



Mercury control technologies for MWC's: The unanswered questions

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Received 8 February 1995; accepted 26 July 1995

Abstract

It is now clear that stricter control of mercury emissions from municipal waste combustors (MWCs) and possibly medical waste incinerators (MWIs) at both the state and federal level is imminent or certain. While some facilities may meet these new standards without additional controls (e.g. refuse derived fuel (RDF) combustors), most will not. This paper will look at the available air pollution control (APC) technologies that lend themselves to retrofit for mercury capture and will suggest that questions remain as to effectivity, interference with other APC devices, and environmental impact. Regulatory considerations are reviewed and research priorities will be suggested.

Keywords: Mercury; Municipal waste combustors; Activated carbon injection; Wet scrubbers; Sodium sulfide injection; Methyl mercury; Testing methods; Emission regulation

1. Introduction

Over the past several years, recognition of the scope of the high levels of bioaccumulated mercury in freshwater fish and its effect on predators, especially humans, has focused attention on point source emissions of mercury. This has led the US Environmental Protection Agency (EPA) and environmental regulators in a number of states, i.e. Minnesota, Florida and New Jersey, to closely investigate anthropogenic sources and require mitigating action.

Municipal solid waste (MSW) incineration is of concern for a number of reasons. As a source of airborne mercury in the US, it is likely that garbage incineration now ranks second only to coal combustion and is growing [1]. Research in Sweden [2] and the Great Lakes area of the upper Midwest [3] indicates that atmospheric deposition is the main source of mercury in freshwater fish. The concentration of mercury in the stack gas from these facilities is high. A number of studies have shown that the

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primary emission form of mercury from MSW incinerators is water soluble oxidized mercury, i.e. HgCl_2 , in vapor form [4–9]. This species should be easily washed out of the stack plume during rain events in high concentrations, close to the source.

This theory was verified when high levels of mercury were found in rainwater downwind of the Warren County, NJ, Resource Recovery Facility [10]. Some of these levels were up to 50 times the upwind concentrations and, when extrapolated to annual deposition rates (in $\mu\text{g}/\text{m}^2/\text{yr}$), exceeded those rates found problematic by Sorensen et al. [11] and Glass et al. [12] ($10 \mu\text{g}/\text{m}^2/\text{yr}$) by more than an order of magnitude.

All of the states that initiated mercury investigations have now issued emission standards for MSW incinerators. New Jersey has a two-step rule for all plants: 65 $\mu\text{g}/\text{dscm}$ (all concentrations at 7% oxygen) by 31 December 1995 and 28 $\mu\text{g}/\text{dscm}$ by 1 January 2000 (based on both source reduction and separation and emission control technology) [13]. Florida requires no more than 70 $\mu\text{g}/\text{dscm}$ for new plants which would also be phased in at existing plants. However, each state allows alternate compliance by reducing mercury emissions by 80% relative to the air pollution control device (APCD) inlet regardless of the concentration. The Federal rule requires a stack concentration of no more than 80 $\mu\text{g}/\text{DSCM}$ or an 85% reduction.

The result of all this is that a large number of MSW incinerators will be required to add (or include) specific controls for mercury capture. Unfortunately, as numerous jurisdictions face the need to commit precious financial resources to install these technologies, serious questions remain as to their effectivity, environmental impact, and long-term cost. Furthermore, detailed knowledge of all the specific emission forms of mercury, their relative abundance, and their fate and impact is lacking.

This paper will examine three mercury control technologies: activated carbon injection, sodium sulfide injection and wet scrubbing. The known disadvantages of each will be reviewed and, more importantly, unanswered and unasked questions about each will be examined. Issues regarding testing methods and regulation will also be discussed. Finally, research priorities are suggested which should be undertaken before widespread use is initiated.

Other mercury mitigation technologies such as deep bed carbon adsorbers, selenium filters, flue gas condensers and flue gas sub-cooling were not included because of high cost or the unavailability of information. This, however, should not preclude their consideration in the future.

2. Mercury capture mechanisms

It is very important to understand the mechanisms that are available for capturing mercury at the temperatures and conditions that exist at MSW incinerators in the US. These mechanisms are:

1. Adsorption onto carbonaceous fly ash particles or deliberately injected activated carbon with subsequent capture in the particulate control device.
2. Conversion to HgS by Na_2S with subsequent capture in the particulate control device.

3. Solvation of soluble oxidized mercury species by water in a wet scrubber.
4. Conversion of elemental mercury into a soluble species by aqueous oxidizing acid or aqueous chelate in a wet scrubber.

