Mercury Emissions Control in Coal Combustion Systems Using Potassium Iodide: Bench-Scale and Pilot-Scale Studies

Ying Li, Michael Daukoru, Acharya Suriyawong, and Pratim Biswas*

Aerosol and Air Quality Research Laboratory, Department of Energy, Environmental and Chemical Engineering, Washington University in St. Louis, St. Louis, Missouri 63130

Received August 12, 2008. Revised Manuscript Received October 23, 2008

Addition of halogens or halides has been reported to promote mercury removal in coal-fired power plants. In this study, bench- and pilot-scale experiments were conducted using potassium iodide (KI) for capture and removal of Hg in air and coal combustion exhaust. Two bench-scale reactor systems were used: (1) a packed-bed reactor (PBR) packed with granular or powder KI and (2) an aerosol flow reactor (AFR) with injection of KI particles. It was found that a higher temperature, a higher concentration of KI, and a longer gas residence time resulted in a higher Hg removal efficiency. A 100% Hg removal was achieved in the PBR above 300 °C using 0.5 g of powder KI and in the AFR above 500 °C with a KI/Hg molar ratio of 600 at a 5.8 s residence time. The low KI injection ratio relative to Hg indicated that KI is highly effective for Hg removal in air. Formation of I2 vapor by the oxidation of KI by O2 at high temperatures, which then reacts with Hg to produce HgI2, was identified as the pathway for removal. The pilot-scale experiments were conducted in a 160 kW pulverized coal combustor. KI was introduced in two ways: as a powder mixed with coal and by spraying KI solution droplets into the flue gas. In both cases the Hg removal efficiency increased with an increase in the feed rate of KI. Mixing KI powder with coal was found to be more effective than spraying KI into the flue gas, very likely due to the higher temperature, longer residence time of KI, and the formation of a secondary reactive sorbent. The Hg removal by KI was less efficient in the pilot-scale tests than in the bench-scale tests probably due to certain flue gas components reacting with KI or I2. Hg speciation measurements in both bench- and pilot-scale experiments indicated no oxidized mercury in the gas phase upon introduction of KI, indicating that the oxidation product HgI2 was captured in the particulate phase. This is very beneficial in coal-fired power plants equipped with electrostatic precipitators where particulate-bound Hg can be efficiently removed.

Introduction

Mercury is a toxic air pollutant, and coal-fired utility plants are the largest anthropogenic emission source in the United States.1 In 2005 the U.S. Environmental Protection Agency (U.S. EPA) issued the Clean Air Mercury Rule (CAMR) to regulate Hg emissions from coal-fired power plants through a cap-and-trade approach.2 However, the U.S. EPA reversed its December 2000 regulatory proposal and removed power plants from the Clean Air Act list of sources of hazardous air pollutants. Both the reversal and the CAMR were vacated by the U.S. Court of Appeals for the District of Columbia Circuit in February 2008.3 As a result, it is likely that the U.S. EPA will have to require power plants to install Hg controls, and a more stringent federal rule is expected in a couple of years. In addition, many states have already promulgated their own regulations on Hg emissions, which are usually stricter than the CAMR.

The extent that Hg can be removed from power plant exhaust gases using conventional air pollution control devices (APCDs) is significantly affected by its speciation.4,5 Elemental Hg (Hg0) is the dominant species that is formed at the high coal combustion temperatures. As the flue gas is cooled along the convective pass in the boiler, a fraction of Hg0 can be oxidized to Hg2+ and/or bound on fly ash as HgP. Hg2+ is soluble in water and is readily captured by wet flue gas desulfurization (FGD) equipment. HgP can be collected together with the particulate matter in electrostatic precipitators (ESPs) and/or baghouses. By contrast, Hg0 is difficult to capture because it is less reactive, volatile, and insoluble in water. Hence, it is of great importance to develop effective Hg0 capture or oxidation technologies.

