

Elemental Mercury Capture Using Activated Carbon: A Review

Stanley R Shewchuk, Ramin Azargohar and Ajay K Dalai*

Department of Chemical and Biological Engineering, University of Saskatchewan, Saskatoon, SK, Canada

Abstract

Elemental mercury in the atmospheric environment has been identified as a significant environmental issue. The primary reason is the increased anthropogenic emissions of this metal into the global atmospheric environment in recent years. This paper provides a review for elemental mercury uptake in a flue gas stream. The objectives are to provide a summary of the carbon materials and effective parameters involved in an elemental mercury emission flue gas stream control system for industry. Activated carbon injection systems into emission stacks of coal fired power plant have been credited with providing a significant elemental mercury emission control technology. Various chemicals including sulfur, halogens and others species have been identified as key capture agents for elemental mercury emission control on an activated carbon. With the successes of the past several years, there is in place an excellent frame work in the literature to build an activated carbon injection control system to further increase the efficiency of uptake for elemental mercury from mixed gas streams.

Keywords: Mercury; Activated carbon; Flue gas; Sulphur; Halogen; Surface chemistry

Introduction

The objective of this review is to summarize relevant information from the literature to describe the value of activated carbon for the control of elemental mercury emissions into the atmospheric environment.

Coal is one of the major energy resources for earth. However, coal emits into the environment many hazardous pollutants including mercury when it is burnt. Mercury emission is an environmental issue. During combustion of coal, the elemental mercury is completely volatilized and is not controlled by conventional particulate control devices. Once elemental mercury is mixed within a steady state global atmospheric environment, it begins to dry deposit out from the atmosphere into soil and water. It is the water systems that are most sensitive to this elemental mercury deposition flux. It is then transformed by bacterial agents in plant life to methylmercury ((CH₃)₂Hg) which is an environmental toxicant [1]. This material accumulates in the food chain and tends to become more concentrated in the food chain. Worldwide mercury emissions from human activities are estimated to be 1,000 to 60,000 t/annum [2]. It is elemental mercury emissions from coal-fired power plants that are believed to be the largest single source of man induced mercury emissions to the environment. However, elemental mercury emission rates into the atmosphere from medical waste and various garbage dump facilities remain a concern at present for this issue. The concentrations of mercury within the atmospheric environment consist of a natural component and an anthropogenic component [3]. These two components have been seen over the years as being approximately equal. However, within recent years with increasing coal burning for energy needs, the anthropogenic component has been considered to be increasing at a more rapid rate than the natural component [4]. In 2013, it was announced that 140 countries have agreed on the first-ever global treaty to curb mercury pollution to the environment [5]. In Canada the issue is driven from the regulatory perspective by the Canada Wide Standards [6] which develops guidelines for elemental mercury and other toxicants emission control for various timelines within the country.

This element can provide neurological health impacts to the human population [1]. There are three forms of mercury in most flue gas streams. They are elemental mercury, oxidized mercury and particulate

bound mercury. Particulate bound mercury and oxidized mercury can be removed by current air pollution control systems quite easily. Elemental mercury, however, is emitted into the atmosphere because of its high volatility as a gaseous product. This elemental mercury gas stream then mixes globally within the troposphere.

Activated Carbon is a form of carbon that has been processed via various thermochemical procedures to make it porous and thus to have a large surface area available for adsorption and chemical reactions [7]. An activated carbon surface has unsaturated carbon atoms on its surface with many unpaired electrons that can play a significant role in adsorption. The activation process and its parameters greatly condition the activated carbon production efficiency and quality [8]. The high surface area is sufficient for good adsorption processes to take place, although often further chemical treatment enhances the adsorbing properties of this material via surface chemical functional agents. Well-developed porosity, chemical structure and oxygen surface functional groups present in activated carbon affect the adsorptive/catalytic activity and selectivity of this product.

The Elemental Mercury Flue Gas Stream Removal Process

There are several methods for elemental mercury sequestrations from industrial flue gas streams. Some of the methods are additions to the process stream with aluminum hydroxide as a precipitate promoting complexed elemental mercury material. Since the amount of elemental mercury in the gas stream from coal combustion is typically in the range of 5 to 10 micrograms/m³, Miller et al. [9] has noted that only a small amount of sorbent needs to be used in an operational facility for efficient control. A mixed gas stream contact with nano-gold

*Corresponding author: Ajay K Dalai, Department of Chemical and Biological Engineering, University of Saskatchewan, Saskatoon, SK, Canada, Tel: 13069664771; Fax: 13069664777; E-mail: ajay.dalai@usask.ca

Received May 27, 2016; Accepted June 23, 2016; Published June 28, 2016

Citation: Shewchuk SR, Azargohar R, Dalai AK (2016) Elemental Mercury Capture Using Activated Carbon: A Review. J Environ Anal Toxicol 6: 379. doi:10.4172/2161-0525.1000379

Copyright: © 2016 Shewchuk SR, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

supported silica and powdered activated carbon [10] can also assist in controlling elemental mercury emissions. Powdered activated carbon is seen to be the material of preference for industrial facilities due to its ease of preparation and its flue gas stream injection efficiencies with the current technologies that are in place.

Carbon materials have been used for many years in heterogeneous catalysis applications because they can act as a direct catalyst or can act as a catalysis support for gas phase reactions involving mercury [11]. Activated carbon adsorption can be configured in two different ways for removal of elemental mercury from industrial activity. They include powdered activated carbon adsorption and fixed bed granular activated carbon adsorption [12]. The former includes injection of the material into the flue gas stream where it collects elemental mercury which is removed farther downstream in particulate collection devices such as fabric filters or Electrostatic Precipitators (ESP). The other is fixed bed control devices that condition the flue gas stream to a defined quality prior to it releasing the material to a storage facility.

An effective mercury control technology was discovered many years ago [13]. The effect of sulfurization of activated carbon for mercury capture at 25°C and 150°C is a well-known fact. At 25°C, for example, the adsorption capacity for mercury sorbents was greatest for carbons with no sulfur and then as the temperature increased the mercury capture amounts decreased. However with the temperature at the higher value of 150°C the adsorption of mercury by the non-impregnated activated carbon material was negligible compared to that of the sulfur impregnated activated carbon material. This observation at the higher temperature is attributed to elemental mercury reacting with the sulfur on the activated carbon surface to form HgS. In the former case, mercury was collected on the carbons by physisorption and in the latter case, mercury was collected on the carbons by chemisorption. Thus, via the chemisorption route, this produces the driving force for the sequestration or removal of elemental mercury atoms from a mixed flue gas stream.

The National Energy Technology Laboratory conducted a series of in-house programs on elemental mercury control technologies [14]. They conducted their work at both laboratory and operational scales of their facilities and were interested in discovering the mechanism of the elemental mercury captured within an industrial setting. They used small packed bed reactor systems to simulate various processes within their operational programs. They compared novel sorbents to commercially available sorbents, with a focus on the elemental mercury capture. They believed that in an Electrostatic Precipitator (ESP) configuration most of the mercury captured by sorbent to occur within the duct up stream of the ESP, whereas in a bag house configuration, most of the mercury capture occurs in the filter cake on the bags.

Another program looked at the mode of occurrence of mercury in coal from a reserve [15]. It was demonstrated in this work that there is a strong relationship between mercury and sulfur in coals. The amount of elemental mercury remaining in coal was seen to be a function of temperature. It was temperatures around 150°C which provide the most stable environment for retention of this species in this medium. Thus it seems reasonable to assume that since sulfur and elemental mercury are so highly correlated in natural reserve systems that as a capture medium functional agent sulfur on an activated carbon surface texture should be an efficient approach for improving activated carbon for elemental mercury emission control within the industrial setting.

