

Bench- and Pilot-Scale Studies on Mercury Removal by Potassium Iodide in Coal-Fired Flue Gas

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Introduction

Mercury (Hg) is a toxic air pollutant with coal-fired utility plants being the largest anthropogenic Hg emission source in the United States.¹ The extent that Hg can be removed from power plants using conventional air pollution control devices (APCDs) is significantly affected by Hg speciation in flue gas.² Oxidized Hg (Hg^{2+}) is preferable to elemental Hg (Hg^0) in that Hg^{2+} is less volatile and soluble in water and thus is easier to be captured through wet scrubbers and/or electrostatic precipitators. Chlorine is the major halogen species in coal and it plays a very important role in both homogeneous and heterogeneous Hg^0 oxidation in flue gas.^{3,4} Other halogen species have also demonstrated their abilities to oxidize Hg^0 .^{5,6} It has also been reported that activated carbon impregnated with sulfur, chlorine, and iodine has greater ability of capturing Hg compared with untreated carbon.^{3,7,8} Particularly, iodine impregnated activated carbon showed superior capacity of Hg capture.^{7,9} Another advantage of using iodine promoted sorbent is the lower volatility of HgI_2 (higher boiling point) compared to other mercury halides, which enhances the stability of the spent sorbent. On the other hand, injection of carbon based sorbents can compromise fly ash properties due to the residual carbon content, and thus, the operation cost will be increased since the fly ash is no longer sellable. Therefore, non-carbon based sorbent with an iodine promoter is preferred.

A simple form of iodine promoter is metal iodide, e.g. KI. I_2 sublimates at a relatively low temperature (113 °C) and it is more expensive than KI, and thus, 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.¹⁰ To the best of our knowledge, no one has directly tested KI as a Hg sorbent in coal-fired combustors. Although it is believed that Hg can be oxidized by I_2 forming HgI_2 ,^{5,11} the interactions between Hg and iodide (e.g. KI) are not clear in the literature. 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. This finding is important to the development of KI-based sorbents for Hg control in full-scale coal-fired power plants.

Experimental

Description of Bench-Scale Tests

The schematic diagram of the bench-scale experimental system is shown in Figure 1. Hg^0 vapor was introduced to the system by passing N_2 through a liquid Hg^0 reservoir. Two types of reactors were used: a packed-bed reactor (PBR) and an aerosol flow reactor (AFR). In

the PBR system (Figure 1a), a certain amount of granular or powder KI (>99.6%, Mallinckrodt Chemicals) was packed in a glass tube (10 mm ID), which was placed inside a tubular furnace (Thermolyne, Type 21100). In the AFR system (Figure 1b), KI aerosols were generated in an atomizer and introduced to the system through atomization. The KI particles mixed with the Hg^0 vapor and then entered a ceramic tube (ID = 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., St. Paul, MN, USA). For both PBR and AFR systems, Hg^0 concentration at the furnace outlet was measured by an online Hg analyzer (Model RA915+, OhioLumex Co.). Since the Hg analyzer only detects Hg^0 , an EPA Method 5 type sampling train developed by Hedrick et al.¹⁰ was used to measure both Hg^0 and Hg^{2+} concentrations in the gas phase. The impinger solutions were then analyzed by inductively coupled plasma mass spectrometry (ICP-MS). The experimental conditions for bench-scale studies are summarized in Table 1.

