CONTROL OF AIR POLLUTION EMISSIONS FROM
MUNICIPAL WASTE COMBUSTORS

James D. Kilgroe
U. S. Environmental Protection Agency
National Risk Management Research Laboratory
Research Triangle Park, North Carolina

Anthony Licata
Licata Energy and Environmental Consultants, Inc.
Yonkers, New York

ABSTRACT

The November 1990 Clear Air Act Amendments (CAAAs) directed EPA to establish municipal waste combustor (MWC) emission limits for particulate matter, opacity, hydrogen chloride, sulfur dioxide, nitrogen oxides, carbon monoxide, dioxins, dibenzofurans, cadmium, lead, and mercury. Revised MWC air pollution regulations were subsequently proposed by EPA on September 20, 1994, and promulgated on December 19, 1995. The MWC emission limits were based on the application of maximum achievable control technology (MACT). This paper provides a brief overview of MWC technologies, a summary of EPA's revised air pollution rules for MWCs, a review of current knowledge concerning formation and control of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans, and a discussion of the behavior and control of mercury in MWC flue gases.[*]

INTRODUCTION

In June 1987, EPA announced its intention to develop new air pollution rules for MWCs.[1] This decision was based, in part, on a study of the potential environmental risk associated with MWCs.[2] Pollutants posing the highest risks included polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and hazardous trace metals. On December 20, 1989, EPA proposed New Source Performance Standards (NSPS) for new MWCs and Emission Guidelines (EGs) for existing MWCs.[3] NSPS and EGs for MWCs larger than 225 Mg/day in capacity were promulgated in February 1991.[4]

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[*] This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative policies and has been approved for publication.

The November 1990 CAAAs directed EPA to establish MWC emission limits for particulate matter (PM), opacity, hydrogen chloride (HCl), sulfur dioxide (SO_2), nitrogen oxides (NO_x), carbon monoxide (CO), PCDDs/PCDFs, cadmium (Cd), lead (Pb), and mercury (Hg).[5] Revised MWC air pollution regulations were subsequently proposed by EPA on September 20, 1994, and promulgated on December 19, 1995.[6-9] These emission limits were based on the application of MACT. For existing units, MACT is defined as the best emission limit achieved by 12 percent of the operating units in a category such as large or small units. For new units, MACT is defined as the best emission limit achieved by the best single unit in a category of units.[5]

This paper provides a brief overview of MWC technologies, a summary of EPA's revised air pollution rules for MWCs, a review of current knowledge concerning formation and control of PCDDs/PCDFs, and a discussion of the behavior and control of Hg in MWC flue gases. The focus of the paper is on the performance of combustion and flue gas cleaning technologies used at MWC facilities in controlling emissions of PCDDs/PCDFs and Hg.

MWC TECHNOLOGIES

Three major types of MWCs are commonly used in the U.S.: field-erected mass burn incinerators, refuse-derived fuel (RDF) combustors, and factory-constructed modular mass burn incinerators.[10] The best combustion technologies ensure adequate waste burnout and produce minimal products of incomplete combustion (PICs) in the flue gas.

In the U.S., dry flue gas cleaning technologies are generally used to control air pollution emissions.[11] Wet scrubbing systems are seldom used. PM is typically collected in

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

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

[b]
GCP	=	Good Combustion Practice
DSI	=	Dry Sorbent Injection into the Combustor Furnace or Flue Gas Duct
ESP	=	Electrostatic Precipitator
FF	=	Fabric Filter Baghouse
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

[c] No NO_x control requirements for small MWC plants or large existing mass burn refractory combustors

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electrostatic precipitators (ESPs) or fabric filters (FFs). Most trace metals such as Cd and Pb are solids at flue gas cleaning temperatures and are efficiently collected in ESPs or FFs. Hg is normally a vapor at flue gas cleaning temperatures, and special methods must be used for its control.[12,13]

Acid gases are controlled in dry or semi-dry scrubbers by injecting either a calcium- or sodium-based reagent into the flue gas to convert HCl and SO_2 into solid compounds that can be collected in a PM control device.[13,14] The most commonly used reagents are quicklime (CaO), hydrated lime [$Ca(OH)_2$], limestone ($CaCO_3$), and sodium bicarbonate [$Na(CO_3)_2$]. Several methods may be used to inject and mix the sorbent with the flue gas: lime spray dryers (SDs), dry sorbent injection (DSI) of limestone or lime into the combustor furnace, or the flue gas duct. Selective non-catalytic reduction (SNCR), the most advanced NO_x control technology being applied in the U.S. on MWCs, uses either ammonia (NH_3) or urea [$CO(NH_2)_2$] as a reagent to reduce NO_x to nitrogen.[15]

The chemistry involved in acid gas and NO_x control and the mechanisms involved in PM control are generally well understood. The major problem associated with control of these pollutants (PM, acid gases, and NO_x) is the engineering optimization of flue gas cleaning processes that are also effective in the control of trace metals and trace organics.

The most difficult to control MWC pollutants of concern are PCDDs/PCDFs and Hg. PCDDs/PCDFs can be formed in MWCs as high temperature PICs, or they can be formed downstream of the combustor by low temperature synthesis

reactions involving fly ash.[10,16] Hg, typically a vapor at flue gas cleaning temperatures, is difficult to collect in flue gas cleaning equipment.

FEDERAL EMISSION CONTROL REQUIREMENTS

On December 19, 1995, EPA promulgated revised NSPS for new MWCs and EGs for existing MWCs.[7-8] These revised rules require the use of good combustion practice (GCP) and MACT flue gas cleaning techniques to continuously limit emissions of PCDDs/PCDFs, CO, PM, Cd, Hg, Pb, HCl, SO_2, and NO_x. The control technologies on which the performance requirements are based are summarized in Table 1. Alternatively, technologies which can provide equivalent or better performance than those on which the standards are based may also be used.

The control of PCDDs/PCDFs is based on the use of GCP in combination with appropriate flue gas cleaning techniques. The objectives of GCP are to maximize furnace destruction of organics and minimize low temperature PCDD/PCDF formation reactions.[16-18] Furnace destruction of organics is controlled by establishing technology-based emission limits for CO (see Table 2). Downstream formation and stack emissions are controlled by a limit on steam load for waste-to-energy plants and a limit on PM control device operating temperature. The load is a surrogate parameter used to limit

TABLE 2. GOOD COMBUSTION PRACTICE FOR MWCs
(DECEMBER 19, 1995)[8,9]

1. CO Requirements

Type of Combustor	CO Emission Limits	
	EG Limit, ppm (Ave. Time, h)	NSPS Limit, ppm (Ave. Time, h)
Mass Burn Water Wall (MBWW)	100 (4)	100 (4)
Mass Burn Refractory Wall (MBRW)	100 (4)	100 (4)
Mass Burn Rotary Water Wall (RWW)	250 (24)	100 (24)
Mass Burn Rotary Wall Refractory (RWR)	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		
- Spreader Stokers (Coal-RDF/SS)	250 (24)	150 (24)
- Pulverized Coal (Coal-RDF/PC)	150 (4)	150 (4)

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

3. PM control device inlet temperature not to exceed a temperature 17 °C above the maximum temperature demonstrated during most recent PCDD/PCDF compliance tests.

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

the relative amount of PM carried out of the combustor with flue gas (PM carryover). The purpose of the inlet temperature limit is to control PCDD/PCDF synthesis reaction rates, and solid- and vapor-phase partitioning of PCDDs/PCDFs in the PM control device. Solid-phase PCDD/PCDF emissions are limited by the use of efficient PM control equipment such as high performance ESPs or FFs.

