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Legal Framework for Control of Mercury Pollution in Ambient Air–A Review on Best Environmental Practices (BEP) and Best Available Technologies (BAT) for Mitigation of Mercury Pollution

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ABSTRACT

Traces of mercury present in the ambient air has led the world to talk about mercury pollution in the environment that consequently resulted in the introduction of the Minamata Convention (MC) on Mercury, an international treaty on mercury. It was signed on 10th October 2013 in Japan that became effective from 16th August 2017. The Minamata Convention is a global treaty that aims to protect human health and the environment from anthropogenic emissions of mercury and its compounds. The MC recognizes mercury as a pollutant of global concern considering mercury to be capable of long-range transport, to be persistent, and to bioaccumulate, which ultimately results in elevated human exposure levels associated with a range of negative health effects. The main concern of the convention is the health impacts of mercury on the human beings and to regulate its emissions by noting its sources. In addition to this, chemistry of mercury and its compounds, long-range transport, prevention and control technologies relating to mercury are the other concerns of the convention. Initially, Mercury, also known as Quicksilver, had been noted for developing public health disasters in Minamata Bay, Japan. Broadly, it exists in two chemical forms, namely, inorganic mercury and organic mercury. The most common form of mercury contributing to the atmosphere due to anthropogenic activities is gaseous elemental mercury. The target organ for inhaled mercury vapor is primarily the brain. Toxicity varies with dosage, large acute exposures to elemental mercury vapor induce severe pneumonitis, that in extreme cases are often fatal. The paper discusses the best available techniques to regulate the mercury concentration in ambient air and mentions the concentration of mercury removal by various control techniques.

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Introduction

Mercury, being a heavy metal of notable toxicity, noted for developing public health disasters in Minamata Bay, Japan [1]. It exists in numerous chemical forms such as inorganic mercury, that includes metallic mercury and mercury vapor (Hg^0) and mercurous (Hg_2^{++}) or mercuric (Hg^{++}) salts; and organic mercury, which includes compounds in which mercury is bonded to a structure containing carbon atoms (methyl, ethyl, phenyl, or similar groups) [2]. Inhaled elemental mercury vapor, for example, is easily absorbed through mucus membranes and the lungs and rapidly oxidized to other forms (but not so quickly as to prevent considerable deposition of elemental mercury within the brain). Methyl mercury easily gets absorbed through the gut and gets deposited in many tissues, but never crosses the blood-brain barrier as efficiently as elemental mercury; but, on getting into the brain it's more and more demethylated to elemental mercury [3]. The target organ for inhaled mercury vapor is primarily the brain. Mercurous and mercuric salts principally harm the gut lining and kidney, while methyl mercury is widely distributed throughout the body. Toxicity varies with dosage: large acute exposures to elemental mercury vapor induce severe pneumonitis, that in extreme cases are often fatal [3]. This paper is intended to review revealed knowledge on best available techniques to mitigate mercury pollution in ambient air since it has been one of the most concerned matter and one must focus on controlling and reducing emissions of mercury released from various sources [4]. As per UNEP, 2013, the most common form of mercury contributing to atmosphere due to anthropogenic activities is gaseous elemental mercury. The remaining emissions are in the form of gaseous oxidized mercury. Oxidised forms of mercury have a shorter atmospheric lifetime than gaseous elemental mercury and are deposited to land or water bodies more rapidly after their release (UNEP, Global Mercury Assessment, 2003). Elemental mercury in the ambient air can undergo transformation into oxidized mercury that is more readily deposited but, once deposited, can be transformed under certain circumstances into organic compounds by bacteria in the environment [4].

Many countries are already concerned about the toxicity of mercury in the environment and are aware of the risks on health and ecology due to which they have accepted it as a priority to control the pollutant [5]. An emission inventory of mercury

indicates that mercury in Asian countries accounts for more than 50% of global anthropogenic emissions of mercury [6]. They have stated that the mercury and carbon monoxide ratio give the satisfactory indication of the Asian industrial flow [7].