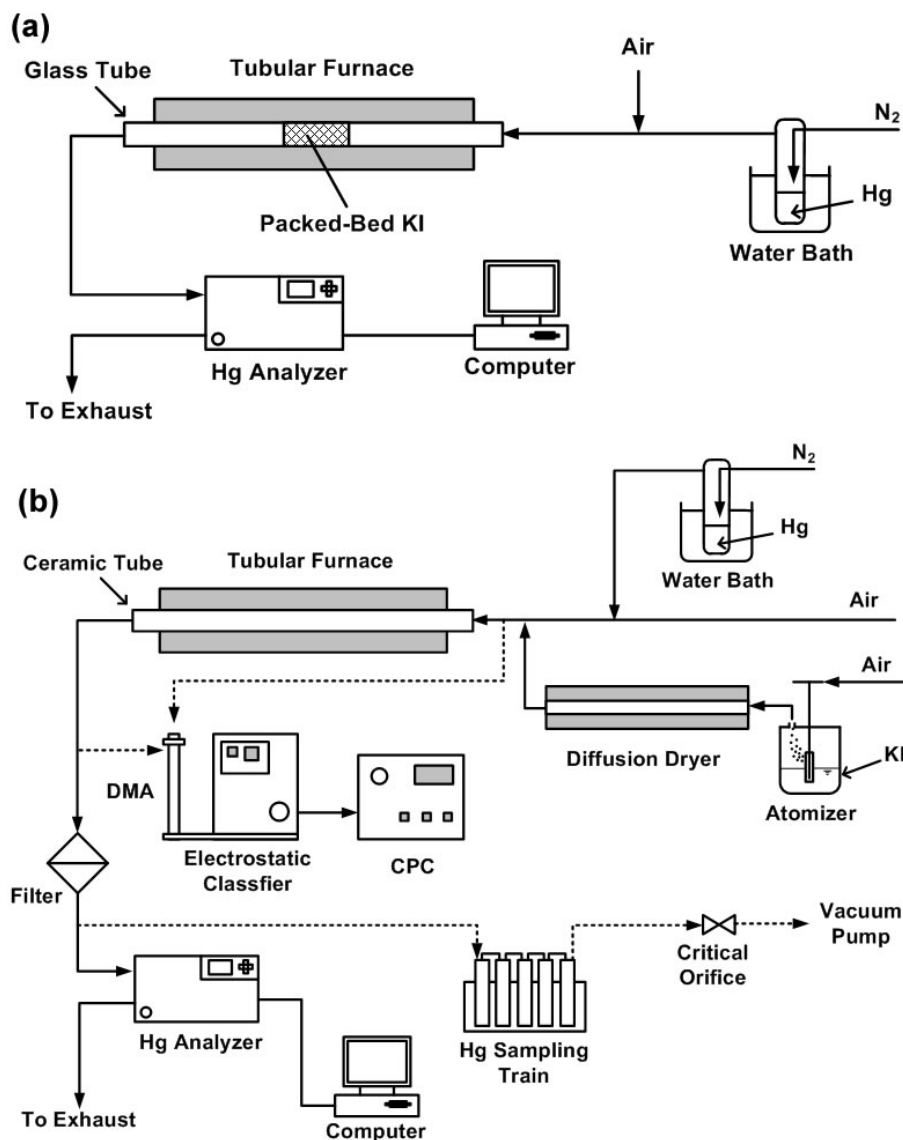


Figure 1. Schematic diagram of bench-scale experimental system: (a) packed-bed reactor (PBR), (b) aerosol flow reactor (AFR).

Table 1. Summary of bench-scale experimental conditions

<i>PBR system</i>				
Inlet Hg conc. (ppb)	Amount of KI (g)	Furnace Temp. (°C)	Gas flow rate (l min ⁻¹)	Residence time in packed-bed (s)
10.5 ± 0.5	2.0 (granule)	25 ~500	1.0	0.21
10.5 ± 0.5	0.5 (powder)	25 ~500	1.0	0.033
<i>AFR system</i>				
Inlet Hg conc. (ppb)	KI/Hg (molar ratio)	Furnace Temp. (°C)	Gas flow rate (l min ⁻¹)	Residence time in reactor (s)
13.5 ± 0.5	15, 30, 60, 600	200 ~ 1100	1.5, 3.0, 4.5	5.8, 2.9, 1.9

Description of Pilot-Scale Tests

The pilot-scale experiments were conducted by burning Powder River Basin (PRB) subbituminous coal in a 160 kW facility at the Energy and Environmental Research Center (EERC) at the University of North Dakota. The schematic drawing of the pilot-scale facility is shown in Figure 2. Coal feeding rate remained constantly at 27 kg/hr and the flue gas flow rate was 130 scfm or 210 Nm³/hr. 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 flue gas. The KI feeding strategies and feeding rates are listed in Table 2.

