



Research and Development

PROCEEDINGS: 1991
INTERNATIONAL CONFERENCE ON
MUNICIPAL WASTE COMBUSTION
Volume 3. Sessions 1C, 2C, 3C, 4C, 6C,
7C, 8C, 9A, and 10A/C

Prepared for

Office of Environmental Engineering
and Technology Demonstration

Prepared by

Air and Energy Engineering Research
Laboratory
Research Triangle Park NC 27711

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EPA-600/R-92-209c
November 1992

PROCEEDINGS:
1991 INTERNATIONAL CONFERENCE ON MUNICIPAL WASTE COMBUSTION

VOLUME 3. Sessions 1C, 2C, 3C, 4C, 6C, 7C, 8C, 9A, 10A, and 10C

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Prepared for:

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PREFACE

The Second International Conference on Municipal Waste Combustion (MWC), held in Tampa, Florida during April 16-19, 1991, was sponsored by the Air and Energy Engineering Research Laboratory and the Risk Reduction Engineering Laboratory of the United States Environmental Protection Agency and the Air and Waste Management Association. The American Society of Mechanical Engineers and Environment Canada were participating organizations.

The Conference program provided an opportunity for exchange of current research developments on MWC and ash disposal as well as unit operating experience. The topics discussed included overviews on MWC in the United States, Canada, and Europe; MWC processes; dry/wet flue gas cleaning experience; ash characterization, treatment, utilization, and disposal; chlorinated dioxin/furan control; novel flue gas cleaning technology; environmental compliance; risk and quality control/quality assurance; municipal waste management; mercury emission control; sampling and analysis; economic and social issues; and regulatory effects.

Conference authors came from Australia, Belgium, Bermuda, Canada, Denmark, Finland, Germany, Italy, Japan, Norway, Sweden, Taiwan, The Netherlands, the United Kingdom, and the United States of America. Panelists related U.S. environmental compliance requirements and MWC plant operation in Session 5 and discussed the international outlook for environmental regulation in the Conference's concluding session, Session 11. Records of the panel discussions are not included in these proceedings. The 82 presentations made in the three concurrent sessions were complemented by the keynote address and international overviews, all of which are contained in these proceedings.

The proceedings have been compiled in three volumes with papers on combustion, ash, and flue gas cleaning grouped separately in different volumes. Papers on related topics have been included in each volume, subject to limiting each volume to approximately the same size. The papers are listed according to sessions in which presented, and the sessions contained in each volume are presented below.

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- Session P: Opening Plenary Session
- Session 0: International Overviews
- Session 1A: Combustion I
- Session 2A: Combustion II
- Session 3A: Combustion III
- Session 4A: Fuel Cleaning
- Sessions 6A/6B: Environmental Effects/Risk and Quality Assurance/Quality Control
- Session 9C: MSW Characteristics and Downstream Effects
- Session 10B: Regulatory Effects

Volume 2 contains papers presented in the following sessions:

- Session 1B: Ash Characterization
- Session 2B: Ash Treatment/Utilization I
- Session 3B: Ash Disposal I
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- Sessions 7A/7B: Municipal Waste Management I/Ash Treatment/Utilization II
- Sessions 8A/8B: Municipal Waste Management II/Ash Leaching
- Session 9B: Economic and Social Issues

Volume 3 contains papers presented in the following sessions:

- Session 1C: Recent Flue Gas Cleaning Experience I
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- Session 3C: Wet and Dry Flue Gas Cleaning Experience
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- Session 5 - Impact of Plant Operation on Environmental Compliance

Moderator: Charles O. Velzy, Roy F. Weston, Inc., Valhalla, NY

Panelists: David S. Beachler, Westinghouse Electric Corporation,
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Francis A. Ferraro, Wheelabrator Technologies, Inc.,
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Gary Pierce, ABB Resource Recovery Systems,
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David B. Sussman, Ogden Martin Systems, Inc., Alexandria, VA

- Session 11 - Outlook for Environmental Regulation

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Panelists: A.G. Buekens, Free University of Brussels, Brussels, Belgium
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The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

OVERVIEW OF AIR POLLUTION CONTROLS FOR MUNICIPAL WASTE COMBUSTORS

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ABSTRACT

The growth in incineration of municipal solid waste has lead to concerns of potential harmful emissions of acid gases, heavy metal and toxic trace organic compounds into the environment. This has lead to the promulgations of emissions control limits in many countries in Europe, the United States and Japan.

