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Short communication

A novel Hg control technology derived from quantum chemistry

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Calculations with quantum theories have predicted that a proprietary substance is an excellent substance for Hg adsorption. Based on this prediction, the adsorptions of Hg with this substance were performed. The tests have shown that the temperature affects the adsorption of Hg on the substance and about 100% Hg removal efficiency was achieved at 300 °C.

Mercury is fast becoming the number one pollutant concern of the U.S. power industry. Although present in coal at levels measured in the parts per billion, mercury is both highly toxic and a bio-accumulator, which means that it is concentrated as it moves through the food chain. The U.S. Environmental Protection Agency is expected to add it to its list of regulated pollutants and the electric utility industry is seeking cost-effective technologies to detect and prevent its emission from coal-fired power plants [1].

Options that have been tested include injection of sulfide-containing liquors oxidation of elemental Hg for enhanced Hg removal by wet scrubbers, the use of solid sorbents, and the use of substrates coated with noble metals such as gold (which are regenerable) to collect Hg vapors [2]. The oxidative methods include the use of solid catalysts, liquid oxidants, photochemical oxidation [3], and corona discharge plasmas. The vast majority of work performed on Hg abatement has involved sorbent injection. Although numerous sorbent materials have been studied, activated carbons [4,5] currently appear to be the most promising and have by far received the greatest attention.

Despite the popularity of activated carbons, problems have been noted with respect to rapid breakthrough of Hg (from fixed beds) in the presence of various flue gas constituents, mass transfer limitations, impacts of SO_2 and HCl on equilibrium adsorption capacity for some activated carbons, and might decrease reactivity and sorption capacity at typical duct injection temperatures [6]. In addition to these technical difficulties, post-combustion control of Hg through sorbent injection may prove prohibitively costly. For example, when using sorbent injection in conjunction with other Hg control strategies, removing 90% of the Hg from coal-derived flue gas is expected to cost billions of dollars annually.

Rather than injected activated carbon in flue gas exiting their boilers for post-combustion control, people are increasingly interested in the removal of mercury from the coal before it is burned. In this approach, the coal is heated to 300 °C in an inert carrier, which drives out most of the mercury as elemental vapor. The concentration of mercury in the carrier gas would be much greater than in flue gas, facilitating mercury recovery compared to post-combustion clean up. Ideally, the carrier gas would not be cooled to recover the mercury but instead stripped of mercury at 300 °C and recycled to the coal pretreatment system.

We have studied a physico-chemical method for the removal of Hg. Based on quantum chemical theories [7,8], the cohesive energies of dimers formed during the physico-chemical adsorption of Hg(V) on selected substances are calculated. Generally speaking, a stable bond may exist if the calculated cohesive energy of the bond formed between Hg(V) and another substance is lower than that (-0.058 eV) between mercury itself (Hg–Hg). One of the substances calculated potentially has a strong Hg adsorption capacity since the cohesive energy of the bond between Hg(V) and this substance is -4.3542 eV, the lowest value among those checked 20 substances.

Mercury removal tests with the proprietary material were conducted under different temperatures. The experimental set-up is shown in Fig. 1. Liquid mercury in a sealed flask

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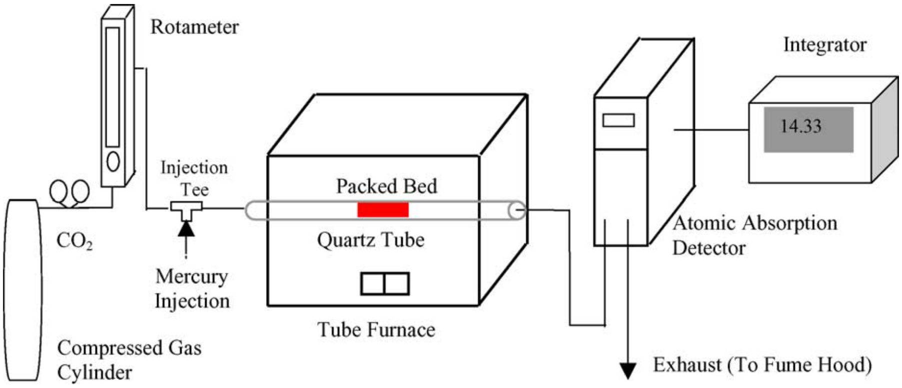

Fig. 1. Schematic diagram of the set-up for mercury removal experiments.

was used as a source for mercury vapor. A 1.0 mL Hamilton gastight syringe was used to withdraw 0.5 mL of mercury-laden air through a 6 mm Teflon faced septum on the top of the flask. The mercury was injected into a carbon dioxide carrier gas stream through a second septum. The carrier gas source was a compressed gas cylinder that supplies carbon dioxide at a constant pressure of 10 psi. The carbon dioxide flow rate was controlled with a rotameter upstream of the mercury injection point to maintain a constant flow of 50 mL/min. Downstream of the mercury injection point, the 1/4″ PTFE lines were connected to a 6 mm OD × 4 mm ID quartz tube using PTFE compression fittings. The quartz tube is 20 inches in length, and a notch was placed 8″ into the tube to hold a packed bed. The packed bed was formed by placing a small piece of quartz wool against the notch, followed by inserting supported tested material (40 mesh, Fisher Scientific), and by another small piece of quartz wool to hold the packed bed in place. The quartz tube was centered in a Lindberg/Blue Model TF55030A tube furnace equipped with an Athena XT16 temperature controller.