A widely held misconception is that elemental mercury and/or mercuric chloride undergo either a heterogeneous or homogeneous condensation and are captured in the particulate control devices. Even at the lowest process temperature involved, i.e. 54 °C, the partial pressure of either is still far below that necessary for condensation based on the mole fraction present [14–16]. Otani et al. [18] shows the saturated vapor concentration of elemental mercury to be $\sim 200,000 \mu\text{g}/\text{m}^3$ in air at 54 °C. This is analogous to the fact that there is water vapor in ambient air even though it is below 100 °C. It is also important to note that even though HgCl_2 is a crystalline salt at room temperature, it has a lower boiling point than elemental mercury (304 °C vs. 357 °C) and is capable of direct sublimation (formerly known commercially as corrosive sublimate) [19].

3. Activated carbon injection

3.1. Mechanism of capture and interferences

Various mechanisms have been proposed for the capture of mercury on activated carbon. These range from physical adsorption in the pore structure of the carbon particles, to catalytic oxidation to mercuric oxide, to a chemically mediated adsorption based on oxygen and/or chloride. Very little data are available on the subject. Those which do exist come from bench-scale investigations [5, 17, 20, 21].

Two observations from these studies suggest that the last of these three mechanisms is the most accurate. First, oxygen deficient inert atmospheres are capable of desorbing previously captured mercury at normal process temperatures (150 °C) [20]. Second, trace levels of SO_2 , a reducing gas, severely affect the mercury capture efficiency of activated carbon. Schager et al. [21] found that 100 ppm of SO_2 in flue gas at 150 °C reduced the capture rate of mercury from 90% to 40%. This effect was largely reversed when this gas mixture also contained 100 ppm of HCl.

These observations are important in the evaluation of activated carbon as a mercury mitigation strategy because they suggest that the capture rate may be affected by variations in levels of pollutants of a reducing nature, such as SO_2 and perhaps NH_3 , and that previously captured mercury may be liberated on the filter cake in a bag-house or after disposal.

Some attempt was made to analyze the interference of reduced lime stoichiometry (hence elevated SO_2 levels) and NH_3 slip (excess injected NH_3 which escapes the boiler) on mercury capture by activated carbon during the activated carbon injection trials conducted by US EPA at Ogden Martin's Stanislaus, California, facility in 1991 [22]. Unfortunately, no significant elevation of either compound was obtained during these tests. With two minor exceptions, the levels of NH_3 measured at the spray dryer absorber (SDA) inlet were all below 5 ppm irrespective of whether NH_3 was being injected. All the authors involved [23] and Ogden Martin [24] concluded that the

results of these tests were inconclusive. Mercury emission results obtained before the activated carbon injection trials suggest a relationship between increasing NH_3 injection rates and increasing mercury emission rates [25]. Some of these tests showed negative capture efficiencies.

Once the process rate of activated carbon injection is optimized at a given facility, the mercury reduction achieved is likely to be due to the combination of the adsorptivity of the ash particles (due to variable levels of unburned carbon) and the injected carbon. Emission reductions obtainable from the presence of unburned carbon alone can be substantial. Test results from the activated carbon injection trials at Stanislaus indicate a mercury removal rate of $\sim 30\%$ without activated carbon injection. At the Camden County, NJ RRF removal rates without carbon injection range up to 90% and average $\sim 50\%$.

Schager et al. [21] found that SO_2 had the greatest effect on mercury capture when using carbonaceous ash from an RDF combustor as a substrate. However, oxidized mercury was captured at high rates regardless of SO_2 concentration (up to 100 ppm). Therefore, the ability of reducing gases to affect capture or create desorption is likely to depend on the underlying rate of capture without carbon injection and the relative proportion of Hg^{2+} to Hg^0 . Those facilities with higher levels of mercury removal without carbon injection may be more susceptible to this possibility.

It is also likely that if this phenomenon exists, it would not be evident from normal stack testing programs. During testing facility operators are, understandably, much more vigilant of plant operating conditions. It is unlikely that an SO_2 or NH_3 excursion would occur during a test run for mercury especially if there is some suspicion of an interference. The author believes that it is essential for regulatory agencies to determine if this effect exists before the use of activated carbon injection for mercury control becomes widespread.

The other aspect of this analysis is the permanency of capture of mercury on activated carbon once landfilled. The research to date has focused on the thermal stability of this material. Tests performed by US EPA on ash generated during the Stanislaus trials [22], as well as data gathered by A.S. Niro on ash samples over a 2 yr period [15], conclude that thermal desorption of mercury in air does not occur below 130°F . However, desorption or bacterial conversions of mercury in the ash when co-disposed with garbage is unresearched and plausible. For the same reasons previously cited, the oxygen deficient methane rich environment (possibly including NH_3) typical in an MSW landfill may desorb previously captured mercury. Based on this analysis and the recommendation of the activated carbon injection vendor [15], NJ DEPE is evaluating whether to require monofilling of all MSW incinerator ash generated in New Jersey [13].

