

Current Management Status of Mercury Emissions from Coal Combustion Facilities: International Regulations, Sampling Methods, and Control Technologies

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Abstract

Mercury (Hg), which is mainly emitted from coal-fired power plants, remains one of the most toxic compounds to both humans and ecosystems. Hg pollution is not a local or regional issue, but a global issue. Hg compounds emitted from anthropogenic sources such as coal-fired power plants, incinerators, and boilers, can be transported over long distances. Since the last decade, many European countries, Canada, and especially the United States, have focused on technology to control Hg emissions. Korea has also recently showed an interest in managing Hg pollution from various combustion sources. Previous studies indicate that coal-fired power plants are one of the major sources of Hg in Korea. However, lack of Hg emission data and feasible emission controls have been major obstacles in Hg study.

In order to achieve effective Hg control, understanding the characteristics of current Hg sampling methods and control technologies is essential. There is no one proven technology that fits all Hg emission sources, because Hg emission and control efficiency depend on fuel type, configuration of air pollution control devices, flue gas composition, among others. Therefore, a broad knowledge of Hg sampling and control technologies is necessary to select the most suitable method for each Hg-emitting source.

In this paper, various Hg sampling methods, including wet chemistry, dry sorbents trap, field, and laboratory demonstrated control technologies, and international regulations, are introduced, with a focus on coal-fired power plants.

Key words : Mercury (Hg), Hg sampling method, Hg control technology, Coal-fired power plants, Coal combustion, Air Pollution Control Devices (APCDs)

1. INTRODUCTION

Major sources of atmospheric Hg are combustion facilities such as fossil-fuel combustors, waste incinerators, and hazardous waste incinerators. Coal-

fired power plants, especially, have been regarded as the largest source of Hg in the US and EU (Gibb *et al.*, 2003; EU, 2001; US EPA, 1997). Once Hg is emitted into the atmosphere, it enters global circulation patterns, and finally deposits in bodies of water and sediment. Major forms of Hg from combustion flue gases include gaseous elemental Hg (Hg^0), oxidized Hg (Hg^{2+}) and particulate bound Hg (Hg_p).

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Hg^{2+} is expected to remove by existing air pollution control devices (APCDs), such as electrostatic precipitators (ESPs), fabric filters (FFs), or wet flue gas desulfurization (FGD), because Hg^{2+} is water soluble and easily attaches to particulate matter in flue gas. By increasing the portion of Hg^{2+} in flue gas, the removal efficiency can be maximized with existing APCDs.

On March 2005, the US EPA announced the Clean Air Mercury Rule (CAMR), aiming to reduce air pollutants such as SO_x , NO_x , and Hg from coal-fired power plants by about 70% by 2018 (US EPA, 2005). This legislative, multi-pollutant approach is managed by a market-based 'cap and trade' program. According to previous FDA/EPA advisories (US EPA, 2004), pregnant women and women of childbearing age should limit their consumption of fish to prevent methyl mercury accumulation, which is known to attack the developing nervous system of an unborn child. Therefore, reducing the total emission of Hg into the atmosphere is necessary to protect humans and wildlife from Hg pollution. The objectives of this study are to review the latest Hg control technologies in coal-fired power plants and their demonstrated efficiencies to provide information on current Hg sampling methods, control technologies, and regulations.

2. MERCURY REGULATIONS

2.1 International agreements

Hg pollution is not a local or regional problem because Hg^0 , one of the major forms of Hg, has the ability to be transported around the world. For example, the Arctic, even though it is far from major sources of Hg, has already been contaminated with Hg compounds (UNEP, 2002). The United Nations Economic Commission for Europe (UNECE), Geneva Convention on Long-range Transboundary Air Pollution (LRTAP) has been extended by eight specific protocols, including the Aarhus Protocol on heavy metals (Gibb *et al.*, 2003). The protocol focused on three major heavy metals: cadmium, lead, and mercury, aiming to reduce their emissions to

below 1990 levels through Best Available Techniques (BAT) on stationary industrial sources, combustion processes, and waste incineration. As of November 2003, seventeen countries in Europe and America ratified or accepted the protocol of initiating controls by December 29th 2003 (Gibb *et al.*, 2003).

In 2002, the United Nations Environment Programme (UNEP) published the Global Mercury Assessment (UNEP, 2002), summarizing broad issues like current Hg exposure and risk evaluation for humans, sources and cycling of Hg in the global environment, and prevention, control technologies and practices. The report concluded that "there is sufficient evidence of significant global adverse impacts to warrant international action to reduce the risk to human health and/or environment arising from the release of mercury into the environment." The working group agreed on the need to submit possible immediate actions on impacts of Hg to the Governing Council (UNEP, 2002).

