TECHNICAL NOTE

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Modified on-line monitoring of total gaseous mercury in flue gases using Semtech® Hg 2000 analyzer

Abstract The Semtech Hg 2000 analyzer continuously monitors the Hg^0 content in flue gas. An on-line measurement method of total gaseous mercury in flue gas developed in our laboratory is described, which uses the absorption cell of the Semtech Hg Analyzer connected to a converter that is located in a furnace heated up to 650 °C. The converter can be heated up to 800 °C by both the furnace and an extra heating of a Ni-Cr alloy heating wire. Both the absorption cell and the converter are made of quartz. All gaseous Hg^{2+} species in flue gas are thermally reduced to Hg^0 by the converter and detected by the Semtech Hg 2000 analyzer. The thermal reduction efficiencies of different conversion materials, which were filled in the converter, such as quartz chips, granular MgO, Ni and CoO powder, were tested using different flue gas conditions. Studies have shown that HCl is the major factor to inhibit the thermal reduction of Hg^{2+} to Hg^0, and in the converter and the absorption cell Hg^0 will react readily with HCl to form $HgCl_2$. Both MgO and Ni could be used in the converter to absorb HCl in the flue gas, but Ni has better absorption efficiency. By using an original Semtech and a modified one, both Hg^0 and total gaseous Hg contents in flue gas could be monitored simultaneously and continuously.

1 Introduction

Mercury is one of the most toxic substances in the environment. Human activities have contributed to the mobi-
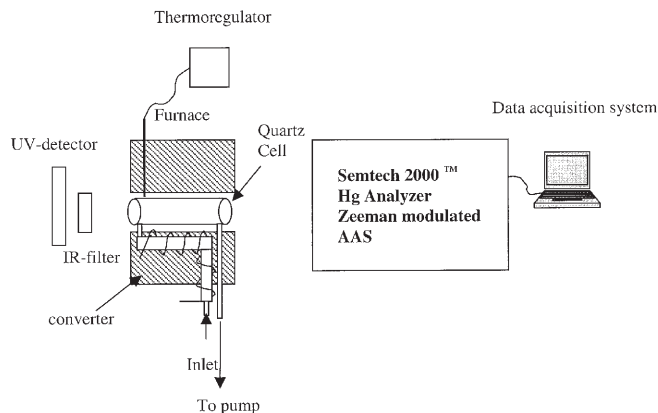
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lization of mercury into biogeochemical cycles. The current airborne mercury concentrations exceed the pre-industrial with a factor of ~3[1]. The anthropogenic pollution derives mainly from combustion facilities, such as coal-fired power plants and waste incinerators [2].

Different approaches exist to measure total mercury contents in flue gases. Most of the samplings have been done in batch mode and the analysis can only produce time-averaged values corresponding to sampling periods, which are normally at least 30 min [3–7]. In addition to the batch sampling and manual testing methods, on-line mercury analysis instruments have also been developed [8, 9]. Hall and co-workers [10] and Lindqvist and Schager [11] tried to speciate mercury on-line in flue gas by a commercial Semtech® mercury analyzer, which is based on Zeeman modulated atomic absorption spectrometry (AAS). The concentrations of elemental and total mercury were measured separately, and the difference between the two concentrations resulted from the presence of Hg(II). Elemental mercury was detected directly by AAS, while the total mercury was measured by driving the flue gas through a tube, where a 20% $SnCl_2$ solution was delivered to meet the incoming gas and Hg(II) was reduced by the solution before being transferred to the AAS detector. This is called wet method, since a chemical reaction in solution is used. Wang and co-workers [12] developed a dry physical pyrolysis converter that was able to thermally reduce Hg(II) into Hg^0. The dry thermal converter consisted of a quartz glass tube filled with crushed quartz chips together with a small amount of soda lime. In this paper, a new dry method in which the converter was connected to the detection cell of the AAS was developed and tested both in the laboratory and the pilot scale flue gas simulator.

