Regenerable sorbents for mercury capture in simulated coal combustion flue gas

Jorge Rodríguez-Pérez, M. Antonia López-Antón*, Mercedes Díaz-Somoano, Roberto García, M. Rosa Martínez-Tarazona

Instituto Nacional del Carbón (CSIC), Francisco Pintado Fe, 26, 33011, Oviedo, Spain

*Corresponding author:
Phone: +34 985 119090
Fax: +34 985 297662
Email: marian@incar.csic.es
Abstract

This work demonstrates that regenerable sorbents containing nano-particles of gold dispersed on an activated carbon are efficient and long-life materials for capturing mercury species from coal combustion flue gases. These sorbents can be used in such a way that the high investment entailed in their preparation will be compensated for by the recovery of all valuable materials. The characteristics of the support and dispersion of gold in the carbon surface influence the efficiency and lifetime of the sorbents. The main factor that determines the retention of mercury and the regeneration of the sorbent is the presence of reactive gases that enhance mercury retention capacity. The capture of mercury is a consequence of two mechanisms: (i) the retention of elemental mercury by amalgamation with gold and (ii) the retention of oxidized mercury on the activated carbon support. These sorbents were specifically designed for retaining the mercury remaining in gas phase after the desulfurization units in coal power plants.

Keywords: mercury, gold, coal combustion, regeneration
1. Introduction

The environmental and health consequences of exposure to toxic mercury species are a matter of great concern. [1-2]. Governments, organizations and scientists worldwide devote significant efforts to prevent mercury pollution [3-6]. However, it was not until January 2013 that more than 140 nations adopted the first legally-binding international treaty aimed at reducing anthropogenic mercury [7].

Coal combustion constitutes one of the main sources of mercury emissions [8], representing 24% of global anthropogenic [9]. Mercury released from coal during combustion in power plants may be present in three forms: elemental mercury (Hg$^0$(g)), oxidized mercury (Hg$^{2+}$(g)) and particulate-associated mercury (Hg$^p$). Hg$^p$ and Hg$^{2+}$(g) can be retained in particle control devices and gas cleaning systems (e.g. flue gas desulphurization, FGD) units. However, Hg$^0$(g) is a species that is more difficult to capture.

Mercury emissions from coal combustion can be controlled by pre-combustion and post-combustion strategies. Pre-combustion not only involves preparing coal blends or cleaning the coal to reduce the amount of mercury in the combustible [10], but also adding reactants, such as bromides, which produce reactive mercury species in the gases that can easily react or be adsorbed by the sub-products [11]. Post-combustion technologies are mainly based on sorbents that are generally injected into the gaseous stream and subsequently retained in particulate control devices [12-13]. Although field tests have been relatively successful, several aspects such as the amount of carbon to be injected, sorbent costs, implications for the fly ashes or effects on the operation of the plant, still require further investigation [14-15].

Hg$^0$ is the most difficult species to retain and requires a specially adapted retention method. A reliable method of Hg$^0$ capture would be to exploit the tendency of
this species to amalgamate with metals [16-18]. The flue gas from coal combustion could be passed over a metal-loaded material where the Hg\textsuperscript{0} would amalgamate. The amalgam-containing sorbent could then be recycled in order for the mercury and the raw material to be recovered. The MerCap\textsuperscript{TM} (Mercury Control Adsorption Process) project [19] is based on this concept. It consists in placing gold-coated metal structures into a flue gas stream to amalgamate the mercury and then thermally regenerating the sorbent, so as to recover the mercury. The drawback to this technology is that large amounts of gold are needed to coat the support. This problem could be reduced if sorbents, containing minimal amounts of gold are developed [19-21]. The present study explores the capacity of an activated carbon loaded with gold dispersed nano-particles, prepared in a previous work [22], to act as a sorbent for mercury. The carbon gold-loaded materials were developed to be used at the end of the coal combustion cycle, where the species of mercury in the outgoing gases will be mainly Hg\textsuperscript{0} as most of the oxidized mercury will have already been retained in the particle control devices and desulfurization plants.