Implementing measures to manage mercury emissions can, however, typically involve some value [4]. Detailing of control technologies for Mercury include pre-treatment, recovery and treatment technologies for the reduction of Mercury emissions from the number of well-known sources; whether natural or anthropogenic [8]. In case of atmosphere, the total contribution of mercury annually is estimated to be around 5500 to 8900 ton/yr. out of which 3,780 to 6,350 ton/yr. is said to be contributed by natural sources such as from oceans, forest fires, volcanoes etc. [9]. The major anthropogenic generators of mercury include dental use and amalgam, paint and pesticides, mercury mining and production, Artisanal and small-scale gold and silver mining, chlor-alkali plants etc. of which different treatment facilities already exist like incinerators, landfill treatment and wastewater treatment processes [9]. When mercury is released in the atmosphere by any means, planktons and other small fishes becomes the target and it gets accumulated in them as methyl mercury. Ultimately, this is termed as bio-accumulation and bio-magnification as its concentration gets magnified when larger fishes eat smaller ones. Similarly, the concentration goes up the food chain [10].

Legal Framework for Mercury Pollution Control

Regulation and working of the actions depend on the regularised framework that lead to its success. Therefore, before going into the mercury pollution techniques it is important to see how it is managed internationally as well as at national level.

International Level

In United States, there is a systematic framework for handling the issues of mercury emitting from different sources. Federal and state statutes are responsible for the easy and smooth regulation of mercury such as United States Environmental Protection Agency (USEPA) is responsible for controlling of mercury emissions from pesticides, US Food and Drug Administration (FDA) regulates presence of mercury in cosmetics, food and dental products. The Occupational Safety and Health Administration (OSHA) regulates exposure of atmospheric mercury at workplaces [11]. Apart from this, Clean Air Act (CAA), Clean Water Act (CWA) and Resource Conservation and Recovery Act (RCRA) are some of the statutes accountable for developing the regulations in order to control the emissions of mercury.

As per Environment Protection Agency (EPA), mercury-specific laws namely, Mercury-containing Rechargeable Battery Management Act of 1996 and Mercury export ban Act of 2008 that basically intends to reduce the availability, usage as well as disposal of mercury based-items.

International Agency for Research on Cancer (IARC) addresses the health effects of mercury on human health in addition to other carcinogenic chemicals. International Programme on Chemical Safety (IPCS) addresses the environmental and health impacts of mercury and suggest the appropriate precautionary measures [11].

National Level

According to 42nd Amendment of the Indian constitution, regulation of toxic metals has extensively dealt. Pollution Control Boards (PCB) have actively adopted the various control measures under the concerned topic.

Table 1: Environmental Legislations Related to Mercury in India

S. No.	Legislations	Objectives	Remarks
1	The Environment (Protection) Act/ Rules, 1986	Act provides for the protection and improvement of environment by giving Central Government powers to take measures whereas Rules regulate environmental pollution, with power given to Central & State Pollution Control Boards.	Mercury is included in the standards of all the major emitting industries, but there are no regulations or standard for thermal power plants emitting mercury in the air.
2	The Water (Prevention & Control of Pollution) Act, 1974 (amendment 1988)	To provide for the prevention, control and abatement of water pollution, and the establishment of central and state boards to implement that objective.	It specifies areas affected by water pollution in the country and prohibits the use of streams or wells for disposal of polluting matter but doesn't concern with the disposal of sludge.
3	The Water (Prevention & Control of Pollution) Cess Act/ Rules, 1978	Act was primarily intended to levy and collect a cess for the abatement of pollution whereas rule specifies quantity of water to be consumed by industries.	Rule specifies the maximum quantity of water to be used for the production of caustic soda by mercury cell process.
4	The Hazardous and other wastes (Management & Transboundary movement) Rules, 2016	To establish a control mechanism for the management of hazardous wastes.	Mercury is included in the waste category.
5	The Manufacture, Storage and Import of Hazardous Chemical Rules, 1989 (amendment 2000)	Formed to regulate hazardous chemicals in the country	Chemicals are included according to the degree of toxicity
6	The Solid Wastes Management Rules, 2016	Regulates municipal solid waste	Standards set for mercury in groundwater, composts and leachate
7	The Central Insecticides Act, 1968	Regulates the import, manufacture, sale transport, distribution and use of insecticides to prevent risk to people and animals	Prohibits the import of most mercury based agro-chemicals

Source: Central Pollution Control Board. December 2009. Mercury - environmental implications & toxicity, Parivesh Publication.