2 Experimental

2.1 The set-up of the analytical instrument. The instrument used was a commercial instrument Semtech® Hg 2000, which is essential a cold vapor AAS using a mercury lamp as the light source. By putting the lamp under a strong pulsed magnetic field, the wave-

Fig. 1 The set-up of the Semtech for on-line measurement of total mercury in the flue gases
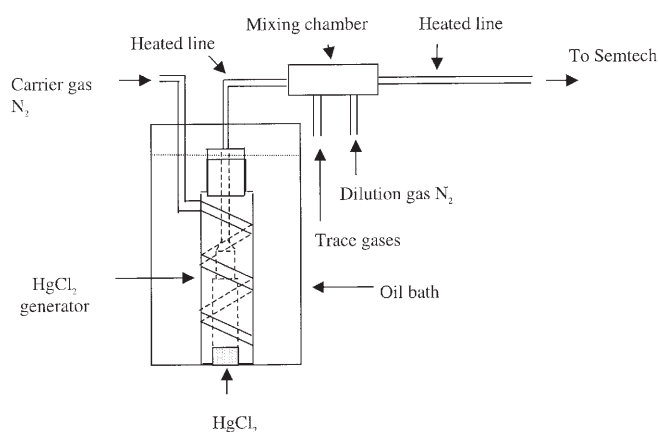
Fig. 2 The set-up of HgCl$_2$ source in the laboratory

length is modulated by the Zeeman effect, which makes it possible to eliminate interfering absorption that compass the 253.7 nm line due to the presence of substances such as SO$_2$, hydrocarbons, particles. This is the most outstanding feature of the instrument, since many combustion processes produce such pollutants. Hg^0 concentration in flue gases can be measured on-line by the instrument with a time resolution from 1 to 60 s. The detection limit that depends on the length of the chosen absorption cell is 2 µg/m^3 with an upper limit of 400 µg/m^3 when a 200 mm long absorption cell is used. The results of the measurements can be displayed directly in units of concentration on the digital screen of the instrument, and the data can also be collected by a personal computer by an RS232 interface for storing and further processing the data. The instrument is calibrated by inserting a 3 mm long absorption cell, in which a drop of metallic mercury is enclosed.

The set-up of the instrument for total gaseous mercury measurement is shown in Fig. 1. Both the absorption cell and the converter are made of quartz glass. The thermal converter used is similar to those described by Schroeder and Jackson [13] and Wang and co-workers [12]. The inner diameter and length of the converter are 18 mm and 150 mm, respectively. The absorption cell is kept at a temperature of 650 °C in a furnace. The converter connected directly to the absorption cell is heated both by the furnace and an extra heating wire to 800 °C. The tested conversion materials that are filled in the converter are quartz chips, granular MgO, Ni, and CoO powder. The total gaseous mercury concentration in the flue gas was measured by using this instrument set-up. In this study, a 200 mm long absorption cell was used. The absorption cell is heated to about 650 °C, the actual detection limit of the in-

strument is 6 µg/m^3 with an upper limit of 1170 µg/m^3. Simultaneously, Hg^0 concentration was measured by using an original Semtech 2000 Hg analyzer.

2.2 Standard HgCl$_2$ sources in the laboratory. Thermodynamic calculations predict that Hg will be in the form of HgCl$_2$ and Hg^0 at the temperature typical in flue ducts (80–250 °C) [14]. Therefore, mercury dichloride was chosen as the standard Hg source. Gas phase HgCl$_2$ was generated using the system according to Wang and co-workers[13] and Larjava[15]. Figure 2 shows the laboratory set-up for generating gas phase HgCl$_2$. The Teflon tubing downstream of the diffusion cell was heated by heating bands in order to prevent the condensation of HgCl$_2$ at the surfaces of the tubing. The mercury concentrations from the source depend on both the temperature of the oil bath and the flow rate of the carrier gas and are checked by using Swedish standard method for flue gas Hg sampling. N$_2$ is used as carrier gas, with a total flow rate to the detection system of 1 L/min.

