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MERCURY EMISSION MONITORING AND CONTROL IN INDIA

BEST TECHNOLOGIES, TECHNIQUES AND PRACTICES FOR COAL-FIRED POWER PLANTS

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INTERNATIONAL CENTRE FOR
SUSTAINABLE CARBON

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PREFACE

This report has been produced by the International Centre for Sustainable Carbon (ICSC) and is based on a survey and analysis of published literature and on information gathered in discussions with interested organisations and individuals. Their assistance is gratefully acknowledged. It should be understood that the views expressed in this report are our own and are not necessarily shared by those who supplied the information, nor by our member organisations.

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BACKGROUND

This technical report represents the results of a piece of work that forms part of a significant project undertaken by the ICSC on behalf of the US Department of State (USDOS), Agreement Number: SLMAQM19CA238: Capacity building in Southeast Asia to reduce mercury and other pollutant emissions from the coal combustion sector. The project comprises two major areas of work to reduce emissions from the coal-fired power sector: one in Indonesia focusing on mercury emissions; and the second in India which addresses additional pollutants – sulphur dioxide (SO_2), nitrogen oxides (NOx), and particulate matter (PM) as well as mercury. The project in India is focused on knowledge sharing and capacity building, in three pillars of work:

- Pillar 1 – emissions monitoring;
- Pillar 2 – emissions reduction, and ash management;
- Pillar 3 – flexibility of plant operation.

This report presents work from Pillar 2: emission reduction, and ash management. The report will help industries, regulators, and related stakeholders to learn about mercury emission issues, monitoring practices, and best practices for control, in order to align with Minamata Convention obligations and goals.

More details on the US Department of State project can be found on the ICSC website www.sustainable-carbon.org.

ABSTRACT

India is the second largest national emitter of mercury in the world and coal contributes 80% of India's national emissions. It is therefore inevitable that mercury emissions must be monitored and controlled from the coal sector as a priority in India. The complex behaviour of mercury in a coal plant must be fully understood to achieve emission reduction, which can be cost effective, but only if the correct techniques and technologies are applied. This report summarises best practices to measure and reduce mercury emissions from the coal utility sector in India, focusing on the regional challenges.

ACRONYMS AND ABBREVIATIONS

ACI	activated carbon injection
BAT	best available technology
BEP	best environmental practice
CEM	continuous emissions monitor
CFBC	circulating fluidised bed combustion
COMET	Cormtech oxidised mercury emission technology
CEN	Comité Européen de Normalisation (European Committee for Standardization)
CFR	Code of Federal Regulations, USA
CPCB	Central Pollution Control Board, India
DBD	dielectric barrier discharge
ECO	electrocatalytic oxidation
ELV	emission limit value
EPRI	Electric Power Research Institute, USA
ESP	electrostatic precipitator
EU	European Union
FF	fabric filter (baghouse)
FGD	flue gas desulphurisation
FTIR	Fourier transform infrared spectroscopy
ICR	information collection request
ICSC	International Centre for Sustainable Carbon
IEA	International Energy Agency, France
MACT	maximum achievable control technology
MATS	Mercury and Air Toxics Standard, USA
MEP	Ministry of Environmental Protection, China
MOEFCC	Ministry of Environment, Forest, and Climate Change, India
PM	particulate matter
POG	process optimisation guidance
PRB	Powder River Basin
ROM	run of mine
SCR	selective catalytic reduction
SDA	spray dry absorber
SNCR	selective-non catalytic reduction
SES	Source Evaluation Society, USA
RATA	relative accuracy test audit
UNEP	United Nations Environment Programme
USEPA	United States Environmental Protection Agency
WESP	wet electrostatic precipitation
WFGD	wet flue gas desulphurisation

Note: all monetary values are in United States dollars ($) unless otherwise stated.

UNITS

Btu	British thermal unit
g/h	gramme per hour
kg/h	kilogrammes per hour
kPa	kilopascal
mg	milligramme
mg/m^3	milligramme per cubic metre
ppm	parts per million (concentration)
t	metric tonne (1 tonne = 1000 kg)
t/y	tonnes per year
$\mu g/m^3$	microgramme per cubic metre

CHEMICALS

$CaBr_2$	calcium bromide
CH_3Hg	methyl mercury
CuO	copper oxide
Fe_2O_3	iron oxide
H_2SO_4	sulphuric acid
HCl	hydrogen chloride
Hg^{2+}	ionic mercury
Hg^0	elemental mercury
Cl_2	chlorine gas
NOx	nitrogen oxides
Hg(p)	particulate mercury
SeO_2	selenium dioxide
SO_2	sulphur dioxide
SO_3	sulphur trioxide
TiO_2	titanium dioxide
V_2O_5,	vanadium pentoxide
WO_3	tungsten trioxide

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1 INTRODUCTION

The coal-fired power sector is one of the most polluting in India, contributing around 60% of the total particulate matter (PM), 45% of the total sulphur dioxide (SO_2), 30% of the total nitrogen oxides (NOx), and more than 80% of the total mercury (Hg) emissions from all industrial sectors in 2020.

Emission limits for PM, SO_2 and NOx have become common for the coal sector in many countries over the past 3-4 decades. Recently, limits for mercury have also been added to many national policies. In 2003, the United Nations (UN) declared mercury to be the pollutant of greatest global concern because, at that time, environmental concentrations were rising and there was no international coordination on reducing emissions. Mercury is a toxic element which can spread globally in the air. In aquatic systems, mercury can be converted into extremely toxic methyl mercury (CH_3Hg). This methyl mercury bioaccumulates in the aquatic food chain and enters the human body mainly through the consumption of fish. High levels of mercury exposure can harm the brain, heart, kidneys, lungs, and immune systems of people of all ages but is especially toxic to developing infants. In the 1950s, the industrial pollution of Minamata Bay in Japan with methyl mercury caused decades of contamination and significant health effects. This incident led to the development of the Minamata Convention, which India ratified on 18 June 2018.

In the past two decades, the focus on mercury emissions has grown significantly and internationally and national emissions inventories are being collated. The United Nations Environment Programme (UNEP, 2018) report estimated annual global mercury emissions at 2220 tonnes per year (t/y), as shown in Figure 1.

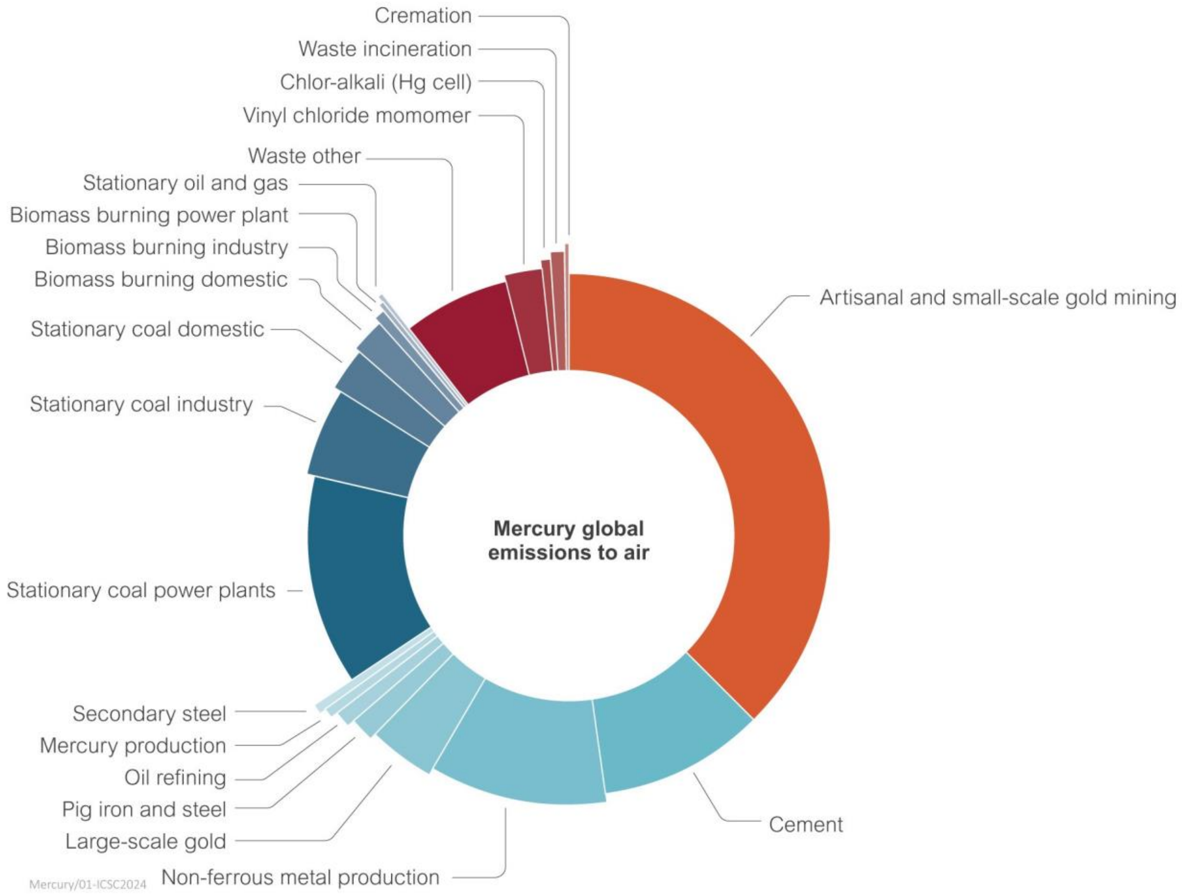


Figure 1 Global mercury emissions by sector in 2018 (AMAP, 2021)

Fossil fuels contribute 24% of global emissions and coal-fired power plants alone contribute 13.1%. The artisanal and small-scale gold mining (ASGM) sector is by far the largest source of emissions. However, since ASGM activities are illegal and generally carried out by small remote communities, data are scarce and reducing emissions is a complex social and economic challenge. Reducing emissions from sectors such as coal is therefore seen as being easier and more cost-effective.

With respect to the geography of emissions almost 40%, of mercury arises from activities in southeast Asia, as shown in Table 1.

TABLE 1 GLOBAL MERCURY EMISSIONS, 2015 (UNEP, 2018)

small-scale	Sector group (emissions, t)					
Mercury emissions to air from anthropogenic sources in 2015, by sector and region, t	**Fuel consumption**	**Industry sectors**	**Intentional use (including product waste)**	**Artisanal and small-scale gold mining**	**Regional total (range), t**	**% of global total**
Australia, New Zealand, Oceania	3.57	4.07	1.15	0	8.79 (6.93-13.7)	0.4
Central America and the Caribbean	5.69	19.1	6.71	14.3	45.8 (37.2–61.4)	2.1
CIS and other European countries	26.4	64.7	20.7	12.7	124 (105–170)	5.6
East and Southeast Asia	229	307	109	214	859 (685–1430)	38.6
EU28	46.5	22.0	8.64	0	77.2 (67.2–107)	3.5
Middle Eastern States	11.4	29.0	12.1	0.225	55.8 (40.7–93.8)	2.4
North Africa	1.36	12.6	6.89	0	20.9 (13.5–45.8)	0.9
North America	27.0	7.63	5.77	0	40.4 (33.8–59.6)	1.8
South America	8.25	47.3	13.5	340	409 (308–522)	18.4
South Asia	125	59.1	37.2	4.50	225 (190–296)	10.1
Sub-Saharan Africa	48.9	41.9	17.1	252	360 (276–445)	16.2
Global inventory	**533**	**614**	**239**	**838**	**2220 (2000–2820)**	**100.0**

According to the AMAP (2021) report, which was produced in support of the Minamata Convention, India is the second largest emitter of mercury after China. The latest data available for 2021 indicate the total mercury emission from India at 144.7 t/y, over 89 t of which comes from the coal combustion sector (*see* Figure 2).

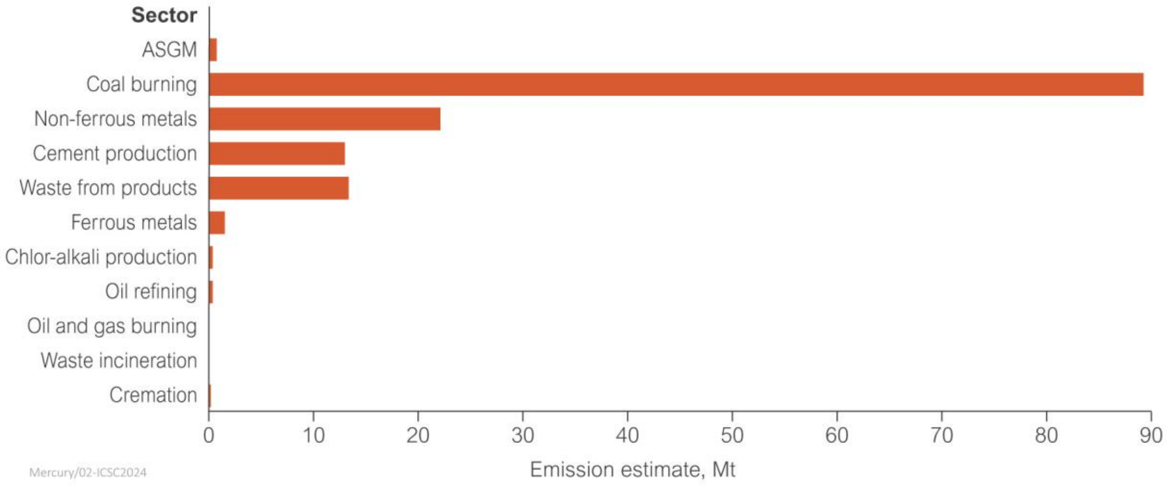


Figure 2 Mercury emissions from different sectors in India (Tableau, 2023)

As the coal sector is by far the largest source of mercury emissions in India it should be the main target for reduction strategies.

A recent and related ICSC report (Sloss and others, 2021) found that mercury monitoring and reporting is virtually non-existent in India. Without data, it is not possible to evaluate appropriate strategies for emission reduction. Under national and international commitments to reduce pollutant emissions, India is likely to step up its action to clean up coal-fired power plants. Although it can learn from experience in countries that have already developed emission reduction strategies, the path for India may be more challenging due to issues such as high ash coals, low water availability, limited national skillsets and experience and financial limitations.

This report is intended to summarise knowledge and best practice in mercury emission monitoring and control specifically for the Indian coal-fired power sector, regulators, and related stakeholders. Chapter 2 covers relevant emission legislation. Chapter 3 explains mercury behaviour in a standard coal-fired plant and Chapter 4 then looks at how mercury capture can be maximised in such plants. Chapter 5 focuses on mercury-specific control technologies with Chapter 6 providing guidance on technology selection. Finally, Chapter 7 reviews monitoring technologies that will be vital for compliance reporting as well as for the development and implementation of effective emission reduction strategies.

2 LEGISLATION FOR MERCURY CONTROL

As a result of growing concern over increasing concentrations of mercury worldwide, international conventions and national policies are evolving to target relevant sources to halt the rise in global emissions ultimately leading to a reduction in emissions.

2.1 INTERNATIONAL – UN MINAMATA CONVENTION

The UN Minamata Convention recognises 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 Convention is a multilateral environmental agreement (MEA) which entered into force on 16 August 2017 with the aim of protecting human health and the environment from emissions and releases of mercury and its compounds. As of January 2024, there are 128 signatories and 147 parties to the convention. India signed on 30 September 2014 and ratified on 18 June 2018 (https://minamataconvention.org/en).

The Minamata Convention comprises 35 Articles and 5 Annexes, the most relevant for coal-fired power plants being Articles 8 and 9 and Annex D, relating to controls on air emissions and releases to land and water (UNEP, 2021). Annex D of the Convention covers emissions from five types of point sources:

- coal-fired power plants;
- coal-fired industrial boilers;
- smelting and roasting processes in non-ferrous metal production;
- waste incineration; and
- cement clinker.

Article 8, which applies to coal-fired power plants, requires parties to implement the following measures in a national plan as soon as practicable and not beyond 10 years after the date of entry into force of the Minamata Convention (UNEP, 2019):

- a quantified goal for controlling and, where feasible, reducing emissions from relevant sources;
- emission limit values (ELV) for controlling and, where feasible, reducing emissions from relevant sources;
- the use of best available techniques (BAT) and best environmental practices (BEP) to control emissions from relevant sources;
- a multipollutant control strategy to deliver co-benefits for control of mercury emissions; or
- alternative measures to reduce emissions from relevant sources.