The Minamata Convention on Mercury

The Minamata convention on mercury is an international treaty signed on 10th October, 2013 in Japan that became effective from 16th August, 2017 in order to protect the environment and human health from untreatable effects of mercury poisoning. The convention consists of 35 Articles and 5 Annexes. The story lies behind the Minamata disease which was firstly diagnosed in two young girls in the year 1956 in Minamata Bay, Japan [12]. This happened due to the presence of a contaminant, known as, methyl mercury $[CH_3Hg]^+$ in the wastewater discharged from a chemical industry [12]. The disease spread all over in infants, children and adults that shifted the world's focus on mercury poisoning.

The agreement focused on reducing the mercury pollution world-wide by addressing the entire life cycle of mercury and controlling its various sources [13]. The Minamata Convention follows and builds on the basis of Rotterdam, Basel and Stockholm conventions. Therefore, altogether it contributes to a comprehensive global system for regulation of hazardous substances. Following are the concerned topics of the convention that have been taken care of in addition to a global assessment of mercury and its compounds:

- Chemistry of mercury and its compounds;
- Health effects;
- Sources;
- Long-range transport;
- Prevention and control technologies.

The problem of mercury pollution was recognised due to its significant neurological and adverse health impacts particularly in infants and unborn children. Worldwide transport of mercury led to this decision of taking global action to address the problem of mercury pollution from various identified sources. According to the Article 16, namely, health impacts, countries are encouraged to promote the development and implementation of preventive programmes on occupational exposure to the mercury, identifying the population at risk, setting treatment facilities and establish institutional health care monitoring facilities.

Mercury, a hazardous substance has prolonged persistence in the environment. It has the ability to accumulate in the body of living organisms that poses negative impacts on them. The strategy of developing the legal norms to withstand the mercury-free environment has resulted in strengthening the national capabilities for the management of mercury. In 2009, the governing council of the United Nations Environment Programme (UNEP) established an Inter-Governmental Negotiating Committee (INC) to construct a legally-binding tool for efficient and effective management of mercury [14].

National Assessment of the Situation

India signed the convention on 30th September, 2014 and participated actively in all the sessions of INC. The convention gives the flexibility in adapting the national development plans in order to control the emissions of mercury by setting the reducing levels. Also, the Mercury wastes and contaminated sites are regulated by setting the environmentally sound measures. For example, controlling of newly borne atmospheric emissions of mercury governed by the convention must be done using best available technology (BAT) and best environmental practices (BEP) [15]. National implementation plans and strategies were developed by the parties to meet the objective of the convention including public awareness and education, Research & Development (R&D), information exchange facilitation etc. [15]. Primarily, mercury is used in the manufacture of thermometers, batteries, thermostat switches, lighting equipment and pharmaceuticals. In India, import of mercury was reported to be 228.19 tons in 2015-16 mainly from Japan, Singapore, USA, Indonesia and Mexico.

As per general emission standards in the country, concentration of mercury must not exceed beyond 0.2 mg/Nm3. On the other hand, standards for concentration of mercury and its compounds in cement plant with co-processing of wastes is 0.05 mg/Nm3 and for chlor-alkali industry (from hydrogen gas holder stack) is 0.2 mg/m3. In dental practices, 2 tons per annum of mercury is used in the country. 99% of producers in chlor-alkali industry have been shifted to membrane cell technology (cleaner technology), recommended by Charter on Corporate Responsibility for Environmental Protection (CREP).

In India, according to Environment (Protection) Act, 1986, there is prohibition of mercury mining activities and fortunately there is no primary mining of mercury has been reported. Mercury used in case of gold mining located in the fields of Kolar and Hatti in the state of Karnataka through cyanide process was also discontinued. Artisanal and small-scale gold mining is considered as insignificant, because it is commonly not practiced in the country. According to E-waste (Management) Rules, 2016 states the permissible limits of mercury used in fluorescent lamps. Provisions of Drugs and cosmetics Act, 1940 and rules 1945 prohibit the manufacture and import of mercury used in cosmetics. Mercury used in pesticides, biocides and topical antiseptics have been prohibited by Ministry of Agriculture and Farmer's welfare but the use of methoxy ethyl mercuric chloride (MEMC) in fungicides are still in practice for seed treatment in potato and sugarcane only.

