Scientific research journal

RESEARCH MANAGEMENT INSTITUTE

SCIENTIFIC RESEARCH JOURNAL

Scientific
Research
Journal

An Overview of Mercury Emission Sources and Application of Activated Carbon for Mercury Removal from Flue Gas

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ABSTRACT

Mercury emission into the atmosphere is a global concern due to its detrimental effects on human health in general. The two main sources of mercury emission are natural sources and anthropogenic sources. Mercury emission from natural sources include volcanic activity, weathering of rocks, water movement and biological processes which are obviously inevitable. The anthropogenic sources of mercury emission are from coal combustion, cement production and waste incineration. Thus, in order to reduce mercury emission it is appropriate to investigate how mercury is released from the anthropogenic sources and consequently the mercury removal technology that can be implemented in order to reduce mercury emission into the atmosphere. Many alternatives have been developed to reduce mercury emission and the recent application of activated carbon showed high potential in the adsorption of elemental mercury. This paper discusses the ability of activated carbon and variable parameters that influence mercury removal efficiency in flue gas.

Keywords: mercury sources, removal technology, adsorption, activated carbon, flue gas

Introduction

Mercury is a heavy metal that cannot be destroyed and remains unchanged in the environment. Mercury has been used in many applications such as in batteries, electrical and electronic devices, thermometer, measuring and control equipment and dental amalgams due to its unique chemical properties [1]. Besides that, mercury is used in some cosmetics, pharmaceuticals, paints, and laboratory.

Mercury emission into the atmosphere comes from anthropogenic and natural sources [2]. Natural sources of mercury released into the atmosphere are due to natural mobilization that occurs in Earth's crust such as volcanic activity, weathering of rocks, water movement, and biological process [3]. Release of mercury is also from remobilization of historic anthropogenic mercury releases, which are previous emission to soil, sediments, water bodies, landfill and waste piles. Anthropogenic sources of mercury emission are released from mercury used intentionally in products and processes including hazardous waste incineration, municipal waste incineration, batteries and thermometer production [4]. Mercury emission from anthropogenic sources that are released from mobilization of mercury impurities include coal combustion, oil combustion, cement production and pulp and paper production.

Mercury has high volatility and can stay up in the atmosphere for a year. Therefore it can be transported and deposited globally and enters rivers, oceans, and lakes directly from atmosphere. The toxicity of mercury can be very harmful to human health. The direct inhalation of mercury vapour can affect the nervous, digestive and immune system and may lead to fatality [3]. Hence, effects of mercury are of grave concern due to its negative impact on human health and the environment. In 2001, the Global Mercury Assessment of mercury was initiated and concluded, there was sufficient evidence of global impact of mercury exist and further action need to be taken to overcome the impact. In response to this assessment, the United Nations Environment Programme (UNEP) Mercury Programme was established in February 2003. The main objective of this program is to eliminate the mercury emissions from anthropogenic sources. It is necessary to make mercury emission inventory in order to make the reduction plan for the mercury emissions.

There are several mercury control technologies which has been explored for the remediation of mercury emission, including sorbent

adsorption, photochemical oxidation and the existing pollution control devices [5]. However, existing pollution control devices such as flue gas desulfurization, fabric filter and baghouses are ineffective for the removal of elemental mercury. Meanwhile, sorbent adsorption is one of the most promising and effective technology to capture elemental mercury in flue gas [5, 6] and it has been proven by many researchers. Activated carbons as adsorbents are the most versatile and commonly used as they have an extremely high surface areas micropore volumes, large adsorption capacities, fast adsorption kinetics, and relative ease of regeneration [7]. The most common feedstock used for the production of activated carbon is organic materials having rich carbons [8]. Agricultural wastes are considered as being very important feed stock for activated carbon preparation because they are a renewable source and low cost materials. From previous studies, the quality and characteristics of activated carbons are not only dependent on physical and chemical properties of the starting materials but also dependent on the preparation conditions [9].

This paper aims to review the mercury emissions to the atmosphere from mainly the anthropogenic sources and the application of activated carbon for mercury removal from flue gas.

Mercury Emission Sources

Natural Sources

Mercury exists naturally in the earth's crust. The release of mercury occurs during volcanic activity and weathering of rocks. Re-emissions of mercury occur from soil, sediments, water bodies, landfill, and sea surfaces. As stated by Pirrone *et al.* (2010), the natural sources of mercury emission is 5207 Mg including the contribution from re-emission process of historic anthropogenic and natural sources of mercury release previously to the environment[10]. The total amount of mercury released into the atmosphere from natural sources was estimated to increase and the indicated amount is by 2000 Mg annually [11]. Table 1 shows the summary global mercury emissions from natural sources.