2.3 The pilot scale combustion simulator. The pilot scale 10 kW natural gas-fired simulator system is mainly the same as described previously[16]. In short, it consists of a burner, a combustion chamber and a flue gas duct about 12 m long. The scheme of the set-up of the pilot-scale flue gas generator is given in Fig. 3. The inner diameter of the duct is 80 mm. Desired concentrations of O$_2$, SO$_2$, NO$_X$, HCl, and Hg^0 were fed to the system via the burner. HgCl$_2$ was injected at port *a*, and the sampling for Semtech total Hg was done at port *d* (see Fig. 3). A Testo 33 electrochemical gas analyzer was used for on-line monitoring the temperatures and the concentrations of O$_2$, SO$_2$, NO$_X$, and CO in the flue gas. A portable FTIR was used to measure the concentration of HCl in the flue gas. The flow rate in the duct was maintained around 680 L/min. The temperature in the combustion chamber was kept about 700 °C, and the temperature in the duct was maintained by using a heating jacket. The temperature at the sampling port was about 120 °C. O$_2$ concentration of about 10% and water content of about 6% were used throughout the investigation. Total gaseous Hg concentration in the flue gas was also measured by using the Swedish standard method.

2.4 The Swedish standard method for total Hg measurement in flue gases. A washing bottle containing 100 mL solution of 0.6% KMnO$_4$ (w/v) and 1.8 M H$_2$SO$_4$ was connected to the gas generating system providing the total concentration of Hg. Mercury, thus collected in the KMnO$_4$ solution, was analyzed by SnCl$_2$ reduction and cold vapor atomic fluoresceence spectrometry (CVAFS) detection (PSA Millennium Merlin Hg Analyzer).
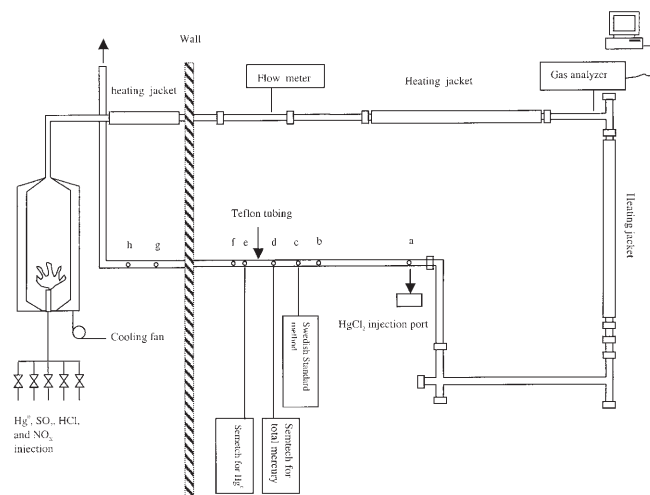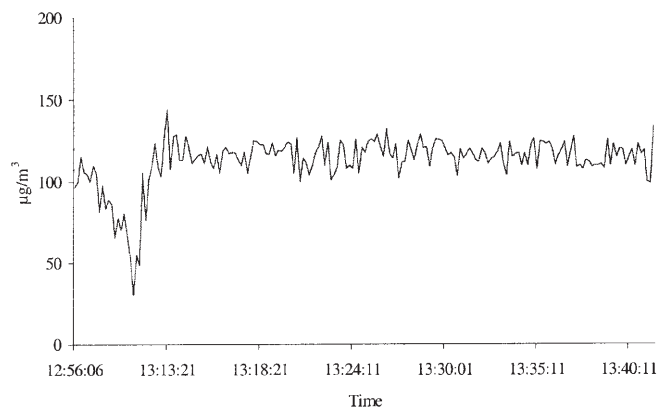

Fig. 3 The schematic diagram of the pilot scale flue gas simulator system

3 Results and discussion

3.1 Laboratory test results

In the laboratory, the thermal conversion efficiency of $HgCl_2$ to Hg^0 has been tested in an N_2 matrix without any

Fig. 4 Measurement results of total mercury obtained by the Semtech method in the laboratory

Table 1 The thermal reduction efficiencies of the converter at laboratory conditions

Experiment date	Hg concentration from source $(\mu g/m^3)^a$	Average Hg concentration from Semtech $(\mu g/m^3)$	Reduction efficiency (%)
28/08/98	262.3	259.6	99.0
28/08/98	262.3	251.9	96.0
31/08/98	107.0	115.2	108.0
31/08/98	107.0	107.1	100.0
01/09/98	117.8	111.3	94.5
01/09/98	117.8	113.9	96.7
01/09/98	117.8	118.9	100.9
02/09/98	143.9	151.1	105.0
	Average reduction efficiency		100.0

