Simultaneous Control of Hg⁰, SO₂, and NO_X by Novel Oxidized Calcium-Based Sorbents

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ABSTRACT

Efforts to develop multipollutant control strategies have demonstrated that adding certain oxidants to different classes of calcium-based sorbents leads to a significant improvement in elemental mercury vapor (Hg⁰), sulfur dioxide (SO₂), and nitrogen oxides (NO_X) removal from simulated flue gases. In the study presented here, two classes of calcium-based sorbents (hydrated limes and silicate compounds) were investigated. A number of oxidizing additives at different concentrations were used in the calcium-based sorbent production process. The Hg⁰, SO2, and NOx capture capacities of these oxidant-enriched sorbents were evaluated and compared to those of a commercially available activated carbon in bench-scale, fixed-bed, and fluid-bed systems. Calcium-based sorbents prepared with two oxidants, C and P, exhibited Hg⁰ sorption capacities (about 100 µg/g) comparable to that of the activated carbon; they showed far superior SO₂ and NO_X sorption capacities. Preliminary cost estimates for the process utilizing these novel sorbents indicate potential for substantial lowering of control costs, as compared to other processes currently used or considered for control of Hg⁰, SO₂, and NO_X emissions from coal-fired boilers. The implications of these findings toward development of multipollutant control technologies and planned pilot and field evaluations of more promising multipollutant sorbents are summarily discussed.

INTRODUCTION

Of all trace metals emitted during fossil fuel combustion and waste incineration, mercury is likely considered the most problematic. This concern is based on a combination of issues, including: the propensity of mercury to concentrate and bioaccumulate by up to a factor of 10,000 within the aquatic food chain; 1,2,3,4 documented adverse health effects associated with mercury exposure; 5,6,7,8 and, most importantly, the inability of current pollution control technologies and strategies, designed primarily for particulate matter (PM), NO_X, and SO₂, to effectively control volatile mercury species. Modifying existing technologies or developing a one-step multipollutant control technology capable of simultaneous control of mercury species, PM, NO_X, and SO₂, would seem to be sensible and cost-effective approaches to solve this problem.

Research on mercury emissions control from coal-fired combustors is currently focused on activated carbon sorption of mercury compounds ^{9, 10, 11, 12, 13, 14, 15} or changing the mercury speciation in the flue gas to water-soluble ionic mercury species (Hg⁺²) that can be absorbed by conventional wet SO₂ scrubbers. ¹⁶ While activated carbon is effective for the capture of both major mercury species, Hg⁰ and Hg⁺², it represents an expensive additional technology specifically designed to control mercury emissions only. As shown in this study, activated carbons are not effective SO₂ sorbents; thus, activated carbon injection cannot be considered as a viable multipollutant control technology. Wet SO₂ scrubbers are employed only on a fraction of coal-fired boilers and are capable of removing only Hg⁺². Some data suggest that Hg⁰ vapor concentration can actually increase across a wet limestone scrubber, presumably due to the reduction of Hg⁺² by sulfite in the scrubber. ¹⁷

In addition, recent data analyses by the U.S. Environmental Protection Agency (EPA) conclude that in 1999, utility boilers emitted 43 tons of mercury or 57% of mercury contained in coal burned. An evaluation of these data shows mercury to be retained by fly ash and collected in PM control devices. Potential multipollutant mercury control strategies therefore include:

- Enhancement of PM control technologies with sorbent injection and/or gas cooling
- Addition of oxidation catalysts, flue gas oxidants, or scrubber liquor oxidants, which increase the collectible Hg⁺², in conjunction with wet SO₂ scrubbers

The development of better sorbents for mercury can lead to better ways of augmenting PM devices, but the most cost-effective use of improved mercury sorbents would appear to be in absorption technologies that remove several pollutants. By using sorbents that also offer oxidation potential, all mercury species may be removed with acid gases in certain types of semidry absorbers, and NO_X reductions (through conversion of NO_X species to more reactive forms) may also be obtained. This type of application is the focus of the remaining discussions on multipollutant sorbent development.