Anthropogenic Sources

The anthropogenic sources of mercury can be divided into two; primary anthropogenic sources and secondary anthropogenic sources [1]. The primary anthropogenic sources are mercury which is released from its geological origins. The categories that contribute to these sources are from mining (either for mercury or contamination due to mining of other minerals) and extraction of fossil fuels (mercury present as trace amount). The secondary anthropogenic sources involve emissions from intentional use of mercury in industry, artisanal gold mining, and products. Table 1 shows the summary of global mercury emissions from anthropogenic sources.

Table 1: Global mercury emissions from natural and anthropogenic sources

Source Category	Hg Emission (Mg/yr)	Reference
Natural sources		
Oceans	2682	[12]
Lakes	96	[12]
Forests	342	[12]
Tundra/Grassland/Savannah/Prairie/Chaparal	448	[12]
Desert/Metalliferous/Nonvegetated zones	546	[12]
Agricultural areas	128	[12]
Evasion after mercury depletion events	200	[12]
Biomass burning	675	[12]
Volcanoes and geothermal areas	9	[12]
Anthropogenic sources		
Coal and oil combustion	810	[12]
Cement production	236	[12]
Non-ferrous metal production	132	[13]
Pig iron and steel production	54	[13]
Gold mining	400	[14]

Table 1: contd.

Caustic soda production	163	[12]
Waste disposal	187	[12]
Mercury production	50	[12]
Vinyl chloride monomer (VCM)	24	[12]
Others	65	[12]

Coal Fired Power Plant and Industrial Boilers

In 2005 global emissions of anthropogenic sources, about 26% (500 metric tonnes per 1921metric tonnes) of the emissions come from combustion of fossil fuel in power plants and industrial boilers [15]. In this industry, mercury is released from the process of pre-combustion measures such as coal washing where sulphur and ash contents are reduced from the coal. As stated by Pirrone *et al.* (2010), the mercury concentrations in coals vary between 0.01 to 1.5g per Mg of fuel.

Mercury is a trace amount in coal and oil. When these fuels are burned in the boilers, the mercury will be emitted to the air along with the exhaust gases [16]. Mercury enters coal fired power plant as feed into the boiler. Coal burned in the boiler furnace chamber at high temperature around 500˚C to 600˚C to produce great heat to convert water circulates in the boiler tubes into high pressure steam to generate electricity. When coal is burned, bottom ash is generated. Bottom ash is collected from the boiler and sent to the ash pond. Fly ash is collected from electrostatic precipitator. The exhaust gases are discharged into the atmosphere through stack gas that probably contains mercury.

Mercury emitted from coal fired power plants has three forms which are elemental form, oxidized form and particulate form. Oxidized mercury and particulate mercury have the tendency to travel near the source of emission, while the elemental form can travel farther and stay up in the environment for one year. The elemental mercury may enter the global pool and remain longer in the atmosphere; therefore it becomes a global issue. This is due to the effects on humans and the environment when the mercury falls to the earth and enters the water and soils. The formations of mercury depends on the power plant specification profile, type of coal

burned and air pollution control devices in the plant [17].

The mercury emission in coal fired power plant are influenced by the rank of coal, temperature of flue gas, efficiency of the plant and its emission control technology [18]. The rank of coal is increasing from lignite, sub-bituminous, bituminous and anthracite. The higher the grade the coal has the lower is its ash and moisture content. On the other hand, the low rank coal has moisture content in excess of 30% while the moisture of bituminous coal is around 1-5% [19]. The presence of chlorine also influences the mercury capture in combustion process. The oxidation of mercury occurs when reacting with chlorine to form $HgCl_2$. Besides that, the gas phase transformation involves the oxidation of $Hg^°$ by atomic Cl. The heterogeneous reactions can lead to the adsorption of gas phase Hg to particulate mercury and the formation of oxidized mercury. Unburned carbon can increase the mercury capture due to the ability of unburned carbon to adsorb oxidized mercury. Bituminous coals generally produce more unburned carbon compared to others [18], 5-30wt.% as loss of ignition [19]. Mercury has high affinity for sulphur compounds. The sulphur can reduce the reactive chlorine to oxidized Hg because of the sulphur compounds may limit the mercury capture on the fly ash. Therefore, the highest content of sulphur leads to an increase in the mercury emissions to the atmosphere. The temperature of flue gas can affect the amount of mercury captured. The ability of oxidized mercury formation is highest at high temperature. However, formation of oxidized mercury decreased at temperature more than 873K. At low temperature, mercury oxidized to $HgCl_2$ and it increases the possibility of mercury to capture at the electrostatic precipitator.

