCR. Sorbents were hydrated from 1 to 6 h at temperatures from 60 to 90 °C. Conversion in the sand-bed reactor increased as sorbent surface area increased.

Pilot Scale

Verification of Grinding Effect. Pilot-plant tests were conducted with UCA to provide a baseline for reactivity with SO_2 . These results were compared with data from injection of the moist GCA. Each sorbent was injected at approximately 30 to 35 percent residual moisture and at Ca/S stoichiometric ratios (SR) of 1, 2, and 3. All tests were conducted at a humidifier inlet temperature of 350 °F at a ΔT_s of 11 °C (20 °F) throughout the system. The inlet concentration of SO_2 was 1500 ppm, and only the baghouse inlet data were reported to simulate duct SO_2 removal in a field operation.

The UCA and GCA results are shown in Figure 10. Previous data showed that $\text{Ca}(\text{OH})_2$ alone yielded approximately 28 percent in-duct SO_2 removal at a SR of 2.0 and a concentration of 2000 ppm. At 1500 ppm SO_2 and a SR of 2.0, the unground calcium silicate solids yielded approximately 56 percent in-duct removal. This demonstrates the much higher reactivity associated with the silicate-based solids. Even at a SR of 1.0, the UCA yielded 26 percent removal. The effective calcium utilization in Figure 10 increases gradually with increasing stoichiometric ratio. At a SR of 1.0, the UCA indicated an in-duct utilization of 26 percent; whereas, at SRs of 2.0 and 3.0, utilizations of 28 and 32.2 percent, respectively, were noted. One possible explanation for this slight increase in utilization is the increase in humidity of the gas stream owing to the increased grain loadings. Normally, an increase in humidity would correspond to a decrease in gas temperature but, because of the duct heat trace, no change in temperature was noted. As indicated above, all sorbents were fed at 30 to 35 percent residual moisture, but analysis of the baghouse catch indicated that all material had dried to approximately 5 to 10 percent. This suggests that, even at a SR of 3.0, the sorbent was releasing all possible moisture.

Previous data reported⁴ indicated that in-duct SO_2 removals of 20 to 35 percent were achieved when unground oven-dried sorbent was injected at a SR range of 1.0 to 3.0 for a ΔT_s of about 11 °C (20 °F). Current data, shown in Figure 12, indicate SO_2 removals of 25 to 95 percent for comparable conditions. The lower removals associated with previous data can be mostly attributed to the initial inherent solids moisture content. Solids used in previous tests⁴ were oven dried to a "crisp" product that could be easily crushed into a fine, dry powder suitable for dry injection. These solids normally possessed 5 percent residual moisture before injection. The UCA solids recently tested contained approximately 35 percent moisture. Because the solids were identically prepared, the large difference in SO_2 removal can

be attributed to the additional inherent moisture contained by the UCA. This inherent moisture provides the media for the reaction between the sorbent particle and SO_2 ; whereas, the low-moisture sorbent must rely on the moisture in the gas stream to provide a basis for reaction to occur.

When comparing UCA and GCA, it is apparent that only a marginal increase in reactivity is noted for the ground solids. Although the increase in reactivity is very small, the important underlying factor is that, by grinding the fly ash prior to hydration with $\text{Ca}(\text{OH})_2$, its hydration time could be reduced from 12 h to an optimum of 3 h. This confirms the bench-scale results discussed earlier (Figure 6).

Recycle Tests. The sorbents used in the above dry-injection tests were prepared by oven drying the ADVACATE slurry to a desired moisture content. However, on a commercial scale, a continuous operation, such as recycle mixing, would be a more practical and efficient way to produce a manageable, free-flowing product for feeding into a duct. Spent material from the first pass of GCA testing was used to prepare fresh solids for subsequent recycle tests.

One part $\text{Ca}(\text{OH})_2$, 2 parts recycle product (RR=2.0), and 1.5 parts ground CR were hydrated at 90 °C (194 °F) for 3 h. The resultant slurry was then mixed with sufficient recycle product to obtain a moist, free-flowing ADVACATE product of approximately 30 percent residual moisture. The mixture appeared sufficiently dry to be handled by a dry-solids feeder. Injection of these solids resulted in an immediate lowering of the flue gas temperature. For this reason, tests were conducted with the temperatures initially set sufficiently high to allow for the decrease in bulk gas temperature to the desired ΔT_s of 11 °C (20 °F). Moist solids were injected into the simulated flue gas at approximately 93 °C (200 °F), and they consequently lowered the duct temperature to 54 °C (130 °F).