^{a} Hg concentration obtained by the Swedish standard method for total Hg in flue gases

trace gases such as HCl, NO_X, SO_2 and O_2. Gaseous $HgCl_2$ was generated as described above. The total mercury concentrations from the source were determined both by the modified Semtech method and the Swedish standard method for total Hg in flue gases. The conversion material filled in the converter was quartz chip. Figure 4 shows typical total gaseous mercury measurement results obtained by the Semtech method in the laboratory. Table 1 lists the results of thermal reduction efficiencies of $HgCl_2$ to Hg^0 tested at laboratory conditions. It can be seen from Table 1 that under the experimental conditions, $HgCl_2$ is quantitatively reduced to Hg^0 by the thermal converter with reduction efficiencies from 94.5 to 108.0%.

3.2 Test results from the pilot-scale flue gas simulator

Real flue gases contain many gases, such as O_2, SO_2, NO_X and HCl, some of which react readily with Hg[16]. The typical concentrations of these gases in the crude flue gas of coal combustion are 4–10% O_2, 0.3–3 $\mu g/cm^3$ SO_2, 0–0.09 $\mu g/cm^3$ NO_X and 0.0016–0.16 $\mu g/cm^3$ HCl, while the corresponding concentrations in that of waste incineration are 6–15%, 0.3–1.0 $\mu g/cm^3$, 0–0.18 $\mu g/cm^3$ and 0.64–1.6 $\mu g/cm^3$ [16]. However, the concentrations of SO_2, NO_X, and HCl in chimney flue gas should be much lower due to the installations of flue gas cleaning devices in both coal combustion and waste incineration plants. In order to evaluate the effects of these gases on the thermal reduction of $HgCl_2$, a certain amount of these gases and as well Hg was injected in the pilot scale flue gas simulator system. The total gaseous Hg concentration in the flue gas was measured by using both the modified Semtech Hg analyzer method and the Swedish standard method for total Hg measurement in flue gases.

Table 2 shows the test results from the pilot scale flue gas simulator. Without any trace gases such as SO_2, HCl, and NO_X injected in the flue gas simulating system, and no matter which kind of mercury species added to the flue gas, there was a quite good agreement between the total mercury concentrations obtained from the modified Semtech method and the Swedish standard method, which demonstrated that at these conditions Hg^{2+} in the flue gas

Table 2 Experiment results from the pilot scale flue gas simulator

Experiment date	Type of Hg source	Trace gases	Total Hg in flue gas $(\mu g/m^3)^a$ A	Average Hg concentration from Semtech $(\mu g/m^3)$ B	B/A
15/09/98	Hg^0	No	204.3	190.0	0.93
16/09/98	Hg^0	No	40.8	39.1	0.96
16/09/98	$HgCl_2$	No	20.4	18.9	0.93
17/09/98	$HgCl_2$	No	113.1	115.9	1.02
17/09/98	$HgCl_2 + Hg^0$	No	171.0	162.6	0.95
17/09/98	$HgCl_2 + Hg^0$	1.94 $\mu g\,cm^{-3}$ SO_2	156.7	146.0	0.93
18/09/98	$HgCl_2 + Hg^0$	1.94 $\mu g\,cm^{-3}$ SO_2	71.5	75.5	1.06
18/09/98	$HgCl_2 + Hg^0$	0.8 $\mu g\,cm^{-3}$ HCl	105.8	0	0
12/03/99	$HgCl_2 + Hg^0$	0.8 $\mu g\,cm^{-3}$ HCl	110.5	0	0
23/09/98	$HgCl_2 + Hg^0$	0.08 $\mu g\,cm^{-3}$ HCl, 0.36 $\mu g\,cm^{-3}$ NOx, 1.43 $\mu g\,cm^{-3}$ SO_2	280.7	270.3	0.96