Several different technologies are currently available and new approaches are emerging for improved control of specific pollutants of concern. Technology transfer is such that a successful application of a new technology anywhere in the world may rapidly lead to applications throughout the world.

This paper presents an overview of technologies being applied to MWC's for the control of NO_x, acid gases, particulate matter, heavy metals and toxic trace organic compounds (PCDD's/PCDF's). The technologies presented are reviewed as to their state of development and control efficiencies.

INTRODUCTION

Environmentally sound disposal of municipal and industrial refuse has become a major issue in the past decade. The volume of waste generated has continued to grow annually and traditional disposal methods (land filling or ocean dumping) are becoming less acceptable because of cost and environmental concerns. Incineration of refuse in modern high efficiency combustors is being employed to a growing fraction of the waste stream to achieve significant reduction in refuse volume while in many instances achieving energy recovery in the form of steam or electricity. This increase in incineration has been coupled with an increase in the complexity and efficiency of air pollution controls to limit incinerator emissions. This paper presents a discussion of the air pollution controls applied to municipal waste combustors.

REFUSE INCINERATION

Refuse or municipal solid waste includes non hazardous waste generated in households, institutions, (excluding hospital wastes) commercial and light industrial facilities, agricultural wastes and sewage sludge. In 1988 the United States generated approximately 180 thousand tons of refuse.⁽¹⁾

The refuse per capita generation rate in the U.S. is the highest in the world and has shown an annual growth over the past several decades. Because of this continual refuse growth, environmental concerns with land filling or ocean dumping and the lack of availability and cost of landfills, the public has began looking into alternate ways to handle its refuse. This has included composting, recycling and incineration. Of these three alternatives, incineration has shown the ability to achieve the greatest reduction in refuse volume (70 - 90%) and can be used in conjunction with the other two alternates to achieve even greater reduction in disposal volume. Incineration is currently being used to treat about 15% of the refuse stream with this percentage expected to increase to 25-30 % by 1995.⁽²⁾

This increase in refuse incineration has lead to increased concern over air pollution from these incinerators, which in turn has lead to the promulgation of air emissions standards and the application of modern air pollution controls to limit these emissions. The U.S. Environmental Protection Agency in response to the public's concerns issued "New Source Performance Standards and Emissions Guidelines for Existing Facilities" in February 1991. Table 1 summarizes these proposed standards and guidelines.

Table 1. Municipal Waste Combustion Emission Standards.⁽³⁾

	New Source Performance Standards	Emission Guidelines For Existing Facilities	
Capacity-Tons/day	<u>Unit</u>	<u>Unit</u>	<u>Facility</u>
	>250	>250 ≤ 2200	>2200
Particulate Matter-(gr/dscf)	0.015	0.030	0.015
Opacity-%	10	10	10
Organic Emissions-ng/dscm Total Chlorinated PCDD Plus PCDF			
-Mass burn units	30	125	60
-RDF fired units	30	250	60
Acid Gas Control % Reduction or Emissions-(ppm)			
HCl	95 (25)	50 (25)	90 (25)
SO ₂	80 (30)	50 (30)	70 (30)
NO _x	(180)	None	None
Carbon Monoxide, ppm	50-150*	50-250*	50-250*

^o All emissions limits are referenced to dry gas conditions at 7% oxygen concentration.