3.2. Compatibility with electrostatic precipitators (ESPs)

The results of the activated carbon injection trials at the Camden County RRF (SDA/ESP) indicate that, on average, an injection rate of greater than 3–5 times that used at Stanislaus (SDA/fabric filter) is necessary to achieve capture rates above 90% [8, 22]. This is understandable given the shorter residence time in ESP equipped units.

The only other ESP equipped MWC to use carbon injection is the Joseph Strasse facility in Zurich, Switzerland [15]. It is important to recognize that the ESPs at Camden and Zurich are reported to be significantly oversized [27]. It is conceivable that units with ESPs more closely sized to the combustors would require even higher rates of injection due to shorter residence times.

The introduction of a semiconductor such as activated carbon into an ESP could decrease particulate capture efficiency by compromising dielectric strength or by shortcircuiting the field. EPA conducted simultaneous particle emission tests at the Camden RRF before, during and following the introduction of carbon and found no increase in the emission of particulate matter [8]. However, a significant reduction in ESP efficiency was observed in the days following a proprietary activated carbon injection trial at an SDA/ESP equipped facility [28]. The ESP at this facility is very similar to that at Camden in size and configuration and is also oversized [29]. It is unclear whether this was related to the injection of activated carbon. Given that new Federal rules will require some MWCs in the US to meet a reduced particulate emission standard of 0.007 gr/DSCF a potential degradation in particulate control is of concern.

3.3. Future cost of activated carbon

Widespread use of activated carbon for mercury control, perhaps as a result of federal emission standards, would create a great new demand for activated lignite coke (the most economical form of activated carbon). The highest consumption estimate might be if 200 facilities of average capacity (800 tpd) were to require 150 000 lb/yr each (based on an injection rate of 0.6 lb of carbon per ton of waste or ~60 mg/dscm of flue gas). This would equate to ~30 million lb of annual new demand. The most recent figures available indicate a significant industry-wide over-capacity in the US [30, 31] (on the order of tens of millions of pounds per year).

Even though this estimate represents production of all types of carbon, i.e. lignite, bituminous, vegetative, etc., production can apparently be switched from one type to another without difficulty [31]. It would then appear that there is more than sufficient capacity to meet the highest expected demand and the price of carbon should remain stable. The only possible exception would be if this technology is adopted at coal fired utility boilers for mercury control.

However, it is important to note that the rate of injection necessary at the Camden County RRF to achieve compliance with New Jersey's proposed interim standard of 65 µg/dscm equates to several hundred tons of carbon per year and even at present carbon prices represents a substantial annual expenditure (> \$400 000/yr).

4. Sodium sulfide injection

Sodium sulfide injection has been used on a number of European facilities [32] and has been tested at two plants in North America, i.e. the Burnaby MWC in Vancouver, BC [33], and Stanislaus, CA [7]. This technology has shown good rates of mercury

reduction ranging from 73% to > 99%, and is desirable because of the stability of the reaction product produced, i.e. HgS.

Unfortunately, testing at Stanislaus [7] revealed relatively poor capture rates (57% mass average). This is of interest because the test method used, 101A, employed an additional step in the analysis of the impingers and filter which was not previously used in this country. This procedure required more complete acidic digestion of the precipitate formed during and after sampling in the impinger solution and the sample filter. As a result, outlet concentrations were found to be higher during Na₂S injection than would have been determined without digestion of the filtrate and filter. Attempts to determine if this procedure is incorporated in European protocols have been unsuccessful.

This casts great doubt on the results obtained in other trials or from operating units. The cause of this phenomenon is unknown but is speculated to be due to the presence of sulfide on the sampling filter or the penetration of sulfide into the impinger solutions causing precipitation of HgS.

Another possible problem associated with Na₂S injection is the potential for the generation of H₂S especially if the stock solution becomes acidified. This was not found to be a problem at either Burnaby or Stanislaus, but given that H₂S is ranked as more acutely toxic than HCN [19], constant vigilance would be essential.

It has been reported that HgS is generated as a fine particulate in this process which may prove difficult to capture in less efficient ESPs. Note that the data available have been from facilities with fabric filters [34].