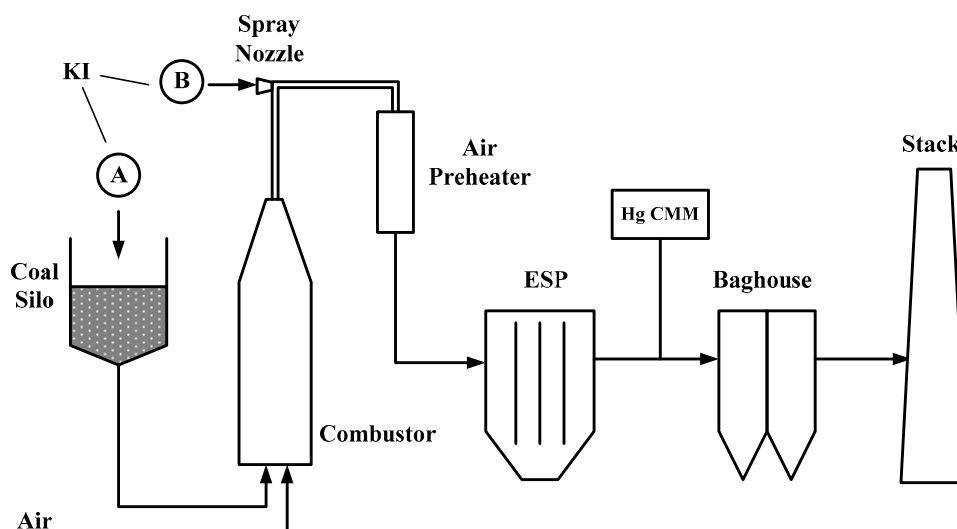


Figure 2. Schematic diagram of the 160 kW pilot-scale facility with KI injection

Table 2. Summary of pilot-scale experimental conditions

	KI powder mixed in coal (ppm _w)	KI solution sprayed (ml/hr)	KI feeding rate (g/hr)	KI conc. in flue gas (mg/m ³)
KI powder	235		6.4	31
	389		10.6	51
	777		21.2	101
KI solution (1.4 M)		200	46.5	221
		800	185.9	885

Results and Discussion

Results of Bench-Scale Tests

The PBR experiments were conducted using 2.0 g granular KI and 0.5 g powdered KI, respectively. The results are shown in Figure 3. For 2.0 g 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 involves chemical reaction and certain activation energy is required. When N_2 (99.99%) 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) and 100% Hg^0 removal was reached at above 400 °C. The result indicated that O_2 can promote 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 which has much smaller size and higher total surface area.

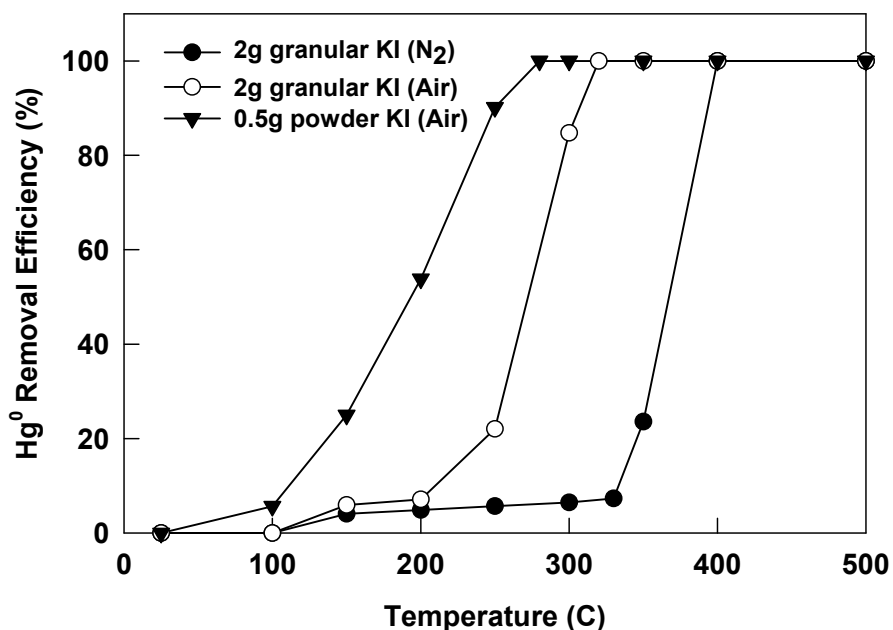


Figure 3. Hg^0 removal by KI in PBR as a function of temperature.