Three consecutive recycle passes were tested in the pilot plant to demonstrate the effect recycle has on overall sorbent reactivity and utilization. The results of these three passes, in addition to the baseline pass, are shown in Figure 11. Results indicate that the first pass of recycle (Recycle I) yielded 66 percent utilization at a SR of 1.0 which is better than previous data reported for unground fly ash⁴. One possible explanation is that using unground ash as the basis for ADVACATE sorbents provides much less overall surface area per gram of sorbent for calcium silicate formation than if ground ash is used. The recycle solids that were used in the current testing emanated from ground fly ash, which provided higher initial surface area for calcium silicate formation.

Figure 11 also shows the overall results of the second and third passes of recycle testing (Recycle II and III, respectively). These passes were tested at a SR of less than 1 owing to the increased grain loadings and the consequent difficulty in maintaining stable conditions. This difficulty in maintaining stable conditions can be attributed greatly to small (2 in. I.D.) duct size used with an 85 m³/h (50 ft³/min) pilot system. This thermal and mass transfer instability region has not been encountered in larger, and therefore more turbulent flow, systems under comparable duct conditions, and should not prove a problem in commercial applications. Several tests were conducted for each pass to ensure consistent operation of the pilot plant. Recycle II material was injected at a moisture content of 35 percent and yielded 80 percent utilization at a SR of 0.61. Recycle III material, at 38 percent moisture, was injected at a SR of 0.75 and yielded 85 percent utilization. When compared with the first pass and Recycle I in Figure 11, these two data points suggest that equilibrium, or steady-state operation, is being approached owing to the diminishing increase in utilization. The above results demonstrated that utilization of $\text{Ca}(\text{OH})_2$ increased using recycle solids as a basis and indicate that SO_2 removals of up to 90 percent in-duct are possible at a SR of 1.2 and complete equilibrium.

COMMERCIAL ACTIVITIES⁷

Figure 12 represents the commercial scheme of the ADVACATE process as envisioned for the 10 MW_e pilot evaluation in 1991-1992. Key process features include:

- In-duct sorbent drying and SO_2 absorption
- One-step sorbent mixing/injection
- Sorbent preparation with two slurry tanks and one tower mill (attritor)

As envisioned, spent sorbent and boiler fly ash are collected in the electrostatic precipitator (ESP) or baghouse, which have been modified mechanically for higher loadings. A portion of the waste material is fed to a slurry tank along with fresh CaO, a larger portion is diverted directly to the mixer, and the remainder discarded as waste. From the first tank, CaO/fly ash slurry is pumped to a constant stir tank reactor (CSTR), where the slurry is constantly recirculated through a tower mill. The combination of particle abrasion and heated water promotes the lime/silica reaction to form a calcium silicate phase on fly ash surfaces. The product silicate slurry is then routed to the mixer and blended with dry recycle solids to form a damp, free-flowing powder that is then injected into the duct at least 0.75 sec upstream of the dust collector. Duct velocities greater than 15 m/sec are necessary to ensure good gas/sorbent contact and to keep duct walls swept clean of agglomerates. Although no studies have been made of silicate waste disposal, the waste is physically and chemically similar to spray dryer FGD waste except that it is more hygroscopic and pozzolanic. Results of one study show capital costs of \$60-85/kW and operating costs of 6 to 7 mills/kWh, assuming 2.7% sulfur Midwestern coal and a SR of 1.2⁷.

Optimism that 90 percent SO₂ at a SR of 1.2 or less will be achieved on a commercial scale is based on in-house pilot and two previous field evaluations. EPA's in-house pilot (85 m³/hr) plant has consistently shown 80 percent utilization with tower mill-ground sorbent (GCA) (Figure 11). The first field evaluation on a 1700 m³/h slipstream at the University of Tennessee pilot plant showed 80+ and 90+ percent calcium utilization in-duct and in-duct/baghouse, respectively, using unground sorbent, when ADVACATE was integrated with the Moist Dust Injection process (Figure 13).⁷ When the Limestone Injection Multistage Burner (LIMB) process was augmented by ADVACATE injection on a 3400 m³/hr slipstream with ESP control, up to 97 percent additional SO₂ removal was realized.⁶ Field tests on a 10 MW_e slipstream pilot plant at TVA's Shawnee facility are currently scheduled to begin in January 1992. From this effort, design and operating data for a full-scale system should be derived.