In coal combustion flue gases, Hg0 is oxidized and/or captured in two ways: (1) homogeneously oxidized in the gas phase, predominantly by Cl2, HCl, or Cl radicals, forming HgCl2,5–9 and (2) heterogeneously oxidized and captured on fly ash or sorbent particles, as well as across selective catalytic reduction (SCR) catalysts.10–13 The gas-phase homogeneous oxidation of Hg0 is kinetically limited because of the short residence time...
in flue gas, while the heterogeneous capture of Hg\(^0\) is limited by the equilibrium adsorption capacity of the sorbent, the mass transfer of Hg\(^0\) to the sorbent surface, and the concentration of chlorine species in the flue gas.\(^{14}\)

Chlorine is the major halogen species in coal, and it plays a very important role in both homogeneous and heterogeneous Hg\(^0\) oxidation.\(^{10,14}\) Other halogen species have also been shown to oxidize Hg\(^0\). The addition of bromine gas\(^{15}\) and hydrogen bromide gas\(^{16}\) to flue gas was demonstrated to enhance Hg\(^0\) oxidation, but the extent of enhancement was significantly affected by the injection temperature and flue gas composition. Cao et al.\(^{17}\) investigated Hg\(^0\) oxidation by four hydrogen halides and reported that HBr and HI are more effective than HCl and HF. Senior et al.\(^{18}\) recently developed an integrated process model for predicting mercury behavior in coal-fired utility boilers, which included bromine chemistry using a set of elementary, homogeneous and heterogeneous reactions involving bromine and Hg species. It has also been reported that activated carbon impregnated with sulfur, chlorine, and iodine has greater ability of capturing Hg compared with untreated carbon.\(^{14,19,20}\)

Two brominated powder activated carbons (PACs)—NORIT Americas’ DARCO Hg-LH and Sorbent Technologies’ B-PAC—showed significant Hg control potential at the DOE/NETL’s phase II field testing.\(^{21}\) As a result, the commercialization of brominated sorbents has been accelerated in recent years, and the cost of Hg control has decreased due to a reduction in the AICI injection rate. However, if the byproduct impacts are taken into consideration, the cost of brominated carbon injection for Hg control is estimated to increase by nearly 3-fold from the range of $6000–17700 (without byproduct impacts) to the range of $18000–42500 per pound of Hg removed, with a target of 90% Hg removal.\(^{22}\) Bromine-containing reagents (e.g., KNX coal additive) have also been tested as commercial products in full-scale coal-fired power plants, and Hg removal rates up to 90% were reported.\(^{22}\)

Other studies showed that iodine-impregnated activated carbons (containing I\(_2\) or KI or both) also have superior capacity of Hg capture.\(^{11,19}\) Another advantage of using an iodine-promoted sorbent is the lower volatility of HgI\(_2\) (higher boiling point) compared to other mercury halides (see Table 1), which enhances the stability of the spent sorbent. On the other hand, since Hg control via AICI will lead to additional costs for byproduct management and nonhazardous disposal,\(^{23}\) a noncarbon-based sorbent with an iodine promoter is preferred.

A simple form of iodine promoter is metal iodide, e.g., KI. I\(_2\) sublimes at a relatively low temperature (113 °C) and is more expensive than KI. Therefore, I\(_2\) is not an appropriate candidate for direct injection. KI is soluble in water, and it has been reported that an acidic KI solution was effective in capturing gas-phase Hg.\(^{23}\) To the best of our knowledge, no one has directly tested KI as a Hg removal reagent in coal-fired combustors. Although it is believed that Hg can be oxidized by I\(_2\), forming HgI\(_2\),\(^{17,24}\) the interactions between Hg and iodide (e.g., KI) are not clear from reports in the literature. Lee et al.\(^{20}\) reported Hg removal by KI-impregnated activated carbon and suggested mechanisms of Hg\(^0\) oxidation involving both KI and I\(_2\). However, no evidence was given in this study on the presence of I\(_2\) or how KI was converted to I\(_2\).

The purpose of this study was to investigate the effectiveness of Hg\(^0\) removal by KI in a coal-fired flue gas and to explore the reaction mechanisms. Feasibility studies were first carried out in bench-scale systems using air as a carrier gas, and the factors that affect Hg\(^0\) removal efficiency were investigated. Guided by the bench-scale findings, pilot-scale tests were then conducted in a pulverized coal combustor. Findings in the bench- and pilot-scale experiments in this study are important to the development of KI-based sorbents/oxidants for Hg control in full-scale coal-fired power plants.