Article 8 also requires each party to establish, ‘as soon as practicable and no later than five years after the date of entry into force of the Convention for it, and maintain thereafter, an inventory of emissions from relevant sources. The same Article obliges parties to use BAT and BEP and provides support for parties to implement these measures by determining goals and setting ELVs. For this, UNEP has developed a guidance document (UNEP, 2019). This current project – *Capacity building in Southeast Asia to reduce mercury and other pollutant emissions from the coal combustion sector* – being executed by the ICSC on behalf of the US Department of State – aims to inform, assist, and accelerate India’s compliance with the Convention.

Prior to the entry-into-force of the Minamata Convention, India had implemented several international environmental regulations for pollutants including those specified in MEAs such as the Rotterdam, Basel, and Stockholm Conventions. The Minamata Convention follows the structure of these conventions and sets out similar basic substantive obligations for parties to manage mercury pollution while providing some differentiation and flexibility in specific provisions. The Convention requires signatory countries to mobilise, within national capabilities, financial resources for implementation. Since India is a party to all these conventions, their enforcement in India has led to formulating and amending several important national environmental regulations in the country (Sharma and others, 2019). These regulations include:

- the Environment (Protection) Act, 1986;
- the Environment (Protection) Act, 1986;
- the Water (Prevention and Control of Pollution) Act, 1974; and
- the Hazardous and Other Wastes (Management, Handling and Transboundary Movement) Rules, 2016.

The major regional mercury emitters - China, India, and the USA - have all stipulated mercury emission standards or norms for coal-fired power plants. The USA has the strictest norms and, currently, China and India have significantly fewer challenging norms. After several years of delays, the EU established emission limits for mercury emissions from coal plants in 2017 which are similarly challenging to those in the USA.

2.2 NATIONAL LEGISLATION

Countries have set their own emission limits for mercury specifically for coal-fired power plants. The format and stringency of these vary according to national targets and regional units of measurement.

2.2.1 USA

The US Environmental Protection Agency (USEPA) National Emission Standards for Hazardous Air Pollutants (NESHAP) for coal- and oil-fired utility boilers, commonly known as the Mercury and Air Toxics Standards (MATS), were promulgated on 16 February 2012 (77 FR 9304) (2012 MATS Final Rule), under title 40 part 63, subpart UUUUU. An existing affected source is any single or collection of coal- or oil-fired electricity-generating boilers in a subcategory within a single contiguous area and under common control. The stringency of the applicable limit varies with fuel type and the age of the unit but applies to any commercial fossil-fired unit over 25 MW in size. 'New' plants are defined as those for which construction or reconstruction began after 3 May 2011. The emissions limits are summarised in Table 2 (USEPA, 2023).

TABLE 2 MERCURY EMISSION STANDARDS FOR POWER PLANTS IN THE USA (NRDC, 2012)

EPA MACT FINAL Rule, 2012	
Existing power plants	**Mercury emission limit (lb/GWh)**
Regular coal	0.013
Designed for low rank coal/lignite	0.12 or 0.040
IGCC (integrated gasification combined cycle)	0.030
Solid-oil-derived/ Continental liquid oil	0.0020
Non-continental liquid oil	0.0040
New power plants	**Mercury emission limit (lb/GWh)**
Regular coal	0.00020
Designed for low rank coal/lignite	0.040
IGCC	0.0030
Solid-oil derived	0.0020
Continental liquid oil	0.00010
Non-continental liquid oil	0.00040
Note: Lignite or low rank coal power plants in the USA have a much less stringent standard	

It is important to note that the US emission standards are expressed in lb/GWh to take into account the efficiency of the plant rather than just the concentration of pollutants being released from the stack. If the US limits are converted into a concentration basis, as mg/m^3, by factoring in an average coal heating value, they work out as 0.0017 mg/m^3 (0.013 lb/GWh) for a bituminous coal plant and 0.0153 mg/m^3 (up to 0.12 lb/GWh) for a lignite coal plant (NRDC, 2012).

2.2.2 European Union

Emission limits for mercury in Europe were adopted in July 2017 but, following significant debate, only became applicable in August 2021. The limits, which vary by coal type and by plant age and size, were determined based on assumptions relating to the emission values which are achievable using BAT. The limits are as shown in Table 3 (EIPIE, 2021).

TABLE 3 MERCURY EMISSION LIMITS FROM COAL AND LIGNITE POWER PLANTS IN EUROPE (EIPIE, 2021)

Combustion plant total rated thermal output, MWth	Annual average or average of samples obtained over one year, µg/m^3			
	New coal	New lignite	Existing coal	Existing lignite
<300	<1–3	<1–5	<1–9	<1–10
>300	<1–2	<1–4	<1–4	<1–7

The values are shown in ranges as the achievability of mercury reduction, even with state-of-the-art technologies, varies with coal chemistry and plant configuration. The actual emission limit for each unit will be determined in agreement with the local authority and written into the plant-specific compliance plan.

These EU limits are in different units from those set in the USA (Section 2.2.1) but are similarly challenging.

2.2.3 China

China's Ministry of Environmental Protection (MEP) adopted air pollutant emission standards for coal-fired power plants on 18 July 2011 to be effective from 1 January 2012. In addition to mercury, the new standards regulate emissions of PM, SO_2 and NOx. The emission limit for mercury and mercury compounds is 0.03 mg/m^3, for both new and existing coal-fired power plants beginning on 1 January 2015 (NRDC, 2012). This limit is significantly more lenient (around an order of magnitude) than the limits set in the USA and EU.

2.2.4 India

Prior to 2015, there were only lenient PM emission limits, or 'norms', (in the range of 150–350 mg/m^3) and there were no limits set for SO_2, NOx or mercury (CSE, 2017). The Ministry of Environment, Forest, and Climate Change (MOEFCC) of the Government of India (GOI) announced new norms for Indian power plants in December 2015 which were expected to be effective two years from the date of notification. However, the regulations faced multiple hurdles and delays. As of January 2024, the norms have varying deadlines as far as 2025, depending on the plants' proximity to densely populated areas. The new norms and their implementation in India are covered in previous ICSC reports:

- *Status of continuous emission monitoring systems at coal-fired power plants in India* (Sloss and others, 2021);
- *Achieving 100% ash utilisation in coal-fired power plants in India* (Sloss and others, 2023a); and
- *Accelerating emission control at coal-fired power plants in India* (Sloss and others, 2023b).

The mercury emission norm for coal-fired power plants in India is 0.03 mg/m^3, which is the same as that in China, at present. This is 2–20 times more lenient than those in the USA and EU. The norm was initially proposed in December 2015 and was to be applicable by January 2017 but, as with the norms for other air pollutants, the compliance deadline has been delayed.

Under the current applicable staged implementation plan, introduced in April 2021, the compliance deadlines vary depending upon the three plant categories – Category A, B and C – defined by their proximity to populated areas. Plants in more densely populated areas are obliged to comply sooner than those which affect fewer people. Depending on the plant ranking, the deadlines for compliance published by MOEFCC start from December 2022 and continue until December 2025 as shown in Table 4.

TABLE 4 RANKING OF PLANTS FOR COMPLIANCE DEADLINE (MOEFCC, 2021)

Rank	Category	Location/area	Timeline for compliance	
			Non-retiring units	Retiring units
1	Category A	Within a 10 km radius of the national capital region or cities with a population >1 million*	Up to 31 Dec 2022	Up to 31 Dec 2022
2	Category B	Within a 10 km radius of a critically polluted area† or non-attainment city†	Up to 31 Dec 2023	Up to 31 Dec 2025
3	Category C	Other than those included in Category A and B	Up to 31 Dec 2024	Up to 31 Dec 2025

* as per the 2011 population count † as defined by CPCB

Retiring units which are not in compliance by the deadline should close immediately. However, units declaring retirement before the date specified in the 'retiring units' column of Table 4 will not be required to meet the specified limits, provided that they submit a petition to the Central Pollution Control Board (CPCB) and Central Electricity Authority (CEA) for an exemption. If these units continue to operate beyond the date specified in their petition, they will be subject to penalties at the rate of 0.20 rupees per unit of electricity generated (kWh) (equivalent to around 0.002 $/kWh or less).

Schedules of penalties for non-retiring, non-compliant units are shown in Table 5. The penalties increase with the growing length of the non-compliance period and depend on the plant's category classification. The values in Table 5 are equivalent to around 0.001 $/kWh or less.

TABLE 5 PENALTIES FOR NON-COMPLIANT POWER PLANTS (MOEFCC, 2021)

Non-compliant operation beyond the timeline, days	Category A	Category B	Category C
0–180 days	0.10	0.07	0.05
181–365 days	0.15	0.10	0.075

2.3 COMMENTS

The USA was one of the first countries to set mercury emission limits for coal-fired power plants which would require remedial action to be taken in order to achieve compliance. The emission limits in Europe are similarly challenging for some plants, especially lignite units (which have more challenging mercury chemistry, *see* Chapter 3). The emission limit in India is currently relatively lax and is only now becoming applicable to plants in densely populated areas; plants in less populated areas will be targeted later. The current mercury limit is not likely to require significant mercury-specific control.

The UN Minamata Convention on Mercury, to which India is now a ratified party, does not oblige signatory countries to set strict emission limits. However, it does require parties to quantify emissions and to control, and where, feasible, reduce these emissions through appropriate action. India is one of the largest regional emitters of mercury and the majority of this mercury comes from the coal sector. As a result, the emission limit for coal-fired plants in India may tighten in future as the country strengthens its commitments under the Convention.

3 MERCURY CHEMISTRY IN COAL AND COAL COMBUSTION

Coal-fired power plants contribute nearly 80% of total mercury emissions in India, as mentioned in Chapter 1 (CSE, 2020). Mercury is released from coal during combustion and its behaviour and ultimate emission are determined by several factors including the coal characteristics and combustion chemistry as well as the presence and performance of downstream pollution control devices.

Mercury chemistry is the key to mercury control – certain species of mercury are captured more easily than others. By understanding mercury behaviour and influencing the changes in mercury chemistry as it passes through the entire coal plant it is possible to maximise mercury control and reduce emissions.

3.1 MERCURY CONTENT IN COAL

The mercury concentrations of coals vary greatly and, even though average mercury contents are often published for different coal types and ranks, actual coal mercury contents can vary considerably even from seam to seam.

The National Coal Resources Data System (NCRDS) of the US Geological Survey (USGC) is the largest publicly available database intended to assess coal quality and quantity of in-ground coal resources in the USA. The US Geochemical Database (USCHEM) includes a subset of the database called COALQUAL. This contains an analysis of large number of samples representing the wide distribution of US coal quality and characteristics. The database can be accessed at: https://ncrdspublic.er.usgs.gov/coalqual/

According to the COALQUAL database, the mean concentration of mercury in US coal is approximately 0.2 ppm, with the lowest value reported as 0.08 ppm for coal from the San Juan River coal area and the highest reported as 0.22 ppm for coal from the Gulf Cost lignite area. If estimated on an energy basis, mercury concentrations tend to be lower in higher rank coals. This is because high rank coals have lower moisture and a higher calorific value, therefore less coal is required per kWh of energy produced, and so less mercury is released.

Mercury concentrations also vary globally. The mercury concentrations of Australian coals are reported to be considerably lower than US coals at between 0.016 and 0.076 ppm mercury (Newman-Sutherland and others, 2001). South American coals are reported to have similarly low mercury contents (Mukherjee and others, 2008). A study by the Mineral and Energy Economy Research Institute, Poland, found that the bituminous coal deposits in the three coal basins – Upper Silesian (USCB), Lublin (LCB), and Lower Silesian (LSCB) – differ greatly in mercury content. The highest mercury concentrations were found in the Lower Silesian Coal Basin where the average mercury content in the Nowa Ruda mine was 0.399 ppm. A much lower average mercury content was recorded for both the LCB and USCB coal basins at 0.074–0.092 ppm and 0.105 ppm in the LCB (Auguścik-Górajek and Niec, 2020). Mercury contents in coals are therefore considered highly variable and care must be taken when assuming the mercury content of any coal.

Indian plants use bituminous and subbituminous coal in coal-fired power plants and, as with other countries, research shows a wide range of mercury contents in Indian thermal coal. Tarit and others (2020) studied a total of 165 Indian coal samples and found a wide variation of mercury content in the coal from 0.003 to 0.554 g/t with an average of 0.175 g/t of coal.

The complementary ICSC report by Sloss and others (2023b) reported on the quality of coal from key mines of Coal India Limited (CIL) which produce over 80% of India's coal in the Northern Coalfields Limited (NCL), Southeastern Coalfields Limited (SECL) and Mahanadi Coalfields Limited (MCL). The coal quality and mercury content are given in Table 6.

TABLE 6 INDIAN COAL QUALITY ANALYSES (UNEP, 2014)

	Production, Mt (2020-21)	Moisture, %	Ash, %	GCV*, kcal/kg	Sulphur, %	Mercury, µg/g
NCL Coal	115.04	7.1	31.5	4437	0.37	0.21
SECL Coal	150.61	6.2	25.4	5318	1.09	0.14
MCL Coal	148.01	5.9	40.1	3779	0.46	0.20
'Average' coal		6.4	32.3	4511	0.64	0.18

* Coal properties from UNEP, 2014; GCV: Gross calorific value

Another study by Agarwalla and others (2023) found the mercury content in the coal from Southeastern Coalfields (SECL) to be in the range of 0.011 to 0.188 ppm (Agarwalla and others, 2023). UNEP (2018) reported a wider range of estimates for the mercury content in Indian coal of 0.003–0.34 ppm with average concentration of 0.14 ppm.

Sloss and others (2023a) compiled data on the average mercury concentrations in coals from China, India, USA, Australia, Russia, Indonesia, and South Africa, as shown in Table 7.

TABLE 7 AVERAGE MERCURY CONCENTRATIONS IN REGIONAL COALS (SLOSS, 2023A)

Country	Mercuryconcentration, ppm (dry basis)
China	0.009–1.527
USA	0.003–1.800
India	0.100–0.300
Australia	0.018–0.114
Russia	<0.002–0.065
Indonesia	0.022–0.190
South Africa	0.170–0.450

Although coals with higher concentrations of mercury will release more mercury, the mode of occurrence of mercury in the coal influences how it will behave. However, since mercury is present in very low concentrations in coal and volatilises at low temperatures (150°C), it is difficult to establish the mode and occurrence of mercury in the coal through direct data. Following classic research such as that of Toole and others (1998), it is now commonly assumed that a substantial proportion of mercury in coal is associated with pyrite (iron disulphide, FeS_2) and some with organic constituents and other minerals.

Surprisingly, other coal components such as halogens and unburnt carbons can have a more prominent effect on mercury emissions than the coal mercury content itself. Coal, which is inherently high in halogens (such as chlorine and bromine) releases more mercury in the oxidised form during combustion which is easy to capture. Coals or combustion conditions which produce a high unburnt carbon content may also help enhance mercury capture in the particulate fraction. However, unburnt carbon is often a sign of inefficient combustion which is not optimal for plant operators.

3.2 MERCURY CHEMISTRY IN COAL-FIRED BOILERS

During combustion, the mercury in coal is volatilised and converted to elemental mercury (Hg^0) vapour in the high-temperature regions of the boiler. Almost all of the mercury in coal is released into the flue gas in the form of Hg^0 during combustion over 1000°C. With the decrease of flue gas temperature, as it flows out of the boiler, a portion of Hg^0 is oxidised to Hg^{2+} mainly by active atomic chlorine (Cl). Ionic mercury (Hg2+) compounds and any forms of mercury which are in a solid phase at flue gas cleaning temperatures (for example, from 120°C to around 180–200°C in a typical subcritical plant) can be adsorbed onto the surface of other particles to create particulate mercury, Hg(p). Mercury behaviour during coal combustion is affected by many important factors including:

- mode of occurrence in the fuel;
- temperature and pressure;

- oxidising or reducing conditions;
- the presence of halogens, most importantly native chlorine or added bromine; and
- the presence of compounds that can act as sorbents such as calcium.

Mercury enters the flue gas cleaning device(s) as a mixture of Hg^0, Hg^{2+}, and Hg(p). The cycling of chlorine is the dominant mechanism of continuing mercury oxidation. This reaction is driven by thermodynamic equilibrium but restricted by reaction kinetics. However, it is commonly established that the greater the amount of chlorine (or bromine) in the flue gas, the higher the oxidation rate of mercury. Conversely, SO_2 and NO in flue gas inhibit the oxidation of mercury (Zhang and others, 2013).