The main objectives of this study were to determine the effectiveness of these sorbents for mercury retention as well as the effect of multiple regeneration cycles on their lifetime and to evaluate the effect of acid gases upon the performance of the sorbent. This work also lays the foundation for developing procedures to recover other valuable products present in the used up sorbents and offers a tentative economic analysis.

2. Experimental

Gold-loaded carbon sorbents (Au-RB3) were prepared by the tetrakis (hydroxymethyl)phosphonium chloride (THPC) method which is based on the
formation of gold colloids [22]. The support was a commercial activated carbon (Norit RB3). The Au coating was almost 100% effective with THPC, which acts both as a reducing agent and as an inhibitor of large particle formation. The carbon support was impregnated with 0.1 and 5 wt% of gold to obtain two sorbents labelled Au0.1-RB3 and Au5-RB3, respectively. The support was ground to a size of 0.2-0.5 mm before impregnation.

A schematic diagram of the experimental device employed to retain and to recover the Hg$^0$ for sorbent regeneration is shown in Figure 1. The fixed sorbent bed (80.0 mg) is placed in a glass reactor where it is kept at a temperature of 40ºC. This is the usual temperature of a flue gas stream at the exit of desulphurization plants. Elemental mercury in gas phase (100 µg m$^{-3}$), obtained by means of a permeation tube, was passed through the sorbent at 0.5 L min$^{-1}$. A simulated flue gas (SFG) consisting of N$_2$ with 6% O$_2$, 135 mg Nm$^{-3}$ SO$_2$, 100 mg Nm$^{-3}$ NO, 25 mg Nm$^{-3}$ HCl, 16% CO$_2$ and 3% H$_2$O was employed as carrier gas. The temperature of the gas was maintained at 120ºC. Regenerable sorbents were developed for use after the DeNOx, particle control devices and desulphurisation units (i.e., in an atmosphere relatively free of acid gases). For this reason the composition of the gas was similar to what one might expect to find just before the stack in a coal combustion power plant (i.e., with a low sulphur, halogen and nitrogen species content). The results were compared with those obtained in an atmosphere of N$_2$ and O$_2$, SO$_2$ or HCl in N$_2$ in proportions identical to those in the SFG atmosphere. The Hg$^0$ not retained in the sorbents was measured using a continuous mercury monitor (VM-3000). The mercury content of the sorbent after retention was determined by means of AMA equipment. The duration of each cycle of retention was 3 days.
The oxidation of mercury was evaluated by capturing the Hg$^{2+}$ in an ion exchanger resin (Dowex® 1x8). The resin was treated with a mixture of HCl:H$_2$O (1:1) at 90°C for 30 minutes. It was then placed at the exit of the reactor prior to the Hg$^0$ continuous analyzer ((1) in Figure 1). The Hg$^{2+}$ in the resin was determined by AMA. Atmospheres of O$_2$, SO$_2$, NO or HCl in N$_2$, and combinations of these gaseous species were evaluated to assess the influence of each gas upon mercury speciation.

To evaluate the regeneration, the post-retention sorbents were heated in the same experimental device from room temperature to 550 °C at a heating rate of 10°C min$^{-1}$ under N$_2$. The desorbed mercury ((2) in Figure 1) was monitored as a function of temperature using the VM3000 analyzer. The gold-doped regenerated sorbent was then re-used to retain mercury. The experimental set-up was equipped with a device for the recovery of Hg$^0$ ((3) in Figure 1). This device consists of a series of 44 tubes of 0.5x30 cm, arranged in rows of three and immersed in ice where Hg$^0$ is recovered and collected in a container.

The gold was recovered by burning the Au-RB3 sorbent in a furnace at 700°C under air to obtain a gold-containing residue. The metal was separated from the other components of the residual ash by adding elemental mercury at a ratio of 2:1 (Hg:Au) to form the Hg-Au amalgam. The suspension was maintained under stirring for 24h and the amalgam was separated from the ashes by sieving (212 μm). The process was repeated until the gold had been totally recovered. Finally, the mercury and gold were separated by heating the amalgam to 450°C. The mercury was collected in a container ((3) in Figure 1) and the gold was recovered in the reactor.

