**A CANDIDATE MATERIAL FOR MERCURY CONTROL IN ENERGY
PRODUCTION PROCESSES: CARBON FOAMS LOADED WITH GOLD**

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Abstract

Tighter control of pollutant emissions in energy generation from coal combustion is essential for the maintenance of coal as a member of the energy panel in coming years. Coal-fired power plants are the primary source of mercury emission in Europe and the second in the world. This study focuses on the development of regenerable sorbents to mercury capture avoiding the generation of new toxic wastes. The sorbents based on carbon foams impregnated with gold have been optimized to achieve the maximum mercury retention efficiency using the minimum amount of gold. Moreover, the sorbent has been designed to facilitate the recovery of the gold once the sorbent has been exhausted. Although this technology requires a higher initial investment than other alternatives, such as the injection of activated carbons, the apparent high cost of the sorbent is offset by the possibility of using the same material over several cycles. A mercury retention mechanism is proposed based on mercury amalgamation and mercury oxidation/adsorption through the double function of gold and support. The results confirm that the reactions between the mercury and gold depend on the size of the gold nanoparticles and the presence of oxygenated groups on the surface of the carbon support.

Keywords: mercury; combustion; energy generation; regenerable sorbent; gold

1. Introduction

Despite the increasing incorporation of alternative sources of energy, fossil fuels continue to be the main energy resource worldwide. By 2014, about 81% of the total primary energy supply was derived from these fuels [1]. Of them coal contributed to 41% of the world's electricity output [1]. Although this percentage has decreased in recent years, especially in OECD countries (29.3% in 2015) as a result of the increasing involvement of renewable sources, the input of coal to production of energy worldwide remains at around 40% [1]. Future forecasts indicate that coal consumption will remain constant up until 2030 [2]. Given this situation the control of emissions from combustion is an inescapable requirement for a healthy environment in the coming years. Furthermore, provided that contamination can be kept under control, the maintenance of coal as a member of the energy scenario even beyond 2030 cannot be ruled out at least from a strategic point of view. The enormous effort made over the years to reduce pollutant emissions from coal combustion has paid off in many cases. Particle emissions have been controlled by different capture systems (electrostatic precipitators or bag filters), NO_x emissions have been prevented by the development of DeNO_x plants, such as selective catalytic reduction (SCR), and SO_x emissions have been reduced considerably by desulfurization systems [3-4]. Nowadays, the problems that still remain unresolved are those related to emissions of CO₂ and Hg [5-9]. In the case of Hg, according to the latest data published in the European pollutant register [10], thermal power plants and other combustion facilities account for 54.5% of its emissions to the air.

In response to this problem, new regulations have entered into force in 2017 [11]. The new specifications derive from the review of the Best Available Techniques (BAT)

Reference Document for Large Combustion Plants (LCP), the so-called LCP BREF, produced by the Commission's Joint Research Centre. The BAT conclusions of the LCP BREF set, for the first time in the EU, limits for the emissions to air of mercury, hydrogen chloride and hydrogen fluoride from the combustion of solid fuels in LCPs. In addition to coal combustion, other sectors such as large volume organic chemical industry, waste treatment, waste incineration, surface treatment using organic solvents (including wood and wood-preservation products with chemicals) and ferrous-metals processing are included in this document. Addressing these emissions can reduce the environmental impact from many of Europe's largest point emission sources and will help the implementation of the Minamata Convention, which came into force in August 2017. The document includes measures to control the supply and trade of mercury, including setting limitations on specific sources of mercury such as coal-fired power plants, primary mining, and to control mercury-added products and manufacturing processes in which mercury or mercury compounds are used, as well as artisanal and small scale gold mining.

The high toxicity of Hg for humankind and ecosystems is well known. Once Hg species are incorporated into the atmosphere, they can travel thousands of miles, causing global contamination of plants, animals and humans. Of all the Hg compounds, methyl mercury (MeHg), is the most dangerous. This species is assimilated by fish in contaminated waters and then incorporated into the food chain.