The specific surface area of fly ash particles and the quantity of unburnt carbon, often referred to as loss-on-ignition (LOI), will affect the amount of mercury which will be captured on particulates. Inorganic components such as CuO, TiO_2, and Fe_2O_3 may also have significant impacts on the mercury oxidation and adsorption processes (Zhang and others, 2016).

Although coal chemistry is important and variable, in general, the majority of gaseous mercury in bituminous coal-fired boilers is produced as Hg^{2+} whereas the majority of gaseous mercury in subbituminous- and lignite-fired boilers is produced as Hg^0. As mentioned above, together, the total chlorine and mercury content of the coal have the most significant impacts on the percentage of mercury as Hg^{2+}, while the ash content and chemistry have a stronger influence on the proportion of Hg(p). The proportions of Hg^0, Hg^{2+} and Hg(p) in the flue gas released from a pulverised coal-fired boiler average around 55%, 35% and 10%, respectively. However, the proportion of Hg^{2+} can range from 5% to 82% while Hg(p) ranges from 1% to 28%.

Besides coal properties, the boiler type also affects mercury speciation in flue gas; a circulating fluidised bed (CFB) boiler can generate as much as 65% Hg(p) in the flue gas due to more contact between gaseous phase mercury and the fly ash inside the boiler (Zhang, 2012).

The behaviour of mercury in combustion systems is complex and variable but it can be modelled with the use of the interactive process optimisation guidance tool iPOG, developed by the UN Mercury Coal Partnership. The iPOG is discussed in more detail in Chapter 6.

3.3 COMMENTS

Mercury emissions from coal combustion are determined less by the concentration of mercury in the coal and more by its chemical state. Oxidised and particulate mercury are easily captured on fly ash and/or in downstream pollution control devices whereas elemental mercury can pass through a plant unhindered. Mercury chemistry varies as it passes through the plant depending on temperature, pressure, and the presence of other chemicals, especially those such as halogens which have the potential to oxidise elemental mercury. Understanding, predicting, and controlling mercury chemistry is the key to cost-effective mercury control.

4 OPTIMISING MERCURY CONTROL IN EXISTING PLANTS

Mercury chemistry is the key to mercury capture, as discussed in Chapter 3. By understanding how mercury can be converted to more easily captured forms, plant operators can maximise mercury control within the plant. This means maximising 'co-benefit' control to achieve cost-effective emission reduction with minimal additional plant modification.

Table 8 includes the potential mercury reduction which can be achieved at coal-fired power plants by maximising the performance of the plant and by taking advantage of existing control systems.

TABLE 8 MERCURY REDUCTION EFFICIENCY WITH DIFFERENT POLLUTION CONTROL SYSTEMS (SLOSS, 2023)

	Control Method	Mercury reduction potential, %	Co-benefits
Pre-combustion	Reduced coal use (efficiency improvement methods)	Up to 34	Efficiency improvement, reduced emissions
	Coal treatment (washing, beneficiation, blending, additives and so on)	10–78	Efficiency improvement, reduced emissions
Post-combustion	PM control	1–90	Reduced emissions
	PM control and sorbent injection	2–98	Reduced emissions
	PM control and wet flue gas desulphurisation (FGD)	10–98	Reduced emissions

The effectiveness of these systems for mercury control is extremely variable with coal characteristics and so the ranges quoted are wide.

4.1 PRE-COMBUSTION OPTIONS

Pre-combustion measures to control mercury emission are intended to reduce the mercury entering the system and, if possible, to optimise the coal and combustion chemistry to maximise the capture of the remaining mercury entering the plant. Operators can use a combination of the options below:

- selection of low-mercury content coal (rarely, if ever, an economically viable choice);
- coal washing or improvement of existing coal washing technologies;
- coal blending with cleaner coals; and
- cofiring with lower mercury fuels such as natural gas and biomass.

4.1.1 Coal mercury content

As mentioned in Chapter 3, the mercury content of coal can vary significantly. Further, the amount of mercury released from coal combustion is more dependent on combustion conditions and the presence of oxidants than the mercury content itself. It is therefore not common for coal to be selected according to the mercury content – factors such as ash content, sulphur content and coal quality (heating value) take priority.

4.1.2 Coal washing

Raw coal contains mineral impurities such as rock and clay that are referred to as ash. Where appropriate, this raw coal should be processed or cleaned. Coal washing is a beneficiation process to enrich the coal quality by removing these non-combustible impurities. Removing impurities helps promote efficient power production, reduced wear and tear, higher plant availability, lower auxiliary power consumption, lower ash generation, and improved emission control.

The mercury content of coal may be lowered by washing the coal before it is fed into the boiler. However, the slurry generated from coal washing carries mercury which can contaminate the ground water and soil if not managed properly. Conventional coal washing can remove mercury associated with non-combustible mineral materials but will not remove any mercury associated with the organic fraction of the coal. In India, coal beneficiation is primarily focused on reducing the ash content in domestic coal from as much as 45% down to 34% or less. The MOEFCC stipulates that any coal-fired power plant situated beyond 500 km from the pithead producing the coal should use raw, blended, or beneficiated coal with an ash content not exceeding 34%, measured on a quarterly average basis (PIB, 2018).

Coal beneficiation begins with the crushing and screening of run-of-mine (ROM) coal, which removes some of the inorganic material. Commonly, the coal is then advanced to one of two main types of coal beneficiation techniques – wet or dry. Wet techniques, the predominant choice, involve using water and mechanical techniques to remove impurities (mainly minerals, ash, and sulphur) from the raw coal. Jigs and dense media bath technologies are common for washing coarse coal (exceeding 10 mm) and medium coal (1–10 mm) and operate through stratification based on specific gravity differences. Dry beneficiation techniques exploit coal particle properties such as coal density, particle shape, friction, electrostatics, and magnetism, to separate coal fractions. The choice of cleaning technology depends on factors such as washability characteristics of the coal, fines content, market statistics, regulatory and taxation environment, capital and operating costs, cost of waste treatment and disposal, and the value of the separated coal products. These factors may vary by country and therefore the technology and process design need to be carefully considered before adoption. Any coal beneficiation process improves the heat content of coal on a weight basis (TERI, 2020). Coal washing is an additional cost, but this is generally recovered by the improved efficiency and reliability of the installation (Weem, 2011).

The efficiency of coal washing for mercury removal varies, data reported in the USA range from 3% to 78% (mean range 20–30%), depending on the type of coal and the washing process. More specialised coal-washing treatments using chemicals or special physical parameters are required to achieve the 78% removal rate, but the efficiencies are coal-specific (Weem, 2011).

Commercial coal cleaning systems are available which can be relevant for mercury. For example, the K-Fuel process used both physical separation and thermal processing to upgrade subbituminous or lignite coal, including the removal of moisture and ash. The K-Fuel pre-combustion multipollutant reduction technology is a two-step process: physical separation by gravity, either wet or dry, and thermal processing in vessels operating under high temperature and pressure (240°C and 340 kilopascals [kPa]), removes ash along with other pollutants such as sulphur and mercury). Although K-Fuel was included in the options for mercury reduction. Amar (2003) quoted up to 30% ash reduction, up to 36% sulphur reduction, and up to 66% mercury reduction. However, few if any examples of K-Fuel can be found in the published literature to confirm this claim. More recently, the WRITECoal™ coal upgrading process for high-moisture coals has been reported to remove up to 87% of the mercury from some coals. The process is a two-stage system of heating where the first phase drives off the moisture and the second phase drives off the mercury. Demonstrations at pilot scale showed that between 50% and 80% of the mercury in lignite and Powder River Basin (PRB) coal, USA coals can be removed, the mercury being captured in a solid sorbent system (Sloss, 2015).

THE LACK OF RECENT LITERATURE ON COAL CLEANING PROCESSES TO REMOVE MERCURY SUGGESTS THAT THIS OPTION IS EITHER CHALLENGING IN PRACTICE AND/OR NOT COST-EFFECTIVE.

4.1.3 Coal blending

Coal blending or cofiring is another cost-effective option for reducing emissions. By maximising the fuel properties, less fuel may be required and/or fewer pollutants are introduced to the boiler.

Generally, coal-fired power plants blend coals to maintain the characteristics required for the designed system and to ensure efficient combustion. Low quality coal can be mixed with higher quality coal to achieve optimum calorific value at an affordable cost. Low sulphur coal can be mixed with high sulphur coal to keep SO_2 emissions under any compliance limit. High ash coal can be mixed with low ash coal to reduce the ash load on pollution control systems and to comply with other relevant regulatory requirements. Most commonly, managing sulphur content, ash generation and achieving optimum calorific value are the kay factors driving coal blending at the power plants. Coal blending for mercury control alone is unlikely to be cost-effective or practical.

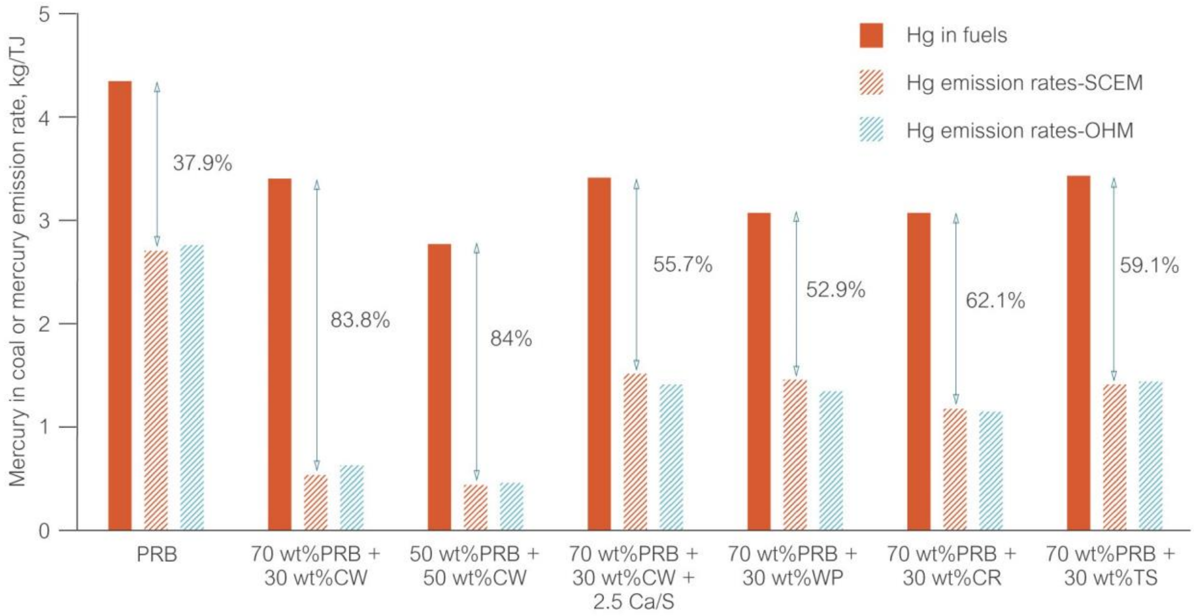
Some coals, despite having a high mercury content, tend to release less mercury to the stack due to enhanced capture/retention of mercury in the fly ash. The blending of coal can help optimise the combustion chemistry to produce more mercury in the oxidised form, enhancing its capture in pollution control devices such as electrostatic precipitator (ESP) and FGD units. Bituminous coals tend to have higher halogen contents (chlorine and bromine) and lower calcium. Bituminous coals therefore typically produce more oxidised (soluble and easy to capture) mercury than subbituminous coals and lignite. Blending up to 20% western bituminous coal with subbituminous coal can increase mercury capture in an FGD system from virtually zero to around 80% in some cases. The effect can be even more encouraging where both FGD and selective catalytic reduction (SCR) systems are installed. SCR systems can convert even more mercury into the soluble oxidised form resulting in up to 97% mercury capture with some blends. Coal blending is therefore an inexpensive option for power plants to control mercury emissions. For example, the 360 MW Holcomb station in the USA fires PRB coal and is fitted with spray dry scrubbers and fabric filters for SO_2 and particulate control. It was shown that the addition of a small amount of western bituminous coals to the fuel mix increased the vapour phase mercury capture from below 25% to nearly 80%.

Coal blending has been a proven economic approach for emission reduction at many plants in North America and could be adopted in developing countries and emerging economies (Sloss, 2015). The effectiveness of this approach is likely to be site-specific and would need further evaluation. It is also possible that blending coals could change boiler slagging and fouling characteristics or the performance of the air pollution control system, potentially increasing operational and maintenance costs (Srivastava and others, 2006).

4.1.4 Cofiring

Improving plant efficiency and reducing the coal consumption rate remains a priority for any plant; more power from less coal makes economic sense. Some coal plants are cofiring biomass or other materials with coal as a move towards lowering CO_2 emissions. This can have an effect on mercury emissions, usually achieving mercury reduction due to the lower concentration of mercury in most biomass materials and due to the change in combustion and ash conditions. Currently, the contribution of the additional fuel is commonly limited to below 20% of the blend. However, cofiring biomass can cause problems of increased slagging and fouling and a reduction in boiler efficiency. More importantly, this may cause chemical and physical changes to the ash that hinder mercury absorption. Since biomass characteristics are so variable, it is important to determine on a case-by-case basis the effect on mercury capture. Even if mercury capture is enhanced, cofiring biomass is unlikely to be considered a major mercury reduction strategy for a coal-fired power plant.

Cao and others (2008) assessed various combinations of PRB coals with different biomass to measure changes in mercury emission rates, as summarised in Figure 3.



CW – chicken waste, WP – wood pellets, CR – coffee residue, TS – tobacco stalks,
SCEM – a PS® analytical continuous emissions monitoring (CEM) system;
OHM – the Ontario Hydro method, a wet chemical method based on impinger solutions

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Figure 3 Variation of mercury emission with cofiring of biomass with subbituminous coals (Cao and others, 2008)

Figure 3 shows that when firing coal alone, around 38% of the mercury was captured in the existing pollution control system (quartz filters). Cofiring high chlorine fuels such as chicken waste (22,340 ppm Cl, by weight) could reduce mercury emissions by over 80% whereas low chlorine fuels such as wood pellets (132 ppm) only reduced mercury emissions by 50%. Although tobacco stalks had a high chlorine content (4237 ppm) the co-combustion in the FBC system did not reduce mercury emissions as significantly as expected for such a high chlorine content. So, although the mercury emissions were strongly correlated to the gaseous chlorine concentration, they were not necessarily correlated to the chlorine content of the fuels. The behaviour of mercury and chlorine was found to be more dependent on the chemistry of these species in the coal and the conditions of combustion than the actual concentrations themselves (Sloss, 2010).

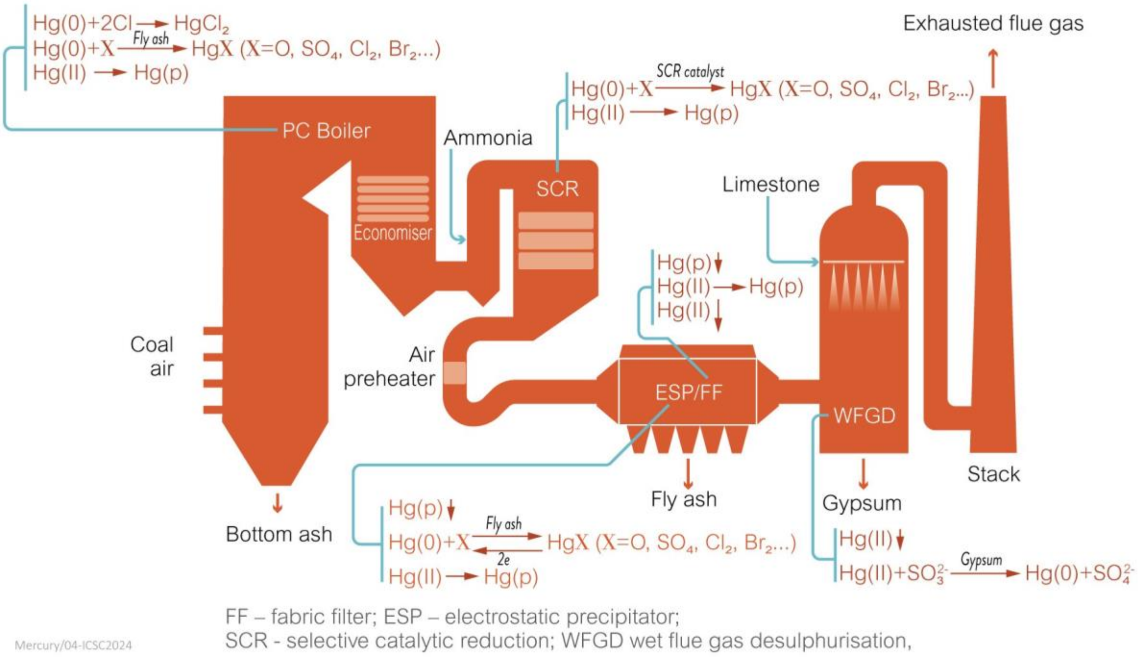
Zhuang and Miller (2006) have studied the effect of cofiring tyre-derived fuel and western subbituminous lignite. With 100% coal firing there was only around 17% oxidised mercury whereas this increased to almost 48% when 5% (mass basis) tyre-derived fuel was added (Zhuang and Miller, 2006).