### Experimental Section

**Description of Bench-Scale Tests.** The schematic diagram of the bench-scale experimental system is shown in Figure 1. Two types of reactors were used: a packed-bed reactor (PBR) and an aerosol flow reactor (AFR). Hg\(^0\) vapor was introduced to the system by passing N\(_2\) through a liquid Hg\(^0\) reservoir which was placed in a constant-temperature water bath. In the PBR system (Figure 1a), a certain amount of granular or powdered KI (>99.6%, Mallinkrodt Chemicals) was packed with glass wool in a glass tube (10 mm i.d.) and placed inside a tubular furnace (Thermolyne, type 21100). The size of granular KI was approximately 2–3 mm, and that of powdered KI was in the range of 100–150 µm (produced by grinding the granular KI and sieving).

In the AFR system (Figure 1b), KI aerosols were generated and introduced to the system through atomization. A certain amount of KI was dissolved in deionized water and used as a precursor in the atomizer (TSI Inc., model 3076). A diffusion dryer was used after the atomizer to dry the particles. The KI particles were mixed with Hg\(^0\) vapor and introduced into a ceramic tube (i.d. = 1.9 cm, L = 50 cm) which was heated by the tubular furnace. The size distributions of the KI particles before and after the furnace were monitored by a scanning mobility particle sizer (SMPS; TSI Inc.),

### Table 1. Physical Properties of Hg and Iodine Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting Point (°C)</th>
<th>Boiling Point (°C)</th>
<th>Decomposition Temp (°C)</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>KI</td>
<td>681</td>
<td>1330</td>
<td>N/A</td>
<td>white</td>
</tr>
<tr>
<td>I(_2)</td>
<td>113 (sublimes)</td>
<td>183</td>
<td>N/A</td>
<td>gray</td>
</tr>
<tr>
<td>HgI(_2)</td>
<td>140 (sublimes at 40°)</td>
<td>N/A</td>
<td>290(^a)</td>
<td>yellow</td>
</tr>
<tr>
<td>HgI(_2)</td>
<td>259</td>
<td>354</td>
<td>N/A</td>
<td>red</td>
</tr>
<tr>
<td>HgBr(_2)</td>
<td>236</td>
<td>322</td>
<td>N/A</td>
<td>white</td>
</tr>
<tr>
<td>HgCl(_2)</td>
<td>277</td>
<td>N/A</td>
<td>100(^a)</td>
<td>yellow</td>
</tr>
<tr>
<td>K(_2)HgI(_4)</td>
<td>N/A</td>
<td>N/A</td>
<td>100(^a)</td>
<td>N/A</td>
</tr>
<tr>
<td>KI(_2)</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

\(^{a}\) Data from ref 21.

