Mercury and Dioxin Control for Municipal Waste Combustors

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ABSTRACT

The control of mercury and dioxins from waste-to-energy plants has been of prime concern for facilities around the world. In the U.S., waste-to-energy plants are called Municipal Waste Combustors (MWCs). Control technologies that were developed in Germany in the 1990's became very elaborate and often uses up to five control stages. In the U.S., simpler systems were developed based on the German experience that incorporated good control technologies on a cost-effective basis.

Today in Germany, it is common to find disposal fees at MWCs in the range of $150 to $350/ton. This is due to the high cost of air pollution control systems and the lack of competition from landfills. In the U.S., there are many landfills available with disposal fees less than $32/ton that compete with MWCs for waste. Therefore, U.S. MWCs had to implement control technologies that meet world recognized standards for dioxin and mercury emissions at cost competitive bases as well as considering local economics when selecting control technologies.

The use of carbon-based technologies is effective in controlling emissions. In addition, a new technology sodium tetra sulfide, is being considered to reduce mercury emissions. This paper discusses the current technologies being used at MWCs in the U.S.

INTRODUCTION

The November 1990 Clear Air Act Amendments directed the U.S. EPA to establish MWC emission limits for particulate matter (PM), hydrogen chloride (HCl), sulfur dioxide (SO_2), nitrogen oxides (NOx), carbon monoxide (CO), PCDDs/PCDFs, cadmium (Cd), mercury (Hg), and lead (Pb). These emission limits were to be based on the application of maximum achievable control technology (MACT). Revised MWC air pollution regulations were subsequently proposed by EPA on September 20, 1994. EPA proposed New Source Performance Standards (NSPS) for new MWCs and Emission Guidelines (EG) for existing MWCs. NSPS and EGs for MWCs larger than 225 Mg/day in capacity were promulgated in February 1991. Tables 1, 2, and 3 present a summary of these emission standards. Table 4 is a summary of U.S. emission standards converted to the metric system which is more commonly used in the rest of the world. Tables 5a and 5b are summaries of emission standards from European countries for comparison.

DIOXIN AND MERCURY CONTROL TECHNOLOGIES

Control technologies in the U.S. for PM and acid gas control also provide a degree of control for PCDDs/PCDFs and Hg. Both PCDDs/PCDFs and Hg may be in a vapor-phase at flue gas temperatures and collection of trace quantities of these compounds is dependent on the absorption on fly ash with subsequent collection in a PM control device. The capture efficiency of PCDDs/PCDFs and Hg in conventional MWC air pollution control equipment depends primarily on the amount of carbon in the fly ash and the operating temperature of the PM control device.

The Hg capture efficiencies of mass burn combustors equipped with ESPs ranges from 0% at 300°C to approximately 30% at 150°C. Modern mass burn combustors have relatively small amounts of carbon in their fly ash. When equipped with SD/FF systems, these combustors exhibit Hg collection efficiencies in the range of 20 to 50%. RDF combustors which contain higher amounts of carbon in the fly ash and when equipped with SD/FF systems often exhibit Hg collection efficiencies greater than 90%.

Field tests have also shown that in semi-dry scrubbing systems, PCDDs/PCDFs emission decrease with the increased amount of carbon in the fly ash. The formation and emission of PCDDs/PCDFs also increases with the increased operating temperature of the PM control device.

Methods which can be used to enhance control of PCDDs/PCDFs and Hg in MWCs equipped with conventionally dry and semi-dry flue gas cleaning systems include:

Enhanced PCDDs/PCDFs Controls Used in the U.S.
- Good combustion practices
- Injection of activated carbon
- Injection of enhanced lime sorbents such as Sorbalit or Sorbalime

Enhanced Control of Mercury Used in the U.S.
- Injection of Sodium Tetra sulfide (Na$_2$S$_4$)
- Source separation
- Injection of activated carbon
- Injection of enhanced lime sorbents such as Sorbalit or Sorbalime

PCDD/PCDF Formation Mechanisms

There are three primary routes for PCDD/PCDF formation: gas-phase reactions involving chlorinated precursors such as chlorobenzenes (CBs), chlorophenols (CPs), or polychlorinated biphenyls (PCBs); condensation reactions involving gas-phase precursors and fly ash; and solid-phase reactions on the surface of fly ash involving metal chlorides and fly ash carbon. The third route of formation, which involves the reaction of unburned carbon in fly ash to form PCDDs/PCDFs, is called de Novo synthesis.

Gas-phase precursors can originate as waste thermal decomposition products or as high temperature products of incomplete combustion (PICs). Low temperature oxidation reactions involving fly ash carbon can also produce CP or other precursor compounds that in turn react to form PCDDs/PCDFs by surface mediated reactions (condensation, absorption, desorption, etc.).

De Novo synthesis consists of low temperature carbon oxidation reactions which provide the biaryl ring structures for PCDD/PCDF formation and metal ion catalyzed reactions which provide the necessary chlorine (Cl) for PCDD/PCDF formation. Low temperature carbon oxidation reactions may be catalyzed by metal ions or carbon structures similar to activated carbon. The Cl for (oxy)-chlorination reactions can be provided from either metal chlorides in the fly ash or HCl in the flue gas.

