

Perin A. Cengiz  
Illinois Institute of Technology  
Chemical and Environmental Eng. Dept.  
10 W 33<sup>rd</sup> St.  
Chicago, Illinois, 60616  
e-mail: cengper@iit.edu  
Telephone: (312) 567-5715  
Fax: (312) 567-8874

Ken K. Ho  
Illinois Clean Coal Institute  
5776 Coal Drive, Suite 200  
Carterville, Illinois, 62918-3328  
e-mail: kenh@icci.org  
Telephone: (618) 985-3500  
Fax: (618) 985-6166

Javad Abbasian  
Illinois Institute of Technology  
Chemical and Environmental Eng. Dept.  
10 W 33<sup>rd</sup> St.  
Chicago, Illinois, 60616  
e-mail: abbasian@iit.edu  
Telephone: (312) 567-3047  
Fax: (312) 567-8874

Francis S. Lau  
Gas Technology Institute  
1700 South Mt. Prospect Rd.  
Des Plaines, IL 60018  
e-mail: francis.lau@gastechnology.org  
Telephone: (847) 768-0592  
Fax: (847) 768-0600

## **High Temperature Flue Gas Desulfurization In Moving Beds With Regenerable Copper Based Sorbents**

**Key Words:** Flue Gas, SO<sub>2</sub> Removal, Copper Oxide, Regenerable Sorbents

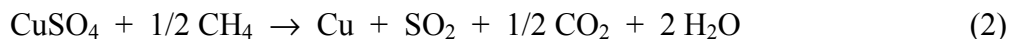
### **Introduction**

In recent years with the enforcement of stricter environmental regulations on coal combustion flue gases, the need for higher treatment efficiencies has become crucial for SO<sub>2</sub> (sulfur dioxide) and NO<sub>x</sub> (nitrogen oxides) removal. In general, higher removal efficiencies require more sophisticated technologies with higher overall process costs. Among various technologies developed for removal of these pollutants from combustion effluents those utilizing dry regenerable sorbents such as the moving-bed copper oxide process are attracting considerable attention. (Darguzas et al., 1996; Hoffman et al., 1992)

The copper oxide process is a process capable of simultaneous SO<sub>2</sub> and NO<sub>x</sub> removal from flue gases. It is based on the utilization of an alumina supported copper oxide sorbent. Sulfur dioxide is removed by reacting with copper oxide through Equation 1. In this process up to 99% of SO<sub>2</sub> can be removed from the flue gas. (Chen and Yeh, 1998)



The sulfated sorbent is regenerated in a separate vessel by reacting with a reducing gas such as methane (CH<sub>4</sub>) according to Equation 2. Thus the sorbent becomes ready to be oxidized and sulfated again (Equation 3) while a highly concentrated SO<sub>2</sub> stream is generated and channeled to a recovery process.





In such processes sorbent properties are crucial in defining the cost associated with the sorbent, which is the key factor determining the overall process cost. Improvement on sorbent properties, that determine the extent of its use, will reduce its replacement cost. However, this is not a straightforward task to accomplish. In traditional sorbent preparation techniques various qualities that extend the use of a sorbent, cannot be improved simultaneously. (Knudsen, 1959; Wagh, 1993) For example, high temperature induration utilized to improve the crush strength will usually results in reduction of surface area and thus effective sorption capacity of the sorbent. On the other hand to increase the capacity of the sorbent active metal content can be increased, which means to reduce the percentage of the support material that provides the strength of the sorbent.

Sol-gel technology has been used for various ceramic applications over the past three decades. In recent years it has become more popular among researchers trying to improve on mechanical properties of sorbents/catalysts while maintaining comparable performance. (Lin and Deng, 1998; Buelna and Lin, 2001; Castillo et al., 1998; Hoang-Van et al., 1998; Lecloux and Pirard, 1998) In this study the application of the sol-gel technique in its various modifications to improve the alumina supported copper oxide sorbent is explored.

### **Objective**

The objective of this study was to develop new and improved regenerable copper based sorbent for high temperature flue gas desulfurization in a moving bed application. The targeted areas of sorbent improvement included higher effective capacity, strength and long-term durability for improved process control and economic utilization of the sorbent.

