

INVESTIGATION OF THE MOVING-BED COPPER OXIDE PROCESS FOR FLUE GAS CLEANUP

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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 SO_2 and NO_x emissions from flue gas generated by coal combustion. This process can meet the goals of a Department of Energy (DOE) initiative to develop flue gas control technologies to remove 99% and 95% of SO_2 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 Low-Emission Boiler System (LEBS) or the High-Performance Power System (HIPPS) [1]. This flue gas cleanup technique 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, SO_2 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 a selective catalytic reduction-type reaction occurs that reduces the nitric oxides in the flue gas. In the regeneration step, the copper sulfate is reduced in a regenerator with a reducing agent, such as natural gas, producing a concentrated stream of SO_2 . Another advantage of the process is that the low 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 SO_2 based on the metal oxide loading on the alumina sphere) can be realized in a moving-bed design.

In this communication, the results from several process parametric test series with the LCTS are discussed. The effects of various absorber and regenerator parameters on sorbent performance (e.g., SO_2 removal) were investigated. Sorbent spheres of 1/8-in diameter were used as compared to 1/16-in sized sorbent of a previous study [2]. Also discussed are modifications to the absorber to improve the operability of the LCTS when fly ash is present during coal combustion.

EXPERIMENTAL

The process has been investigated using the LCTS, which has been diagrammed and described previously [3]. The LCTS has the capability of operating in a continuous integrated mode, specifically related to the absorption and regeneration steps. The sorbent performance in the moving-bed configuration has been characterized by using flue gas that can be produced by combusting natural gas or by combusting pulverized coal (34 lb/hr of an Illinois Old Ben Mine No. 24) with some natural gas support, resulting in a nominal flue gas flow rate of 110 scfm. The flue gas is spiked with SO₂ and NO supplied from cylinders to adjust these concentrations to those of the desired test levels. Ammonia is injected into the flue gas upstream of the absorber to facilitate the catalytic reduction of nitrogen oxides to nitrogen and water vapor in the absorber. The sorbent process stream in the LCTS involves a closed-loop cycle of sorbent transported through four major vessels: the moving-bed absorber, a fluidized-bed sorbent heater, the regenerator, and a fluidized-bed air cooler. Sorbent hoppers located between the vessels isolate the activities occurring in each vessel and provide for metered transport of the sorbent around the closed-loop cycle.

An earlier study with the LCTS entailed using a 1/16-in diameter sphere of copper oxide/alumina sorbent [2]. However, recent economic and industrial considerations related to bed pressure drop and sorbent transport have guided the scope of the study to include a larger-sized sorbent. Unless noted, the results in this communication allude to those obtained while using 1/8-in diameter sorbent spheres that were produced by Alcoa and contain a copper loading of about 6.6 weight percent. The sorbent was formulated by an incipient wetness technique using a solution of copper sulfate as the impregnant. Initial activation of the sorbent was conducted in the regenerator, either in a batch or continuous mode.

Modifications to the LCTS were required to effectively transport, heat, and cool the larger and denser Alcoa sorbent. The major changes consisted of inserting a sleeve into the fluidized-bed cooler and the fluidized-bed heater to reduce the effective cross-sectional area at the available fluidizing gas supply, since the fluidization velocity of the larger 1/8-in sorbent was much greater than that of the 1/16-in sorbent used in the past.

Also, operational difficulties while burning coal in the LCTS needed to be eliminated. If the original absorber design was used during coal burning, sorbent performance in the absorber would degrade as fly ash accumulated within the bed and/or on the sorbent retention screens. Removal of SO₂ in the absorber typically decreased while pressure drop through the absorber increased. Two modifications were made to the absorber to negate this problem: a new design of the sorbent retention screens and an increase in the pulsing capability of the absorber. The initial design of the sorbent retention screen (an inlet and outlet screen envelop the moving-bed of sorbent in the absorber) incorporated a square, stainless steel wire mesh (35 mesh -- 0.0176-in square opening by 0.011-in wire diameter) affixed by tack-welding to a stainless steel perforated plate (0.125-in thick, 1-in diameter holes on a hexagonal pattern with 1.25-in center-to-center spacing). However, due to the aforementioned ash plugging problem, a new retention screen design using vertical bars fabricated by Hendrick Manufacturing Company was conceived. The new retention screen consists of stainless steel vertical bars spaced slightly apart, resulting in vertical slots that retain particles of a certain diameter. The cross-sectional area of each bar is shaped like a truncated "golf tee" so that any particle able to penetrate the minimum slot opening encounters a diverging nozzle arrangement, and thus the particle is free to migrate through the rear of the screen. At the sorbent/screen interface, the bar measures 0.140-in width and spaced 0.030-in apart (i.e., the minimum slot opening) so that particles less than 0.030 inches slip through the minimum slot opening.