De Novo synthesis reactions generate a variety of chloro-organic compounds including CPs, chloro-benzonitriles, -thiophenes, -benzofurans, -benzothiophenes, PCDDs, -naphthalenes, PCDFs, and -benzenes. Laboratory experiments show that de Novo reactions occur at temperatures ranging from approximately 250° to 600°C with maximum formation rates near 300°C. At temperatures above 600°C, chloro-organics are rapidly destroyed and at temperatures below 250°C, reaction rates result in minimal formation.

PCDD/PCDF Control at MWCs

Stack emission of PCDDs/PCDFs from MWCs has been found to range from < 0.01 to > 400 ng TEQ/dscm (< 1.0 to > 20,000 ng/dscm), depending on combustion and flue gas cleaning conditions. Although the stack emissions are dependent on combustion conditions, the highest emissions are generally obtained with MWCs equipped with only ESPs followed in order of decreasing emissions by DSI/ESP, SD/ESP, DSI/FF and SD/FF.

Factors affecting the formation and subsequent emission of PCDDs/PCDFs from MWCs include the:
- ❑ Composition and properties of waste
- ❑ Combustion conditions
- ❑ Composition of flue gas
- ❑ Amount of entrained PM
- ❑ Flue gas time/temperature profile
- ❑ PM control device operating temperature, and
- ❑ Method of acid gas and PM control

Details on formation and the factors stated above are found in the papers listed in the Reference section.

The implementation of good combustion practices and carbon-based technologies has resulted in dioxin emission well below U.S. and German standards. Table 6 presents typical controlled dioxin emissions from different MWC operations. The data summary shows that various carbon injection or Sorbalit technologies both dry and wet injection can meet both the U.S. and German dioxin emission regulations.

Mercury Control in MWCs

The capture of Hg in flue gas cleaning devices depends on the:
- ❑ Waste composition
- ❑ Flue gas properties (temperatures, gas composition, moisture, etc.)
- ❑ Hg form (speciation and phase [vapor or solid])
- ❑ Fly ash and sorbent properties, and
- ❑ Type of control device

Mercury in MWCs

At higher temperatures, mercury compounds are not very thermally stable, therefore, the mercury is gaseous at a temperature of 850°C in the combustion chamber, independent of the kind of compound that is taken into the refuse combustion plant. The minimal retention of mercury in the slag is due to its high vapor pressure and is less than 5% of the total mercury input as shown in various investigations. Other metals such as copper, chromium, or nickel have a slag retention rate of more than 90%.

The mercury vapor in the combustion chamber is mixed with the flue gas and enters the convective section of the boiler. In this section, the flue gas cools down while producing hot water and steam. Due to the decreasing gas temperature, the elementary mercury is able to react with other flue gas components.

The main reaction of the mercury vapor is the formation of mercury (II) chloride ($HgCl_2$) out of the gaseous hydrochloric acid (HCl) and elemental mercury (Hg^0) under oxidizing conditions of the off-gases downstream of the refuse incinerator. The exact mechanism of this reduction reaction has not yet been completely understood but is usually described as follows:

$$HgO + 2\ HCl + \tfrac{1}{2}\ O_2 \leftrightarrow HgCl_2 + H_2O \qquad\qquad \text{(R-1)}$$

In case of decreasing temperature, the equilibrium of this reaction shifts more and more to the right side. However, the reaction is not only dependent on temperature. Other flue gas components such as O_2 and sulfur compounds, as well as the residence time in a certain temperature range, influences the reaction equilibrium.

The thermodynamic balance of the above-mentioned reaction is blocked kinetically. Therefore, a complete transformation of the Hg^0 into $HgCl_2$ cannot be expected. The mercury chloride thus formed has a high volatility and is found in the gas phase in the boiler (see Table 7).

Beside the formation of mercury (II) chloride other reduction reactions of mercury in the gaseous phase are possible:

- **elementary mercury can be oxidized to mercury(I) chloride (Hg_2Cl_2):**

$$2\ Hg^0 + 2\ HCl + \tfrac{1}{2}\ O_2 \leftrightarrow Hg_2Cl_2 + H_2O \qquad\qquad \text{(R-2)}$$
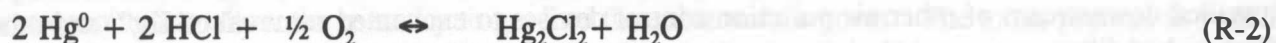
- **elementary mercury can be oxidized to mercury oxide (HgO):**

$$2\ Hg^0 + O_2 \leftrightarrow 2\ HgO \qquad\qquad \text{(R-3)}$$

However, the above described reaction possibilities (R-2 and R-3) are of less importance as Hg_2Cl_2, and HgO are not stable at temperatures above 400°C. Above this temperature, Hg_2Cl_2 decomposes into Hg^0 and $HgCl_2$ respectively and Hg^0 into $Hg^0 + \tfrac{1}{2}\ O_2$.

A higher amount of mercury (I) chloride can be formed out of $HgCl_2$ in the presence of fly ash creating a reducing atmosphere.