^{*} Range of values reflect differing types of MWC's

In proposing these standards, the EPA recognized differences in facility size, the type of incineration (mass burn fired versus refuse derived fuel fired) and new sources versus existing sources. The facility capacity refers to the total burn rate for all refuse combustors at a single site. EPA selected total particulate matter emissions limits as the way of controlling trace heavy metal emissions limits. EPA will add emission limits for mercury, cadmium and lead emissions in the coming year.

Emissions limits are established for the total emissions of the poly-chlorinated dibenzyl-dioxins (PCDD) plus polychlorinated dibenzyl-furans (PCDF). These compounds were selected as surrogates for organic emissions because of their potential adverse health effects. In addition EPA has established carbon monoxide (CO) emission limits as a measure of good combustion practices which limit the formation of PCDD, PCDF and their key precursors. The proposed CO limits vary from 50 to 250 ppm (@ 7%O₂ dry gas conditions) depending on the type of combustion.

Acid gas emissions (HCl and SO₂) are based on either a percent reduction or a maximum stack emission level whichever is the least stringent. Nitrogen Oxides (NO_x) emissions levels are proposed only for large new sources.

of MWC facility operating supervisors and site specific training for operating personnel.

In addition to EPA standards, many states and local air pollution control districts have developed their own sets of emission standards for new sources. Many of these standards (or permit conditions) are more stringent than the proposed EPA standards.

INCINERATION SOURCES

Several different technologies are employed in refuse combustion. These include mass burn combustors (modular, traveling grate and rotary combustors) refuse derived fuel-fired combustors and to a lesser extent fluid-bed combustors.

MASS BURN COMBUSTORS

Mass burn combustors are the predominant type of incinerators currently being employed for refuse. These are characterized by accepting refuse which has undergone very limited preprocessing other than removal of large oversized items. Mass burn combustors may be of the modular (or starved air) type, the traveling grate type or the rotary combustor type. Figure 1 shows a cutaway view of a traveling grate mass burn incinerator.

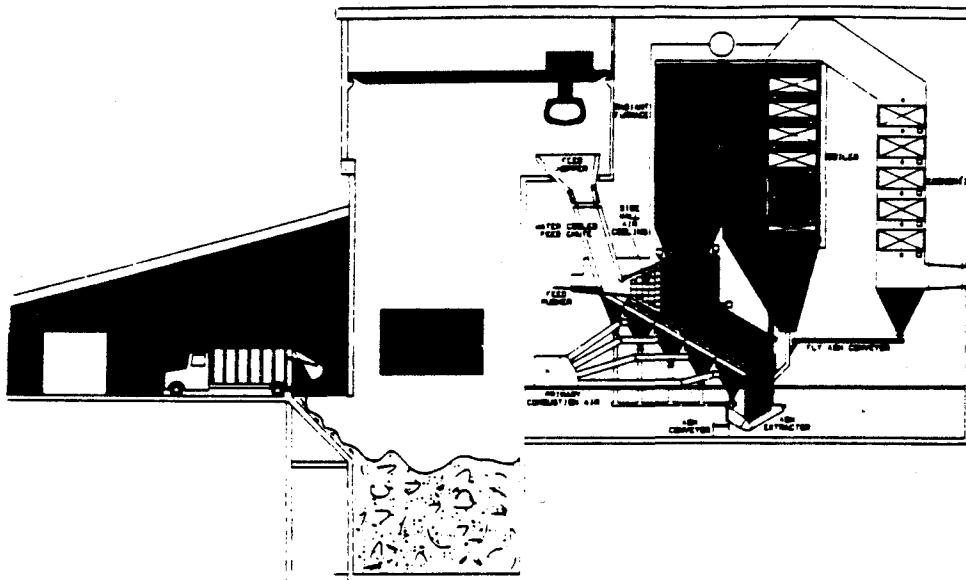


Figure 1. - Mass Burn Incinerator.⁽⁴⁾
(Courtesy - Joy Technologies Inc.)