2.2 United States of America

On March 15, 2005, the US EPA issued a rule to permanently cap and reduce Hg emissions from coal-fired power plants, making the United States the first country in the world to regulate Hg emissions from coal-fired power plants (US EPA, 2005). The EPA believes trading is the most cost effective mechanism for reducing Hg emissions from coal-fired power plants. In addition to this, the added benefit of the cap-and-trade approach is that it fits well with the sulfur dioxide (SO_2) and nitrogen oxides (NO_x) emission caps under the Clean Air Interstate Rule (CAIR). CAIR establishes cap-and-trade programs that considerably limit SO_2 and NO_x emissions from the power sector. The advantage of Hg regulation using the same regulatory mechanism for SO_2 and NO_x means significant reductions in Hg emissions because reductions of oxidized Hg will be achieved by the air pollution controls already designed and installed to reduce SO_2 and NO_x . Thus, the coordinated regulation of Hg, SO_2 , and NO_x allows Hg reduction to be achieved in a cost-effective manner.

CAMR aims to reduce Hg emissions from coal-fired power plants from 48 ton/yr to 38 ton/yr by 2010 (first phase), and to 15 ton/yr by 2018 (second phase). This reduction corresponds to approximately 70% of Hg emissions in 1999. This mandatory rule will enact significant penalties for noncompliant facilities. However, if emissions at a facility fall below the cap level, the plant owner can sell emission 'credits' to another facility (US EPA, 2005). The EPA believes that the cap-and-trade program can reduce Hg emissions and provide active motivation for the reduction of pollutant emissions from power utilities.

2.3 European commission

The European commission published a position paper on Hg in 2001 (EU, 2001). The position paper was based on the most up-to-date knowledge of European sources, natural and anthropogenic, and major processes/mechanisms influencing Hg cycles in Europe and in the global environment and its impact on human health. The working group recommended a specific action plan for reducing the atmospheric Hg input into terrestrial and aquatic ecosystems in Europe, including the reduction of Hg emissions from major anthropogenic sources (EU, 2001). European communities must follow the following policies that will directly or indirectly contribute to the emission reduction of trace elements from coal-fired combustion and gasification plants.

2.3.1 Directive 96/61/EC, Integrated Pollution Prevention and Control (IPPC) (Gibb *et al.*, 2003)

The IPPC directive is applicable to specified industrial activities, including combustion installations with a thermal input exceeding 50 MW. It covers metals and their compounds from the sources and must be based on the principle of Best Available Technology (BAT). It has been applied to new installations since 1999, while existing facilities had to comply by October 2007. This will help to establish the European Pollutant and Emission Register (EPER) that reports annually on emissions of many chemical species in air, land, and aquatic systems.

2.3.2 Directive 2001/80/EC, Large Combustion Plant Directive (LCPD) (Gibb *et al.*, 2003)

This directive applies to the emission of trace elements from coal-fired furnaces. Like the IPPC directive, the LCPD applies only to plants with over a 50 MW capacity and applies to new plants licensed after 1987. However, old plants are required to comply from 2008 onwards. The Commission had to submit a report to the Council and European Parliament by December 2004, focusing on the amount of heavy metals emitted by large combustion plants, along with a detailed reduction plan.

3. MERCURY SAMPLING AND MEASUREMENTS

3.1 Wet chemistry-based sampling methods

Wet chemistry-based Hg sampling methods for the measurement of combustion based emissions have been updated in documents US EPA 29, 101A, 101B, Tris-Buffer, Ontario Hydro Method (OHM), among others. In Table 1, information on wet chemistry-based Hg sampling methods is summarized (Linak *et al.*, 2001). Shaded impingers are used to collect oxidized Hg (Hg^{2+}), while a $\text{H}_2\text{SO}_4\text{-KMnO}_4$ solution is able to absorb elemental Hg (Hg^0) or total Hg from the source. Among these methods, OHM is mainly used for Hg sampling and speciation measurement from coal-fired power plants, which is registered in the American Society for Testing and Materials (ASTM) D 6784.

The absorbed liquid sample and particulate is treated and measured with a CVAAS (Cold Vapor Atomic Absorption) or CVAFS (Cold Vapor Atomic Fluorescence spectrometry) analyzer. Usually, a stannous chloride solution (SnCl_2) is used as the reducing agent for Hg^0 . Table 1 shows a summary of Hg sampling methods and the relevant set-up of impinger trains and reagent content.

3.2 Dry sorbents trap sampling methods

Although OHM is widely used for field Hg sampling, some disadvantages of this method include the use of hazardous chemicals, large sample volumes due to high Hg blanks, lack of data due to ex-

Table 1. Summary of mercury sampling methods and their impinger train settings.