At the boiler's outlet temperature the Hg_2Cl_2 is solid and will be separated together with the fly ash (sublimation temperature 383°C) (see Table 7.) Consequently, up to 10% of the total mercury amount can be removed.

Usually, the mercury at the boiler outlet consists mainly of 5 to 15% Hg^0 and 85 to 95% $HgCl_2$. Characteristic for both species is their high vapor pressure, even at temperatures of about 200°C. Thus, the particulate removal equipment usually arranged downstream of the boiler is unable to act as an effective mercury sink.

Mercury Speciation and Control Mechanisms

The form of Hg in flue gas depends on:

- ☐ Flue gas residence time in the combustor,
- ☐ Flue gas composition (HCl) and
- ☐ Temperature.

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For combustion systems containing substantial amounts of Cl in the waste (or fuel), the two predominant forms of Hg at flue gas cleaning temperatures (<300°C) are believed to be ionic mercury (Hg^{2+}) and elemental mercury (Hg^0). Thermo-chemical equilibrium calculations indicate that the Hg^{2+} will be predominantly mercuric chloride ($HgCl_2$).

Most metals condense to form solid particles as flue gas is cooled so that they can be collected as PM. However, both Hg and $HgCl_2$ are vapors [$Hg^{(v)}$] at typical flue gas cleaning control device operating temperatures (140°C), and special methods must be devised for their capture.

Hg in MWC flue gases can be captured if it is in the solid-phase [Hg(s)] or is absorbed on fly ash or special sorbents such as activated carbon or enhanced lime-based sorbents containing activated carbon. $Hg^{(v)}$ capture without the use of special sorbents depends on the amount of carbon in the fly ash. Well-designed and operated mass burn combustors have little carbon in their fly ash and, even when equipped with SD/FFs or SD/ESPs, they exhibit Hg control levels below 50%. Conversely, RDF combustors contain relatively high amounts of carbon in the fly ash (> 2%) and they commonly exhibit control efficiencies above 80 and 90% when equipped with SD/ESPs and SD/FFs, respectively.

Activated carbon can be used in three ways to control $Hg^{(v)}$ emissions. It can be in injected as a power in dry or semi-dry scrubbers to absorb $Hg^{(v)}$ for subsequent collection in an ESP or FF. It can be used in a lime enhanced sorbent system to replace lime. Finally, flue gas can be filtered through a carbon bed polishing filter installed downstream of other air pollution control devises to enchanted removal of $Hg^{(v)}$ and other pollutants. Carbon bed filters are currently being applied to European MWCs where they are primarily used to the lowest possible emission level of PCDDs/PCDFs, Hg, and other trace metals. EPA has sponsored two major field tests on the wet and dry injection of powdered activated carbon for Hg control and has selected this technology as the basis for Hg emission control requirements on MWCs.

Carbon Capture Mechanism

The adsorption of mercury and organics by activated carbon and coke is controlled by the properties of both the carbon and the adsorbate, and by the conditions under which they are contacted. This phenomenon is generally believed to result from the diffusion of vapor-phase molecules into the pore structure of carbon particles. These molecules are retained at the surface in the liquid state because of intermolecular or Van der Waals forces.

As the temperature falls, or as the partial pressure of the vapor above the carbon rises, the average time that a molecule resides on the surface increases. So does the fraction of the available surface covered by the adsorbate. However, the carbon surface is not uniform and consists of sites whose activities vary. More active sites will become occupied first and, as the activity of the remaining available sites decreases, the adsorption energy will change.

The physical structure of activated carbon and coke is not known in detail, but it is believed to contain randomly distributed pores in the carbon, between which lies a complex network of irregular interconnected passages. Pores range in diameter down to a few angstroms and provide a internal surface area from 300 to 1,000 m^2/gram of carbon. The volume of pores at each diameter is an important variable that directly affects carbon performance.

Since adsorption takes place at the carbon-gas interface, the surface area of the carbon is one of the most important factors to consider. The second factor is the pore radius. Laboratory bench scale tests have shown that both increasing the surface area and the addition of sulfur compounds result in higher adsorption rates of Hg^0. Most of the laboratory work on carbon adsorption has been done on Hg^0 not with the Hg compounds we normally see in MWC emissions and without humidification.

The actual adsorption capacity of carbon is affected by:

- Gas Temperature
- Flue gas moisture
- Type of carbon used and surface area
- Contact time
- Acid content of the flue gas
- Inlet concentrations of Hg
- Species of Hg
- Concentration of organics such as dioxin

Enhanced Lime-based Sorbents

Several enhanced lime-based sorbents are commercially available for use in MWCs. Sorbalit is a patented system for controlling emissions of acid gases, mercury, and organics in a single application. The sorbent component of the technology is produced by mixing lime with surface-activated substances such as activated carbon and sulfur-based components in a proprietary process. Sorbalit can be produced with carbon contents ranging from 4 to 65% depending on the technical and economic requirements of each project.