3. Results and discussion

3.1. Mercury retention
3.1.1. Effect of gold content

In a previous work [22], the RB3 activated carbon was impregnated with different amounts of gold (0.05-5 wt%), using the polyvinyl alcohol (PVA) and tetrakis (hydroxymethyl) phosphonium chloride (THPC) methods. The quantities of mercury retained in the sorbents prepared by these methods were similar for a given gold content, but the THPC was the more efficient for loading the gold. When freshly prepared sorbents are used, even the samples with only 0.1 wt% of gold had a mercury retention capacity and efficiency comparable to that of the commercial activated carbon RBHG3 [22], which is specifically designed for mercury retention at low temperatures. However, RBHG3 is not regenerable. These promising results led us to investigate whether these sorbents are regenerable and maintain their good retention properties after several cycles.

Figure 2 shows the mercury breakdown curves for the sorbent with the lowest gold content (Au0.1-RB3), over three regeneration cycles under N_2 and O_2+N_2 atmospheres. The presence of O_2 (12.6 vol%), did not have any significant effect on mercury retention since the results were similar to those in the inert atmosphere. What is remarkable is that mercury retention decreased sharply after the first cycle of regeneration. After 3 days, the mercury retention capacity of the fresh Au0.1-RB3 sorbent achieved retention values of 2.5±0.3 mg g\(^{-1}\) with an efficiency of 100% for more than 24 hours and maximum retention capacity was still not reached even after 3 days. With the second cycle, mercury capture decreased to 0.4±0.1 mg g\(^{-1}\), remaining constant thereafter over successive cycles of regeneration. In the case of the sorbent loaded with 5% gold (Au5-RB3), the qualitative behaviour was similar, but the quantity of mercury retained after regeneration was considerably higher (Figure 3). In this case, the mercury
retention capacity reached values similar to those of Au0.1-RB3 (2.3±0.2 mg g⁻¹) during
the first cycle with 100% efficiency for approximately 1700 minutes, but in subsequent
cycles, the mercury retention capacity remained constant at 1.1±0.2 mg g⁻¹. It should be
noted that the amount of mercury retained over successive cycles was about 3 times
higher in the sample loaded with 5% gold than in that loaded with 50 times less gold
(0.1%). Therefore, increasing the amount of gold improves the performance of the
sorbent but not in a directly proportional way. Nevertheless, the regenerated sorbent
loaded with 5% gold fulfills the objectives. On the one hand, a high retention capacity
was attained and, on the other, maximum retention capacity was reached after an
acceptable breakdown time with 100% efficiency.

The different performances observed after the first cycle of retention may have
been due to the degradation of the support or to degradation of the loaded gold.
Theoretically, changes in the characteristics of the gold particles after the evaporation of
mercury should not occur, especially in the case of Au5-RB3. The Au-Hg phase
diagram reported by Okamoto and Massalski [23] (Figure 4), shows the path of mercury
desorption in the sorbents. The Au/Hg ratio in the amalgam was 71/29 and 96/4 for
Au0.1-RB3 and Au5-RB3, respectively. During the regeneration of Au0.1-RB3 the
amalgam went through different solid phases until the mercury had been completely
desorbed at 450 °C, but during the regeneration of Au5-RB3 the amalgam remained in
the same solid phase (Figure 4). No changes in the morphology of the gold deposited on
the sorbent before and after desorption (as observed by TEM) or in the oxidation state
of the gold (as identified by XPS) were observed.