During coal combustion Hg may be emitted to air as elemental mercury (Hg^0) and oxidized mercury species (Hg^{2+}). Both are toxic and may be transformed into MeHg in the environment. Of the species formed during coal combustion, the most difficult to capture is Hg^0 , (as it is insoluble and unreactive), while Hg^{2+} can be retained in the gas cleaning systems incorporated in most coal combustion plants [12]. The Hg^0 present in

combustion flue gases causes both environmental and operational problems [13-14] and currently there is no technology for its control. Therefore, it is essential to develop systems capable of retaining Hg^0 in an environmentally effective manner. Of the technologies evaluated for Hg^0 capture from combustion flue gases, the injection of activated carbons is the only one that has been tested at industrial scale [15]. A high level of Hg retention can be achieved by the injection of activated carbon, but this process entails the generation of a new waste containing Hg. This problem can be avoided by using regenerable sorbents such as those impregnated with noble metals, which can react with Hg^0 by amalgamation. This method is becoming increasingly attractive as it is possible to isolate the mercury after the sorbent has been depleted [16].

In recent years there has been renewed interest in the use and role of Au in various applications, since Au not only amalgams with certain metals as Hg, but also may be catalytically active for several chemical reactions when is as nano-dispersed particles size [17-19]. Both amalgamation and catalysis are particularly attractive properties for the development of a sorbent for retaining gaseous Hg species from coal combustion processes, and when a highly efficient regenerable sorbent for Hg^0 , with the minimum amount of Au, is being searching. The application of sorbents based on Hg-Au amalgamation in coal-fired power plants is not new. The MerCapTM (Mercury Control Adsorption Process) project [20] is an example of one such application. In this project, Au-coated structures were placed into a flue gas stream to retain any Hg^0 in its path. The Au-coated structure was then thermally regenerated to recovering the Au and isolate the Hg. The drawback of this technology is that it requires large amounts of Au. This can be avoided by developing sorbents containing Au dispersed nano-particles, with the right properties. To achieve this, a support with optimal textural and chemical characteristics is required so that the Au can be efficiently impregnated. This was one of the objectives

of the present study. The second was to find a material that can be easily separated from Au, to allow the recovery of this metal after the sorbent has been exhausted.

Carbon-based materials such as activated carbons [21-22] and carbon monoliths [23-24], are potential options as Au supports since their surface chemistry can be modified to favour the dispersion of the Au in the form of nanoparticles. Previous studies carried out by the authors using activated carbons as supports of Au, exhibited promising results, with high levels of mercury retention efficiency over several cycles of regeneration, and the possibility of recovering the Au from the exhausted sorbent by simple combustion [21-22]. However, some drawbacks were encountered in these previous studies: 1) the mineral matter present in the carbon support makes it more difficult to recover pure Au, and additional purification step via amalgamation with Hg^0 is necessary which increases the cost and handling of the process and 2) the activated carbon has to be extruded to avoid a pressure drop when the sorbents are used in the fixed bed. Therefore, the support needs to be upgraded, for the purpose of which, carbon foams can be used as an alternative to activated carbons [25]. It has been proved that these materials can be easily mechanized during or after their preparation and can be obtained with channels, which would prevent pressure drops when used at industrial scale. Activated carbon foams can also be tailored in such a way that they are free of mineral matter, thereby avoiding the presence of ash which would impede the recovery of the noble metal.

Within the framework outlined above, the objective of the present study was to develop a regenerable sorbent capable of retaining Hg^0 from a gas stream both efficiently and affordably cost, to allow it to be implemented on an industrial scale. To achieve this objective, the amount of Au required and the appropriate nanoparticle size to ensure maximum (100%) Hg retention over a high number of cycles was determined.

Moreover a procedure for tailoring the method to achieve total recovery of the Au was established. This work also attempts to clarify the mechanism of Hg adsorption on solids loaded with gold nanoparticles, which is imperative for the advance of cost-efficient technologies for Hg retention in future fossil fuel energy generation processes.