Impinger train No.	M101A ^a	M29 ^a	M101B ^b	Tris-Buffer ^b	OH ^b	AMS ^b
1	10% H_2SO_4 - 4% KMnO_4	Empty (Optional)	Deionized H_2O	Tris/EDTA*	1N KCl	1N NaOH
2	10% H_2SO_4 - 4% KMnO_4	5% HNO_3 - 10% H_2O_2	Deionized H_2O	Tris/EDTA*	1N KCl	1N NaOH
3	10% H_2SO_4 - 4% KMnO_4	5% HNO_3 - 10% H_2O_2	5% HNO_3 - 10% H_2O_2	10% H_2SO_4 - 4% KMnO_4	1N KCl	Deionized H_2O
4	Silica gel	Empty	Empty	10% H_2SO_4 - 4% KMnO_4	5% HNO_3 - 10% H_2O_2	Empty
5	–	10% H_2SO_4 - 4% KMnO_4	10% H_2SO_4 - 4% KMnO_4	Silica gel	10% H_2SO_4 - 4% KMnO_4	10% H_2SO_4 - 4% KMnO_4
6	–	10% H_2SO_4 - 4% KMnO_4	10% H_2SO_4 - 4% KMnO_4	–	10% H_2SO_4 - 4% KMnO_4	10% H_2SO_4 - 4% KMnO_4
7	–	Silica gel	Silica gel	–	10% H_2SO_4 - 4% KMnO_4	Silica gel
8	–	–	–	–	Silica gel	–
Source	US EPA Method	US EPA Method	US EPA Method	DOE/EPRI (1996)	ASTM D 6784	DOE/EPRI (1996)

^aUS EPA Method 101A and 29 can measure total Hg only

^bUS EPA Method 101B, Tris-buffer, Ontario Hydro Method (OH), Alkali Mercury Speciation (AMS) attempt to separate Hg^{2+} and Hg^0 species. For these methods, Hg recovered from the shaded impingers train can be regard as Hg^{2+} and the other sampling train can absorb Hg^0

*Tris (Hydroxymethyl)aminomethane (Tris) buffer solution/ethylene diamine tetraacetic acid (EDTA) chelating agent (Table adapted from: Linak *et al.*, 2001)

tended sampling time, high cost, and labor intensity (Brunette *et al.*, 2004; Laudal *et al.*, 2004). To prevent the aforementioned problems, new sampling methods are needed.

The US EPA proposed a novel Hg sampling method, draft method 324, using dry sorbent material for the capture of Hg from combustion flue gas (Fig. 1) (US EPA, 2004). The sorbent trap, KCl-coated quart beads, is placed in front of the sampling probe and followed by iodine-impregnated, activated carbon. The former adsorbs Hg^{2+} and the latter chemisorbs Hg^0 , if flue gases are withdrawn semi-isokinetically from combustion flue gas. In addition, German studies show that some special resins can adsorb HgCl_2 selectively (Gutberlet and Tembrink, 2004). Dowex[®] resin may replace KCl-coated beads for Hg field sampling. According to previous thermodynamic studies, a major form of oxidized Hg from combustion flue gas is HgCl_2 . Therefore, Dowex[®] resin is advantageous for the

study of Hg speciation and field sampling. This kind of ‘sorbent trap’ sampling method has the following advantages: no hazardous chemicals, low Hg blank, low sampling volume leading to shortened sampling time and more data, and low cost/labor (Gutberlet *et al.*, 2004; Laudal *et al.*, 2004; US EPA, 2004b).

3.3 Continuous Emission Monitoring (CEM) methods

Although wet chemistry-based Hg sampling methods are used widely in the field and provide good results, they have several disadvantages such as a high level of QA/QC and well trained personnel, lack of real-time data, lengthy testing time, and inability to provide long-term results showing Hg emission variations (Laudal *et al.*, 2004). For those reasons, on-line monitoring Hg analyzers are being developed to measure total Hg and Hg speciation in combustion flue gas.