Although the costs for alternative fuels may be low, there can be associated plant problems such as requirements for specialist handling or separation and flame stability can be an issue. Sourcing fuels such as tyre-derived fuel may also be an issue (Pavlish and others, 2005)

The GOI has recently (2023) started to promote biomass cofiring at coal-plants in India. As mentioned above, this is unlikely to be an important part of any mercury emission reduction strategy. However, noting the importance of mercury chemistry on the effectiveness of mercury control options, biomass cofiring will need to be included within any plant-specific strategy.

4.2 ENHANCING CO-BENEFIT EFFECTS

Even after mercury has left the boiler and flows into cooler areas of the coal plant, its behaviour can be affected by chemical and physical changes in the flue gas, as shown in Figure 4. Some mercury control can therefore be obtained, cost-effectively by utilising the co-benefits of multipollutant control technologies used for PM, SO_2 and NOx. The co-benefits can be further enhanced by coal blending (as discussed) and by promoting mercury oxidation through the addition of oxidising chemicals such as bromine (*see* Chapter 5).



FF – fabric filter; ESP – electrostatic precipitator;
SCR - selective catalytic reduction; WFGD wet flue gas desulphurisation,

Figure 4 Mercury chemistry through pollution control systems (Zhang and others, 2016)

Co-benefit mercury control is the preferred option for mercury reduction by plants worldwide as it takes advantage of the existing plant design and operation. The co-benefits of standard pollution control technologies can be summarised as follows:

- PM emission control system will capture mercury and any sulphur or other trace elements associated with particulates, or which will attach to any solid materials being captured in an ESP, baghouse, or similar technology;
- NOx emission control systems such as SCR catalysts will oxidise mercury and enhance its capture in downstream control systems; and
- SO_2 emission control system, FGD, will capture additional particulates together with any trace elements associated with these solids and soluble materials such as oxidised mercury.

The following sections summarise how mercury behaves in standard flue gas control equipment.

4.2.1 PM control devices

ESP capture particulates by creating an electric charge and attracting particles to surfaces where they are collected and removed. Due to their high PM removal efficiency and relatively low cost, ESPs are the most widely used PM control systems in coal-fired power plants, especially in India.

Over 99% of Hg(p) is removed inside an ESP (Wang and others, 2010). A small portion of Hg^{2+} can also be adsorbed onto fly ash and removed by an ESP. The Hg^{2+} capture rate is largely determined by the unburnt carbon on the fly ash (Senior and Johnson, 2005). The total mercury removal efficiency of an ESP is usually in the range of 20–40% when there is around 5% unburnt carbon in the ash. Lower unburnt carbon contents, which would be expected in more efficient boilers, would produce lower mercury capture efficiencies as a result. In addition to the unburnt carbon content of the ash, the surface property, size, porous structure, and mineral composition will also affect the mercury capture rate of an ESP (Lu and others, 2007).

When coal with a high chlorine content is burned, and unburnt carbon is present, more Hg^{2+} and Hg(p) will be formed and captured. If an ESP is optimised for fine particulate capture (such as smaller than PM_{10}) the mercury capture efficiency will also be improved.

Inter-conversion between Hg^0 and Hg^{2+} can occur inside an ESP. The charging anode of an ESP can neutralise Hg^{2+} and convert it to Hg^0 while Hg^0 in the flue gas continues to be oxidised to Hg^{2+} through heterogeneous reactions in the ESP at temperatures of 150–200°C. Therefore, the Hg^0 concentration can either increase or decrease inside the ESP depending on the flue gas chemistry and temperature (Zhang, 2012). Various research (such as Wang and others, 2010; Zhang and others, 2013) indicate an average mercury removal efficiency of 29% for ESPs, but this is within a wide possible range of 1–74%. Research (for example, Chen and others, 2007; Zhang, 2012) suggests that an ESP installed after a CFBC can achieve a higher average of 74% mercury removal due to the high proportion of Hg(p) in the flue gas.

Fabric filters (FF), or baghouses, have a better PM capture efficiency than ESP and therefore also offer greater potential for mercury capture. Numerous studies (such as Chen and others, 2007; Shah and others, 2008; Wang and others, 2009) report that FF have total mercury removal efficiencies of 9–92% with an average of 67%. Besides capturing over 99% of the Hg(p), baghouses can also remove over 50% of the Hg^{2+}. During the filtration of the flue gas through the baghouse, contact between the flue gas and the particles on the cake layer promotes the adsorption of Hg^{2+} onto fly ash maximising capture on unburnt carbon and any other absorptive surfaces (Zhang, 2012). If the chemistry is suitable, the dust cake layer can also facilitate the oxidation of Hg^0 (Wang and others, 2016).

Some plants apply hybrid ESP-baghouse systems to improve fine particle removal efficiency. Limited studies suggested an overall mercury removal rate of 39% in ESP-baghouse hybrid precipitators (Wang and others, 2016).

4.2.2 NOx control devices

The major options for NOx control in coal-fired systems are low NOx burners, SCR, and selective non-catalytic reduction (SNCR). Low NOx burners and SNCR systems have limited (if any) effect on mercury emissions.

SCR installed for NOx control can be the first air pollution control device installed downstream of the boiler. The operational temperature in an SCR is typically 300–400°C. SCR catalysts, usually composed of vanadium pentoxide (V_2O_5), tungsten trioxide (WO_3), and titanium dioxide (TiO_2), significantly promote the Hg^0 oxidation process and increase the concentration of Hg^{2+} which can be effectively captured in further downstream control devices, such as FGD systems; *see* Section 4.2.3 (Niksa and Fujiwara, 2005). The concentrations of NO, SO_2 and total mercury as well as the type and age of the SCR catalyst will affect its performance. SCR catalysts may have to be replaced more frequently to maintain their mercury reduction potential (Zhang and others, 2013b).

4.2.3 SO_2 control devices

Wet flue gas desulphurisation (WFGD) is the most common pollution control system for SO_2 control in coal-fired power plants. During the SO_2 scrubbing process in WFGD systems, Hg^{2+} is also removed. The average Hg^{2+} removal efficiency of WFGD ranges from 56% to 88% (Lee and others, 2006; Chen and others, 2007; Wang and others, 2010). Insoluble Hg^0 passes through WFGD without being captured.

The chemical reduction of the dissolved Hg^{2+} within the WFGD itself reduces the total mercury removal efficiency, due to the re-volatilisation of Hg^0 (Wo and others, 2009). Flue gas and slurry composition, operating temperature, limestone injection rate, and slurry pH are the key factors affecting the re-volatilisation of Hg^0 (Schuetze and others, 2012).

WFGD is commonly regarded as the best option to achieve co-benefit mercury control technologies in coal-fired power plants. The applications of high-chlorine coal, SCR and halogen addition can increase the Hg^{2+} proportion in flue gas before WFGD, which will enhance the overall mercury capture efficiency. The optimised strategy for WFGD is then to stabilise the Hg^{2+} in the WFGD slurry to prevent mercury re-volatilisation. The overall mercury removal efficiency of a WFGD is on average 45% with a range of 10–85 % (Wang and others, 2010).

Seawater FGD (SWFGD)systems use seawater as the medium to capture sulphur emissions and the effluent is discarded into the local water. In such systems, it is likely that the mercury is also concentrated in the liquid effluent and, since there is no removal of gypsum or other solid by-products, all the capture mercury could be concentrated in local waters. Thus, care must be taken when using them. This potential side-effect should be determined on a site-by-site basis and, where necessary, pre-treatment for mercury removal upstream of the SWFGD system may be necessary.

4.3 COMMENTS

Mercury's behaviour in a coal combustion system is complex. However, it is clear that emission control technologies installed to reduce emissions of PM, SO_2 and NOx can have significant effects on mercury reduction. It is therefore cost-effective to take advantage of this co-benefit mercury control. This is most effective if applied during the technology selection stage but can sometimes be applied retrospectively, for example:

- baghouses can be twice as effective at reducing mercury emissions as ESP systems;
- WFGD systems can capture 70% or more of the oxidised mercury in the flue gas; and
- if an SCR system is installed for NOx control, placing it upstream of the baghouse and/or the WFGD system will maximise co-benefit mercury capture.

By considering mercury control during any retrofit, it will be possible to reduce mercury emissions at little or no additional cost.

5 MERCURY-SPECIFIC CONTROL FOR COAL-FIRED POWER PLANTS

The amount of mercury control which can be achieved with each of the technologies discussed in Chapter 4 is not listed as it is extremely variable and is affected by such factors as coal chemistry. However, most commercial suppliers will work with plant operators on a case-by-case basis to modify the performance of their systems and even combine approaches to ensure that the final system provides the required level of pollutant control. With time, as emission norms are tightened for common pollutants such as PM, SO_2 and NOx and norms for new pollutants such as mercury, trace metals, halogen and fine particulates are introduced, plant operators should explore site-specific strategies on a case-by-case basis (Zhang and others, 2016).

In addition to the control efficiencies and the costs of equipment, installation, and outage timelines, especially for retrofits, are important. Table 9 shows control technologies for co-benefit with respective installation timelines and outages required for retrofit (Hutson, 2016).

TABLE 9 CONTROL TECHNOLOGIES FOR CO-BENEFIT WITH INSTALLATION TIMELINES AND OUTAGES (HUTSON, 2016)

Emission control system	Primary pollutant controlled	Co-benefit reduction	Installation times (design to installation), months	Outage time, weeks
Baghouse	PM, non-Hg metals	Hg (with or without ACI), acid gases (with DSI)	12–24	1–4
ESP upgrade	PM, non-Hg metals	Hg (with ACI), acid gases (with DSI)	6–24	0–4
DSI	Acid gases (including halogens)	SO_2, SO_3, SeO_2	9–12	None
Dry scrubber	Acid gases (including halogens)	SO_2, SO_3, SeO_2, Hg	24–36	1–4
Scrubber upgrades	Acid gases (including halogens)	SO_2, SO_3, Hg	12–36	4–8 (in two parts)
Activated carbon injection	Hg	–	12–18	None
Oxidant addition	Hg		3–12	None

ACI – activated carbon injection, DSI – dry sorbent injection

Table 9 emphasises that most retrofitted control technologies are now considered multipollutant technologies to some extent due to the co-benefit capture of additional pollutants. It also indicates a significant timeline requirement for upgrading or installing new control systems in a plant. As far as the effectiveness of the control system in standalone or multipollutant control cases is concerned, it is much dependent on the coal chemistry and plant configuration, on a case-to-case basis.

5.1 POST-COMBUSTION MEASURES TO CONTROL MERCURY EMISSION

Various factors affect the behaviour of mercury in a power plant process particularly: coal characteristics, boiler type, operation type, presence of other pollutants, and air pollution control devices (APCDs). Installation of APCDs plays a critical role in mercury emission, post-combustion. However, the choice of APCDs also requires consideration of multiple plant-specific variables. Since the APCDs control key pollutants PM, SO_2 and NOx from the flue gas, mercury also gets captured in the due process using the solid or liquid media available. There are three essential steps which take place for mercury control at coal-fired plants:

1. elemental mercury converts into oxidised mercury;
2. the oxidised mercury contacts with a carrying solid/liquid medium to get removed from the flue gas; and
3. mercury from carrying media gets captured, removed, and secured.

Therefore, overall mercury control depends on all three key factors: mercury conversion efficiency, carrying media contact efficiency and capture efficiency (Looney and others, 2014).

Mercury emission control using co-benefits refers to any emission reduction achieved by methods or APCDs applied for the control of other pollutants. These include:

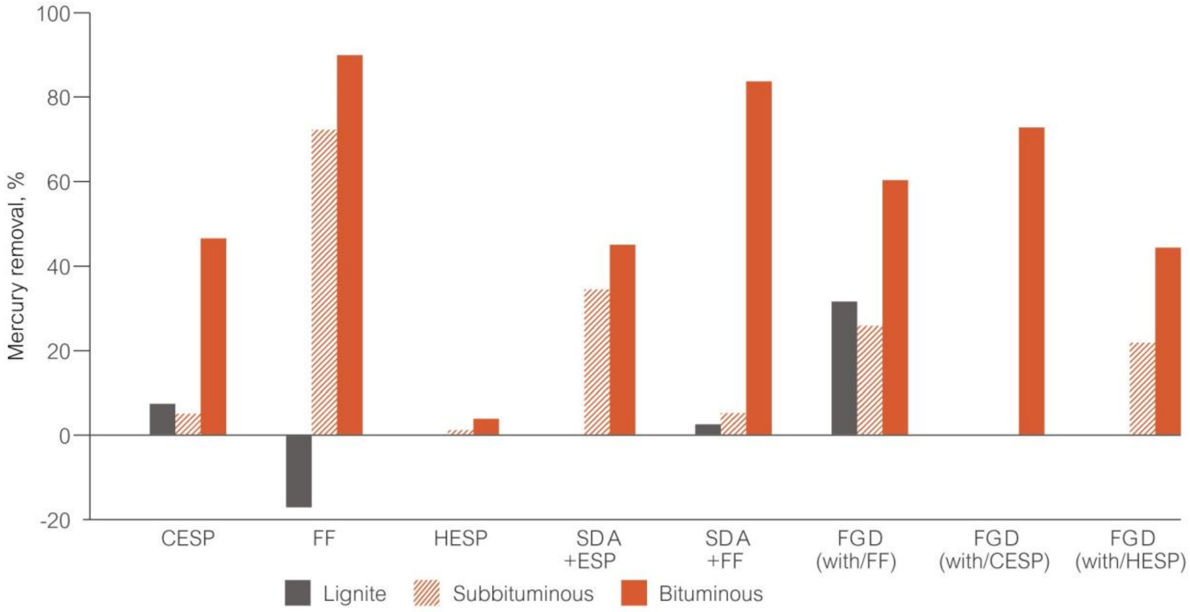
- PM control using ESP (cold-side ESP (CESP) and hot-side ESP (HESP) and, or FFs;
- SO_2 control using FGD and spray dry absorber (SDA); and
- NOx control using SCR.

Depending on the configuration of pollution control equipment, varying amounts of mercury removal could be accomplished. General trends of co-benefit mercury removal for different configurations of existing air pollution control equipment are shown in Table 10.

TABLE 10 CONFIGURATION OF POLLUTION CONTROL SYSTEMS AND THEIR CONTRIBUTION TO MERCURY EMISSION CONTROL (UNEP, 2011)

Existing control equipment	Qualitative mercury capture
CESP only	Good capture of particulates – or sorbent-bound; better co-benefit capture for low sulphur bituminous coals than low rank coals
HESP only	Low co-benefit capture; may require specially formulated sorbents for high-temperature mercury capture
FF only	Good co-benefit capture of Hg^{2+}; Hg^0 may be oxidised across the fabric filter
CESP + wet FGD	Generally, good co-benefit capture for bituminous coals is due to the presence of soluble Hg^{2+} in the flue gas. Relatively poor capture for low ranks coals. Hg^0 re-emission may decrease the amount of co-benefit
HESP + wet FGD	Moderate co-benefit capture for bituminous coals; poor co-benefit capture for low rank coals
SDA + FF	Very high co-benefit capture is expected for bituminous coals; somewhat less co-benefit capture is expected for low rank coals
FF + wet FGD	Good co-benefit capture for bituminous coals, comparable co-benefit capture for low rank coals; Hg^0 may be oxidised across the fabric filter and captured in the wet scrubber
SCR + CESP	Good capture of particulate – or sorbent-bound Hg; better co-benefit capture for bituminous coals than low rank coals
SCR + HESP	Low co-benefit capture
SCR + CESP + wet FGD	Good capture of particulates – or sorbent-bound Hg; better co-benefit capture for bituminous coals than low rank coals. SCR enhances capture for bituminous coals by oxidising Hg^0 to Hg^{2+}
SCR + SDA + FF	Very high co-benefit capture for bituminous coals, less for low rank coals. SCR enhances capture by oxidising Hg^0 to Hg^{2+}, given the availability of chlorine in the flue gas
SCR + HESP + wet FGD	Generally, poor capture of particulate-bound mercury and total mercury for low rank coals. SCR enhances capture for bituminous coals by oxidising Hg^0 to Hg^{2+}, given the availability of chlorine in the flue gas
SCR + FF + wet FGD	Generally, high levels of mercury are captured for all coals. SCR enhances capture for bituminous coals by oxidising Hg^0 to Hg^{2+} form, given the availability of chlorine in the flue gas
CESP – cold-side ESP; HESP – hot-side ESP; FF– fabric filter; SDA – spray dry absorber; SCR – selective catalytic reduction	

Figure 5 shows mercury emission control co-benefits by various combinations of pollution control systems for different qualities of coal, based on information from the USEPA's information collection request (ICR) (Sloss, 2008).



