

FLUE GAS CLEANUP STUDIES WITH THE MOVING-BED COPPER OXIDE PROCESS

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INTRODUCTION

The Moving-Bed Copper Oxide Process is a dry, regenerable sorbent technique that uses supported copper oxide sorbent to simultaneously remove SO₂ and NO_x emissions from flue gas generated by coal combustion. This process can meet the goals of a Department of Energy initiative to develop flue gas control technologies to remove 99% and 95% of SO₂ and NO_x, respectively, at a low cost for emission control. The process can be integrated into the design of advanced power systems, such as the High Performance Power System (HIPPS) [1,2]. This process has been the subject of a small scale experimental test program with Rockwell and is currently being evaluated in a Life-Cycle Test System (LCTS) with a moving-bed flue gas contactor at DOE's Pittsburgh Energy Technology Center. An experimental data base being established will be used to verify reported technical and economic advantages, optimize process conditions, provide scaleup information, and validate absorber and regenerator mathematical models.

The chemistry of the process is relatively straightforward. In the absorption step, SO₂ in the flue gas reacts with copper oxide, supported on small spheres of alumina, to form copper sulfate. Ammonia is injected into the flue gas before the absorption reactor and an SCR-type reaction occurs that reduces the nitric oxides in the flue gas.

In the regeneration step, the copper sulfate is reduced in a regenerator via a reducing agent, such as natural gas, producing a concentrated stream of SO₂. Another advantage of the process is that the lower pressure drop across the moving-bed configuration reduces power consumption and thus influences the overall economic costs. The moving-bed process also has a lower projected sorbent attrition rate compared with other reactor configurations. Lastly, high sorbent utilization (the degree to which the sorbent absorbs its theoretical maximum level of SO₂ based on the metal oxide loading on the alumina sphere) can be realized in a moving-bed design.

In this paper, the results from four process parametric test series (MBCUO-2 through MBCUO-5) with the LCTS are discussed. During MBCUO-2 and MBCUO-3, the effect of absorber parameters on sorbent performance (e.g., SO₂ removal) and operational performance was investigated. UOP sorbent was used in this work. During MBCUO-4, natural gas regeneration was evaluated with the UOP sorbent. In MBCUO-5, Grace sorbent with a slightly higher copper loading (7.0% versus 6.4% in UOP sorbent) was used to further evaluate natural gas regeneration and initially investigate hydrogen regeneration.

EXPERIMENTAL

The process has been investigated using the LCTS designed, constructed, and operated at PETC. Figure 1 shows the schematic diagram of the LCTS. The LCTS has the capability of operating in a continuous integrated mode, specifically related to the absorption and regeneration steps. Flue gas can be generated by a combustor that burns approximately 40 lbs/hr of pulverized coal, resulting in a nominal flue gas flow rate of 110 scfm. The combustor can also be fired using natural gas. Only tests with natural gas firing are discussed here. The flue gas exiting the combustor passes through heat exchangers so that a prescribed inlet absorber temperature can be maintained. The flue gas can be spiked with SO₂ and NO supplied from compressed gas cylinders to adjust these concentrations to those of the desired test levels. Typically, NO is spiked for a 1-3 hour period after steady-state is reached at a set of parameters. Consequently, ammonia is injected into the flue gas upstream of the absorber to initiate the catalytic reduction of nitrogen oxides to nitrogen and water vapor in the absorber. A controlled flue gas bypass provides a slip stream around the absorber, enabling the desired flow of flue gas through the absorber to be maintained. After passing either through or around the absorber, the flue gas is cooled by humidification and then passed through a baghouse for removal of any residual fly ash.