**Table 1. Physical Properties of Hg and Iodine Compounds**

(18) Senior, C.; Fry, A.; Adams, B. Modeling Mercury Behavior in Coal-Fired Boilers with Halogen Additions. Presented at The Power Plant Air Pollution Control Mega Symposium, Baltimore, MD, 2008; Paper No. 150.
(22) Rini, M.; Vosteen, B. Full-Scale Test Results from a 600 MW PRB-Fired Unit Using Alstom’s KNX Technology for Mercury Control. Presented at The Power Plant Air Pollution Control Mega Symposium, Baltimore, MD, 2008; Paper No. 73.
Pilot-Scale Tests. The pilot-scale experiments were conducted by burning powder river basin (PRB) subbituminous coal in a 160 kW combustor facility at the Energy and Environmental Research Center (EERC) at the University of North Dakota. On a dry basis, the PRB coal burned in this study contained 67.28% carbon, 6.97% ash, 0.29% sulfur, 10 ppmw chlorine, and 0.05 ppmw Hg. The schematic drawing of the pilot-scale facility is shown in Figure 2. The combustor is oriented vertically to minimize wall deposits. A refractory lining helps to ensure an adequate flame temperature for complete combustion and prevents rapid quenching of the coalescing or condensing fly ash. Coal was introduced to the primary air stream via a screw feeder and eductor. The coal nozzle fired axially upward from the bottom of the combustor. The secondary air was introduced concentrically to the primary air with turbulent mixing. An electric air preheater was used for precise control of the combustion air temperature. The flue gas flow rate was 130 scfm or 210 (N m$^3$)/h, and the mean residence time of a coal particle in the combustor was approximately 3 s. An ESP operated at 40–60 kV was used to collect fly ash particles. A heat-traced and insulated baghouse was located downstream of the ESP. It contained three bags, and each bag was cleaned separately with its own diaphragm pulse valve. Hg speciation and concentration were measured at the ESP outlet using a continuous mercury monitor (CMM) (PSA Sir Galahad). KI was fed to the system in two ways as shown in Figure 2: (a) KI powder mixed with coal and (b) aqueous KI solution sprayed into the flue gas. KI powder was obtained by grinding granular KI into small sizes comparable to that of the pulverized coal powders (∼50 μm). KI solution (1.4 M) was prepared by dissolving KI granules in deionized water. The KI feeding strategies and feeding rates are listed in Table 3.

Results and Discussion

Bench-Scale Tests. PBR Results. Background tests without KI were first performed in the PBR and verified that the empty reactor (with glass wool) had no effect on Hg$^0$ removal in the temperature range tested. Then experiments were conducted using 2.0 g of granular KI and 0.5 g of powdered KI. The results are shown in Figure 3. For 2.0 g of granular KI with air as the carrier gas, no Hg$^0$ removal was observed when the temperature was below 100 °C. When the temperature increased over 100 °C, a slight removal of Hg$^0$ (∼7%) was observed. A sharp increase in Hg$^0$ removal occurred at around 200 °C and reached 100% when the temperature was higher than 320 °C. This positive temperature dependence suggests that Hg$^0$ removal is via a chemical reaction with a certain activation energy barrier. When N$_2$ (99.99%, Cee Kay Supply, Inc.) was used as the carrier gas, a similar shape of curve was observed except that the sharp increase in Hg$^0$ removal occurred at a higher temperature (330 °C), with 100% Hg$^0$ removal observed above 400 °C. The result indicated that O$_2$ promoted Hg$^0$ removal by KI. When 0.5 g of powder KI was tested in air, the Hg$^0$ removal curve shifted to the lower temperature region, even though the amount of powder KI was less than the granular KI used. This is likely due to the better contact of Hg$^0$ with KI powder because the powders have a much smaller size and a much higher total surface area than...
the granules. The temperature dependence of Hg\textsuperscript{0} removal by KI observed in this study is consistent with the findings reported by Lee et al.\textsuperscript{20} that the removal of Hg\textsuperscript{0} by KI-impregnated activation carbon increased as the temperature increased from 80 to 140 °C.

**AFR Results.** Experiments in the AFR system investigated the effectiveness of KI aerosols on Hg removal by varying the KI concentration and residence time in the temperature range of 200–1100 °C. The inlet Hg\textsuperscript{0} concentration was maintained constant for all tests. The mass concentration of KI aerosols introduced to the gas stream was varied by changing the concentration of KI in the solution in the atomizer, assuming a linear relationship between those two concentrations. The residence time was controlled by varying the total gas flow rate. Background tests without KI aerosols were first performed, and no Hg\textsuperscript{0} removal was detected in the temperature range tested. Figure 4 shows that for all the test conditions the Hg\textsuperscript{0} removal as a function of temperature followed a trend similar to that observed in the PBR tests; i.e., Hg\textsuperscript{0} removal became notable above a certain temperature, then increased with increasing temperature, and finally reached a plateau at high temperatures.