The Sorbalit process produces a homogeneous powder containing calcium, carbon, and sulfur compounds that will not dissociate (demix) when used, either in a slurry or dry form, in the air pollution control systems. The addition of sulfur compounds to the process plays a major role in the adsorption of mercury but not in the adsorption of dioxin. Sulfur's role in the adsorption is two fold. First the sulfur compounds maintain the active state of the carbon. Activity is defined as the amount of open pores in the carbon. Sulfur's role is to keep these pores open and to allow the mercury to get into the substructure pores. The exact process in which the sulfur keeps the pores open has not been defined. One theory is that the sulfur reacts with water which is adsorbed or is on the surface of the carbon particles to form an acid that penetrates the pores. The second role for sulfur is converting elemental mercury to a sulfate.

Since the lime used in spray dryers or the lime component of Sorbalit removes the SO_2 from the flue gas, some adsorption capacity of the carbon for Hg^0 is diminished. The sulfur component in Sorbalit added during manufacturing, replaced the missing SO_2 and enhanced the adsorption of Hg^0. Mercuric chloride does not react with the sulfuric acid but is dissolved in sulfuric acid. No studies concerning the necessary sulfuric acid loading for quantitative precipitation of mercury have been made.

Performance of Activated Carbon Systems

The performance of activated carbon systems depends primarily on the carbon injection rate, carbon injection method, carbon properties, flue gas temperature, and PM control method. Performance tests in the U.S. and Europe have primarily been limited to the application of carbon injection to mass burn MWCs equipped with SD/FF or SD/ESP systems.

Two major test projects have been conducted in the U.S. to evaluate the use of carbon injection on mass burn MWCs. The first was conducted on an MWC in Stanislaus County, California equipped with a SD/FF system. The second was conducted on two MWCs in Camden County, New Jersey equipped with SD/ESP systems. These tests show that stack concentrations of Hg depend on the Hg concentration in the flue gas (SD inlet concentration), the carbon content of fly ash, and the operating conditions of the carbon injection system.

Mercury concentrations in MWC flue gas are highly variable with time. In MWCs, the total solid-phase flue gas carbon (carbon in fly ash plus the carbon injection rate) appears to be the key determinant of Hg capture. In the absence of carbon injection, the amount of Hg captured depends on the amount of carbon in the fly ash. When the fly ash carbon content is low or when Hg concentrations are high, poor removal efficiencies are obtained. When the fly ash carbon content is high and the Hg concentration is low, high removal efficiencies are obtained.

Injection of powdered activated carbon into the flue gas can be used to increase solid-phase carbon concentration. Increasing the carbon injection rate reduces both the average and variability of emissions. At high carbon injection rates, there is generally sufficient carbon to capture low or high levels of Hg. The amount of excess carbon needed for continuously high levels of capture will depend on the variation of Hg concentration in the flue. Highly variable Hg inlet concentrations will require high excess carbon injection rates to ensure continuous Hg capture.

In SD/FF tests at the Stanislaus County MWC, Hg capture without carbon injection ranged from 16 to 46%. Outlet Hg concentrations for these tests ranged from 311 to 538 μg/dscm. Hg capture increased with increasing carbon injection rates and, at the highest injection rates of approximately 70 to 100 mg/dscm, Hg outlet concentrations ranged from 17 to 77 μg/dscm. SD outlet temperatures at Stanislaus County normally ranged between 136° and 145°C.

Recent tests with an enhanced lime based sorbent (Sorbalit) has demonstrated the significance that sulfur plays in capturing Hg in MWCs equipped with SD/FF systems. The test program conducted at the Marion County, Oregon MWC showed Sorbalit captured more Hg (total and vapor-phase) than dry carbon injection. To determine the equivalent performance of carbon and Sorbalit, both were injected at the same carbon feed rate of 5 lbs./hr. Sorbalit captured 87.7% of the total Hg while carbon injection captured 84.2%. More importantly, Sorbalit captured 83.2% of the vapor-phase Hg while carbon collected 77.6%.

Hg emissions from coal fired plants are significantly different in two ways from those of MWCs. First, the uncontrolled Hg emissions from U.S. eastern coal ranges from 8 to 30 μg/dscm while a typical mass burn MWC would emit 600 μg/dscm (uncontrolled). Secondly, since there is a relatively low chlorine content in coal, the percentage of $Hg^{(v)}$ is much higher than in a MWC. As a result, the capture of Hg emissions is more difficult via dry injection. In a test conducted in late 1993 on a coal fired plant, Sorbalit captured between 44 and 55% of the $Hg^{(v)}$ while carbon injection only captured 10 to 15%. These tests were conducted under difficult Hg capture conditions: high temperatures and low moisture.

During the Camden County SD/ESP carbon injection test project, Hg capture without carbon injection ranged from 18 to 92%. When dry carbon injection rates exceeded 150 mg/dscm and the ESP inlet temperature was 132°C, stack emissions of Hg were generally less than 80 μg/dscm .

The performance of activated carbon in absorbing Hg is dependent on temperature. The temperature at the inlet to the PM control device is normally used as a parameter in evaluating the performance of the device in collecting condensed or absorbed pollutants. The PM control device inlet temperature for SD/FF and SD/ESP systems on MWCs is normally between 135° and 145°C. Tests on the Camden County SD/ESP system at 177°C indicated only moderate reduction in Hg capture relative to similar tests at 132°C. Temperature variations over the normal operating range of SD/FFs and SD/ESPs can be expected to have only minor effects on Hg capture. Similar tests on European MWCs have shown that carbon injection can be used to reduce Hg emissions in SD/FF and SD/ESP systems to less than 80 μg/dscm.