All MWC plants must comply with an Hg emission limit of 80 ug/dscm or an 85 percent reduction in Hg emissions.[6] The Hg emission limit is based on the use of powdered activated carbon in conjunction with dry scrubbing. The activated carbon adsorbs gas-phase Hg and is collected in the PM control device. Acid gases (HCl and SO_2) and metal (Cd, Hg, and Pb) emission limits require equipment and operating conditions that are also needed for PCDD/PCDF control.

Acid gas sorbents may reduce PCDD/PCDF formation rates and allow for reductions in the PM control device operating temperature. The use of activated carbon for Hg control improves PCDD/PCDF control.

The 1995 EPA emission requirements for new and existing sources are summarized in Table 3. The rules have different requirements for new and existing plants, and for small (> 35 to 225 Mg/day) and large (> 225 Mg/day) plants. Emission limits are expressed either in mass concentration per dry standard cubic meter (dscm) or parts per million on a dry volumetric basis (ppmv), corrected to 7 percent O_2 and standard conditions at 20 °C (68 °F) and 101.3 kPa (14.7 psi).

The PCDD/PCDF limits are: 125 ng/dscm for small existing plants, 60 ng/dscm for large existing plants with ESP-based air pollution control systems, 30 ng/dscm for existing non-ESP-based systems, and 13 ng/dscm for large and small new plants.[6,7] Each MWC will be subject to annual PCDD/PCDF compliance tests unless they qualify for less frequent testing. MWC plants are allowed to conduct PCDD/PCDF performance tests on only one unit per year if all units achieve emission levels for 2 consecutive years of 30 ng/dscm for small existing plants, 15 ng/dscm for large existing plants, and 7 ng/dscm for all new plants.[6,7]

Although PCDD/PCDF emissions cannot be continuously monitored, operating and emission parameters which correlate with PCDD/PCDF emissions will be continuously monitored and controlled. These continuous compliance parameters include CO emission limits, boiler steam load, PM control device inlet temperature, and activated carbon hourly feed rates. Opacity and SO_2 are to be continuously monitored to guarantee proper operation of the flue gas cleaning equipment. The use of these continuous monitoring and compliance parameters will ensure that each MWC operates at conditions necessary to control emission of PCDDs/PCDFs, Hg, and other regulated pollutants.

DIOXIN AND MERCURY CONTROL METHODS

Control technologies in the U.S. for PM and acid gas control also provide a degree of control for PCDDs/PCDFs

TABLE 3. EMISSION LIMITS FOR MWCs[a]
(DECEMBER 1995)[8,9]

Pollutant/ Measurement	Guideline Limits - Existing Plants (or % Reduction)		NSPS Limits - New Plants (or % Reduction)
	Small >35 to 225 Mg/Day	Large >225 Mg/Day	Large and Small ≥35 Mg/day
ng/dscm [ ][b]	125 [30]	60[c][15]	13 [7]
PM,mg/dscm	69	27	15
Opacity[d], %	10	10	10
Cd, mg/dscm	0.10	0.04	0.01
Pb, mg/dscm	1.6	0.50	0.10
Hg, mg/dscm	0.08 (85)	0.08 (85)	0.08 (85)
HCl, ppmv	250 (50)	35 (95)	25 (95)
SO₂, ppmv[e]	80 (50)	35 (75)	30 (80)
NOₓ, ppmv[e]	None	200 -250[d,f]	150[d,g]

[a] All emissions corrected to 7 percent O_2.

[b] Average of three stack tests using EPA Method 23. Values are weight of total tetra- through octa- cogeners. Values in brackets for [emission limits to qualify for less frequent testing].

[c] Emission limit for ESP-based air pollution control systems. Non ESP-based systems must comply with a 30 ng/dscm limit or the "less frequent testing" requirement.

[d] EPA Method 9. Limit for 6-minute averages.

[e] 24-hour averaging time.

[f] 200 ppmv for MBWW, 250 ppmv for RWW, 250 ppmv for RDF, 240 ppmv for FBC, no NOₓ control requirement for MBRW, and 200 ppmv for others.

[g] Applies to large plants only. 150 ppmv, except 180 ppmv is allowed for the first year of operation.

and Hg. Both PCDDs/PCDFs and Hg may be in a vapor phase at flue gas temperatures, and collection of these pollutants is primarily dependent on sorption on fly ash particles or flue gas cleaning sorbent particles with subsequent collection in a PM control device. The capture efficiency of PCDDs/PCDFs and Hg in MWC air pollution control equipment typically used in the U. S. depends primarily on the amount and properties of carbon in the fly ash, the amounts and properties of sorbents injected into the flue gas, and the operating temperature of the PM control device.

Field tests have shown that in semi-dry scrubbing systems, PCDDs/PCDFs and Hg emissions decrease with increasing fly ash carbon content. Variations in combustion conditions affect the amounts of carbon in fly ash and its capacity for adsorbing semi-volatile trace organics and Hg. Increased combustion efficiencies needed to maximize destruction of organics reduce the absorption capacity of fly ash and its ability to capture semi-volatile pollutants in PM control devices. The formation and emission of PCDDs/PCDFs and emission of Hg are affected by the PM control device operating temperature as the sorption of semi-volatile pollutants is reduced with increasing operating temperatures.

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

Enhanced PCDDs/PCDFs control
- Good combustion practices,
- Injection of activated carbon, and
- Injection of specialized multipollutant sorbents.

Enhanced control of Hg
- Injection of sodium sulfide,
- Injection of activated carbon, and
- Injection of specialized multipollutant sorbents.

PCDD/PCDF FORMATION MECHANISMS

There are three primary routes for PCDD/PCDF formation: (1) gas-phase reactions involving chlorinated precursors such as chlorobenzenes (CBs), chlorophenols (CPs), or polychlorinated biphenyls (PCBs); (2) surface reactions involving gas-phase precursors and fly ash; and (3) solid-phase reactions on the surface of fly ash involving metal chlorides and fly ash carbon.[19-24] Formation route (3), which involves the reaction of unburned carbon in fly ash in the presence of oxygen and water vapor to form PCDDs/PCDFs, is called *de novo* synthesis.[20,21] The reactions associated with formation routes (2) and (3), which involve both gas- and solid-phase reactions, are called heterogeneous reactions.

Gas-phase precursors can originate as waste thermal decomposition products or as high temperature PICs. Low temperature oxidation reactions involving fly ash carbon can also produce CPs or other precursor compounds that in turn react to form PCDDs/PCDFs by surface mediated reactions (condensation, absorption-desorption, etc.).[25]

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.[26,27] The Cl for (oxy)-chlorination reactions can be provided from either metal chlorides in the fly ash or Cl in the flue gas.[27,28]

De *novo* synthesis reactions generate a variety of chloro-organic compounds including CPs, chloro-benzonitriles, -thiophenes, -benzofurans, -benzothiophenes, PCDDs, -naphthalenes, PCDFs, and -benzenes (see Figure 1).[23] Laboratory experiments (see Figure 2) show that *de novo* reactions occur at temperatures ranging from approximately 250 to 600°C with maximum tetra- to octa-PCDD formation rates near 300°C. Maximum tetra- to octa-PCDF formation rates also occur at 300°C with a lower peak near 450°C.[23] Maximum PCDD/PCDF formation rates are typically reported to occur near 300°C.[20-23] 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 emissions of PCDDs/PCDFs from MWCs have been found to range from < 1.0 to > 20,000 ng/dscm depending on combustion and flue gas cleaning conditions (see Figure 3).[29-32] 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
- Methods of acid gas and PM control.

Composition and Properties of Waste

Rapid changes in waste composition or properties may cause combustion upsets and lead to PCDD/PCDF formation. Although PCDDs/PCDFs are formed during steady state combustion conditions, the amounts formed are believed to increase substantially during combustion upsets associated with improper feed conditions. It is important to blend or mix waste prior to combustion to reduce variations in heating content, volatility, and moisture content.[16-18]

While waste composition probably affects the amounts of specific organics formed during combustion, there is no conclusive scientific evidence that specific solid waste components, such as polyvinyl chloride (PVC), are primarily responsible for the formation and emission of PCDDs/PCDFs.[32,33] Sufficient Cl is available from other waste components to account for observed levels of PCDDs/PCDFs in MWCs.