Previous investigations 19, 20 have shown that modified calcium (Ca)-based sorbents have a potential to be viable multipollutant (Hg⁰, Hg⁺², and SO₂) sorbents, thus providing the operators of coal-fired power plants and waste incinerators with a practical multipollutant control strategy. It was previously established that mercuric chloride (HgCl₂) vapor is readily adsorbed as an acid gas by conventional Ca-based sorbents such as hydrated lime¹², while Hg⁰ is partially adsorbed by Ca-based sorbents when significant modifications are implemented in the sorbent production process. 19, 20 Further improvement in the Hg⁰ uptake capabilities of these modified Ca-based sorbents was necessary before they could be considered as attractive total mercury sorbents. Current efforts, described in this paper, have attempted to improve the uptake of Hg⁰ by increasing the number of active sites and adding oxidative species to Ca-based sorbents. Based on the previous investigations, 19, 20 the key assumptions for this study were that Ca-based sorbents, modified or unmodified, will adsorb SO₂ and Hg⁺²; and that modified Ca-based sorbents, having both fine pore structure and oxidizing species in the pore structure, can oxidize and sequester Hg⁰ and NO_X from flue gas. The improvement in the capture of Hg⁰ and NO_X by the oxidant-enriched Ca-based sorbents makes them an attractive choice for a multipollutant control technology.

PREVIOUS STUDIES ON OXIDANT-ENRICHED Ca-BASED SORBENTS

An earlier study demonstrated that adding oxidants to Ca-based sorbents during their production process could significantly increase the Hg⁰ uptake capabilities of these sorbents.²⁰ One class of these Ca-based sorbents, termed "oxidized hydrated limes," was prepared by hydrating commercial quicklime in the presence of an oxidant in solution. Different concentrations of oxidant in solution were used. It was shown that the hydration process in the presence of oxidant solution (as opposed to water) had no effect on the total surface area of these sorbents (13-15 m²/g). Oxidized hydrated limes, on average, exhibited a 2-3 times higher Hg⁰ uptake than the baseline hydrated lime prepared in the presence of water. Increasing the strength of oxidant solution (from 6 to 30%) increased the Hg⁰ uptake by a factor of 2. It was hypothesized that the hydration of quicklime in the presence of an oxidant creates active sites. The presence of oxidizing sites was further confirmed by thermal decomposition to oxygen using thermogravimetric analysis (TGA) coupled with residual gas analysis (RGA). Although an improvement in Hg⁰ uptake could be achieved by oxidized hydrated lime, the overall uptake was a factor of 10 lower than a commercially available activated carbon (DARCO FGD, Norit Americas Inc.). This lower activity was then attributed to the much lower surface area of oxidized hydrated limes (13-15 m²/g), as opposed to the FGD activated carbon (514 m²/g).

Another class of high-surface-area Ca-based sorbents, silicate sorbents, has been prepared extensively in EPA laboratories. Silicate sorbents are hydrated lime and silica source reaction products, a calcium silicate gel. This calcium silicate gel has high surface area (100-200 m²/g), thin layers of free lime [Ca(OH)₂], and substantial moisture that allows simultaneous in-duct absorption of acid gases and flue gas cooling. ^{21, 22, 23}

It was hypothesized that adding oxidant to silicate sorbents should result in a more efficient Hg^0 sorbent due to improved dispersion of active sites over a larger surface area. Placing the oxidant on the calcium-silicate sorbents proved to be problematic due to oxidant decomposition. Rather than incorporating the oxidant solution in the calcium-silicate reaction, oxidant solution was added to the finished dry silicate sorbent. No significant improvement in Hg^0 uptake was observed. The oxidant was believed to have decomposed prior to the formation of significant active sites. This observation, and the fact that oxidized hydrated limes described above were significantly less efficient in capturing Hg^0 than an activated carbon, prompted the exploration of more effective oxidants.