The sorbent process stream in the LCTS involves a closed-loop cycle of sorbent transported through four

major vessels. The sorbent absorbs flue gas contaminants in the moving-bed absorber, passes through a fluidized-bed sorbent heater where the sorbent is heated with air and the products of a natural gas combustor, enters a regenerator where sulfur-containing species are released after treatment of the sorbent with a reducing gas, and lastly passes through a fluidized-bed air cooler prior to returning to the absorber. The sorbent is gravity fed through all four vessels, except for the line connecting the absorber exit with the fluidized-bed sorbent heater. In this line, a pneumatic transport system sends the sorbent to an elevated location (i.e., the sorbent heater) to repeat the gravity-fed sorbent cycle. The hot air from the sorbent heater is vented through a baghouse for dust removal, and the regenerator off-gas is vented through an incinerator.

The entire system operates at pressures close to ambient; the various vessel pressures are maintained by forced draft and induced draft blowers and control valves. The absorber and regenerator have externally mounted heaters for temperature maintenance, and typically operate at 750 and 850°F, respectively. Gas analyzers and various instrumentation have been used in the experimental characterization of the process.

Steady-state at a set of process parameters was typically determined by achieving set points for key parameters and calculated quantities (e.g., SO₂ removal, certain thermocouple readings from the absorber and regenerator, regenerator off-gas composition, etc.). Once at the steady-state condition, operation of the LCTS continued for an additional period of time. Data was then averaged over this period of time or a smaller representative era within the period. The parameters and calculated quantities in the summary tables represent the average of this data or calculation over the designated steady-state period. Absorber removal efficiencies are corrected for air in-leakage. Also, inlet and outlet analyzer readings for the absorber are adjusted to reflect a constant inlet oxygen concentration of 3.6%. (Calculated quantities are defined in reference [3].) Tables 1-4 are summaries of the results from the respective tests MBCUO-2 through MBCUO-5.

DISCUSSION AND RESULTS

Absorber Parametric Testing

Sorbent performance and operational performance of the LCTS are presented in the attached tables for various parametric conditions. The UOP sorbent used was 1/16-inch diameter spheres of alumina with a 6.4 weight percent copper loading.

During earlier shakedown studies, several issues were resolved so that a baseline test could be defined. One concern was that the regeneration step with natural gas was not entirely effective. A batch test in the regenerator identified the regeneration conditions that would be used throughout Tests MBCUO-2 and MBCUO-3. A temperature of 850°F and a 3-hr sorbent residence time with an excess of natural gas (typically twice the stoichiometric requirement) was sufficient to regenerate the sorbent.

The moving-bed absorber mathematical model of Young and Yeh [4] was used to define a baseline test so that changes in parameters could be quantified in the parametric study. The shakedown tests also indicated that sorbent flow in the original reactor design was not ideal, and cold flow studies dictated that the reactor width be reduced from 2 ft to 1 ft. Final absorption conditions for the baseline were a cross-sectional area of 8-ft², bed thickness of 5 inches, temperature at 750°F, sorbent flow of 1-lb/min, and a flue gas flow of 110-scfm produced by burning natural gas and spiking to a level of 2250 ppm of SO₂. Regeneration conditions described above were employed. Periodically during the parametric testing, the baseline condition was repeated to assure that the activity of the sorbent, as well as the operational response of the LCTS, was maintained.

The effects of absorption temperature, inlet SO₂ concentration, sorbent flow, and flue gas flow on the pollutant removal efficiencies in the absorber were systematically investigated. Absorber model predictions were also compared to the actual SO₂ removals at a set of conditions.

Temperature. In the temperature study, four temperatures of absorption were investigated: 591, 705, 749, and 801°F, corresponding to the test periods MBCUO-3-8, MBCUO-3-2A, MBCUO-3-1A, and MBCUO-3-3, respectively.