Possible modifications of the characteristics of the activated carbon support
between cycles were also considered, and it was concluded that the different behaviour
after the first and subsequent cycles was due to the presence of chlorine in the fresh
sorbent which evaporated after the first regeneration. The Au-loaded RB3 sorbents, prepared by impregnation using gold chloride [22], contain a small and slightly variable amount of chlorine (<15%) that may affect mercury capture on carbonaceous materials [24]. This explains the decrease in the retention of mercury after the first regeneration (Figures 2-3), since after regeneration at 550°C all the chloride is desorbed. In conclusion, when the Hg⁰ in gas phase passes through the sorbent, some of the mercury remains as Hg⁰ which is retained by amalgamation, while some is oxidized on the support in the presence of chlorine to form Hg²⁺ which is retained in the carbon support. When the sorbent loses the chlorine after the first regeneration, amalgamation is the only capture mechanism. Figure 5 shows the mercury desorption curves of Au5-RB3 after successive cycles of regeneration in N₂. The amount of Hg⁰ desorbed during the first cycle, as determined by VM3000, is lower than the total amount of mercury retained in the sorbent, as analyzed by AMA. However, with the second cycle the amounts of mercury desorbed and retained are similar which confirms that, during the first cycle, mercury is oxidized and retained as Hg⁰ and Hg²⁺, whereas during the second and successive cycles it is retained as Hg⁰. Nevertheless, it is important to note that mercury retention remains constant over a large number of cycles, which makes the Au5-RB3 a promising material for mercury capture.

3.1.2. Effect of the gas composition

The literature data show that flue gas components, such as SO₂, can poison the gold, making it ineffective for mercury capture [25]. This needs to be taken into account when considering regenerable sorbents. In Figure 6(a) it can observed that the capture of mercury by Au5-RB3 in the presence of SO₂ is slightly lower than in the presence of N₂ and N₂+O₂ during the first cycle of retention (1.9±0.3 mg g⁻¹). However, no significant
differences between the two atmospheres (Figures 3 and 6(a)) are apparent in the subsequent cycles of retention (0.9±0.2 mg g\textsuperscript{-1}). Mercury capture after the first cycle is again lower than that achieved by the fresh sorbent. Although the time during which mercury is retained with 100% efficiency is shorter in the atmosphere of SO\textsubscript{2}+N\textsubscript{2} than in that of O\textsubscript{2}+N\textsubscript{2} during the first cycle, indicating that SO\textsubscript{2} might slightly reduce the effectiveness of gold-doped activated carbon, total poisoning of the gold does not occur, even after several cycles of regeneration (Figure 6(a)). A mercury retention capacity of the order of mg g\textsuperscript{-1} is still reached and maintained over several cycles. The influence of HCl on the adsorption of mercury by Au5-RB3 is shown in Figure 6(b). It can be seen that, unlike SO\textsubscript{2}, HCl improves mercury capture. Indeed, after successive regeneration cycles the mercury retention capacity remains constant at 2.7 mg g\textsuperscript{-1} with an efficiency of 100% for more than 2000 minutes during every cycle. These results again suggest that Hg\textsuperscript{0} may be oxidized in the sorbent, with retention being favored by the presence of HCl [26]. This would explain why retention is maintained over successive cycles in the presence of HCl but not in the case of O\textsubscript{2}, N\textsubscript{2} and SO\textsubscript{2} (Figures 3 and 6(a)). In a previous study carried out by the authors [27] it was concluded that an atmosphere containing only HCl increased mercury retention considerably and promoted heterogeneous mercury oxidation in the presence of carbonaceous matter, which may have catalyzed the reaction between Hg and HCl [28]. Therefore, when HCl is present in the flue gas, mercury is retained as HgCl\textsubscript{2} in the carbonaceous support while the non-oxidized mercury is retained by the nano-dispersed gold throughout all the retention cycles.