Chemistry of Atmospheric Mercury

Mercury is found freely in nature. It is mainly present as Cinnabar ore (HgS) which is a bright red crystalline solid. Mercury is a lustrous liquid metal that can even sink in water. It is mobile and so it is used in thermometers and blood pressure instruments. It is malleable, ductile and can solidifies at -39^{0}C that can be cut with a knife. Mercury is an excellent conductor of electricity.

Three most important species of mercury are as follows:

- Elemental mercury (Hg): Mercurous (Hg^0), low solubility in water.
- Divalent inorganic mercury: Mercuric (Hg^{2+}), more soluble in water.
- Methyl mercury [CH3Hg+ or MeHg]: It is toxic and is strongly bio-accumulated in living organisms.

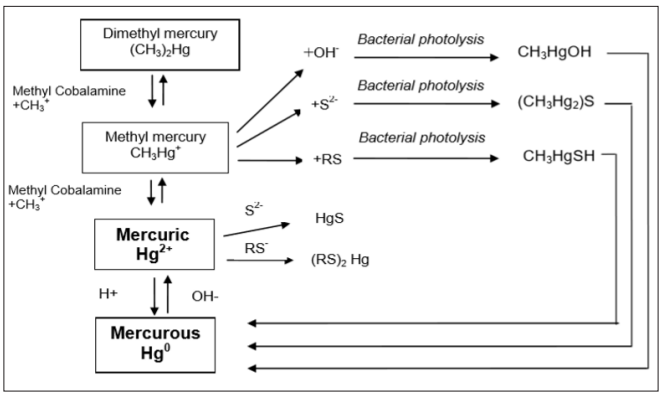

Figure 1: Environmental Chemistry of Mercury in Environment

Source: Central Pollution Control Board. December 2009. Mercury - environmental implications & toxicity, Parivesh.

Reactive gaseous mercury (RGM) that consists Hg(I) & Hg(II) compounds and particle bound mercury (PHg) are reactive forms of mercury that are deposited in the atmosphere near the emission source and are said to have short lifetime. In Northern Hemisphere, the global concentration of mercury is found to be 1.5 to 1.7 ng/m^3 and in Southern Hemisphere, 1.1 to 1.3 ng/m^3 [16].

Techniques for Controlling Mercury Emission

The extent of control of mercury is dependent on its chemical nature as well as on its form, that is oxidised or elemental. Oxidised mercury is usually captured in dust-cleaning devices such as bag filters and electrostatic precipitators (ESP) but elemental mercury does not. Therefore, to remove the atmospheric mercury efficiently, it becomes necessary to enhance by oxidising the gaseous mercury [17]. There are numerous technologies for controlling Mercury and following are the few controlling devices/techniques of primary particulates e.g. asbestos and heavy metals:

- Bag filters
- Electrostatic precipitator (ESP)
- Wet scrubbers
- Activated carbon
- Coconut pith

Bag Filters

It is one of the effective mechanism or the particulate collector with almost 99% efficiency that consists of fabric filter bags, inlet, outlet, shaker device and a dust hopper. The filter bag is usually made of a material i.e. fabric which gives the support for the filtering mechanism. When air comes in, it passes through these filters and eventually comes out as a clean air through outlet. The particulates get attached on the surface of the filters and are removed via dust hoppers simply. The thin layer of particles or rather a filter cake that settles on the filter surface is known as precoat [18].