New Approach to Mercury Control

Several states have proposed lower Hg emission standards than required by the U.S. EPA. New Jersey has already adopted an Hg emission standard of 28 μg/dscm or 85% reduction whichever is less restrictive. Massachusetts has proposed an emission standard of 28 μg/dscm without a reduction allowance. The State of Maine is considering an annual emission standard for Hg of 50 pounds per year. The proposed Maine standard on a concentration basis is about 32 μg/dscm for a 500 TPD MWC. These new proposed Hg emission standards have raised certain concerns in the industry since at this time there is little reliable data based on long-term operations at 28 μg/dscm. In addition, the lower limit of carbon adsorption using injection technology has not been determined.

One approach to achieve lower Hg emissions is to use sodium tetra sulfide (Na_2S_4) injection by itself or in combination with carbon injection. Na_2S_4 can capture both ionic $HgCl_2$ and Hg^0 in accordance with the following simplified reactions:

$$Na_2S_4 + HgCl_2 \leftrightarrow HgS + 2\,NaCl + 3\,S^0 \qquad \text{(R-4)}$$

$$S^0 + Hg^0 \leftrightarrow \qquad \text{(R-5)}$$

The only requirement is to inject the aqueous Na_2S_4 solution into the flue gas duct. Such a system can be easily retrofitted to an existing flue gas cleaning plant at a minimal cost. The Na_2S_4 reacts with the mercury to form mercury sulphide (HgS) whose red allotrope is known as cinnabar. This is a non-poisonous, insoluble salt which is thermally stable up to 400°C (see Table 7) and thus, effectively immobilizes the mercury by chemical binding. The black allotrope meta-cinnabarite is to be found in refuse incineration plants which, in the course of several years, changes into the stable red allotrope.

Apart from the heat exchange with the flue gas, there is also a mass transfer between the droplet of the additive and the flue gas. The most likely mass transfer process between the liquid and the gaseous phase is the dissolving of HCl in the droplets of the Na_2S_4 as aqueous alkaline liquids show a strong affinity towards the gaseous HCl.

The dissolved HCl will decompose the existing Na_2S_4 in the droplets as follows:

$$Na_2S_4 + 2\,HCl \leftrightarrow H_2S + 3\,S + 2\,NaCl \qquad \text{(R-6)}$$

After evaporation of the droplet, the H_2S injected into the flue gas is gaseous at a temperature of approximately 220°C. The elementary sulphur which is formed (melting point of sulphur = 119°C, boiling point = 445°C) exists in liquid form as an aerosol with a diameter of < 1 μm, (see Table 7).

However, it is most unlikely that all Na_2S_4 molecules will be decomposed by the HCl. Because Na_2S_4 (melting point = 275°C) is stable at the existing temperatures, it is most probable that Na_2S_4 particles can still be found in the flue gas after evaporation of the droplet.

In the entrained-flow phase, the mercury reacts with $H_2S^{(g)}$, $S^{0(l)}$, and Na_2S_4. According to the predominant opinion in literature and also according to the steam pressure curve for pure components, Hg^0 and $HgCl_2$ can be found in the gaseous phase due to their high volatility. However, the existence of aerosols cannot be denied. Therefore, a different reaction mechanisms must be responsible for the formation of HgS within the entrained-flow phase.

It is most probable that Hg^0 and $HgCl_2$ are dissolved in the droplet of the additive where they react as follows:

$$HgCl_2 + H_2S \leftrightarrow HgS + 2\,HCl \qquad \text{(R-7)}$$

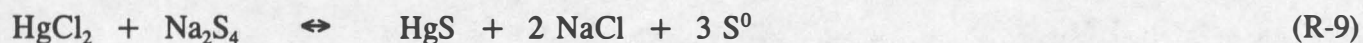$$Hg^0 + S^0 \leftrightarrow HgS \qquad \text{(R-8)}$$
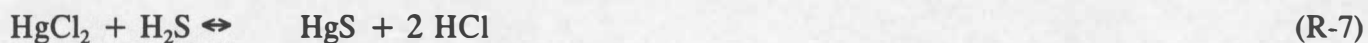
These reactions are not only dependent on the distribution of educts, but also on the time limited existence of a liquid phase.

Other reaction schemes exist (melting temperature Hg^0 and $HgCl_2$: -40°C and 280°C, boiling temperature: 360°C and 303°C) to account for the presence of Hg^0 and $HgCl_2$ as aerosols (see Table 7).

Hg⁰ and HgCl₂ Aerosols

Hg^0 and $HgCl_2$ aerosols respectively, can be combined with Na_2S_4 particles, and can be absorbed and react as follows:

$$HgCl_2 + Na_2S_4 \leftrightarrow HgS + 2\,NaCl + 3\,S^0 \qquad \text{(R-9)}$$

$$Hg^0 + Na_2S_4 \leftrightarrow HgS + Na_2S \qquad \text{(R-10)}$$

According to R-7, $H_2S^{(g)}$ can react to form HgS in the gaseous phase as well as in the liquid phase with the $HgCl_2$ aerosols. $S^{0(l)}$ can also be combined with $Hg^{0,(g)}$ and Hg^0 aerosols and react to form HgS as mentioned in R-8.