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 to 1100 °C. 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. The residence time was controlled by varying the total gas flow rate. Figure 4 shows the results when the residence time was 5.8 s. The curves of Hg^0 removal as a function of temperature followed a similar trend as observed in the PBR tests, i.e. Hg^0 removal became notable above a certain temperature and then increased with increasing temperature and finally reached a plateau at high temperatures. A higher temperature was needed to achieve observable Hg^0 removal at a lower KI concentration (i.e. smaller KI/Hg molar ratio). When the molar ratio of KI/Hg decreased subsequently from 600 to 60, 30, and 15, the temperature above which Hg^0

removal took place increased from 300 to 350, 380, and 400 °C, respectively. In the plateau region (500 – 1100 °C) where Hg^0 removal was relatively stable, a higher KI concentration also resulted in higher Hg^0 removal efficiency. A maximum of 98% and 100% Hg^0 removal was achieved at KI/Hg = 60 and 600, respectively. As the residence time decreased from 5.8 s to 2.9 s and 1.9 s (results not shown), the Hg^0 removal efficiency decreased accordingly. The Hg speciation analysis did not detect gaseous Hg^{2+} at the reactor outlet. Thus, it is believed that all the Hg^0 reduced in the gas-phase across the reactor was converted to particulate phase, possibly collected on the filter downstream.

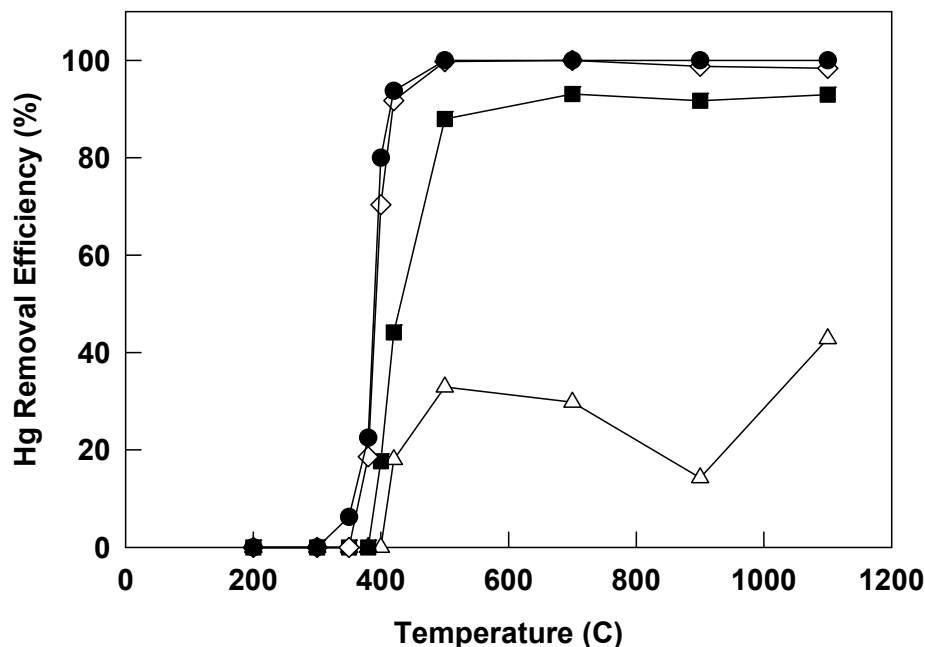


Figure 4. Hg removal efficiency as a function of temperature; resident time = 5.8s. Legend: \triangle KI/Hg (molar ratio) = 15, \blacksquare KI/Hg = 30, \diamond KI/Hg = 60, \bullet KI/Hg = 600.

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 was reported that by using activated carbon a carbon-to-Hg mass ratio of 2,000 – 15,000 was required to achieve 25% to 95% removal of Hg in coal-fired power plants.³ Typical flue gas residence time from coal-fired boiler furnace exit to 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^0 removal at a residence time of 5.8 and 2.9 s, respectively. This demonstrates that KI is a highly effective sorbent for Hg^0 removal.

