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A Systematic Review on Mercury Toxicity and Removal Processing

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ABSTRACT

Toxic metals, including "heavy metals," are individual metals and metal compounds that negatively affect people's health. In very small amounts, many of these metals are necessary to support life however, in larger amounts they become toxic. They may build up in biological systems and become a significant health hazard. Mercury is one such most hazardous air pollutants due to its neurological toxicity, volatility, persistence, and bioaccumulation, all of which pose a great threat to both human health and organism security. Common sources of mercury exposure include mining, production, and transportation of mercury, as well as mining and refining of gold and silver ores. It poses a great threat to the well being of an individual. Therefore there is an urgent need to develop methods efficient enough to remove mercury from various sources. Many technologies have been implemented to control Hg^0 *emissions, such as catalytic or photochemistry oxidation, sorbent injection and air pollution control devices (APCDs). Adsorption using porous carbon (PC), particularly PC impregnated with sulfur (S), chlorine (Cl), or iodine (I), has excellent potential for* Hg^0 *removal from flue gases.*

Keywords:— *Mercury, hazardous, catalytic oxidation, sorbent injection, adsorption*

I. INTRODUCTION

Toxic substances that accumulate in the environment and in food chains disrupt biological processes[1, 2]. Several industrial operations release various toxic heavy metals in their effluents which eventually find their way into water sources, such as lakes, rivers and streams. Mercury, lead and cadmium are regarded as contaminants of the environment. The main sources of these metals pollution in the urban areas are anthropogenic while contamination from natural sources predominates in rural areas[1]. Some amounts of these metals have been known to cause serious damage to various human tissues and aquatic life. Lead used by humans, has a long history of beneficial use to humankinds, but now been recognized as toxic, poses a widespread threat to humans and wildlife. Cadmium has no beneficial effect on any living organism. In man, it can cause kidney damage, high blood pressure, and destruction of testicular tissues and blood vessels[3]. Because of the toxic nature of these metals, the need for their removal from the environment arises. Various researchers have reported the removal of Pb(II), Hg(II) and Cd(II) ions from aqueous solutions[4, 5, 6, 7] using Thais coronata (grastropoda) and Crasstrotea gasar (bivalve) shells, Activated carbon or coconut shells.

In particular, mercury is one of the most hazardous air pollutants due to its neurological toxicity, volatility, persistence, and bioaccumulation, all of which pose a great threat to both human health and organism security [8, 9, 10, 11]. Among human activities, coal combustion makes the greatest contribution as an anthropogenic source of mercury emission. Coal-fired flue gas can contain three forms of mercury: elemental mercury (Hg^0), oxidized mercury (Hg^{2+}) and particle-bound-mercury (Hg^P) [12, 13]. During coal combustion, elemental mercury is released and partly oxidized to Hg^{2+} in the flue gas. The adsorption of Hg^0 and Hg^{2+} on solid surfaces leads to the formation of the particle-bound mercury. Particle-bound mercury (Hg^P) can be easily removed by dust collection processes. Furthermore, oxidized mercury is soluble in water and easily adsorbed on solid surfaces, which aids its removal[14]. However, Hg^0 is neither soluble in water nor easily adsorbed. It has a lifetime of 1-2 years in the atmosphere and can be transported over long distances to cause widespread mercury pollution. Therefore, the removal of Hg^0 emitted from flue gas is an important part of minimizing mercury emissions[15]. Many technologies have been implemented to control Hg^0 emissions, such as catalytic or photochemistry oxidation, sorbent injection and air pollution control devices (APCDs). Adsorption using porous carbon (PC), particularly PC impregnated with sulfur (S), chlorine (Cl), or iodine (I), has excellent potential for Hg^0 removal from flue gases.