Typically, refuse is dumped into a tipping bay where it is mixed and oversize objects are removed by an overhead crane. The overhead crane dumps the mixed refuse into a feed chute where it is fed into the grate system by a hydraulic ram. The traveling grates move the refuse through the various zones of the combustion chamber in a tumbling motion. Air is added at multiple points through the grate to assist in refuse dry out, combustion and burnout. Additional combustion air may be added above the grate to assist in flue gas mixing and complete combustion.

Residual ash falls from the grate into a wet quench system and then is removed and sent to a landfill. Flue gases pass upward to a burnout zone where the temperature is maintained at about 1800°F for 1 to 2 seconds to ensure complete destruction of organic compounds. The flue gas then passes through the boiler and economizer where its temperature is reduced to 350 - 450°F prior to entering the flue gas cleaning system.

REFUSE DERIVED FUEL (RDF) COMBUSTORS

RDF fired combustors are designed to burn a fuel which has been pre-processed to produce a fuel with a more uniform size, composition and heat rate. A variety of combustor designs can be employed with RDF depending on the degree of preprocessing. The simplest form and most commonly employed method of RDF processing is shredding of refuse followed by magnetic separation, to remove ferris metals, and in some cases air classification to remove ash. This type of fuel is often burned in a spreader stoker combustor or suspension fired over a stoker.

The RDF may be further processed to produce; a densified fuel, by pelletizing; a recovery prepared RDF in which a larger portion of metals and glass are removed; or a fluff RDF for co-firing with coal in suspension fired combustors.

RDF combustors range in size from approximately 400 to 1000 TPD capacity. Because of the nature of the fuel and firing, particulate matter carry over to the air pollution control system is generally much higher than for a mass burn combustor.

EMISSIONS CHARACTERIZATION

Refuse incineration has the potential of emitting a wide range of pollutants to the environment. These potential emissions arise from compounds present in the refuse stream, are formed as a part of the normal combustion process, or are formed due to incomplete combustion. Table 2 lists principal potential MWC emissions and the prime source for each.

Table 2. Principal MWC Emissions and Sources.

<u>Pollutant</u>	<u>Principal Source</u>
Particulate Matter	Ash In Waste Stream
Acid Gases	
HCl	Chlorinated Plastic In Waste Stream
SO ₂	Sulfur Compounds In Waste Stream
SO ₃	Oxidation of SO ₂ In Flue Gas
HF	Fluorocarbons In Waste Stream
NO _x	Air & Fuel Nitrogen Conversion
CO	Incomplete Combustion
Heavy Metals (Arsenic, Cadmium, Lead, Mercury)	Metal Compounds In Waste Stream
Organic Compounds (Dioxins, Furans)	Products of Incomplete Combustion or Contained in Waste Stream

Particulate matter consists primarily of non-combustible inorganic material entrained in the flue gas. Particulate matter typically ranges in size from less than one micron to about 50 microns. The uncontrolled particulate matter emission rate varies substantially for the different types of MWC's. Modular incinerators produce the lowest levels of uncontrolled emissions with RDF fired units having the highest.

Acid gases; hydrogen chloride (HCl), sulfur dioxide (SO₂) and hydrogen fluoride (HF) are formed during the combustion of chloride, sulfur and fluoride containing compounds found in the waste stream. A small fraction (approximately 1 to 5 percent) of the SO₂ in the flue gas is oxidized to sulfur trioxide (SO₃). These gases, in the presence of water or water vapor, react to form hydrochloric, sulfurous, hydrofluoric or sulfuric acid.

Nitrogen oxides (NO_x) are found predominantly in the form of Nitrous Oxide, NO, and are formed primarily through the conversion of fuel bound nitrogen although some nitrogen in the combustion air may also be converted. Carbon monoxide (CO) is formed through the incomplete combustion of organic compounds in the waste stream and is used as an indicator of combustion conditions.