By changing oxidants, decomposition of these compounds may be manageable, resulting in dispersed oxidant in the pore structure of the Ca-based sorbents. These active sites will be available to oxidize and sequester Hg^0 , NO_X , and SO_2 , upon exposure. A series of oxidants and Ca-based sorbent production processes were investigated. Oxidant-enriched hydrated limes and silicate sorbents were screened based on Hg^0 , NO_X , and SO_2 capture efficiency. The capture efficiency of sorbents toward Hg^0 and SO_2 was further compared to that of an activated carbon.

SORBENT PREPARATION

Oxidant-Enriched Hydrated Lime

Lime sorbents were prepared with commercial powdered quicklime (Marblehead Lime Co.) and degassed deionized (DI) water. The indicated oxidant was added to the quicklime prior to hydration at a rate of 0.1 equivalents per mole of quicklime. Four oxidants were screened, and designated S, N, M, and C. Quicklime was hydrated in a scaled Parr Bomb reactor with stoichiometric water for 30 minutes. As a precaution against further oxidant decomposition, sorbents were then stored in sealed containers without further drying. The surface areas of these sorbents are shown in Table 1.

Sorbent	BET Surface Area, m ² /g	
Baseline lime	11.03	
S lime	14.39	
N lime	9.54	
M lime	14.28	
C lime	11.36	

Table 1. Specific surface area of screened hydrated lime sorbents.

Oxidant-Enriched Silicate Sorbents

Silicate sorbents were prepared in glass beakers in a double boiler configuration. Equal parts of silica fume and reagent grade hydrated lime were slurried in a 90 °C solution of a wetting agent and degassed DI water for 2 hours. The slurry was vacuum filtered through Whatman #42 paper, and the filter cake was dried overnight in a vacuum oven at 100 °C. Five milliliters of a 1 mM lime solution was added to a 60 °C heated mortar containing 0.5 g of the indicated oxidant. Ten grams of dry silicate was added to the solution in the mortar and mixed. Contents of the mortar were transferred to a watch glass and dried overnight in a 100 °C vacuum oven. Selected physical properties of these sorbents are shown in Table 2. Silicate surface areas do not appear to be greatly affected by the addition of oxidant; however, the surface area remains substantially less than that of FGD activated carbon (514 m²/g).

Table 2. Specific surface area of screened silicate sorbents.

Sorbent	BET Surface Area, m ² /g	
Baseline silicate	101.79	
M silicate	te 95.54	
C silicate	90.90	

EXPERIMENTAL APPARATUS

Bench-scale Hg⁰/SO₂ removal tests were performed on a vertical fixed-bed reactor apparatus; operation and construction details of this apparatus have been previously described. ^{12, 19} A simulated flue gas was generated containing 40 ppbv Hg⁰, 4 mole% oxygen (O₂), 10 mole% carbon dioxide (CO₂), 1 mole% water vapor (H₂O), and 500 ppmv SO₂. Simulated flue gas was then passed through the sorbent bed, a Lindberg furnace, a NAFIONTM Dryer, and serial ultraviolet Hg⁰ and SO₂ analyzers. Sorbent was exposed to 300 cm³/min [dry at standard temperature and pressure (STP)] simulated flue gas for 2 hours at 80 °C reactor temperature. The Lindberg furnace was maintained at 100 °C to prevent condensation and to avoid undesirable reactions. Breakthrough curves from Hg⁰ and SO₂ analyzers were integrated to obtain uptake during the 2-hour exposure.