It should be noted that the operating temperature for a commercially designed absorber would be 750°F, because the flue gas temperature from a utility boiler economizer is typically near 750°F. A nominal temperature of 750°F would allow the absorber to be placed after the economizer but before the air preheater. Results of the LCTS testing (see Figure 2) would indicate that temperature fluctuation between 700 to 800 °F due to upsets in a commercial process would not have an appreciable impact on SO₂ removal. However, lower temperatures than 700°F result in higher rate of drop in sorbent activity as depicted by the 76.6 percent removal at the 591°F temperature level. The line in Figure 2 represents the prediction for SO₂ removal using the absorber model of Young and Yeh [4].

Inlet SO₂ Concentration. The impact of the inlet flue gas SO₂ concentration was also investigated. Essentially, as the SO₂ concentration increases, the effective Cu/S feed ratio decreases, thus causing a decrease in removal efficiency. Results can be seen in Figure 3 when the concentration levels of SO₂ were 1500, 2242, 3059, and 3244

ppm, simulating the concentrations in flue gas when a mid- to high-sulfur coal is combusted. The respective SO₂ percent removals for periods MBCUO-3-4, MBCUO-3-1A, MBCUO-2-3, and MBCUO-3-5 were 96.3, 93.2, 85.9, and 81.2, respectively. The line in Figure 3, which closely follows the experimental data, represents the absorber model prediction.

Sorbent Flow. The effect of changing the sorbent flow on the SO₂ removal efficiency was also investigated. During this set of parametric tests, sorbent samples were withdrawn from the regenerator to verify that the regeneration step was complete. Thus the sorbent flowing into the absorber should have the same available copper for each sorbent flow variance. Effects of varying the sorbent flow can be seen at two gas flow conditions. The first is at a 55 scfm gas flow where sorbent flow was increased from 0.5 to 1.0 lb/min. A corresponding increase in SO₂ removal (94.0 to 95.2 percent) occurred as seen in MBCUO-2-1 and MBCUO-2-2A. At 110 scfm, the sorbent flow rates for three sets of conditions for periods MBCUO-3-6, MBCUO-3-1A, and MBCUO-3-7 were 0.75, 1.0, and 1.25 lb/min, respectively, with corresponding SO₂ removals of 86.5, 93.2, and 91.1 percent. Except for the latter point as seen in Figure 4, the trend is the same, indicating that a higher sorbent flow of regenerated sorbent will enhance the SO₂ removal efficiency of the absorber.

NO_x Removals. As mentioned previously, NO was injected after certain test period conditions attained steady-state. Once the chemiluminescent analyzers established the NO spike concentration, ammonia was injected to a flow that established a 90 or 95% NO_x removal by again following the chemiluminescent analyzers. The molar flow of ammonia was determined by the flow settings, and a molar ratio of ammonia to nitric oxides was then calculated. From Table 2, the ratio in MBCUO-3 was between 0.96 and 1.06, and most conditions were below 1.0. A similar NH₃/NO ratio had been found to be adequate in earlier copper oxide work, indicating that a molar ratio less than one can reduce a vast majority of the NO_x. A wet chemical sampling technique that bubbled a slip-stream of flue gas through a hydrochloric acid solution was used to determine if ammonia slippage occurred. The solution is then analyzed by using an ion electrode technique. No ammonia slippage has been detected.

Sulfur Analysis of the Spent Sorbent. During the course of the testing, sorbent samples were withdrawn from the absorber and regenerator at various locations along the length of each respective reactor. While sampling sorbent from the absorber, the flue gas bypassed the reactor; for the regenerator, the reactor was purged with nitrogen before the samples were taken. A metal probe (thief) was inserted at the port and a vacuum drew the sample into a container. The probe was gradually moved back and forth within the vessel in an attempt to obtain a representative sample at a horizontal cross-section of the reactor. These samples were then analyzed for total sulfur content by using a LECO sulfur analyzer. Caution must be used in interpreting these results since some locations prior to a change after MBCUO-5 may not have given a representative sample.

For the MBCUO-2 and MBCUO-3 tests, the extent of regeneration was substantial with a high sorbent residence time and with an excess natural gas flow. The sulfur content on the regenerated sorbent was typically low. However, residual sulfur was always present on the sorbent; the form of the residual sulfur is still to be determined. It is speculated that some residual sulfur could exist in the form of aluminum sulfate [5].