Currently, a pretreatment or conversion system is

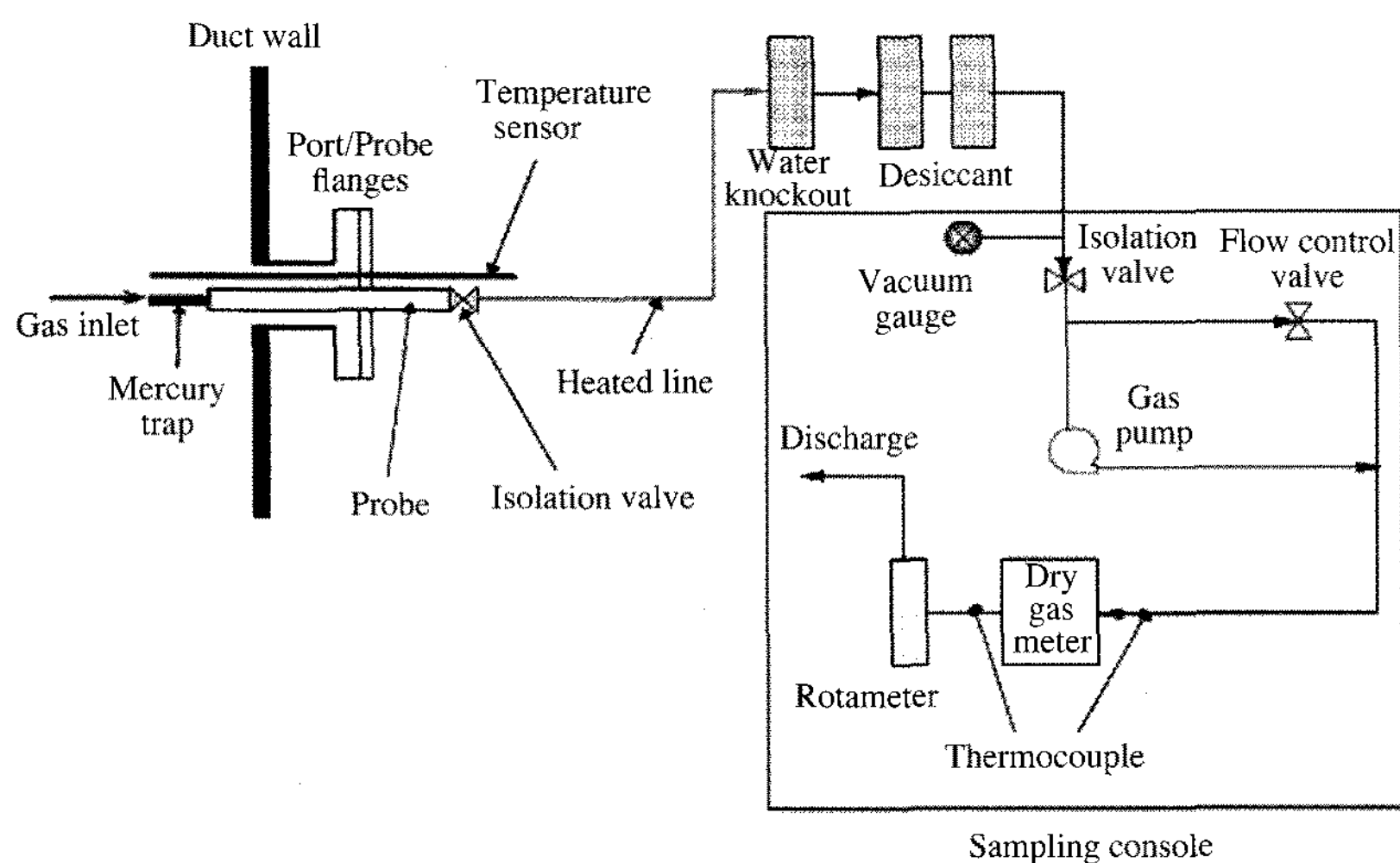


Fig. 1. Schematic diagram of US EPA draft method 324.

needed to measure total Hg and Hg speciation because Hg analyzers such as AA (Atomic Absorption) or AF (Atomic Fluorescence) read only Hg^0 . Semi-kinetically withdrawn flue gas goes into a wet/dry type pretreatment system where Hg^{2+} is converted to Hg^0 to measure total Hg concentration, while another flue gas stream goes into a chiller to condense moisture and Hg^{2+} . Only Hg^0 is released, and the concentration is measured. The portion of Hg^{2+} is calculated using the difference of these two results (Laudal *et al.*, 2004; Meischen *et al.*, 2004; Schmid, 2002).

3.3.1 Wet chemistry conversion systems

Usually wet chemistry conversion systems use a SnCl_2 solution for the reduction of Hg^{2+} to Hg^0 prior to analysis. A SO_2 removal scrubber solution is employed because SO_2 can interfere with the analysis of mercury.

3.3.2 Dry/thermal conversion systems

Gas-phase Hg^{2+} can be reduced to Hg^0 by heating or using a catalyst. The major concern is re-oxidation or re-combination of reduced Hg^0 to an oxidized form of Hg. To prevent this problem, specially developed catalysts convert Hg^{2+} to Hg^0 at much lower temperatures, decreasing the possibility of re-combination. Another method is thermally reduced

Hg rapid quenching to decrease re-oxidation of Hg. This method uses a gold trap and diluted flue gas.

Hg concentration and speciation can be affected by particulate matter in the flue gas, especially fly ash, thus both types of Hg CEM require fly ash treatment devices. One available device is a specially designed particulate separation probe. Unfortunately, there are still several difficulties while operating Hg CEMs. For example, at high temperature conditions, a high moisture content results in condensation with acidic gases thereby causing corrosion of the equipment and plugging at high particulate conditions.

3.4 Evaluation of mercury sampling and analysis methods

The most widely-applied Hg sampling method is the wet chemistry-based OHM. As described above, wet chemistry-based sampling methods have a lot of disadvantages such as high cost/labor, long test times, few data points, use of hazardous materials, and so on. In addition, Hg^{2+} can be over-estimated by impinger oxidation when a high chlorine content exists in flue gas (Linak *et al.*, 2001).