2. Experimental

2.1 Preparation of the activated carbon foam support

The methodology followed to prepare the activated coal-based carbon foams, referred to as carbon foams (CFs) from here on, has been described elsewhere [26]. A high bituminous coal from USA (Pondfork), ground to $<212\ \mu\text{m}$ and demineralized, was selected as the precursor of the carbon foams. The results of the fluidity assay and proximate analysis of the coal have been reported elsewhere [26]. The chemical activation was carried out using ZnCl_2 . The coal was added to a solution of the chemical activating agent in ethanol (coal/ ZnCl_2 mass ratio of 1:1). The suspension was stirred and heated at $60\text{--}75\ ^\circ\text{C}$ for 2 h. Afterwards, the solvent was removed by heating at $105\ ^\circ\text{C}$ for 2 days. The resultant mixture was loaded into a cone-trunk-shaped stainless steel reactor coated with aluminum foil. The loaded reactor was then purged with argon to obtain an inert atmosphere. Subsequently all the valves were closed to prevent volatile matter from leaking during the foaming process. The foaming process was carried out in a fluidized sand bed oven at the temperature of coal maximum fluidity ($450\ ^\circ\text{C}$), for 2 h. The “green” foam thus obtained was carbonized in a horizontal tubular furnace by heating under an argon flow at 5°C min^{-1} up to $500\ ^\circ\text{C}$ and maintaining this temperature for 2 hours (CF500). An additional 20 hour-heat treatment step at $800\ ^\circ\text{C}$ under a flow of CO_2 was performed to obtain the activated coal foam labelled CF800.

2.2 Impregnation of the activated carbon foam with Au

The CF500 and CF800 activated carbon foams were impregnated with 1 to 5 wt% of Au, following the THPC method, which is based on the formation of Au colloids [21]. The amounts of reagent used were those necessary to obtain sorbents with 1, 2, 3, 4 and 5 wt% Au. For example, to obtain a sorbent with a 4% gold content, 0.8 mL of a tetrakis-(hydroxymethyl)phosphonium chloride (THPC) solution was added to a solution of 0.6 mL of NaOH (0.2 M) in 4 mL of H₂O under stirring (150 rpm). Then 6.0 mL of HAuCl₄·3H₂O (0.127 M) was added to form an Au solution. A suspension of 150 mg of CF500 or CF800 in 8 mL of H₂O prepared in an ultrasonic bath during 15 min was then added to the Au sol. The mixture was stirred at 200 rpm until the solution became colorless. The resultant solid sorbent was filtered, washed, and dried. The THPC remaining in the solid sorbent was removed by heating at 350 °C for 3 hours under an argon flow (100 ml min⁻¹). The sorbents prepared with the CF500 and CF800 supports and Au contents of from 1 to 5% were labelled CF500-1, CF500-2, CF500-3, CF500-4, CF500-5, CF800-1, CF800-2, CF800-3, CF800-4, and CF800-5.

2.3 Characterization of the sorbents

The functionalized groups present on the surface of the carbon support were identified by Temperature Programmed Desorption (TPD). The specific surface area was determined by the standard BET method, using nitrogen adsorption data in the 0.01–0.2 relative pressure range. The microporosity volume (<2.0 nm; V_{DR-N₂}) and the narrow porosity (<0.7 nm; V_{DR-CO₂}) were determined by fitting the Dubinin-Radushkevich (DR) equation to the N₂ and CO₂ adsorption isotherms, respectively. The total macropore volume (V_{Hg}) and the percentage of open porosity (*s*) were calculated by means of Eqs. (1) and (2).

$$V_{\text{Hg}} = (1/\rho_{\text{Hg}}) - (1/\rho_{\text{He}}) \quad \text{Eq. (1)}$$

$$s = [1 - (\rho_{\text{Hg}}/\rho_{\text{He}})] \cdot 100 \quad \text{Eq. (2)}$$

The apparent density, ρ_{Hg} , and the true density, ρ_{He} , of the samples were measured by means of mercury porosimetry and helium pycnometry, respectively. The macroporosity of the carbon foam was ascertained by mercury measurements performed between 0.0007 and 227 MPa.

The Au distribution and Au particle size were identified by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) equipped with an energy-dispersive X-ray spectroscope (EDX). The quantity of Au loaded onto the sorbent was determined by analyzing the Au remaining in the solution after foam impregnation, by means of inductively coupled plasma-mass spectrometry (ICP-MS). The speciation of the Au on the carbon surface was identified by X-ray photoelectron spectroscopy (XPS).