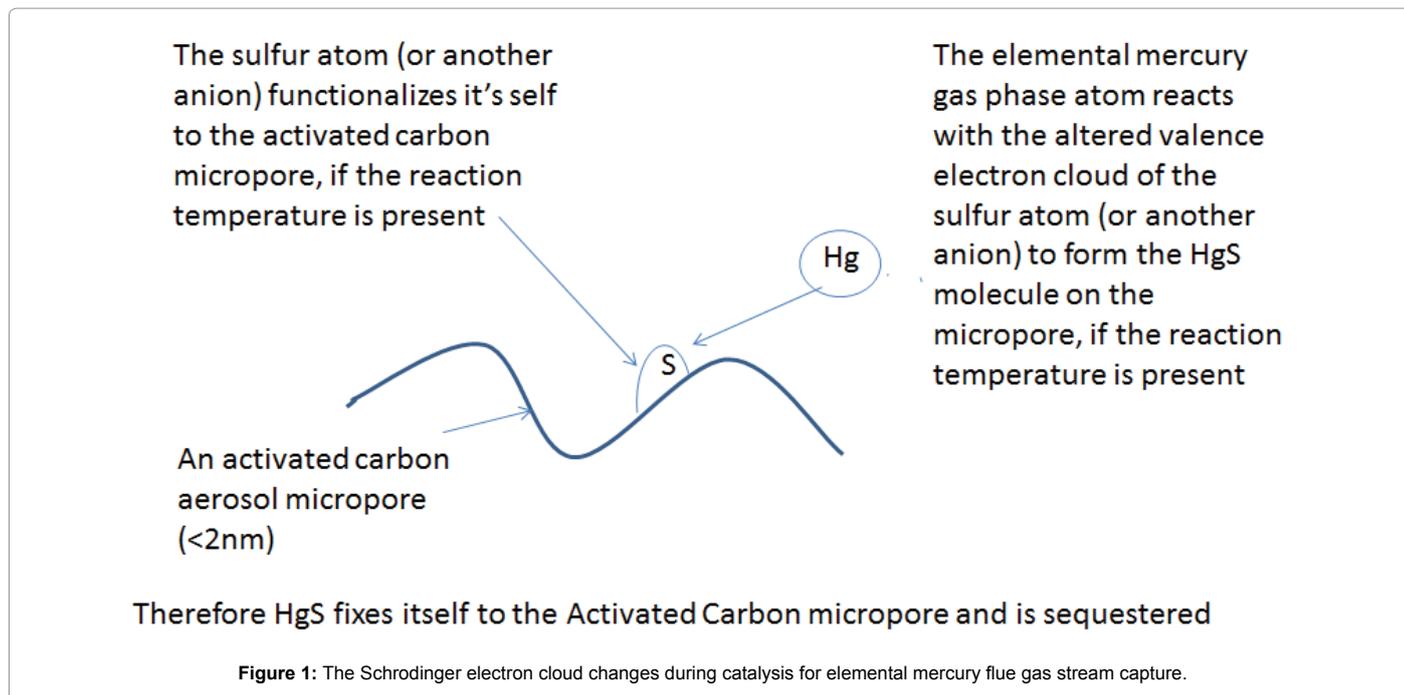
Activated Carbon as an Effective Adsorbent for Elemental Mercury Emission Control

Parameters involved in the carbonization process have been reviewed [8]. Various forms of the activation process are discussed with slow to high heating rates. Key factors in the design of an activated carbon surface are peak temperature, pressure, vapor residence time and moisture. All of these various factors do have an effect on the rate the surface chemistry conditioning of the activated carbon and do have an influence upon the uptake of elemental mercury atoms in a mixed flue gas stream situation.

Activated carbon materials exhibit a fundamental flexible nature in applying their physical and chemical properties to specific applications. Surface chemistry and the carbon porous structure are the two determinant factors which are the keys to the value of these compounds in their use in the laboratory and field setting. These two features can be tailored for various given applications in designing a catalyst. This section discusses the performance of these activated carbons used for elemental mercury capture.

It is important to note that the carbon surface itself can be considered as a catalysts support or a catalyst in a reaction. When a solid catalyst interacts with a gaseous feed stock, the adsorption of the mixed gas stream reactant molecule on the catalyst surface creates a chemical bond with the surface. This alters the electron cloud density around the reactant molecule and allows it to undergo chemical reactions that would normally not be available to it. It has been shown that oxygen, for example, can be catalyzed onto an activated carbon surface [16]. Then this oxygen reacts with elemental mercury via an electron transfer process if the temperature for this reaction is appropriate for the conditions of the experiment. Specifically with a mixed gas stream containing SO₂, it has been shown that the formation of sulfur groups on the activated carbon surface can act as the elemental mercury chemisorption sites via this electron cloud reaction mechanism. Laumb et al. [17] conducted a study on the chemical changes that take place on the surface of activated carbons. They tested Norit FGD lignite activated carbon's ability to retain elemental mercury in a simulated flue gas stream containing high concentrations of SO₂, NO₂ and HCl. The authors identified that part of the elemental mercury binding mechanism on the activated carbon involves the oxidation of SO₂ and that the form of sulfur absorbed from the flue stream is mostly S(IV). In general most authors support the hypothesis that it is the interaction of acidic species in the mixed flue gas stream with the activated carbon surface that is the important mechanistic process which is responsible for the creation of active sites for mercury capture by the chemisorption process [1,18].

Electrons that compose an atom or molecule can be described as relativistic waves about the nucleus of an atom [19]. In this model, electrons in their orbits set up as standing waves about the nucleus. Figure 1 displays the electron changes about an atom that can occur during anion catalysis to the activated carbons microporous surface. As the temperature of this chemical arrangement changes, the electron cloud can be made available for a chemical reactions with the neighboring cations. As the reaction proceeds between the catalyzed anion and the elemental mercury cation a molecule of HgS is formed on the microporous surface of the activated carbon. In the case seen in Figure 1 the result is a mercuric sulfide molecule. However with other anions, there are many other molecules that can be catalyzed to the activated carbon surface including HgO, HgSO₄, etc. This is the main mechanism of elemental mercury atoms capture in a mixed gas stream in either the laboratory or field situation.



The construction and design of carbon based sorbents for elemental mercury efficient capture conditions was undertaken by Lee and Park [20]. The work focused upon the comparison of virgin activated carbons with that of sulfur doped material. It was found that on several different methods of sulfur addition to the carbon for efficient capture that the virgin activated carbon with oxygen functional groups was an efficient collection route on an activated carbon surface for elemental mercury. The elemental mercury adsorption rate was dependent upon the pore size characteristics of the virgin activated carbon and that the type of sulfur not the amount of sulfur as a dopant was contingent on the elemental mercury capture rate. Pore diameters in excess of 2 nm were necessary for efficient capture rates.

A series of low cost carbon sorbents for industrial systems was ranked for the purpose of elemental mercury sequestration [21]. In these experiments, a stream of nitrogen and mercury is used for the temperature range of 130 to 220°C. It was reported that the coal ashes were also effective in elemental mercury capture. Other materials such as the solid product of pyrolysis of scrap rubber tires tested well against commercial material (supplied by Norit). In the simulated laboratory flue gas stream, it was noted that the introduction of NO and NO₂ significantly improves mercury capture. It was shown that the effect of increasing temperature, decreased the elemental mercury capture efficiency in these tests. This phenomenon is attributed to a low temperature efficient capture rate related to physisorption and with a high temperature HgO capture rates being more attributed to chemisorption.

Undoped activated carbon in a mixed flue gas stream is an effective adsorber of various components from the mixed gas stream. Some of those are the selective incorporation of various gaseous components that can act as chemical functional agents. Then selective capture of various of the chemicals onto the carbon that react with elemental mercury in the mixed gas stream, as an example sulfur or bromine, can functionalize itself to the surface and then capture flue gas stream elemental mercury as a HgS or a HgBr molecule which can be

subsequently removed from the flue gas stream via a selective capture process.

Yang et al. [22] has looked at the advances in the development of sorbents for mercury capture for industrial systems. These authors have reported that it was activated carbon injected downstream of the coal fired boiler flue gas stream that had the best chance of cost effectively sequestering industrially focused elemental mercury in a mixed gas emission stream. The authors looked at the bench scale and utility scale of elemental mercury emission streams and concluded that virgin commercial material with brominated carbon enhancements were seen to perform the best in the industrial situation with cost effective options taken into consideration.

Activated carbons from two biomass sources of olive residue and wheat straw were also investigated [23]. The authors studied the effect of chlorine and alkali metals on the elemental mercury capture efficiency. They found that the biochar based carbons performance for elemental mercury capture was better than that for lignite derived carbon product and similar to that for commercial grades of activated carbon.

The effect of the carbon surface on the elemental mercury capture from a flue gas stream has also been reported [24]. The authors focused upon cost based alternatives to commercial carbon suppliers. These authors noted that sulfur has been identified as being superior for the removal of elemental mercury from a flue gas stream. They used petroleum coke as a feedstock because it does have high sulfur content in its domestic state. They reported that the specific surface area of the coke increased by about an order of magnitude during the activation procedures and it resulted in an increase in the mercury capture efficiency by a corresponding amount. This activated petroleum coke was considered to be a candidate for sorbent development for removing elemental mercury from a flue gas stream.

The sorption of elemental mercury by activated carbon as a functional agent of flue gas stream composition shows that an extended surface area and a development of micropores structure combined

with a small volume of mesopores in an activated carbon specimen enhanced mercury capture [16]. A full scale value of activated carbon injection application to mercury emission systems in industry was reported by Sjostrum et al. [25]. Operational flexibility is available with these systems and it is making all quite attractive for further reductions to emission rate into the environment as necessary. According to these authors activated carbon from flue gas streams can be used effectively to sequester elemental mercury in flue gas streams from operational systems. Industrial flue gas streams with low halogen gas composition can get elemental mercury controls by using various levels of halogen doped activated carbon.

In other work Yang et al. [22] provide a review of adsorbents for industrial elemental mercury control and it has identified activate carbon injection as the best of a series of aerosol formulations that are available for elemental mercury flue gas control. Within the commercial scene activated carbon can provide a cost effective control package for industry.

It is seen that activated carbon if prepared in an appropriate manner can act as a catalysis support for the flue gas stream capture of elemental mercury atoms. However various chemical functional agents, such as, the application of sulfur, various halogens and other surface active agents applied to the catalysts surface can significantly enhance the elemental mercury flue gas stream capture process both in the laboratory and industrial setting.