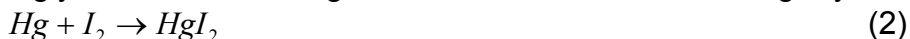
Reaction Mechanisms

In this study, a starch-iodine test was carried out to verify whether I_2 was generated and participated in the removal of Hg^0 . It is known that I_2 dissolved in aqueous KI solution (forming I_3^- ion) reacts with starch producing a deep black-blue color. Neither I^- nor I_2 alone will lead to the color change. In this study, a white-color 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 KI powder. Air or N_2 (99.99%) was passed through the PBR at 1.0 l/min without feed of Hg^0 . If gas-phase I_2 was produced from the KI powder in the PBR, it would be captured in the impinger and color change should be observed.

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, probably due to the trace amount of I₂ captured from the gas-phase. When the furnace temperature further increased to 450 °C, the solution turned to blackish blue in one min, which clearly indicated the presence of I₂. The tests were then repeated using N₂ 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, very likely due to the impurity O₂ (<100 ppm) in the N₂ cylinder. The results of starch-iodine tests indicated that I₂ vapor was produced from the oxidation of KI by O₂.



Accordingly, the removal of Hg⁰ was due to the oxidation of Hg⁰ by I₂ forming HgI₂.



This reaction mechanism was further verified by examining the number concentration and particle size distributions of the KI aerosols (without feed of Hg⁰) at the AFR outlet measured by SMPS. The KI aerosol concentration was observed to decrease above 300 °C and dropped to the background level (no KI) at 600~700 °C. Because the melting point of KI is 681 °C, the decrease in the particle number concentration below this temperature is very likely due to oxidation of the fine KI particles to I₂ vapor. The melting and boiling points of HgI₂ are 259 °C and 354 °C, respectively. Considering that 100% Hg⁰ removal was achieved when the AFR was operated at above 500 °C and no gaseous Hg²⁺ species was detected, the HgI₂ produced in the furnace should stay in gas phase at that high temperature and then possibly deposited along the tubing or adsorbed on unreacted KI particles at lower temperatures downstream of the AFR (most likely on the filter), forming KHgI₃ or K₂HgI₄.



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. Figure 5a shows the effect on Hg⁰ removal by adding KI powder to coal and co-combusted at over 1400 °C. Without KI addition, the baseline Hg^T and Hg⁰ concentrations at the ESP outlet were around 5.0 µg/m³ and no Hg²⁺ was in the gas phase. Soon after 235 ppm_w (6.4 g/hr) KI powder was added to the coal, the Hg^T concentration decreased to around 3.6 µg/m³. Temporarily cutting off the KI powder feed caused the Hg^T concentration to increase to the baseline level. When the KI powder was added again at 389 ppm_w, the Hg^T concentration decreased to 2.4 µg/m³. Measurement of Hg⁰ concentration at this condition showed the same level as Hg^T, indicating that no Hg²⁺ existed in the gas phase which agrees with that in the bench-scale experiments. It is very likely that the reaction product, HgI₂, was condensed in particulate phase or captured on the fly ash as the flue gas cools down. Increasing the KI powder mixing ratio further to 777 ppm_w reduced Hg^T concentration to an average level of 1.9 µg/m³. Finally, the KI powder feed was cut off and the Hg^T concentration increased but at a slower rate toward the baseline level. Figure 5b shows the effect of spraying KI solution to the flue gas where the temperature was around 900 °C. The average baseline Hg^T and Hg⁰ concentrations were again equal to each other at around 5.8 µg/m³. When spraying KI solution equivalent to 46.5 g/hr of KI, the Hg^T concentration gradually decreased to 4.1 µg/m³. Increasing the spraying rate by four times to 185.9 g/hr, the Hg^T concentration slightly decreased to 3.5 µg/m³. The average Hg⁰ concentration at this condition was also close to Hg^T concentration.