A design change to the back-pulsing assembly was also incorporated. The original assembly consisted of eight chambers segmenting the cross-sectional area of the rear retention screen. Each chamber provided screen coverage of 6-in bed width by 4-ft bed height. Two horizontal rows, each containing 4 chambers,

provided total screen coverage of 2-ft bed width by 8-ft bed height. Each chamber contained one venturi nozzle to deliver the back-pulse. In an effort to minimize any flow disruption to the furnace, the chambers were sequenced to pulse such that only a quarter of the total bed area was back-pulsed at one time. An increase in back-pulsing capability was implemented by doubling the number of venturi in each chamber from one to two. Also, better sealing of the chamber to the rear screen was incorporated.

DISCUSSION AND RESULTS

Sorbent performance and operational performance of the LCTS are presented in Tables 1 and 2 for absorption and regeneration parametric studies, respectively. A similar study was conducted with a 1/16-in diameter sorbent using spiked flue gas from natural gas combustion [2]. However, in the present study, some testing periods were conducted to confirm an adequate performance with the larger sorbent and to validate the design of the modified absorber while burning coal. The absorber bed had dimensions of 8-ft height, 1-ft width, and 5-in depth throughout the testing. Periodically during the parametric testing, a baseline condition was repeated to assure that the activity of the sorbent, as well as the operational response of the LCTS, was maintained. The parameters and calculated quantities in the tables represent the average of the data or calculation over a designated steady-state period. Nitric oxide was injected after certain test period conditions attained steady-state, followed by ammonia injection to reach a desired level of NO_x removal. During coal combustion, spiking with NO was not necessary.

During the absorption study, the regeneration parameters were typically held at 850°F, a residence time of 180 min, and a natural gas-to-sulfur molar ratio of at least 1. The effects of inlet SO_2 concentration and sorbent flow on the pollutant removal efficiencies in the absorber were systematically investigated. A temperature scan was not conducted since past investigations with copper oxide indicated the optimum temperature of absorption is near 750°F. Absorber model predictions were also compared to the actual SO_2 removals at a set of conditions. Modifications to the previous modeling effort [4] included a factor for pore diffusional effects with the larger sorbent [5]. The SO_2 removal of the baseline test was 85 percent.

The impact of the inlet flue gas SO_2 concentration was investigated. Essentially, as the SO_2 concentration increases, the effective Cu/S feed ratio decreases, thus causing a decrease in SO_2 removal efficiency. Results can be seen in Table 1 when periods A, B, and G are compared at the lower sorbent flow rate of 0.75 lb/min, and when periods E and F are compared at the sorbent flow rate of 1.5 lb/min. The concentration levels of SO_2 were nominally 1500, 2250, and 3250 ppm on a dry basis and simulate the concentrations in flue gas when a mid- to high-sulfur coal is combusted.

TABLE 1: Absorption Study Results								
Test Period	A	B	C	D	E	F	G	H
Flue Gas Flow, SCFM	108	109	109	108	111	108	110	100
Absorber Temp, F	747	747	747	766	747	762	791	747
Sorbent Flow, lb/min	0.76	0.75	1.0	1.0	1.5	1.5	0.75	0.75
Inlet SO ₂ , ppm dry	1529	2259	2291	2048	2042	2985	3004	2430
Actual SO ₂ Removal, %	96	85	93	92	98	93	73	87
Model Predicted SO ₂ Removal, %	95	85	95	96	97	96	78	87
Inlet NO _x , ppm dry	-	-	528	574	516	588	524	496
NO _x Removal, %	-	-	94	94	94	88	94	89
Firing Mode: Coal (C) or Natural Gas (NG)	NG	NG	NG	C	C	C	C	NG

The effect of changing the sorbent flow on the SO₂ removal efficiency was also investigated. Effects of varying the sorbent flow can be seen at two different inlet gas SO₂ concentration conditions. The first is at a nominal 2250 ppm inlet concentration for periods B, C, and E; SO₂ removals increased with increasing sorbent flow. The second is at a nominal 3000 ppm inlet SO₂ concentration for periods G and F. The trend is the same indicating that a higher sorbent flow of regenerated sorbent will enhance the SO₂ removal efficiency of the absorber.

Several additional items should also be noted with respect to these absorption tests. A return to the baseline conditions after a duration of time (periods B and H) indicated that no decrease in sorbent activity occurred during the testing. Also, the reactivity of the sorbent was not impacted when flue gas produced by coal combustion was substituted for that produced by natural gas combustion (periods C and D). The revised sulfation model predicted the SO₂ removals quite well as seen in Table 1. Also, NO_x removals were around the designed levels of 90% and 95% as seen in Table 1.

A regeneration study listed in Table 2 investigated the effects of temperature, residence time, and natural gas-to-sulfur molar ratio on regeneration. Constant nominal absorption conditions of 110 scfm of flue gas, 750°F, 0.75 lb/min sorbent flow, and 2250 ppm inlet SO₂ concentration were maintained. The effect of temperature can be seen in periods I and L where a 50F° drop in temperature decreases the effectiveness of regeneration, as depicted in the larger concentration of methane in the off-gas and a decrease in absorber SO₂ removal. The impact of sorbent residence time was studied at constant natural gas-to-sulfur ratio and temperature in periods J, K, and M. Although the results appear similar at

residence times of 180 min and 120 min, the effectiveness of regeneration diminishes below a residence time of 120 min as determined by an increase in regenerator outlet CH₄ concentration and a decrease in SO₂ removal in the absorber. The influence of natural gas-to-sulfur molar ratios can be determined by comparing periods I and J, where the larger ratio condition resulted in the outlet gas diluted with methane. At these two particular ratios, the impact on the overall capacity of the sorbent for SO₂ removal was minimal.