5. Wet scrubbers

5.1. Description

For the purpose of this paper, wet scrubbers are divided into two categories, single stage and two-stage. In a single-stage wet scrubber, the circulating scrubber water is maintained at a pH of 6.5 or above by the addition of an alkaline reagent such as sodium hydroxide or lime. The purpose of this pH level is to maximize the absorption of SO₂ from the flue gas. In a two-stage wet scrubber, two distinctly different pH levels are maintained in the circulating loops. In the first section, absorption of HCl lowers the pH to between 0.5 and 3 and creates a high chloride concentration. The second section is the same in pH and function as a single-stage wet scrubber. Since the only mechanism of mercury removal available (without chemical dosing) in a wet scrubber is solvation of soluble species [35, 36], the ultimate emission level attainable is primarily dependent on the proportion of elemental vapor in the flue gas. However, the fate of the captured mercury can be very different in these two types of scrubbers.

5.2. Mercury capture and fate, single-stage wet scrubber

Soluble oxidized mercury is reported to be easily reduced in alkaline solutions [37, 38] or by SO₂ in the same medium [4, 39, 40]. Therefore, some of the captured

oxidized mercury, probably HgCl_2 , is likely to be reduced to elemental mercury which may then either homogeneously agglomerate and precipitate or revolatilize. The degree to which this may occur is likely to depend on the chloride concentration. Reimann reports that as much as 60% of the mercury originally present may remain in solution, possibly as a chloride complex, even after the addition of lime [41]. The wet scrubber on the MSW incinerator at Fort Dix, NJ, operates at a pH of > 6.5 in both the venturi and packed tower [42]. During a testing program in 1988, the wet scrubber demonstrated a range of capture efficiencies of 17–75% with a mass average removal rate of 47% [43]. The operator has observed deposits of metallic mercury in the scrubber water circulation piping [42]. This would support the theory that captured oxidized mercury may be reduced and precipitated. The overall poor removal shown in the stack tests is consistent with revolatilization of some of the reduced mercury assuming that HgCl_2 is the predominant species entering the scrubber. Metallic mercury accumulations in the piping have been observed at a number of other wet scrubber installations [44].

5.3. Mercury capture and fate, two-stage wet scrubber

The reduction of soluble oxidized mercury is avoided in the acidic first section of a two-stage wet scrubber for two reasons. First, the low pH limits the solubility of SO_2 . Second, the low pH and high chloride concentration favor the formation of the stable chloride complex HgCl_4^{-2} [45] over the unstable intermediary $\text{Hg}(\text{SO}_3)_2^{-2}$ which is likely at higher pH and SO_2 concentrations [46]. Vogg et al. [39] recommend a pH of < 3 and a chloride concentration of 0.1 M (or > 3500 ppm) for stabilization.

When the first stage of this type of scrubber is used solely for mercury control and retrofitted onto a facility which already achieves good acid gas removal, the amount of HCl available for acidification will be much lower. Careful control of the scrubber water bleed rate will be necessary to achieve optimum stabilization conditions. Since there would be no need for the alkaline stage for SO control in this situation, this yields a third wet scrubber variant, i.e. an acidic single-stage spray tower for retrofit onto MWCs with good acid gas control and exit temperatures below 350 °F for the sole purpose of controlling mercury emissions.

5.4. Treatment of waste water

The bleed water from these scrubbers must be treated before disposal. This involves pH adjustment by mixing the separate stage bleed-streams together (if applicable) and/or neutralization with lime. Again, the conditions are right for oxidized mercury to be reduced and precipitated as metal. Also, as Reimann observed, a significant fraction may remain in the liquid and be discharged either into the sewage system or receiving body. In the former case the mercury appears to partition mainly to the solids [47], the disposal of which portends separate environmental impacts. The latter case may be undesirable since, in some cases, mercury concentrations in lake water

of less than 10 ppt have been linked to problematic methyl mercury levels in fish (>0.5 ppm) [2, 3].

To some extent, the problem of mercury discharge with the waste water can be avoided by using a specific precipitant. This has become common practice at a number of European installations. The precipitants are usually based on sulfur and include sodium sulfide, dithiocarbamate, and trimercapto-s-triazine (known commercially as TMT-15) [32, 35, 36]. Reimann reports that the use of TMT-15 at the Bamberg facility has reduced average mercury levels in the treated scrubber water discharge from 2.5 ppm to 45 ppb [41]. The manufacturer (Degussa Corp.) claims that TMT-15 is capable of reducing mercury levels to below 1 ppb [36]. It is unclear whether the 45 ppb level at Bamberg is due to the inefficiency of the sand filter or some other factor (e.g. organic mercury). Other constituents in the waste water may also present a disposal problem. For example, Reimann also reports average chloride concentration at 12 000 ppm (1.2%) [41].

5.5. Zero water discharge option

An alternative to waste water discharge is to evaporate it either using process heat or in an upstream quench or spray dryer. The former method is in use in Japan but requires the use of process energy capacity [35]. The resulting salt mixture is sold to industry. Disposal via the spray dryer is used in Europe at some facilities [48]. This appears to be a viable alternative which directly reduces the water consumption of the wet scrubber. However, if unprecipitated mercury remains, it is likely to be revolatilized in the quench/SDA [48].

