PREPARATION AND EVALUATION OF MODIFIED LIME AND SILICA-LIME SORBENTS FOR MERCURY VAPOR EMISSIONS CONTROL

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Abstract

Previous work has shown that mercury chloride vapor is readily absorbed by calcium-based sorbents as an acid gas in environments typical of coal-fired boiler flue gas, while elemental mercury vapor is absorbed by calcium-based sorbents only when sulfur oxides are also present. Current efforts are attempting to improve uptake of mercury species by increasing active sites and adding oxidative species to the sorbent. Preparation of modified lime and silica-lime sorbents and their behavior toward mercury species are compared to those of commercially available lime on a fixed-bed, bench reactor. The implications of findings toward development of multipollutant control technologies and planned field pilot evaluations of more promising multipollutant control concepts are discussed.

Introduction

Title III of the 1990 Clean Air Act Amendments (CAAA) requires the U.S. Environmental Protection Agency (EPA) to submit a study on 189 hazardous air pollutants (HAPs). This study would include emissions and a risk (to public health) assessment of the 189 HAPs. Of these pollutants, mercury has drawn special attention due to its increased levels in the environment and the well documented food chain transport and bioaccumulation of this element and its compounds such as methyl mercury [1,2]. An EPA report to Congress cites the largest emitters of mercury as coal-fired utilities, medical waste incinerators (MWIs), municipal waste combustors (MWCs), chlor-alkali plants, copper and lead smelters, and cement manufacturers [3]. These sources are estimated to account for over 90% of all anthropogenic mercury emissions. Utility boilers account for nearly 25% of the total anthropogenic emissions, of which more than 90% are attributed to coal-fired utility boilers.

Mercury, a trace constituent of coal and waste, is readily volatilized during combustion processes. Mercury is the most volatile trace metal, and major portions of it can pass through existing particulate matter (PM) control devices [4]. A sorbent reacting with this metallic vapor can effectively convert it to a sorbed liquid or solid phase, facilitating its removal with sorbent particles in a PM control device. Emission control processes which use dry sorbents do not pose the problem of the treatment and stabilization of a waste liquid stream and, therefore, seem very attractive for coal combustors and waste incinerators.

Several methods of controlling mercury emissions are in either commercial use or development for MWCs and MWIs [5]. Dry sorbent injection (DSI) of activated carbon, followed by fabric filtration (FF), has shown high (>90%) mercury removal in MWC applications. Spray drying (SD) followed by FF, and wet scrubbing (WS) have been both successfully applied for acid gas control, and found to remove substantial (60-90%) amounts of mercury in MWCs. However, all three technologies have been less successful in removing mercury from coal-fired flue gases [6].

Previous investigations conducted in EPA laboratories have indicated that mercury control strategies are dependent upon the mercury species that exist in the coal/waste combustion flue gases [7-9]. These studies have shown the relative ease of controlling oxidized mercury. specifically mercuric chloride (HgCl₂), as opposed to elemental mercury (Hg⁰) in fixed-bed applications. Reagent grade hydrated lime exhibited as high as 85% removal of HgCl₂ sustained for at least 24 hours [9]. The same sorbent under identical conditions showed no Hg⁰ capture, indicating the degree of difficulty in the capture and control of Hg⁰. Since Hg⁰ is expected to be present in coal combustion flue gases, it is therefore not surprising that the MWC mercury control technologies have been less successful in removing mercury from coal-fired flue gases. Furthermore the operators of some waste incinerators also need to be concerned about Hg⁰ emission control. While the mercury in most incinerator streams is predominantly HgCl₂, this is not always the case. Prior compliance measurements from the Ft, Dix municipal Waste-To-Energy Plant in New Jersey, for example, indicated a high degree of Hg⁰ in flue gases [10]. Thus, the focus of this study was to optimize the development of novel calcium (Ca)-based sorbents so that maximum capture of Hg⁰ could be achieved. As discussed previously, HgCl₂ can be controlled using any alkaline sorbent such as unmodified reagent grade lime [7-9].

Development of novel sorbents for the control of mercury is the subject of a number of current research programs [11-14]. Our previous studies [8,15,16] have shown that a potential method of cost reduction in controlling mercury emissions in coal-fired utilities (applicable to waste incinerators as well) would be to utilize cheaper Ca-based sorbents. These results also showed that further modifications and improvements in these Ca-based sorbents are needed in order to augment their Hg⁰ sorption capabilities.