As shown in Figure 4a, when the residence time was 5.8 s, a higher temperature was needed to achieve observable Hg\textsuperscript{0} removal at a lower KI concentration (i.e., smaller KI/Hg molar ratio). When the molar ratio of KI to Hg decreased subsequently from 600 to 60, 30, and 15, the temperature above which Hg\textsuperscript{0} removal took place increased from 300 to 350, 380, and 400 °C, respectively. In the plateau region (500–1100 °C) where Hg\textsuperscript{0} removal was relatively stable, a higher KI concentration also resulted in a higher Hg\textsuperscript{0} removal efficiency. A maximum of 98% and 100% Hg\textsuperscript{0} removal was achieved at KI/Hg = 60 and 600, respectively. As the residence time decreased from 5.8 to 2.9 s (Figure 4b), the temperature needed for removal of Hg\textsuperscript{0} increased while the removal efficiency in the plateau region decreased for all the KI concentration levels. For example, at KI/Hg = 600, Hg\textsuperscript{0} removal occurred at 380 °C (compared to 300 °C at a 5.8 s residence time) and reached approximately 90% in the plateau region (compared to 100% at 5.8 s). No Hg\textsuperscript{0} removal was observed at a KI/Hg ratio of 15 for the entire temperature range. As the residence time further decreased to 1.9 s (Figure 4c), for all the KI concentrations the temperature required for Hg\textsuperscript{0} removal shifted toward an even higher value and the removal efficiency decreased further. Again, there was

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**Table 3. Summary of Pilot-Scale Experimental Conditions\textsuperscript{a}**

<table>
<thead>
<tr>
<th>concn of KI mixed in coal (ppm\textsubscript{w})</th>
<th>rate of KI spraying into flue gas (mL/h)</th>
<th>KI feeding rate (g/h)</th>
<th>KI concn in flue gas (mg/m\textsuperscript{3})</th>
<th>KI/Hg mass ratio\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>KI powder</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>235</td>
<td></td>
<td>6.4</td>
<td>31</td>
<td>4700</td>
</tr>
<tr>
<td>389</td>
<td></td>
<td>10.6</td>
<td>51</td>
<td>7780</td>
</tr>
<tr>
<td>777</td>
<td></td>
<td>21.2</td>
<td>101</td>
<td>15540</td>
</tr>
<tr>
<td>KI solution (1.4 M)</td>
<td></td>
<td>200</td>
<td>46.5</td>
<td>34000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>800</td>
<td>185.9</td>
<td>136000</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The coal feeding rate remained constant at 27 kg/h. \textsuperscript{b} The Hg concentration in the PRB coal burned was 0.05 µg/g.

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Figure 3. Hg\textsuperscript{0} removal by KI in PBR as a function of temperature.

Figure 4. Hg removal efficiency as a function of temperature at varied resident time: (a) $t = 5.8$ s, (b) $t = 2.9$ s, (c) $t = 1.9$ s. Key: (Δ) KI/Hg (molar ratio) = 15, (□) KI/Hg = 30, (○) KI/Hg = 60, (●) KI/Hg = 600.
no Hg\textsuperscript{0} removal at a ratio of KI to Hg of 15, with approximately 70\% Hg\textsuperscript{0} removal at a KI/Hg ratio of 600.

The AFR results indicated that Hg\textsuperscript{0} removal by KI in air was affected by three important parameters: temperature, KI concentration (or KI/Hg ratio), and residence time. A higher KI concentration or longer residence time leads to a higher Hg\textsuperscript{0} removal efficiency. This work for the first time thoroughly studied the temperature dependence of Hg\textsuperscript{0} removal by KI. In practical applications, KI- and/or I\textsubscript{2}-impregnated activated carbon is normally injected into the low-temperature region of the boiler convective pass (e.g., before the ESP at 120–160 °C),\textsuperscript{24} because the adsorption capacity of activated carbon decreases as temperature increases. The findings in this study, however, indicated that KI removes Hg\textsuperscript{0} more efficiently at higher temperatures (e.g., > 400 °C). Hence, activated carbon may not be an appropriate substrate for KI. It is recommended that non-carbon-based substrates or pure KI be used, so that these can be injected into a higher temperature zone to enhance Hg\textsuperscript{0} removal.