^{a} Hg concentration obtained by the Swedish standard method for total Hg in flue gases
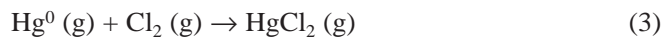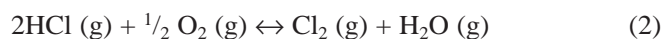
is quantitatively thermally reduced by the converter. For high concentrations of SO_2 in the flue gas, the total mercury concentrations obtained from the modified Semtech still agreed very well with those obtained by the Swedish standard method. This implied that SO_2 would not deteriorate the thermal reduction efficiency of the converter. At simulated coal combustion flue gas conditions with low HCl concentration, but high NO_X and SO_2 concentrations, the thermal converter reduced Hg^{2+} efficiently to Hg^0. It is confirmed that NO_X as well as SO_2 would not deteriorate the thermal reduction efficiency of the converter at all. However, when $0.8 \ \mu g/cm^3$ of HCl was added to the flue gas, the modified Semtech method cannot detect any mercury. At this condition, in the detection cell and the converter, mercury might occur in the form of $HgCl_2$. Briefly, from the test results it can been concluded that HCl is the major factor in the flue gas to inhibit the thermal reduction of Hg^{2+} to Hg^0, and SO_2 and NO_X will not change the thermal reduction efficiency of the converter.

3.3 Test results of different conversion materials

The addition of HCl in the flue gas causes an oxidation of Hg^0 to $HgCl_2$ in the analytical cell or in the converter, where the temperature was higher than 650 °C. Regarding the reaction mechanism, the direct reaction of Hg^0 with HCl (1) was ruled out since this is thermodynamically unfavorable at temperatures > 350 °C.

$$Hg^0 \text{ (g)} + 2HCl \text{ (g)} \rightarrow HgCl_2 \text{ (g)} + H_2 \text{ (g)} \qquad (1)$$

The reaction of Hg^0 and HCl was examined at 500 °C in a flue gas generator, and also at varying temperatures with a quartz reactor[16]. The results indicated that the reaction rate increased with temperature; more than 90% of the original Hg^0 was converted at 900 °C with a residence time of 0.7 s. The possible reaction mechanism could be as follow:

$$2HCl \text{ (g)} + {}^1/_2 \ O_2 \text{ (g)} \leftrightarrow Cl_2 \text{ (g)} + H_2O \text{ (g)} \qquad (2)$$

$$Hg^0 \text{ (g)} + Cl_2 \text{ (g)} \rightarrow HgCl_2 \text{ (g)} \qquad (3)$$

Since HCl can oxidize Hg^0 into $HgCl_2$ even at high temperatures, one possibility to eliminate the effect is to absorb HCl before the gas reaches the converter and the absorption cell. Several kinds of materials have been tested for this purpose.

3.3.1 Magnesium oxide

The granular MgO, which has been used as thermal converting material for Hg^{2+} to Hg^0 in the measurement of the total particulate mercury in the ambient air by Lu and co-workers[17], was crushed into small pieces, and filled into the converter. Two tests were run at the pilot-scale flue gas simulator system with $HgCl_2$ as the mercury source. The results depicted in Figs. 5 A and 5 B show that first of all MgO eliminates the effect of HCl to a certain extent.
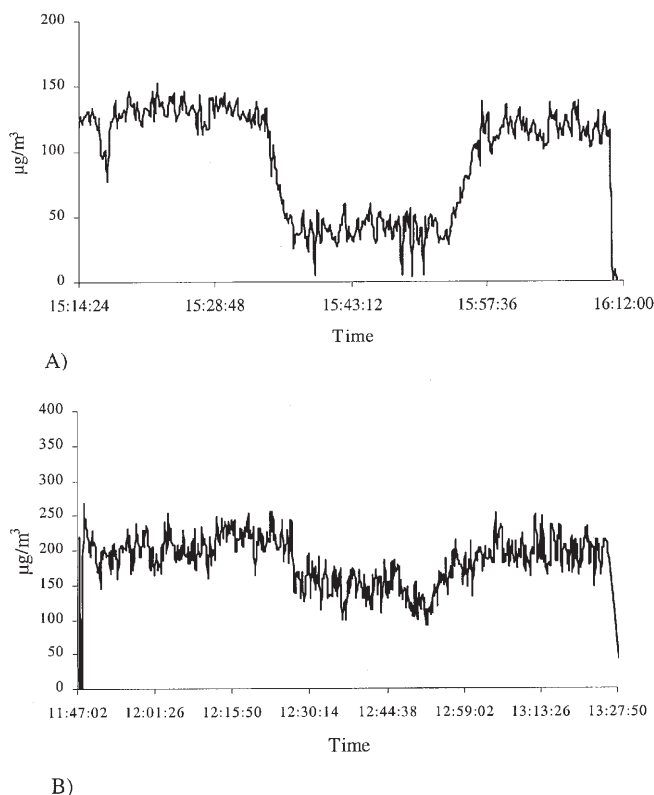
Fig. 5 Measurement results of total mercury obtained by Semtech with MgO filled in the converter. **A)** Between 12.22.00 and 12.54.00 0.64 $\mu g/cm^3$ HCl was injected into the flue gas; **B)** Between 15.34.00 and 15.54.00 0.32 $\mu g/cm^3$ HCl was fed into the flue gas