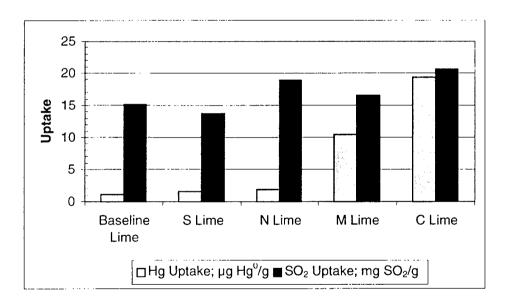
Simultaneous evaluations of Hg⁰, NO_X, and SO₂ on the fixed-bed reactor were confounded by experimental artifacts encountered with the NAFIONTM Dryer. The further desire to more closely simulate anticipated field activity led to the construction of a fluidized-bed reactor apparatus designed to accommodate high-moisture simulated flue gas. Bench-scale NO_x/SO₂ removal tests were performed on the fluidized-bed reactor apparatus. An NO/SO₂ span gas mixture, nitrogen, and dry air were metered through rotometers to produce 12 scfh of a dry simulated flue gas of 300 ppmv NO_X, 600 ppmv SO₂, 8% O₂, and the balance nitrogen. This gas was preheated to reaction temperature (80 °C) and humidified with vaporized water to an average 10.5 mole% water. The resulting wet simulated flue gas was passed through a vertical reactor loaded with fluidized sorbent and sand; it was then passed through a filter to remove any entrained particulate and to protect the downstream equipment. The reactor and filter assembly were housed in an oven maintained at 80 °C. The test stand was equipped with a bypass of the reactor and filter assembly to allow for bias checks. Sorbent was exposed to simulated flue gas for 30 minutes. Water was removed from the spent flue gas with a NAFIONTM Dryer. Dry gas was then serially analyzed with SO₂ and NO_X continuous emission monitors (CEMs). Breakthrough curves from NO_x and SO₂ analyzers were integrated to obtain uptake during the 30-minute exposure. Though NO_x was introduced to the system as NO, the convention of reporting in terms of NO₂ was adopted. Activated carbon could not be evaluated on this system due to excessive carryover to the filter.

RESULTS AND DISCUSSION

Effectiveness of Oxidant-Enriched Hydrated Lime Sorbents

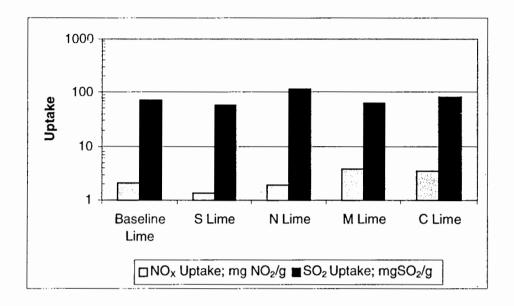
Oxidants were screened by testing oxidant-enriched hydrated limes in duplicate for Hg^0 and SO_2 removal in the fixed-bed reactor. Uptakes of Hg^0 (in $\mu g \ Hg^0/g$ sorbent) and SO_2 (in $mg \ SO_2/g$ sorbent) by these sorbents are illustrated in Figure 1. Despite a lower surface area, the C lime exhibited the highest Hg^0 uptake (19.3 $\mu g/g$), followed by the M lime (10.4 $\mu g/g$). The other oxidant-enriched hydrated limes did not show any improvement in Hg^0 uptake over the baseline, hydrated lime (1.04 $\mu g/g$). The pooled standard deviation of the replicates was 0.77 $\mu g \ Hg^0/g$. In terms of SO_2 uptake, C lime (20.6 mg/g) and M lime (16.6 mg/g) were not significantly different from the baseline lime (15.2 mg/g). The pooled standard deviation of the SO_2 uptake was 1.8 $mg \ SO_2/g$. Hg^0 and SO_2 uptakes did not show any correlation to the physical parameters (such as total surface area) of the sorbents, indicating that the generation of active sites (oxidation sites) in certain oxidant-enriched hydrated limes (C and M limes) was instrumental in the improvement in Hg^0 and SO_2 uptake.

Figure 1. Fixed-bed Hg^0 and SO_2 uptake by the oxidant-enriched hydrated limes at 80 °C. Flue gas consisted of 40 ppbv Hg^0 , 4 mole% O_2 , 10 mole% CO_2 , 1 mole% H_2O , and 500 ppmv SO_2 .