To support these efforts, Acurex Corporation and AEERL/EPA will continue research in the following process areas with federal funds and funding from appropriate vendors:

- Optimization of particle attrition
- Optimization of slurry/solids mixing
- Integrated small pilot evaluation
- ESP performance
- Evaluation of fly ashes and alternative calcium sources
- Effects of additives and impurities

Concurrent with the above efforts, Acurex and EPA will be developing non-fly-ash ADVACATE technology for possible use on non-coal-fired combustion sources of acid gases, including waste combustors, smelters, and industrial boilers.

CONCLUSIONS

1. Hydration time and temperature have significant effects on sorbent reactivity for sorbents prepared from ground fly ash and lime. Sorbent reactivity increases with increasing hydration time and temperature. Sorbents prepared from ground fly ash were always more reactive than sorbents made from unground fly ash at the same hydration conditions.
2. For sorbents hydrated at 90 °C (194 °F) for 3 h, reactivity tends to increase as the amount of fly ash grinding increases prior to sorbent preparation.
3. Reactivity tends to increase as sorbent surface area increases for sorbents hydrated from 1 to 6 h at 60 to 100 °C.
4. Pilot-plant results verify that initially grinding the fly ash before hydration with Ca(OH)₂ decreases the optimal hydration time from 12 to 3 h.

5. The inherent moisture content of the ADVACATE sorbent greatly affects its overall reactivity toward SO_2 .
6. Initially using ground rather than unground fly ash provides for a more reactive sorbent in subsequent passes, owing to the higher initial surface area associated with the ground ash.
7. Pilot-scale data suggest that possible equilibrium, or steady-state operation, can be achieved by the third or fourth pass of recycle material. Recycle III material demonstrated $\text{Ca}(\text{OH})_2$ utilization of up to 86 percent.

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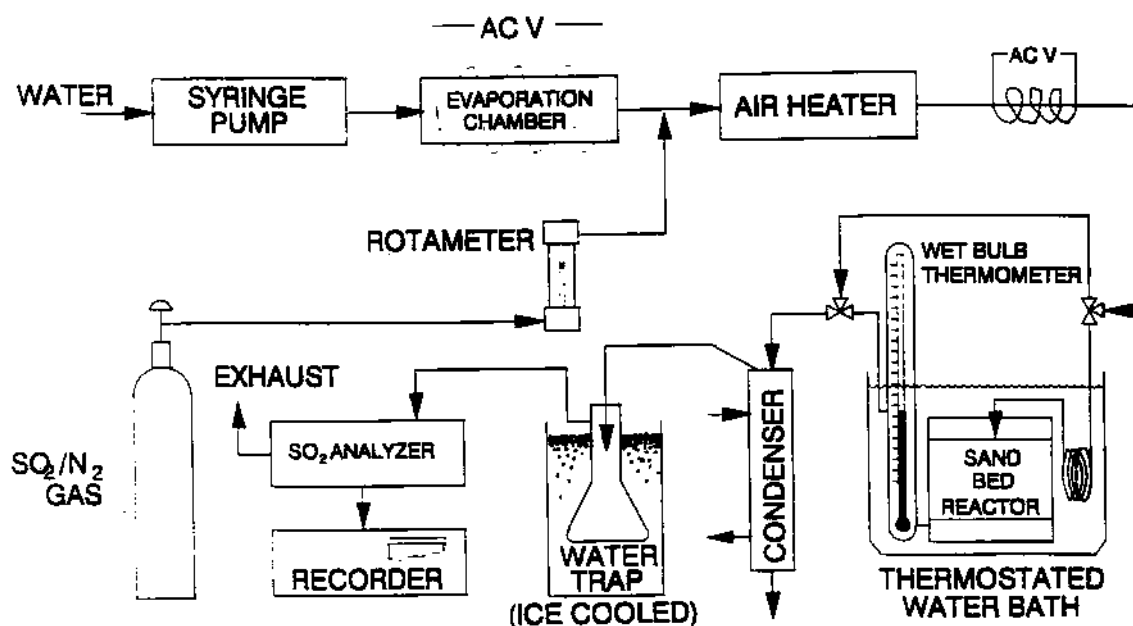


FIGURE 1. Schematic of sand-bed reactor bench-scale facilities.