Finally, mercury retention was evaluated in synthetic gas mixtures typical of coal combustion with and without water vapor in their composition. For comparison purposes Table 1 shows the mercury retention capacity recorded for Au5-RB3 in these
two atmospheres and that observed in the N\textsubscript{2} atmosphere. Also listed are the data obtained for the raw activated carbon without gold (RB3). Figure 7 shows the mercury adsorption curves for Au5-RB3 over several regeneration cycles under the two gas mixtures. In these reactive gas-containing atmospheres, the sorbent proved to be 100% efficient over successive cycles of utilization as when HCl was present in the flue gas. After successive regeneration cycles the mercury retention capacity remained constant at 2.9 mg g\textsuperscript{-1} with an efficiency of 100% for more than 4000 minutes during every cycle. The presence of H\textsubscript{2}O does not seem to have any effect on mercury retention or regeneration (Figure 7(a)). However, when the mercury desorption curves corresponding to cycles of regeneration in N\textsubscript{2}, SFG and SFG without H\textsubscript{2}O, are compared (Figure 8), it can be seen that the peak temperatures differ. The desorption of mercury starts at approximately 120 °C but its total decomposition does not occur until 280±20 °C in N\textsubscript{2} and SFG. However, in SFG without H\textsubscript{2}O the desorption of mercury shows two peaks with maxima at approximately 210 and 340°C, which indicates that the species of mercury retained are different. From the results obtained for RB3 (Table 1), it can be seen that, whereas in N\textsubscript{2} mercury retention was very low, in SFG both with and without H\textsubscript{2}O, it reached values of 0.6 and 1.5 mg g\textsuperscript{-1}, respectively, suggesting that mercury compounds may have formed as a result of homogeneous oxidation (gas-gas interactions) or interactions between the activated carbon and the gases (heterogeneous oxidation).

Figure 9 shows the percentages of Hg\textsuperscript{0} and Hg\textsuperscript{2+} detected for each of the gas compositions studied. The results indicate that no homogeneous oxidation reactions occurred in the single gases O\textsubscript{2}, SO\textsubscript{2} and HCl under the experimental conditions tested. However, in the NO atmosphere, approximately 28% Hg\textsuperscript{2+} was formed. When O\textsubscript{2} was present with SO\textsubscript{2} and NO, oxidation was 3 and 48%, respectively. This would suggest
that O$_2$ has a synergistic effect on mercury oxidation not only via SO$_2$ which is in agreement with the results of a previous study [27], but also and mainly via NO. When the other components were added to the gas composition (i.e., O$_2$+NO+SO$_2$+HCl+CO$_2$+N$_2$) the percentage of mercury oxidation was similar (around 40%) to that obtained with O$_2$+NO+N$_2$ (48%) (Figure 9), but it differed in the presence of H$_2$O. It can be deduced, therefore, that SO$_2$ in O$_2$, and mainly NO, with or without O$_2$, are the main gas combinations responsible for the homogeneous oxidation of mercury. The gas species might be HgO which would form through reactions (I-V).

$$\text{Hg}_0^0 (g) + \text{SO}_2 (g) + \text{O}_2 (g) \rightarrow \text{HgO}_x (s,g) + \text{SO}_3 (g) \quad (I)$$

$$2 \text{Hg}_0^0 (g) + 2 \text{NO} (g) \rightarrow 2 \text{HgO}_x (s,g) + \text{N}_2 (g) \quad (II)$$

$$\text{NO} (g) + \text{O}_2 \rightarrow \text{NO}_2 (g) + \text{O} \quad (III)$$

$$\text{Hg}_0^0 (g) + \text{O} \rightarrow \text{HgO} (g) \quad (IV)$$

$$\text{Hg}_0^0 (g) + \text{NO}_2 (g) \rightarrow \text{HgO}_x (s,g) + \text{NO} (g) \quad (V)$$

It is, however, remarkable that mercury oxidation decreased when H$_2$O was present in the gas (Figure 9). Oxygen has a positive effect on mercury oxidation but when both water vapor and oxygen coexist in the simulated flue gas the conversion of Hg$_0^0$ to Hg$^{2+}$ may decrease due to competition between the O and OH, which would prevent the above reactions. It was found that a small amount of moisture may enhance oxidation (<0.74%) whereas a large amount (in this study 3%) may have the opposite effect [29].