Regeneration Parametric Study

A regeneration parametric study was conducted to determine efficient and economical ways to reduce copper sulfate in the spent sorbent to copper. The regenerated sorbent is then reused, through closed-loop recycling, to remove SO₂ and NO_x from flue gas. Regeneration parameters investigated were the inlet CH₄/S molar ratio, sorbent residence time, and temperature. The inlet CH₄-to-S molar ratio is defined as moles of inlet CH₄ to the regenerator per unit time to moles of inlet SO₂ to the absorber per unit time. To simplify the computation, natural gas, which was used as a regenerant, was assumed to be 100% CH₄, although in actuality it is closer to 90% with additional hydrocarbons in the natural gas. Test information was not affected when this method of calculation was consistently applied throughout the research effort.

Test data are presented in Table 3 for the regeneration study using natural gas as regenerant. Absorber process conditions were held constant throughout the tests with the realization that a regeneration parametric change would not only affect the regeneration results (e.g., gas and sorbent composition from the regenerator) but also the SO₂ removal efficiency of the absorber. Unlike Tests MBCUO-2 and MBCUO-3, certain nitrogen purges around the regenerator were shut off during this test. Thus, the CH₄, SO₂, and CO₂ compositions from regenerator off-gas should add up to 100%. These components were obtained from the continuous gas analyzers and were periodically checked by taking a grab gas sample and having it analyzed by gas chromatography. Comparisons are usually excellent (within +/- 3%). Again the UOP sorbent with copper content of 6.4% was used in this test.

Inlet CH₄/S Molar Ratio. During the test, an excess of natural gas was present at all times and results from varying

the ratio from 0.59 to 1.17 are shown in Figure 5. Excess natural gas was used to ensure no shortage of regenerant in the regenerator. Results are from Periods MBCUO-4-3, MBCUO-4-2, and MBCUO-4-1. It can be seen that as the molar ratio increases, the methane concentration in the regenerator off-gas increases and the corresponding SO₂ concentration decreases because of the dilution effect of the methane. However, as the ratio approaches the stoichiometric amount required from the process chemistry (0.5/1), the activity of the sorbent in the absorber decreases. This would probably be magnified if the residence time were not 3 hr. Also, the sulfur on the sorbent out of the regenerator appears to be higher at the lower molar ratio.

Sorbent Residence Time. The impact of the residence time within the regenerator was also investigated. Residence times of 60 min (MBCUO-4-7), 120 min (MBCUO-4-4), and 180 min (MBCUO-4-1) were studied, and the results are shown in Figure 6. Attempts were made to hold constant all other parameters within the regenerator. From the results, it appears that as the residence time increases, better regeneration occurs as noted by a decreasing methane gas exit concentration and an increasing SO₂ concentration. The SO₂ removal efficiency in the absorber increased with increasing regenerator residence time; the residual sulfur on the sorbent decreased slightly with increasing residence time.

Temperature. The impact of temperature on regeneration is shown in two separate comparisons: at a 120 min residence time and at 850°F (MBCUO-4-4) and 937°F (MBCUO-4-6A); at a 60 min residence time and at 815°F (MBCUO-4-8) and 876°F (MBCUO-4-7). In the first case, the absorber activity after regeneration at the extremely high temperature of 937°F was lower (probably within the limits of uncertainty) than after the 850°F regeneration. This could indicate that at 850°F and 120 min residence time, the sorbent is being adequately regenerated. It must be recognized that after the high temperature regeneration, the sulfur content on the sorbent was the lowest seen (0.6 versus 0.93 wt%).