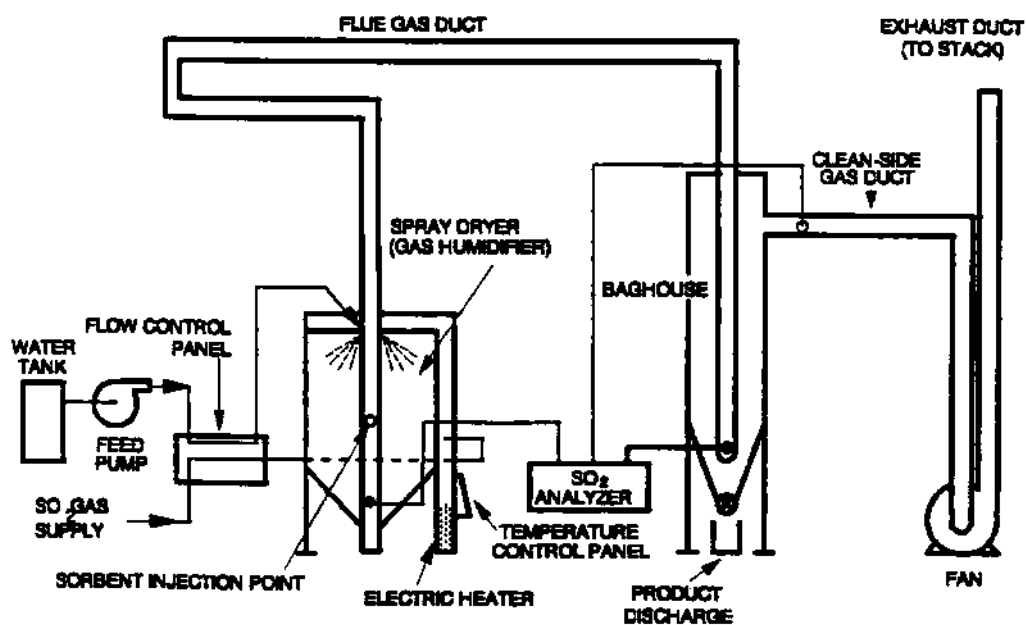


FIGURE 2. Schematic of duct injection pilot-plant facility.



FIGURE 3. SEM photomicrograph of "as received" Clinch River fly ash (CR) sample, x2000.



FIGURE 4. SEM photomicrograph of ground Clinch River fly ash (UPCR) sample, x5000.



FIGURE 5. SEM photomicrograph of sorbent made from ground Clinch River fly ash (BCR) hydrated with Ca(OH)_2 , at a 3:1 weight ratio, for 3 h at 90 °C (194 °F).