Effects of Surface Functional Groups on the Activated Carbon Surface Chemistry and on the Elemental Mercury Reaction Kinetics

The sorption of elemental mercury atoms by an activated carbon surface can be related to the functional surface chemical agents [16]. It has been shown that the presence of HCl, O₂ and SO₂ tended to contribute to the surface chemisorption of elemental mercury atoms on activated carbon. Among these agents HCl provided the strongest elemental mercury sequestration ratios. The oxidation of elemental mercury on the acidic sites was promoted on the carbon surface by the HCl and other anions.

The exact form of elemental mercury uptake on activated carbons can be either of a physisorption or chemisorption route. Physisorption occurs at primarily low temperatures (~ 50°C) and chemisorption occurs at higher temperatures with the form of surface functional agents [26] in the order of 150°C. Others also reported that elemental mercury adsorption complex species uptakes on various carbon sorbent surfaces at higher temperatures 200°C. Data from synchrotron based radiation

programs indicated that species such as sulfur in the mixed flue gas stream situation is an important species for surface based active sites on the carbons for mercury capture by the chemisorption process [27].

Pavlish et al. [28] presented an overview of mercury emission control technology for coal fired power plants. They mentioned that acid gases do influence the oxidation of elemental mercury as it is captured on adsorbents, while HCl, NO and NO₂ all promoting oxidation and capture of elemental mercury atoms both individually and in combination to the surface. However, the combination of SO₂ with NO₂ greatly reduces the capture of elemental mercury on sorbents.

Experimental results have shown that SO₂ and NO in a mixed gas stream, particularly with Cl₂ present as a powerful chlorinating reagent, have a significant effect on the oxidation of HgO at high temperatures to Hg²⁺ when H₂O was present in the mixture [29]. These authors also mentioned that reduction of Hg²⁺ back to its elemental form took place under homogeneous catalysis conditions when the H₂O was removed from this blend.

The nature of the interaction between elemental mercury, various mixed gas stream components and the activated carbon surface has been reviewed and put in the form of a model by Olsen et al. [30]. Their work showed that NO₂ or HCl-O₂ is required for effective HgO adsorption on the activated carbon surface. Thus the chemisorption of HgO in their experiment was significantly affected by the various mixed gas stream components. The oxidation of HgO occurred to form a bound Hg(II) species on the carbon surface with the electrons donated to the carbon. In their laboratory experiments both NO₂ and H₂O in the mixed flue gas stream contributed to the enhanced capture of HgO onto the carbon surface. However, with the presence of HCl on the carbon surface, HCl is displaced at the surface by the presence of other species such as sulfur owing to the high volatility of HCl. Hence the effect of various surface functional groups on elemental mercury reaction kinetics in a mixed gas stream can be quite complex.

Sulfur as a Surface Functional Group and an Impregnating Agent

From the literature, an important functional group for elemental mercury capture from a simulated or industrial mixed gas streams on an activated carbon surface is sulfur. Many authors [4,10,31-40] have shown the important role of sulfur in this process. Table 1 shows the effects of sulfur on the adsorption of HgO on activated carbon.

Research on sulfur coated flux systems and non-sulfur coated systems of activated carbons was conducted by Uddin et al. [39].

Research work	Experimental conditions	Outcomes
Feng et al. [34]	-AC treated with H ₂ S -temp range 400-600°C	-higher temps favor organic sulfur on AC -lower temps promote elemental sulfur on AC -HgO uptake is related to elemental sulfur on AC
Hsi et al. [31]	-coal derived AC for HgO capture studies	-high sulfur coals adsorb more HgO than low sulfur coals
Karatz et al. [4]	- adsorption studies of HgO on commercial carbon	- HgO is absorbed on carbon surfaces where high sulfur concentrations exist
Morimoto et al. [32]	- effect of H ₂ S to remove HgO on AC - temperature range 60-100°C	- suggested partial oxidation of H ₂ S with O ₂ to elevate the presence of sulfur on the AC - suggested the primary reaction for Hg removal is S ₈ +HgO=HgS
Uddin et al. [47]	- the value of SO ₂ in HgO capture - temperature range 60-100°C	- the presence of sulfur from the flue gas stream SO ₂ was essential for HgO capture - the lower temperature ranges favored the reaction of HgO capture

Table 1: The effects of sulfur on the adsorption of HgO on activated carbon (AC).

They examined the input loading for mixed gases situations. Their conclusion was that the sulfur coated activated carbons was nearly 40% more efficient at the collection of elemental mercury in these mixed gas situations than non-sulfur coated activated carbons.

The behavior of activated carbons prepared from raw and demineralized lignite for gas-phase elemental mercury removal was evaluated [35]. These authors looked at various activated carbon structural properties and surface chemistry impregnation features. Their experiments were conducted with and without sulfur additions to the activated carbon surface and their results are shown in Table 2. These experiments with elemental mercury adsorption were conducted with activated carbon prepared from lignite of the raw and demineralized carbon forms. The addition of sulfur to the carbons in each case significantly increased the elemental mercury capture efficiency to the surface area of the carbons. Loading of sulfur on activated carbon can decrease the BET surface area, micropore surface area and the volume of active micropores remaining on the carbon surface. However, the sulfur on these carbons creates a significant opportunity for the elemental mercury capture via the chemisorption route if the temperature of the surface conditions is appropriate.

The form of sulfur on the activated carbon surface is another major factor for effective elemental mercury uptake. Many authors [12,20,41] have identified that it is the elemental sulfur component that is the best sulfur form for elemental mercury capture and its activity is strongly related to reaction temperature [35]. Higher temperatures promote organic sulfur on the activated carbon surface. It was the temperature range of 400-600°C that was the most efficient at the take up of elemental mercury atoms from a flue gas stream in their experiments. In addition, it is shown that elemental mercury is adsorbed on particular sites on the activated carbon where high elemental sulfur exists [4]. These authors worked at temperatures in the range of 120 and 150°C and the main sulfur compound product on their activated carbon surface was mercuric sulfide (HgS).

Yan et al. [42] have reported that many different gaseous components can have a significant impact on elemental mercury uptake collectively but that the sulfur gaseous components is by far the best capture agent for elemental mercury atoms in a mixed gas stream [42]. All of these reactions are a chemisorption process and are strongly dependent upon temperature. The cooler temperatures in the flue gas stream experiments are the most efficient at reacting with elemental mercury atoms and other authors [37,39] support this position. Higher sulfur impregnations temperatures [31,34] tend to promote organic sulfur on the activated carbon surface and this product discriminates against the elemental mercury capture process at these higher flue gas stream temperatures.

In a series of experiments, involving SO₂ and HCl on a mixed gas stream elemental mercury removal by a commercial activated carbon, was reported by Ochiai et al. [41]. They reported that HCl in the presence of SO₂ and mercury in a mixed simulated flue gas stream interacted

with each other to influence mercury capture. The characteristics of the mercury species formed on the carbon was investigated with a temperature programmed decomposition desorption technique. It was found that the presence of HCl and SO₂ in the mixed flue gas stream affected the mercury adsorption characteristics on the carbons. The mercury removal rate from the carbons increased with the HCl concentration in the mixed gas stream. A mercury desorption peak was noted at about 300°C. The authors suggested that the peak may be related to the decomposition and desorption of the mercury chloride species under these conditions.

As identified by Feng et al. [34] under mixed gas situations elemental mercury uptake has been associated with thiophene sulfur and sulfate sulfur in the mixed gas stream. But elemental sulfur uptake onto the activated carbons in these mixed gas streams has been identified by these authors as being one of the most effective elemental mercury capture agent. As a general statement the presence of SO₂ in a flue gas stream tends to enhance the elemental mercury capture and the presence of SO₃ tends to suppress the efficient capture of elemental mercury atoms within a flue gas stream. In addition several other authors [25,33] have investigated the direct impact of an SO₃ flue gas stream component on the uptake of elemental mercury capture from a mixed gas stream and all report that, unlike sulfur dioxide, SO₃ in a flue gas stream can significantly reduce the elemental mercury capture rates on an activated carbon surface.

Specifically focusing upon mercury vapor removal from a simulated coal combustion flue gas stream in a laboratory, Morimoto et al. [32] used H₂S gas to enrich the sulfur deposition onto a commercial variety of activated carbon products. It was suggested by these authors that at low temperatures (<150°C) the key feature for the capture of the elemental mercury component was the presence of oxalating agents in the flue gas steam which would essentially result in elemental forms of sulfur to be deposited on the carbon surface. However, it was suggested by these authors that the subsequent reaction of sulfur elemental adsorbed +HgO=HgS on the activated carbon surface was the key mechanism for the elemental mercury capture on the surface. As the mercury capture began to be observed by these authors in their experiments, the presence of elemental sulfur was confirmed on the carbon surfaces by visual observation.