Cement Production

An up-to-date assessment of global mercury emission shows about 236 Mg/yr emission comes from cement production [10]. In 2000, the mercury emission inventory estimated that the emissions from cement plants are about 5.6% of total mercury emission[20]. Mercury exists as trace metals in raw material and fuel in cement production. Mercury content varies and depend on the raw materials and fuel used in the cement production. The origin of raw materials, fuel source and type of fuel gives varieties of mercury content [21]. Some industries use recycled fly ash from electric power plant as raw materials for cement production. Mercury is

also present in the fly ash that contributes to the mercury emissions from cement industry. Alternative fuels such as chemical waste, sewage sludge and domestic waste has been used in cement plants. This type of fuels have high content of mercury, therefore it leads to high mercury emission from cement plants [22]. Nevertheless, the major contributors of total mercury in cement production comes from the raw materials and not the fuels [21].

There are four major types of cement manufacturing process such as long-wet, long-dry, preheater and precalciner [23]. The long-wet process, the feedstock slurry enters kiln. The drying, calcining and sintering occur inside the kiln, while for long-dry process, the dry feedstock enters the kiln and the same process occurs inside the kiln. However, this type of process always shut down, thus, it has been improved by preheater and precalciner facilities. There are three fundamental stages of cement manufacturing process; preparation of feedstock, production of clinker and production of cement. The preparation of feedstock is the crucial process, since it consumes more than 90% of input energy and leads to more than 90% of air pollution emissions from cement plant [24]. Desorption of Hg also occur in the cement kiln, where the temperature of the kiln is approximately 1450°C. In cement clinker process, mercury is present in different forms (Hg^{2+} and Hg_p) that can be removed easily. The clinkers that produce in the kiln then are milled and mixed with other materials to produce cement.

The study by Won and Lee (2012) shows that the highest mercury concentration in raw materials comes from solid waste derived fuel (221ng/g), followed by fly ash (144ng/g) and tire derived (39.2ng/g). The other raw materials including limestone, clay, silica stone, bituminous coal, and liquid waste derived has slightly lower mercury content, mostly are below 20ng/g. Although the concentration of mercury in limestone is lower compared to others feed stocks, the input amount of limestone contributes about 81%, making it the major source of mercury contributions in cement plant. It was concluded from the study, about 1.71-1.53 tons of mercury per year from cement plant, which represents about 9-12% of total mercury emissions in Korea.

Waste Incineration

Waste incineration covers all the types of waste burned in the incinerator. From UNEP Toolkit, the waste incineration is divided into four categories

including incineration of municipal solid waste, incineration of hazardous waste, incineration of medical waste and incineration of sewage sludge incineration. Most of the mercury is released from waste containing mercury like batteries, dental applications, lamps, thermometers, measurement and electronic devices and other application. Mercury can be emitted from these wastes due to its breakdown, incineration and land filling.

Global mercury emissions into the atmosphere from waste incineration is 187 Mg/yr [10] that contributes ~8% of the total anthropogenic mercury emissions [25]. In Poland, the mercury emissions from waste incineration are 160 kg/year in 2005 and the projection in 2020 is reduced to 48 kg/year. This projection is based on the Extended Emission Control scenario where the projection is estimated after taking into consideration the control measures to reduce the emissions. The control measures that are suitable for mercury reduction in waste incineration including adsorption due to the injection of activated carbon with bag filter, adsorption using fixed (static) beds with suitable adsorbent replenishment rate and others [26]. In Cambodia, the mercury emission from waste incineration is 67.329 kg/yr that includes mercury emission from municipal solid waste incinerators and medical waste incinerators [27]. Most of the incinerators don't have air pollution control measures to treat the flue gas. In China, the rapid expansion of the municipal solid waste incineration industry was observed, hence leading to the fastest growth of mercury emissions from the incineration, from 0.6 tonne in 1995 to 10.4 tonnes in 2003 [25].