This exact condition has been observed at the 'state-of-the-art' MSW incinerator at Coburg-Neuss, Germany, which began operation in 1989 [49]. The air pollution controls consist of an SDA, a fabric filter baghouse, a two-stage wet scrubber and a wet ESP. Neutralized and filtered scrubber discharge is introduced into the SDA with lime slurry. There is no specific precipitant added for mercury. Mercury emissions at the stack range from 224 to 560 $\mu\text{g}/\text{NM}^3$ (11% oxygen). The APCD vendor guarantee was 280 $\mu\text{g}/\text{NM}^3$ (11% oxygen).

Apparently, it is also possible for dissolved ionic mercury to be revolatilized in a wet scrubber. This occurs as entrained droplets of scrubber water escape through the stack or evaporate before reaching the demister if the flue gas is above the saturation temperature [50]. This condition might occur if an operator were trying to minimize water consumption.

5.6. Flue gas discharge considerations

A consequence of discharging water saturated flue gas from a wet scrubber is that any further temperature reduction in the duct-work or stack flue (or induced draft (ID) fan, if applicable) creates corrosive condensation. This requires either reheating the flue gas or lining the duct-work and flue with corrosion resistant materials or coatings. All of these options increase capital cost. Reheat can be accomplished by the use of a heat exchanger loop, by fossil fuel combustion, or by process heat. In a reheat

loop, heat removed from the flue gas at the boiler exit is used to raise the gas temperature above the saturation point after the demister. This reduces water consumption but may limit the ability to evaporate all of the waste water in a zero discharge system if the temperature reduction produced by the first heat exchanger is too great. This process does not reduce electric generation except for that needed to run the circulation pumps. A common misconception is that the hot side heat exchanger condenses the flue gas; it does not [27]. Flue gas condensers and zero water use systems exist but are not covered in this paper.

Another aspect of low flue gas temperature is decreased plume buoyancy and dispersion. Hahn [51] estimates that this may increase ground level concentrations of pollutants by a factor of two. While this must be evaluated on a site-specific basis, given the large margin of safety demonstrated by the ground level concentrations predicted from a 'state-of-the-art' plant operating at 285–300 °F, this should not be of concern. However, without reheat a large water vapor plume will be visible which may be of concern in some jurisdictions.

5.7. Dioxin toxicity enhancement

A worrisome phenomenon regarding dioxin and furan emissions has been observed at two MWCs in Europe [51, 52] and at a number of MWIs in this country [53]. The total toxic equivalency seems to be enhanced after passing through the wet equipment even though the total amount of dioxin and furan decreases. This has been linked to dechlorination of higher substituted isomers, particularly octa-substituted, or chlorination of tri-substituted isomers resulting in higher concentrations of more toxic isomers, i.e. tetra and penta [53].

Belco Technologies/Lab S.A. has found that the addition of a common, but unidentified, reagent to the scrubber water can destroy captured dioxins and furans with >98% efficiency across all isomer classes. They also report very low dioxin emission from these same units (<0.13 ng/dscm). If this process is substantiated by commercial application and testing, then it would not only eliminate enhanced dioxin emission, but could serve as the basis for the destruction of dioxin and furan as well. A patent application has reportedly been filed for this process [35].

5.8. Capture of elemental mercury

Even at low pH and high chloride concentration, a wet scrubber will be limited to capturing only soluble species of mercury. Therefore, the relative abundance of elemental mercury will dictate the lowest achievable emission rate. This effect alone may not be sufficient to achieve compliance with the low limits soon to be required. Assuming an inlet concentration of 600 µg/dscm, HgCl₂ would have to exceed 89% of the total to equal New Jersey's proposed interim standard of 65 µg/dscm. If this is not the case, it may be possible to add specific reagents to chemically convert and capture some of the elemental mercury. These include hypochlorite and chelates [6]. Hypochlorite addition would probably create chlorine. Hall et al. [5], found that chlorine

reacted with mercury even at room temperature. The effect that chlorine would have on the emission of chlorinated products of incomplete combustion (PICs) is unknown.

6. Organic mercury emissions

It has been speculated that organic (methyl) mercury may be a component of the emissions from combustion sources including MWCs [38, 54]. Test results from coal fired power plants published by Nicholas Bloom under contract from the Electric Power Research Institute (EPRI) indicated that as much as 15% of the total mercury emitted was in the form of methyl mercuric chloride. Subsequent re-examination of the test method employed revealed that some or all of the methyl mercury present was created by one or more of the reagents employed; therefore, these results have been withdrawn. The author knows of no other test results for methyl mercury at any combustion facility including MWCs.