2.4 Experimental device for mercury retention and regeneration

The laboratory scale device used for retention of Hg has been described in a previous work [25] (Fig. S1). It consists of: (1) a gas blending station equipped with mass flow controllers for preparing the gas composition (73% CO₂, 27% N₂, and in some cases traces of HCl and SO₂). The development of the regenerable sorbents is mainly thought to be used at the end of the cycle, i.e., a predominance of CO₂ in the flue gas with very low amounts of other gases like SO₂ or HCl, (2) a calibrated permeation tube placed inside a glass “U” tube which is immersed in a water bath, to incorporate 100 µg m⁻³ of Hg⁰ to the gas stream, (3) a glass reactor containing a sorbent bed of carbon foam kept at 40-50 °C (the total volume of the gas flow through the sorbent was 500 mL·min⁻¹), and (4) a continuous mercury analyser (VM 3000), to monitor the Hg⁰ leaving the

sorbent bed. A Dowex® 1×8 ion exchanger resin is also incorporated to the device to capture the outgoing oxidized mercury (Hg^{2+}), the origin of which could be the homogeneous or heterogeneous oxidation of the Hg^0 incorporated to the gas stream [27-28]. The total amount of Hg retained in the sorbent and the Hg^{2+} captured in the resin were analysed using AMA equipment.

The post-retention sorbent was regenerated in the same experimental device by temperature controlled heating from 40 to 450 °C, at 3 °C min⁻¹, under a N₂ flow of 500 mL min⁻¹. In these conditions all of the Hg retained in the sorbent is released. The desorbed Hg was continuously monitored as a function of temperature using the VM3000 analyser.

3. Results and discussion

3.1 Characterization of the activated carbon foam

The morphology and textural properties of the activated foams has been described in previously published works [26,29]. However, it is necessary to mention here some important characteristics essential for the interpretation of the results to be discussed. The activated carbon foams have a bimodal porosity (macro- and microporosity) with an open network of interconnected macropores. CF500 and CF800 have BET surface areas of 880 and 738 m² g⁻¹, and $V_{\text{DR-N}_2}$ volumes of 0.36 and 0.28 cm³ g⁻¹, respectively. The $V_{\text{DR-CO}_2}$ underwent a slight decrease from 0.30 for CF500 to 0.19 cm³ g⁻¹ for CF800, indicating that activation at 800°C with CO₂ reduces the narrow microporosity. In terms of macroporosity, Table 1 lists the textural properties obtained for the foams under study. As can be seen, the samples show low values of apparent density (< 0.5 g cm⁻³) and high values of true density (> 1.5 g cm⁻³), in concordance with their porosity structure. A rise in the temperature from 500 to 800 °C produced an increase in the

values of open porosity from 72 % for CF500 to 84% for CF800 while the total pore volume also increased from 1.7 cm³ g⁻¹ to 2.7 cm³ g⁻¹, respectively.

Table 1. Textural properties of the activated carbon foams.

Carbon foam	True density (ρ_{He} , g cm ⁻³)	Apparent density (ρ_{Hg} , g cm ⁻³)	Open porosity (s, %)	Total pore volume (V_{Hg} , cm ³ g ⁻¹)
CF500	1.52	0.42	72.3	1.71
CF800	1.91	0.31	83.7	2.69

As well as the textural properties, the presence of oxygen functional groups, such as, carboxyl, lactone, phenolic and carbonyl, may influence Hg⁰ adsorption on carbonaceous surface sites [30-32]. The presence of surface functional groups detected by TPD in CF500 and CF800 (Fig. 1), indicates that treatment at 800 °C under a CO₂ atmosphere modifies the surface chemistry of the material. In general, carboxylic acids and lactone groups release CO₂ upon heating, while carboxylic anhydride produces both CO and CO₂. CO is derived from phenols, ethers and carbonyl/quinone groups [33]. In the case of CF500, CO decomposition is centred at 650°C, which suggests the presence of phenols and ethers, whereas in CF800 it occurs at 880°C, indicating the presence of carbonyls and quinones.