Mercury emission into the atmosphere depends on the mercury input from waste and flue gas cleaning technology in the incineration [25]. Products containing mercury are fed into the incinerator at solid waste feed inlet. The temperature of the primary chamber is between 600-800 ˚C where bottom ash is generated. The organic substances from waste are broken down at this temperature [28]. Since mercury is volatile, it is oxidized to form $HgCl_2$ if HCl is present [29]. The study by [29] shows the concentration of mercury was higher in fly ash compared with bottom ash with 0.203 mg/L and 0.0134 mg/L respectively. The fly ash is classified as hazardous waste due to the high content of heavy metals, therefore it needs to be treated before disposal into landfill or re-incinerated. This oxidized form of mercury is captured in the air pollution control and transferred to fly ash. Then, the remaining materials released into the atmosphere through the stack. Some of flue gas cleaning equipment such as fabric filters, wet scrubbers, spray absorbers, electrostatic precipitator etc are co-benefits to

remove mercury and its compounds from waste incineration[30]. Therefore, the air pollution control equipment can facilitate in reducing the mercury concentration in the flue gas.

Since the mercury contained in the waste will be emitted into the air when incinerated; one of the best solutions is to reduce the input of products containing mercury into the incinerator. Before incineration, a sorting process in needed by sorting out mercury containing product in order to reduce the emissions of mercury from the incineration process [15]. Besides that, the programs on collection and replacement of mercury-containing devices from batteries, thermometer, and fluorescent lamps should actively implement to control mercury emissions.

Other Sources

There are other sources that contribute to mercury emissions into the atmosphere. The anthropogenic sources such as artisanal gold mining, oil combustion, primary zinc, lead and copper smelting, landfill and crematoria leads to mercury emissions. China, as the largest anthropogenic mercury emissions in the world has contribute about 543 tonnes of mercury emissions from primary zinc, lead and copper smelting [31]. The study by Wu *et al.* (2010) indicated that the mercury emissions from non ferrous metal smelters in 2010 was 72.5 tonnes which is slightly lower compare with the emissions from primary metal smelters. Mercury can be found in metal ores and fossil fuel in primary metals smelting process. Mercury is evaporated at the high process temperature during zinc, lead and copper production. In 2004, the mercury emissions from zinc, lead and copper production in India are 1.90 Mg, 1.83 Mg and 11.78 Mg respectively.

Besides that, iron and steel production also emit mercury. Steel is produced by the chemical reduction of iron ore from the blast furnace, oxygen furnace or by melting steel scrap in an electric arc furnace. Coke can be obtained by coking in ovens at 1000°C or more. In this process, Hg from coal is released and passes through the gas and other products. Therefore, a small amount of mercury is in coke and the others will pass into the atmosphere. The emission factor of mercury emission from iron and steel in India is 0.08 g Mg^{-1} where it's quite high compared to other countries [32]. This is because the coal used in iron and steel production is categorised as poor quality with high ash content (30 – 40%). Therefore, it needs more

coal per Mg of steel and iron production. The mercury concentration in dust was 56mg kg^{-1} and the atmospheric deposition of mercury in the vicinity of iron and steel works was in the range of 60 to 836 g/km^2/month as reported by Murkherjee *et al.* (2009).

Mercury is used in many applications due to its unique physical and chemical characteristics. Mercury is a liquid at room temperature and can expand precisely due to changes in temperature. Therefore, mercury is used in many products such as batteries, thermometer, relay and switches, measuring and control equipment, fluorescent lamp, dental amalgam and laboratory chemicals. Mercury can be released from these products in many ways. Mercury is released during production and manufacturing of these products, due to breakage during use of product containing mercury, released through associated treatment of final disposal of mercury waste such as incineration and other. The average mercury use for all products and processes from 1994-2000 is about 3600 Mg/year [10]. The amount of mercury in solid waste depends on the mercury content of the products, the life time of the products and also the treatment of disposal waste. Mercury concentration in medical devices is in the range 0.5g for medical thermometer and 200g for industrial an special applications [33]. In Australia, the mercury emissions from measuring devices are 92 kg/year by using default emissions factor of UNEP Toolkit. However, it is estimated that the emission is quite high as 200-300kg per year [34].