The possibility of methyl mercury emissions from MSW incinerators is of great importance for two related reasons. First, one of the greatest uncertainties in attempts to model the transport and fate of point source mercury emissions is the rate and mechanism of the formation of methyl mercury from the known emission forms, i.e. HgCl_2 and Hg^0 . That portion of mercury emitted in the organic form would bypass most of this uncertainty and could potentially increase environmental impact by a large factor. Second, the ability of any of the control technologies discussed here to permanently capture methyl mercury is unknown. Even if a pollution control device removes 95% of the mercury present in the flue gas, if the water soluble organic form constitutes most of the remaining emission, the resulting environmental impact may still pose a very serious problem.

The observations of the residual levels of mercury in treated scrubber water discharge would take on new importance. The limiting factor preventing quantitative removal of mercury by the precipitant may be that some or all of this residual level is organic. Even if only 1 ppb (1000 ppt) of total mercury remained in the discharge water, of which a small fraction was methyl mercury, e.g. <10% or 100 ppt, this could still portend an unacceptable impact given that the bioaccumulation factor for methyl mercury in piscivorous game fish is reported to be 10^7 over the water concentration. This is also significant when compared to the Federal Ambient Surface Water Quality Standard for methyl mercury of 12 ppt. Some Great Lakes states have set even lower standards [47].

7. Regulatory considerations

7.1. Implications of the carbon/mercury relationship

It has been widely reported that the degree of mercury capture at an MWC is primarily dependent on the amount of unburned carbon in the fly ash [32]. This phenomenon is most evident at certain RDF combustors which, in some cases,

already achieve mercury emission rates low enough to meet the strictest standards under consideration, i.e. New Jersey's interim standard of 65 $\mu\text{g}/\text{dscm}$. Consistent with this observation, White and Jackson [34] suggest that it may be possible to adjust combustion conditions at some MSW incinerators to obtain more carbon carryover and lower mercury emissions. While they conclude that this is not feasible for continuous operation, it points out two potential problems for regulators.

First, it is highly likely that creating a carbonaceous burn condition during a mercury stack test would give better results than during normal operation. Second, a jurisdiction considering building an MWC might become convinced that choosing a unit with poorer combustion characteristics, e.g. certain types of RDF combustors, might be more economical than selecting a clean burning system that would require specific controls for mercury with the associated capital and operating expenses.

The former case illustrates the importance of having *all* air emissions tests monitored and analyzed by trained, knowledgeable regulators. Another possible answer may be to require simultaneous testing for both mercury and products of incomplete combustion (PICs), e.g. dioxin/furan/polycyclic aromatic hydrocarbons (PAHs). NJ DEPE is currently considering just such a requirement [55]. Of course, this assumes that the permit limit for the PIC selected is meaningfully low. Unfortunately, New Jersey's PIC limits do not meet this requirement. For example, NJ only regulates one dioxin isomer, 2,3,7,8-TCDD, not the toxic equivalent or the total, and allows an extremely high emission rate. A typical MWC carbon monoxide limit in NJ is 400 ppm (1 h average) or 100 ppm (4 d average) [56].

Over the past decades, great strides have been made in the area of 'good combustion practice' at MSW incinerators. This includes clean burning grate systems, automatic combustion controls, advanced furnace designs, etc. For the reason previously cited, this progress could be partially undone if regulators set low mercury emission limits but fail to set low CO requirements and limits for PICs at new plants that closely mirror the capabilities of the best combustion and APC technologies. This includes creating special categories for different combustor types with disparate PIC permit limits. Hopefully, US EPA's new CO limits and combustion rules will prevent this possibility and overcome previous regulatory shortfalls.

7.2. Permit compliance for mercury

Due to the variability of inlet concentrations of mercury, even MWCs with specific mercury controls with very high removal rates may fail to meet strict limits based on the average of a small number of tests. There are two potential remedies: raise the permit limit to account for this phenomenon, or base compliance on the average of a larger number of test runs.

Relaxing a health based emission standard, such as New Jersey's proposed limits, runs counterintuitive to the reason for establishing low limits and may create a disincentive for MWC operators to run their mercury control devices at their optimum capability. A larger number of individual test runs means greater expense for the jurisdiction. A yearly requirement to conduct three mercury stack tests can be included in an annual test program for other pollutants at nominal expense. However,

the need to have multiple mobilizations of a testing contractor each year strictly for mercury engenders a dramatic increase in costs.