Fig. 1. TDP profiles of (a) CO evolution and (b) CO₂ evolution in the activated coal foams

3.2 Au deposition on CF500 and CF800 activated carbon foams

The impregnation method described in section 2.2 resulted in a 100% Au impregnation efficiency. This efficiency is a considerable improvement on that achieved in a previous work [25] where it was of 60%. The improvement is a consequence of the strict control of several conditions. One is related with the concentration of the reactants: the concentration of THPC needs to be higher than that of the salt of Au⁺³ to reduce particle growth. Another is associated with the duration of the deposition: the Au sol/carbon mixture needs to be stirred at 200 rpm until the color of the solution changes from dark red to colorless. The time needed for this to occur can vary considerably between 2 and 24 hours depending on the Au concentration and characteristics of the surface of the carbon material. It was observed that CF500 needs more stirring time than

CF800, suggesting that the C=O groups present in CF800 favors the adsorption kinetics of the sol by the carbon. Moreover, the stirring time needs to be longer as the percentage of Au to be loaded increases.

According to TEM and SEM analyses, the average size of the Au particles was smaller in the samples with 1-3% Au contents (5-16 nm) than in those with 4-5% Au contents (23-40 nm) reaching an average Au particle size of 116 nm in the case of the CF800 loaded with 5% Au (Fig. 2). Fig. 3 shows SEM micrographs of the CF800 loaded with 1 and 5% Au where it can be observed that an increase in the concentration of Au widens the range of particle sizes. Fig. 4 shows TEM micrographs of CF500 and CF800 loaded with 5% Au. The distribution and particle size of Au particles is more homogeneous in CF500.

Fig. 2. Relationship between the average gold particle size and the amount of gold in the activated coal foams

Fig. 3. SEM micrographs of activated coal foam CF800 with (a) 1% Au and (b) 5% Au

Fig. 4. TEM micrographs of the activated coal foams (a) CF500 with 5% Au and (b) CF800 with 5% Au

The Au deposited by the THPC method on the CF500 and CF800 supports is in its elemental state. The analysis of the Au-loaded sorbents by XPS shows two Au 4f peaks corresponding to the binding energy of metallic Au (84.0 eV and 87.7 eV) (Fig. S2). The absence of oxidized Au, within the detection limit of XPS, corroborates the THPC method as suitable for the deposition of elemental Au which is necessary for its amalgamation with elemental mercury.

3.3 Hg retention on sorbents impregnated with Au particles

The Hg retention capacities for the CF supports before impregnation and for the Au-coated sorbents are shown in Fig. 5. The retention capacities were calculated at the breakthrough time (t_b), which is defined as the time at which a sample retains the Hg with 100% efficiency. The capacity of the supports to retain mercury before impregnation is very low demonstrating that the capture of Hg is mainly due to the presence of Au. However, it can also be observed that the quantity of Au in the sorbents is not the only variable that improves Hg retention. In both CF500 and CF800, Hg retention increases until the sorbent has a Au concentration of 3% but then decreases while the Au content continues to increase from 3 to 5%. This behaviour is due to the formation of Au aggregates resulting from impregnation of the carbon foam with high quantities of Au (Figs. 3-4). Au aggregates would reduce the accessibility of Hg [34-35]. In fact, mercury retention capacity decreases more markedly in CF800-4 and CF800-5 than in CF500-4 and CF500-5, where the Au particle sizes were estimated by SEM/TEM to be between 32-113 and 23-26 nm, respectively (Figs. 2 and 5). Also the activated foam CF800 has a higher macropore volume (between 50 and 100 μm) than CF500 which might favor the formation of agglomerates in impregnations with high Au concentrations (4-5%) (Fig. S3). From the SEM and TEM micrographs it can be seen that Hg retention improves when the Au distribution is more homogeneous, i.e. for Au concentrations of between 1 and 3% (Figs. 3-5). The optimum Au concentration to reach the maximum Hg retention for sorbents prepared from both carbon foam supports CF500 and CF800, is around 3% (Fig. 5). A comparison of CF500-3 and CF800-3 reveals that CF800-3 retains Hg more efficiently than CF500-3 (Fig. 5), showing that the amount of Au is not the only factor that influences mercury capture in this kind of sorbent. As has been observed in previous studies with similar sorbents [22, 25], the

amalgamation of Hg with Au is not the only mechanism determining the retention of Hg in carbon materials impregnated with Au.