II. MERCURY CHARACTERISTICS

Mercury is characterized as a highly malleable liquid at normal temperature and pressure[16]. Its name is derived from the Latin word hydrargyrum, meaning metal that resembles liquid silver[16]. Mercury is classified into three main groups: elemental mercury, inorganic mercury, and organic mercury. Mercury exists in several forms: inorganic mercury, among which there have been the metallic mercury and mercury vapor (Hg^0) and mercurous mercury (Hg^+) or mercuric mercury (Hg^{++}) salts; organic mercury, also called organometallic, which results from a covalent bond between mercury and a carbon atom of an organic functional group such as a methyl, ethyl, or phenyl group. The biological behavior, pharmacokinetics, and clinical significance of the various forms of mercury vary according to its chemical structure [17].

2.1 Inorganic Mercury Compounds

1. Elemental Mercury or Metallic Mercury Compounds.

In its liquid form, the elemental mercury (Hg0) is poorly absorbed and presents little health risk. However, in the vapor form, metallic mercury is readily absorbed through the lungs and can produce body damage[18-20] Elemental mercury is used in thermometers and sphygmomanometers because of its uniform volumetric expansion, high surface tension, and lack of vitreous adherence to surfaces. Low electrical resistance and high thermal conductivity allow metallic mercury to be used in electrical and electronic materials. Because of its high oxidation power, metallic mercury is used in electrochemical operations in the chlorine and soda industries. Metallic mercury is also used in metallurgy, mining, and dentistry because of the easy amalgam formation with other metals. In addition, gold extraction with archaic and dangerous methods predisposes miners to mercury poisoning. The burning of metallic mercury on the gravel promotes the separation of gold, a process called amalgamation, which causes emission of large amounts of mercury vapor that is inhaled immediately by the miner, since they do not use appropriate personal protective equipment[21-22].

2. Mercurous Mercury and Mercuric Mercury Compounds.

The mercurous mercury in the form of mercurous chloride (Hg_2Cl_2) is little absorbed in the body. It is believed that in the body the form of metallic mercury is changed to elemental mercury and mercuric mercury [23]. Mercuric mercury compounds, such as mercury salts, result from the combination of mercury with chlorine, sulfur, or oxygen. Mercuric mercury can be found in different states when combined with other chemical elements, including mercuric chloride ($HgCl_2$), which is highly toxic and corrosive; mercury sulfide (HgS), which is often used as a pigment in paints due to its red color; mercury fulminate ($Hg(CNO)_2$), which is used as an explosive detonator[24].

3. Organic Mercury

Organic mercury compounds, also called organometallic, result from a covalent bond between mercury and the carbon atom of an organic functional group such as a methyl, ethyl, or phenyl group. Methylmercury (CH_3Hg^+) is by far the most common form of organic Hg to which humans and animals are exposed. CH_3Hg^+ in the environment is predominantly formed by methylation of inorganic mercuric ions by microorganisms present in soil and water [25-27].

Thimerosal is an organomercurial compound that since 1930 has been widely used as a preservative in biological material such as vaccines and serums used to prevent microbiological growth[28]. Thimerosal is metabolized in the human body and degraded into ethyl mercury and thiosalicylate. The chemical difference between these compounds is an important determinant of their toxicity [29, 30].

4. Forms of Mercury Exposure

Mercury is now considered an environmental pollutant of high risk to public health because of its high toxicity and mobility in ecosystems [31]. Exposure to mercury can occur from both natural and artificial sources. Human activities that can result in mercury exposure include the burning of fossil fuels, chlor-alkali industries, mining, the burning of waste, and the use of coal and petroleum.

More natural sources of mercury include volcanic activity, earthquakes, erosion, and the volatilization of mercury present in the marine environment and vegetation[32, 33, 34]. Mercury emitted both naturally or as a result of human activity is primarily found as inorganic metal vapor (Hg^0). Among the natural sources of mercury, the largest emissions are from the degassing of the earth’s crust. More than five tons of mercury is estimated to be released into the sea every year as a result of erosion and geochemical cycles [35].

Mercury contaminates the environment through a cycle involving the initial emission, the subsequent atmospheric circulation of the vapor form, and the eventual return of mercury to the land and water via precipitation. The emission of mercury is an important part of this cycle of contamination and can occur through natural processes or as a result of human activities, as mentioned above. Mercury present in seas and rivers after methylation can contaminate fish [36, 37]. The consumption of fish contaminated with mercury is a major source of mercury exposure in the Amazon basin. Studies show that the concentration of mercury in the muscles of fish that are widely consumed in the Amazon region are greater than the limit set by WHO (World Health Organization) as safe for human consumption (0.5 g/kg).