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HESP = hot side ESP; FF = fabric filter; SDA = spray dry absorber; FGD = flue gas desulphurisation

Figure 5 Average mercury removal across APCDs in coal-fired power plants (Kolker and others, 2006)

The ICR was a USEPA survey of mercury behaviour across all plants in the USA in the mid-2000s. The study showed that fabric filters were far more efficient than ESP for removing mercury. Spray dry adsorption (SDA) systems, which used limestone sprayed into the flue gas to capture sulphur, were also highly effective for mercury control, often more so than wet FGD systems. The effectiveness of each system varied significantly with the coal type – mercury emissions from bituminous coals were relatively easy to capture but those from subbituminous coals and lignite were much more challenging (*see* also Chapter 3).

5.1.1 Mercury control co-benefits of PM emission control systems

Mercury emission control using co-benefits of PM control systems is limited. Only a small fraction of mercury in the particulate form, Hg(p) is found in the flue gas since the majority is in the gaseous form. However, the oxidised mercury can also bind to the absorbent surface of particulates such as unburnt carbon and can be captured in particulate control systems. The overall mercury capture in the particulate format is coal and condition specific. Mercury capture in particulate control systems depends on the following key factors:

- choice of pollution control – ESP or FF;
- location of ESP: CESP or HESP;
- coal type and quality;
- sulphur content in the coal;
- chlorine content in coal;
- unburnt carbon in fly ash; and
- temperature of the flue gas before the fabric filter.

ESP systems generally remove only PM-bound mercury in the process of collecting PM. PM-bound mercury is preferentially bound to unburnt carbon and its absorption capacity is better than that of fly ash particles. Between 20% and 40% mercury capture can be expected in an ESP when capturing fly ash containing about 5% unburnt carbon. For higher unburnt carbon contents, mercury capture as high as 80% has been reported which is likely to be because of the presence of halogens (Senior and Johnson, 2008). Higher concentrations of mercury in ESP fly ash were observed when bromide was added to the boiler, compared to the no-addition case (Vosteen and others, 2003; *see* Chapter 6).

Since FF are more efficient at PM emission control than ESP in general, they are also more effective at capturing mercury. This is due to the increased residence time between particles, which contain unburnt carbon and other species with adsorptive properties, and the oxidised mercury in the flue gas. ESP systems are moderately effective for capturing mercury, as the cold-side systems (installed after the air preheater) provide greater capture than hot-side systems (installed before the air preheater) due to the reduced volatility of mercury in the colder system.

The effectiveness of any particulate control system for mercury capture increases with the amount of mercury in the oxidised form since oxidised mercury is stickier and more soluble. Bituminous coals tend to produce more mercury in the oxidised form than lower grade coals and lignite, probably due to a higher content of halogens and other species which have oxidising properties. Table 11 shows mercury emission control using PM control in combination with other APCDs in the pulverised coal-fired boilers using different types of coal.

TABLE 11 MEAN MERCURY EMISSION REDUCTION FROM PULVERISED COAL-FIRED BOILERS IN THE USA (TRAVOULAREAS AND JOZEWICZ, 2005)

Emission control system		Average mercury reduction, %		
		Bituminous	Subbituminous	Lignite
PM control only	CESP	35	3	0
	HESP	14	12	Not tested
	FF	89	73	Not tested
	Particulate scrubber	12	0	33
PM and spray dry absorber (SDA)	ESP and SDA	Not tested	50	Not tested
	FF and SDA	98	23	17
	FF and SDA and SCR	97	Not tested	Not tested
PM control and wet FGD system	CESP and FGD	81	30	42
	HESP and FGD	45	25	Not tested
	FF and FGD	97	Not tested	Not tested
	FF and FGD	97	Not tested	Not tested

PM – particulate matter; ESP – electrostatic precipitator; CESP – cold-side EPS; HESP – hot-side ESP; FF – fabric filters; SDA – spray dry absorber; FGD – flue gas desulphurisation
Table 11 shows the mean mercury emission reductions achieved in different APCD combinations in coal-fired power plants in the USA. This is based on actual plant data collected during the USEPA's ICR (Sloss, 2015)

As mentioned before, the mercury removal efficiency varies greatly with coal rank. Afonso and Senior (2001) found that higher chlorine contents increased the mercury control in particulate control systems. Coal with more than 200 ppm chlorine content resulted in most of the mercury being converted into the particulate phase before it enters PM control systems. Fabric filters were found to oxidise 40–85% of the elemental mercury, the highest values in this range being for bituminous coals. ESP systems appeared to oxidise only 25–40% and negligible oxidation was seen for low rank coals.

Sjostrom and others (2001) found that increased carbon in the fly ash correlated with higher mercury removal in cold-side ESPs for both bituminous and subbituminous coal-fired power plants in the USA and Canada. These ESPs with higher special collection also led to higher mercury removal with lignite coal-fired power plants, although the highest mercury removal was only 7%. A review of data from the USEPA's ICR by the Energy and Environment Research Centre (EERC), USA, found consistently lower mercury removal in the power plants using low-chlorine coals such as western US coals. For example, mercury removals across an ESP averaged 35% for bituminous coals compared with 10% for western low rank coal (CATM, 2001).

A pilot scale study with a low-sulphur coal-based combustion facility found negligible mercury control if the unburnt carbon level was below 1%, and increased mercury control if the unburnt carbon content increased. It is important to remember that other variables – such as the oxidation state of the mercury and the baghouse temperature – also play a role in such conditions. Any increase in unburnt carbon is also counterproductive for plant efficiency. The properties of an unburnt carbon particle such as surface area, particle size, porosity, and composition, may also affect the amount of mercury captured in the ESP as these provide adsorption surface to mercury. The lower the particle size, the higher the mercury capture due to the larger surface area. Unburnt carbon particles are usually larger in size but are more absorptive (Lu and others, 2007).

Coal ash content and temperature in the control system also have an impact on mercury control. The effect of temperature seems to be predominant as cooler FF temperatures capture more mercury in the ash even at low ash carbon contents. The mercury adsorption of the fly ash was found to increase as the flue gas temperature decreased and, at each temperature, increased with the content of fly ash carbon, until a saturation point was reached. However, there appeared to be a complex relationship between mercury adsorption and the proportion of different petrographically recognisable carbon forms (Sloss, 2012).

Wet PM scrubbers are not common for PM control in coal-fired power plants. However, mercury capture, especially oxidised mercury, is expected to be significant in these systems as they have a similar working chemistry to wet FGD. The mercury removal by wet PM scrubber could be augmented by coal switching/blending or the addition of oxidants or halogens. Mechanical collectors (such as cyclones) are expected to be less efficient in mercury collection due to their limited capability to separate submicron particles from the flue gas (UNEP, 2011).

5.1.2 Mercury control co-benefits of SO_2 emission control systems

Dry and wet scrubbers or FGD are the two main technologies used for SO_2 emission control in a coal-fired power plant. In dry FGD the flue gas is sprayed with dry sorbent such as limestone, it is not saturated with water and the by-product is dry. Wet FGD involves saturating the flue gas with a water-limestone mix to produce a wet by-product. Wet FGD systems commonly produce gypsum as a by-product whereas sulphite is produced by dry systems. Both dry and wet FGD can have a significant effect on mercury emissions, especially for bituminous coals. Wet FGD systems are the most popular method for sulphur control on large coal-fired boilers worldwide, which is useful for mercury control as it can also be captured effectively in most FGD systems.

PM control is usually installed before the FGD which takes care of the Hg(p) in the flue gas. Oxidised mercury in the gaseous form ($Hg^{2+)}$ is generally water-soluble and thus captured in wet FGD systems in the slurry. Data from actual facilities has shown that over 90% capture of Hg^{2+} can be expected in calcium-based wet FGD systems, although there are cases where significantly less capture has been measured as a result of unfavourable scrubber equilibrium chemistry (Niksa and Fujiwara, 2004). However, gaseous Hg^0 is insoluble in water and therefore does not absorb in FGD slurries.

Previous ICSC reports by Sloss (2008, 2012, 2015) have reviewed the complex chemistry of mercury in these systems. Under some conditions, Hg^{2+} absorbed in slurry may be reduced to Hg^0 in a wet FGD, which could then be re-emitted. For this reason, preservation of the Hg^{2+} is required to avoid its conversion and re-emission. The dissolved species are believed to react with dissolved sulphides from the flue gas, such as hydrogen sulphide (H_2S), to form mercuric sulphide (HgS); the HgS precipitates from the liquid solution as sludge. In the absence of a sufficient concentration of sulphides in the liquid solution, a competing reaction with sulphites that reduces dissolved Hg^{2+} to Hg^0 is believed to take place. This re-emission may be more significant in magnesium-enhanced lime scrubbers as these operate with a much higher sulphite concentration than limestone systems. Transition metals in the slurry and appreciable mercury concentration in the liquor phase also play a role in re-emission. In some cases, the reduction of Hg^{2+} to Hg^0, and subsequent re-emission, has been abated with the help of a sulphide-donating liquid reagent.

Mercury capture in pulverised coal-fired power plants equipped with wet FGD scrubbers depends on the relative amount of Hg^{2+} in the inlet flue gas and on the PM control technology. The USEPA ICR data reflected that average mercury capture ranged from 29% for subbituminous coal in plants fitted with ESP and FGD to 98% for bituminous coals in plants with FF and FGD (Table 11 and Figure 5). The high mercurycapture in plants with both FFs and FGD was attributed to increased oxidisation and capture of mercury in the FF followed by capture of any remaining Hg^{2+} in the wet scrubber.

Wet FGD can typically remove 75–99% of the oxidised mercury present in flue gases. Total mercury removal efficiencies average around 55% (Sloss, 2015). A classic report by Meij and others (2001) reviewed data on the effect of FGD and found that studies in Austria, Canada, Denmark, Germany, Japan and the USA, all agree that wet FGD systems remove at least 50% of the mercury (Sloss, 2008).

Looney and others (2014) estimated that if the maximum mercury oxidation using SCR, halogen and other additives could reach 95% and if wet FGD is added then, assuming a 98% mass transfer, the maximum mercury capture of 93% (95% x 98%) could be achieved. However, if the mercury content in coal is high, even a 93% mercury removal may result in a failure to comply with the tight mercury emission standard under the MATS rules in the USA. So, for tighter emission limits, plants may have to consider additional mercury-specific approaches to ensure compliance (Sloss, 2015; *see* Sections 5.2 and 5.3).

Spray dry absorption (SDA), a dry scrubber technology usually installed in combination with FFs for particulate control operates by the same principle as a wet FGD system using a lime scrubbing agent. However, in SDA systems the flue gas is mixed with a fine mist of lime slurry instead of a bulk liquid (as in wet scrubbing). The SO_2 is absorbed in the slurry and reacts with the hydrated lime reagent to form solid calcium sulphite and calcium sulphate. Hg^{2+} may also be absorbed. Sorbent particles containing SO_2 and mercury are captured in the downstream ESP or FF. Having a fabric filter instead of ESP gives the potential for additional capture of gaseous Hg^0 as the flue gas passes through the bag filter cake composed of fly ash and dried slurry particles.

SDA systems have been shown to reduce mercury emissions by up to 95% but, as always, this depends on the coal type and combustion conditions. SDA systems are less common than wet FGD systems due to more challenging operating requirements. SDA systems have been developed specifically for some CFBC systems, such as those offered by Lurgi, Wulff GmbH and FLS Miljo. Mercury removal rates for these systems range from 50–89% (Travoulareas and Jozewicz, 2005).

As shown in Table 11, the USEPA ICR data reflects the plants equipped with SDA scrubbers (SDA/ESP or SDA/FF systems) exhibited average mercury capture ranging from 98% for bituminous coals to 24% for subbituminous coal.

Alstom has patented the NID™ system, a semi-dry FGD system which reduces mercury emissions by 90%, in addition to controlling SO_2 and PM. The system is used at the 585 MW Boswell Energy Centre plant of Minnesota Power in Cohasset, MN, USA. The NID technology has also been bought for 2 x 66 MW coal units at the Homer City Generating Station in Indiana County, Pennsylvania and there are now over 60 NID units worldwide (Sloss, 2015).

5.1.3 Mercury control co-benefits of NOx emission control systems

SCR and SNCR are the two main NOx control technologies adopted in coal-fired power plants. They are applied in the flue gas downstream from the boiler. Primary NOx control measures include combustion optimisation techniques such as low NOx burners (LNBs) and overfire air (OFA).

Combustion optimisation techniques do not have a direct effect on mercury emissions but can influence mercury capture by increasing the unburnt carbon in the ash. LNBs or low NOx combustion systems can cause a 5–30 wt% increase in unburnt carbon. As mercury can concentrate on the carbon-rich fraction of the fly ash it can thus be captured more efficiently in particulate control systems (Kolker and others, 2006). However, as discussed before, increasing unburnt carbon in the fly ash is not preferred as it affects the plant efficiency and reduces fly ash quality.

A patented combustion system staging process of GE Environmental Services (GEES) improves the reactivity of the ash for mercury adsorption. Using CO/O_2 sensors, coal dampers and air flow control actuators, the combustion is optimised within a narrow range with optimum unburnt carbon content in fly ash which maximises mercury removal with a minimum negative effect on efficiency and fly ash quality. This approach is recommended to optimise natural mercury removal in the fly ash and can be used in conjunction with activated carbon. By enhancing the mercury capture in natural fly ash, the amount of activated carbon required is reduced (Sloss, 2008). Tested on the Green Station, a 255 MWe wall-fired boiler firing bituminous coal with cold-side ESP and wet scrubbers, the GEES process achieved 80% mercury removal at 8–12% unburnt carbon and ESP at below 150°C temperature. The mercury removal efficiency was temperature sensitive with greater removal efficiencies at lower temperatures (for example, around 80% at 127°C to 40–60% at 155°C). At full scale, 80% mercury control was achieved with 10–11% unburnt carbon and ESP at a temperature range of 132–140°C (Lissianski and others, 2005). The re-burning system has the potential to reduce NOx and mercury emissions simultaneously whilst reducing the cost of any further activated carbon treatment. However, loss of ash sales and reduced boiler efficiency are likely with such high unburnt carbon contents.

SCR comprises a reagent (usually ammonia) dosing system and a catalyst (usually porous ceramic material such as titanium oxides with active catalytic coating components such as zeolites or oxides of metals like vanadium, molybdenum, and tungsten). An SCR system does not capture mercury but it does oxidise elemental mercury (Hg^0) in the flue gas into oxidised mercury (Hg^{2+}) which is easily captured in the downstream APCD, such as ESP or FGD. SCR catalysts can deliver 30–98% mercury oxidation, higher for bituminous coal (average 72%) and much lower for subbituminous coal (Kolker and others, 2006). The oxidation of mercury by SCR catalysts may be affected by the following factors (USEPA, 2007):

- space velocity of the catalyst;
- temperature of the reaction;
- concentration of ammonia;
- age of the catalyst; and
- concentration of chlorine in the gas stream.

The effectiveness of the catalyst reduces with time due to the exposure of the catalyst to the fly ash, sulphur trioxide (SO_3) and other chemical components of the flue gas. This causes erosion, particulate plugging, and chemical reactions such as poisoning, more so for widely used hot-side SCR. Mercury also reduces the effect of catalysts and reduces the NOx reduction rate. Systems such as COMET (Cormtech oxidised mercury emissions technology) are being marketed which characterise SCR reactor performance and determine the correct catalyst formation for maximum NOx and mercury control. The performance of catalysts can be enhanced by halogen injection and by efficient management of catalyst surface replacements (Sloss, 2015).