The other impact of temperature was determined at a residence time of 60 min and temperatures of 815°F and 876°F. The lower temperature adversely affected the regeneration as denoted in the higher concentration of methane in the exit gas stream at the lower temperature and the corresponding lower concentration of carbon dioxide. The absorber SO₂ removal was significantly lower (76.6 versus 83.5) and the sulfur content of the sorbent at the lower temperature was high (1.47 versus 1.02 wt%).

Natural Gas and Hydrogen Regeneration. A Grace sorbent that contained 7.0 wt% copper was used during MBCUO-5. The initial test condition was identical to a previous test period with the UOP sorbent using natural gas as the regenerant. Parametric conditions for this base case were chosen to match a test period from MBCUO-4. Additionally, hydrogen regeneration was investigated.

Four test periods during MBCUO-5 were devoted to hydrogen regeneration. The initial operation in going to hydrogen from methane was complicated because of the exothermic nature of the hydrogen regeneration. The regenerator was run at an elevated temperature during the first test period under hydrogen, but the next two periods were conducted at an 850°F regenerator temperature followed by a 750°F condition. Heater controls on the regenerator were observed frequently. All tests were at the same absorption conditions and used hydrogen at a 120 min sorbent residence time in the regenerator and at H₂/S molar ratio of approximately 4.7. The high concentration of water in the regenerator exit gas caused some operational problems.

Test period MBCUO-5-1 can be compared with MBCUO-5-5B. Conditions were approximately the same except that a nitrogen diluted hydrogen gas was used in the latter period rather than natural gas. Results indicate that the sorbent absorption reactivity was a little lower after the hydrogen regeneration due to higher residual sulfur levels entering the absorber. The nitrogen dilution was used in the hydrogen test because of operational problems downstream of the regenerator. Without the added nitrogen dilution with the hydrogen flow, regenerator gas concentration results would be similar to that of MBCUO-5-5A, with about 80% of the exit gas as SO₂.

From MBCUO-5-5B, negligible hydrogen was seen in the regenerator off-gas, as determined from gas chromatography. Also, the sulfur content on the sorbent from the regenerator was greater than in any previous testing. Duplicate runs confirmed this.

The impact of temperature of hydrogen regeneration can be seen in test periods MBCUO-5-5, MBCUO-5-5B, and MBCUO-5-7, where the temperatures were 962, 851, and 755°F, respectively. Results from these tests indicate that the SO₂ removal efficiencies did not vary significantly and the concentration of SO₂ exiting the regenerator was near the same for all three cases. Again, no excess hydrogen was seen in the exit gas stream, and the sulfur content on the sorbent exiting the system was high in all these cases. This could indicate that the sorbent sulfur was not entirely regenerated to a gaseous form such as SO₂. Rather, some solid compound or intermediate of sulfur formed on the surface of the sorbent. Findings by McCrea et al. [5] and Bjornbom et al. [6] indicate that more hydrogen than predicted by the simple copper sulfate/hydrogen reduction equation is needed due to the occurrence of side

reactions. This result with respect to hydrogen regeneration will be further investigated.

SUMMARY

A parametric study of the Moving-Bed Copper Oxide Process was conducted using the LCTS. The effects of various parameters on the absorption step of this flue gas cleanup technique were systematically investigated. High removals of SO₂ were obtained at most conditions. Removal efficiencies within the temperature range of 700-800°F did not vary significantly. A decrease in the flue gas flow rate, a decrease in the inlet SO₂ concentration, and an increase in the sorbent flow rate would all tend to enhance the SO₂ removal capabilities of the absorber. The computer-simulation model [4] of the moving-bed reactor agrees very well with the experimental SO₂ removal data.

Regeneration studies investigated the optimization of the natural gas regeneration step regarding temperature, reducing gas stoichiometric ratio, and sorbent residence time. A sufficient regeneration temperature with natural gas is near the reported 850°F temperature, although a higher regeneration temperature improves the level of sorbent regeneration. As the CH₄/S molar ratio increases or the sorbent residence time increases, the regeneration improves.

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