The level of capture of the Hg$^{2+}$ produced by homogeneous oxidation was evaluated using sorbent beds made up of RB3 and Au5-RB3. Figure 10 shows the
percentages of Hg$^{2+}$ and Hg$^{0}$ in the outlet gas and the percentage of mercury retained in
the sorbent (Hg$_{r}$). The atmospheres employed were N$_2$ and the mixtures
O$_2$+NO+SO$_2$+HCl+CO$_2$+N$_2$ (SFG without water) and O$_2$+NO+SO$_2$+HCl+CO$_2$+H$_2$O
+N$_2$ (SFG with water). As can be observed in Figure 10(a), RB3 does not retain mercury
in the inert atmosphere. However, in the gas mixtures mercury was captured and a slight
amount of Hg$^{2+}$ coming from the reactor was identified. In the SFG without water the
amount of Hg$^{2+}$ outside the sorbent was around 2% compared to 34% Hg$^{2+}$ resulting
from homogeneous oxidation (Figure 9). In the case of SFG only 1% Hg$^{2+}$ was
collected at the exit of the reactor. This percentage was also lower than that produced by
homogeneous oxidation in this atmosphere (4%) (Figure 9). These results demonstrate
that most of the Hg$^{2+}$ produced by homogeneous oxidation was retained in the RB3
sorbent. The mercury species formed after interaction with the sorbent Au5-RB3 are
shown in Figure 10(b). If we compare the percentages of the three species in RB3 and
Au5-RB3 important differences can be observed. In the N$_2$ atmosphere where there was
no homogeneous oxidation (Figure 9) and all the mercury is in the form of Hg$^{0}$, part of
the Hg$^{0}$ is retained, whereas the rest is released as Hg$^{0}$ (Figure 10(b)). As in the case of
RB3, in the atmosphere containing reactive gases, the amount of mercury oxidized at
the exit of the sorbent bed is minimal. As for RB3, most of the Hg$^{2+}$ is retained in the
carbonaceous support in Au5-RB3. As might be expected, the main difference between
the results obtained with RB3 (Figure 10(a)) and Au5-RB3 (Figure 10(b)) is that no Hg$^{0}$
was detected at the exit of the reactor containing the Au5-RB3 sorbent since a 100%
efficiency was attained in both atmospheres.

We should also consider the possibility that, in addition to reactions (I-V), which
explain homogenous oxidation, the sorbent may act as a support for the formation of
HgSO₄ (reaction VI) [27] and/or different mercury nitrites and nitrates (reactions VII and VIII) [30-32] in the SFG without water atmosphere.

\[ \text{Hg}^0 (g) + \text{SO}_2 (g) + \text{O}_2 (g) \rightarrow \text{HgSO}_4 \]  (VI)

\[ 4 \text{Hg}^0 (g) + 6 \text{NO} (g) + 3 \text{O}_2 (g) \rightarrow \text{Hg}_2(\text{NO}_3)_2 + \text{Hg}_2(\text{NO}_2)_2 + 2 \text{NO} (g) \]  (VII)

\[ 4 \text{Hg}^0 (g) + 4 \text{NO} (g) + 3 \text{O}_2 (g) \rightarrow \text{Hg}_2(\text{NO}_3)_2 + \text{Hg}_2(\text{NO}_2)_2 \]  (VIII)

In summary, the carbon material loaded with 5% gold (Au5-RB3) is able to capture mercury with 100% efficiency in both O₂+NO+SO₂+HCl+CO₂+N₂ and O₂+NO+SO₂+HCl+CO₂+H₂O+N₂ atmospheres over several cycles of regeneration. The retention mechanism involves both the support and the gold. The RB3 support captures Hg²⁺, whereas the gold amalgamates Hg⁰.

3.2. Economic analysis

3.2.1 Gold recovery

Although a procedure for recovering gold from the sorbent has not been optimized in this work, a possible way of retrieving the gold used in the process would be to separate the gold from the carbonaceous support by burning the organic matter. Because the support (RB3 activated carbon) contains 6% of mineral matter, the key to the process is to separate this mineral matter from the gold after combustion of the carbon support. The separation would involve amalgamating the gold present in the residue with the very same mercury recovered in the regeneration process. The global process is, in fact, intended as a relatively re-established sequence. The gold recovered in the first process of amalgamation with mercury was approximately 82% of the total. The second amalgamation step increased the amount recovered 92% (Figure 11). This
amount could probably be improved upon by using successive amalgamation cycles but this must be the subject of a future study.