An alternative to both might be to initially (and periodically) test the capture efficiency of the mercury control device to determine its ability to meet the permit limit based on an *average* inlet concentration. Between test programs the system could be monitored to insure proper operation. For example, for an activated carbon injection system installed on an SDA/fabric filter equipped facility, the permit could specify the carbon injection rate based on the previous period's test results. At any time, a regulator could perform an audit to make certain that the required amount of carbon was purchased, delivered, and used on site. Unannounced spot-checks could be part of such a program.

7.3. Testing methods

United States

Two methods are available for measuring emissions of total mercury from MWCs. These are Method 101A and Method 29 (also known as the draft multi-metals method). Both methods rely on a filter followed by a number of impingers containing 4% KMnO_4 /10% H_2SO_4 (Method 101A), or both this solution and 5% HNO_3 /10% H_2O_2 in separate impingers (Method 29) [34]. The correct use, recovery, laboratory preparation and analysis of either method is a complicated affair with a high potential for loss due to mishandling. This is compounded by the proposed inclusion of the new lab filter step (previously discussed under sodium sulfide injection) [57]. White and Jackson analyzed the results of the tests done at Stanislaus with both methods simultaneously. They found that, on average, Method 29 produced higher results than Method 101A ($\sim 30 \mu\text{g}/\text{dscm}$) and had greater precision [34]. US EPA will require the use of Method 29 for Federal compliance.

A simple dry canister method known as the HEST method has been developed by Cooper [58]. This method employs carbon impregnated filter pads and is conducted in the stack. Published results have shown good agreement with the two aforementioned methods and is the best hope for a simple replacement for both M101A and M29 for measuring total mercury.

Speciating methods

Two very similar methods have been independently developed for determining the quantity of mercury emitted as ionic and elemental. Bloom has developed a two-stage procedure based on a mixture of KCl and soda lime ($\text{NaOH} + \text{Ca}(\text{OH})_2$), and iodized carbon [38]. Braun et al. [4] use a chloride saturated exchange resin, also followed by an iodized carbon trap. In theory, ionic oxidized mercury, e.g. HgCl_2 , is captured in the first portion (KCl/soda lime or chloride resin) and elemental mercury is captured in the carbon trap. Separate analysis of these sections yields the concentrations of each form. Bloom still believes that his method is capable of quantifying methyl mercury. However, given recent experience, this awaits a thorough validation program.

Some have suggested that Method 29 is capable of speciating ionic and elemental mercury if the filter and two impinger sections are all separately analyzed [59, 60].

The operative theory is that soluble ionic chloride will be captured in the two $\text{HNO}_3/\text{H}_2\text{O}_2$ impingers and that elemental mercury will be captured in the $\text{KMnO}_4/\text{H}_2\text{SO}_4$ impingers. Because an increasing amount of mercury emission data are becoming available using this method including the separate analyses of the two impinger groups, this bears closer examination.

The critical factors are whether the optional empty impinger located between the filter and the first $\text{HNO}_3/\text{H}_2\text{O}_2$ impinger is used and what the capture rate of elemental mercury is in the two $\text{HNO}_3/\text{H}_2\text{O}_2$ impingers. Braun et al. [4] used a condensing impinger in the design of their continuous emission monitor for mercury. They found that passing a stream of flue gas through the flue gas condensate gave quantitative reduction of oxidized mercury to elemental mercury in most cases. This is essentially identical in function to the optional impinger. Therefore, if this condensing impinger is used, there appears to be little hope of accurate speciation, especially with high SO_2 levels such as are encountered in untreated flue gas.

For the capture of elemental mercury, Shendrikar and Ensor [54] reported that three consecutive impingers of acidified 10% H_2O_2 had a total efficiency of 18%. Lindquist [61] found that two consecutive impingers of 4.8 M HNO_3 had very poor efficiency for elemental vapor. It would seem then that the maximum amount of elemental mercury likely to be trapped in the $\text{HNO}_3/\text{H}_2\text{O}_2$ impingers is <20% of the total. From this, one could conclude that if none of the soluble ionic mercury is reduced in the $\text{HNO}_3/\text{H}_2\text{O}_2$ impingers by SO_2 and if the optional condensing impinger is not used, then the amount of elemental mercury in the flue gas sampled is equal to the KMnO_4 catch plus 0–25% (to account for that elemental mercury which may be trapped in the peroxide impingers), and the amount of soluble ionic mercury present is equal to the H_2O_2 impinger totals minus 0–25% of KMnO_4 fraction (to also adjust for any captured elemental mercury). Therefore, until specific research into this subject is done, any speciation reported by Method 29 should be presented as a range according to the foregoing.