Doses of Mercury and Safety Legislation:

The chemical form of mercury in the air affects its time of permanence and its dispersion in the atmosphere. The elemental mercury form can persist for more than four years in the air, while its compounds are deposited in a short time at locations near their origin. In the northern hemisphere, their average concentration in the atmosphere is estimated at

2ng/m^3 and in the southern hemisphere is less than 1ng/m3. In urban areas, there is a great variability of these concentrations being found up to 67 ng/m^3 with a mean of 11 ng/m^3 in Japan[38]. FUNASA standards of mercury in the air consider a mean of 1ng/m^3 in the period of one year. In 2004, the Joint FAO (Food and Agriculture Organization of the United National)/WHO Expert Committee on Food Additives (JECFA) established that the safe concentration of methyl mercury intake, without the appearance of neurological disorders, is 1.6 mg/kg of body weight. However, in 2006, JECFA stated that this concentration is not safe for intrauterine exposure, because fetuses are more sensitive to the onset of neurological disorders after exposure to methyl mercury[39]. Currently, the general population is exposed to mercury by the following main sources: the consumption of contaminated fish, the use and manipulation of dental amalgam, thimerosal contained in vaccines, workers in industries of chlorine, caustic soda, miners, and workers in industries of fluorescent lamps [40, 41]. Each of these sources of exposure contains specific toxicological characteristics[42].

In Brazil, the rules for vaccination of the Ministry of Health, published in June 2001, shows that thimerosal is used in many vaccines. These vaccines prevent flu (influenza vaccine), rabies (rabies vaccine), infection with meningococcus serogroup b, and hepatitis B [43]. The US Environmental Protection Agency recommended a reference blood concentration of mercury to be 5.8 ng/mL; concentrations below this level are considered to be safe [44, 45]. Some studies have reported that the blood mercury concentration in the control population is approximately

1 ng/mL. On the other hand, levels of 7–10 ng/ mL have been reported in workers exposed to mercury or in residents of Guizhou (China), an area that is known to suffer mercury contamination[46, 47]. In a recent biomonitoring study in New York City, the blood mercury concentration was found to be 2.73ng/mL, and levels reached 5.65ng/mL in adults that consumed fish regularly[48]. WHO states that an allowable concentration of mercury in human hair is less than 6 μg/g. In the Amazon basin, where fish is the main source of dietary protein, mercury concentrations in hair reached up to 150 μg/g.

Furthermore, only two of 40 cities studied have average mercury concentrations below the recommended amount [49]. In individuals who have amalgam, the daily release of mercury amalgam is approximately 4-5 μg/day, and a positive correlation exists between the blood concentration of mercury and the number of amalgams. It is estimated that each dental amalgam releases 3–17 μg mercury vapor per day and that the blood concentration of mercury after removal or the restoration can reach 5 nmol/L[50, 51, 52]. However, even at concentrations below recommended levels, there is strong evidence that exposure to ethyl mercury, the major component of thimerosal, is associated with the onset of neurological and heart disorders in children[53].

Mercury Generation Potential:

Mercury and its compounds are everywhere in our environment. Between 2,700 and 6,000 tons of mercury are released annually from the oceans and the earth’s crust into the atmosphere. Another 2,000 to 3,000 tons are released from human activities, primarily burning household and the industrial waste and especially from burning fossil fuels, such as coal[54]. The Asian countries contributed about 54 percent to the global mercury emission from anthropogenic sources in 2000, followed by Africa (18 percent) and Europe, including the European part of Russia (11percent)[55]. Among the various regions Asia has become the largest contributor of anthropogenic atmospheric mercury, responsible for over half of global emission[56].