Combustion Conditions

PCDDs/PCDFs contained in the waste are believed to be destroyed in active flame zones or the high temperature regions of MWCs.[10,16] However, the waste composition and combustion conditions determine the availability of specific precursors needed for PCDD/PCDF formation. These precursor compounds are formed by the thermal destruction,
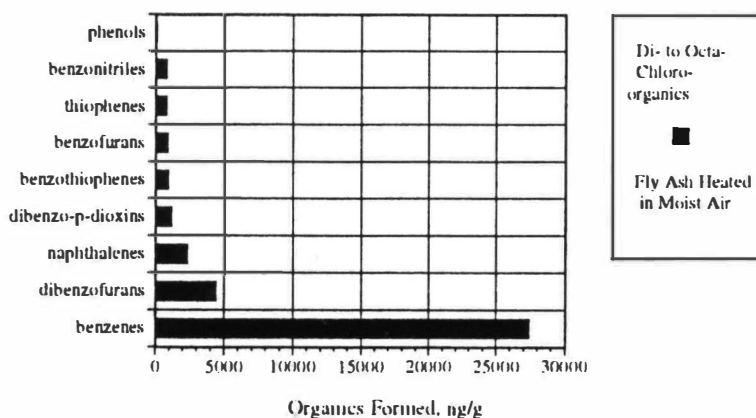

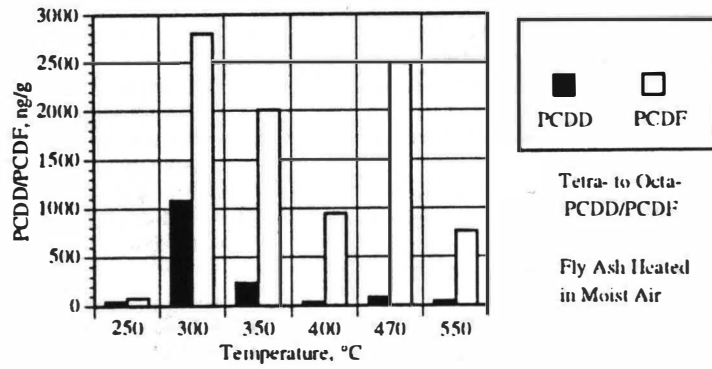FIGURE 1.   CHLORO-ORGANICS FORMED DURING *DE NOVO* SYNTHESIS

FIGURE 2. EFFECT OF TEMPERATURE ON *DE NOVO* FORMATION
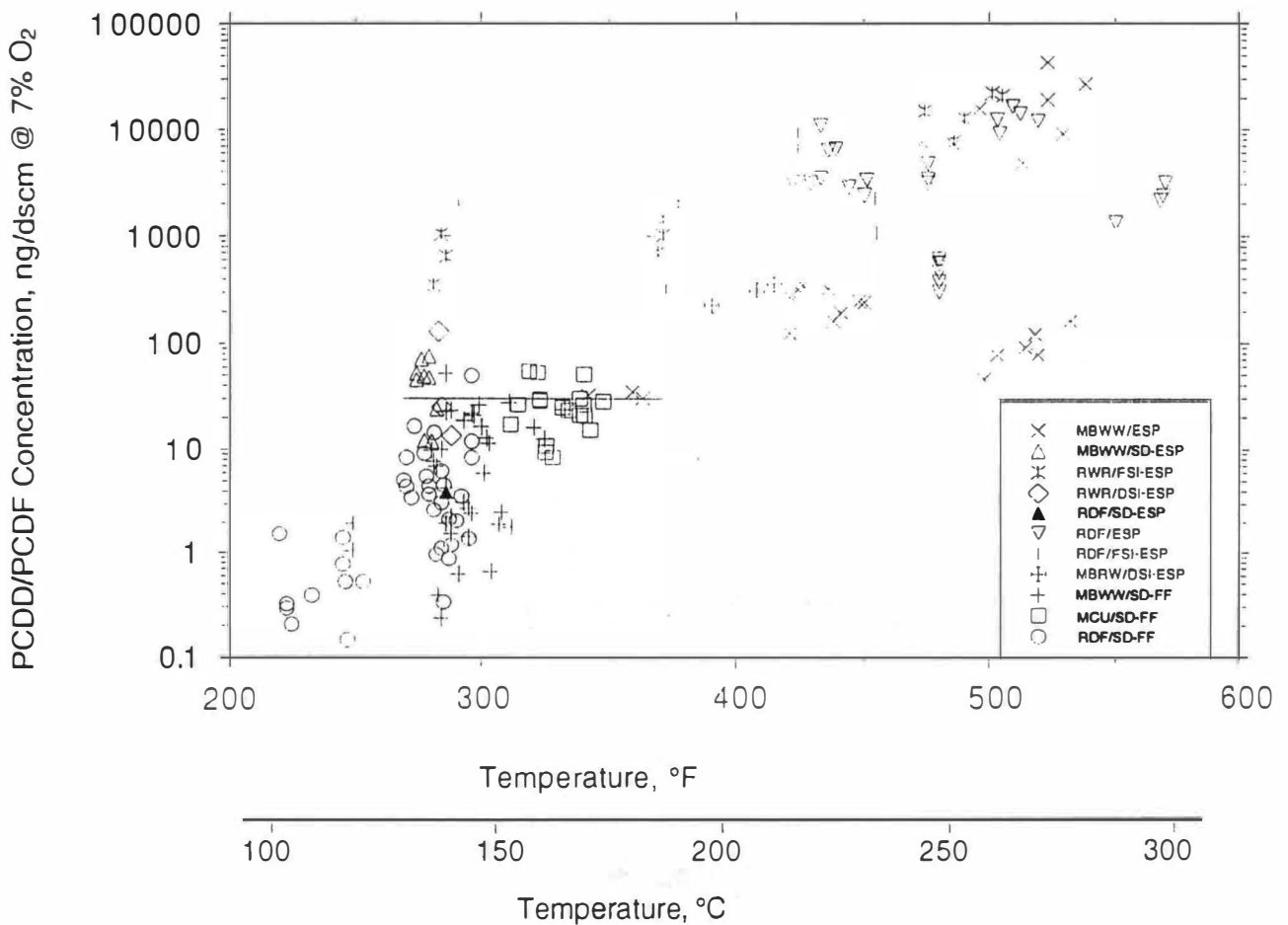RATES OF TETRA - TO OCTA - PCDD/PCDF

FIGURE 3.   DEPENDENCY OF PCDD/PCDF EMISSIONS ON TECHNOLOGY
AND PM CONTROL DEVICE OPERATING TEMPERATURE

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oxidation, and synthesis reactions which occur in the burning waste bed, the active flame region above the bed, and the high temperature regions of the furnace. Combustion conditions and the time/temperature profile in the cooling zones.downstream of the combustor determine the amounts of PCDDs/PCDFs precursor material entering flue gas cleaning devices and the potential for formation within the devices. Organics that have been implicated in PCDD/PCDF formation include: CBs, CPs, PCBs, and the carbon in fly ash.[25-28]

GCP can be used to maximize the furnace destruction of organics and minimize the downstream formation of PCDDs/PCDFs by controlling the amounts of PM carried out of the furnace with flue gas. Furnace destruction of organics must include destruction of both gas- and condensed-phase organics. Field test experiments have shown that formation of PCDD/PCDF and other trace organics correlates with the CO and the amounts of PM carried out of the combustor with flue gases (see Figures 4 and 5).[16,17,34-36] In extensive tests at a RDF combustor, CO and total hydrocarbons (THCs) were found to be the two best parameters for predicting PCDDs, PCDFs, CBs, CPs, and PAHs at the SD inlet.[36]