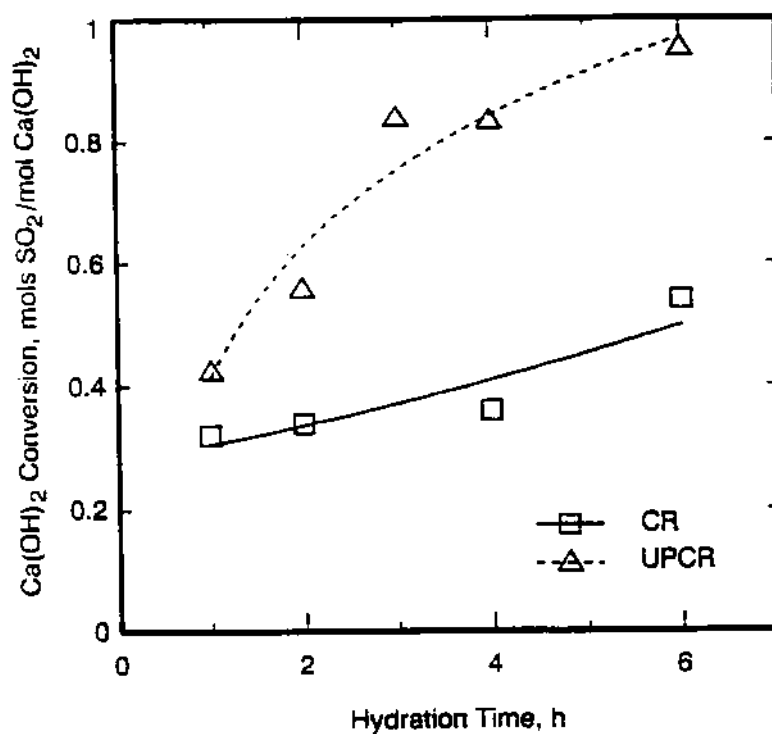


FIGURE 6. Conversion as a function of hydration time at 90 °C (194 °F), fly ash to Ca(OH)_2 weight ratio of 3:1 (conditions in the sand-bed reactor: 60 percent relative humidity, 1000 ppm SO_2 concentration).

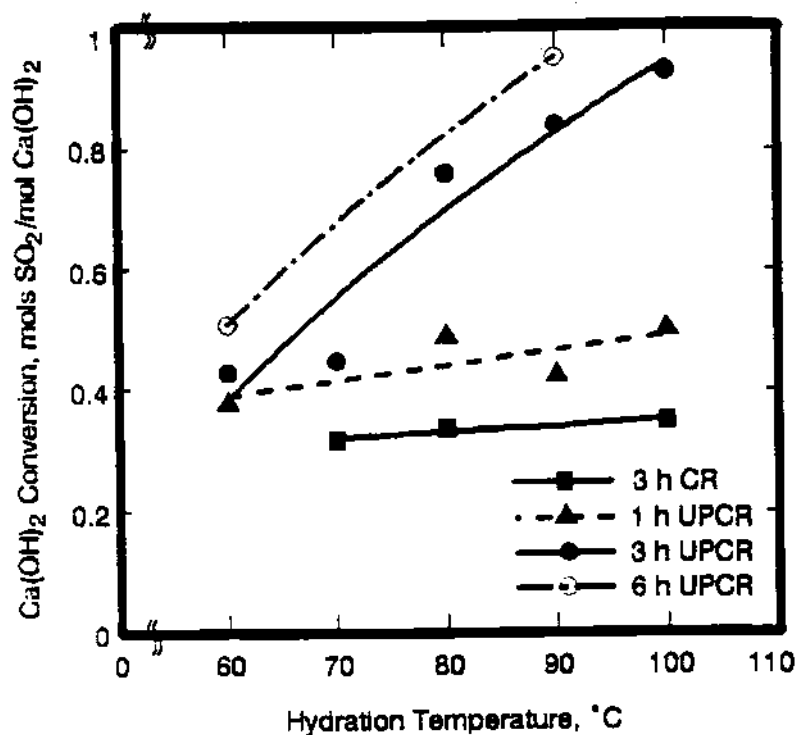


FIGURE 7. The effect of hydration temperature and time on the conversion of $\text{Ca}(\text{OH})_2$, (conditions in the sand-bed reactor: 60 percent relative humidity, 1000 ppm SO_2 concentration).