3.2.2 Cost analysis

The data obtained in this study were employed for a preliminary economic analysis (y) based on the cost of the sorbent, which mainly took into account the cost of the gold employed (A), the cost of the support (B) and the cost of preparing the sorbent (C). In this preliminary analysis, the expenses derived from the installation of the facility in the power plant were not included because at this stage (i.e., laboratory scale), any attempt to estimate the costs at industrial scale would be premature. It is also too early to evaluate the operating costs that would include the energy necessary for overcoming pressure drops and for producing the heat required for regeneration and maintenance. What follows therefore is an estimation of the investment required for the sorbent material.

The cost of the sorbent (y) will depend on the amount of sorbent (m) needed to retain all of the mercury emitted in gaseous phase.

Therefore

\[ y = m (A + B + C) \]  

(1)

where y is the cost in dollars ($) and m is the mass of sorbent (kg).

A simple relationship can be established between the amount of sorbent and the concentration of mercury in the gas phase, the breakthrough time, defined as the time during which the sorbent retains the mercury with 100% efficiency, and the retention capacity of the sorbent. This relationship can be expressed as:

\[ m = \frac{Q \cdot C \cdot tb}{RC} \]  

(2)
where $Q$ is the flow rate ($m^3\cdot h^{-1}$), $C$ is the mercury concentration ($\mu g\cdot m^{-3}$), $t_b$ is the breakthrough time (h) and $RC$ is the mercury retention capacity ($\mu g\cdot Hg^0\cdot kg^{-1}$ sorbent).

The cost of the gold employed ($A$) can be estimated as:

$$A = 0.05 \cdot C_g$$

(3)

where 0.05 is the mass of gold per unit of mass of the sorbent Au5-RB3 ($gAu\cdot kg^{-1}$ sorbent) and $C_g$ is cost of the gold per unit mass ($\$\cdot kg^{-1}$ Au).

The cost of the support ($B$) is calculated as:

$$B = C_s$$

(4)

where $C_s$ is the cost of the support ($\$\cdot kg^{-1}$ support ~ $\$\cdot kg^{-1}$ sorbent).

Finally, the cost of preparation ($C$) is estimated as:

$$C = 40.9 + 8044 \cdot H$$

(5)

where 40.9 is the cost of the reagents per unit of sorbent ($\$\cdot kg^{-1}$ sorbent), 8044 is the cost of the energy employed per unit of sorbent (kW$\cdot h\cdot kg^{-1}$ sorbent) and $H$ the cost of kW$\cdot h$ ($\$\cdot kW^{-1}\cdot h^{-1}$)

Therefore:

$$y = m(0.05 \cdot C_g + C_s + 40.9 + 8044 \cdot H)$$

(6)

This analysis was carried out assuming that the sorbent Au5-RB3 is able to retain mercury with an efficiency of 100% for at least three days, which represents in our experiment a mercury retention capacity of 2.9 mg g$^{-1}$ in a simulated coal combustion flue gas. If this type of sorbent were employed in a 1200 MW pulverized coal combustion power station equipped with a flue gas desulphurization unit, and a mercury concentration of 8.6 $\mu g\cdot m^{-3}$ were produced with a flow rate of 131147 $m^3/h$, the amount of sorbent required for the complete retention of the emitted mercury would be approximately 28 kg. This would imply a total sorbent cost of approximately 126000$, as is shown in Table 2. However, this would be the initial investment. The recovery of
the gold for this or other applications would considerably make up for the cost of the regenerable sorbent used in the plant.

4. Conclusions

A regenerable sorbent prepared by the dispersion of gold nanoparticles on a carbon material using 5% doped gold was found to be highly effective for mercury capture, exhibiting a 100% efficiency over several cycles of regeneration. The activated carbon loaded with gold was able to retain Hg$^{2+}$ on its own carbonaceous support in the presence of chloride and Hg$^{0}$ by amalgamation with the noble metal. The sorbent was thermally regenerated at approximately 240 ºC and the Hg$^{0}$ was recovered and collected in a container. Although a high level of investment due to the cost of gold must be accepted as inevitable, the gold can be recovered which makes this type of sorbent a very attractive option for retaining elemental mercury during coal combustion without producing toxic waste.