Test Period	I	J	K	L	M	N	O
Natural Gas/S Molar Ratio	1.2	0.8	0.8	1.2	0.8	1.2	1.2
Regenerator Temp, F	855	854	863	797	858	846	854
Residence Time, min	180	180	120	180	60	180	180
Gas Outlet, %, dry basis							
SO ₂	42	46	47	40	47	40	40
CO ₂	42	44	40	37	38	38	37
CH ₄	14	6	5	25	14	17	19
Absorber SO ₂ Removal, %	86	85	87	83	82	87	85
Firing Mode: Coal (C) or Natural Gas	NG	NG	NG	NG	NG	C	C

Table 3 reports the findings of the absorber modification changes with two different sorbent sizes. For all the test periods reported, flue gas flow was obtained from natural gas firing of the combustor. The total pressure drop across the bed was the largest with the old retention screen design (2.5 in of water) as compared to the new design (1.4 in of water). The screen substitution did not impact the SO₂ removal but did successfully lower the pressure drop across the absorber. A benefit in going to the larger-sized sorbent can be observed by the decrease in pressure drop from 1.4 to 1.0 in of water. As seen by the SO₂ removal, it is also noteworthy that the sorbent reactivity of the smaller sorbent was greater than the larger material, indicating that pore diffusional resistance is greater for the larger sorbent.

As stated before, the SO₂ removal was not significantly impacted when flue gas produced from coal firing was substituted for that produced from natural gas firing. (See Table 1 periods C and D and Table 2 periods I, N, and O.) Typically, an increase in absorber pressure drop was experienced due to fly ash accumulation in the bed, but either continuous pulsing or a pulse after a certain pressure drop was obtained (similar to a baghouse operation) would reduce the pressure drop. Most of the fly ash ends up in the sorbent stream from the absorber and in the flue gas exit stream from the absorber.

SUMMARY

A parametric study of the Moving-Bed Copper Oxide Process was conducted with 1/8-in sorbent in the LCTS. The effects of various parameters on the absorption and regeneration steps of this flue gas cleanup technique were systematically investigated. High removals of SO₂ were obtained at most conditions. A decrease in the inlet SO₂ concentration or an increase in the sorbent flow rate would enhance the SO₂ removal capabilities of the absorber.

TABLE 3: Effect of Retention Screen Design					
Test Period	MBCUO 6-9	MBCUO 7-1	MBCUO 8-1	MBCUO 9-1	MBCUO 10-1
Sorbent	1/16" Grace	1/16" Grace	1/8" Alcoa	1/8" Alcoa	1/8" Alcoa
Screen	Square Weave & Perforated Plate	Bar	Bar	Bar	Bar
SO ₂ Removal (%)	94	93	87	85	86
Total Absorber Pressure Drop (in H ₂ O)	2.5	1.4	1.0	0.8	1.1

Note:

- 1) Identical flow in each case.
- 2) Bed dimensions: 8 Ft(H) x 1 Ft(W) x 5 In(D).
- 3) Similar absorber and regenerator conditions for all test periods.

Regarding regeneration, a high temperature or a large residence time has a major influence on the regeneration of the sorbent. A new absorber design facilitates the use of particulate-laden flue gas in the current bed configuration.

REFERENCES

[1] Hoffman, J.S., Pennline, H.W., Yeh, J.T., Ratafia-Brown, J., and V.A. Gorokhov, Integration of a High Efficiency Flue Gas Cleanup Process Into Advanced Power Systems. Proceedings of the 19th International Technical Conference on Coal Utilization and Fuel Systems, pp 541-552, March 1994,

Clearwater FL.

[2] Yeh, J.T., Pennline, H.W., Hoffman, J.S., Resnik, K.P., and P.A. Vore, Life-Cycle Tests of the Moving-Bed Copper Oxide Process For SO₂ and NO_x Control. Paper No. 96-RP105B.03 presented at the 89th Annual AWMA Meeting, Nashville, TN, June 1996.

[3] Pennline, H.W., Yeh, J.T., Hoffman, J.S., Longton, E.J., Vore, P.A., Resnik, K.P., and F.N. Gromicko, Design, Construction, and Operation of a Life-Cycle Test System for the Evaluation of Flue Gas Cleanup Processes. U.S. DOE Topical Report, DOE/PETC/TR-96-01, December 1995.

[4] Young, R.J. and J.T. Yeh, Computer Simulation of a Flue Gas Desulfurization Moving-Bed Reactor. Environmental Progress, 12(3), pp. 200-207, 1993.

[5] Hedges, S.W., private communication, August 1995.

DISCLAIMER

Reference in this paper to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement by the U.S. Department of Energy. Proceedings of the 13th Annual Pittsburgh Coal Conference, pp. 1468-1473, September 1996.