Fig. 5. Mercury retention capacity on the raw activated coal foams and containing 1, 2, 3, 4 and 5% Au.

The catalytic activity of gold-based catalysts has been demonstrated for gold particle diameters of less than 10 nm [36]. This catalytic activity needs to be taken into account to explain the differences observed between CF500-3 and CF800-3. The distributions of Au in CF500-3 and CF800-3 are similar, both having an average particle size of 11 and 16 nm, respectively (Fig. 2). Therefore, the gold nanodispersed in both carbon foams can act as catalyser. However, as already mentioned, the mercury retention capacity by CF800-3 is higher than CF500-3 indicating an additional factor other than that connected with the particle size of the gold. One of the differences between both sorbents is the surface chemistry. According to the TPD analysis (Fig. 1), CF800 contains carbonyl and quinone groups and these groups may be responsible for the oxidation and retention of Hg in the activated carbon foams, as in activated carbons [32, 37]. Hg^0 may be converted to Hg^{2+} losing its two 6s electrons of the electronic

configuration. The mechanism of oxidation is favoured by reactions of type I (quinonoid complexes) which can accept mercury electrons.

Oxygenated surface groups, such as lactones and carbonyls or quinones, will then act as electron acceptors facilitating the electron transfer process (mercury oxidation) on the activated carbon foam surface which acts as an electrode. When the oxidation of Hg was evaluated in the laboratory-scale device (Fig. S1) by analysing the Dowex® 1×8 ion exchanger resin that is capable of retaining Hg^{2+} , it was found that the percentage of mercury oxidation was higher with CF800-3 than with CF500-3, their percentages of oxidation being 5 and 1%, respectively. Scheme 1 illustrates the double functions of these novel materials, as supports of Au particles and as oxidants of Hg^0 .

Scheme 1. Pictorial illustration of gold nanoparticles on a) CF500 and b) CF800 with two different functions depending on the surface chemistry of the support: i) amalgamation and ii) oxidation of elemental mercury

It must be also considered that CF800 has a higher open porosity than CF500 (Table 1) favouring the diffusion of Hg through the carbon foam and then its interaction with the Au particles. The resulting sorbent (CF800-3) contains well dispersed gold

nanoparticles embedded inside the macropores of the activated carbon foam, with a promising activity in the mercury oxidation.

3.4 Regenerability of the sorbent

The regenerability of the sorbent was evaluated with the sorbents with the highest mercury retention capacity, CF500-3 and CF800-3. Fig. 6 shows the mercury adsorption curves for these sorbents over 5 cycles of adsorption-desorption. A mercury retention capacity of the order of 150 and 340 $\mu\text{g g}^{-1}$ was achieved and maintained over several cycles for CF500-3 and CF800-3, respectively.

Fig. 6. Mercury adsorption curves for a) CF500 and b) CF800 with 3% Au in an atmosphere containing CO_2 and N_2 .

It must be borne in mind that the performance of regenerable sorbents to be used in coal-fired power plants needs to satisfy certain conditions, out of which at least two should be mentioned: 1) the need for a 100% mercury retention efficiency and 2) once no longer 100% efficient, the sorbent must be able to reach its saturation point quickly for its immediate regeneration (Fig. 6).

Previous studies have evaluated the influence of SO_2 , HCl , NO_x and H_2O , etc., [22, 25, 38-39] on Au-based sorbents. Although gases such as HCl , frequently improve the

mercury retention capacity of sorbents [25] (Fig. S4), others such as SO₂ may poison the Au and make it ineffective. In this study, the effect of SO₂ on the Hg capture and cyclability of the sorbent was evaluated using 100 ppm of SO₂, a concentration slightly higher than would normally be expected in a process of CO₂ purification. Fig. 7 shows the mercury adsorption-desorption curves for CF500-3 and CF800-3 in the presence of SO₂. It was observed that after successive regeneration cycles the 100% mercury retention capacity of the sorbent remained constant over several cycles, evidencing that SO₂ does not have any effect on mercury retention or regeneration in the case of these sorbents (Figs. 6-7).

Fig. 7. Mercury adsorption curves for a) CF500 and b) CF800 with 3% Au in an atmosphere containing CO₂, N₂ and SO₂.