To overcome the sampling problems with wet chemistry-based methods, the US EPA has developed EPA method 30B, which is a dry sorbent type

sampling method. Method 30B can measure vapor phase Hg compounds including Hg^{2+} and Hg^0 and can be applied to reference methods for relative accuracy test audits (RATAs) of Hg CEM and Hg emission tests on coal-fired boilers.

Hg CEM is very useful for reading and recording Hg emission levels in real time. Since Hg emissions, as well as speciation in flue gas, fluctuate, Hg CEM has more advantages than manual sampling methods (dry or wet chemistry-based sampling methods). Under CAMR, in the USA, Hg CEM or Method 30B are to be installed at coal-fired power plants to report Hg emission levels by Jan. 1, 2009.

4. MERCURY CONTROL TECHNOLOGIES

4.1 Hg control by conventional APCDs

APCDs installed for removing NO_x , SO_x , and particle matter (PM) can also be used to capture Hg (US EPA, 2002, 1998). Field data indicate that the highest level of Hg control for bituminous-fired plants is on facilities equipped with FGD for SO_2 control and FF for PM control (US EPA, 2002). Of course, the degree of removal efficiency depends on the coal type and configuration of APCDs. Coal can be classified into two groups: high rank coal, such as bituminous, and low rank coal, including sub-bituminous coal and lignite. According to ICR (Information Collection Request) data from US EPA (1999), generally, bituminous coal tends to have a higher chlorine content and higher levels of unburned carbon in fly ash than low rank coal. As a result, the flue gas from bituminous coal combustion has higher levels of Hg^{2+} , which is easily removed by conventional particulate controls such as ESP, FF, and SO_2 scrubbers, as wet FGD. Fig. 2 shows the Hg removal efficiencies with existing APCDs based on ICR data.

Based on the same configuration of bituminous coal-consuming plants, interesting trends can be observed. FF systems are more efficient than CS-ESP and HS-ESP for bituminous and sub-bituminous coal. However, the results indicate that native

Hg control levels are affected by the chlorine content in coal, carbon in the fly ash, flue gas temperature, and flue gas composition, besides coal type and APCD configurations.

4.1.1 Hg capture in Particulate Matter (PM) control devices

The FF system is very effective for Hg control because the contact time is increased, resulting in formation of a filter cake on the FF with fly ash and unburned carbon. The filter cake reacts like a fixed-bed reactor, enhancing heterogeneous oxidation and adsorption of Hg. However, the filter cake on the FF can cause the filter to catch on fire because the heat of adsorption increases during the adsorption process between activated carbon or unburned carbon in the fly ash and Hg compounds.

Compared to FF, ESP systems show poor removal efficiencies, due to less contact time between particulate matter and Hg compounds in the flue gas, as well as the high temperature at the HS-ESP. With sorbent or activated carbon injection technology, particulate matter control equipment is considered an integral part of achieving higher efficiency.

4.1.2 Hg capture in a FGD system

Usually, a wet FGD system is employed to control SO_2 emitted from coal-fired power plants. Fortunately, due to the high water solubility of Hg^{2+} , high removal efficiencies can be obtained through calcium-based wet FGD. However, reduction of removed Hg^{2+} to Hg^0 can occur in the scrubber solution, with possible Hg^0 re-emission into the outlet stream of FGD. Thus the concentration of Hg^0 at a FGD outlet is sometimes higher than at the inlet (Chang and Ghorish, 2003). Effective Hg removal can be expected using wet FGD with high Hg^{2+} coal combustion flue gas and a SCR-equipped power plant, because SCR catalysts have the ability to oxidize Hg. Power plants equipped with various configurations of APCDs such as SCR, CS-ESP and wet FGD results in higher total Hg removal efficiency than ordinary power plants equipped with PM and SO_x removal equipment. The impacts of the SCR catalyst on oxidation and speciation of Hg will be considered in the following paragraphs.