Mercury also can be emitted through gold mining where mercury is contained in the ore as a trace metal. The emissions from large scale industrial production is about 6% of total global emissions and about 18% from small scale and artisanal gold mining and production [34]. Due to this high emission, it has become the most critical environmental issues especially in developing countries. Artisanal gold mining is active in 70 countries with total emissions of 1000 Mg/year to the environment [10]. In South Africa, about 8000-20000 small scale gold mining activities operating in this country contribute to mercury emissions. However, the emissions is lower compared to the mercury emissions in Zimbabwe with 3 to 5 Mg/year [35].

The emissions from crematoria are also significant and contribute to mercury emissions into the atmosphere. Mercury release in crematoria is through the incineration of amalgam tooth filling in dead bodies. The decomposition of tooth filling occur at temperature below the operating temperature of incineration (870-980˚C) [36]. Mercury contains 50% of

mixture in dental amalgams. Therefore, each filling may contain about 0.4-0.6g Hg [36]. In Massachusetts, mercury emissions from crematoria activity release 23.3 kg of mercury in 2008 with 15 680 deaths was cremated. In Northeast, about 165 kg/year of mercury emissions from crematoria was estimated. The emissions factor use in this estimation is 4.8 E^{-02} lbs mercury per ton body charged [37].

Mercury Removal by Activated Carbon

Activated carbon system is well established as a commercial air pollution control process for a variety of volatile organic compounds, dioxin-furan, and heavy metals control applications [38]. Activated carbon adsorption offers the potential for controlling mercury emissions since it has a high specific surface area and considered as an excellent adsorbent. Factors affecting adsorption capacity are specific surface area, pore size distribution and affinity between adsorbate (Hg) and adsorbent (AC). Activated carbons that are used to adsorb mercury can be divided into two categories which are virgin or impregnated with chemical substances.
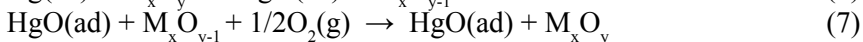
Virgin Activated Carbon

Generally, for virgin or unimpregnated activated carbon only pure physisorption process is involved and occurs at low temperature. At high temperature, activated carbon showed a weaker Hg^0 capture ability [39] because its bind material by Van der Waals or London dispersion force. Commonly, the higher specific surface area of the activated carbon (especially higher micropore surface area) the larger it is adsorptive capacity for the removal of gaseous pollutants. Diamantopoulou *et al.* (2010), has studied two commercial activated carbons in fixed bed (F400, Norit) with different micropore volume (0.40, 0.22cm^3/g) and different BET surface area (827, 620m^2/g) at temperature 150°C. The results revealed that the high BET surface area and the large pore volume of microporous F400 activated carbon presented higher mercury efficiency because inside the micropores, the mechanism of adsorption is taking place where Hg filled the pores [40]. According to Vidic and McLaughlin (1996), reduction of particle size activated carbon gained higher adsorptive capacities [41].

Developing activated carbon with high surface area, high porosity, and low cost is essential to economically remove mercury from flue gas. To achieve this goal, producing activated carbon from agricultural wastes such as corn cob, coconut shell, rice bran, jackfruit shell waste, palm oil waste and jathropha fruit shell is considered more cost-effective and effective to adsorb mercury in flue gas. According De *et al.* (2013), activated carbon from biomass has low ash contents and large micropore surface areas than coal derived activated carbon. With higher ash content, surface area of the activated carbon is reduced because high level of impurities leads to blockage pores [42].

Impregnated Activated Carbon

Impregnation of activated carbon using promoters such as halides, chemical, metal halides or metal oxides had shown great potential to increase the mercury removal capacity. The amount of mercury adsorbed onto the impregnated activated carbon attributed to a combined physisorption and chemisorption meanwhile for unimpregnated activated carbon is only via physisorption [43]. When activated carbon was loaded with chemical substances, automatically the BET surface area decreased. At this moment, adsorption of Hg^0 was not related with BET area but depended on reaction occurred between adsorbate (Hg) and adsorbent (loaded AC).