Competitive reactions such as the oxidization of Na_2S_4, H_2S or S into Na_2SO_3, SO_2, SO_3, or S_2O_3 cannot be excluded. Such competitive reactions would prevent the sulphur from further reactions with mercury. Moreover, sulphide formation of other heavy metals can cause competitive reactions as well. However, in the case of injection after upstream dust removal, such reactions are of no consequence regarding the sulphur balance. Even if all heavy metals in the flue gas flow react to sulphide, only 4 to 10% of the feed sulphur could be used up via the Na_2S_4 injection.

Finally, the equations R-7 and R-8 have to be indicated as the basic reaction equations responsible for the transformation of Hg^0 and $HgCl_2$ during the entrained-flow phase which is started by the reaction of Na_2S_4 with the dissolved HCl.

Na_2S_4 is a proven Hg control technology in Germany. Recent test on a U.S. facility have demonstrated that Na_2S_4 injection, either by it self or in combination with carbon injection, can meet the proposed Hg emission limit of 28 $\mu g/dscm$. The tests have just been complete and the results will be presented at the conference. The tests were conducted on a limited time basis. A long-term testing program will be required to determine if the new lower Hg emissions standards can be met under all operating conditions. One limitation of the Na_2S_4 technology is that it does not control dioxins. Therefore, it can only be applied to facilities that do not need dioxin control or it has to be used in combination with other technologies.

CONCLUSIONS

• Dioxin formation is predominantly associated with heterogeneous reactions involving fly ash. These low temperature synthesis reactions can occur downstream of the combustor at temperatures ranging from approximately 250° to 600°C.

• The flue gas cleaning systems most commonly employed on MWCs in the U.S. include: ESPs, DSI/FFs, SD/ESPs, and SD/FFs.

• Spray dryers and FFs can be used to continuously reduce PCDD/PCDF emissions to less than 20 ng/dscm. Carbon-based technologies, which are needed for Hg control in many MWCs, will provide additional PCDD/PCDF control.

• Spray dryers and ESPs can be used to reduce typical PCDD/PCDF emissions from mass burn combustors to less than 75 ng/dscm. Injection of activated carbon and other additives to control Hg emissions, can be used to further reduce PCDD/PCDF emissions to less than 30 ng/dscm (about 0.5 ng TEQ/dscm).

- The Hg in MSW is volatilized during combustion and converted to elemental and ionic Hg. Hg in MWC flue gas is believed to be predominantly $HgCl_2$ and Hg^0. Both are predicted to be in a vapor-phase at stack gas temperatures (boiler exit).

- In dry flue gas cleaning systems, $Hg^{(v)}$ can be absorbed onto the surface of particles for collection in PM control devices. $Hg^{(v)}$ can be absorbed either on the residual carbon in fly ash or on activated carbon or enhanced lime-based sorbents such as Sorbalit which have been injected into the flue gas.

- MWCs, such as waterwall mass burn combustors, may require the injection of activated carbon or enhanced lime-based sorbents to obtain efficient $Hg^{(v)}$ control.

- Nearly all of the uncontrolled Hg in MWC stack gas is in a vapor-form. Data suggest that carbon absorption methods collect $Hg^{2+(v)}$ more efficiently than $Hg^{0(v)}$. As Hg removal efficiencies increase, $HgCl_2{}^{(v)}$ is selectively removed and the proportion of Hg that is $Hg^{0(v)}$ increases. In MWCs equipped with SD/FFs and SD/ESPs, the relative amount of Hg(PM) in stack gas will generally be less than 5%.

ACKNOWLEDGMENTS

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Table 1. Basis for Proposed MACT Performance Requirements[a]
(September 20, 1994)

Proposed Requirements	Basis for Emission Limits[b]
Emissions Guidelines (EG) - Existing Plants	
Small (>35 to 225 Mg/day)	GCP + DSI + ESP + CI
Large (>225 Mg/day)	GCP + SD/ESP (or SD/FF) + CI + SNCR
New Source Performance Standards (NSPS) - New Plants	
Small (>35 to 225 Mg/day)	GCP + SD/FF + CI
Large (>225 Mg/day)	GCP + SD/FF + CI + SNCR

[a] Technologies which provide equivalent or better performance may also be used.