The effect of sulfur functional group impregnation temperatures onto activated carbon fibers and the subsequent sequestration of elemental mercury for a simulated flue gas stream was reported by Hsi et al. [31]. This study focused upon the micropore structure of the carbons. The authors found that the total sulfur content of these carbons decreased with increasing temperature. They reported that in this simulated flue gas situation that the sulfur on these carbons was in both the inorganic and organic form with the inorganic form being more predominant at the lower temperatures. Sulfur impregnation at any temperature decreased the surface area of the carbons by a much a two orders of magnitude below the virgin activated carbon surface area. Interestingly these authors suggested that elemental sulfur was the

Sample	BET surface area (m ² /g) using N ₂ -adsorption	BET surface area (m ² /g) using CO ₂ -adsorption	Total pore volume (cm ³ /g)	Micropore volume (% of total pore volume)	HgO adsorption capacity (Hg/mg)
Raw AC	183.2	385.2	0.155	54	209.1
Raw AC with a surface sulfur addition	163.2	327.9	0.169	40	346.0
Demineralized AC	134.5	751.9	0.141	34	176.7
Demineralized AC with a surface sulfur addition	10.9	686.6	0.015	20	416.7

Table 2: Activated carbon (AC) pore structure characteristics and elemental mercury adsorption capacity with and without sulfur from Skodras et al. [35].

main form of the sulfur functional groups that collected the elemental mercury to the surface of their carbons and that these functional groups were associated with the activated carbon's microporosity features and both of these features improve mercury removal efficiencies from their simulated flue gas streams. From this work, they concluded that carbon-based adsorption processes whether they are either direct injected or fixed bed processes, they have the best potential to remove very low trace gas phase concentrations of elemental mercury in the order of micrograms per cubic meter from industrial flue gas streams.

The sulfur exists on the surfaces of the activated carbons associated with elemental mercury capture in various forms as an acidic species arrangement, prior to elemental mercury capture. While one can have various forms of sulfur on the activated carbon surface including organic and inorganic structures, it is primarily the elemental sulfur form, within a given series of temperature ranges that is the primary determinant of elemental mercury uptake by chemisorption on the activated carbon surface within a mixed gas flue stream.

Halogens as a Surface Functional Grouping

With regard to halogen functional agents, many authors [2,43-48] have noted that halogens have positive impact upon elemental mercury uptake within a mixed gas situation. The mechanism of elemental mercury uptake involves chemisorption. Chlorine [2] is best in the laboratory setting in one case, according to De et al. [45] iodine is best in the laboratory setting for efficient element mercury capture from a mixed flue gas stream on another case. A summary of characteristics of the elemental mercury capture via halogens is seen summarized in Table 3.

The research work done by Zeng et al. [26] shows the effect of chlorine doped on activated carbon and subsequent elemental mercury adsorption. Their work showed that chloride impregnation significantly enhances the adsorptive capacity of mercury vapor. ZnCl₂ impregnation from 0 to 5 wt% onto an activated carbon surface significantly enhanced the adsorptive capacity of the mercury vapor by nearly an order of magnitude (Figure 2).

It is known that activated carbons chemically modified with bromine compounds are most effective at sequestering vapor phase mercury from industrial flue gas streams. Tong et al. [49] investigated the leaching potential of elemental mercury captured with four activated carbons. These activated carbons were a raw lignite derived carbon and the three specific activated carbon chemically treated with Br₂, KClO₃, and SO₂. The authors clearly show the effects of bromine treated material on the stability of the captured mercury. The elemental mercury captured with bromine was likely in the form of a mercurous bromide complex on the carbon surface.

In a series of experiments Hu et al. [2] looked at the oxidative adsorption of elemental mercury by activated carbon in a laboratory setting. In this setting, they used a commercial brand of activated carbon Injection material. These authors also concluded that it was brominated activated carbons that had the best chance of significantly removing the HgO in complex flue gas stream.

In the temperature range of 100 to 200°C, Ghorishi et al. [48] used HCl and reported that the chlorine component on the activated carbon surface provided an effective elemental mercury uptake onto the carbon surface. In general, they reported that activated carbons with metal catalysts are efficient elemental mercury capture agents. Shen et al. [50] identified in a complex series of halides groupings that chlorides are the most efficient capture agents of elemental mercury in a flue gas stream. These authors identify that once the oxidation reaction with elemental mercury takes place that these metal oxides reside on the activated carbon surface as the chemical compounds of either HgCl or HgBr.

Uddin et al. [39] worked in the temperature range of 80 to 300°C with halogens. These authors concluded that within a simulated flue gas stream HCl contributed most significantly to the removal of elemental mercury. However, in a mixed gas situation, such as with the presence of SO₂, within an HCl flue gas stream that each component gas contributed quite significantly to the uptake and the stability of elemental mercury on the activated carbon surface.

Synchrotron Science via X-ray absorption fine structure (XAFS) technique has been used to examine the adsorption complexes of elemental mercury onto an activated carbon surface under mixed flue gas stream conditions by Huggins et al. [1]. These authors concluded that the sorption complex with mercury compounds on the activated

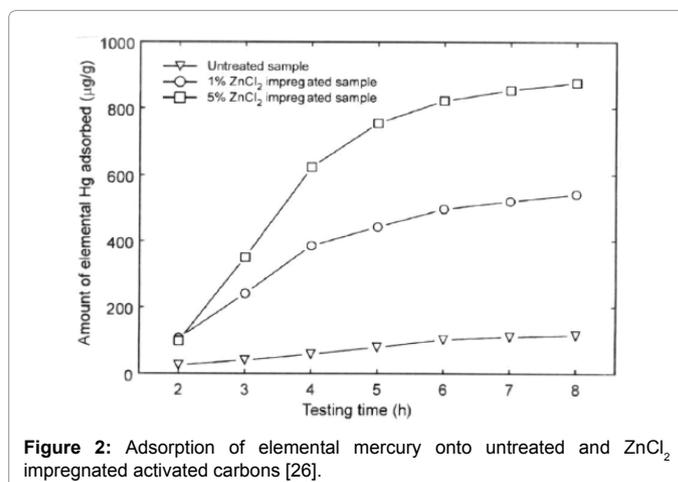


Figure 2: Adsorption of elemental mercury onto untreated and ZnCl₂ impregnated activated carbons [26].

Research work	Experimental conditions	Outcomes
De et al. [45]	-looked at process temperature -Halides on HgO removal from bio-char AC Used various halides and NH ₄ ⁺	-all halides used significantly improved HgO capture with Cl and NH ₄ ⁺ being best in their classes
Hu et al. [58]	-effect of chemical activation of AC for HgO capture studied	-steam AC did not absorb HgO -AC activated with ZnCl ₂ was shown to significantly adsorb elemental mercury -HgO adsorption by AC is a chemical adsorption process
Hutson et al. [44]	-HgO capture upon brominated AC	-By XAS & XPS indicated that HgO is bound on the carbon in an oxidized form -Bromination is seen to be a strong determinant for HgO oxidation in a mixed flue gas stream
Lee et al. [43]	-Iodine & chlorine were tested for HgO capture -two types of AC were tested	-HgO removal increases with temperature for iodine -HgO removal decreases with temperature for chlorine -active surface area decreases with increasing chemical content

Table 3: The presence of various halogens and adsorption of HgO on Activated carbon (AC).

carbon surface is related to acid species of the halogens that were present in the flue gas. They examined both chlorine and bromine species on the activated carbon, and found that chlorine complexes on the activated carbon are more superior capture agents for elemental mercury in a flue gas as compared to iodine complexes. They speculated that their experimental results implied that significant volatilization of the iodine species had occurred from the carbons during exposure to the flue gas streams of their study. Hutson et al. [44] used X-ray absorption spectroscopy (XAS) to determine information about the binding of elemental mercury on commercial activated carbons. They specifically looked at the sorbent structure of brominated activated carbons and at the binding of mercury on two commercially available brominated activated carbons. Results showed that mercury consistently introduced as a vapor into the system was bound on the carbon as an oxidized form.

Huston et al. [44] have noted that bromine is a more efficient capture agent than chlorine under their individually different flue gas stream circumstances. Otten et al. [51] has indicated that while halogens are effective flue gas stream capture agents for element mercury in a flue gas stream, these authors suggested that elemental mercury oxidation by bromine in combustion systems is different from that for the same system with chlorine. They suggested that bromine may be more stable for elemental mercury control in complex industrial systems.

In summary, halogens can be important flue gas stream elemental mercury uptake agents under various conditions. However, their individual reaction kinetics with the activated carbon surface and the mixed gas steam components containing elemental mercury can be quite different and complex from one halogen species to another.

Oxygen as a Surface Functional Group

It is known that the type of oxygen groups present on an activated carbon surface can be significantly altered by activation conditions [35]. Thus in the process of creating an activated carbon product, the surface characteristics can be efficiently designed via the activation processes to uptake elemental mercury atoms under various different mixed gas stream conditions. Rodriguez-Reinoso [7] has attributed this large amount of oxygen chemisorption variability on the activated carbon surface to edge areas having varying amounts of unpaired electrons available for a chemical surface reaction with oxygen. The characteristics of the elemental mercury capture via oxygen are summarized in Table 4.