Based on previous study by Shen *et al.* (2010), activated carbon that loaded with metal oxide and metal chloride showed a high Hg^0 capture capacity because have active elements such as Cl which could react with Hg^0 and change it to mercury oxide or mercury chloride, as proved by diction of $HgCl_2$ and HgO [39, 44].
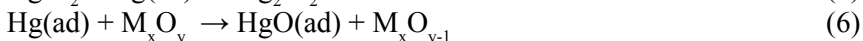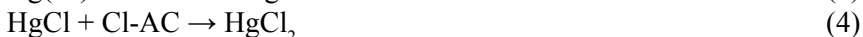
$$MCl_x(s) + AC \rightarrow M_xO_y + Cl\text{-}AC \qquad (1)$$
$$Hg + AC\text{-}surface \rightarrow Hg(ad) \qquad (2)$$
$$Hg(ad) + Cl\text{-}AC \rightarrow HgCl \qquad (3)$$
$$HgCl + Cl\text{-}AC \rightarrow HgCl_2 \qquad (4)$$
$$HgCl_2 + Hg(ad) \rightarrow Hg_2Cl_2 \qquad (5)$$
$$Hg(ad) + M_xO_y \rightarrow HgO(ad) + M_xO_{y-1} \qquad (6)$$
$$HgO(ad) + M_xO_{y-1} + 1/2O_2(g) \rightarrow HgO(ad) + M_xO_y \qquad (7)$$
[M: metal elements, s: solid, ad: adsorption, g: gaseous]

These reactions showed that sorbents loaded with metal chlorides processed a joint catalytic effect of valence variable metal and chlorine oxidation [5,39].

In addition, impregnation of activated carbon using halides has shown great potential to increase the mercury removal efficiency. The halides group consists of F, Cl, Br, and I. The iodide impregnated activated carbon was the most effective to remove mercury in flue gas [42,45] even at high temperature. The iodide ions are expected to have highest surface exposure compared to others since the size of the halide ions increases in the order of $Cl^- < Br^- < I^-$ [42]. Therefore, it is expected that iodide ions have better contact with Hg^0 and finally increased the mercury removal efficiency. The reactions for iodine can be expressed as follows [42, 46]:

$$Hg + I_2 + 2KI \rightarrow K_2HgI_4, \tag{8}$$
$$Hg + I_2 + KI \rightarrow KHgI_3, \tag{9}$$
$$Hg + 1/2I_2 \rightarrow HgI, \tag{10}$$
$$2KI + HgI + 1/2I_2 \rightarrow K_2HgI_4, \tag{11}$$
$$KI + HgI + 1/2I_2 \rightarrow KHgI_3. \tag{12}$$
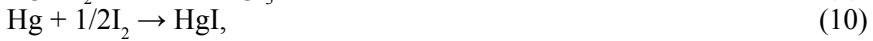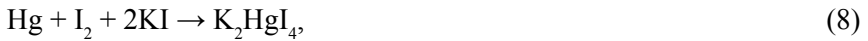
However, mercury removal amount depend on the loading values and types of impregnating precursor that are used.

Factors Affecting Mercury Adsorption by Activated Carbon

There are a large number of variables that affect the adsorption of mercury in flue gas. These include mercury speciation and concentration, flue gas temperature, flue gas composition and carbon physical and chemical properties such as particle size distribution, pore structure and distribution, and surface characteristic.

Inlet Mercury Concentration

Vidic and McLaughlin (1996) used different types of virgin activated carbon to uptake elemental mercury vapor. Adsorption of mercury at high concentration ($25 - 115 ug/m^3$), resulted in high adsorption outlet mercury

concentration (90% or higher). This may be caused by the fact that when concentration of inlet mercury in feed gas is higher, the Hg atoms have more chances to interact and be attached with the carbon surface [42]. Meanwhile, Ping *et al.* (2012) stated that the mercury removal efficiency was slightly affected by mercury concentration because when concentration of inlet mercury is increased, the gas phase driving force for mass transfer also increased and make the reaction rate increases [47]. However, with increasing temperature above $140^{\circ}C$, the adsorption capacity decreases. The author also found there existed a decrease in adsorptive capacity with an increase in temperature and a decrease in influent mercury concentration [41, 47].

Flue Gas Temperature

In pilot plant studies, activated carbon injection indicated the mercury removal efficiency is strongly dependent on the gas temperatures. In technical paper by Takaoka *et al.* (2002), stated that Hg reduction ratio increases as the flue gas temperature decreases. When the temperature is increased from $150^{\circ}C$ to $180^{\circ}C$ in spray tower the Hg reduction ratio decreased. This is because at high temperature mercury becomes a hot vapor and unstable to be adsorbed in activated carbon [43]. According Zeng *et al.* (2004), when the temperature of virgin activated carbon is increased, the amount of Hg^0 adsorbed decreased progressively, indicating a typical physisorption mechanism due to van de Waals forces between the adsorbate (Hg^0) and the adsorbent (AC). However, the trend was entirely different for impregnated activated carbon. When temperature is increased up to $150^{\circ}C$, there were more and more active site adsorbate molecules and chemisorption occurred by forming chemical bonds between the adsorbate and chemical additives present on the adsorbent [43, 48]. Therefore, it can be concluded that at this positive temperature, Hg^0 removal was typical in a chemisorption mechanism. However, further increasing the temperature to $200^{\circ}C$, the adsorptive capacity of Hg^0 dropped because of exothermic nature of adsorption process.