IV. MERCURY TOXICITY

One of the important areas of concern is mercury toxicity. Mercury exists in many chemical forms and the differential toxic effect manifested by each, from the primary route of exposure to metallic mercury is inhalation, this is because of its low vapour pressure. It is essentially odorless and has limited warning properties. Workers at risk of experiencing biological effects because of chronic exposure are often unaware that significant exposure is occurring[57]. In particular public health concern has been possible neurologic impairment associated with prolonged exposure to elemental mercury[58,59]. Elemental mercury easily diffuses across the Blood-Brain Barrier especially in children. Ionized mercury deposits in various tissues in the body over a period of time. Elemental mercury vapor, such as may be present in the workplace, is readily absorbed through the lung tissue and is then taken up by several tissue types through passive diffusion, in particular are the kidney tissue and RBCs. As amount of mercury exposure levels go up, the kidneys are gradually damaged and their excretion of mercury becomes impaired.

In children urinary mercury levels were reported to be highly correlated with both number of amalgam fillings and time since placement[60]. Release of mercury vapour from amalgam restorations is known to occur but intensive research over the past three decades have failed to identify deleterious health outcomes[61, 62]. This is likely to be due to insufficient mercury being released from dental amalgam restorations to cause a medical problem[63, 64].

As a vapor, metallic mercury can be inhaled and absorbed through the alveoli in the lungs at 80 % efficiency. This is clearly the major route of entry into the human body. Metallic mercury is poorly absorbed through the skin or the gastrointestinal tract [65]. The acute toxicity by mercury vapor appears to occur in three phases. The initial phase is characterized by flu like symptoms lasting 1-3 days. The intermediate phase is dominated by signs and symptoms of severe pulmonary toxicity. The victim in final phase will experience gingivostomatitis, tremor, and erethism (memory loss, emotional liability, depression, insomnia, and shyness) [66].

Effect of Mercury on the Central Nervous System (CNS):

Among the compounds of mercury, the methyl mercury is primarily responsible for the neurological alterations present in humans and experimental animals. It is believed that the mechanisms are related to the toxic increase in reactive oxygen species (ROS). Oxidative stress is associated with the etiology of neurodegenerative diseases such as amyotrophic lateral sclerosis, Parkinson’s disease, and Alzheimer’s disease[67, 68], but these mechanisms have yet to be fully recognized. Studies also demonstrate that mercury has the ability to reduce the number of neuron and cytoarchitecture in individuals with prenatal exposure to mercury.

Effect of Mercury on the Cardiovascular System:

For decades, the toxic effects of mercury were associated mainly with the central nervous system; however, inorganic mercury also produces profound cardiotoxicity[69-73]. Halbach and collaborators[74] showed that mercury concentrations in hair reached up to150 μg/g in populations living in the Amazon basin. Furthermore, nearly all of the inhabitants of 40 cities studied have blood concentrations above the reference values. In this population, it has been demonstrated that exposure to mercury by frequent consumption of fish has a strong positive correlation with increased arterial blood pressure[75]. Other studies also correlate mercury exposure with increased risk of hypertension, myocardial infarction, coronary dysfunction, and atherosclerosis[76-78].

Exposure to mercury increases the production of free radicals, potentially because of the role of mercury in the Fenton reaction [79-81] and a reduction in the activity of antioxidant enzymes, such as glutathione peroxidase. The Me Hg reaction with the glutathione peroxidase occurs via thiol (–SH) and/or selenol (–SeH) groups from endogenous molecules[82].

Taken together, these data show that chronic low doses of mercury have an important and deleterious effect on vascular function by reducing NO bioavailability. The degree of severity of mercury exposure is comparable to traditional cardiovascular risk factors, such as hypertension diabetes or hypercholesterolemia. Therefore, mercury could be considered an important risk factor for cardiovascular disease that could play a role in the development of cardiovascular events. The association between mercury exposure and an increased risk of developing cardiovascular and neurological diseases is apparent. Thus, continuous exposure to mercury can be dangerous, and current reference values, once considered to be without risk, should be reevaluated and reduced.