Waste and its associated thermal decomposition products must be exposed to elevated temperatures for a sufficient time to completely destroy their organic components. Time scales required for destruction are typically measured in milliseconds for gaseous compounds in active flame zones. Combustion reaction times in the order of seconds to minutes may be required for the complete destruction of small solid particles. Combustion temperatures and residence times of 980°C (1800°F) and 1 to 2 seconds, respectively, are generally believed sufficient to thermally destroy gas-phase compounds.[10] However, even at temperatures of 980°C or higher, residence times needed for the complete combustion of entrained solid particles may be insufficient, and residual unburned carbon in fly ash may lead to reactions which form PCDDs/PCDFs.[16]

The amount of air used for combustion must be high enough to minimize the existence of fuel-rich pockets and low enough to avoid quenching of combustion reactions.[10,16] The distribution of combustion air is also important. Burning refuse beds contain drying, devolatization, combustion, and burnout zones. Each zone requires a different amount of combustion air. State-of-the-art MWCs often use zoned underfire air supplies to provide proper air distribution to the refuse bed and overfire air to complete combustion of unburned material leaving the bed.[10]

Poor mixing increases the amount of organic material available for the formation of PCDDs/PCDFs. It may result in local stoichiometries that are insufficient for the complete oxidization of gas- and solid-phase organics. Poor mixing may also lead to the formation of difficult-to-destroy soot particles. Methods of achieving good mixing include the use of furnace configuration and overfire air jets.[10,16]

Composition of Flue Gas

The effects of flue gas composition on PCDDs/PCDFs are complex.[24,25] Oxygen is required for the low temperature carbon oxidation reactions that are associated with *de novo* synthesis. Oxygen and H_2O are also required for the Deacon process reaction which provides Cl for the chlorination of

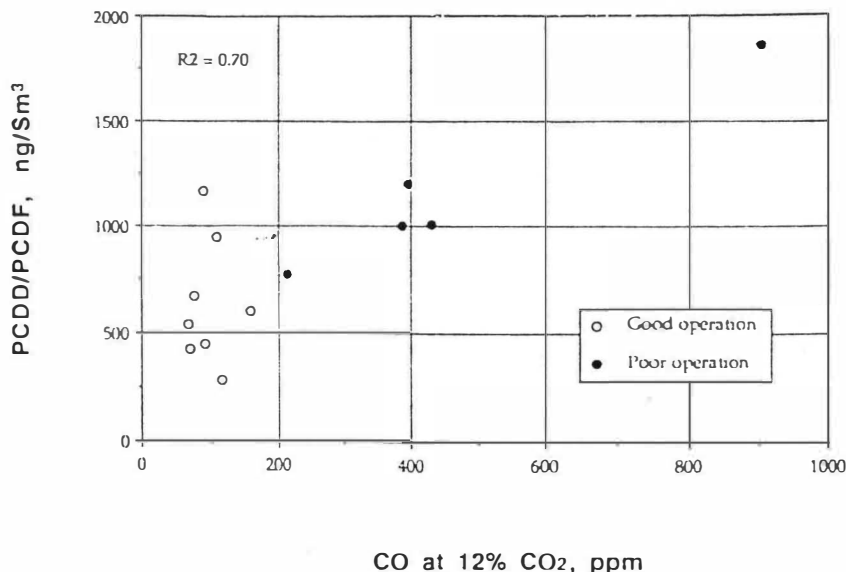CO at 12% CO_2, ppm

FIGURE 4.   RELATIONSHIP BETWEEN CO AND PCDD/PCDF CONCENTRATIONS AT SD INLET, MID-CONNECTICUT MWC
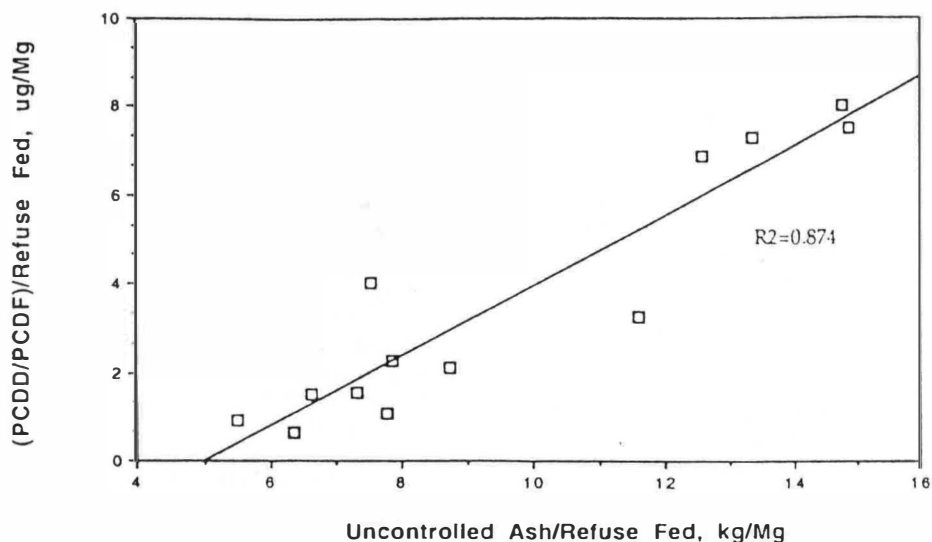
FIGURE 5.   RELATIONSHIP OF PM CARRYOVER TO PCDD/PCDF
EMISSIONS, QUEBEC CITY MWC

PCDDs/PCDFs or their precursor compounds. The Cl for the Deacon process reaction may come from either the inorganic chlorides in fly ash or the HCl in flue gas. Some bench and pilot scale experiments show that PCDD/PCDF formation increases with increasing levels of HCl or Cl_2 in combustion gases.[28,37] Although the flue gas concentrations of O_2 and H_2O may affect the rate of PCDD/PCDF formation, the waste moisture content and excess air levels determine the concentrations of these two constituents. The amount of excess air must be fixed at levels needed to obtain good combustion, and it is generally not practical to control the moisture content of wastes to the extent needed to control formation of PCDDs/PCDFs.

Entrained Particulate Matter

The entrainment and carryover of fly ash into the cooler regions of MWCs may lead to the formation of PCDDs/PCDFs and other trace organics. Metal ions or fly ash carbon can catalyze condensation formation reactions, and fly ash carbon can serve as the source of organics for the *de novo* synthesis of PCDDs/PCDFs. PM carryover is determined by the aerodynamic properties of particles, the method of waste combustion, and combustor gas flow characteristics. Methods of limiting PM carryover include proper furnace design, control of the underfire-to-overfire air ratio, the amount of excess air, and load (refuse burn rate).[16,18]

The correlation between PM carryover and PCDD/PCDF emission rates from tests at the Quebec City, Canada, mass burn combustor is shown in Figure 5.[34] These data, which are measured in the stack downstream of an ESP, show the effects of changing combustion conditions on emission of PCDDs/PCDFs. Changes in the PM carryover rate can be attributed primarily to changes in the flue gas flow rate and the ratio of underfire-to-overfire air. At higher loads,

increased gas flow rates increase entrainment and carryover of PM. Higher underfire air flow rates also increase PM entrainment. During the low combustion temperature tests at Quebec City, Canada, excess air rates were increased to lower the combustion temperature. This had the effect of increasing volumetric flow rates and particle entrainment. During the poor combustion air distribution tests, the underfire-to-overfire air ratio was increased, thereby increasing PM carryover. Increasing emission rates of PCDDs/PCDFs with increasing amounts of fly ash is consistent with heterogeneous formation theories.