Summary of Previous Studies

Two novel Ca-based sorbents and a reagent grade hydrated lime were evaluated with regard to their Hg⁰ capture capabilities in our previous investigations (fixed-bed applications). Hydrated lime with a total surface area of 13 m²/g exhibited no Hg⁰ capture. The two novel Ca-based sorbents exhibited relatively good Hg⁰ capture in the presence of sulfur dioxide (SO₂), removing 35 and 18% of gas-phase Hg⁰, respectively, during a 30-minute test. Under identical conditions, a commercially available activated carbon (Darco FGD, Norit Americas Inc.) removed about 70% of inlet Hg⁰. It was hypothesized that activated carbon was effective (as compared to Cabased sorbents) in adsorption of Hg⁰ in large part due to its large surface area (about 550 m²/g) and large population of small pores as was illustrated in its pore size distribution results [8,15]. The two novel Ca-based sorbents that exhibited some reactivity toward adsorption of Hg⁰ were also found to have significantly higher numbers of small pores and relatively high surface areas (compared to hydrated lime) [8,15]. This previous work was conducted using a different approach than the work reported herein, and results are not directly comparable.

From this previous work, the conclusion was that Hg^0 capture requires small pores (and subsequently higher surface area) in the Ca-based sorbents normally used for SO₂ control. It should be noted that the two novel Ca-based sorbents exhibited measurable Hg^0 capture only in the presence of SO₂ in the gas phase. It was concluded that SO₂ reacts with Ca-based sorbents and creates active sites inside the fine pore structure and facilitates the capture of Hg^0 molecules. It was determined that the extent of Hg^0 capture by modified Ca-based sorbents, upon further improvements, could provide an economic alternative to commercially available activated carbons.

As reported at the 1997 Mega Symposium, subsequent testing of two higher-surface area (and pore volume) calcium silicates exhibited high affinities for Hg⁰.[16] Sorbent 43 had a surface area of 205 m²/g, compared to 74.5 m²/g for sorbent 40. For sorbent 43, Hg⁰ uptake continued beyond 200 minutes of exposure. On the other hand and despite a higher initial rate of uptake, sorbent 40 showed a relatively small uptake capacity, reached after 30-40 minutes of exposure to the Hg⁰-laden simulated flue gas. Hg⁰ sorption directly correlated with the total surface area of the two sorbents.

It has been hypothesized that fine pores (< 100Å) are instrumental in capturing Hg⁰. The number or volume of pores smaller than 100Å was noticeably higher in sorbent 43. Activated carbon, FGD, was also tested under similar conditions, and continued to remove Hg⁰ beyond 200 minutes. Capacities of Sorbents 40, 43, and FGD after 200 minutes of exposure are plotted in Figure 1. The initial rate of Hg⁰ uptake (in μ g Hg⁰/g sorbent-min) for silicate sorbents in comparison to FGD is shown in Figure 2. Unlike slaked limes, modified silicates did not exhibit the same trends as capacities (Figure 1). Sorbent 43, despite a far superior Hg⁰ capacity, showed a lower initial rate of uptake. At that time the reasons for these observations were not understood, or proposed. As expected, activated carbon exhibited a better initial rate of Hg⁰ uptake.

Present Work

Since it has been established that Hg^0 is more difficult than $HgCl_2$ to control, and that Hg^0 control by alkaline sorbents requires fine pore structure and an SO_2 presence, this paper focuses on developing calcium-based sorbents for Hg^0 control. The key assumptions are that (a) alkaline sorbents will sorb $HgCl_2$, and (b) alkaline sorbents, having both fine pore structure and and an oxidizing species in the pore structure, can oxidize and sequester Hg^0 from flue gas.

Apparatus and Methodology

Bench-scale Hg^0 removal tests were performed on the vertical fixed-bed reactor apparatus illustrated in Figure 3. Operation and construction details of this apparatus have been previously described[8,15]. A simulated flue gas was generated containing 40 ppb Hg^0 , 4% oxygen, 10% carbon dioxide (CO₂), and 1% water vapor. Although some tests were performed with no SO₂ present, the majority of tests were on simulated flue gas containing 500 ppm SO₂. Simulated flue gas was then passed through the sorbent bed, a Lindberg furnace, a NAFIONTM dryer, and to serial Hg^0 and SO₂ analyzers. A total of 250 mg of sorbent was exposed to 300 cm³/min (dry@STP) simulated flue gas for 2 hours. Sorbents were tested at either 70 or 100°C reactor temperature. The Lindberg furnace was maintained at 100°C to prevent condensation and avoid undesirable side reactions. Breakthrough curves from the Hg⁰ and SO₂ analyzers were evaluated to determine initial and total Hg⁰ uptake rates; initial removal rates were calculated as the average removal rate during the first 5 minutes of sorbent exposure to the simulated flue gas.