Heavy metals compounds of concern emitted from MWC's include the oxides and chlorides of arsenic, cadmium lead and mercury. These compounds are formed from the combustion of heavy metal containing components of the waste stream such as batteries, plastics, paper products and metal alloys. A number of these compounds have boiling points or sublime at temperatures below the 1800°F typical of incineration systems and are thus vaporized into the flue gas. As the flue gas temperature cools, they tend to condense out and are concentrated on fine particulate matter in the flue gas. For the compounds of mercury and lead, a significant fraction may remain in the vapor state at typical incinerator exit flue gas temperatures.

Organic Emissions are a result of incomplete combustion of compounds found in the waste stream. The prime organic compounds of concern are polychlorinated dibenzyl-dioxins (PCDD) and polychlorinated dibenzyl-furans (PCDF). These emissions can arise from; incomplete thermal destruction of PCDD and PCDF containing materials in the waste stream, incomplete thermal destruction of other organic compounds that produce PCDD/PCDF precursors and through chemical reactions that occur at relatively low temperatures downstream of the combustor.

Table 3. shows typical uncontrolled and controlled emissions for a number of pollutants of concern from refuse incineration. Percent reduction ranges typical of levels being achieved utilizing best available control technologies are also shown for each pollutant.

Table 3. Typical Refuse Incinerator Uncontrolled and Controlled Emissions.

Pollutant	Uncontrolled Emissions	Controlled Emissions	Percent Reduction
Particulate Matter, gr/dscf	0.5-4.0	0.002-0.015	99.5+
Acid Gases ppm dv			
HCl	400-100	10-50	90-99+
SO ₂	150-600	5-50	50-90+
HF	10-0	1-2	90-95+
NO _x	120-300	40-120	30-65*
Heavy Metals mg/nm ³			
Arsenic	<0.1-1	<0.01-0.1	90-99+
Cadmium	1-5	<0.01-0.5	90-99+
Lead	20-100	<0.1-1	90-99+
Mercury	<0.1-1	<0.1-0.7	10-90+
Total PCDD/PCDF ng/nm ³	20-500	<1-10	80-99

Reference conditions - Dry Gas @ 12%CO₂

* Reduction associated with non-selective catalytic reduction

Modern refuse incinerator installations achieve very low emissions due to the proper application and operation of available air pollution control systems. The average incinerator emissions levels for all pollutants has decreased substantially over the past five years as more modern installations have been brought into service.

AIR POLLUTION CONTROL SYSTEMS

Air pollution control systems for refuse incinerators can be classified by either the pollutant they control or their operating principals. Often more than one control device will be used in series to control a number of pollutants. The most common examples of this are the use of an electrostatic precipitator followed by a wet scrubber or a spray dryer absorption system including an electrostatic precipitator or fabric filter. The following sections discuss control techniques for the major stack emissions from municipal waste combustion.

CARBON MONOXIDE CONTROLS

Carbon monoxide emissions are controlled by employing "Good Combustion Practices". These practices include operational and incinerator design elements for controlling the amount and distribution of excess air in the flue gas to ensure there is enough oxygen present for complete combustion. The design of modern efficient combustors is such that there is adequate turbulence in the flue gas to ensure good mixing, a high temperature zone (greater than 1800°F) to complete burnout and a long enough residence time at the high temperature (1-2 seconds).

The feed to the combustor is controlled to minimize fuel spikes that lead to fuel rich firing. The combustor is equipped with adequate instrumentation and combustion air controls to adjust for rapid changes in fuel conditions. These types of controls can limit CO formation to 150 ppm or less depending on the combustor design.

Good combustion practices also limit PCDD/PCDF emissions exiting the incinerator. This is accomplished by maintaining firing conditions that destroy PCDD/PCDF's found in the fuel and by destroying PCDD/PCDF's precursors that may be formed from the combustion of other chlorinated and organic compounds.