Time/Temperature Profile

Pilot scale experiments have shown that the concentration of PCDDs/PCDFs in flue gas downstream of the furnace depends on the time/temperature profile in the cooling sections of combustion systems.[37-39] The time/temperature profile is determined by the time required by flue gas and suspended PM to pass through the heat extraction regions of boilers, superheaters, and economizers. High flue gas temperature quench rates reduce the time that gas-phase organics and entrained particles spend in the temperature range associated with high PCDD/PCDF formation rates.

PM Control Device Operating Temperature

ESPs and FFs can function as chemical reactors that generate and emit PCDDs/PCDFs.[40] A large fraction of the PCDDs/PCDFs entering PM control devices is commonly associated with collectible fly ash. However, the large mass of particles within the device can serve as a source for the synthesis of PCDDs/PCDFs. Limiting the temperature at which PM control devices are operated is important in controlling the formation and emission of PCDDs/PCDFs.[16-18,40,41]

The ESP operating temperature is perhaps the most important variable affecting the formation and emission of chloro-organics in ESP systems. At PM control device operating temperatures above 250°C, *de novo* synthesis reaction rates become significant and the partitioning of PCDDs/PCDFs into a vapor phase increases with increasing temperature.

The results of tests to evaluate the effects of ESP operating temperature on the formation and emission of PCDDs/PCDFs are depicted in Figure 6. These tests were conducted on a mass burn refractory MWC with a water spray flue gas quench chamber and an ESP located in Montgomery County, Ohio.[40] Quench water flow rates were adjusted to obtain nominal ESP inlet temperatures of 300 , 200 , and 150 °C. The test conditions included: normal and poor combustion (low temperature) tests at 300 °C inlet temperature; normal combustion with and without furnace injection of $CaCO_3$ at 200°C inlet temperature; and normal combustion with furnace injection of $CaCO_3$ and duct injection of $Ca(OH)_2$ at 150°C ESP inlet temperature.

The flue gas concentrations of PCDDs/PCDFs were higher at the ESP outlet than at the inlet for all tests, indicating PCDD/PCDF formation within the ESP. Under normal combustion conditions at the high ESP inlet temperature (300 °C), ESP inlet concentrations of PCDDs/PCDFs averaged 200 ng/dscm while stack concentrations averaged 17,000 ng/dscm. Reducing the ESP inlet temperature to 200°C without sorbent injection reduced average stack emissions to 870 ng/dscm. For tests with furnace injection of $CaCO_3$, stack emissions of PCDDs/PCDFs averaged 1480 ng/dscm at an ESP inlet temperature of 200°C and 670 ng/dscm at 150°C inlet temperature. The lowest emissions (57 ng/dscm) were

obtained using duct injection of $Ca(OH)_2$. Operating at the lowest practical ESP operating temperature is critically important in minimizing PCDD/PCDF emissions.

Methods of Acid Gas and PM Control

The methods of acid gas and PM control are major determinants of PCDD/PCDF emissions. Acid gas controls modify the chemistry of the PCDD/PCDF formation environment, affect flue gas quench rates, and allow operation of PM control devices at low temperatures. Low operating temperatures are necessary to minimize *de novo* synthesis rates and partitioning of trace organics between solid and vapor phases. Efficient collection of PM is necessary to collect solid-phase organics. Vapor-phase organics can be absorbed onto the surface of PM as it passes through the fly ash filter cake in FFs. DSI and SD can be used to reduce acid gases, modify PCDD/PCDF formation chemistry, and allow for lower PM control device operating temperatures.

Experiments in a 14.7 kW (63,000 Btu/hr) pilot scale combustor have shown that injection of $Ca(OH)_2$ into the flue gas at temperatures greater than 800°C significantly reduces the formation of PCDDs/PCDFs.[37] The reduction in PCDD/PCDF yield appears to result from both a reduction in the HCl content of flue gas and an inhibitory effect on fly ash surface reactions. DSI can also be used to remove HCl and reduce heterogeneous formation rates in the PM control device, but substantial amounts of PCDDs/PCDFs may be
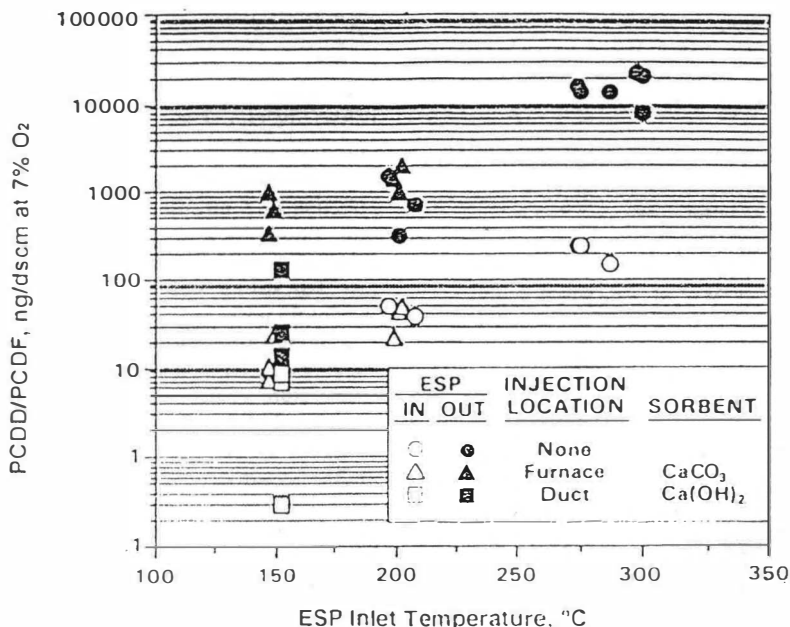

FIGURE 6.   EFFECT OF ESP INLET TEMPERATURE ON PCDD/PCDF FORMATION, MONTGOMERY COUNTY MWC

formed upstream of the sorbent injection locations near the inlet to the PM control device. Most of the PCDDs/PCDFs formed upstream will be retained in the PM control device if the PM control device operating temperatures are low enough. SD systems combine the advantages inherent in high flue gas quench rates, sorbents which probably modify PCDD/PCDF synthesis reactions, and low PM control device operating temperatures.

Flue gas concentrations of PCDDs/PCDFs can either decrease or increase across an ESP.[30] Increases are associated with high rates of PCDD/PCDF synthesis within a PM control device. PM control devices containing collected fly ash can function as reactors for formation of PCDDs/PCDFs.[40] The amount formed will depend on the temperature, the mass of PM within the control device, the composition of the fly ash, the composition of the flue gas, and the residence time of PM within the device. Maximum *de novo* synthesis reaction rates occur at temperatures near 300°C.[23] Lowering PM control device operating temperatures to less than 250°C results in low PCDD/PCDF formation rates and alters the partitioning of vapor- and solid-phase PCDDs/PCDFs. In ESPs, operating temperature is critical, and it may be necessary to scrub acid gases from the flue gas to permit lowering of the PM control device operating temperature to a level where acid gas corrosion of the device is not a problem.

PM control device collection efficiencies >99 percent are probably necessary to adequately control PCDD/PCDF emissions. At the lower PM control inlet device temperatures typically employed by dry scrubbing systems, formation rates are greatly reduced and PCDDs/PCDFs are predominantly retained on captured fly ash. Although substantial quantities of trace organics may be formed during the combustion process, most of the semi-volatile organics are effectively collected in dry scrubbing systems. This is especially true of SD/FF systems.