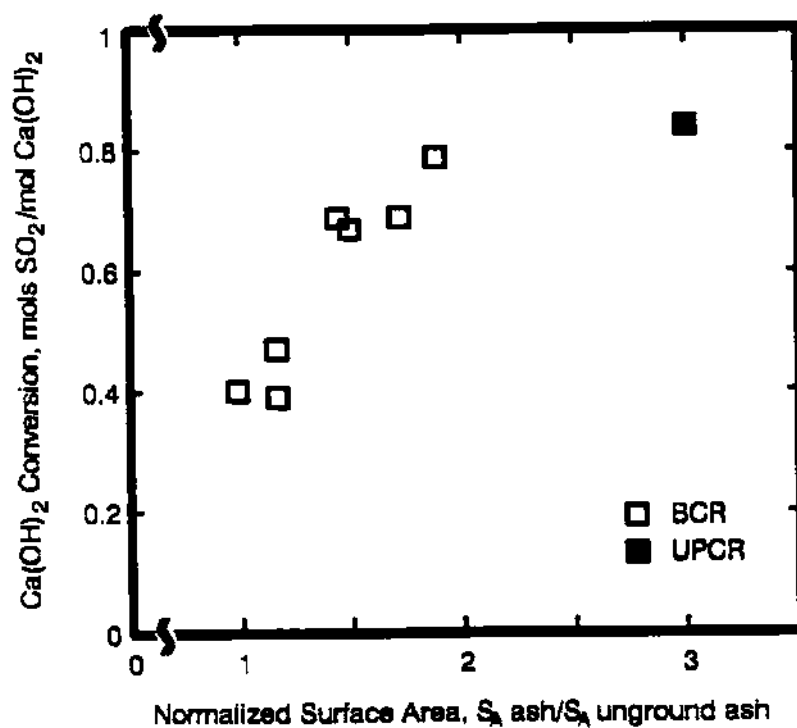


FIGURE 8. Effect of fly ash initial surface area on conversion of sorbents hydrated at 90 °C (194 °F) for 3 h at a fly-ash-to- $\text{Ca}(\text{OH})_2$ weight ratio of 3:1 (conditions in the sand-bed reactor: 60 percent relative humidity, 1000 ppm SO_2 concentration).

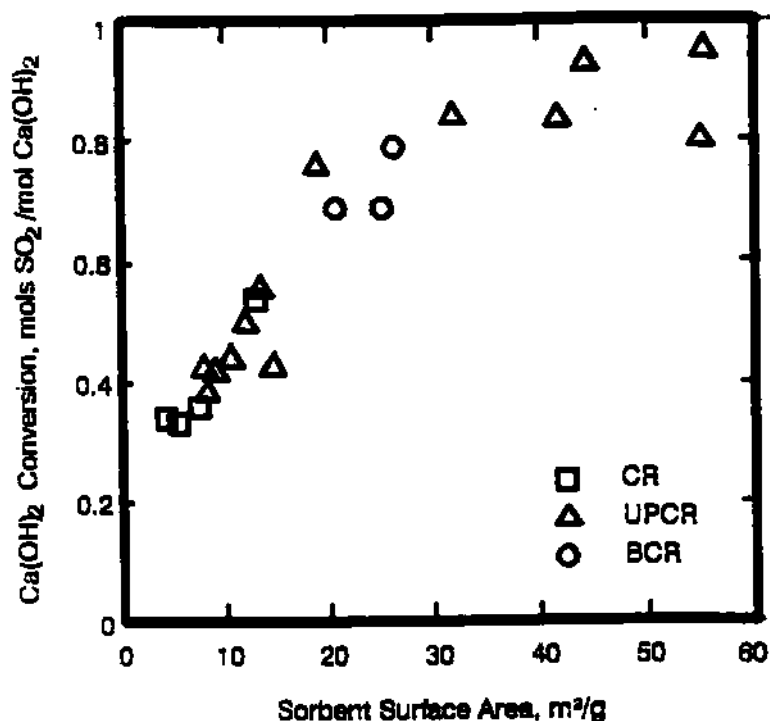


FIGURE 9. Effect of sorbent surface area on conversion for sorbents prepared at a fly-ash-to- Ca(OH)_2 weight ratio of 3:1 (conditions in the sand-bed reactor: 60 percent relative humidity, 1000 ppm SO_2 concentration).