Overall, the Hg removal efficiency increases with increasing KI feeding rate. 61% and 53% Hg removal were achieved at the feeding rates of 21.2 g/hr and 10.6 g/hr KI powder, respectively. It clearly shows that mixing KI powder with coal was more effective than spraying an aqueous KI solution into the flue gas. One important reason why co-combusting KI powder with coal was superior to spraying KI is because of the higher temperature and longer residence time, both of which favor the production of I_2 .

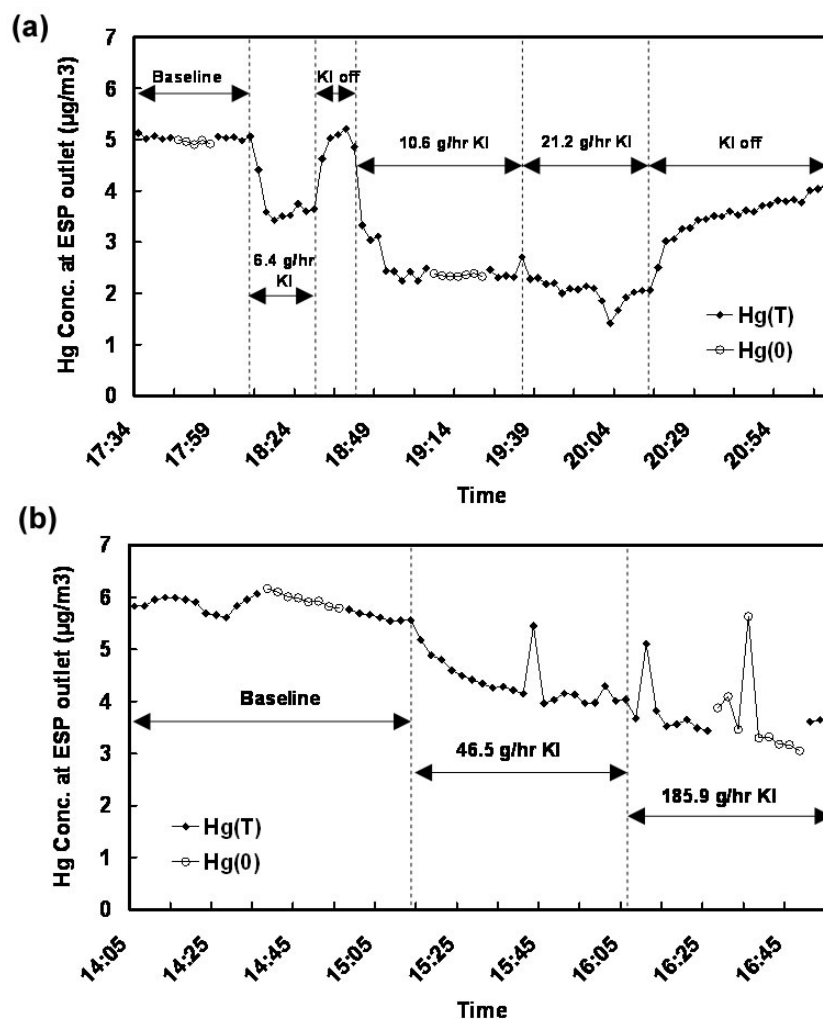


Figure 5. Hg concentration at ESP outlet under the condition of (a) KI powder mixed with coal (b) KI solution sprayed into flue gas.

Conclusions

It has been demonstrated that KI is an effective reagent for Hg^0 removal in both bench- and pilot-scale experiments. In the bench-scale 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 granular and 0.5 g 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 removal was 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. Higher KI concentrations and longer residence time in the reactor also enhanced Hg⁰ removal efficiency. Guided by the bench-scale results, pilot-scale experiments were conducted in a 160 kW pulverized coal combustor. First, KI powder was mixed with coal and fed to the combustor (>1400 °C); second, KI was sprayed to the flue gas where the temperature was approximately 900 °C. 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 to the flue gas, possibly due to the higher temperature of the combustion zone and the longer residence time of KI in the flue gas that favor the generation of I₂. No gaseous Hg²⁺ species was measured in the flue gas, indicating that the oxidation product HgI₂ was captured on the fly ash and removed by the ESP.

Acknowledgements

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