SNCR technology for NOx control, which simply uses reagent dosing for NOx reduction, has not been reported to affect mercury emissions and so is not discussed further.

5.2 USE OF OXIDANTS FOR MERCURY CAPTURE ENHANCEMENT

Several oxidants can be used to enhance the co-benefits of multipollutant control systems. These are delivered via solutions and sprays into the boiler or at some point upstream of the PM and SO_2 control systems. The most common oxidants are halogens in the form of halides. Bromine in the form of calcium bromide ($CaBr_2$) is the most widely used halogen for its high oxidation potential for mercury. KNX™, marketed by Alstom and MercPlus™, is a bromine-based oxidant marketed by Babcock and Wilcox.

The efficiency of SCR catalysts to oxidise mercury can reduce over time (*see* Section 5.1.3). In this case, the addition of a sorbent, especially a sorbent activated with a halogen, provides another surface for mercury to attach to, increasing mercury capture while extending the lifespan of the SCR catalysts. The most popular commercial oxidants in use are bromine or bromine-based materials. Vosteen Consulting Ltd, Germany holds the patent for bromine use for mercury capture enhancement (Sloss, 2017).

Even for mercury capture in FGD, additives can provide significant enhancement. Since wet FGD systems capture oxidised mercury only, additives such as bromine can enhance mercury oxidation for capture in liquid or solid form. However, the effects of additives on the wet chemistry of FGD must be evaluated and controlled to ensure that the primary purpose of sulphur removal is not reduced and to check for other possible issues such as corrosion and wastewater generation.

There are also reagent-based systems to enhance mercury capture in wet FGD and to control potential mercury remission. Nalco's MerControl 8034 and Babcock and Wilcox's Absorption Plus (Hg)™ trap the dissolved mercury in an insoluble form which can be precipitated and removed from the wet scrubber. Nalco's MerControl technologies have been noted to reduce over 90% of the mercury resulting in emission rates below 1.0 ug/m^3. MerControl technologies cost nearly half of that required for activated carbon injection (ACI) which can also control delivery by controlling the re-emission of mercury from wet FGD (Carpenter, 2013).

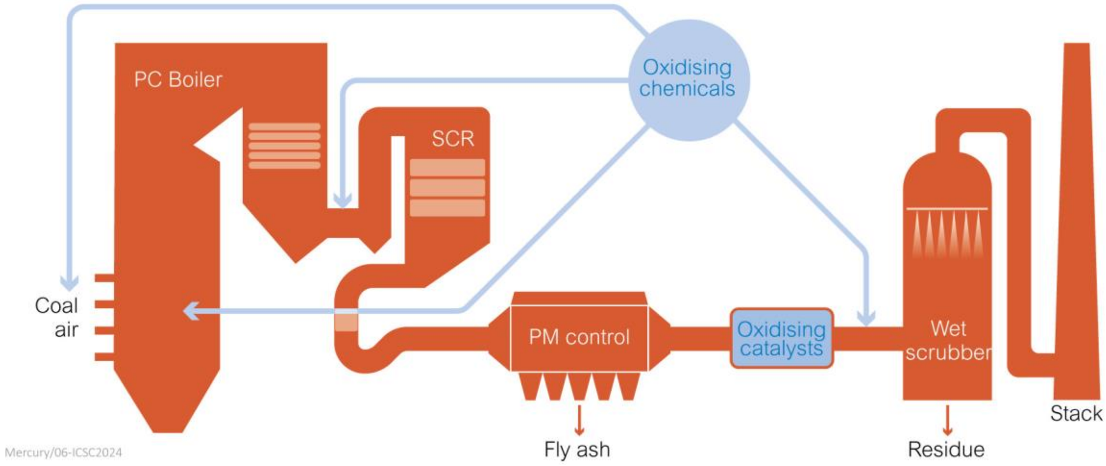


Figure 6 Use of oxidants for mercury capture enhancement in a coal-fired power plant (Sloss, 2017)

The addition of bromine has been applied at many plants. For example, Plant Millar of the Alabama Power Company, USA, has injected calcium bromide ($CaBr_2$) directly onto the coal being fed into the boilers. Mercury oxidation through this bromine addition ensured mercury emissions from the plant were reduced from 10 µg/m^3 to less than 2 µg/m^3. Calcium bromide was applied as KNX-Technology by Alstom/Vosteen Consulting. This high-temperature bromine technology has also been applied successfully at the Pleasant Prairie Plant (2 x 600 MWe) in Wisconsin (Vosteen and Hartmann, 2012).

As mentioned previously, FFs are a better PM control system for mercury than ESP. Tighter mercury emission norms in the USA have guided many coal-fired power plants in the USA to use activated carbons and sorbents and to switch from ESP to FFs to maximise mercury capture (Sloss, 2017).

The EPPSA (European Power Plant Suppliers Association, 2015) has estimated costs for mercury reduction under the following assumptions:

- a typical 800 MW plant with ESP operating 7500 h/y;
- 0.2 mg/kg mercury in the coal; and
- bromine as an additive.

The estimate includes a one-time cost for the feed system and integration with the control system at €400,000; and reagent cost (at 30 kg/h bromine) at €750,000. It is important to note that the effectiveness of additives and cost will depend on coal and plant characteristics and the oxidative effect of SCR systems which can reduce oxidant requirements up to a factor of 10 (EPPSA, 2015). Further, the cost of these technologies and reagents will have changed since 2015. However, the magnitude of the cost is still relevant, emphasising the ongoing additional cost for reagent for the full lifetime of the system.

Lignite is usually a challenge for mercury control because of the low inherent mercury oxidation rate. However, successful mercury control was demonstrated at Great River Energy's 2 x 600 MW lignite-fired plant in North Dakota, USA, over a 30-day period in 2014. A combination of calcium bromide addition to the coal feed plus the injection of ‘Kleenscrub’, an organic-sulphide liquid, into the FGD reaction tanks was shown to be highly effective (Larson, 2014).

5.3 USE OF SORBENTS FOR ENHANCING MERCURY CAPTURE

Sorbents such as activated carbon are widely used for mercury control. The sorbent is injected upstream of existing particulate control devices. The efficiency of a sorbent to capture mercury depends on a number of variables including:

- sorbent average particle size, pore size and size distribution;
- sorbent capacity with mercury speciation and at different gas temperatures;
- residence time in the flue gas;
- type of particulate control (ESP or FF); and
- inlet mercury concentrations.

Activated carbon injection (ACI) has the potential to achieve moderate to high levels of mercury control. The performance of an activated carbon is related to its physical and chemical characteristics. ACI can achieve mercury emission in the range of 0.2–0.5 ug/m^3 with 85–95% emission control (Jozewicz, 2023). The capacity for mercury capture generally increases with increasing surface area and pore volume. The ability of mercury and other sorbates to penetrate into the interior of a particle is related to pore size distribution. The pores of the carbon sorbent must be large enough to provide free access to the internal surface area by Hg^0 and Hg^{2+} while avoiding excessive blockage by previously adsorbed reactants. As particle size decreases, access to the internal surface area of the particle increases along with potential adsorption rates. The selection of carbon for a given application would take into consideration the total concentration of mercury, the relative amounts of mercury and Hg^{2+}, the flue gas composition, and the air pollution control systems installed.

The addition of a sorbent increases the particulate load in ESP or FF which may demand capacity enhancement. Since the sorbents used are generally very fine, in order to maximise the active surface area, enhanced particulate control may be required to capture the finer PM. Rubin and others (2001) suggest that the use of activated carbon would increase particulate emissions by 9%. The total cost of using activated carbon (including humidification and waste disposal) was estimated to increase the cost of electricity in the USA by 23% (2002 data). The amount of sorbent needed can be reduced by water injection into the flue gas. This is due to the cooling effect (Sloss, 2002). These data are somewhat dated and the cost of ACI is much lower now – the cost of sorbent varies from 1.5–2 €/kg, depending on the type of sorbent. For the typical plant in the EU, as discussed above, the requirement would be 100–400 kg/h leading to costs of €850,000–3,400,000 for 7500 hours per year, excluding any additional operation and maintenance costs. This is significantly more than the cost of oxidant injection. Sorbent also adds to control the reemission of mercury from the wet FGD. EPPSA (2015) estimated a cost of around €500,000 for an activated carbon dosing station to reduce re-emission.

Table 12 shows the combination of pollution control technologies in combination with additives and sorbent options with tentative costs estimated by EPPSA for the EU plants.

TABLE 12 POLLUTION CONTROL IN COMBINATION WITH ENHANCEMENT TECHNIQUES AND THE ESTIMATED COST OF MERCURY CONTROL (EPPSA, 2016)

Technique	Fuel chlorine content	Oxidant	Separation	Treatment	Investment, €/MW	Operation, €/MW.y
SNCR + DSI + FF	Low	Br_2	ACI	None	2000	2250
	High	NA	ACI	None	1250	1500
SCR + SDA/CDS + FF/ESP	Low	Br_2	ACI	None	1500	1300 (FF) 3700 (ESP)
	Low	OXI	ACI	None	1250	1100 (FF) 3500 (FF)
	High	NA	ACI	None	1000	1000 (FF) 3400 (ESP)
SCR + ESP + WFGD (with unsaleable gypsum)	Low	Br_2	ACIW/OSW	WTP	1000	300
	Low	OXI	ACIW/OSW	WTP	850	150
	High	NA	ACIW/OSW	WTP	500	50
SCR + ESP + WFGD (with saleable gypsum)	Low	Br_2	ACIW	GPT	2000	275
	Low	OXI	ACIW	GPT	1700	125
	High	NA	ACIW	GPT	1400	30

N/A – not applicable
ACI – activated carbon injection, ACIW – activated carbon injection into wet scrubber, CDS – circulating dry scrubber, DSI – dry sorbent injection, GPT – gypsum pretreatment, OSW – organosulphide addition to wet scrubber, OXI – oxidation catalyst, SCR – selective catalytic reduction, SNCR – selective non-catalytic reduction, SDA – spray dry absorber, WFGD – wet flue gas desulphurisation, WTP – water treatment plant, WTPS – water treatment plant with sludge concentration

Note: Movement of mercury, selenium, bromine by-products in the water discharge which may require a change in water processing and separation systems have not been considered. Licence fee is also not considered in the above cost estimates.

Although the data are dated, the relative costs are still relevant. Table 12 shows that mercury control costs are lower for those plants which have FFs rather than ESP. Costs go down significantly if wet FGD systems are in place, although treatment of wastewater and by-products also have to be considered. Plants with low chlorine coals and no FGD would have to compare the economics of using oxidants and ACI in the existing ESP system with moving to a FF. There are numerous sorbents on the market with much investment in the improvement of capture characteristics; the newer sorbents are cheaper and more effective than the original materials.

5.4 EMERGING MERCURY-SPECIFIC TECHNOLOGIES

Technologies with various improvements for multipollutant control are being developed. ICSC has published several reports to review such emerging technologies (Zhang, 2016). Table 13 below lists emerging technologies for multipollutant control in coal-fired power plants.

TABLE 13 EMERGING MULTIPOLLUTANT CONTROL TECHNOLOGY (SLOSS, 2017)

System	Format	Demonstration status	Marketed by
Wet ESP (WESP)	WESP	Full scale at many plants	Various
COHPAC™	ESP plus FF or pulse-jet FF	1700 MW installed on coal plant and waste to energy incinerators	EPRI, via Babcock and Wilcox, Hamon Research-Cottrell
TOXECON™	Sorbent, and pulse-jet FF (COHPAC plus sorbent)	Fitted in 8 plants in the USA	EPRI, via Babcock and Wilcox, Hamon Research-Cottrell
EFIC, Electrostatic Fabric Integrated Collector	Similar to COPAC with pulse-jet FF	50 units in operation	China Fujian Longking
ESFF, ESP-Fabric Filter Hybrid System	Split-level filters either integrated or separated	3 plants in China and 1 in India	Zheijian Feida Environmental Science and Technology Co
ECO™ Technology	Dielectric barrier discharge, ammonia-based scrubber, and WESP	Slip-stream demonstration	Powerspan
ReACT™	Regenerative activated coke technology	Full scale – Isogo, Japan; Weston, USA; industrial plants in Germany	J-Power, Haldor Topsoe
SNOX™	Dry catalyst/reactors with ammonia addition	Full scale, Nordjyllandsvaerket, Denmark, plus industrial sites	Haldor Topsoe
SNRB™ (SOX-NOx-Rox-Box)	Alkali sorbent injection and high-temperature FF	Demonstration	Babcock and Wilcox
Airborne™ Process	Sodium bicarbonate injection with wet sodium scrubbing and oxidation	Pilot and small scale	Airborne Clean Energy
Neustream™ Technology	Dual-alkali FGD with upstream ozone injection	Pilot scale	Neumann Systems Group
Gore mercury and SO_2 control modules	Passive, modular, fixed absorption media modules	2100 MW installed in coal-fired power plants in the USA and demonstration pilots in European plants	Gore
Skymine™ Process	Electrochemical sodium hydroxide scrubbing	Pilot scale	Skyonic Corporation
Tri-Mer™	Modular ceramic catalyst and oxidant units	Pilot scale	Tri-Mer

WESP systems have been used commercially for over 30 years to control sulphuric acid and particulate emissions. However, historically they are not a preferred choice for large coal-fired power plants. WESP operates similarly to ESP but washes the collecting electrodes with liquid rather than mechanically rapping the collection plates. WESPs can be installed in coal-fired plants, with dry ESP for primary PM control before FGD, or standalone after the wet FGD as a final ‘polishing’ stage to remove very fine particulates, sulphuric acid, and any other mist. A WESP system was installed after a dry ESP and a wet FGD at AES Deepwater high sulphur coal-fired power plant, Texas, USA, showing control of 95–97% PM and 90% sulphuric acid. With no dry ESP installed, the WESP used in Units 1 and 2 at Xcel Energy's Northern States Power Sherco coal-fired power plant achieved a particulate collection efficiency of over 90% and a stack opacity below 10% (Zhang, 2016).

The following summarises examples of the most successful or promising advanced mercury control technologies taken from the more detailed ICSC review (Sloss, 2017):

- **Compact Hybrid Particulate Collector (COHPAC)** was developed by the Electric Power Research Institute (EPRI), USA, in 1991. The FF is located in a separate casing downstream of the ESP (known as COHPAC I) or within the existing ESP casing, by replacing one or more fields with FF modules (COHPAC II). Since the pulse-jet collector operates as a polisher to achieve lower PM emissions, it gives a small footprint on-site, longer bag life, lower pressure drops, and lower parasitic load. The system can be retrofitted on existing units and achieve high PM removal efficiencies at a relatively low cost. Full-scale demonstrations of COHPAC were conducted at the 272 MWe Unit 3 of EC Gaston low sulphur coal-fired power plant and 2 x 575 MWe units at the Big Brown Plant, resulting in 99.9% collection efficiencies, allowing fuel flexibility, reducing opacity, increasing bag filter life, and decreasing operating costs. The technology has been commercial since 2000.
- **TOXECON™ and TOXECON II™ technologies** were developed by EPRI, USA, for removing mercury and fine particulates, by coupling COHPAC with a sorbent injection system upstream of a FF. Babcock & Wilcox and Hamon Research-Cottrell are licensed suppliers of EPRI's COHPAC™ and TOXECON™ systems.
- **Electrostatic-Fabric Integrated Collector (EFIC)** developed by China Fujian Longking, is similar to COHPAC II where the ESP fields are replaced with a pulse jet FF for better fine PM control. The system includes pulsing valves, step-down arrangement of bag compartments, sizing of clean air chamber exit valves, a large clean gas chamber, and a filter bag bypass system for online overhaul. Utilising electric fields causes particle agglomeration and enables easier capture. The first EFIC was installed in 2009 in the last three fields of a four-field ESP on a 660 MWe unit at the Boasham coal-fired power plant in China. EFIC collection efficiency is as high as 99.8% with low pressure drops of 900–1000 Pa, and a lower parasitic load.
- **ESP-fabric filter hybrid system (EFF)** Zhejiang Feida Environmental Science & Technology Co Ltd developed an ESP-FF hybrid system (EFF), which has a split-level filter. Feida's EFF has two types: integrated and separated. The integrated type has the ESP and FF in one case, with a direct connection between the two elements. The dust collector is separated into several passages; each chamber has an exit damper. In the separated type, the ESP and FF are connected by a duct, and the FF area acts as the independent dust collector consisting of several separate chambers. Each chamber is designed with a built-in bypass duct, and entrance and exit dampers. Feida's first EFF system was installed at the Tianjin Chentang coal-fired power plant achieving PM emissions of 5 mg/m³.