8. Summary and conclusions

All three mercury control technologies suffer from disadvantages or potential deficiencies. The problems and potential drawbacks of each must be more fully explored before scarce public resources are expended on technological fixes for mercury which may not perform as reported. This is not meant to argue for delay in the development of stricter mercury emission standards. This research must be expedited as the problem of mercury bioaccumulation is real and growing, especially if organic mercury is found to be an emission from MWCs, which the author believes is a strong possibility. Regulators must be aware of the unwanted ramifications of greatly reduced mercury emission limits and of the cost of compliance testing. Simpler (possibly speciating) test methods are also needed.

The tests of activated carbon at both Stanislaus and Camden have added greatly to the data base for this technology and have demonstrated high removal rates and low emissions under 'ideal conditions'. EPA justifies these trials as necessary for the

development of a mercury emission standard since they must know what the performance range is. Nonetheless, these trials represent an enormous, cost free, engineering and market development study for the activated carbon injection vendors and the activated carbon producers. No similar investigation has been made of the best type of wet scrubbers even though they enjoy great popularity in Europe and are widely used (in a less sophisticated form) on medical waste and sewage sludge incinerators in this country, both of which are significant emitters of mercury.

Table 1 shows the proportion of wet scrubber equipped MSW incinerators in Switzerland. It is of interest to note that the only 'dry' process system (SDA/fabric filter/carbon injection) is the Joseph Strasse facility in Zurich. This plant has now contracted for an expansion which will be equipped with wet scrubbers [62]. Table 2 shows similar data for the former West Germany. Two of the largest MWCs to recently commence operations in Europe are the retrofitted AVR facility in Rotterdam [63] and the new AVI plant in Amsterdam [35]. Both utilize wet scrubbers in the APCD train. Holland has what are arguably the strictest emission standards in the world for MSW incinerators [63]. A thorough, objective trial of this technology on an MWC is long overdue.

Table 1
APCD utilization on MWCs in Switzerland, 1990 [36]

APCD type	Number of plants	Share (%)	Annual capacity ^a (10 ³ t/y)	Share (wt%)	Plant size range (10 ³ t/r)
Wet	30	97	2117	95	8–298
Semi-dry	1	3	103	5	123
Dry	0	0	0	0	—
Total	31	100	2220	100	—

^a 1988 data.

Table 2
APCD utilization on MWCs in the former West Germany, 1992 [36]

APCD type	Number of plants	Share (%)	Annual capacity (10 ³ t/y)	Share (wt%)	Plant size range (10 ³ t/y)
Wet	25	53	5138	56	60–592
Semi-dry	14	30	2748	30	62–386
Dry	8	17	1352	14	25–400
Total	47	100	9238	100	—

9. Recommendations

9.1. Regulatory

- For new MWCs, when adopting low mercury emission standards, also reduce PIC and CO emission limits to reflect the best performing technologies.
- Consider permit requirements that would insure effective and dependable operation of the mercury control device as an alternative to relaxed mercury emission limits or more frequent testing. For sorbent injection systems, include an audit provision to verify procurement and use.
- Require the use of Method 29 for compliance testing for mercury instead of Method 101A.
- All air emissions tests should be monitored and analyzed by regulatory personnel. EPA should produce a compendium of known and suspected operating interferences for all emission test methods.
- Require that stack tests for mercury be done concurrently with one of more PIC type emission tests, e.g. Method 23 for dioxins, furans and PAHs.
- Permit limits for mercury should be based on flue gas concentrations and *not* mass emission rates. This removes the uncertainty in determining how much material was burned during the tests.
- Tests for mercury capture efficiency *must* be simultaneous at both the inlet and outlet (except for travel time from the inlet point to the outlet point).

9.2. Research

- Determine whether organic (methyl) mercury is emitted from MWCs, and, if so, in what quantities.
- If organic mercury is found to be an emission form, quantify its capture by the various control technologies and establish its subsequent fate.
- Assess the ability of trace reducing gases (SO₂, NH₃, etc.) to depress the capture rate of mercury by activated carbon and to desorb previously captured mercury on the filter cake. This could be accomplished by repeating a portion of the Stanislaus activated carbon injection trials and deliberately generating high levels of SO₂ (30–300 ppm) and NH₃ (20–70 ppm).
- Determine the stability of mercury species adsorbed onto activated carbon and carbonaceous fly ash in landfill atmospheres.
- Develop a simpler dry method for measuring total emissions of mercury from combustion sources and begin assessment of the speciating methods for the determination of organic, soluble ionic, and elemental mercury. The purpose of this effort should be to develop a speciating replacement for Methods 101A and 29 for mercury.
- Perform a comprehensive trial similar to Camden and Stanislaus utilizing a pilot-scale advanced wet scrubber on an MWC.
- Explore the aqueous chemistry of mercury in wet scrubbers and their associated waste water treatment systems.

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