NITROGEN OXIDES CONTROLS

Nitrogen oxides (NO_x) emissions are controlled by limiting their formation in the incinerator using staged combustion or applying selective non catalytic reduction to reduce the NO_x content in the flue gas. Staged combustion is accomplished by splitting up the introduction of combustion air into the combustor so that areas of fuel rich and fuel lean firing are established. This will lower the peak flame temperatures and limit the amount of oxygen available to react with nitrogen in the air at the peak temperature. Introduction of additional secondary air downstream in the combustor will ensure complete combustion and minimize CO formation. Generally staged combustion is effective in reducing NO_x formation due to air nitrogen conversion but is not very effective in limiting conversion of fuel bound nitrogen to NO_x .

NO_x present in the flue gas can be reduced by employing either a selective catalytic or non catalytic reduction process. The selective catalytic reduction (SCR) process utilizes ammonia injection upstream of a catalytic reactor, at about 600-650°F, to reduce NO_x to nitrogen. Selective catalytic reduction has been applied to a wide range of combustion sources where 80-85 percent NO_x reduction has been demonstrated. However, because for the nature of the compounds found in refuse incinerator flue gas, the successful application of SCR requires installation downstream of the acid gas and particulate control systems with subsequent reheat to the reactor operating temperature. Because of these constraints, only limited SCR applications to refuse incinerator flue gases have been attempted.

Selectively, non-catalytic reduction (SNCR) reduces flue gas NO_x through the reaction with ammonia in a temperature range of 1700-1900°F. The ammonia may be supplied as anhydrous ammonia, aqueous ammonia or as urea. At flue gas temperatures above 1900°F, the oxidation of ammonia to NO_x increases and SNCR can actually result in an increase in overall NO_x . At temperatures below about 1700° NO_x reduction falls off and ammonia break through increases leading to the potential for a visible ammonium chloride plume.

Ammonia injection, also known as Thermal De- NO_x , has been applied to many different combustion sources including mass burn refuse incinerators. NO_x reduction levels of up to 65 percent have been demonstrated at an ammonia to NO_x ratios of about two with ammonia break through as low as 5 ppm. This corresponds to an NO_x emission level as low as approximately 60 ppm. Thermal De- NO_x operates most efficiently under steady state operating conditions. Changes in fuel feed rate, excess air rate or incinerator load can significantly change flue gas conditions at the ammonia injection point leading to a major change in control efficiency.

Urea injection has been demonstrated full scale on refuse combustors in the U.S. and Europe. Urea injection offers the advantage of not requiring a hazardous material for operation. At the injection temperatures employed (1600-1900°F) the urea quickly breaks down to form the active reagent. In some cases, reaction enhancers are added to the urea to expand the effective temperature window to as low as 1200°F. Tests with urea injection have achieved greater than 65 percent NO_x reduction with very low (approximately 5 ppm) ammonia slip.⁽⁵⁾

Activated carbon reactors are under development in Germany for the removal of NO_x , PCDD/PCDF, and mercury from incinerator flue gases. These reactors are placed downstream of a dry scrubbing system in cleaned flue gases at temperatures between 60 and 150°C. Ammonia is injected upstream of the reactor. Test work has shown 50-75% NO_x reduction and NO_x emissions between 60 and 120 ppm.⁽⁶⁾

PARTICULATE MATTER CONTROLS⁽⁷⁾

Particulate emissions are primarily controlled by electrostatic precipitators (ESP's) or fabric filters, although wet scrubbers are sometimes used on small incinerators or in series with ESP's for additional control. ESP's are installed either alone, to control particulate emissions, or after a

spray dryer, as a part of an acid gas cleaning system. Fabric filters are typically installed downstream of a quench tower or spray dryer where the conditions of increased flue gas moisture and lowered temperature aid in protecting filter bags from hot embers.