Removal Processing Methods:

1. Catalytic oxidation: Catalyst-enhanced elemental mercury (Hg^0) oxidation, when combined with a wet flue gas desulfurization system, provides a promising method to simultaneously control mercury and SO_2 emission. Zeng et al. [83] studied the removal capabilities of elemental mercury from coal combustion flue gas of chloride-impregnated activated carbon. The experiment results showed that impregnation with $ZnCl_2$ significantly enhanced the adsorptive capacity for mercury vapor but decreased the specific surface area of the activated carbon.

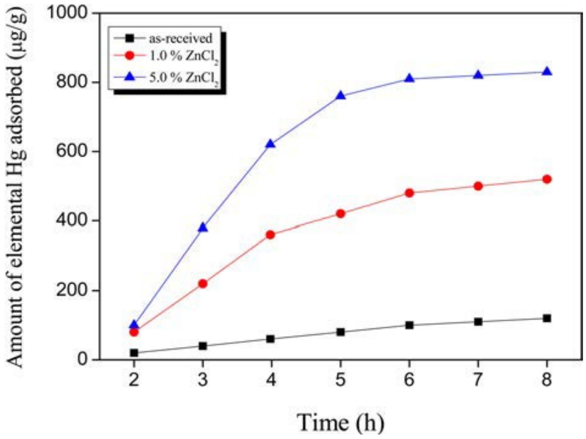

Figure 1. Adsorption of elemental mercury onto the ZnCl2-impregnated activated carbon for a testing time up to 8 hr [24].

Hu et al.[84] investigated oxidative adsorption of elemental mercury by activated carbon in simulated coal-fired flue gas. Figure 2 shows the Hg^0 adsorption of chlorine-impregnated activated carbon. The adsorption of Hg^0 by activated carbon was a complete chemical adsorption process in N_2 gas or in simulated flue gas. Hg^0 was oxidized to Hg^{2+} by chlorine on the carbon surface and absorbed by activated carbon in N_2 gas. The oxidizing elements were consumed during the adsorption process.

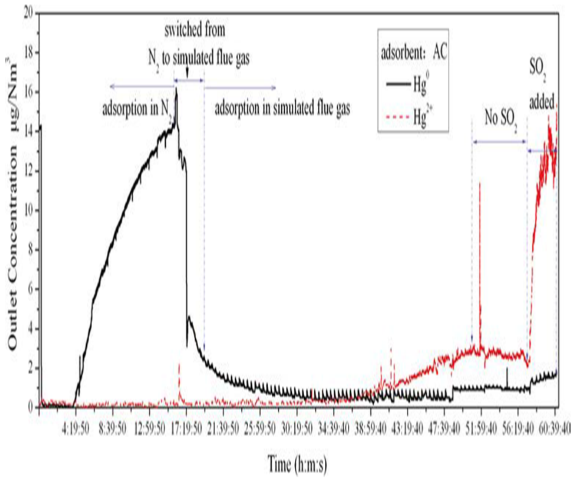

Figure 2. *Hg^0 adsorption by activated carbon in N_2 and in simulated flue gas*

Mercury removal with catalytic oxidation, particularly when used in conjunction with sulfur (S), chloride (Cl), or iodine (I) impregnation, has also been studied for the removal of Hg^0 from flue gas. Recently, catalysts employing manganese oxides as the active ingredient have attracted substantial attention in the selective catalytic reduction field owing to their high catalytic activity in a wide range of temperatures.

2. Photochemistry oxidation:

Photochemistry oxidation of mercury with various components in flue gas may be an attractive alternative to sorbent[85, 86] or scrubber-based[87] processes for mercury capture applications. One widely studied area and relevant has been the photochemistry oxidation of mercury using 253.7 nm ultraviolet light[88]. Dickinson and Sherrill demonstrated the photochemical formation of mercuric oxide via the sensitized formation of ozone in 1926. The mechanism between mercury and oxygen in the presence of 253.7 nm radiation is expressed below as Eq. (1).

$$\mathrm{Hg} + 2\mathrm{O}_2 + \mathrm{UVlight} \rightarrow \mathrm{HgO} + \mathrm{O}_3$$