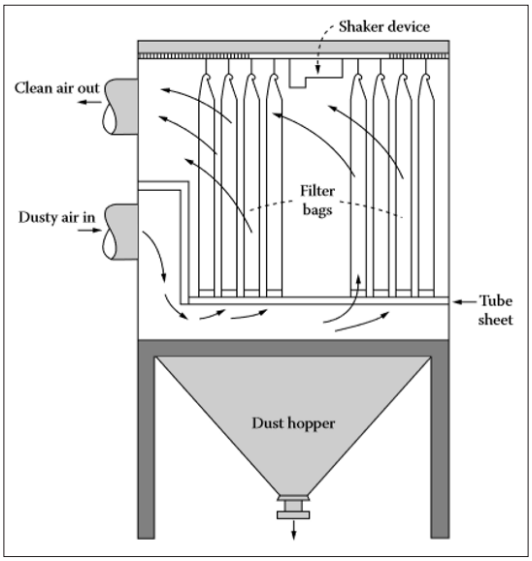

Figure 2: Single compartment baghouse filter

Source: Griffin RD (2007) Principles of Air Quality Management. Second Edition. Boca Raton: Taylor & Francis Group 170

It works efficiently when the passed gas is not too hot and wet. Often working can be enhanced by using it with the combination of dry or semi-dry sorbent injection [17]. The instantaneous flow rate through the filter is described by the following equation [19]:

$$V_s = \frac{(P_1 - P_3)}{\mu[(\Delta x/k)_{\text{cake}} + (\Delta x/k)_{\text{f.m.}}]} = \frac{Q}{A_{\text{filter}}}$$

The Δx / k terms are called the cake resistance and the cloth resistance [19].

Although, when the gas steam is cooled to the dew point of the specific material, some metals and toxic air pollutants might form condensable particulate fume. Therefore, its operation must be at temperatures above the dew point so that the metal compound is passed leaving behind the toxic metals [18].

Mercury removal has been observed better by fabric filters as compared to that of electrostatic precipitator. Their performance has been recorded by observing the results before and after the passing of the flue gas. The location for taking the samples was at five coal-fired power plants [20].

Electrostatic Precipitator (ESP)

Electrostatic precipitators use electrostatic forces for the separation of dust particles from exhaust gases. Main factors that affect the collection efficiency are particle size distribution and electricity resistivity in addition to the temperature, moisture content and flow rate [17].

Toxic metals are significantly controlled by wet ESPs as compared to that of dry ESPs [18]. Operation of a wet ESP takes place with the help of water vapour saturated air streams i.e. humidity is 100% [17]. The working principle is based on electrical ionisation and charging of particles or droplets in the steam. The charged particles migrate towards the concerned electrode after passing through an electrical field. Ultimately, collected particulates are removed mechanically or washed online with a water solution.

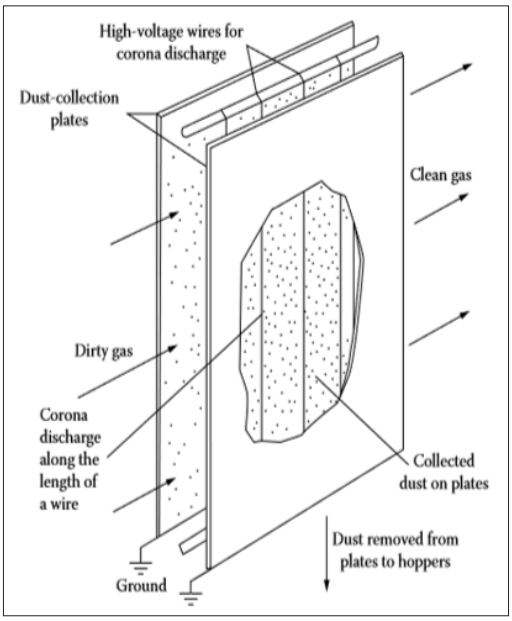

Figure 3: Single-stage Electrostatic precipitator

Source: Griffin RD (2007) Principles of Air Quality Management. Second Edition. Boca Raton: Taylor & Francis Group 173

Wet Scrubber

Wet scrubber provides control for gaseous emissions by the process of chemical absorption. The efficiency of dust removal is said to be 98% but the final concentration of dust is relatively high i.e. over 5 mg/Nm^3 [17]. Common types of wet scrubber

are as follows:

- Spray chambers
- Plate (tray) chambers
- Centrifugal
- Dynamic (Wet fan)
- Venturi