Diamantopoulou et al. [16] looked at the effect of O₂ on the collection of HgO in a chemical stream. Activated carbons with higher levels of microporosity structure and increased BET surface areas exhibited a greater elemental mercury capture capacity. It was also noted that the presence of an increasing oxygen concentration on the carbon surface was directly related to the mercury captured via the chemisorption process.

The stability of the elemental mercury taken up on the activated carbon surface was investigated by Liu et al. [40]. They studied the impact that various gas stream constituents found in an industrial flue mixed gas streams had on elemental mercury atoms that had been fixed to their sulfur-impregnated activated carbons. They showed that CO₂ had no effect on these carbons. However, the presence of oxygen in their flue gas streams increased the absorptive capacity up to 30%. They postulated that the enhanced performance was due to the formation of HgO catalyzed to the surface of their carbons. Moisture increases up to 10% can decrease the mercury up take by as much as 25%. These authors noted that the elemental mercury absorptive effect of their prepared carbons decreased significantly with the reaction temperature increases from 140 to 400°C due to the pronounced exothermic nature of HgS formation.

It is not only activation conditions that can control the oxygen functional groups on the activated carbon surface but it is also known that the type of edge effects on the texture of the activated carbon surface can have an influence on these oxygen functional groupings. It has been reported by Uddin et al. [47] that it is the activated carbon edge effects that can uniquely capture oxide species prior to elemental mercury uptake. These edge effects are produced under specifically designed activation conditions.

Several authors have reported that the presence of oxygen functional groups associated with the activate carbon surfaces have been efficiently linked to captured elemental mercury in the laboratory setting [52,53]. Their results suggest that it is oxygen surface functional groups in addition to lactones such as carbonyl groups that are important for elemental mercury reaction kinetics under various temperatures. Hall et al. [54] reported that oxygen within the surface structure of activated carbon in the temperature range of 100 to 300°C chemisorbs elemental mercury quite efficiently.

Li et al. [52] looked at the moisture, in the range of ~2%, and elemental mercury uptake on activated carbon. The results suggested that elemental mercury bonding on activated carbon was associated

Research work	Experimental conditions	Outcomes
Li et al. [52]	-role of surface H ₂ O on HgO capture	-H ₂ O reduces HgO capture on AC -HgO bonding on AC is associated with oxygen surface complexes -by reducing flow rate of O ₂ the HgO capture is lowered
Li et al. [52]	-AC were treated to vary their oxygen surface functional groups	-O ₂ surface complexes are active sites for HgO capture
Liu et al. [40]	-Sulfur impregnation on AC with O ₂ complexes -temperature range of 140-400°C	-the presence of O ₂ increased HgO uptake -CO ₂ and H ₂ O had no effects -HgO uptake decreased with increasing temperature
Moroto-Valer et al. [55]	-effect of porous structure and surface functional groups on HgO capture	-Oxygen functional groups promote HgO capture on AC -Surface area is not important for HgO capture
Olsen et al. [46]	-Sorption kinetics of HgO for various coals were compared for temperatures of 107, 150, and 163°C	-O ₂ was required for best reactivates in each case -HgO capture is inversely proportional to temperature
Wang et al. [59]	-V ₂ O ₅ AC catalyst for HgO Capture	-with V ₂ O ₅ /AC, HgO capture was found to be more significant than with virgin AC injection of HgO -the reaction is promoted by the presence of O ₂ -the main capture sites for HgO on the AC are associated with HgO and HgSO ₄

Table 4: The presence of oxygen and adsorption of HgO on Activated carbon (AC).

with the oxygen component of the moisture. Maroto-Valer et al. [55] have reported that not only is oxygen functionality an important factor in elemental mercury control but the presence of halogen species in a mixed gas situation on the carbon surface with the oxygen present promote a more efficient mixed flue gas stream elemental mercury adsorption scenario.

Effect of mixed gas conditions on elemental mercury atoms uptake of sulfur doped activated carbon surfaces was considered by Liu et al. [40]. They showed that sulfur impregnated activated carbons demonstrated effective elemental mercury up take capacities under various mixed gas stream conditions. However, it was noted that the presence of oxygen increased the mercury adsorption capacity on their carbon significantly in this mixture gas stream situation with increased oxygen concentrations. As seen in Figure 3, these authors increased the concentration of O₂ in a mixed gas carrier gas stream with elemental mercury in place from 0 to 9%. When the concentration of oxygen was in the 0 to 3% in this mixed gas stream, the uptake of elemental mercury atoms remained unchanged. However, as the concentration of oxygen was increased from 6 to 9%, the overall flue gas stream mercury capture increased from 16 to 33% respectively. In general the presence of moisture in their fixed bed arrangement decreased the effectiveness of their system for mercury capture due to increasing temperature from 140 to 250°C had the effect of decreasing the effectiveness of the carbons for elemental mercury capture.

In summary, many authors have identified oxygen as a parameter for elemental mercury adsorption under mixed flue stream conditions. Edge effects on the activated carbon tend to be the focal points for the chemical oxidation of various species resulting to the formation of HgO. Oxygen atoms associated with the activated carbon surface cannot only act as a direct route for the chemisorption of mercury to the carbon surface itself, but also directly influence the reaction kinetics of other species for elemental mercury chemisorption reactions on the activated carbon.

Other Features of Importance to Activated Carbon Elemental Mercury Uptake

Porosity structure

Regarding porous structure, Lee et al. [20] looked at the pore

structure of the activate carbon surface as it is related to elemental mercury emission stream capture, they conclude that pore characteristics on the activated carbon surfaces above 2 nm were more active collectors of elemental mercury atoms. These authors do point out, however, that the type of sulfur on the surface of their carbons regardless of pore structure was more important than the amount of sulfur on their activated carbons for efficient elemental mercury flue gas stream capture.

In an attempt to increase the economic value of commercial carbons, Shamsijazeyi et al. [56] treated commercial activated carbon material with nitric acid. The focus was to examine the changes to the inherent pore structure of a commercial carbon with acidity. Mercury removal tests were conducted on iodized and nitrogen enhanced carbons. They used Fourier transform infrared spectroscopy (FTIR) to evaluate the effects of acid treatment on the surface functional groups. It was shown via this method that nitric acid treatment enhanced the elemental mercury adsorption capacity of these carbons. These authors with this procedure pointed out the value of changes to the external surface configuration of the carbons for elemental mercury chemisorption and that pore structure of the activated carbon was an important feature for elemental mercury capture.

Both micro and mesoporosity roughness on activated carbon within certain temperature ranges are seen to be a primary determinant of the elemental mercury capture. Highly developed microporosity has been shown by Diamantopoulou et al. [16] and Hsi et al. [31] to be an important requirement for effective elemental mercury chemisorption onto the activated carbon surface. It has been shown that both micropores and mesopores are involved in elemental mercury capture with mesopores acting as conduit routes for the elemental mercury from mesopores to the micropore surface features [35]. It is on micropore structures that these authors have shown the main elemental mercury capture process by chemisorption takes place.

Mineral base

Arvelakis et al. [23] examined biochar vs coal char activated carbon surfaces as capture medium for elemental mercury flue gas stream. The principle difference between biochar and coal char is that bio char coming from a biological source which has significantly less mineral content than for coal char or inorganic carbon material. Both types of char materials collected elemental mercury from a mixed flue gas stream quite efficiently. However, coal char material is somewhat less efficient at mixed gas stream collection of elemental mercury than biochar. The difference in degree of activity is directly related to the amount of mineral content of the activated carbon.

De et al. [45] investigated the elemental mercury capture from flue gas stream capture using biological carbon. The activated biological carbon specimens were produced by the steam activation of biochar obtained from the fast pyrolysis of whitewood. The carbons were impregnated with potassium and ammonium halides. The halide addition to these carbons significantly enhanced the elemental mercury capture rate from a simulated and industrial scale flue gas streams. The authors showed that ammonium halides were more effective at collecting elemental mercury than potassium halides and hypothesized that the former provided better access of the elemental mercury into the carbon pore structures. Biological based carbons were shown to provide a significantly more attractive carbon to mercury ratio of the sequestered elemental mercury than for that of commercial activated carbons.

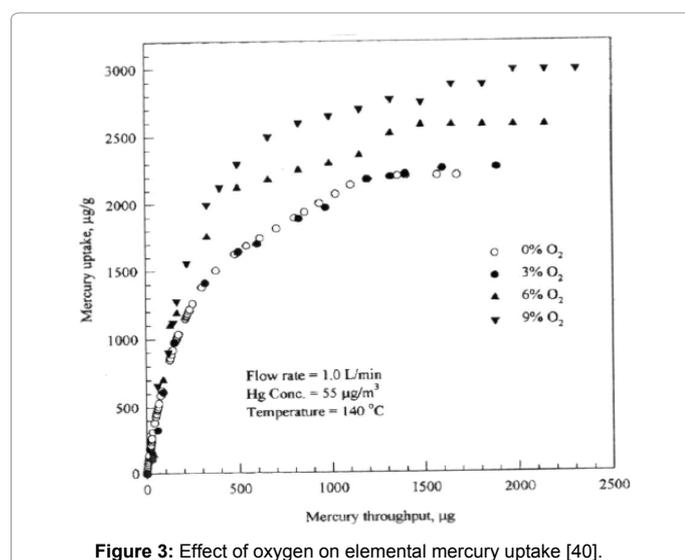


Figure 3: Effect of oxygen on elemental mercury uptake [40].