Oxidants were also screened in oxidant-enriched hydrated lime sorbents for their ability to enhance NO_X removal in the fluidized-bed test stand. Screening results are shown in Figure 2. A significant improvement in NO_X removal was observed for C lime (3.4 mg NO_2/g) and M lime (3.9 mg NO_2/g) compared to baseline lime (2.1 mg NO_2/g). Though the enhancement at test conditions proved modest, the same additives effective for mercury control show promise with respect to NO_X activity. Duplicate testing of the baseline lime performance indicates a standard deviation of 0.06 mg NO_2/g . No significant difference in SO_2 removal was observed between baseline lime and C or M lime.

Figure 2. Fluid-bed NO_X and SO_2 uptake by oxidant-enriched hydrated limes at 80 °C. Flue gas consisted of 300 ppmv NO_X , 600 ppmv SO_2 , 8% O_2 , and 10.5% H_2O .



Effectiveness of Oxidant-Enriched Silicate Sorbents

The screening process identified two oxidants as effective in enhancing Hg^0 and NO_X removal from simulated flue gas with hydrated limes. The next step was to place these oxidants on a Ca-based silicate sorbent with higher surface area. The Hg^0 and SO_2 uptake of the oxidant-enriched silicates was measured in duplicate on the fixed-bed reactor and compared to those of the FGD activated carbon and a baseline silicate (no oxidant). As shown in Figure 3, C silicate exhibited the highest Hg^0 uptake capacity (101 $\mu g/g$). Despite a much lower surface area than FGD, C silicate exhibited Hg^0 removal indistinguishable from that of the FGD activated carbon (95.5 $\mu g/g$). The pooled standard deviation of the Hg uptake was 7.5 $\mu g/g$. C silicate also showed a far superior SO_2 uptake capacity than the activated carbon (101 as compared to 8.9 mg/g). C silicate is a superior multipollutant sorbent for Hg^0 and SO_2 than the activated carbon.

The oxidant-enriched silicates were also evaluated on the fluidized-bed test stand for NO_X and SO_2 removal. These results are summarized in Figure 4. Baseline silicate sorbent exhibited NO_X removal (7.0 mg NO_2/g) far superior to the baseline lime (1.6 mg NO_2/g) evaluated in this block of testing. The silicate sorbent is presumed to enhance an oxidation mechanism similar to that proposed for mercury removal on similar sorbents. Addition of oxidants in C silicate and M silicate further enhanced NO_X removal with these silicate sorbents (14.0 and 15.7 mg NO_2/g , respectively). Despite reduced alkali content of the silicate sorbents, SO_2 removal has been dramatically increased in the silicate sorbents, most notably in C silicate (176 mg/g) and M silicate (177 mg/g), sorbents at conditions tested. Neither NO_X nor SO_2 concentrations returned to baseline prior to the end of the test for the silicate sorbents, indicating the sorbent was not exhausted in these tests.

Figure 3. Fixed-bed Hg^0 and SO_2 uptake by the oxidant-enriched calcium-silicate at 80 °C. Flue gas consisted of 40 ppbv Hg^0 , 4 mole% O_2 , 10 mole% CO_2 , 1 mole% H_2O , and 500 ppmv SO_2 .

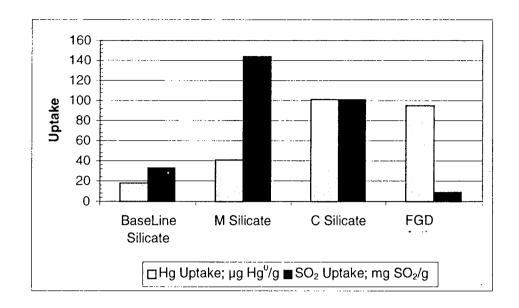
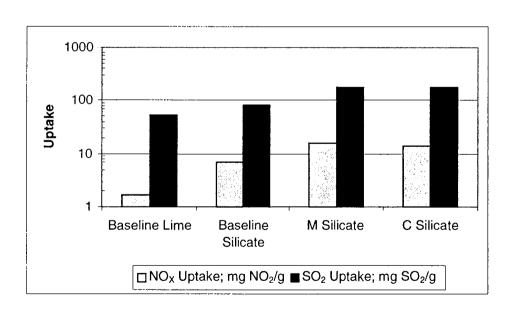


Figure 4. Fluid-bed NO_X and SO_2 uptake by silicates at 80°C. Flue gas consisted of 300 ppmv NO_X , 600 ppmv SO_2 , 8% O_2 , and 10.5% H_2O .