Hydrated lime sorbents were prepared from commercial powdered quicklime (Marblehead Lime Co.) in a Parr reactor. The solution used for hydration was prepared from 30 % oxidant solution and deionized water as required. Quicklime was added to the reactor at ambient temperature prior to assembly. The hydrating solution at ambient temperature was injected into the reactor, and the reactor was scaled. Hydrations were performed with a substoichiometric amount of solution, estimated at 0.85, to ensure that liquid water was eliminated from the sorbent in an attempt to minimize oxidant decomposition. Thirty minutes after hydrating solution injection, the reactor was vented and sorbent was removed from the reactor. Due in part to the large thermal mass of the reactor, reaction temperatures did not exceed 100°C. No further drying was performed prior to testing. Sorbents were tested on the mercury apparatus within 48 hours of preparation.

The physical properties of the hydrated lime sorbents are shown in Table 1 with respective test conditions. The surface area and pore diameter of hydrated lime prepared with 6 and 30 %

oxidant were similar. Thermogravimetric Analysis (TGA) coupled with Residual Gas Analysis (RGA) confirmed the presence of oxidant on the solid sorbent in the form of a low decomposition temperature oxygen peak. Each sorbent preparation was tested once in the mercury test stand.

Hydrating Solution, % Ox	BET Surface Area, m²/g	Average Pore Diameter, Å	SO ₂ Concentration, ppmv	Reactor Temperature, °C
30	15.49	204.3	500	70
6	14.61	188.1	0	100
30	15.64	182.9	0	100
30	16.09	199.4	500	100
6	15.33	195.2	500	100
6	14.02	188.4	. 0	70
30	15.88	199.0	0	70
6	13.55	185.0	500	70

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Calcium silicate sorbents were prepared in a Parr reactor from reagent grade hydrated lime and ground amber post-consumer glass. An inorganic additive was dissolved in de-ionized water prior to addition of hydrated lime or ground glass. Glass, hydrated lime, and water were added to the Parr reactor at room temperature, and the reactor was sealed. Reagents were heated to 150° C and maintained at this temperature for 1 hour. Pressure was then released from the reactor and the slurry was vacuum filtered through Whatman #42 paper. The filter cake was dried overnight in a vacuum oven at 100°C and was removed and allowed to cool. A freshly regenerated molecular sieve scrubber was installed on the inlet air side of the vacuum oven each day to minimize CO₂ contamination. Dried sorbents were ground with a mortar and pestle. Recovered solids were then slurried at ambient temperature by adding solids to a wetting solution. The wetting solution was either de-ionized water or 30 % aqueous oxidant used in previous lime hydrations. After mixing for 5 minutes, the slurry was vacuum filtered through Whatman #42 paper and the filter cake was dried overnight in a vacuum oven at 100°C. Sorbents were tested for on the mercury test stand within 48 hours of preparation.

Sorbents were tested in the same manner as the hydrated limes on the bench-scale apparatus. All were evaluated with 500 ppmv SO_2 and at a 100°C reactor temperature. While each preparation was tested once on the mercury test apparatus, each preparation was replicated. The average physical properties of the calcium silicate sorbents are summarized in Table 2. The additive significantly enhanced the surface area of the silicate sorbent. In addition, wetting the sorbent in aqueous oxidant appears to both increase the surface area and decrease the average pore diameter compared to wetting the sorbent in water.

Silicate Preparation	Wetting Solution	Average BET Surface Area, m²/g	Average Pore Diameter, Å
3:1 glass/Ca(OH) ₂ with additive	water	167.8	164.8
1:1 glass/Ca(OH) ₂ with additive	water	130.0	231.2
1:1 glass/Ca(OH) ₂ no additive	water	50.48	233.7
1:1 glass/Ca(OH) ₂ no additive	30 % Oxidant	76.51	176.4
1:1 glass/Ca(OH), with additive	30 % Oxidant	156.8	202.6

Table 2. Silicate Sorbent Preparation and Physical Parameters

Results

Figure 4 illustrates the effects of oxidant-enriched lime on the initial rate of mercury removal. With 500 ppmv of SO₂ present in the simulated flue gas, calcium oxide (CaO) with 6% oxidant hydration removes Hg⁰ at an initial rate of 0.06 μ g/g-min at 70°C and 0.13 μ g/g-min at 100°C. Without SO₂ present, the effects of oxidant hydration are more pronounced, and initial mercury uptake rates are higher, indicating an interference between the oxidant and SO₂. Also the impact of adding the more concentrated oxidant solution, 30 vs 6%, is to further increase the rate of uptake in the absence of SO₂. With SO₂ present, the effect of increased oxidant concentration above 6% is negligible. For comparison, lime hydrated with water only has an initial Hg⁰ uptake of less than 0.01 µg/g-min.