MWCs equipped with SD/ESP systems are less effective in controlling PCDD/PCDF emissions than similar MWCs equipped with SD/FF.[30,42] The latter devices often have better PM control efficiencies, and the flue gas is passed through a filter cake where PCDDs/PCDFs can be absorbed on fly ash and sorbent particles. A review of data from eight different combustion units equipped with SD/ESPs indicated PCDD/PCDF emissions ranging from 9 to 173 ng/dscm (mass). All but one of these units had emissions of less than 75 ng/dscm, and the average for the range of typical emissions was 38.1 ng/dscm.[42]

The performance of SD/ESP systems for controlling PCDDs/PCDFs in mass burn MWCs can also be improved by the injection of activated carbon into the flue gas at the entrance to the SD system or by use of a carbon-enhanced lime-based sorbent in place of lime.[43-45] During three EPA-sponsored tests at the Camden County, New Jersey, MWC, stack concentrations of PCDDs/PCDFs without activated carbon averaged 46.8 ng/dscm. During three tests in which 360 mg/dscm of dry activated carbon was injected into the flue gas upstream of the SD/ESP, stack concentration of PCDD/PCDF averaged 5.6 ng/dscm.[44,45] Tests in Europe on MWCs equipped with SD/FF and SD/ESP systems have also shown the effectiveness of carbon injection for reducing PCDD/PCDF emissions.[43]

An EPA review of data from 20 different combustion units equipped with SD/FF systems indicated PCDD/PCDF emissions ranging from 1 to 22 ng/dscm. Nineteen units had emissions <12 ng/dscm, and the average for these units was 6.6 ng/dscm. Two large MWCs with DSI/FF systems had PCDD/PCDF emissions of 5 and 18 ng/dscm.[42]

CONTINUOUS CONTROL OF PCDDs/PCDFs

There is currently no feasible method for continuously measuring PCDD/PCDF emissions. Continuous control of PCDDs/PCDFs is of concern from regulatory and risk assessment perspectives. EPA's strategy to ensure continuous compliance with PCDD/PCDF emission limits is to place limits on CO concentrations, steam load, PM control device operating temperature, carbon feed rate, and opacity. The first four parameters are used to limit formation and partitioning of PCDDs/PCDFs, and the final parameter (opacity) will ensure proper operation of the PM control device which is needed for effective collection of solid-phase PCDDs/PCDFs. The effectiveness of these parameters for continuously controlling PCDD/PCDF emissions is verified by periodic compliance tests on each MWC that is subject to regulation.

CONTROL OF OTHER ORGANICS

Field test measurements show that a wide variety of trace organics are formed during combustion of municipal solid waste. Trace organics formed include semi-volatile organics such as PCDDs/PCDFs, CBs, CPs, PCBs, PAHs, and a variety of volatile organics. Analysis of data from the Quebec City MWC mass burn tests and the Mid-Connecticut RDF combustor tests show that flue gas concentrations of PCDDs/PCDFs, CBs, CPs, and PAHs all correlate with each other and with flue gas concentrations of CO and THC.[30,36] Measures taken to control emission of PCDDs/PCDFs are also effective in controlling CBs, CPs, and PAHs. (It is expected that these measures will also control PCBs, but the concentrations of PCBs in MWC flue gases are generally so low that strong statistical correlations with other pollutants are not found.)

Combustion controls are effective in controlling all trace organics. Dry and semi-dry scrubbers with FFs and temperature control are effective in controlling semi-volatile organics, but the degree of control is probably related to the amounts of carbon in the fly ash. Activated carbon or multipollutant sorbent containing calcium and carbon (lime enhanced sorbents) should also enhance capture of all semi-volatile organics in MWCs equipped with dry and semi-dry scrubbing systems. Dry and semi-dry scrubbing systems are probably not effective for controlling volatile organics, and the best method for controlling these pollutants is the use of GCP as a preventive measure.

MERCURY CONTROL AT MWCs

The capture of Hg in flue gas cleaning devices depends on the

- Waste composition,
- Flue gas properties (temperature, gas composition, moisture, etc.),
- Hg form [speciation and phase (vapor or solid)],
- Fly ash and sorbent properties, and
- Type of control device.

The waste composition and the relative amounts of Hg in each component determine the concentration of Hg in MWC flue gas. Hg mass balances from Environment Canada's Quebec City mass burn test project indicated that more than 96 percent of Hg in the MWC output streams was in either the collected ESP ash or the flue gas, indicating the volatile nature of Hg in MSW.[34]

MERCURY SPECIATION AND CONTROL MECHANISMS

The form of Hg in flue gas depends on the flue gas composition and temperature. Thermal-chemical calculations indicate that Hg is converted to elemental mercury (Hg°) in the high temperature regions of the combustor. As the flue gas cools, some or all of the Hg° is converted to other Hg species.[46,47] 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 Hg°.[46-49] Thermochemical equilibrium calculations indicate that the Hg^{2+} will be predominantly mercuric chloride ($HgCl_2$).[49]

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 (300 to 140°C), and special methods must be devised for their capture.[12,13]

Hg in MWC flue gases can be captured if it is in the solid phase [Hg(s)] or is adsorbed 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 and properties of carbon in the fly ash. Well-designed and well-operated mass burn combustors have little carbon in their fly ash and, even when equipped with SD/FFs or SD/ESPs, they often exhibit Hg control levels below 50 percent. Conversely, RDF combustors contain relatively high amounts of carbon in the fly ash (> 2 percent). And, they can exhibit control efficiencies above 80 and 90 percent when equipped with SD/ESPs and SD/FFs, respectively. Figure 7 shows the distribution of Hg stack concentrations for RDF and non-RDF MWCs equipped with SD/FF and SD/ESP systems.[42]

Two techniques employed for Hg capture in dry flue gas cleaning systems are the use of activated carbon and sodium sulfide (Na_2S).[12,13] Na_2S, a crystalline solid, is dissolved in water and injected upstream of the flue gas cleaning equipment. Hg°(v) and Hg^{2+}(v) are converted to a solid form of Hg [mercury sulfide (HgS)] that can be collected in a PM control device. Na_2S has been used at MWC facilities in Europe and Canada for Hg control. Na_2S test results from European facilities show Hg emissions ranging from 40 to 70 μg/dscm and removal efficiencies from 65 to 90 percent.[10] Na_2S is not currently being used in the U.S. Activated carbon can be used in three ways to control Hg(v) emissions: (1) it can be injected as a powder in dry or semi-dry scrubbers to
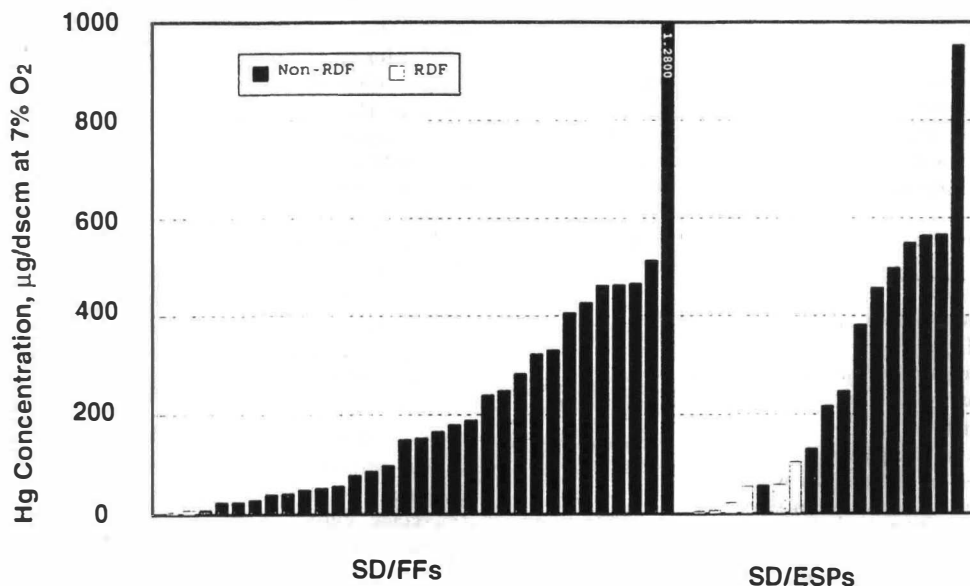
FIGURE 7.   HG CAPTURE IN MWCS WITH SD/FFS AND SD/ESPS, LARGE PLANTS (>225 MG/D)

absorb Hg(v) for subsequent collection in an ESP or FF.[12,13] (2) it can be used in a sorbent system combining both lime and carbon in a single multipollutant sorbent,[50] and (3) flue gas can be filtered through a carbon bed polishing filter downstream of other air pollution control devices to enhance removal of Hg(v) and other pollutants.[51] Carbon bed filters are currently being applied to European MWCs where they are primarily used to improve emission control of PCDDs/PCDFs, Hg, and other trace metals.[51]