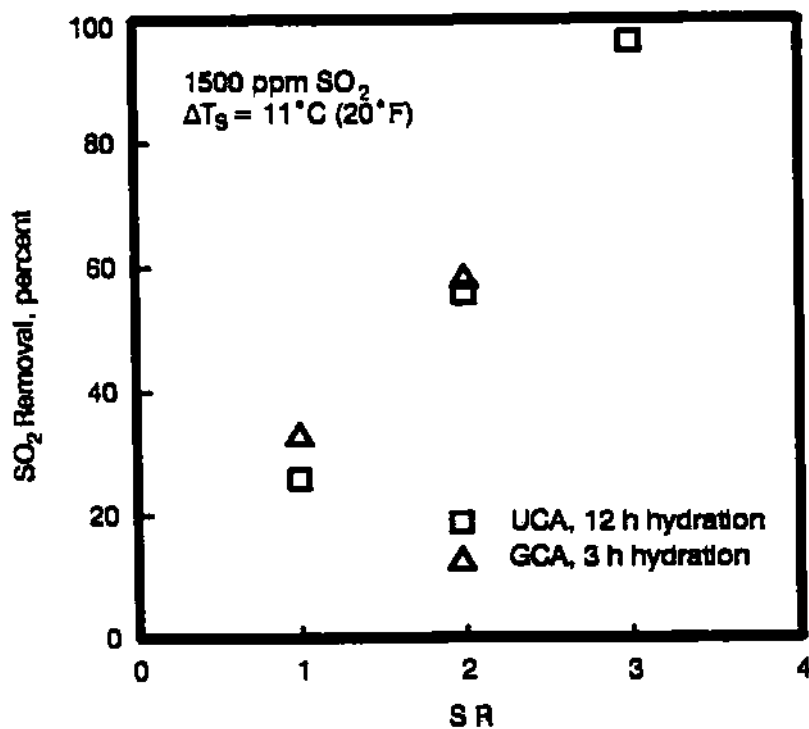


FIGURE 10. Comparison of CR ADVACATE (UCA and GCA).

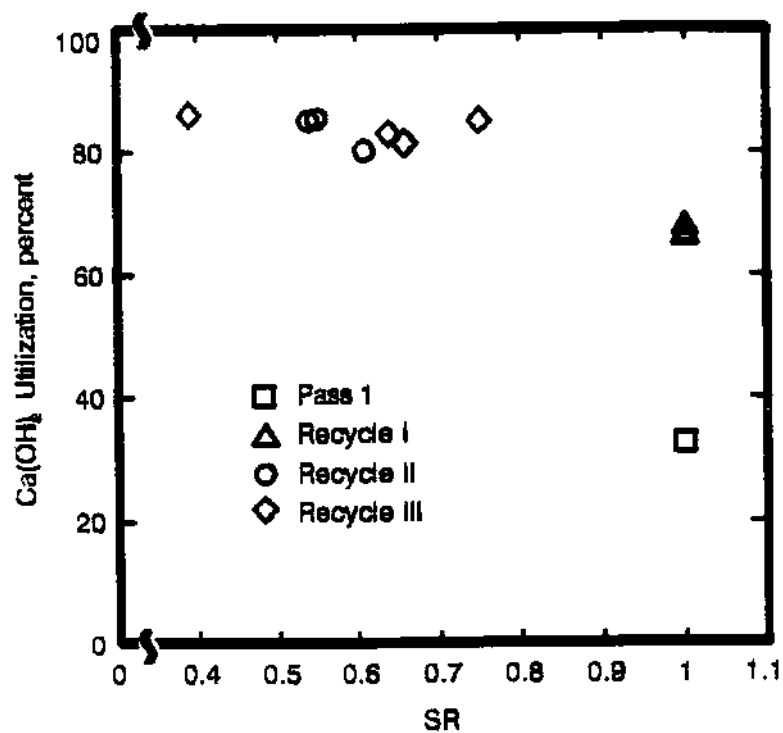


FIGURE 11. Calculated utilization of $\text{Ca}(\text{OH})_2$ in ground CR (GCA) sorbent.