Elemental mercury uptake was looked at by Scala et al. [57] in an in-duct incinerator flue gas stream by activated carbon powder. They found that improvements in the mercury capture performance can be obtained by increasing the sorbent particle sizes and decreasing the in-duct residence time.

Within this category of compound structures on the activated carbon surface, several authors have reported that activated carbons with the oxidizing compound of $ZnCl_2$ on their surface did collect elemental mercury most effectively [26,58]. The zinc chloride uptake is most strongly dependent upon temperature. It is important also to note that there are several other compounds such as that once they are collected on an activated carbon surface with the appropriate conditions in place will capture elemental mercury atoms on the activated carbon surface in this manner. Another compound that captures elemental mercury on activated carbon is V_2O_5 . The gas phase elemental mercury capture by the V_2O_5 on carbon was studied for a simulated flue gas stream by Wang et al. [59]. It was shown that the elemental mercury capture onto the carbon surface with this compound was much greater than that by virgin activated carbon. The capture rate increases with V_2O_5 loading and was enhanced by the presence of O_2 in the flue gas stream and inhibited by H_2O in the gas stream complex. Using spectroscopy techniques, Wang et al. [59] have reported that the elemental mercury is sequestered onto the activated carbon in the forms of HgO and $HgSO_4$. They argued that mercury was catalytically oxidized to Hg^{2+} on V_2O_5 .

The mercury vapor oxidation and adsorption onto chemically treated carbons were reported by Lee et al. [24]. They studied the elemental mercury oxidation and adsorption characteristics of $CuCl_2$ -AC (a commercially available activated carbon from Norit Americas) and a carbon from DARCO. The results suggested that $CuCl_2$ -AC has different site available for elemental mercury capture than does the DARCO product. These authors considered that the mineral base differences explained the differences in reactivity.

An approach to sequestering mercury from the environment is to place it into the composition of concrete material. Then once it is in place, it will remain fixed in this permanent storage form and safe from environmental interaction. Golightly et al. [60] looked at the release of mercury in fly ash that was placed into concrete material. The concrete material showed an effective performance for holding the mercury material quite strongly. A small fraction of this mercury was released during the curing process. However, once within the concrete mix it was deemed secure from environmental release. Within the complex of un-burnt fly ash carbon and activated carbon injected aerosols used, they noticed that activated carbon held the mercury in the complex more securely than the un-burnt fly ash carbon particles.

The control of mercury in the air emissions for coal-fired power plants was looked at by Hower et al. [61]. The unburned carbons in fly ash can capture varying amounts of HgO depending upon the temperature and composition of the flue gas stream. They found that HgO capture increases with the increase in the amount of carbon in the fly ash. Increases in the surface area of these fly ash carbons are also credited with increasing the in-stream mercury capture. Acid gases including HCl and H_2SO_4 also enhanced in flue gas stream HgO capture.

Temperature

The temperature of the chemisorption of elemental mercury on activated carbon is an important parameter in capture from a mixed gas stream.

Murakami et al. [18] used a simulated coal combustion flue mixed gases (including HCl , SO_2 , O_2 , CO_2 and H_2O) to study the mercury sorption/desorption mechanism onto a commercial activated carbon. The bed reactor temperature was $80^\circ C$. The thermal stability of the mercury species on the activated carbon under various sorption/desorption conditions were investigated by a temperature programmed desorption (80 to $500^\circ C$) technique. These authors identified that the mercury species formed on the activated carbon at higher temperatures was $HgCl_2$ and that these species decomposed and desorbed on the activated carbon at around $300^\circ C$. They suggested that chlorine present in their simulated flue gas resulted in high temperature decomposition of the mercury compound.

The effect of temperature has been reported by Ho et al. [62] for elemental mercury capture. The activated carbon bed temperature had a profound effect on the mercury adsorption process in a mixed flue gas stream. A simple and direct effect of temperature on the elemental mercury capture is seen by De et al. [45]. The effect of temperature on mercury removal efficiency for their carbons is shown by Figure 4. They showed that by changing the temperature, from 25 to $160^\circ C$, the activated carbon mercury removal efficiency was increased by at least 50% . The study looked at the influence of various mercury deposition fluxes onto an activated carbon surface at these temperatures. These authors suggested that physisorption may be responsible for mercury removal from the flue gas stream by impregnated activated carbon. An increase in temperature clearly lowers the elemental mercury adsorption efficiency on these activated carbons. It is the cooler temperatures within the activated carbon elemental mercury capture processes that are responsible for the strongest elemental mercury mass flux to the carbon surface.

For efficient elemental mercury capture on activated carbon, temperature has been identified [18,62] as an important process parameter. In most cases, reported elemental mercury capture for impregnated activated carbons are shown as inversely proportional to temperature in the range of 50 to $300^\circ C$. Indeed higher temperatures (in the order of $600^\circ C$) promote organic sulfur species on activated carbon material which discriminates against elemental mercury capture. Whereas other authors have reported that lower temperatures ($<200^\circ C$) tend to favor the formation of elemental sulfur on the activated carbon surface and hence promote elemental mercury atom uptake via the chemisorption route from a mixed flue gas stream.

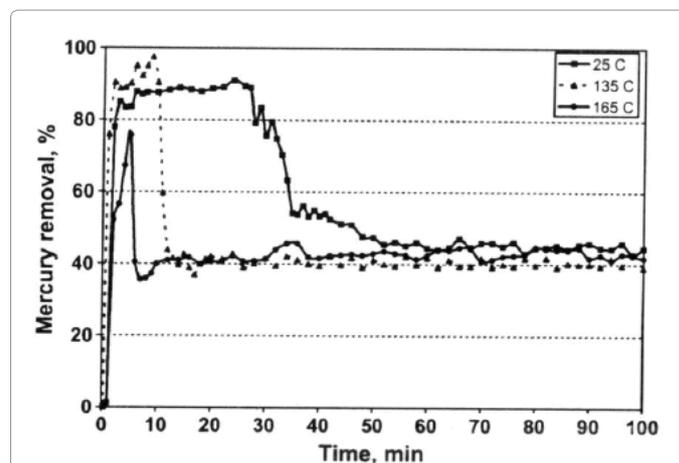


Figure 4: Effect of temperature on mercury removal efficiency [45].

Many of these authors acknowledge that adsorption temperature is a key determinant that provides the best platform for activated carbon to uptake elemental mercury atoms in a mixed gas stream. However, most note that it is temperatures in the approximate range of 120 to 180°C that provide the best chemisorption platform for efficient capture of the elemental mercury species from a flue gas.

Industry Operational Conditions

Many industrial flue gas streams are a complex of several different gaseous species. These complex gas streams support the hypothesis that the interaction of acidic species (HCl, HNO₃, H₂SO₄, etc.) in the flue gas with the activated carbon sorbent surface is an important mechanism that is responsible for the creation of active acid sites for elemental mercury capture by chemisorption on these activated carbon surfaces [27]. This being the case, the value of especially designed and prepared activated carbons for specific industry based activity are enormous.

In Canada Companies such as Trans Alta, ATCO, EPCOR and GE Energy, together, evaluated a full scale sorbent injection technology for elemental mercury control [63]. They concluded that the injection technologies are capable of achieving at least a 70% reduction of control of mercury emission. They also looked at the value of stack gas mercury capture via fly ash and concluded that stack gas fly ash concentrations are of value in an industrial emission control strategy and should be looked at for operational mercury emission control scenarios.

The University of North Dakota has conducted research on providing a cost effective system for elemental mercury emission rates control from their coal burning power plant facilities [64]. Their focus was to provide a 50 to 90% reduction of elemental mercury flue gas stream control cost. The most widely held strategy for removing elemental mercury from a coal combustion flue gas stream is the adsorption of elemental mercury by sorbent injection up stream of the control devices such as fabric filters and Electrostatic Precipitators.

Within the industrial context, Yan et al. [65] have reported that adsorption of elemental mercury is greatly dependent on operational conditions. Sulfur adsorption is best at lower temperatures in many industrial situations. The cost for the commercial product for mercury emission suppression has been estimated by Jones et al. [66]. These authors quote a typical range of cost as being 40,000 to 60,000 dollars per one kilogram of elemental mercury emission removed from a typical industrial flue gas stream. Industrial concerns do consider that this cost can be considerably reduced by moving away from activated carbon for elemental mercury emission control and focusing upon recycling and using partially burnt coal ash as an elemental mercury capture medium.