3.5 Gold recovery and cost analysis

Regenerable sorbents impregnated with a noble metal provide a means to achieve 100% mercury retention efficiency over several cycles of regeneration, while avoiding the generation of toxic wastes during the generation of energy from coal. However, in the case of Au-based sorbents it is necessary to implement the best techno-economical Hg removal technology in order to reduce the costs of the process. To achieve this, the recovery of the main participants involved in the processes has to be the goal.

The simplest way to recover the Au deposited in the sorbent designed for the sorbents of this study is to eliminate the support by combustion. Once the CF500-3 and CF800-3 are depleted and the Hg has been eliminated and condensed, the sorbents can be burned in air to obtain a residue that consists mainly of gold (Fig. S5). Since the activated coal foam-based support contains <5% of mineral matter, the Au recovered after combustion needs to be purified.

The costs derived from the installation of this type of technology in the power plant cannot be included in this study at this stage (i.e., laboratory scale) and any attempt to estimate the costs at industrial scale would be premature and it would be 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. However, an estimation of the price of the sorbent material can be made (Table 2). As might be expected, the cost of the CF500-3 and CF800-3 materials reveals that the highest charge for preparing of the sorbent is due to the price of the gold. Although the cost depends on the useful life of the sorbent, which can be extended for several years if the regeneration process is effective, it is estimated a cost for the sorbent of approximately 70.000-80.000 €/year useful life. This estimate is based on the assumption that the sorbent will be employed in a coal combustion power station emitting $10 \mu\text{g m}^{-3}\text{N}$ of Hg. Excluding the installation costs and regeneration of the sorbent, this would entail an initial investment higher than the technology of activated carbon injection [40]. However, the key advantages of these regenerable sorbents are that the initial cost can be recuperated by using the same material for several cycles and by recovering the Au.

Table 2. Estimation of the cost of preparation CF500-3 and CF800-3 at laboratory scale.

Cost of preparation at laboratory scale (€/kg)	CF500-3	CF800-3
Coal: 0.06 €/kg. CF500 and CF800 require 2 and 5 kg, respectively	0.12	0.30
Reagents: HCl (0.05€/kg); HF (0.3€/kg); ZnCl ₂ (3€/kg)	9.6	22
Gas for activation: Ar (0.02 €/l); CO ₂ (0.007 €/l)	0.5	1.5
Energetic cost for activation: 0.13 €/kWh	14	16
Impregnation: H ₂ AuCl ₄ (40000€/kg); NaOH (70€/kg); THPC (278€/l)	2600	2600
Energetic cost to eliminate THPC: 0.13 €/kWh	1.3	1.3
TOTAL	2626	2641

4. Conclusions

The development of regenerable sorbents for elemental mercury capture provides a way to avoid having to choose between achieving 100% mercury retention efficiency and the generation of new toxic wastes in processes for energy production from coal. Regenerable sorbents based on activated carbon foams impregnated with gold are novel materials with a huge potential for use on an industrial scale. Moreover, they provide an open network of interconnected macropores which would avoid the over pressure when used as a bed in coal-fired power plants. Mercury retention is mainly controlled by i) the homogeneity and size of the gold particles on the carbonaceous support rather than the amount of gold and ii) the presence of carbonyl and quinone groups on the support surface.

The commercial applicability of sorbents loaded with gold in coal-fired power plant could be disputed owing to the price of gold. However, the main issue to be considered in processes of energy generation is the durability of the sorbent. The durability or life span of the sorbent is related to the cyclability and resistance to acid gases that were

confirmed high in this study. Moreover, one of the keys of the feasibility of these sorbents is that the gold in exhausted sorbents can be recovered and recycled, in which case the use of gold-based regenerable sorbents may be economically affordable.

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Supplementary information

Fig. S1. Experimental device for the Hg capture experiments

Fig. S2. XPS spectrogram of the activated coal foams. Au 4f with peaks corresponding

Fig. S3. Pore size distribution obtained by mercury porosimetry for activated coal foams.

Fig. S4. Mercury adsorption curve for CF800 with 3% Au in an atmosphere containing CO₂, N₂, SO₂ and HCl.

Fig. S5. SEM/EDAX analysis of the residue after the combustion in air of CF800-3