- **ReACT Technology –** marketed by Haldor Topsoe has been running since 2002 at J-POWER's Isogo plant in Yokohama, Japan. The plant burns low sulphur coal and incorporates high-efficiency ultrasupercritical boilers, low NOx burners and controls, primary SCR and ESP and uses the ReACT system as a flue gas polishing technique. The system has been in operation since 2002 and demonstrates excellent emissions control. The technology shows over 98% SO_2 removal, over 90% mercury removal, and 20–40% NOx reduction as a co-benefit. The ReACT system is also being applied at the Weston plant in Wisconsin, USA.
- **SNOX system –** marketed by Haldor Topsoe, is an FGD system which includes residual dust removal in the catalyst upstream in an ESP or FF, catalytic reduction of NOx by adding ammonia (NH_3)) to the gas upstream of the SCR DeNOx reactor, catalytic oxidation of SO_2 to SO_3 in the oxidation reactor; and cooling of the gas to about 100°C whereby the sulphuric acid (H_2SO_4) condenses and can be withdrawn as a concentrated sulphuric acid product. The system has an advantage over FGD and SCR/SNCR systems, as it takes up less space and the sale of sulphuric acid as a by-product will also offset installation and running costs. The system has been demonstrated at the Nordjyllandsværket coal-fired combined heat and power plant in Vodskov, Denmark.
- **Airborne Process™** – developed by Airborne Clean Energy, uses a sodium bicarbonate scrubbing technology combined with post-scrubbing oxidants to remove SO_2, SO_3, NOx, mercury, and other chemicals such as sulphuric acid, HCl, and HF acid from flue gases while producing a saleable fertiliser by-product. Sodium scrubbing has been in operation at PacifiCorp's Jim Bridger Power Plant, Naughton Station in Wyoming, and Nevada Power's Gardner Station, USA. Airborne Clean Energy (ACE) has developed a process where the sodium sulphite byproduct can be used to regenerate sodium bicarbonate reagent, while simultaneously producing an agricultural-grade fertiliser. ACE is offering this technology in combination with oxidants to achieve additional NOx and mercury removal. The first demonstration of the integrated technology was installed at LG&E's Ghent Generating Station located in Carroll County, Kentucky, USA. As a part of the USDOE's Clean Coal Power Initiative, the technology was installed on a 5 MW equivalent slipstream of Unit 2, between January and July 2003, which achieved 99.9% SO_2 removal, up to 90% NOx removal with the addition of an oxidant and 60–80% mercury removal.
- **NeuStream^{TM} technology**, developed by Neumann Systems Group, is a compact technology for SO_2 emission reduction using dual FGD and upstream ozone injection. Still under demonstration, the technology is expected to be economical and with a smaller footprint than traditional technology. Colorado Springs Utilities and Neumann Systems Group (NSG) have executed an agreement for the design and installation of new emissions control technology for Colorado Springs Utilities' Martin Drake Power Plant, USA.

- **GORE mercury and SO_2 control system (GMCS)** developed by GORE is a fixed sorbent system based on discrete stackable modules that are installed downstream of a particulate collection system. The modules are designed with a unique open channel structure which provides extremely low pressure drop, avoiding the need for an additional booster fan. The system contains a catalyst (in addition to mercury adsorption and sequestration chemicals) to promote the oxidation of mercury but also of SO_2 into hydrogen sulphate which can be captured separately. The combined system therefore provides both SO_2 and mercury control without the need for any injection of oxidant and does not produce any materials which then have to be captured in existing particulate control systems. Rather the sorbent units themselves can be replaced when necessary. GORE Mercury Control Systems operate in five absorbers in the coal-fired power industry and the total installed operating capacity is currently over 2100 MW (GORE, 2023).
- **SkyMine® process** by Skyonic Corporation is primarily meant for CO_2 mineralisation and capture but also gives additional benefits of capturing SO_2, NOx and mercury. The process uses a packed column scrubber and electrochemical cell to capture hydrogen, chlorine, and sodium bicarbonate. The demonstration was conducted at the Big Brown plant, Texas. It is claimed to deliver 99–100% of SO_2 and NOx removal, and over 97% mercury removal while converting and capturing 80–92% CO_2 (Skyonic, 2008).
- **Tri-Mer's Catalytic Ceramic Filter system – UltraCat** produced by Tri-mer Global Technologies (TGT) is an advanced version of PM, SO_2 and NOx control systems in series, but in a more modular, controllable, and potentially compact manner. Its modular format allows a plant operator to select the individual parts of the process separately to ensure the capture of the pollutants required. UltraCat ceramic filters are embedded with NOx or volatile organic compound (VOC) catalyst particles dispersed within the filter walls. PM, SO_2, HCl, and metals such as chrome-6, and NOx are removed by this single, all-in-one system. A full-scale demonstration of the Tri-Mer system on coal-fired power plants is expected (Tri-Mer Corporation, 2023).

5.5 COMMENTS

Although mercury control in existing air pollution control systems can be significant, it is not guaranteed. When mercury reduction is insufficient, additional techniques and technologies can be applied. Adding oxidants, such as halogens, can increase the amount of mercury in the oxidised form, allowing more to be captured in existing control systems. Sorbents such as activated carbon can also be added to pull down extra mercury in the PM control devices.

Mercury-specific control technologies, which commonly combine oxidation and enhanced PM capture, have been tested and some have proven highly effective. However, these systems are commonly only used in the USA, where the tight mercury emission limits for coal plants require this level of action.

Commercial systems have also been developed in China on plants which are built to demonstrate maximum emission control rather than to comply with emission standards. For the moment, most coal plants do not need to consider mercury-specific control systems. However, this may change in future if, and when, emission limits are tightened.

6 TECHNOLOGY SELECTION

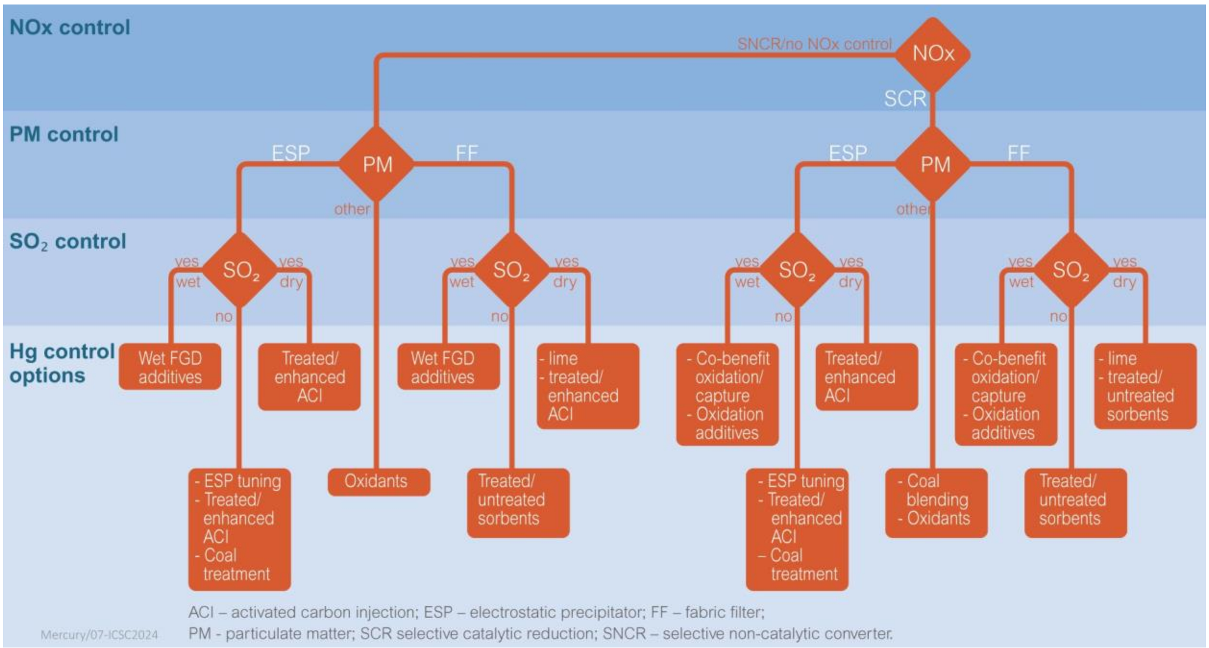
Various pollution control technologies and enhancement options are available to reduce mercury emissions, but the effectiveness of mercury capture also varies from plant to plant depending on the coal quality and plant characteristics, as discussed. It can therefore be a challenge to determine which mercury control strategy is appropriate in each situation.

In India, the emission norms are the most relevant factor for determining what, if any, action needs to be taken. Each plant will need to determine, on a case-by-case basis, what emission reduction is required and to investigate, with the assistance of technical experts, the most appropriate means of mercury reduction. Although many plants in India may currently comply with the relatively lenient emission limit for mercury, it would be wise for plant operators to start to build mercury control into current emission reduction strategies to avoid any expensive additions in future, for if and when the legislation is tightened.

Cost-effectiveness will be a priority, so co-benefit options, which take advantage of pollution control systems which are already in place, or which will be installed soon, should be considered first. For example, in Indian coal-fired power plants; ESP are already widely installed, and FGD has been chosen for significant SO_2 control at many plants. These pollution control systems will provide some co-benefit mercury reduction and, since the mercury emission norms are currently relatively lenient, compared to those in the USA, the co-benefit effects of ESP and, where relevant, FGD, should be more than sufficient to ensure mercury emission compliance.

6.1 PROCESS OPTIMISATION GUIDANCE, POG

The UNEP Coal Partnership has produced the Process Optimisation Guidance (POG) document to summarise mercury control strategies for coal-fired power plants. The POG recommends a technology selection decision-making tool which takes the form of a flow chart (UNEP, 2010). The chart, shown in Figure 7, shows the most likely suitable options, but without any commercial bias. The POG document then provides summaries of each of the technology options, from coal cleaning and fuel switching through to activated carbon injection.



ACI – activated carbon injection; ESP – electrostatic precipitator; FF – fabric filter;
PM - particulate matter; SCR selective catalytic reduction; SNCR – selective non-catalytic converter.

Figure 7 Decision-tree to determine the most appropriate mercury control options (UNEP, 2010)

The decision-tree presents two broad options for mercury emission control: first, for the plants which can have SCR/SNCR for NOx control; and second, for those with no SCR/SNCR options. The plant operator can choose the 'best fit' technology options for mercury control according to the current or planned plant configuration. The POG does not list the costs of the various options, as they are likely to vary with location and to reduce over time. However, it does include a table ranking the relative costs of different control options.

6.2 IPOG

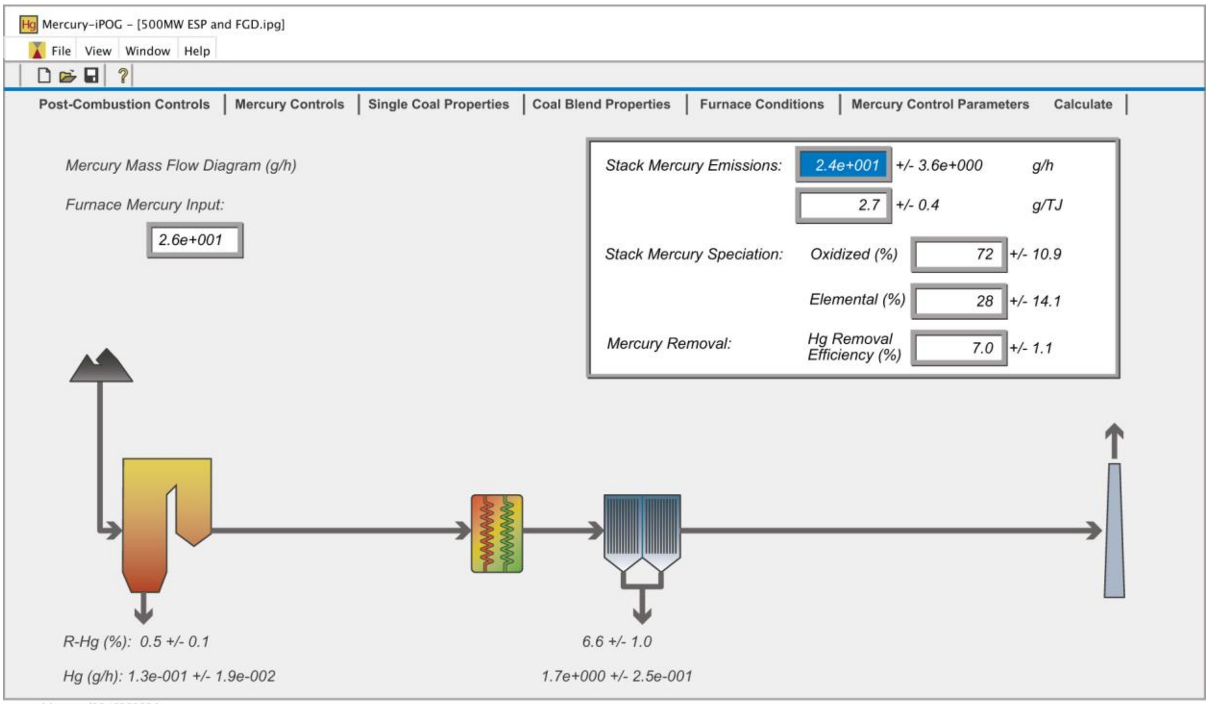
Based on UNEP's POG concept, a calculation model, in the form of a user-friendly software application named iPOG has been developed by Niksa Energy Associates. This application allows plant operators to input plant operation-specific data on coal, technology, and technique availability to predict the mercury emissions from the plant. The application can be used with generic data, such as without any mercury control, but also, with all sets of possible combinations for co-benefits and mercury-specific controls. The iPOG estimates mercury emission rates from power plants with any coal or coal blend, given a few coal properties, the gas cleaning configurations selected firing and gas cleaning conditions, and an assortment of mercury control technologies.

The user can input data from their own plant quickly – coal characteristics, plant configuration and so on – to determine estimated baseline mercury emissions. They may then go back and test the programme to predict what changes will occur in mercury emissions with plant variations, as listed in Table 14. All of the most common gas cleaning configurations are available, and users can assess mercury emission reductions by coal pretreatment and blending, co-benefits to mercury capture from existing pollution control equipment for NOx, PM, and/or SO$_2$, and mercury-specific control technologies, such as halogen addition with or without ACI with untreated or brominated sorbents. Licensed commercial mercurycontrol technologies, such as TOXECON-I and TOXECON-II and bromine addition, can also be examined.

TABLE 14 MERCURY CONTROL OPTIONS SUGGESTED IN POG AND IPOG (UNEP, 2011)

POG	**iPOG**
Mercury control options	Mercury control options
Coal treatment	Coal treatment
Co-benefits for mercury oxidation/capture	Co-benefits for mercury oxidation/capture
Hg^0 oxidation additives	Hg^0 oxidation additives
Untreated ACI	Untreated ACI
Treated/enhanced ACI	Treated/enhanced ACI
Untreated non-carbon sorbents	
Lime injection	
ESP tuning	
Oxidants for wet PM	
Wet FGD additives	
The application can be downloaded from: https://www.unep.org/resources/report/interactive-process-optimization-guidance-ipogtm	

The screenshot of the iPOG application in Figure 8 below shows the various tabs to select applicable and suitable options and to enter the available data across post-combustion pollution controls, mercury-specific controls, coal properties, furnace conditions and mercury control parameters, in order to calculate mercury emission in the far-right tab.



Mercury Mass Flow Diagram (g/h)

Furnace Mercury Input: 2.6e+001

Stack Mercury Emissions: 2.4e+001 +/- 3.6e+000 g/h

2.7 +/- 0.4 g/TJ

Stack Mercury Speciation: Oxidized (%) 72 +/- 10.9

Elemental (%) 28 +/- 14.1

Mercury Removal: Hg Removal Efficiency (%) 7.0 +/- 1.1

R-Hg (%): 0.5 +/- 0.1

Hg (g/h): 1.3e-001 +/- 1.9e-002

6.6 +/- 1.0

1.7e+000 +/- 2.5e-001

Mercury/08-ICSC2024

Figure 8 iPOG application screenshot (Jozewicz, 2023)

The ICSC used the iPOG model to estimate mercury emissions for an Indian coal-fired power plant using average coal quality with a gross calorific value of 4,511 kcal/kg, sulphur 6.4%, mercury 0.18%, ash 32.3% and moisture 6.4% to be used in 500 MW unit with 35% efficiency, 110% excess air and 10% preheater air leakage.