Effect of O$_2$ Concentration

The influence of O$_2$ concentration on the mercury adsorption was investigated and the results showed that adding O$_2$ in the simulated flue gas system can lightly increased the Hg^0 removal efficiency [47, 49]. This is because O$_2$ can oxidize Hg^0 to oxidized mercury (solid or gaseous) and easily captured by activated carbon and subsequently removed from the system. Following, there are mainly two ways of oxidation proposed [5] (the expression "ad", "g" and "s" in the parentheses are abbreviation of "adsorption", "gaseous" and "solid", respectively):

$$Hg^0(g) + 1/2O_2(g) \rightarrow HgO(g) + HgO(s, ad) \qquad (13)$$
$$Hg^0(ad) + 1/2O_2(g) \rightarrow HgO(s, ad) \qquad (14)$$
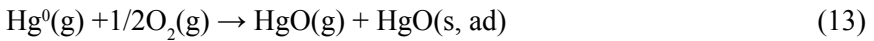
In addition, oxygen element also exist in activated carbon [6]. So, this functional group can help mercury adsorption because oxygen will be reacted with elemental mercury to form mercuric oxide which is more easily adsorbed and captured by using existing abatement pollution control technologies.

Effect of CO$_2$ Concentration

The presence of CO$_2$ in the simulated flue gas, in the range 0-20%, generally did not cause a decrease of mercury adsorption efficiency however showed a decrease when used non-sulfur-impregnated activated carbon is used. This is probably due to the reduction in the active sites that resulted from the competitive adsorption between CO$_2$ and Hg^0 on activated carbon [49]. Indeed, CO$_2$ was filled in a part of activated carbon microporous structure in order to prevent increasing mercury adsorption [40].

Moisture Content

Water vapor is contained in flue gas as one of the products of combustion or entrained from the evaporation of moisture originally in the combustible raw material. There has been observation that indicates high moisture levels in the flue gas will suppress the capture of mercury by activated carbon

because water molecules can block adsorption site for mercury with fill the micropores and reduces active sites available for Hg removal [38]. However, in a lab-scale study by Li *et al.* (2002), the presence of moisture on the carbon surface was reported to promote mercury bonding [50] and OH radicals in water vapor can be generated to oxidize Hg^0 [51]. He reported that moisture levels around 5% can be significant because when increasing to 10 vol. %, the adsorption decrease to 25% instead.

Effect of HCl

The effect of HCl, in the range of 10-50ppm$_v$ on Hg removal was found to be promotional. The efficiency of Hg removal was directly proportional to HCl concentration. However, according to Ying et.al (2008), Hg removal was not apparently related to HCl concentration but HCl promotes heterogeneous Hg oxidation. In the presence of catalyst such as metal oxides or metal chlorides, a Decon process could convert HCl in the flue gas to Cl_2 at high temperatures, thereby enhancing Hg^0 oxidation or chlorination [51]. Meanwhile, Zheng *et al.* (2012) stated the difference in capture efficiency between Hg^0 and $HgCl_2$ is small because Hg^0 is oxidized by a fast reaction to $HgCl_2$ over the carbon sorbent [38]. However, these observations depends on the presence of the others gases.

Conclusion

Natural and anthropogenic sources are two major sources that contribute to mercury emissions into the atmosphere. For anthropogenic sources, coal combustion, cement production and waste incineration have high mercury emissions compare to other sources. Since the mercury emission is increasing globally, the application of activated carbon in mercury removal technology has become more important. From the literature reviewed, modified activated carbon is considered as a highly potential adsorbent for mercury removal in flue gas compared to unmodified activated carbon because chemisorption process occurred and is capable to remove Hg at high temperature. Besides that, Hg removal have a large of variables that influenced mercury removal in flue gas such as flue gas temperature, mercury concentration, flue gas composition, types and characterization of activated carbon.

Acknowledgement

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