It should be noted that even the highest KI injection rate (KI/Hg = 600) tested in this study was actually very low compared to the full-scale injection rates of other types of sorbents. It is reported that, on using activated carbon, a carbon-to-Hg mass ratio of 2000–15000 is required to achieve 25–95\% removal of Hg in coal-fired power plants.\textsuperscript{14} Typical flue gas residence times from a coal-fired boiler furnace exit to the ESP inlet is 3–5 s. At a comparable time scale, this study showed that a KI/Hg mass ratio of 500 (molar ratio = 600) achieved 100\% and 90\% Hg\textsuperscript{0} removal at a residence time of 5.8 and 2.9 s, respectively. This demonstrates that KI is a highly effective reagent for Hg\textsuperscript{0} removal.

**Hg Speciation Results.** Results of gas-phase Hg speciation at the AFR outlet are shown in Figure 5. In the baseline test (no KI was injected), as expected, 100\% Hg\textsuperscript{0} was detected at the AFR outlet, and collected on the filter downstream. Future research is needed to close the Hg mass balance by measuring the amount and form of particulate Hg collected on the filter.

**Discussions on Hg—KI Reactions in Air.** A starch—iodine test was carried out to verify whether I\textsubscript{2} was generated and participated in the removal of Hg\textsuperscript{0}. It is known that I\textsubscript{2} dissolved in aqueous KI solution (forming I\textsuperscript{3}– ion) reacts with starch, producing a deep black-blue color. Neither I\textsuperscript{−} nor I\textsubscript{3}– alone leads to the color change. In this study, a white-colored solution consisting of 0.3\% (w/w) starch and 0.01 M KI was used as the reagent, and an impinger containing 15 mL of such solution was connected to the outlet of the PBR that was packed with 0.5 g of KI powder. Air or N\textsubscript{2} (99.99\%) was passed through the PBR at 1.0 L/min without a feed of Hg\textsuperscript{0}. If gas-phase I\textsubscript{2} were produced from the KI powder in the PBR, it would be captured in the impinger and a color change would be observed. Table 4 summarizes the results of the starch—iodine tests. When air was the carrier gas and the furnace was operated at 25 °C, no color change was observed for a collection time of 120 min. When the furnace temperature increased to 300 °C, a pink color was observable in 120 min, due to the trace amount of I\textsubscript{2} captured from the gas phase. When the furnace temperature was increased to 450 °C, the solution turned to black-blue in 1 min, which clearly indicated the presence of I\textsubscript{2}. The tests were then repeated using N\textsubscript{2} as the carrier gas. In this case, no color change was observed at 300 °C in 120 min but a pink color at 450 °C in 3 min. The results of starch—iodine tests indicated that I\textsubscript{2} vapor was produced from the oxidation of KI by O\textsubscript{2} at elevated temperatures:

\[
\text{O}_2 + 4\text{KI} \rightarrow 2\text{I}_2 + 2\text{K}_2\text{O} \tag{1}
\]

At room temperature almost no I\textsubscript{2} was produced. A higher temperature and a higher O\textsubscript{2} concentration result in a higher I\textsubscript{2} production rate. The pink color observed with N\textsubscript{2} at 450 °C is very likely due to the impurity O\textsubscript{2} (<100 ppm) in the N\textsubscript{2} cylinder that oxidizes KI to I\textsubscript{2}. Note that the experimental conditions under which Hg\textsuperscript{0} was removed in the PBR agree very well with the I\textsubscript{2} production observed in the starch—iodine tests. Hence, it is very likely that the removal of Hg\textsuperscript{0} is by the oxidation by I\textsubscript{2}, resulting in the formation of particulate HgI\textsubscript{2}:

\[
\text{Hg} + \text{I}_2 \rightarrow \text{HgI}_2 \tag{2}
\]
°C) is close to the temperature at which Hg⁰ removal started to occur (Figure 4). This validates the reaction mechanism that Hg⁰ reacts with I₂ vapor produced from KI oxidation. A larger amount of I₂ was generated at a higher KI concentration, which resulted in a higher Hg⁰ removal efficiency as shown in Figure 4.