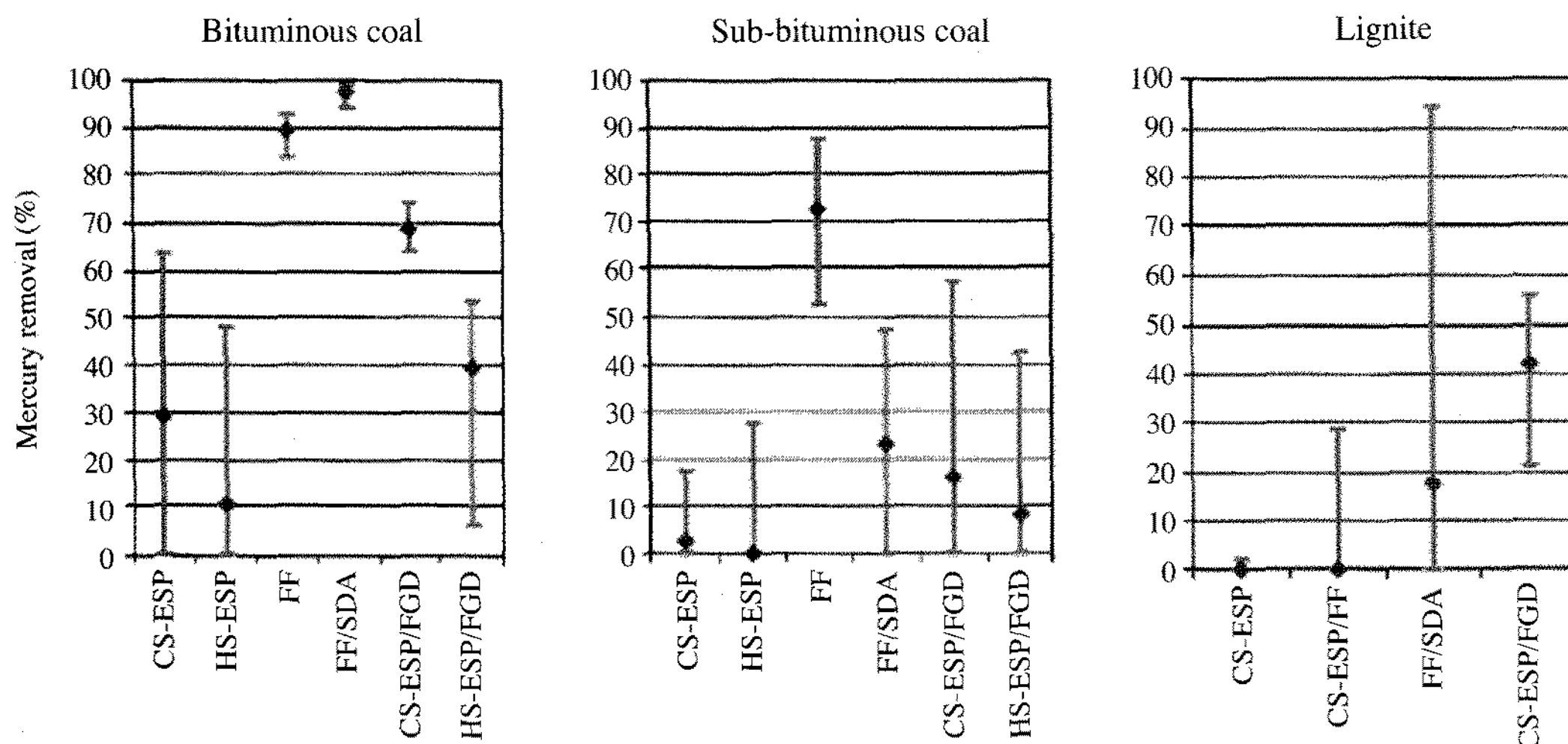


Fig. 2. Mercury removal efficiencies depending on coal type and APCD configuration (results from US EPA ICR data, 1999). CS-ESP (Cold-Side ESP), HS-ESP (Hot-Side ESP), FF (Fabric Filter), SDA (Spray Dry Adsorber), FGD (Flue Gas Desulfurization).

4.2 Available Hg control technologies

4.2.1 Carbon injection method

Powdered Activated Carbon (PAC) is usually injected upstream of PM control devices such as ESP and FF. The PAC injection method is reasonable, and is a widely applied Hg control technology for coal-fired power plants. US DOE (Department of Energy)/NETL (National Energy Technology Laboratory), and EPRI (Electric Power Research Institute) have implemented numerous pilot and field demonstration tests with the PAC injection method to control Hg from coal-fired power plants. The results indicate that generally, Hg removal increases with increasing sorbent injection rate; however, the removal efficiency is limited. Flue gas temperature is an important parameter in the PAC injection method, with Hg removal relatively higher when the temperature upstream of the PM control device is approximately 300°F. But if the temperature is over 350°F, the efficiency of Hg removal decreases rapidly. In addition, HCl concentrations in the flue gas, particle size of PAC, and SO₃ concentration also affect the Hg removal efficiency.

In the case of high HCl concentration and fine particle size (< 20 μm in diameter), PAC shows very

effective Hg removal. But SO₃ can compete with Hg for active sites on the PAC, so although PAC injection has been widely demonstrated to be effective in coal-fired power plants, there are some limitations.

Activated carbon (AC) injections increase the carbon content in fly ash. Because fly ash from coal-fired power plants is used as an additive for cement manufacturing, a high content of carbon in fly ash can have an adverse effect on its reuse or recycling. For this reason, non-carbon based sorbents or high performance/cost-effective halogenated PACs are being developed and tested in the field. Recently, bromine (Br)-impregnated ACs showed efficient Hg removal in field tests, but the high cost of chemically-treated AC results in a relatively high cost of Hg removal.

