



# 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.

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## 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<sub>x</sub> emissions have been prevented by the development of DeNO<sub>x</sub> plants, such as selective catalytic reduction (SCR), and SO<sub>x</sub> emissions have been reduced considerably by desulfurization systems [3,4]. Nowadays, the problems that still remain unresolved are those related to emissions of CO<sub>2</sub> 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

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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 ( $\text{Hg}^0$ ) and oxidized mercury species ( $\text{Hg}^{2+}$ ). 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  $\text{Hg}^0$ , (as it is insoluble and unreactive), while  $\text{Hg}^{2+}$  can be retained in the gas cleaning systems incorporated in most coal combustion plants [12]. The  $\text{Hg}^0$  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  $\text{Hg}^0$  in an environmentally effective manner. Of the technologies evaluated for  $\text{Hg}^0$  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  $\text{Hg}^0$  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  $\text{Hg}^0$ , 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 MerCap™ (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  $\text{Hg}^0$  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 favor 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  $\text{Hg}^0$  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  $\text{Hg}^0$  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  $\text{ZnCl}_2$ . The coal was added to a solution of the chemical activating agent in ethanol (coal/ $\text{ZnCl}_2$  mass ratio of 1:1). The suspension was stirred and heated at 60–75 °C for 2 h. Afterwards, the solvent was removed by heating at 105 °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 °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  $\text{min}^{-1}$  up to 500 °C and maintaining this temperature for 2 h (CF500). An additional 20 h-heat treatment step at 800 °C under a flow of  $\text{CO}_2$  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 1–5 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

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