Acknowledgments

The authors thank CSIC (PIF-06-050) and the Spanish Ministerio de Ciencia e Innovación (CTQ2008-06860-C02-01) for financial support. The corresponding author would like to thank CSIC for the award of a JAE-Doc position (European Social Fund).

References


Table 1. Mercury retention by raw activated carbon (RB3) and activated carbon impregnated with 5% gold (Au5-RB3) in different atmospheres.

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>Hg retention (mg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RB3</td>
</tr>
<tr>
<td>N₂</td>
<td>10ᵇ</td>
</tr>
<tr>
<td>6%O₂ + 16%CO₂ + 135mgNm⁻³SO₂ + 25 mgNm⁻³HCl + 100mgNm⁻³ NO + N₂</td>
<td>1.5±0.3</td>
</tr>
<tr>
<td>6%O₂ + 16%CO₂ + 135mgNm⁻³SO₂ + 25 mgNm⁻³HCl + 100mgNm⁻³ NO + 3% H₂O + N₂</td>
<td>0.6±0.2</td>
</tr>
</tbody>
</table>

ᵃ retention after 3 days, no saturation;ᵇ maximum retention capacity (μg g⁻¹)

Table 2. Preliminary analysis of costs

<table>
<thead>
<tr>
<th>Initial investment</th>
<th>Cost ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold</td>
<td>92000</td>
</tr>
<tr>
<td>Support</td>
<td>3640</td>
</tr>
<tr>
<td>Reagents</td>
<td>1145</td>
</tr>
<tr>
<td>Cost of energy for preparing the sorbent</td>
<td>29000</td>
</tr>
<tr>
<td>Cost of installing the device</td>
<td>Not applicable</td>
</tr>
<tr>
<td>Operating costs for regeneration and maintenance</td>
<td>Not applicable</td>
</tr>
<tr>
<td>Total</td>
<td>125785</td>
</tr>
</tbody>
</table>
Figure captions

Figure 1. Schematic diagram of the experimental device used for the mercury retention and the thermal regeneration test.

Figure 2. Mercury adsorption curves of Au0.1-RB3 over three regeneration cycles under N2 (a) and O2+N2 (b) atmospheres.

Figure 3. Mercury adsorption curves of Au5-RB3 over successive regeneration cycles under N2 (a) and O2+N2 (b) atmospheres.

Figure 4. Diagram of the Au-Hg phase (data extracted from Okamoto and Massalski [23])

Figure 5. Mercury desorption curves for Au5-RB3 in repeated regeneration cycles under an N2 atmosphere.

Figure 6. Mercury adsorption curves for Au5-RB3 over successive regeneration cycles under SO2+N2 (a) and HCl+N2 (b) atmospheres.

Figure 7. Mercury adsorption curves for Au5-RB3 over repeated regeneration cycles under O2+NO+SO2+HCl+CO2+H2O+N2 (a) and O2+NO+SO2+HCl+CO2+N2 (b) atmospheres.

Figure 8. Mercury desorption curves for Au5-RB3 in the first cycle of regeneration under N2, O2+NO+SO2+HCl+CO2+N2 (SFG without H2O) and O2+NO+SO2+HCl+CO2+H2O+N2 (SFG) atmospheres.

Figure 9. Percentages of Hg0 and Hg2+ in the different atmospheres studied.

Figure 10. Mercury speciation in the presence of RB3 (a) and Au5-RB3 (b) under N2, O2+NO+SO2+HCl+CO2+N2 and O2+NO+SO2+HCl+CO2+H2O+N2 atmospheres.

Figure 11. Image of the gold recovered.
Figure 1

Figure 2
Figure 3

Figure 4
Figure 5

Figure 6

[Au5-RB3 (SO2+N2)]

[Au5-RB3 (HCl+N2)]
Figure 7

Figure 8
Figure 9
Figure 10
Figure 11