CARBON CAPTURE MECHANISMS

The adsorption of Hg and organics by activated carbon 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 because of intermolecular 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 is not known in detail, but it is believed to contain randomly distributed pores in the carbon, between which lies a complex network of irregularly, interconnected passages. Pores range in diameter down to a few angstroms, and provide an internal surface area from 300 to 1,000 m^2/g 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. Another important factor is the pore radius. Bench scale tests have shown that increasing the surface area and adding sulfur compounds to the sorbent result in higher adsorption rates of some Hg species. Until recently, most of the laboratory work on carbon adsorption has been done on Hg°, not with the Hg compounds normally found in MWC flue gas.

The actual adsorption capacity of carbon is affected by:

- Gas temperature,
- Inlet concentrations of Hg,
- Species of Hg,
- Type of carbon and surface area,
- Contact time,
- Flue gas moisture,
- Acid content of flue gas, and
- Concentration of compounds which compete with Hg for sorption sites .

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 been limited primarily to the application of carbon injection to mass burn MWCs equipped with SD/FF or SD/ESP systems.[13,42,43,52]

EPA has sponsored two major field tests on the injection of powdered activated carbon for Hg control and has selected this technology as the basis for Hg emission control requirements on MWCs.[44,45,52-54] Both tests were conducted at facilities with conventional mass-burn waterwall combustors. 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 and properties 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 concentrations are low, stack emissions of Hg are low.

Powdered activated carbon can be injected into the flue gas to increase solid-phase carbon concentrations and improve Hg capture. 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 gas. 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 percent. 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 (see Figure 8).[52-54] SD outlet temperatures at Stanislaus County normally ranged between 136 and 145 °C.

During the Camden County SD/ESP carbon injection test project, Hg capture without carbon injection ranged from 18 to 92 percent.[44,45] 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 (see Figure 9). The dependency of Hg reduction efficiency on the total solid carbon concentration in the flue gas during the Camden County tests is shown in Figure 10.
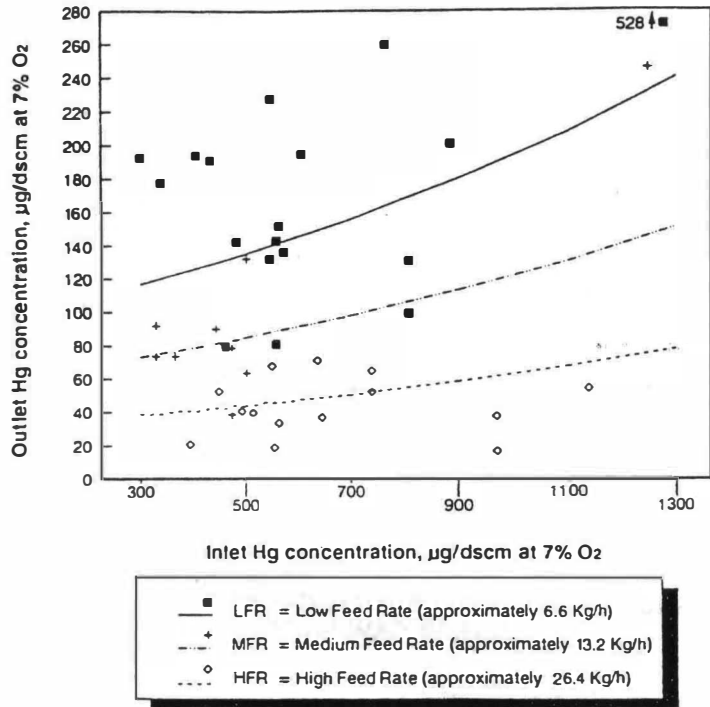
FIGURE 8.   PERFORMANCE OF ACTIVATED CARBON IN SD/FF
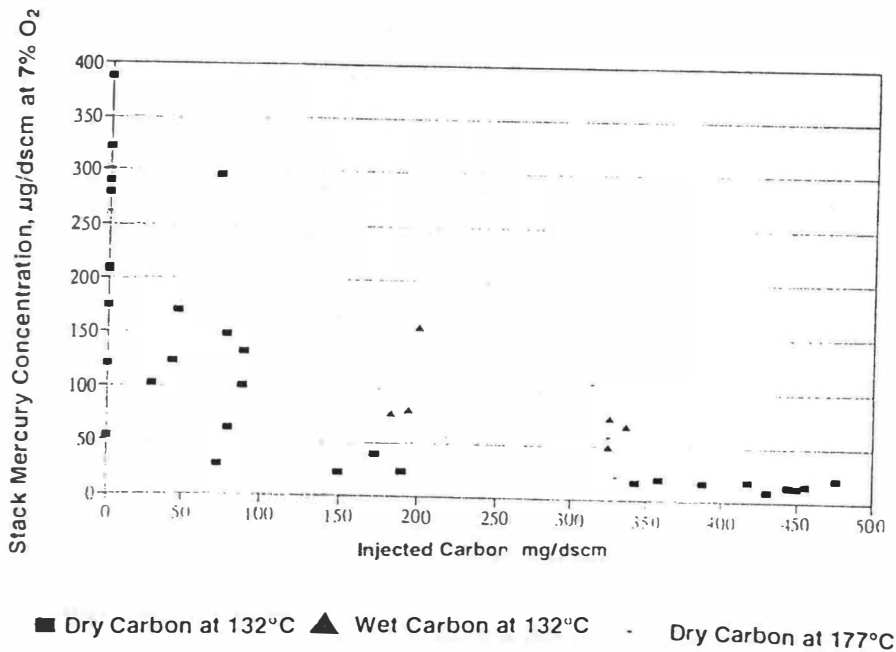   SYSTEM, STANISLAUS COUNTY MWC

FIGURE 9.   EFFECT OF INJECTED CARBON ON MERCURY CONTROL
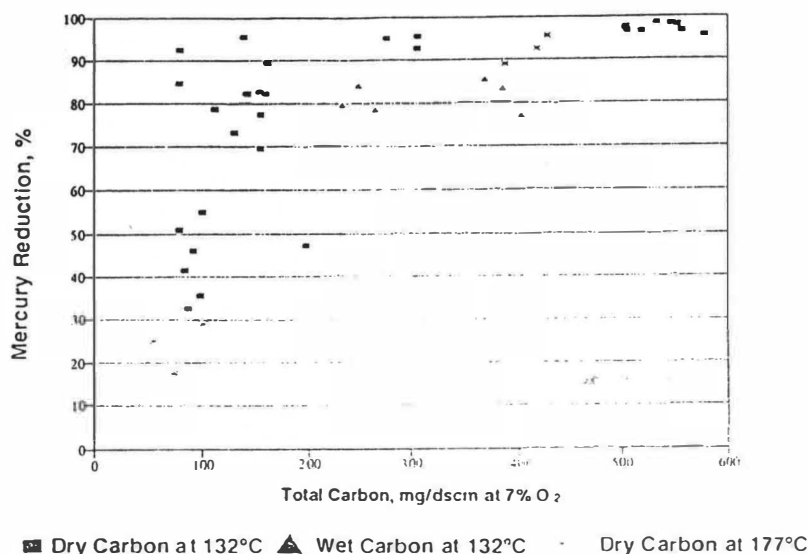   IN SD/ESP, CAMDEN COUNTY MWC