In the reaction mechanism, elemental mercury serves as a sensitizer for the formation of ozone, and the ozone oxidizes mercury to form mercuric oxide [89]. Photochemistry oxidation is a potential means of removing mercury from flue gas. The photochemical formation of mercuric oxide can also have a significant impact on current ultraviolet-based methods of measuring mercury in flue gas as well as potential environmental consequences[86]. Woo et al. [90] studied a PCO process for the photochemical removal of mercury from flue gas. The preliminary tests conducted to date clearly show the ability of the PCO process to oxidize elemental mercury, as shown in Figure 5 and Figure 6. Similar results were observed by Pitoniak etal for silica-titania nanocomposites for elemental mercury vapor removal (Figure 3)

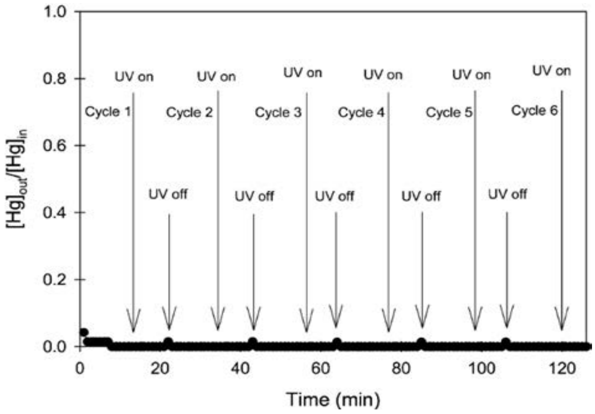

Figure 3. Fractional Hg0 outlet concentration for TiO2 -HgO-doped pellets

Photochemistry oxidation is possible under UV light for the measurement of mercury. Recently, this process of elemental mercury removal has been studied under various light sources.

3. Sorbent injection:

Mercury control via the injection of sorbent materials into the gas stream of coal-fired boilers is under development. Currently, this approach is being demonstrated on selected full-scale systems. A typical implementation of this control technology would entail the injection of powdered sorbent upstream of a particulate matter (PM) control device (electrostatic precipitator [ESP] or fabric filter [FF]). An alternative is the TOXECON configuration, in which a relatively small FF is installed downstream of an existing ESP. Sorbent is injected downstream of the ESP after most of the flue-gas PM has been removed. The sorbent is then collected in the downstream FF, which effectively segregates the fly ash and injected sorbent.

Some of the factors that appear to affect the performance of any particular sorbent include the method and rate of sorbent injection; the flue gas conditions, including the temperature and concentrations of the halogen species (e.g., HCl) and sulfur trioxide (SO_3); the existing APC configuration; and the physicochemical characteristics of the sorbent. The sorbent injection rate is usually expressed as pounds of sorbent per million actual cubic feet of flue gas (lb/MMacf). For a 500-MW boiler, a sorbent rate of 1.0 lb/MMacf corresponds to ~120 lb/h of sorbent [91]

Carey et al. investigated the effectiveness of sorbent injection as a means of mercury control in flue gas streams. Mercury adsorption tests conducted at two different utility sites indicate that the sorbent characteristics are dependent on the flue gas conditions. Based on the sorbent characteristics measured at two field sites using a commercially available form of activated carbon, the predicted carbon injection rates to achieve 80% mercury removal can differ by a factor of 2-5, as shown in Figure 4 and Figure 5.

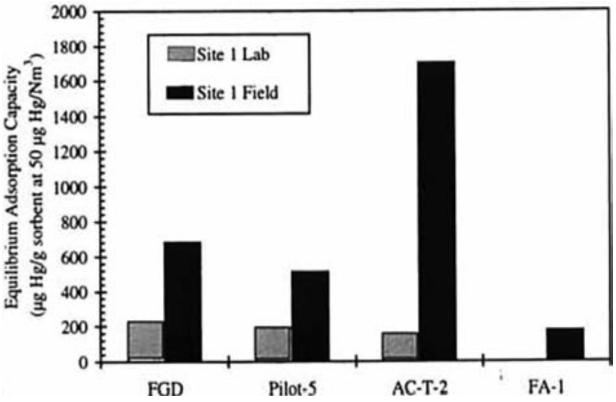

Figure 4. Comparison of mercury adsorption capacities for sorbents tested in the lab and at site