The melting and boiling points of HgI₂ are 259 and 354 °C, respectively (Table 1). Considering that 100% Hg⁰ removal was achieved when the AFR was operated above 500 °C (Figure 4a) and no gaseous Hg²⁺ species was detected, the HgI₂ produced in the furnace should stay in the gas phase at that high temperature and then possibly be deposited along the tubing or adsorbed on unreacted KI particles at lower temperatures downstream of the AFR (most likely on the filter). Ponpon et al. studied the HgI₂ surface etched by KI solution and identified the formation of a KHgI₃ · H₂O complex on the surface. Similarly, in this work gas-phase HgI₂ may be adsorbed on the solid KI surface to produce KHgI₃ or K₂HgI₄ at lower temperatures:

\[ \text{HgI}_2 + \text{KI} \rightarrow \text{KHgI}_3 \]  
\[ \text{HgI}_2 + 2\text{KI} \rightarrow \text{K}_2\text{HgI}_4 \]

The decomposition temperatures of K₂HgI₄ and KHgI₃ are approximately 100 °C (Table 1). Hence, reactions 3 and 4 are less likely to proceed inside the high-temperature furnace. Since the online Hg analyzer requires the sampling gas temperature to be lower than 40 °C, the system after the furnace (e.g., the tubing and the filter) was naturally cooled, where K₂HgI₄ and KHgI₃ were possibly formed and deposited. This explains why no gaseous Hg²⁺ species were detected by the Hg analyzer. The formation of HgI₂ from reaction of Hg and I₂ is less likely to occur because HgI₂ sublimes at very low temperatures (Table 1) and should be detected in the gas phase, if any, by the impinger sampling and subsequent ICP-MS measurement.

Results of Pilot-Scale Tests. Since the bench-scale results showed that high temperatures promote Hg⁰ removal by KI, KI was introduced into two high-temperature zones in the pilot-scale combustor. First, KI powder was mixed with coal and fed to the combustor where the temperature exceeded 1400 °C. Second, aqueous KI solution was sprayed into the flue gas at a location where the temperature was around 900 °C. Figure 7a shows the effect on Hg⁰ removal by adding KI powder to coal. Without KI addition, the baseline Hg⁰ concentrations at the ESP outlet were around 5.0 µg/m³ and very close to each other (within 2%), indicating no Hg²⁺ existed in the gas phase. Soon after 235 ppmw (6.4 g/h or 31 mg/m³) KI powder was added to the coal, the Hg⁰ concentration decreased to around 3.6 µg/m³. Temporarily cutting off the KI powder feed caused the Hg⁰ concentration to increase to the baseline level. When the KI powder was added again at 389 ppmw, the Hg⁰ concentration decreased to 2.4 µg/m³. Measurement of Hg⁰ concentration at this condition showed the same level as Hg⁷, indicating no Hg²⁺ existed in the gas phase. This Hg speciation result agrees with that obtained in the bench-scale experiments. It is very likely that the reaction product, HgI₂, was condensed in the particulate phase or captured on the fly ash as the flue gas cooled. Increasing the KI powder to coal ratio to 777 ppmw reduced the Hg⁰ concentration to an average level of 1.9 µg/m³. Finally, the KI powder feed was cut off and the Hg⁰ concentration increased but at a slower rate toward the baseline level.

iodine promoters. It has been reported that SO$_2$ may react with I$_2$ and H$_2$O to form H$_2$SO$_4$ and HI at temperatures greater than 120 °C:\[26]

\[
\text{SO}_2 + \text{I}_2 + 2\text{H}_2\text{O} \xrightarrow{120 \ ^\circ \text{C}} \text{H}_2\text{SO}_4 + 2\text{HI} \quad \text{(exothermic)} \quad (5)
\]

Meanwhile, HI may decompose to I$_2$ and H$_2$ at temperatures higher than 320 °C:\[26]

\[
\text{HI} \xrightarrow{320 \ ^\circ \text{C}} \text{I}_2 + \text{H}_2 \quad \text{(endothermic)} \quad (6)
\]

Although the PRB coal burned has a low sulfur content (0.29%), the estimated SO$_2$ concentration in the flue gas in the pilot-scale tests was around 300–400 ppm$_v$, at least 1 order of magnitude higher than the concentration of I$_2$ produced by KI injection. Because of the high concentration of water vapor in the flue gas, reaction 5 may proceed and consume I$_2$. Since the rate of I$_2$ production from reaction 6 was lower than the I$_2$ consumption by SO$_2$, a lower Hg removal efficiency was observed in pilot-scale experiments. Further studies are needed to systematically evaluate the effects of flue gas components on Hg removal by KI.