Cost Analysis

Approximately 75% of the existing coal-fired utility boilers in the U.S. are equipped only with electrostatic precipitators (ESPs) for the control of PM. EPA's mercury control cost estimation work considered this configuration as one of the 16 dry sorbent-based technology application cases reflecting differences in flue gas cleaning equipment and type of coal burned. For this configuration, EPA estimated the total annual cost for an 80% mercury control on a 100 MW boiler with 65% capacity factor and flue gas mercury concentration of 10 µg/dscm at 1.79 mills/kWh.²⁴ The cost of activated carbon sorbent used to derive the above estimated total annual cost was \$1.00/kg.

Excellent bench-scale mercury removal was observed with sorbents other than activated carbon. Therefore, it is of interest to estimate total annual cost for the mercury control system installed on an identical boiler, as described above, but operated with sorbents other than activated carbon. As previously discussed, C silicate Hg⁰ removal performance was indistinguishable from that of FGD activated carbon in bench-scale packed-bed tests. Therefore, it was assumed that 80% mercury could be removed by injecting C silicate at the same sorbent-to-mercury ratio as used before with activated carbon injection. The cost of C silicate was taken to be \$0.20/kg of sorbent. Calculations were performed using the same methodology used by EPA for a 100 MWe boiler firing low-sulfur bituminous coal and with 65% capacity factor. Utilizing the above assumptions, the total annual cost was estimated to be 0.36 mills/kWh for 80% mercury removal.

Substitution of C lime for activated carbon results in somewhat smaller, though still significant, cost savings. Based on bench-scale removal, injection rates of C lime necessary to accomplish mercury removal similar to that observed with activated carbon are estimated at 5 times the injection rates of activated carbon. At an estimated cost of \$0.13/kg, total annual cost of C lime injection is estimated at 1.16 mills/kWh for the comparable 100 MWc unit requiring 80% mercury removal.

In summary, the preliminary cost estimate described above indicated that approximately 80% reduction of the total annual cost of mercury control could be possible when using C silicate in lieu of activated carbon. Assuming sorbent injection was carried out for Hg control in the presence of a relative abundance of SO₂, injection of C silicate or similar Ca-based sorbent would result in significant SO₂ removal, resulting in the generation of SO₂ emission credits. Fluidized-bcd reactor data suggest that, without optimizing for SO₂ or NO_X removal, 0.17 tons of SO₂ may be removed per ton of C silicate. This SO₂ emission credit could be sold or contribute to operational flexibility of a plant. NO_X reduction by such sorbents also has the potential to provide direct economic benefit through the production of credits, if and when a NO_X trading system is implemented, but is likely to have a more immediate impact through increased operational flexibility.

CONCLUSIONS

Multipollutant sorbents have been developed that can remove both Hg⁰ and Hg⁺² as effectively as FGD activated carbon in fixed-bed simulations of coal-fired flue gas at 80 °C. Oxidant-enriched calcium-based sorbents proved far superior to activated carbon with respect to SO₂

uptake on the same fixed-bed simulations. These oxidant-enriched, calcium-based sorbents also performed better with respect to NO_X and SO₂ uptake than baseline lime hydrates for fixed and fluid-bed simulations at 80 °C.

Preliminary economic analyses suggest that silicate sorbents with oxidants are 20% of the cost of activated carbon for mercury removal, while oxidant-enriched lime hydrates offer reduced, but significant savings. Credits for SO₂ and NO_X increase the savings for multipollutant sorbents over activated carbon.