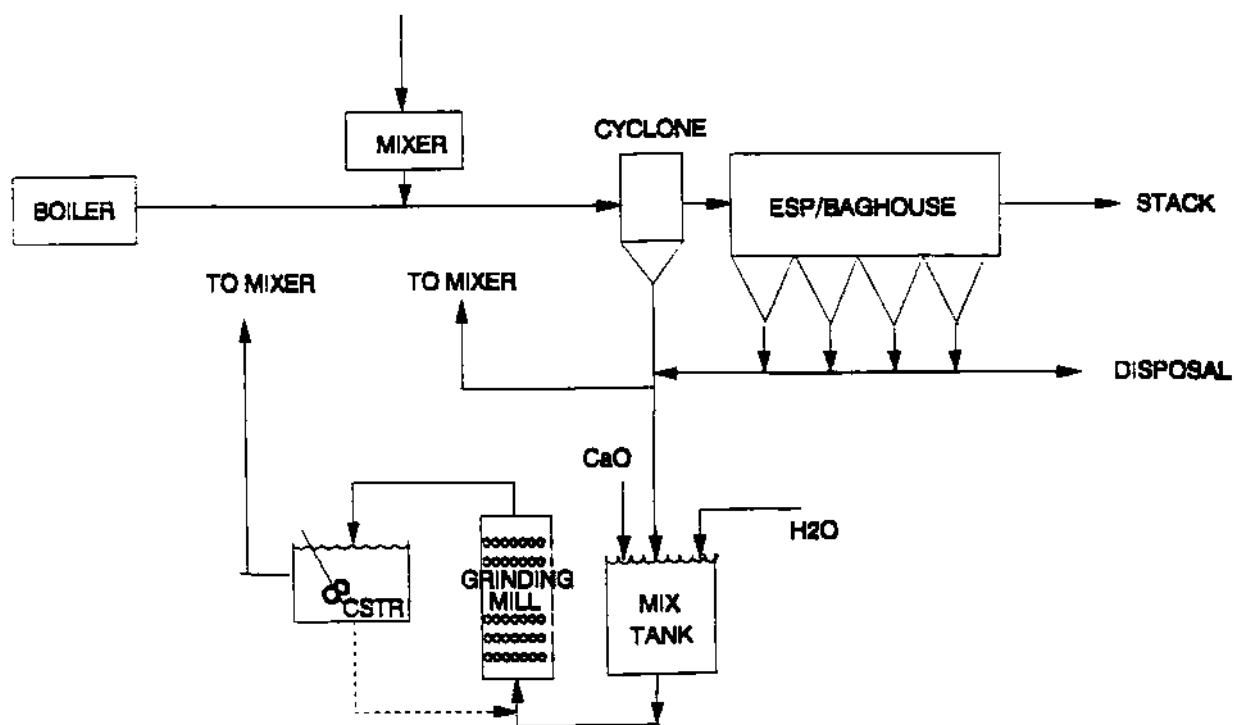


FIGURE 12. Commercial scheme of the ADVACATE process.

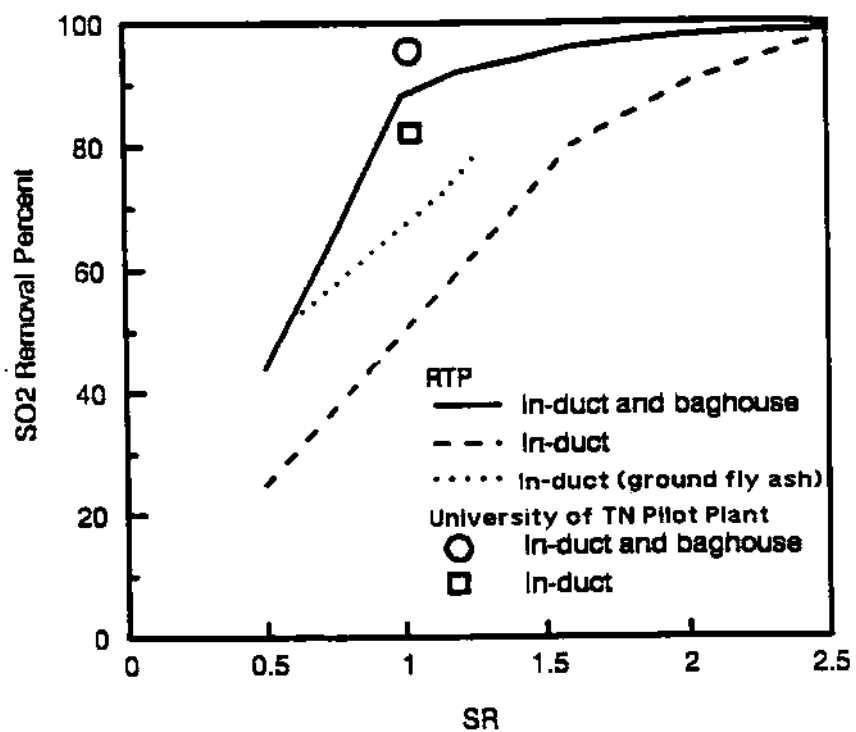


FIGURE 13. The effect of SR on SO₂ removal during calcium silicate damp injection at near equilibrium conditic