It should be noted that the iodine emissions from the flue gas may have negative health effects. Iodine in the flue gas may cause corrosion problems for power plants as well. Further studies are needed to address these potential concerns. On the other hand, studies are being conducted to evaluate the balance-of-plant impact of bromine/bromide injection for coal-fired power plants with regard to flue gas bromine emissions, ash use, bromine leaching, and bromine-related corrosion in the boiler and in the scrubber.\[27\] Since iodine and bromine have similar chemical properties, the results of these bromine studies will help in understanding the balance-of-plant impact of iodine promoter injection.

Conclusions

It has been demonstrated that KI is an effective reagent for Hg$^0$ removal in air in bench-scale experiments. The bench-scale results indicated that the temperature, KI concentration, and residence time were important factors that affect the Hg$^0$ removal efficiency. In both the PBR and AFR experiments, a positive temperature dependence of Hg$^0$ removal by KI was observed. In the PBR, 100% Hg$^0$ removal was observed for either 2 g of granular or 0.5 g of powder KI at temperatures higher than approximately 300 °C. In the AFR, at a 5.8 s residence time and temperature above 500 °C, 98% and 100% Hg$^0$ removals were achieved at KI/Hg molar ratios of 60 and 600, respectively. The starch–iodine tests identified the formation of I$_2$ vapor due to oxidation of solid KI by O$_2$ at elevated temperatures, which resulted in the observed Hg$^0$ removal, with HgI$_2$ being the most likely reaction product. In the low-temperature region downstream of the reactor, HgI$_2$ may condense to the particulate phase or adsorb on KI, forming KHgI$_3$ or K$_2$HgI$_4$. Higher KI concentrations and a longer residence time in the reactor also enhanced the Hg$^0$ removal efficiency.

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(27) Dombrowski, K.; Richardson, C.; Paradis, J.; Chang, R. The Balance-of-Plant Impact of Calcium Bromide Injection as a Mercury Oxidation Technology in Power Plants. Presented at The Power Plant Air Pollutant Control Mega Symposium, Baltimore, MD, 2008; Paper No. 27.
Guided by the bench-scale results, pilot-scale experiments were conducted in a 160 kW pulverized coal combustor. KI in two different forms was injected at two locations (with different temperatures) in the system. First, KI powder was mixed with coal and fed to the combustor (>1400 °C), and second, KI was sprayed into the flue gas where the temperature was approximately 900 °C. The Hg removal efficiency increased with increasing feeding rate of KI. Mixing KI powder with coal resulted in a higher Hg removal efficiency than spraying KI solution into the flue gas, possibly due to the higher temperature and the longer residence time of KI in the flue gas. The mixing of KI with the coal favors the generation of I₂ (due to higher temperatures) and possibly the in situ generation of secondary reactive sorbents from reactions of KI and coal minerals in the combustor. No gaseous Hg²⁺ species was measured in the flue gas, indicating that the oxidation product HgI₂ was captured and removed by the ESP. The removal of Hg by KI in the coal combustion flue gas (pilot-scale tests) was less efficient than in air (bench-scale tests), possibly because certain flue gas components (e.g., SO₂) react with the injected KI or I₂.

Acknowledgment. This work was supported partially by the U.S. DOE (Grant Number DE-FG06-05NT42531) and Ameren UE, St. Louis, through Contract Number W-0001-06, Missouri Department of Natural Resources. We thank Dr. Ye Zhuang, UND-EERC, and his staff for helping perform the pilot-scale experiments.