4.2.2 SCR system for NO_x control

Currently, the Selective Catalytic Reduction (SCR) catalyst is the most widely used post-combustion technology for NO_x emissions control. Recent studies also show significant oxidation of elemental Hg by the SCR system installed for NO_x reduction (Lee *et al.*, 2006; Senior, 2006; Niksa, 2005; DOE, 2004). With an increase in gaseous Hg²⁺, effective Hg

Table 2. Summary of flue gas control technologies and their availability for coal-fired power plants in the USA.

Technology	Mercury control effectiveness	Control of other pollutants	Availability and other notes
Coal Cleaning	0~78% (bituminous) (subbituminous rarely cleaned)	Average 48% reduction in SO ₂ emission potential	Already effective on most eastern and mid-western coal to reduce sulfur and improve boiler performance. Hg removal varies widely, typically from 10% to 50% with mean removal rate of 21% More advanced coal cleaning methods are under development
Low NO _x Burners (LNBs) Overfire air (OFA) Reburn	Unclear-massive range	>50% NO _x reduction possible	Available and in use on most coal-fired boilers. It has been postulated that LNBs/OFA/Reburn will improve Hg capture due to the increase in amount of unburned carbon (i.e., LOI) in the flue gas stream that may act in a manner similar to activated carbon injection
Fuel Switching	>99% for natural gas	>99% SO ₂ , and PM control; 50~75% NO _x reduction	Fuel switching reduces multiple pollutants, including NO _x , SO ₂ , particulates and CO ₂ . Accounting for multiple pollutant benefits reduces control costs for Hg alone
Electrostatic Precipitator (ESP)	35% (CS-ESP) 16% (HS-ESP) (bit) 4% (cold side ESP) 9% (HS ESP) (sub bit)	>99% PM removal	Already in use for particulate removal. CS-ESP shows significantly higher Hg removal than HS-ESP. Coal rank (HCl, LOI, SO ₂) appears to be a crucial factor in determining capture efficiency
Fabric Filter (FF)	84% (bit) 70% (sub-bit)	>99% PM removal	Only filters providing particulate collection efficiencies >99% appear to reduce significant amounts of Hg, but data are limited. Lower temperatures appear to improve performance. FF is more effective than ESP in controlling Hg due to dust cake effect. Less sensitive to coal type than ESP
Wet ESP	Unclear	Fine PM removal	Wet ESP being investigated for "polishing" residual emissions from other controls. May improve Hg removal through lower temperature, and dissolving Hg ²⁺ on wet collection surfaces
Combined ESP/FF (COHPAC/TOXECON ¹)	Low without additional sorbent injection	>99% PM removal	Combination technology to achieve very low PM emissions can improve removal of Hg when used in conjunction with powdered activated carbon
Wet FGD scrubber	Up to 90% removal of oxidized Hg. NO removal of Hg ⁰	80~90% SO ₂ removal further PM removal	Already in use to reduce SO ₂ . Effectiveness of Hg removal highly dependent Hg speciation and hence coal type. Re-emission of Hg ⁰ a concern. Hg-containing FGD residues must be stable
Dry scrubber with ESP or FF	Significant removal of both oxidized and Hg ⁰	80~90% SO ₂ removal	In use on only limited number of boilers (most units apply wet scrubbers). Fabric filter assists with Hg capture. Less sensitive to Hg speciation than wet scrubbers, but still affected by flue gas constituents (HCl)
Selective Catalytic Reduction (SCR)	SCR+wet scrubber combination may result in substantial Hg reduction	70~>90% NO _x reduction	Available and used on larger power plants. SCR catalyst may improve oxidation of Hg ⁰ , which can be captured in a downstream wet scrubber used for SO ₂ control. The ability of SCR to improve the oxidation of Hg for capture in scrubbers may be highly coal-specific

Table 2. Continued.

Technology	Mercury control effectiveness	Control of other pollutants	Availability and other notes
Combined SCR with wet scrubber	> 80% removal of overall Hg may be possible for units firing bit coals; effectiveness for units firing sub bit coal/lignite is uncertain	> 90% SO ₂ , and > 90% NO _x removal possible	SCR already in use to reduce NO _x . Oxidizes Hg ⁰ to soluble form thereby allowing for greater removal by downstream wet scrubber. Results are based on limited but encouraging data. The ability of SCR to improve the oxidation of Hg for capture in scrubbers may be highly coal-specific
Selective Non-catalytic Reduction (SNCR)	Unknown	30 ~ 60% NO _x reduction	Available and used on utility boilers
Sorbent injection	Recent full-scale test results indicate about 80% removal with bit coal+ ESP+COHPAC and 55 ~ 60% with sub bit coal +ESP	Not applicable	The only Hg specific removal technology. The least sensitive to coal type and hence flue gas constituents. Cost and removal effectiveness are directly related to the amount of carbon used. May have serious impacts on opacity and re-use of fly ash. Full-scale demonstrations underway and many new sorbents under development, but is not yet commercially deployed.