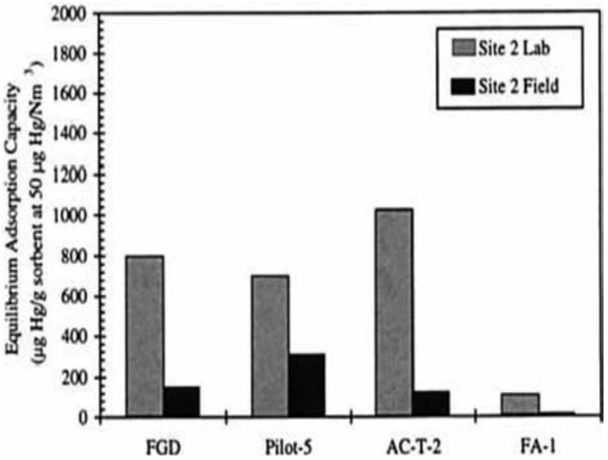

Figure 5. Comparison of mercury adsorption capacities for sorbents tested in the lab and at site

In conclusion, there is a strong correlation between the Cu_2O/Cu ratio and the mercury-removal properties of Cu-coated porous carbonaceous materials. Figure 6 shows the elemental mercury adsorption characteristics of metal/activated carbon hybrid materials. Based on the experimental results, elemental mercury adsorption of all metal/ACs occurred at a level higher than noted with the as-received sample. This demonstrates that metal plating (Cu and Ni) on carbon surfaces can be a feasible method of elemental mercury adsorption.

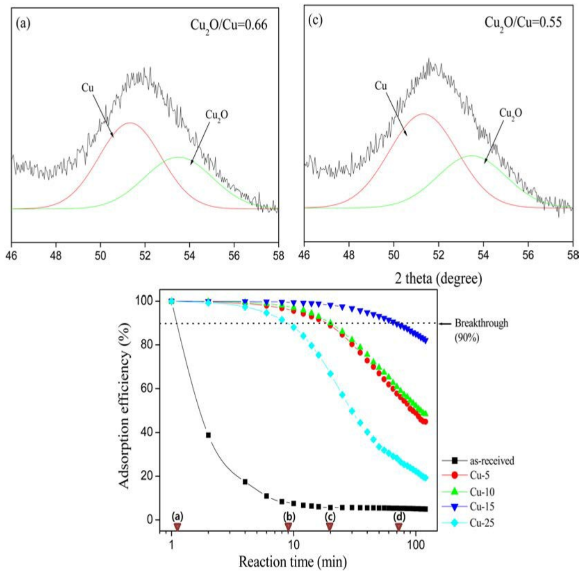

Figure 6. X-ray diffraction patterns and elemental mercury removal efficiency of the Cu/PC as a function of the plating time

4. Air pollution control devices:

Mercury species in coal-fired flue gas include elemental, oxidized and particulate-bound mercury. The most common APCDs in US coal-fired utility power stations include (1) ESP used with or without flue-gas desulfurization (FGD) controls (Figure 7), and (2) FF, which may be used alone or with spray dry absorbers (SDAs). These control devices are designed to remove particulates (FF, ESP) or S (FGD, SDA) from flue gases. The position of an ESP relative to the air pre-heater device, downstream of the boiler, is an important distinction.