During a Hg removal test the temperature of the sorbent samples were varied between 150 and 300 °C. Downstream of the tube furnace, the gas mixture were analyzed for mercury with a Thermo-Separations Products MercuryMonitor® 3200 Atomic Adsorption detector. The analog signal from the detector was connected to a Hewlett-Packard 3395 Integrator and the peak areas from the detector signal were determined. The efficiency was determined by comparing peak area obtained with a packed bed to the peak area obtained when no packed bed was placed in the tube.

These results are shown in Fig. 2, which reveals almost 100% chemisorption of Hg onto microscopic particles of sorbent at temperatures of approximately 300 °C. This occurs near the optimum temperature for thermal evolution of Hg from the coal prior to combustion.

The test results could be explained with the mechanism of physico-chemical adsorption. In the lower temperature range, the atoms of Hg and sorbent were not sufficiently activated to form a strong bond between them, which resulted in lower Hg removal efficiencies. Increase of temperature strengthened the bond formed between Hg and sorbent and consequently enhanced the Hg removal efficiencies. However, when temperature was higher than 300 °C desorption dominated the interaction between Hg and sorbent and consequently the Hg removal efficiency started to decrease.

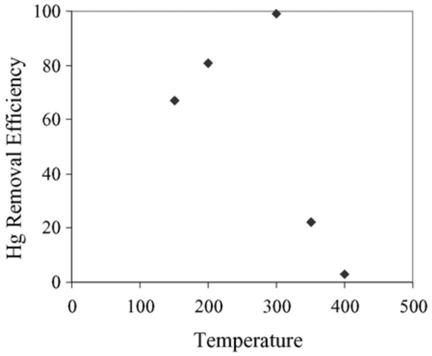

Fig. 2. Experimental results using the proprietary sorbent.

Furthermore, the proprietary sorbent material proved to be regenerable by heating to about 400 °C in a CO$_2$ environment. During the Hg loading step, elemental Hg vapors were injected into a CO$_2$ carrier gas stream flowing over a 2 g sorbent bed at a rate of 500 mL/min. The sorbent bed was heated at a nominal temperature of 225 °C while Hg was being injected. Through a series of injections, a total of about 40 ng of Hg was loaded onto the 2 g sorbent bed. After the Hg was loaded, the sorbent bed was removed from the tube furnace and the temperature of the tube furnace was increased to 450 °C. The sorbent bed was then inserted into the preheated 450 °C furnace while under a continuous CO$_2$ purge at 500 mL/min. Gases exiting the sorbent bed were continuously monitored for Hg during both the Hg loading and thermal regeneration steps. Results of this test are shown in Fig. 3. The signal observed during sample loading was scalloped because of temperature cycling in the tube furnace and because of the high sensitivity of Hg sorption behavior to temperature. The desorption signal looked excellent, and the area associated with the signal from the desorbed Hg was

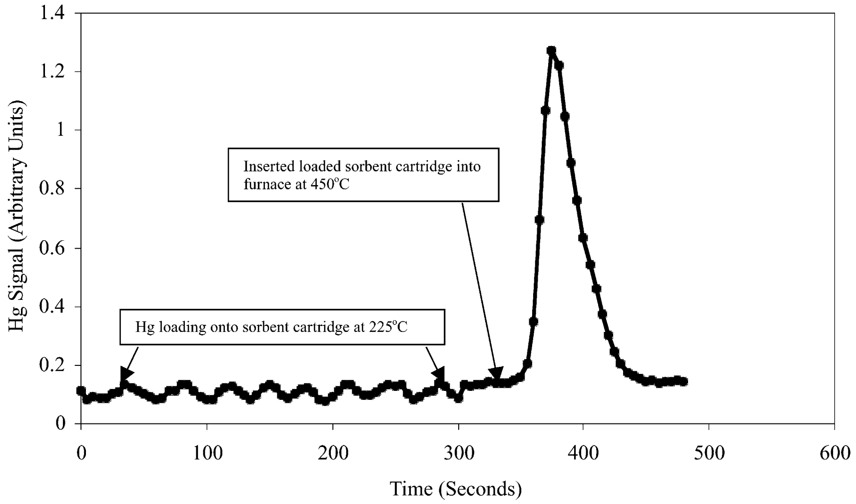

Fig. 3. Hg signal during loading and regeneration of sorbent cartridge with CO_2 as a carrier gas (gas flow rate: 500 mL/min; Hg loaded in gas stream: 40 ng; mass of sorbent bed: 2.0 g).

within 10% of the value expected based on the amount of Hg injected.

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