¹COHPAC (Compact Hybrid Particle Collector); ESP+pulse jet FF

TOXECON (Toxic Emission Control); ESP+sorbents injection+pulse jet FF

Ref.: UNEP (United Nations Environment Programme) Chemicals, Global Mercury Assessment, 2002

removal can be expected when using a wet FGD system. Titanium and Vanadium (Ti/V)-based SCR catalysts can oxidize over 90% Hg⁰ to Hg²⁺. Bituminous coal, especially, is more effective because it contains high levels of chlorine. In contrast, Powder River Basin (PRB) coal shows lower Hg oxidation, which may be due to a lower HCl concentration and CaO content in the flue gas. Previous studies (Lee *et al.*, 2006; Senior, 2006) indicate that HCl concentration is the major parameter determining Hg oxidation in the SCR system. Additionally, flue gas temperature, space velocity (gas flow rate/catalyst volume), age of catalyst, and NH₃/NO_x ratio can effect the oxidation and speciation of Hg in the SCR system. Table 2 indicates the summary of flue gas control technologies for coal-fired power plants in the USA and their availability, which is useful for understanding Hg control technology in its present state.

4.3 Novel Hg control approaches

4.3.1 Chemical additives

To increase Hg oxidation, chemical additives such as HCl, chlorine salts, and NaHS are injected into

the flue gas or fuel coal, with high Hg removal efficiencies expected for the wet FGD system; however, only the short term effects of these treatments have been studied. Long-term effects such as corrosion, plugging, and impacts on equipment still need to be evaluated (US EPA, 2005).

4.3.2 Photochemical processes

Ultraviolet (UV) light can enhance the reactivity of Hg⁰. Excited Hg⁰ is likely to react with oxygen (O₂) and sulfur dioxide (SO₂), forming mercuric oxide and mercurous sulfate (Granite and Pennline, 2002). Using existing particulate collectors or/and wet scrubbers, higher Hg removal efficiency can be achieved. However, this process has only been demonstrated in laboratory scale tests. Thus, feasibility should also be evaluated in field conditions.

4.3.3 Non-carbon based sorbents

Although carbon-based Hg sorbents have shown reasonable effectiveness for Hg control in full-scale tests, a high carbon content in fly ash from coal-fired power plants has an adverse affect on reuse in the cement industries. Hence, non-carbon based sorbents have been investigated for Hg removal. Pota-

ssium iodate aerosols/crystal and calcium based high temperature sorbents (Lee *et al.*, 2007) have been shown to effectively capture as much as 90% Hg⁰. Additionally, Titania, Zeolite, and Sodium tetrasulphide (Na₂S₄) also show promise for effective Hg capture (Gibb *et al.*, 2003).

Non-carbon based sorbents are more advantageous than AC in terms of fly ash recycling for cement manufacturing. However, stable Hg removal efficiency and feasibility in the field with different coal types, and cost-effectiveness compared to AC are the most important evaluation criteria.

4.3.4 Multipollutant control technology

Multipollutant control technology currently employs post-combustion flue gas treatments to remove NO_x, SO_x and acid gases (HCl, HF). Most multipollutant systems use the principal of NO_x and SO_x oxidation to create nitric and sulphuric acids. These kinds of acidic gas vapors should be removed by wet ESPs or a scrubber, which are both quite effective at the removal of trace metal species including Hg in coal combustion flue gas. Sorbent injection technologies can also be involved in multipollutant control technology. Multipollutant control technologies have been considered in the USA under CAMR regulation.

5. CONCLUSIONS

Hg pollution is not a local or regional problem, but a global problem because Hg compounds can be transported over a long range. Technologically-advanced countries including the USA and Canada have set stringent national regulations for the reduction of Hg emission and use. Also, UNEP has set up partnership programs between many related countries concerning Hg. Vigorous research has been performed, and various developed technologies for Hg sampling, analysis, and control have been implemented in the last decade. However, since Hg emission concentrations from anthropogenic sources are quite low (ppbv) and are easily affected by fuel type, flue gas conditions, etc., there are many uncertainties and fluctuations in Hg-related studies. It is

clear that there is no proven technology for Hg control encompassing all combustion conditions. Therefore, applying adequate control technologies for each source based on combustion conditions and characteristics of facilities is important. This paper included the status of Hg emission regulations in technologically-advanced countries and related control technologies that have been developed to reduce emissions from various sources with reference to coal-fired power plants. Hg sampling and analysis methods are not simple, thus various methods that are currently used to measure Hg and its emission characteristics were discussed. This information may be useful in implementing a strategy to deal with the issue of Hg in Korea.

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