[b] GCP	=	Good Combustion Practice
ESP	=	Electrostatic Precipitator
DI	=	Dry Injection of Sorbent (FSI = Furnace Sorbent Injection and DSI = Duct Sorbent Injection)
CI	=	Carbon Injection
SD/ESP	=	Lime Spray Dryer Absorber and ESP
SD/FF	=	Lime Spray Dryer Absorber and Fabric Filter Baghouse
SNCR	=	Selective Non-catalytic Reduction

Table 2. Proposed Good Combustion Practice Requirements for MWCs
(September 20, 1994)

Type of Combustor	EG Limit ppmv (Avg. Time, h)	NSPS Limit ppmv (Avg. Time, h)
		CO Emission Limits
Mass Burn Water Wall (MBWW)	100 (4)	100 (4)
Mass Burn Refractory (MBR)	100 (4)	100 (4)
Mass Burn Rotary Water Wall (MBRW)	250 (24)	100 (24)
Mass Burn Rotary Refractory (MBRR)	100 (24)	100 (4)
Refuse-Derived Fuel Stokers (RDF)	200 (24)	150 (24)
Fluidized Bed Combustors (FBC)	100 (4)	100 (4)
Modular Combustion Units (MCU)	50 (4)	50 (4)
Coal/RDF Mixed Fuel-Fired (Coal/RDF)	150 (4)	150 (4)

A. CO Requirements

B. Load not to exceed maximum load demonstrated during most recent PCDD/PCDF compliance tests.

C. PM control device inlet temperature not to exceed level demonstrated during most recent PCDD/PCDF compliance tests.

D. Chief facility operator, shift supervisors, and control room operators must meet training and certification requirements.

Table 3. U.S. Emission Limits for MWCs[a]
(September 20, 1994)

Pollutant/Measurement	EG Existing Plants	NSPS Limits - New Plants (or % Reduction)
	Large	Large and Small
	>225 Mg/Day	≥35 Mg/day
ng/dscm [ng TEQ/dscm][b]		
Baghouse	30 [0.5]	13 [0.2]
ESP)	60 [1.0]	NA
PM, mg/dscm	27	15
Opacity[c], %	10	10
Cd, mg/dscm	0.04	0.01
Pb, mg/dscm	0.50	0.10
Hg, mg/dscm	0.08 (85)	0.08 (85)
HCl, ppmv	35 (95)	25 (95)
SO$_2$, ppmv[d]	35 (75)	30 (80)
NO$_x$, ppmv	180[e]	180[e]

[a]   All emissions corrected to 7% O$_2$.

[b]   Average of three stack tests using EPA Method 23. Toxic equivalents based on International Toxic Equivalency factors. Values are weight of total tetra- through octa- cogeners. Values in brackets for [toxic equivalents based on 1989 International Toxic Equivalency (TEQ) factors]. Note: TEQ to mass bases is approximate and not a direct conversion.

[c]   EPA Method 9, limit of 6 minute averages.

[d]   24-hour averaging time.

[e]   Applies to large plants only, 24-hour averaging time.

Table 4. Comparison of German and U.S. EPA standards for MWCs [1]

Pollutant	Germany Bundesgeseztblatt -1990 All Sized Units		U.S. EPA Promulgated 12/95 New Large Units
SO₂ mg/Nm³	200	50	61 or
% reduction	N/A	N/A	80%
Avg. time-hrs.	0.5	24	24
HCl mg/Nm³	60	10	28 or
% reduction	N/A	N/A	95%
Avg. time-hrs.	0.5	24	24
PM mg/Nm³	30	1024	18.3
Avg. time-hrs.	0.5		-
Cd mg/Nm³	Included in Class I	0.05	0.0153
Avg. time-hours	Metals [2]	(>½ hr & <2 hr)	-
Pb mg/Nm³	Included in Class	0.5	0.153
Avg. time-hours	III Metals [2]	(>½ hr & <2 hr)	-
Hg mg/Nm³	Included in Class	0.05	0.061 or
% reduction	II Metals [2]	N/A	85%
Avg. time-hours.	-	(>½ hr & <2 hr)	-
Dioxin Furan [3]			
ng ITEQ/Nm³	-	0.1 [4]	≈0.2 [5]
ng/Nm³ mass	-	N/A	13
Avg. time - minutes	-	>500 m & <960 m	-
NOx mg/Nm³	400	20024	219
Avg. time-hrs.	0.5	-	24
CO mg/Nm³	100	5024	89
Avg. time-hrs.	1	-	4

(1)   All emission data based on mass burn water wall technology

(2)   Class I Heavy Metals: Cd & Tl
       Class II Heavy Metals: Hg
       Class III Heavy Metals: As, Co, Cr, Cu, Mn, Ni, Pb, Sb, Sn, & V

(3)   Germany requires a minimum combustion zone temperature of 850°C for 2 seconds.

(4)   U.S. EPA dioxin standards are on a mass basis. There is no direct correlation to ITEQs and only an approximate conversion can be made with a ± error.

(5)   U.S. EPA requires control of temperature at APC system.