The apparent superiority of multipollutant lime and silicate hydrates enhanced with oxidants has been confirmed at conditions typical of gas-cooled, semidry absorption processes on coal-fired boilers; performance of sorbents at higher-temperature conditions of duct sorbent injection technologies remains to be evaluated. Planned field evaluations of both semidry absorption and duct sorbent injection will allow better economic and performance comparisons of activated carbon sorbents to that of oxidant-enriched lime and silicate hydrates.

REFERENCES

¹ Westoo, G. "Methylmercury as Percentage of Total Mercury in Flesh and Viscera of Salmon and Sea Trout of Various Ages." *Science*, 1973, 181, 567-568.

² Carpi, A. "Mercury from Combustion Sources: A Review of the Chemical Species Emitted and Their Transport in the Atmosphere." *Water, Air, Soil Pollut.*, 1997, 98, 241-254.

³ Lindberg, S. E.; Stratton, W.J. "Atmospheric Mercury Speciation: Concentrations and Behavior of Reactive Gaseous Mercury in Ambient Air." *Environ. Sci. Technol.*, 1998, 32(1), 49-57.

⁴ Engstrom, D. R.; Balogh, S. J.; Swain, E.B. "Evidence for historic increases in mercury methylation from the sediments of 14 lakes in northeastern Minnesota," Proceedings of the Air and Waste Management Association Specialty Conference on Mercury in the Environment, Minneapolis, MN, September 15-17, 1999.

⁵ Clarkson, T.W. Environ. Health Perspect., 1987, 74, 59-64.

⁶ Clarkson, T.W. Environ. Health Perspect., 1987, 74, 103-107.

⁷ Clarkson, T.W. "Health Effects Associated with Mercury Contamination," Third International Conference Municipal Waste Combustion, Williamsburg, VA, March 1993.

⁸ Goyer, R.A. "Toxic effects of metals, in Casarett and Doull's toxicology the basic science of poisons, 4th ed., Amdur, M.O.; Doull, J.; and Klaassen, C.D., eds., Pergamon Press: New York, NY, 1991.

⁹ Krishnan, S.V.; Gullett, B.K.; Jozewicz, W. "Sorption of Elemental Mercury by Activated Carbons," *Environ. Sci. Technol.*, 1994, 28(8), 1506-1512.

¹⁰ Krishnan, S.V.; Gullett, B.K.; Jozewicz, W. "Mercury Control in Municipal Waste Combustors and Coal-Fired Utilities," *Environ. Prog.*, 1997, *16*(1), 47-53.

¹¹ Vidic, R. D.; McLaughlin, J. B. "Uptake of Elemental Mercury Vapors by Activated Carbons," *J. Air & Waste Manage. Assoc.*, 1996, 46, 241-250.

¹² Ghorishi, S.B.; Gullett, B.K. "Sorption of Mercury Species by Activated Carbons and Calcium-based Sorbents: Effect of Temperature, Mercury Concentration and Acid Gases," *Waste Manage*. & Res., 1998, 16(6), 582-593.

¹³ Lancia, A.; Musmarra, D.; Pepe, F.; Volpicelli, G. "Adsorption of Mercuric Chloride Vapors from Incinerator Flue Gases in Calcium Hydroxide Particles," *Combust. Sci. Technol.*, 1993, 93, 277-289.

¹⁴ Lancia, A.; Musmarra, D.; Pepe, F.; Volpicelli, G. "Adsorption of Metallic Mercury on Activated Carbon," Proceedings of the Twenty-Sixth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 1996.

¹⁵ Srivastava, R.K.; Sedman, C.B.; Kilgroe, J.D. "Preliminary Performance and Cost Estimates of Mercury Emission Control Options for Electric Utility Boilers," Proceedings of the 93rd Air & Waste Management Association Annual Meeting, Salt Lake City, UT, June 18-22, 2000.