### **Approach**

In line with the objective, the improvements of sorbent performance for the various copper-based sorbents developed need to be determined. To assess the level of improvement first a baseline is established. For this purpose the commercially available wet impregnated sorbent (Alcoa) utilized in the demonstration of the copper oxide process in a pilot scale unit at the Illinois Coal Development Park was used. The copper based sorbents formulated with different sorbent preparation techniques were used in this study (Abbasian et al., 1999; Slimane et al., 2000). The sorbent preparation techniques include various modifications of the sol-gel technique. The sorbents were tested for their physical and chemical characteristics as well as their desulfurization capabilities and long-term durability. The relationship between sorbent characteristics and sulfur removal capabilities were explored. Effect of induration on sorbents prepared with traditional methods was demonstrated.

### **Project Description**

This study was a part of the work completed for two projects (Abbasian et al., 1999; Slimane et al., 2000) that were conducted as collaboration between Illinois Institute of Technology (IIT), Gas Technology Institute (GTI) and Illinois Clean Coal Institute (ICCI). As indicated earlier the objective was to develop new and improved regenerable copper based sorbents for the high temperature removal of sulfur dioxide. The sorbent development was investigated in line with the moving bed application of the copper oxide process. The study required the thorough

investigation of the currently available sorbent for this process to create a baseline for comparison. To achieve sorbent improvement a relatively new sorbent preparation technique, sol-gel technique, was chosen. This technique has shown considerable improvement in strength of the material produced while maintaining the capacity of the sorbent/catalyst. Various modifications of this technique were investigated to gain a better understanding of how sorbent formulation and various stages of the preparation technique impact the sorbent performance.

## **Results**

Among the sol-gel sorbents developed four formulation exhibited more than 23% improvement in sulfur capacity (volume basis) and more than 45% improvement in crush strength compared to the wet impregnated commercial sorbent. The “best” sorbent formulation resulted in 3.5 times sulfur capacity on volume basis (2.6 times on weight basis) and 1.5 times crush strength compared to the commercial sorbent (Figure 1 and 2). (Slimane et al., 2000)

In an attempt to improve the crush strength of the wet impregnated and bulk sorbents, they were calcined at 1000°C. Calcination at this temperature caused the crush strength of the wet impregnated sorbent to decrease to about 3% that of the fresh sorbent (Table 1). When calcined at 1200°C the crush strength still declined to 11% that of the fresh sorbent. When the sorbent calcined at 1200°C was tested for sulfur removal its sulfur loading declined almost to zero resulting in immediate breakthrough. The bulk sorbents on the other hand showed crush strengths comparable to the fresh sorbents when calcined at 1000°C. The crush strengths improved upon calcinations at 1200°C, but similar to the wet impregnated sorbent their sulfur removal capacities dropped to almost zero after calcinations at this high temperature (Figure 3).

The reactivity of the “best” sorbent after 20 cycles was about twice that of the wet impregnated sorbent, while the rates of decrease in the sulfur capacities for the two sorbents were similar (Figure 4). These results indicate that the rate of “fresh sorbent make-up” with the best sorbent is significantly lower than that of the wet impregnated sorbent. The crush strength of the best sorbent does not appear to be adversely affected by long-term durability test. (Slimane et al., 2000)

In general, sorbents prepared with various modifications of the sol-gel technique demonstrated superior crush strength and sulfur removal capacity. Even though, crush strength and sulfur removal capacity of the sorbents were improved compared to the sorbents formulated with traditional preparation techniques, improvement on one of these qualities impeded the improvement on the other. This leaves the choice of preferred sorbent formulation to be determined based on the specific design requirements.

Efforts to indurate the wet impregnated and bulk sorbents resulted in improvement in crush strength only at very high temperatures (1200°C) (Table 1). This induration, however, caused the capacities of these sorbents to reduce significantly.

Repeated sulfation and regeneration of the sol-gel sorbent with the highest sulfur removal capacity indicated higher sorbent durability compared to the wet impregnated commercially available sorbent. Over the 20 cycles of testing the crush strength of the sol-gel sorbent remained unaffected while the wet impregnated sorbent slightly deteriorated. To show the extent of

improvement of durability and its economic implications more accurately, the sorbents will need to be tested for greater number of cycles. (Slimane et al., 2000; Cengiz et al., 2002)

### **Application**

The alumina supported copper oxide sorbents developed in this study are suitable for moving bed copper oxide process for removing sulfur dioxide from flue gases as a regenerable process. The increased crushing strength and sulfur capacity as well as the long-term durability provides for the extended use of these materials.