A lance put into a power plant flue gas stream is called a Thief. The Thief Process for fly ash carbons is described in detail by O'Dowd et al. [67] and Granite et al. [68]. This is a mercury removal process using carbon that may be applicable to a broad range of coal-fired power plant systems. This technology involves the production of a thermally activated sorbent within the power plant's flue gas stream. The sorbent is obtained by inserting a lance into the combustor near the active flame and extracting a mixture of partially combusted coal which has sorbent adsorptive properties that are suitable for removal of vapor phase mercury at flue gas stream temperatures. Although technically it is not an activated carbon, because of the lack of the complete activation, this fly ash stream can be considered as it has been partially pyrolysed. These authors suggest that this sorbent injection into the downstream duct of a furnace reduces cost effectively capturing elemental mercury

in the emission stream. If prepared in an appropriate manner, this adsorbant preparation structural technology could be a promising new approach for in-stack elemental mercury emission control.

In the Thief Process, partially combusted coal from the main combustion furnace is removed from the furnace. It is then collected and injected in an organized fashion into the downstream ducting arrangements from the main boiler of a coal fired power plant to enhance the particulate collection devices, such as, as wet scrubber, bag house etc. The real value of this technology arrangement is that it takes partially combusted carbon aerosols from the coal combustion streams, feeds them in an appropriate manner back into the exhaust system of the power plants combustion process. Essentially these rejected carbon material have already been paid for in this combustion facility as primary combustion destined particles. With some components of the carbon remaining on these aerosols (i.e., they are not an ash product) the particles are then reintroduced downstream as an elemental mercury collection product. Several authors have suggested that the capture of elemental mercury in a mixed flue gas stream by the Thief Process is more efficient as compared to similar mass fluxes of commercially available activated carbon sorbents [24,61,67]. It is stated more research effort should be placed in this research direction to assess commercial viability of the Thief process.

Yang et al. [22] identified recent progress in sorbent design for mercury capture from coal-fired utility boilers. These emissions depend on species of coal burnt, boiler operational conditions such as temperature and type of the air pollution devices in place. They have suggested that it is activated carbon injection that has the best opportunity to function well within an industrial complex for mercury emission control. They used a commercial brand of activated carbon and tested it in both laboratory and field setup. They used sulfur, halogen and other types of enhanced surface chemistry agents for HgO capture in their programs. In their experiments, they have concluded that it is the bromine enhanced structures that are the most attractive for cost effective sequestration of in-stack HgO sequestration.

Once mercury is sequestered from an emission stream, one of the locations for the storage of this product is in the formation material of concrete. Golightly et al. [60] conducted research on gaseous mercury released from concrete material during the curing process. Releases of mercury over the entire curing process ranged from 0.4 to 5.8 nanograms of mercury/kg of concrete. The mercury flux from the exposed concrete surfaces to mercury-free area range was measured which showed similar to the mercury fluxes for natural soils to ambient air. They concluded that the mercury storage from an anthropogenic source can be most efficiently stored via this route in concrete block arrangements. Many related industries are focusing upon concrete as a form of permanent sequestration for their mercury complexed material.

Conclusions

It is clear from this review that activated carbon application to a mixed gas stream control of elemental mercury emission stream is the most important and useful technology in a wide variety of situations. The designing of surface functional agents to activated carbons can significantly improve the elemental mercury capture process and that this can be directly related to an industrial cost benefit analysis. Whether it is the application of surface functional agents or the structures of the mineral base of the activated carbons via surface porosity or mineral structure, activated carbons can be of value as a tool for elemental mercury mixed gas emission control.

There are many factors that influence the rate of elemental mercury capture onto an activated carbon surface in a mixed gas stream. The applications of these factors for elemental mercury emission mixed gas emission can be quite complex. All of the elemental mercury uptake reactions are conditioned by temperature. Most authors identify activated carbons' pore structure, surface chemistry and the presence of sulfur and other functional enhancements on the activated carbon surfaces as being the primary determinants as to the rate and efficiency of the elemental mercury uptake from a mixed gas stream. Edge effects on the activated carbon and surface roughness also play a part in efficiently capturing mercury oxide species that interact with elemental mercury via the chemisorption process.

Temperature is a primary elemental mercury mixed gas stream determinant for emission control. Also, other key factors in the design of an activated carbon surface are process pressure, vapor residence time, and moisture in flue gas. All of these factors do have an effect on the surface chemistry of the activated carbon and will affect the mercury capture capacity of activated carbon from industrial flue gas.

It is clear that there are some primary determinants on an activated carbon surface that strongly dictate elemental mercury mixed gas stream capture efficiency. Chemicals, such as, sulfur, halogens, oxygen and various compounds (such as V_2O_5 , $ZnCl_2$ etc.) for efficient elemental mercury capture in a mixed gas stream. Based on the outcomes from different research workers, it is possible to develop a greater level of emissions control with an elemental mercury mixed gas stream prior to it being emitted into the environment.

References

- Huggins FE, Huffman GP, Dunham GE, Senior CL (1999) XAFS examination of mercury sorption on three activated carbons. *Energy & Fuels* 13: 114-121.
- Hu C, Zhou J, Luo Z, Cen K (2011) Oxidative adsorption of elemental mercury by activated carbon in simulated coal-fired flue gas. *Energy & Fuels* 25: 154-158.
- Nriagu JO (1989) A global assessment of natural sources of atmospheric trace metals. *Nature* 338: 47-49.
- Karatza D, Lancia A, Musmarra D, Zucchini C (2000) Study of mercury absorption and desorption on sulfur impregnated carbon. *Experimental Thermal and Fluid Science* 21: 150-155.
- Miles T, Farge E (2013) More than 140 countries adopt a global treaty to curb mercury emissions. *Globe and Mail*.
- Canadian Council of Ministers of the Environment (2006) Canada - Wide Standards for Mercury emissions from coal-fired electric power generation plants.
- Rodriguez-Reinoso F (1998) The role of carbon materials in heterogeneous catalysis. *Carbon* 36: 159-175.
- Manyà JJ (2012) Pyrolysis for biochar purposes: a review to establish current knowledge gaps and research needs. *Environ Sci Technol* 46: 7939-7954.
- Miller SJ, Dunham GE, Olson ES, Brown TD (2000) Flue gas effects on a carbon-based mercury sorbent. *Fuel Processing Technology* 65-66: 343-363.
- Vitolo S, Pini R (1999) Deposition of sulfur from H_2S on porous adsorbents and effect on their mercury adsorption capacity. *Geothermics* 28: 341-354.
- Padak B, Wilcox J (2009) Understanding mercury binding on activated carbon. *Carbon* 47: 2855-2864.
- Korpiel JA, Vidic RD (1997) Effect of sulfur impregnation method on activated carbon uptake of gas-phase mercury. *Environ Sci Technol* 31: 2319-2325.
- Sinha RK, Walker PL (1972) Removal of mercury by sulfurized carbons. *Carbon* 10: 754-756.
- O'Dowd WJ, Hargis RA, Granite EJ, Penline HW (2004) Recent advances in mercury removal technology at the National Energy Technology Laboratory. *Fuel Processing Technology* 85: 533-548.
- Strezov V, Evans TJ, Ziolkowski A, Nelson PF (2010) Mode of occurrence and thermal stability of mercury in coal. *Energy & Fuels* 24: 53-57.
- Diamantopoulou I, Skodras G, Sakellariopoulos GP (2010) Sorption of mercury by activated carbon in the presence of flue gas components. *Fuel Processing Technology* 91: 158-163.
- Laumb J D, Benson SA, Olson EA (2004) X-ray photoelectron spectroscopy analysis of mercury sorbent surface chemistry. *Fuel processing technology* 85-86: 577-585.
- Murakami A, Uddin MA, Ochiai R, Sasaoka E, Wu S (2010) Study of the mercury sorption mechanism on activated carbon in coal combustion flue gas by the temperature-programed decomposition desorption technique. *Energy & Fuels* 24: 424-4249.
- Schrodinger E (1926) An undulatory theory of the mechanics of atoms and molecules. *Physical Review* 28: 1049-1070.
- Lee S, Park Y (2003) Gas-phase mercury removal by carbon-based sorbents. *Fuel Processing Technology* 84: 197- 206.
- Seneviratne HR, Charpentreau C, George A, Millan M, Dugwell DR, et al. (2007) Ranking low cost sorbents for mercury capture from simulated flue gases. *Energy & Fuels* 21: 3249-3258.
- Yang H, Xu Z, Fan M, Bland AE, Judkins RR (2007) Adsorbents for capturing mercury in coal-fired boiler flue gas. *J Hazard Mater* 146: 1-11.
- Arvelakis S, Crocker C, Folkedahal B, Pavlish J, Spliethoff H (2010) Activated carbon biomass for mercury capture: Effect of the leaching pretreatment on capture efficiency. *Energy & Fuels* 24: 4445- 4453.
- Lee SH, Rhim YJ, Cho SP, Back JI (2006) Carbon-based novel sorbent for removing gas-phase mercury. *Fuel* 85: 219-226.
- Sjostrom S, Dillon M, Donnelly B, Bustard J, Filippelli G, et al. (2009) Influence of SO_3 on mercury removal with activated carbon: Full-scale results. *Fuel Processing Technology* 90: 1419-1423.
- Zeng H, Jin F, Guo J (2004) Removal of elemental mercury from coal combustion flue gas by chloride-impregnated activated carbon. *Fuel* 83: 143-146.
- Huggins FE, Yap N, Huffman GP, Senior CL (2003) XAFS characterization of mercury captured from combustion gases on sorbents at low temperatures. *Fuel Processing Technology* 82: 167-196.
- Pavlish JH, Sondreal EA, Mann MD, Olson ES, Galbreath KC, et al. (2003) Status review of mercury control options for coal-fired power plants. *Fuel Processing Technology* 82: 89-165.
- Zhao Y, Mann MD, Olson ES, Pavlish JH, Dunham GE (2006) Effects of sulfur dioxide and nitric oxide on mercury oxidation and reduction under homogeneous conditions. *J Air Waste Manag Assoc* 56: 628-635.
- Olson ES, Mibeck BA, Benson SA, Laumb JD, Crocker CR, et al. (2004) The mechanistic model for flue gas-mercury interactions on activated carbons: the oxidation site. *Prepr Pap Am Chem Soc Div Fuel Chem* 49: 279.
- Hsi HC, Rood MJ, Rostam-Abadi M, Chen S, Chang R (2001) Effects of sulfur impregnation temperature on the properties and mercury adsorption capacities of activated carbon fibers (ACFs). *Environ Sci Technol* 35: 2785-2791.
- Morimoto T, Wu S, Uddin MA, Sasaoka E (2005) Characteristics of the mercury vapor removed from coal combustion flue gas by activated carbon using H_2S . *Fuel* 84: 1968-1974.
- Presto AA, Granite EJ (2007) Impact of sulfur oxides on mercury capture by activated carbon. *Environ Sci Technol* 41: 6579-6584.
- Feng W, Borguet E, Vidic RD (2006) Sulfurization of a carbon surface for vapor phase mercury removal. *Carbon* 44: 2998-3004.
- Skodras G, Diamantopoulou IR, Sakellariopoulos GP (2007) Role of activated carbon structural properties and surface chemistry in mercury adsorption. *Desalination* 210: 281-286.
- Asasian N, Kaghazchi T (2012) Comparison of dimethyl disulfide and carbon disulfide in sulfurization of activated carbons for producing mercury adsorbents. *Ind Eng Chem Res* 51: 12046-12057.
- Liu W, Vidic RD, Brown TD (1998) Optimization of sulfur impregnation protocol for fixed-bed application of activated carbon-based sorbents for gas-phase mercury removal. *Environ Sci Technol* 3: 531-538.