Table 5a. Waste Incineration Emission Guidelines for Some European Countries (Mg/nm³ Dry at 11% O₂)

Measurement	German 17th BImSchV 11/90 Corrected only when >11% O₂ 24 hr. avg	German max. ½ hr.	Austria LKR-K 15.07. 1988 daily mean	Sweden monthly mean	Netherlands BLA 1993 All Waste Plants Corrected at All Times max. 1 hr. mean	Draft EU Directive for MWC Facilities Corrected only when >11% O₂ 24-hour	Draft EU ½-hour
HCl	10	60	15	100	10	5	10
SO (SO₂ + SO₃)	50	200	100	-	40	25	50
HF	1	4	0.7	-	1	1	2
NOx (NO₂)	200	400	100	-	70	-	-
CO (always corrected)	50	(hr.) 100	100	-	(Boiler) 50	50	-
C (organic)	10	20	20	-	10	10	10
Particulate	10	30	25	20	(8 hr. avg.) 5	5	10
Heavy Metals							
Class I	Cd + Tl Σ = 0.05 (>½ hr & <2 hr)		Hg = 0.05 Cd = 0.05	Hg = 0.6 max 0.3 aim	Hg = 0.05 (8 hr. avg.)	Cd + Tl = 0.05	
Class II	Hg = 0.05 (>½ hr & <2 hr)		-	-	Cd = 0.05 (8 hr. avg.)	Hg = 0.05	
Class III	Sb,As,Pb,Co,Cr,Cu, Mn,V,Sn,Ni Σ = 0.5 (>½ hr & <2 hr)		As,Co,Ni Σ = 1 Pb, Zn, Cr Σ= 4	- -	Sb,As,Pb,Co,Cr,Cu,Mn, V,Sn,Ni,Te,Se Σ = 1 (8 hr. avg.)	Sb,As,Pb,Co,Cr,Cu, Mn,V,Sn,Ni Σ = 0.5 (>.5 hr.)	
PCDD/PCDF (ng/Nm³)	0.1 ITEQ (>500 min & <960 min)		0.1 ITEQ	0.5 -2.0 Stndrd 0.1 ITEQ aim	0.1 ITEQ (8 hr. avg.)	0.1 ITEQ Recommended	
Combustion Temperature	850°C >2 sec. for MSW and MWI >6% O₂; 1200°C >2 sec. for Sludge >6% O₂		-	-	850°C at >6%O₂ >2 sec.	850°C at >6%O₂ >2 sec.	

Table 5b. Waste Incineration Emission Guidelines for Other Selected Countries (mg/Nm³ dry at 11% O₂)

Basis Measurement	Denmark 1991 Standards daily mean	Switzerland 1992 Standards >350 kw	England 1990 Standards	Japan	Taiwan
HCl	65	20	30	700 [1]	50
SO₂	300	50	300	-	100
HF	2	2	2	-	2
NOx (NO₂)	-	80	350	514	370
CO	100	50	-	63	-
C (organic)	20	20	-	-	-
Particulate	40	10	30	20	10
Ammonia (NH₃)	-	5	-	-	-
Heavy Metals					
Hg	Hg + Cd ∑= 0.2	0.1	0.1	-	-
Cd	Hg + Cd ∑= 0.2	0.1	0.1	-	-
Other Metals					
Pb	1	Pb + Zn ∑= 0.2	-	-	-
Ni + As	∑= 1	-	-	-	-
Pb + Cr + Cu + Mn	∑= 5	-	-	-	-
PCDD/PCDF (ng ITEQ/Nm³)	Recommended Value = 0.1	Recommended Value = 0.1	0.1	0.5 [2]	-
Combustion Temperature	-	-	-	800°C at >6%O₂ ; >2 sec.	-

(1)   Dependent on area and stack height

(2)   Guideline only

Table 6: Dioxin Emissions from MWCs

Plant	Control Technology	Measurement Units	Standard	Inlet	Outlet
CH, USA	Spray dryer/ESP with Sorbalime slurry	ng/dscm total at 7% O_2	60	900	40
NF, USA	Spray dryer/FF with Sorbalime slurry	ng/dscm total at 7% O_2	30	n m	5
Berlin-Ruhleben, Germany	Dry injection/FF with dry Sorbalit injection	ng/Nm3 TEQ at 11% O_2	0.1	4.6 to 23.77	0.025 to 0.092
Burgau, Germany	Dry injection/FF with dry Sorbalit injection	ng/Nm3 TEQ at 11% O_2	0.1	n m	0.012 to 0.018
Camden, NJ USA	Spray dryer/ESP with dry carbon injection	ng/dscm total at 7% O_2	60	374	11
Würzburg, Germany	Dry injection/FF with dry Sorbalit injection	ng/Nm3 TEQ at 11% O_2	0.1	9.0 - 10.0	0.02 to 0.06

Table 7: Selected Physical Properties of Hg and Hg-compounds[3]

	Mercury Hg^0	Calomel Hg_2Cl_2	Sublimate $HgCl_2$	'Meta-cinnabarite' black, meta-stable 'Cinnabar' = red, stable HgS	Mercury-oxide HgO	Sulfur S	Sodium tetra-sulfide Na_2S_4
Melting temperature [°C] at p = 1 bar	-38.84	Solid	280	Solid	Solid	118.95	275
Boiling temperature [°C] at p = 1 bar	356.95	-	303	-	-	444.6	-
Sublimation temperature [°C] at p = 1 bar	-	383	-	580	-	-	-
Vapor pressure at p = 1 bar 20°C	0.0017 mbar = 15,000 $\mu g/m^3$	-	-	-	-	-	-
Formation / Decomposition	-	-	-	Decomposition in oxidizing atmosphere and ≥ 400°C	Formation 300-350°C Decomposition > 400°C	-	-