Figure 5 illustrates the effects of oxidant hydration upon long-term (2 hour) Hg⁰ capacities of lime. With 500 ppmv SO₂ present, the Hg⁰ capacities average about 2.5 μ g/g sorbent for oxidant hydration, compared to a base hydrated lime (no oxidant) Hg⁰ uptake of about 1.0 μ g/g sorbent. In the presence of 500 ppmv SO₂, the strength of oxidant solution is not important. With no SO₂ present, the capacities are increased several fold over that with SO₂ present; the strength of oxidant solution is also important, with 30% solution nearly doubling (15.5 vs 8.8 μ g/g) the capacity over 6% solution at 70°C and increasing capacity over threefold (11.7 vs 3.1 μ g/g) at 100°C.

Figure 6 illustrates the effects upon SO_2 sorption capacity by oxidant hydration, and shows slight, but perceptible, improvement with increasing oxidant addition, more so at 70 than 100°C.

Figure 7 illustrates the impact of inorganic additive and oxidant on two sorbents prepared from brown glass and lime at 1:1 and 3:1 glass-to-lime weight ratios. The effects of inorganic additive (added to increase porosity) and oxidant (added to increase the rate of mercury oxidation) are similar, resulting in nearly 100% increases in the initial Hg⁰ uptake rate, when added separately. The effect is confounded when both are added, since the apparent improvement is the same as adding either separately. Limited data suggest that the initial uptake rate may be intrinsically higher for 1:1 glass-lime sorbent than for 3:1. For comparable flue gas temperatures and conditions (500 ppmv SO_2 and 100°C), the initial Hg⁰ uptake rates for unmodified silicates are comparable (~0.12-0.13 $\mu g/g$ -min) to that of oxidant hydrated lime and the modified silicates nearly twice (~0.22-0.23 $\mu g/g$ -min) that of oxidant hydrated lime.

Similar impacts are shown in Figure 8 for the total capacity of Hg⁰ uptake, where about 75% increases in capacity are noted with either additive, but again no synergism between additives is evident. However, the Hg⁰ capacity of one 3:1 glass:lime sorbent with inorganic additive is greater (6.0 vs 4.5 μ g/g) than for the comparable1:1 sorbent, despite having a lower initial uptake rate. Further, the base (no additives) sorbent at 1:1 glass:lime showed Hg⁰ capacities of 2.5 μ g/g sorbent, while the enhanced glass-lime sorbents averaged about 4.4 μ g/g sorbent. These may be compared to similar tests of lime sorbents, where Hg⁰ capacities of 2.5 μ g/g sorbent for oxidant-enriched lime were observed, and 1.0 μ g/g sorbent for base lime hydrate.

Figure 9 illustrates the impact of additives on SO_2 uptake by glass-lime silicates; inorganic additive slightly improves SO_2 uptake capacity, while little effect of oxidant addition is observed. The combined inorganic additive and oxidant effects appear to lower SO_2 capacity significantly, but the mechanism is not yet understood.

Discussion of Results

An explanation of the above results is that the oxidant hydration forms a solid calcium oxidant, CaO_x , which dissociates to oxidize Hg⁰. The oxidized Hg vapor is sorbed onto the alkaline sorbent matrix. The SO₂ present also will promote Hg⁰ oxidation by reacting with the lime to form solid calcium sulfite (CaSO₃) or calcium sulfate (CaSO₄) but, in doing so, blocks the pores, restricting further Hg⁰ diffusion into the reactive zone. The proposed reactions are:

$$H_2O + OX + 2CaO \rightarrow CaOOX + Ca(OH)_2$$
(1)

$$2Hg^{0} + CaOOX \rightarrow Hg_{2}O + CaO$$
(2)

The overall reaction for (1) and (2) is:

$$H_2O + OX + 2Hg^0 + CaO \implies Hg_2O + Ca(OH)_2$$
(3)

 SO_2 interferes with reaction (2) by consuming the solid oxidant phase :

$$CaO'OX + SO_2 -> CaSO_4$$
(4)