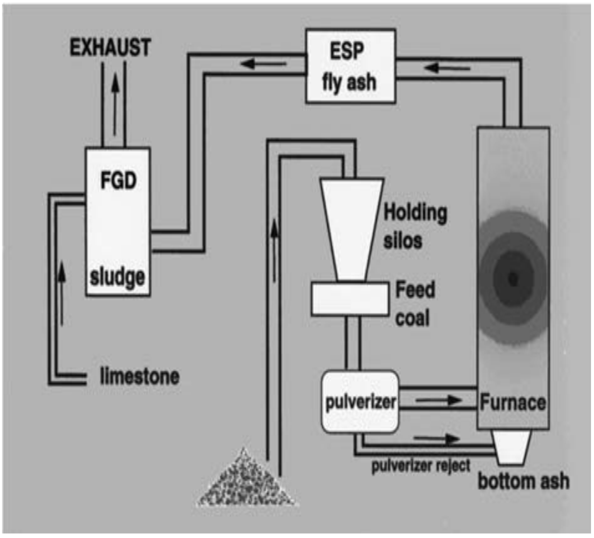

Figure 7. Schematic showing the flow of materials in a coalfired boiler equipped with an electrostatic precipitator (ESP) and flue-gas desulfurization (FGD) air pollution control devices

A cold-side ESP is installed downstream of the air pre-heater whereas a hot-side ESP is installed upstream of the air pre-heater, closer to the boiler. The amount of Hg removed by an APCD depends on its type and on the rank of coal being burned. Empirical results [92] show the most efficient level of Hg removal for bituminous coal (>60%) in FF/SDA and FGD devices (Figure 8). In contrast, a cold-side ESP (CESP) removes only 40% of Hg from flue gases, while a hot-side ESP (HESP) has virtually no effect on the pollutant. At plants burning sub bituminous coal or lignite APCDs are much less capable of removing Hg. For the former fuel, only FFs (60%) and FGD systems (15%) have shown good effectiveness. In the case of lignite-burning plants, the removal of Hg is very low, in some cases apparently negative. Mercury removal is calculated from measurement of Hg in the flue gas at the inlet and outlet of the particulate control device. When little Hg is removed, limitations on the accuracy of the inlet and outlet measurements may result in apparent negative removals. Equations describing the Hg removal behavior of these devices as a function of coal quality parameters have been fit to the ICR data; these results were compared and evaluated.

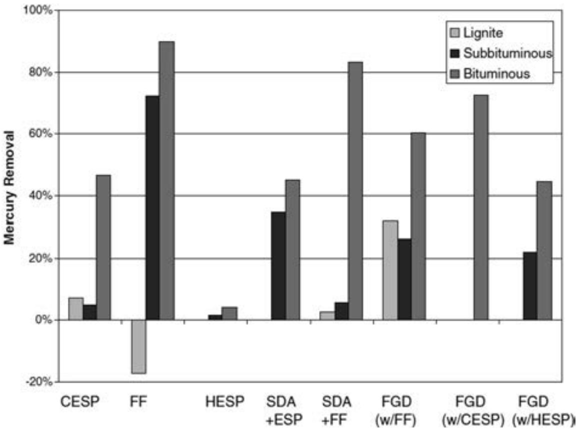

Figure 8. Average Hg removal across air pollution control devices in coal-fired utility boilers from an Environmental Protection Agency (EPA) Information Collection Request

V. CONCLUSION

Mercury is freely available in chemical markets in India. It is sold openly and one does not require any kind of authorization to buy this toxic metal. In developed countries, the use of mercury in various products is either banned or regulated. There are various provisions and acts pertaining to the prevention and control of pollution and protection of the environment. Mercury finds place in some of them, but nothing that deals with it specifically. The nature and extent of threat from the deadly metal makes it a candidate for specific attention. As potential exists for mercury to be transformed into more toxic species, new regulation and methods should be designed to minimize the production of organic mercury. The degree of severity of mercury exposure is comparable to traditional cardiovascular risk factors, such as hypertension diabetes or hypercholesterolemia. Therefore, mercury could be considered an important risk factor for cardiovascular disease that could play a role in the development of cardiovascular events. The association between mercury exposure and an increased risk of developing cardiovascular and neurological diseases is apparent. Thus, continuous exposure to mercury can be dangerous, and current reference values, once considered to be without risk, should be reevaluated and reduced. Also additional research is needed to identify the mercury compounds that are formed and to verify capture mechanisms. Engineering development is also needed to improve the sorbent dispersion and optimize gas–solid contact time.

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