With 0.32 $\mu g/cm^3$ HCl in the flue gas, the thermal reduction efficiency of the converter is about 76%, and the reduction efficiency drops to 35% with 0.64 $\mu g/cm^3$ HCl in the flue gas. The possible mechanism is given in the Eq. (4). Even though MgO can trap HCl, with the dimension of the converter we used here the retention efficiency of MgO for HCl is not sufficient. Increasing the retention time of the flue gas in the converter will definitely increase the retention efficiency of HCl by MgO. On the other hand, increasing the surface areas of MgO will also increase the retention efficiency of HCl by MgO.

$$MgO \text{ (s)} + 2HCl \text{ (g)} \rightarrow MgCl_2 \text{ (s)} + H_2O \text{ (g)} \qquad (4)$$
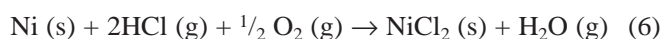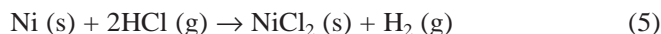
3.3.2 Nickel

Nickel is known as one of the metals that will not amalgamate with mercury even at room temperature. Thermodynamic calculations show that Ni will react with HCl (Eqs. (5) and (6)) at a temperature up to 500 °C[1]. Experimental results show that Ni reacts with HCl at temperatures from 200 and 500 °C, and $NiCl_2$ formation is observed.

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[1] Personal communication with Siemens V from Technical Research Center of Finland, Espoo, Finland, 1998

A)

B)

C)
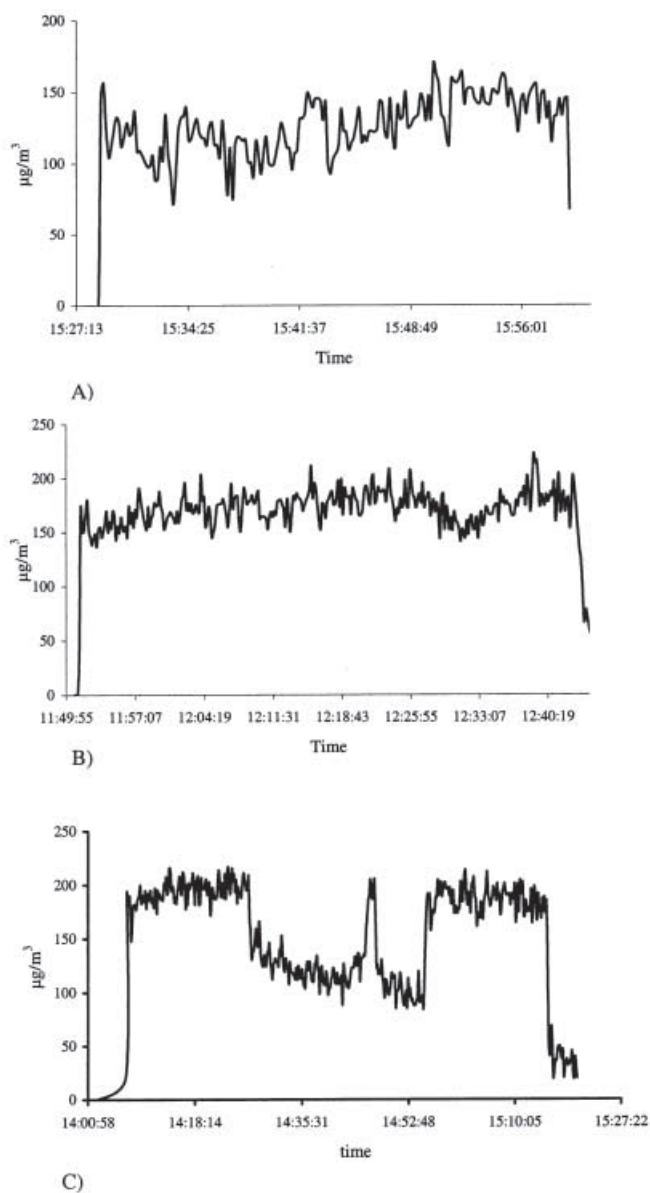
Fig. 6 Measurement results of total mercury obtained by Semtech with nickel and quartz chips packed in the converter. **A**) At 15.41.09, 0.32 $\mu g/cm^3$ HCl was added into the flue gas; **B**) At 12.19.38, the injection of 0.48 $\mu g/cm^3$ HCl into the flue gas was stopped; **C**) Between 14.27.00 and 14.55.00, 0.80 $\mu g/cm^3$ HCl was fed into the flue gas