38. Lopez-Anton MA, Tascon JMD, Martinez-Tarazona MR (2002) Retention of mercury in activated carbons in coal combustion and gasification flue gases. *Fuel Processing Technology* 77-78: 353-358.
39. Uddin A, Ozaki M, Sasaoka EI, Wu S (2009) Temperature-programmed decomposition desorption of mercury species over activated carbon sorbents for mercury removal from coal-derived fuel gas. *Energy & Fuels* 23: 4710-4716.
40. Liu W, Vidic RD, Brown TC (2000) Impact of flue gas conditions on mercury uptake by sulfur-impregnated activated carbon. *Environ Sci Technol* 34: 154-159.
41. Ochiai R, Uddin MA, Sasaoka E, Wu S (2009) Effect of HCl and SO₂ concentration on mercury removal by activated carbon sorbents in coal-derived flue gas. *Energy & Fuels* 23: 4734-4739.
42. Yan R, Ng YL, Liang DT, Lim CY, Tay JH (2003) Bench-scale experimental study on the effect of flue gas composition on mercury removal by activated carbon adsorption. *Energy & Fuels* 17: 1528-1535.
43. Lee SJ, Seo YC, Jurng J, Lee TG (2004) Removal of gas-phase elemental mercury by iodine- and chlorine-impregnated activated carbons. *Atmospheric Environment* 38: 4887-4893.
44. Hutson ND, Attwood BC, Scheckel KG (2007) XAS and XPS characterization of mercury binding on brominated activated carbon. *Environ Sci Technol* 41: 1747-1752.
45. De M, Azargohar R, Dalai AK, Shewchuk SR (2013) Mercury removal by bio-char based modified activated carbons. *Fuel* 103: 570-578.
46. Olson ES, Azenkeng A, Laumb JD, Jensen RR, Benson SA, et al. (2009) New developments in the theory and modeling of mercury oxidation and binding on activated carbons in flue gas. *Fuel Processing Technology* 90: 1360-1363.
47. Uddin A, Yamada T, Ochiai R, Sasaoka E (2008) Role of SO₂ for elemental mercury removal from coal combustion flue gas by activated carbon. *Energy & Fuels* 22: 2284-2289.
48. Ghorishi SB, Keeney RM, Serre SD, Gullett BK, Jozewicz WS (2002) Development of a Cl-impregnated activated carbon for entrained-flow capture of elemental mercury. *Environ Sci Technol* 36: 4454-4459.
49. Tong S, Fan M, Mao L, Jia CQ (2011) Sequential extraction study of stability of adsorbed mercury in chemically modified activated carbons. *Environ Sci Technol* 45: 7416-7421.
50. Shen Z, Ma J, Mei Z, Zhang J (2010) Metal chlorides loaded on activated carbon to capture elemental mercury. *J Environ Sci (China)* 22: 1814-1819.
51. Otten BV, Buitrago PA, Senior CL, Silcox GD (2011) Gas-Phase Oxidation of Mercury by Bromine and Chlorine in Flue Gas. *Energy & Fuels* 25: 3530-3536.
52. Li YH, Lee CW, Gullett BK (2003) Importance of activated carbon's oxygen surface functional groups on elemental mercury adsorption. *Fuel* 82: 451-457.
53. Cai JH, Jia CQ (2010) Mercury removal from aqueous solution using coke-derived sulfur-impregnated activated carbons. *Ind Eng Chem Res* 49: 2716-2721.
54. Hall B, Schager P, Weesman J (1995) The homogeneous gas phase reaction of mercury with oxygen, and the corresponding heterogeneous reactions in the presence of activated carbon and fly ash. *Chemosphere* 30: 611-627.
55. Moroto-Valer MM, Zhang Y, Granite EJ, Tang Z, Pennline HW (2005) Effect of porous structure and surface functionality on the mercury capacity of a fly ash carbon and its activated sample. *Fuel* 84: 105-108.
56. ShamsiJazeyi H, Kaghazchi T (2010) Investigation of nitric acid treatment of activated carbon for enhanced aqueous mercury removal. *Journal of Industrial and Engineering Chemistry* 16: 852-858.
57. Scala F (2001) Simulation of mercury capture by activated carbon injection in incinerator flue gas. 1. In-duct removal. *Environ Sci Technol* 35: 4367-4372.
58. Hu C, Zhou J, He S, Luo Z, Cen K (2009) Effect of chemical activation of an activated carbon using zinc chloride on elemental mercury adsorption. *Fuel Processing Technology* 90: 812-817.
59. Wang J, Yang J, Liu Z (2010) Gas-Phase elemental mercury capture by V₂O₅/AC catalyst. *Fuel Processing Technology* 91: 676-680.
60. Golightly DW, Cheng C, Weavers LK, Walker HW, Wolfe WF (2009) Fly ash properties and mercury sorbent affect mercury release from curing concrete. *Energy & Fuels* 23: 2035-2040.
61. Hower JC, Senior CL, Suuberg EM, Hurt RH, Wilcox JL, et al. (2010) Mercury capture by native fly ash carbons in coal-fired power plants. *Prog Energy Combust Sci* 36.
62. Ho TC, Shetty S, Chu HW, Lin CJ, Hopper JR (2008) Simulation of mercury emission control by activated carbon under confined-bed operations. *Powder Technology* 180: 332-338.
63. Brown T, Lissianski V (2009) First full-scale demonstration of mercury control in Alberta. *Fuel Processing Technology* 90: 1412-1418.
64. Benson SA, Pavlish JH, Holmes HJ, Crocker CR, Galbreath KC, Zhaung Y (2009) Mercury control testing in a pulverized lignite-fired system. *Fuel Processing Technology* 90: 1378-1387.
65. Yan R, Liang DT, Tsen L, Ping Y, Lee YK (2004) Bench-scale experimental evaluation of carbon performance on mercury vapor adsorption. *Fuel* 83: 2401-2409.
66. Jones AP, Hoffman TW, Smith DN, Feeley TJ, Murphy JT (2007) DOE/NETL's phase II mercury control technology field testing program: Preliminary economic analysis of activated carbon injection. *Environ Sci Technol* 41: 1365-1371.
67. O'Dowd WJ, Pennline HW, Freeman MC, Granite EJ, Hargis RA, et al. (2006) *Fuel Processing Technology* 87: 1071-1084.
68. Granite EJ, Freeman MC, Hargis RA, O'Dowd WJ, Pennline HW (2007) The thief process for mercury removal from flue gas. *J Environ Manage* 84: 628-634.