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Figure axis labels: Mercury Reduction, % (vertical); Total Carbon, mg/dscm at 7% O_2 (horizontal)

■ Dry Carbon at 132°C   ▲ Wet Carbon at 132°C   · Dry Carbon at 177°C

FIGURE 10.   EFFECT OF TOTAL CARBON ON MERCURY CONTROL
IN SD/ESP, CAMDEN COUNTRY MWC

The performance of activated carbon in adsorbing 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 adsorbed 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 (see Figure 10).[44,45] 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.[43]

ESPs and wet scrubbers are commonly used to control emissions from European MWCs. Some European plants have installed activated carbon beds downstream of the primary air pollution control devices to act as polishing filters for the control of metals, dioxins, and acid gases. The use of activated carbon filter beds in combination with conventional control equipment has demonstrated Hg reductions exceeding 99 percent and Hg outlet concentrations of less than 1 μg/dscm.[51]

PERFORMANCE OF ENHANCED LIME-BASED SORBENTS

Several enhanced lime-based sorbents are commercially available for use in MWCs. One enhanced sorbent (Scansorb) is designed for improved HCl and SO_2 control in dry injection systems.[55] Another sorbent (Sorbalit) is a multipollutant sorbent designed for control of acid gases, Hg, and trace organics.[50] Sorbalit is produced by mixing lime, surface-activated carbon, a sulfur-based compound, and other additives. The Sorbalit carbon content can range from 4 to 65 percent depending on the technical and economic requirements of each project.

Comparative performance tests between Sorbalit and a typical activated carbon on a mass-burn MWC equipped with an SD/FF system have indicated equivalent or slightly higher capture of Hg by the enhanced lime-based sorbent.[50] The lime-based sorbent captured 87.7 percent of the total Hg, while the conventional activated carbon captured 84.2 percent. Analysis of the sampling train data indicated that it captured 83.2 percent of the vapor-phase Hg, while the conventional carbon captured 77.6 percent. Additional performance testing is being planned to evaluate the effectiveness of Sorbalit in controlling emissions from MWCs with other flue gas cleaning equipment configurations.

FORM OF MERCURY EMISSIONS

In conducting risk assessments, it is important to estimate the form and speciation of Hg stack emissions. The transport, deposition, and environmental uptake of Hg are dependent on the form and speciation of Hg. Several studies estimate the speciation of Hg in MWC flue gases. Metzger and Braun estimate that nearly all Hg in MWCs at flue gas cleaning temperatures is in the form of mercury chlorides.[49] Lindqvist and Schager estimate that the speciation of Hg in raw flue gases is approximately 20 percent Hg°, 60 percent Hg^{2+}, and 20 percent Hg(s).[48] Pacyna estimates that Hg emissions from European waste incinerators consist of 10 percent Hg°, 85 percent Hg^{2+}, and 5 percent Hg(s).[56]

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There is currently no validated U.S. method for determining the speciation of Hg in stack gas. However, information on the chemical behavior of Hg and the distribution of Hg in EPA's multimetal sampling train (Method 29) can be used to estimate the form and speciation of Hg in the MWC stack gas. These estimations are valid only for measurements downstream of the air pollution control devices. The phase and speciation of Hg at inlet sample locations can be significantly affected by PM collected in the Method 29 probe and filter. For outlet samples, Hg found in the probe and filter can be assumed to have been either vapor-phase Hg adsorbed onto PM or a solid-phase Hg compound. Both are associated with PM as designated by Hg(PM). $HgCl_2$ is soluble in water and should be removed in the nitric acid/peroxide (HNO_3/H_2O_2) impingers. Hg found in the downstream permangenate/sulfuric acid $(KMnO_4/H_2SO_4)$ impingers was probably Hg°(v). The distribution of multimetal train samples collected during the activated carbon injection tests at the Camden County MWC and Stanislaus County tests is shown in Figure 11.[44,45]

For the Camden and Stanislaus County tests, the fraction of Hg(PM) was generally below 5 percent and exceeded 10 percent for only one test. Tests with stack concentrations of Hg >100 µg/dscm represent tests without carbon injection or low carbon injection feed rates. For these tests, Hg° ranges from 2 to 26 percent of total Hg. As carbon injection rates and Hg capture increase, the percentage of Hg° as a fraction of total Hg increases. This implies that Hg^{2+} is more easily captured by activated carbon than Hg°. For stack concentrations of Hg <50 µg/dscm, the fraction of Hg° ranges from approximately 14 to 72 percent.

From the results of these tests it can generally be concluded that, for MWCs equipped with SD/ESPs and SD/FFs, the stack emission of Hg(PM) is negligible unless further Hg is absorbed on the surface of PM between the stack sampling location and the stack exit.

At low levels of control, the stack concentration of Hg is probably 15 to 30 percent Hg°(v) and the rest is Hg^{2+}(v) and Hg(PM). In MWCs with SD/FF or SD/ESP systems, stack concentrations of Hg(PM) are probably less than 5 percent. At high levels of control, Hg^{2+}(v) is selectively removed, increasing the relative concentration of Hg° (v). The relative concentration of Hg (v) may be 50 percent or higher.

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.

Spray dryers and FFs can be used to continuously reduce PCDD/PCDF emissions to less than 20 ng/dscm. Activated carbon, which is 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, to control Hg emissions, can be used to further reduce PCDD/PCDF emissions to 60 ng/dscm or less.
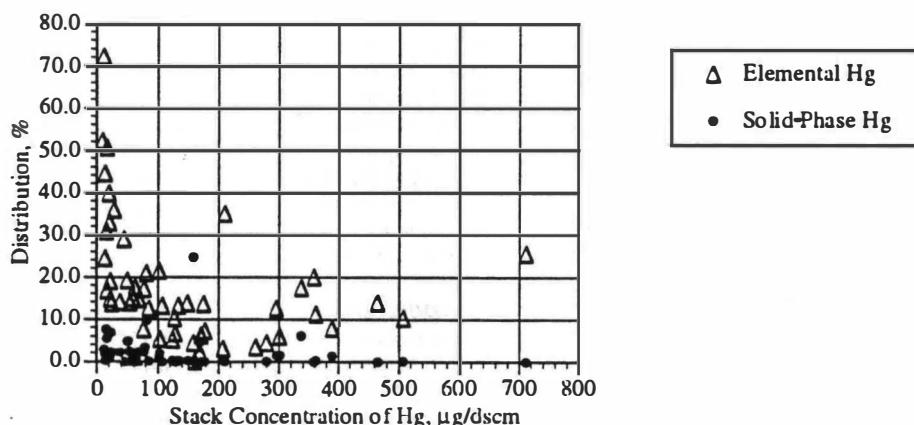

FIGURE 11.   DISTRIBUTION OF Hg IN EPA METHOD 29 SAMPLING TRAIN, CAMDEN COUNTY AND STANISLAUS COUNTY CARBON INJECTION PROJECTS

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°. Both are predicted to be in a vapor phase at stack gas temperatures.

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 adsorbed either on the residual carbon in fly ash, on activated carbon, or on enhanced lime-based sorbents which have been injected into the flue gas.

RDF combustors have relatively high amounts of carbon in their fly ash (>2 percent), and those equipped with SD/FFs may attain Hg removal efficiencies of >90 percent due to adsorption of Hg(v) onto the fly ash carbon. Other types of MWCs, such as mass-burn water-wall 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. Method 29 sampling train data suggest that carbon absorption methods collect Hg^{2+}(v) more efficiently than Hg°(v). As Hg removal efficiencies increase, $HgCl_2$ (v) is preferentially removed and the proportion of Hg that is Hg°(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 percent.

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