The iPOG predicted the following for the 500 MW unit:

- with only ESP present, the mercury reduction will only be 3.5% of the mercury resulting in an emission of 52 g/h (21 µg/m^3) which is below the stipulated norm/emission standard of 30 µg/m^3;
- if a FF replaced the ESP, the mercury emissions would be 25% lower at about 40 g/h (16 µg/m^3);
- with both an ESP and wet FGD, the projected mercury emission would be 43 g/h (17 µg/m^3) (similar to the plant installed with only a FF).

The iPOG results estimate that the ESP-only unit would release about 70% of total mercury emissions as elemental mercury whereas one with ESP + wet FGD would release almost all of its mercury emissions as elemental mercury. The iPOG was then used to estimate the effect of mercury-specific reduction strategies (Sloss and others, 2023b):

- the addition of 200 ppm of bromine would achieve over 40% mercury emission reduction for the unit with wet FGD (about 30 g/h or 12 µg/m^3)

- the same amount of bromine with ESP + FGD would give a 44% emission reduction (22 g/h or 17 µg/m^3)
- if an SCR system was added, there could be over 60% mercury removal (20 g/h or 8 µg/m^3)
- the SCR+ESP+wet FGD system performance could be improved further by the addition of chlorine to the coal - 100 ppm of chlorine addition could reduce mercury emissions to 10 g/h (4 µg/m^3)
- if untreated (non-brominated) ACI were injected at a rate of 0.032 g/m^3, 38% removal (emission rate of 33 g/h or 18 µg/m^3 was predicted. With brominated ACI, 84% removal could be achieved (8.8 g/h or 5 µg/m^3 of mercury in the flue gas), comparable to the US emission limits.

These iPOG estimates suggest that the application of current and impending emission controls for PM, SO_2 and NOx could help reduce mercury mass emissions by up to 50% or more. This reduction could be accomplished by the installation of additional equipment such as SCR and/or wet FGD to achieve NOx and/or SO_2 emission limits, respectively.

Additional measures to improve mercury oxidation in addition to SCR and/or wet FGD could reduce mercury concentration in the flue gas to below 10 µg/m^3 both with ESP+wet FGD+ 200 ppm bromine addition; and SCR+ESP+ wet FGD+300 ppm chlorine addition. Currently, neither of these scenarios may be particularly attractive to Indian utilities. The first scenario relies on the addition of significant amounts of bromine, which may promote corrosion and thus may require enhanced, more expensive, materials for the construction of downstream equipment and ductwork. The second scenario relies on the deployment of SCR which is an expensive technology (Sloss and others, 2023a). However, this theoretical analysis demonstrates that there are options to enhance mercury control at coal plants should it become necessary in future.

6.3 COMMENTS

Although Indian emission limits for mercury are sufficiently lenient that most plants should already be in or near compliance, it is prudent for coal plants to plan for the tightening of this emission limit. Tools provided by the ICSC and UNEP, such as the POG and iPOG, can help existing plants estimate baseline mercury emissions and also future emission values under different plant retrofit configurations. Wet FGD and SCR systems will reduce mercury emissions by up to around 40–50% but this could be increased by the addition of oxidants and/or sorbents. If necessary, these additives could be applied to lower emissions from Indian coal plants down by almost an order of magnitude, although this could come at a significant cost (retrofitting and consumables).

7 MERCURY EMISSION MONITORING

Correct emission monitoring is important in a pollution control strategy. As mercury is a low-concentration pollutant, identifying accurate emissions is a challenge which asks for specialised and suitable technology and proper operation and maintenance. Since the technologies are specialised, these are more costly than those required for broader category pollutants, such as PM, SO_2 and NOx. Achieving emission norms and reduction targets is only successful if emissions can be measured, and compliance assured.

7.1 MANUAL REFERENCE/WET CHEMICAL METHODS

This European standard, EU CEN 13211-2003, specifies a manual reference method for the determination of the mass concentration of mercury in exhaust gases from ducts and chimneys. The method is applicable for the total mercury concentration range of 0.001–0.5 mg/m^3in the flue gases with the following gas composition range: total suspended matter 0–20 mg/m^3; hydrocarbons 0–10 mg/m^3; HCl 0–50 mg/m^3; HF 0–10 mg/m^3; SO_2 0–250 mg/m^3; NOx 0–500 mg/m^3; CO_2 0–15 vol%; moisture (g) 10–25 vol%; O_2 8–15 vol% (dry) and temperature 60–140°C (iTeh Standards, 2023).

The USEPA Method 29, which is the most used method for trace metals, especially mercury measurement (CAS No. 7439-97-6) from sources such as coal-fired plants, is similar. This method requires following the provisions of USEPA Method 5 and Method 12. Mercury emissions can be measured, alternatively, using EPA Method 101A (Appendix B, 40 CFR Part 61) which measures only mercury (USEPA, 2016).

The Ontario Hydro (OH) an ASTM method adopted by USEPA, for reference measurement of total and speciated mercury for coal-fired power plants, is similar to a wet chemical method based on a number of alkali and acidic impingers in sequence. Through additional application and experimentation, these issues have been further investigated and characterised. Experimental data support the application of the OH measurements to concentrations less than 0.001 mg/m^3. Experimental data also support the application of the OH method to other combustion sources, including hazardous and municipal waste combustors (USEPA, 2004).

These methods are not simple, and it is recognised that they should only be performed by qualified specialists. Method 29 is a relatively complex wet chemical method involving the passing of flue gas through several impingers containing different solutions, including nitric acid. Each of these solutions must be collected and analysed separately using chemicals which must be shipped from the field for off-site analysis. The method is time-consuming. Wet chemical methods have been required to calibrate continuous emission monitoring systems (CEMS) for mercury. However, modern CEMS are self-calibrating using mercury standards. They must still be validated against a separate system to ensure that they are functioning correctly.

7.2 SORBENT TUBES

Mercury attaches to activated carbon and similar materials and, in addition to their use in control technologies, sorbents can also be used to capture mercury for quantification by monitoring systems. The USEPA has developed its Mercury Measurement Toolkit, which is mobile and based on sorbent tubes. Mercury passes through the sorbent tube and is captured according to its speciated form over an extended period. The material in the tube is analysed using thermal desorption to measure the mercury content. These measurements, combined with process information (flow rate, fuel calorific value and feed rate), are used to calculate total mercury mass emissions ($\mu g/m^3$) or mass emissions per unit of heat input. The robustness and simplicity of the sorbent tube system make it ideal for both short-term and long-term sampling. UNEP-sponsored projects, led by the ICSC have deployed the toolkit in several countries, including Russia and South Africa, to successfully measure mercury emissions from large coal-fired power plants (Sloss, 2015).

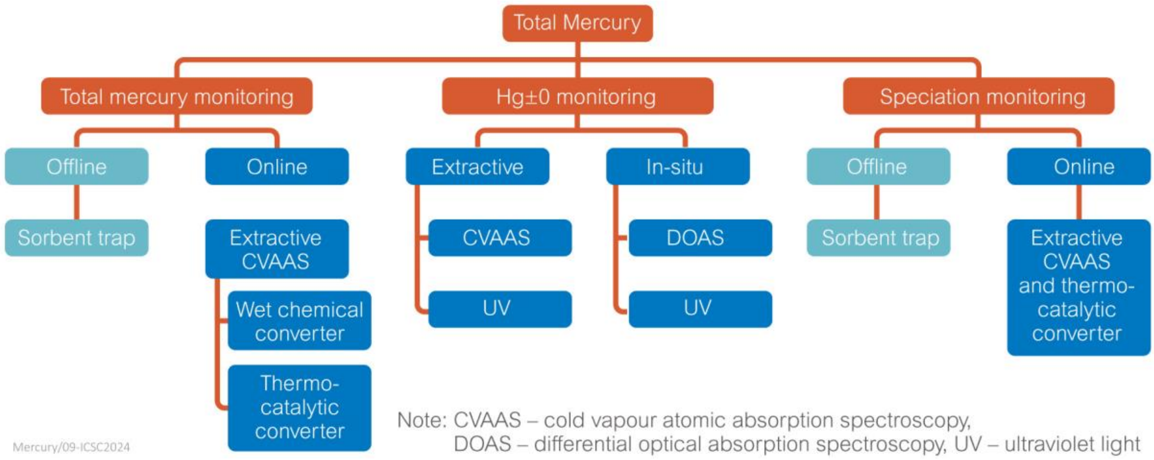
A typical sorbent trap system costs around $130,000–150,000 if the analysis system is included and only $80,000–100,000 if the tubes are sent to a commercial lab for analysis. Consumables and labour are then around $20,000–25,000 per year, significantly lower than the CEMS discussed earlier (Siperstein, 2011).

Method 30A is a procedure for measuring total vapour phase mercury emissions from stationary sources using an instrumental analyser. This method is particularly appropriate for performing emissions testing and for conducting relative accuracy test audits (RATAs) of mercury CEMS and sorbent trap monitoring systems at coal-fired combustion sources (USEPA, 2017).

EERC (Energy and Environmental Research Centre, ND) in the USA have developed their own ME-ST sorbent tube-based system for mercury measurement. They have successfully demonstrated it on pilot-scale standard pulverised coal-fired systems but also on oxycombustion and gasification systems. The ME-ST system can be used for all of the MATS-specified metals and not just mercury, with detection levels significantly lower than those possible with Method 29 (Lentz and Pavlish, 2011).

7.3 MERCURY CEMS

Mercury CEMS (Figure 9) must measure total mercury from flue gases which are at elevated temperatures and often contain acidic and interfering species. Mercury CEMS must therefore be robust and well designed. In order to determine total mercury emissions, these systems must also be able to detect and quantify both elemental and oxidised mercury. This requires a conversion system, which is often the feature that causes problems in mercury CEM maintenance.



Note: CVAAS – cold vapour atomic absorption spectroscopy,
DOAS – differential optical absorption spectroscopy, UV – ultraviolet light

Figure 9 Mercury CEMS measuring technology options (Zepeck, 2022)

Both in situ and extractive-type technologies are available for mercury CEMS. Using the ultraviolet (UV)/Fourier Transform Infrared (FTIR) difference optical absorption spectroscopy technique, the system is non-contact, with a fast response. A basic system includes an analyser spectrometer, an emitter/receiver set, and an optical fibre cable and calibration gas cylinder. Extractive-type mercury CEMS consist of – a gas sampling system, instrument air conditioning system, thermal converter and cell, test gas generator and vaporiser (of test gas generator). In the case of Thermo catalytic converters, the conversion of Hg^{2+} into Hg^0 takes place which is monitored in a UV detector (Zepeck,2022).

In Europe, EN 14884 is the standard for mercury CEM. The standard is general, outlining the methods for calibration, positioning and so on. It does not prescribe any type of CEMS but requires the system to meet defined performance standards. There are numerous commercial CEMS available, the most popular of which appear to be Tekran, ThermoFischer, Lumex, SICK, Durag and PS Analytical systems.

Mercury CEMS can typically cost from around $150,000 up to over $350,000 and site preparation can add another £200,000–350,000 to the total cost. There are ongoing costs associated with maintenance and upkeep but, in the long term, the manufacturers report that these should generally be no more than would be associated with any standard CEM (such as SO_2 and NOx – around $50,000–90,000 per year (Sloss, 2012). Mercury CEM has been prone to problems with reliability. In the past, operators reported problems with low availability, interference, high maintenance costs and issues with heated sample lines. Although manufacturers suggest that mercury CEM can be easy to maintain, users have reported that, in practice, they require far higher levels of maintenance than other CEMS with some systems requiring significant hands-on support at levels of 20 hours per week or more. Some operators switched from CEMS to sorbent traps because of these issues (Kietzer, 2011).

Older systems were reliant on consumables, solutions such as tin chloride or a heated catalyst, to convert mercury oxides to the elemental form to obtain total mercury measurements. Many systems now use extreme heat (>800°C) to crack the mercury compounds into their elemental form thus avoiding the need for any consumables (Kietzer, 2011).

Cross-interference from other species such as SO_2 can also be an issue. This could be avoided by using a gold-trap to capture the mercury, move it and analyse it in a clean gas zone. This, however, made the system more of a batch-process than a CEMS. Many systems avoid this by using the 'Zeeman effect' which uses two magnetically separated wavelengths to exclude cross-interferences. Mercury CEMS have improved significantly in the last few years with maintenance intervals in the range of 3–6 months and relative accuracy results of >5%. NIST standards have also been developed to provide a level of calibration which was not available before 2010 (Kietzer, 2011).

7.4 COMMENTS

Since mercury emission limits have been introduced in India, emissions from sources such as coal-fired power plants must be monitored to ensure that plants are in compliance. Wet chemical methods are available but tend to be cumbersome and only provide results for a short period of sampling. CEMS for mercury are available but can be expensive. However, these CEMS are ideal for sources where the emissions of mercury may vary. For coal plants, which tend to produce similar amounts of mercury per tonne of coal fired, it may be more cost-effective for sources to use the sorbent trap method to produce an average mercury emission value for a set period of time, as long as the coal plant operation does not vary significantly. Sorbent traps can be used annually to confirm that the average mercury emissions from a plant have not changed.

8 CONCLUSIONS AND RECOMMENDATIONS

Coal utility plants in India have been monitoring and controlling PM emissions for many years and, as a result of the new norms, the focus is now on SO_2 and NOx. However, to date, mercury emissions have largely been ignored. The mercury emission limit in India (0.03 mg/m^3) is around an order of magnitude more lenient than the limits in the EU and the USA. Most plants can meet the 0.03 mg/m^3 emission limit by firing average coals, without the installation of any control technologies other than ESP or baghouses for particulate control. However, India is the second largest mercury emitter in the world and the coal-based power sector alone contributes over 80% of these emissions. Because of the risk of significant emissions continuing from the coal sector, the Indian emission limit for mercury will probably be tightened in the future, to align with international emission limits. Further, as a signatory to the UN Minamata Convention on Mercury, India is obliged to "control and where feasible reduce" emissions of mercury. It is therefore prudent for India to ensure that mercury control and monitoring is considered within current plant retrofit plans, as this could significantly offset mercury-specific control costs in the future.

The average mercury content in Indian coal is not reported to be high. However, estimates from various sources vary widely. For example, UNEP reports mercury content in Indian coal to be typically in the range of 0.003–0.34 g/t with an average concentration of 0.14 g/t (UNEP, 2018). Since the power sector burns huge amounts of coal, nearly 700 Mt/y in 2021 (IEA, 2022), a large amount of mercury is released into the environment.

As mentioned in Section 3.1, unburnt carbon and other materials in fly ash can enhance mercury capture. Indian coals are high in ash and, as a result, Indian fly ash tends to have a higher-than-average concentration of mercury. Indian coal ash is reported to have an average mercury concentration of 0.53 mg/kg, based on measurements from a few selected power plants.

Emission estimates for mercury concentrations from Indian coal plants are not published; few plants have mercury emission monitors in place and the emission limit is not yet applicable at many plants. However, assuming that mercury emissions from Indian plants are similar to those at uncontrolled plants in other regions, even unabated emissions are likely to be below 0.03 mg/m^3. The emission limits for the USA and EU, as discussed in Chapter 2, have been set almost an order of magnitude lower than this value in order to make mercury-specific emission reduction a technical requirement. Some Indian coal-fired power plants will therefore argue that they can comply with the 0.03 mg/m^3 limit without taking any action. However, this will need to be confirmed on a plant-by-plant basis under the incoming emission legislation.

The GOI is confident that the new emission limit for mercury will not require additional mercury-specific technologies; the MOEFCC submitted to the Supreme Court of India in February 2018 that:

> ALL UNITS ARE LIKELY TO MEET MERCURY EMISSION NORMS AFTER INSTALLATION OF POLLUTION CONTROL

This declaration assumes the imminent compliance of Indian coal plants with other relevant emission norms. SO_2, NOx and PM control offer additional co-benefit potential for mercury emission reduction. However, for these co-benefits to materialise in the near future, air pollution control equipment for PM, SO_2, and NOx must be installed, operated, and maintained effectively. For mercury, the emission reduction timeline will likely follow the FGD installation timeline since this technology has the greatest co-benefit effect for mercury control (see Chapter 4). Indian plants have not opted for SCR for NOx control so any co-benefit from these systems will be delayed. ESPs are already widely installed across coal-fired power plants for PM emission control.

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