SO₂ promotes a similar oxidation of Hg⁰:

$$Ca(OH)_2 + SO_2 + O_2 -> CaSO_4 + H_2O + O$$
 (5)

$$2Hg^{0} + O \rightarrow Hg_{2}O \tag{6}$$

The overall reaction for (5) and (6) becomes:

$$Ca(OH)_2 + SO_2 + O_2 + 2Hg^0 \rightarrow CaSO_4 + H_2O + Hg_2O$$
 (7)

 SO_2 also inhibits reactions (3) and (7) by forming CaSO₃ and closing off pores:

$$Ca(OH)_2 + SO_2 \rightarrow CaSO_3 + H_2O$$
(8)

The oxidant-enriched lime tests in Figures 4-6 support the theory that the uptake of Hg⁰ by calcium sorbents is a two-step reaction, where Hg⁰ is oxidized at the surface (preferably in < 100Å pores) by reactions (3) and (7) and then further interacts with the alkaline sorbent. While SO₂ likely promotes Hg⁰ oxidation to Hg₂O by reactions (5) and (6), it also forms solid reaction products by equations (4), (5), (7), and (8), gradually closing off pores with CaSO₃ and CaSO₄ layers. Therefore, SO₂ can actually inhibit Hg⁰ uptake capacities by closing off the pore reaction sites for Hg₂O, while simultaneously promoting the formation of Hg₂O. SO₂ apparently intercepts the CaOOX formed by oxidant hydration of lime by reaction (4), thus further inhibiting Hg⁰ sequestering.

The temperature effect upon Hg^0 uptake is similar for oxidant-enriched and base lime hydrates in that decreasing the temperature below 100°C tends to slow down the necessary reactions; this is further indication that the observed reactions do not involve an Hg^0 condensation mechanism, which would increase with decreasing temperature. The significant findings from this work are that the initial rate of Hg^0 uptake can be dramatically increased by oxidant-enrichment of lime hydrates, and the overall capacity for Hg^0 may be significantly increased if a reduced SO₂ environment can be established. Although hydrogen chloride (HCl) was not present in any of the above work, it is expected that the role of HCl in sorbent pore pluggage would be similar to that for SO₂. Other prior studies with combined lime and activated carbon, show dramatically improved mercury uptake, presumably due to the lime's sequestering of acid gases before product chlorides and sulfites/sulfates can deactivate the highly porous activated carbon (17,18).

Silicate sorbents prepared from glass and lime are intrinsically higher in surface area and porosity than hydrated lime (Table 2 vs. Table 1) and, therefore, would be expected to have higher Hg^0 uptake rates and capacities than lime. The only data in Figures 7 and 8 are for 500 ppmv SO_2 present, so the capacities of silicates at low or no SO_2 conditions are yet to be determined. Attempting to increase surface area and oxidation potential by dual additives to silicate sorbents simultaneously appears to have been unsuccessful, although either individual additive shows positive benefits.

CONCLUSION

The practical significance of these results is that it has been shown that for sorbents to be effective for total mercury control, where an appreciable portion of mercury is Hg^0 , pore structure and oxidants are necessary. This implies that sorbents added for acid gas control will not be as effective for mercury control unless steps are taken to reduce the pore closure by solid chlorides, nitrates, and sulfites/sulfates. This further suggests that staging of sorbent addition will be more effective with less expensive alkaline sorbents added upstream for bulk acid gas removal, followed by downstream addition of premium, higher porosity, oxidant-enriched sorbents for mercury control.

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Figure 1- Hg° uptake by calcium silicates, 100 °C, 2 hours of exposure to 40 ppb Hg°, 500 ppm SO₂, 1% H₂O, 4% O₂, 10% CO₂, and balance N₂



Figure 2. Initial rate of Hg° uptake by calcium silicates, 100 °C, 2 hours of exposure to 40 ppb Hg°, 500 ppm SO2, 1% H2O, 4% O2, 10% CO2, and balance N2

7







Figure 4. Initial rate of Hg° uptake for modified lime sorbents; effect of temperature, SO₂, and oxidant



Figure 5. Hg° sorption capacity (2-hour exposure) for modified lime sorbents; effect of temperature, SO₂, and oxidant



Figure 6. SO₂ sorption capacity (2-hour exposure) for modified lime sorbents; effect of temperature and oxidant



Figure 7. Initial rate of Hg° uptake by calcium silicates; 500 ppm SO₂, 100°C



Figure 8. Hg° sorption capacity of calcium silicates: 500 ppm SO₂, 100°C



Figure 9. SO₂ sorption capacity of calcium silicates; 500 ppm SO₂, 100 °C

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