### **Future Activities**

Even though the initial investigation of the sol-gel sorbents revealed improvement of the sorbents long-term durability, before a future attempt to commercialize these sorbents they need to be tested for a longer duration (more cycles of sulfation/regeneration) to establish a healthier understanding of their long-term durability. (Cengiz et al., 2002)

As discussed earlier the sorbent developed possess superior qualities compared to what is currently available in the commercial market. Several of the sorbent developed within the context of this investigation are suitable for the copper oxide process for extended use. The design of the copper oxide process will determine the desired formulations to be pursued. Through proper development the improved sorbents can be utilized in the copper oxide process.

More cost effective methods of production for these sorbents should be investigated further. The cost may be reduced by utilization of cheaper ingredients and creating various shortcuts in the sorbent preparation procedure.

### **References**

- Abbasian, J., Slimane, R.B., Cengiz, P.A., and Williams, B.E., 1999. Development of Improved Sorbents for the Moving-Bed Copper Oxide Process. *Final Technical Report to the Illinois Clean Coal Institute*, Nov. 1, 1998 through Oct. 31, 1999.
- Buelna, G. and Lin, Y.S., 2000. Preparation of Spherical Alumina and Copper Oxide Coated Alumina Sorbents by Improved Sol-Gel Granulation Process. *Microporous and Mesoporous Materials* 42: 67-76.
- Castillo, S., Moran-Pineda, M., Molina, V., Gomez, R., and Lopez, T., 1998. Catalytic Reduction of Nitric Oxide on Pt and Rh Catalysts Supported on Alumina and Titania Synthesis by Sol-Gel Method. *Applied Catalysis B: Environmental* 15: 203-209.
- Cengiz, P.A., Abbasian, J., Khalili, N.R., Slimane, R.B., and Ho, K.K., 2002. Development of Durable and Reactive Regenerable Sorbents for High Temperature Flue Gas Desulfurisation. *International Journal of Environment and Pollution* 17(1/2): 82-101.
- Chen, Z-Y and Yeh, J.T., 1998. A Sorbent Regenerator Simulation Model in Copper Oxide Flue Gas Cleanup Processes. *Environmental Progress* 17(2): 61-69.

Darguzas, J.N., Pennline, H., Sloat, D.G., and Penrose, J., 1996. Moving Bed Copper Oxide Desulfurization and NO<sub>x</sub> Removal Process Development. *Final Technical Report to the Illinois Clean Coal Institute*, Sept. 1, 1994 through Jan. 15, 1996.

Hoffman, J.S., Smith, D.N., Pennline, H.W., and Yeh, J.T., 1992. Removal of Pollutants from Flue Gas via Dry, Regenerable Sorbent Processes. AIChE Spring National Meeting, March 29-April 2.

Hong-Van, C., Zegaoui, O., and Pichat, P., 1998. Vanadia-Titania Aerogel deNO<sub>x</sub> Catalysts. *Journal of Non-Crystalline Solids* 225: 157-162.

Knudsen, F.P., 1959. Dependence of Mechanical Strength of Brittle Polycrystalline Specimens on Porosity and Grain Size. *Journal of the American Ceramics Society* 42(5): 376-387.

Lecloux, A.J. and Pirard, J.P., 1998. High Temperature Catalysts through Sol-Gel Synthesis. *Journal of Non-Crystalline Solids* 225: 146-152.

Lin, Y.S. and Deng, S.G., 1998. Removal of Trace Sulfur Dioxide from Gas Stream by Regenerative Sorption Processes. *Separation and Purification Technology* 13: 65-77.

Slimane, R.B., Abbasian, J., and Cengiz, P.A., 2000. Development of New and Improved Sorbents for the COBRA Process. *Final Technical Report to the Illinois Clean Coal Institute*, Nov. 1, 1999 through Oct. 31, 2000.

Wagh, A.S., Singh, J.P., and Poeppe, R.B., 1993. Dependence of Ceramic Fracture Properties on Porosity. *Journal of Materials Science* 28(13): 3589-3593.

### **Disclaimer**

This paper was prepared by the Illinois Institute of Technology (IIT) and Gas Technology Institute (GTI) with support, in part by grants made possible by the Illinois Department of Commerce and Community Affairs through the Illinois Coal Development Board and the Illinois Clean Coal Institute. Neither IIT, nor GTI, nor the Illinois Department of Commerce and Community Affairs, Illinois Coal Development Board, Illinois Clean Coal Institute, nor any person acting on behalf of either:

- (A). Makes any warranty of representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this paper, or that the use of any information, apparatus, method, or process disclosed in this paper may not infringe privately-owned rights; or
- (B). Assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method or process disclosed in this paper.

Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring; nor do the views and opinions of authors expressed herein

necessarily state or reflect those of the Illinois Department of Commerce and Community Affairs, the Illinois Coal Development Board, or the Illinois Clean Coal Institute.

**Notice to Journalists and Publishers:** If you borrow information from any part of this report, you must include a statement about the state of Illinois' support of the project.

**Figures and Tables**

Table 1. Average Crushing Force per Pellet Diameter or Length of the Sorbents (N/mm)

Sorbent	Uncalcined	Calcined at 1000°C	Calcined at 1200°C
Baseline (Alcoa)	14.23	0.98	1.51
TSR-11	12.50	12.81	20.24
T-4489	20.60	-	145.37

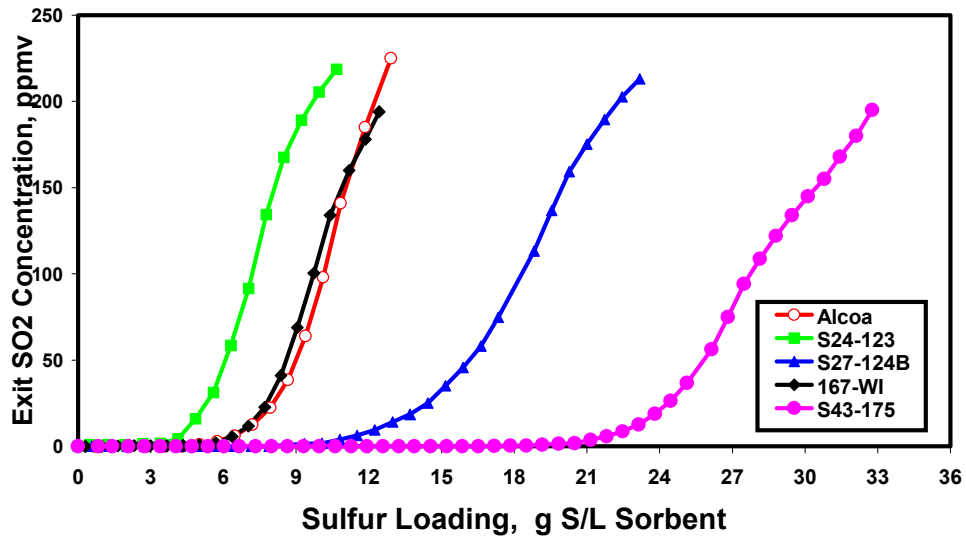


Figure 1. Effective Sulfur Capacities of Various Sorbents

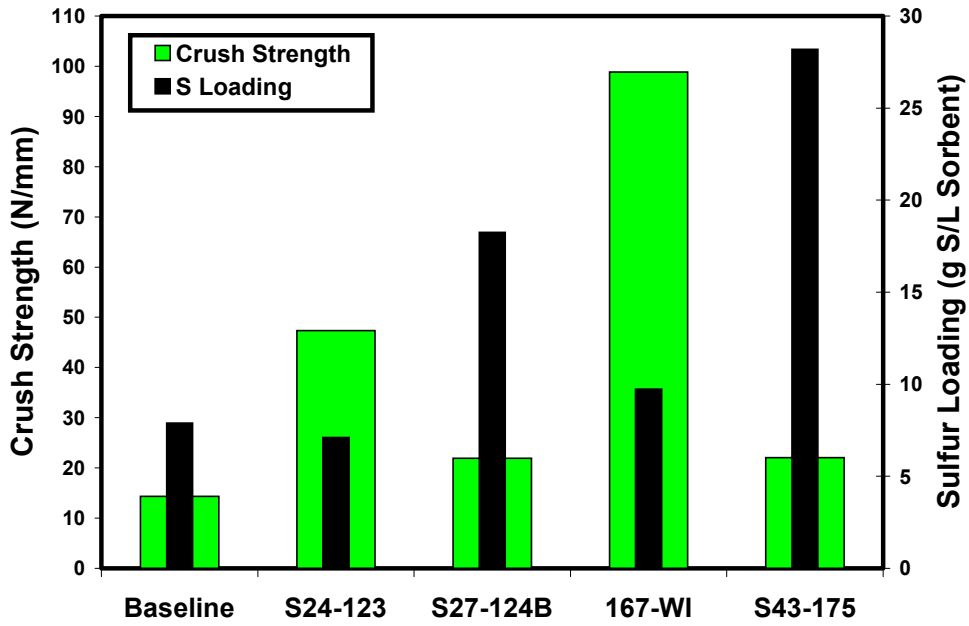


Figure 2. Sulfur Loadings and Crush Strengths of Various Sorbents

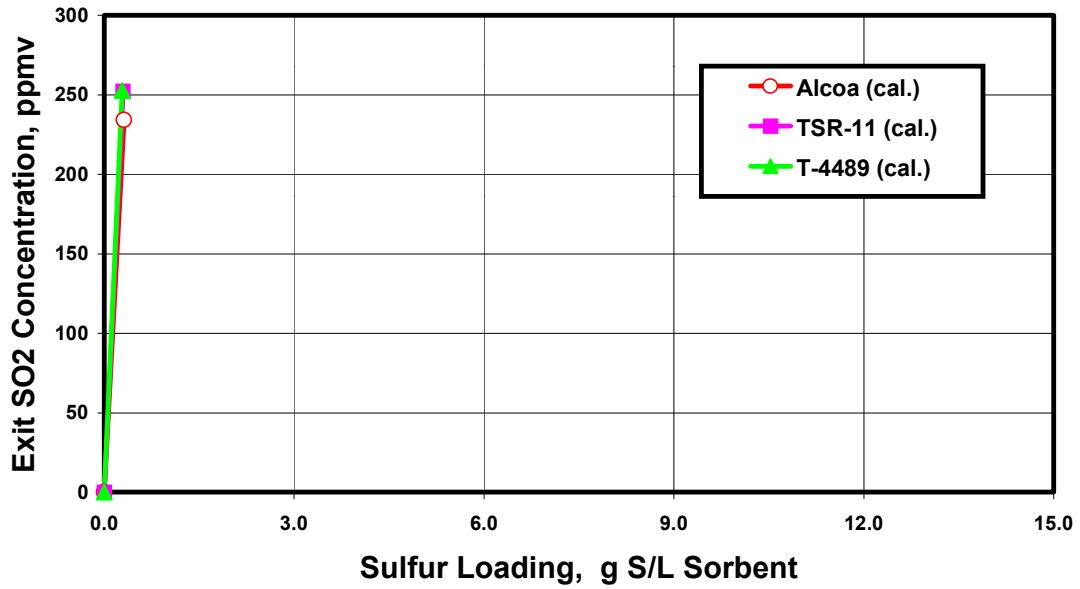


Figure 3. Sulfur Removal with Sorbents Indurated at 1200°C

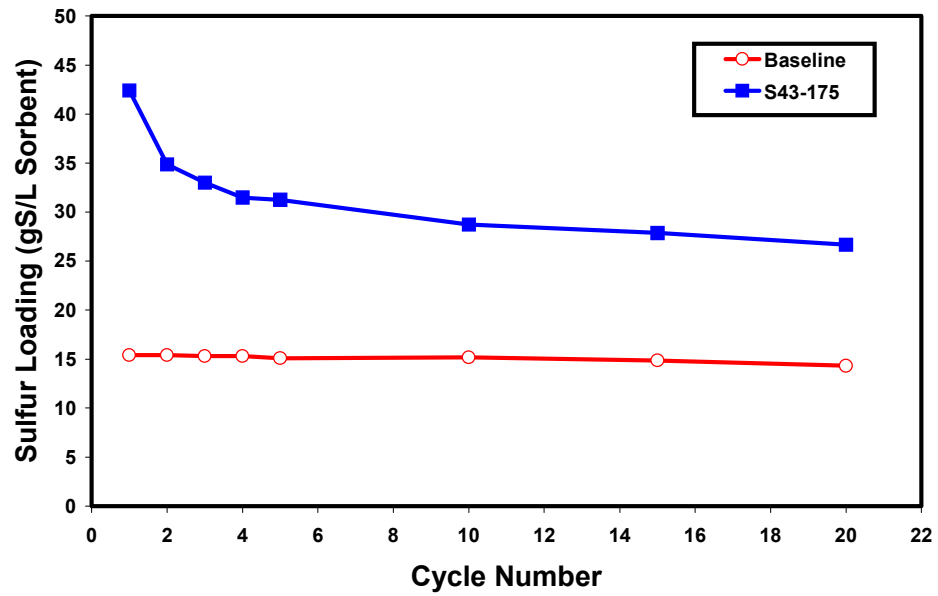


Figure 4. Comparison of Sulfur Capacities of the Baseline and New Sorbent in Long-Term Durability Test