$$Ni\ (s) + 2HCl\ (g) \rightarrow NiCl_2\ (s) + H_2\ (g) \tag{5}$$

$$Ni\ (s) + 2HCl\ (g) + \tfrac{1}{2}\ O_2\ (g) \rightarrow NiCl_2\ (s) + H_2O\ (g) \tag{6}$$

Nickel powder is filled into the inlet end of the converter where the temperature is kept at 450 °C, and the residual part of the converter is packed with smashed quartz chips. Three experiments have been run at the pilot-scale flue gas simulator with $HgCl_2$ as the mercury source and 0.32, 0.48, and 0.80 $\mu g/cm^3$ HCl injected into the flue gas, respectively. The results are illustrated in Fig. 6. When the HCl

concentration in the flue gas is lower than 0.32 $\mu g/cm^3$, 100% thermal reduction efficiency of $HgCl_2$ to Hg^0 by the converter is acquired. When 0.48 $\mu g/cm^3$ HCl is injected into the flue gas, 82% of Hg in flue gas is reduced to Hg^0 by the converter. However, when the HCl concentration in the flue gas is increased to 0.80 $\mu g/cm^3$, the reduction efficiency of the converter drops to 64%. These results demonstrate that there is a breakthrough of HCl from the Ni part of the converter for very high concentrations of HCl in the flue gas, and the re-oxidation of Hg^0 by HCl occurs at the quartz part of the converter and the absorption cell. One way to prevent the breakthrough of HCl from the Ni part of the converter is to increase the retention time of the flue gas in this part of the converter.

According to thermodynamic calculations[1] and laboratory experiments, cobalt(II) oxide can absorb HCl efficiently at temperatures from room temperature to 500 °C. However, experimental results show that CoO can effectively absorb Hg^0 at temperatures higher than 100 °C. According to the studies conducted by Olson and co-workers[18], certain transition metal oxides such as manganese, iron, chromium, nickel and copper oxides can effectively oxidize elemental mercury to produce a mixed mercuric oxide form that is effect bonded to the inorganic matrix. Therefore, CoO might also chemically absorb Hg^0 at temperatures applied for the converter. Hence, the application of CoO in the converter is limited.

4 Conclusions

- At laboratory conditions, $HgCl_2$ could be efficiently thermally reduced to Hg^0 by the converter;
- HCl is the major factor to inhibit the thermal reduction of Hg^{2+} to Hg^0, and in the converter and the absorption cell Hg^0 will react readily with HCl as shown in Eqs. (2) and (3) to form $HgCl_2$;
- Both MgO and Ni could be used in the converter to absorb HCl from the flue gas, but Ni has better absorption efficiency;
- By using both an original Semtech and a modified one, we could monitor both Hg^0 and total Hg contents in flue gas simultaneously and continuously.

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