¹⁶ Richardson, C.; Blythe, G.; Rhudy, R.; Brown, T. "Enhanced Control of Mercury by Wet FGD Systems," Proceedings of the 93rd Air and Waste Management Association Annual Conference and Exhibition, Salt Lake City, UT, June 18-22, 2000.

¹⁷ Redinger, K.E. Babcock & Wilcox to William Maxwell, letter, U.S. EPA, Office of Air Quality Planning and Standards, Durham, NC, November 7, 1996.

¹⁸ Federal Register Vol. 65, No. 245, December 20, 2000, 79825-79831.

¹⁹ Ghorishi, S.B.; Sedman, C.B. "Low Concentration Mercury Sorption Mechanisms and Control by Calcium-based Sorbents: Application in Coal-fired Processes," *J. Air & Waste Manage*. *Assoc.*, 1998, 48, 1191-1198.

²⁰ Ghorishi, S.B.; Singer, C.F.; Sedman, C.B. "Preparation and Evaluation of Modified Lime and Silica-Lime Sorbents for Mercury Vapor Emissions Control," Proceedings of the 2nd EPRI-DOE-EPA Combined Utility Air Pollutant Control Symposium, Atlanta, GA, 1999.

²¹ Jozewicz, W. "Program to Demonstrate ADVACATE Technology in Poland," Proceedings of the Second International Conference on Energy and Environment: Transitions in East Central Europe, Prague, Czech Republic, 1994, 661-669.

²² Jozewicz, W.; Rochelle, G.T.; Stroud, D.E. "Novel Techniques for the Enhanced Utilization of Ca(OH)₂ under Duct Injection Conditions," Proceedings of the Seventh Annual Coal Preparation, Utilization, and Environmental Control Contractors' Conference, Pittsburgh, PA, July 15-18, 1991, 246-253.

²³ Jozewicz, W.; Chang, J.C.S. "Evaluation of FGD Dry Injection Sorbents and Additives, Volume I: Development of High Reactivity Sorbents," EPA-600/7-89-006a (NTIS PB 89-208 920), Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, May 1989.

²⁴ Srivastava, R.K.; Sedman, C.B.; Kilgroe, J.D. "Performance and Cost of Mercury Emission Control Technology Applications on Electric Utility Boilers," EPA-600/R-00-083, National Risk Management Research Laboratory, Research Triangle Park, NC, September 2000.

KEY WORDS

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16. ABSTRACT The paper gives results of an investigation of two classes of calcium (Ca)based sorbents (hydrated limes and silicate compounds). (NCTE: Efforts to develop multipollutant control strategies have demonstrated that adding certain oxidants to different classes of Ca-based sorbents significantly improves the removal of elemental mercury vapor (Hgo), sulfur dioxide (SO2), and nitrogen oxides (NOx) from simulated flue gases.) A number of oxidizing additives were used at different concentrations in the Ca-based sorbent process. The Hgo, SO2, and NOx capture capacities of these oxidant-enriched sorbents were evaluated and compared to those of a commercially available activated carbon in bench-scale, fixed-bed, and fluid-bed systems. Ca-based sorbents prepared with two oxidants, designated C and P, exhibited Hgo sorption capacities (about $100 \mu g/g$) comparable to that of the activated carbon; they showed far superior SO2 and NCx sorption capacities. Preliminary cost estimates for the process utilizing these novel sorbents indicate potential for substantial lowering of control costs, compared to other processes currently used or considered for control of Hgo, SO2, and NOx emissions from coal-fired boilers. The implications of these findings toward development of multipollutant control technologies are summarized.

17. KEY WORDS AND DOCUMENT ANALYSIS						
a. DESCRIPTORS		b.IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group			
Pollution	Flue Gases	Pollution Control	13B	2 1B		
Mercury (Metal)	Calcium Oxides	Stationary Sources	07B			
Sulfur Dioxide	Silicate Minerals			08G		
Nitrogen Oxides	Activated Carbon					
Sorbents	Coal		11G	21D		
Calcium	Combustion					
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