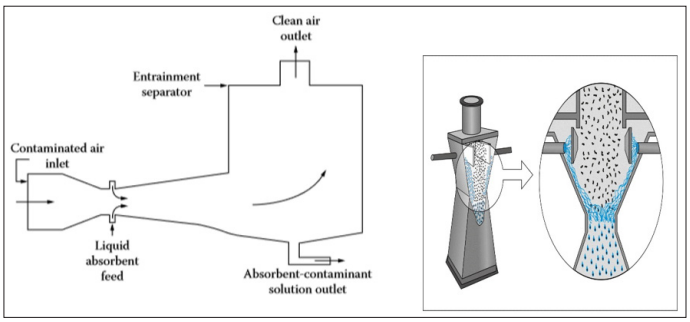

Figure 4: Venturi Scrubber

Source: Griffin RD (2007) Principles of Air Quality Management. Second Edition. Boca Raton: Taylor & Francis Group 172

Venturi scrubbers use liquid steam to remove particles. Gas laden with particulate matter passes through a short tube with flared ends and a constricted middle. This constriction causes the gas steam to speed up when the pressure is increased. The difference in velocity and pressure resulting from the constriction causes the particles and water to mix and combine. The reduced velocity at the expanded section of the throat allows the droplets of water containing the particles to drop out of the gas stream. Absorption of elemental mercury can be improved by the addition of activated carbon or sulfur compounds to the scrubber liquor (Miller et al.,2014). To limit the risk of mercury that is posed to human health, the Environmental Protection Agency (EPA) has announced that it will alter or regulate the mercury emissions and other toxics in the atmosphere from coal and oil-fired power plants [21].

Activated Carbon

It is an effective sorbent for mercury capture from flue gas and it is temperature dependent. Therefore, when temperature decreases, removal become effective (below 175°C) [17]. It can be injected to the upstream of dust-cleaning devices. Although, it may pose a risk of fire and explosion due to its bad quality so dilution of carbon with inert material is suggested.

Table 2: Minimum expected performances of activated carbon techniques for mercury removal expressed as hourly average mercury concentrations

Control techniques	Mercury content after cleaning (mg/m^3)
Carbon filter	<0.01
Sulfur-impregnated carbon filter	<0.01
Carbon injection + dust separator	<0.05
Injection of brominated activated carbon + dust separated	0.001
Source: Guidance document on best available techniques for controlling emissions of heavy metals and their compounds, annex II (ECE/EB.AIR/116,2013)	

Coconut Pith

Coconut pith has very good adsorption capacity of elemental mercury. The adsorption capacity in case of activated carbon is observed to be much lower as compared to coconut pith with a difference of almost 3,023 µg/g of adsorption capacity. Therefore, this indicates that coconut pith can replace activated carbon effectively [22].

Conclusion

Mercury capture by various dust-abatement techniques such as Electrostatic precipitators (ESPs), activated carbon, wet scrubbers etc. poses great help towards the protection of human health which is a main objective of the international agreement, the Minamata Convention on Mercury. The agreement has been a great success in the country and more or less, all over globe. India alone has cut-down mercury pollution to a significant level by prohibition of mercury mining activities, setting permissible limits for mercury in fluorescent lamps, prohibition of manufacture and import of mercury used in cosmetics etc. Also, shifting of mercury thermometers to digital thermometers and blood pressure instruments has been a great achievement in reducing the use of mercury. Almost all the chlor-alkali industries have been shifted to a cleaner technology i.e. membrane cell technology. Mostly, elemental mercury is not captured by these dust-cleaning devices. The remedy of this problem lies in oxidation of gaseous mercury. To improve the efficiency of removal of mercury, oxidising agents such as halogens may be added or injected to the flue gas. The same can be achieved by using activated carbon impregnated in addition to halogens or sulphur.

Concerning the management of mercury emissions associated with coal burning and other sources in India, an important step would be to identify the regions and industries that are leading in atmospheric mercury emission levels for successful implementation of the Minamata Convention on Mercury. Mercury management action plans need to be implemented for selected industries along with a national roadmap that facilitates the development of a National Action Plan for the Minamata Convention. A sound and effective management of mercury pollution in India would be a complement to ongoing efforts to achieve the Sustainable Development Goals [23-25].

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