Electrostatic Precipitators

Electrostatic precipitators collect particulate matter by introducing a strong electrical field in the flue gas which imparts a charge to the particulates present. These charged particles are then collected on large plates which have an opposite charge applied to them. The collected particulate is periodically removed by rapping the collection plates. The agglomerated particles fall to a hopper where they are removed. Key design parameters for electrostatic precipitators include, particulate composition, density and resistivity; flue gas temperature and moisture content; inlet particulate loading and collection efficiency; specific collection area (SCA = square feet of collecting surface per 1,000 acfm of flue gas) and number of fields; flue gas velocity, collector plate spacing; rapping frequency and intensity; and transformer rectifier power levels.

Table 4. presents sizing parameters typical for ESP's applied for incinerator particulate emissions control.

Table 4. Electrostatic Precipitator - Design Parameters.

Particulate Loading, gr/acf	0.5-9	Acid Gas Control
Required Efficiency, %	98-99.9	
Number of Fields	3-4	
SCA, ft ² /1000 acfm	400-550	
Average Secondary Voltage, kv	35-55	
Average Secondary Current mA/1000ft ³	30-50	
Gas Velocity, ft/sec.	3.0-3.5	

Particulate	Acid Gas Control
Flue Gas Temperature, °F	350-450
Flue Gas Moisture, % Vol.	8-16
Ash Resistivity, ohm-om	10 ⁹ -10 ¹²
	10 ⁸ -10 ⁹

The ranges in parameters shown reflect straight ESP particulate control applications and ESP applications as a part of an acid gas cleaning system. Although the inlet particulate loading to the ESP is much higher as part of an acid gas cleaning system, the number of fields and specific collecting area required to achieve a similar outlet emission, don't change significantly. This is due to lower ash resistivity values and increased flue gas moisture contents which improve the

ESP's performance. Incinerators which have had spray dryers retrofitted in front of existing ESP's, have in most cases been able to maintain the same level of particulate emissions (e.g. 0.01 to 0.015 gr/dscf @ 12% CO₂)

Weighted wire, rigid frame and rigid electrode type precipitators are employed for incinerator applications, however, rigid frame and rigid electrode types predominate. This is related to the corrosive gas conditions and sticky nature of the fly ash being collected. Electrode failures associated with rigid frame and rigid electrode systems are less frequent than for weighted wire years. This is especially true where higher rapping forces are needed to dislodge the sticky fly ash. For rigid frame systems, high alloy (e.g. Incoloy 825) spring wound electrodes are also used to minimize electrode corrosion problems.

The insulator compartment ventilation system is designed to minimize the effects of the corrosive nature of the flue gas and fly ash stickiness. A pressurized ventilation system, employing heated air is recommended to maintain clean insulators and reduce potential electrical tracking problems.

Fabric Filters

Both reverse air and pulse jet type fabric filters are used for particulate emission control on refuse incinerators. Each type offers advantages that should be evaluated on a site specific basis. Both types are capable of achieving particulate emissions on the order of 0.01-0.015 gr/dscf @ 12% CO₂ or lower. Table 5 presents design parameters typical of incinerator fabric filter applications.

Table 5. Fabric Filter Parameters Reverse Air.

<u>Reverse Air</u>	<u>Pulse Jet</u>
Operating Temperature, °F	230 -450
Type Fabric	Woven Fiberglass
Fabric Coating	10% Teflon B or Acid Resistant
Fabric Weight, Oz/Yd ²	9.5
Bag Diameter, Inches	8
Net Air to Cloth Ratio	1.5 - 2.0:1
Minimum Compartments	6
Overall Pressure Drop, in W.G.	4 - 6
Estimated Bag Life, Years	3 - 4
	16 or 22
	6
	3.5 - 4.0:1
	4
	8 - 10
	1.5 - 2

The temperature ranges shown represent both operation after a dry quench chamber

(350-450°F) and a spray dryer (230-300°F). For these temperatures ranges woven fiberglass is typically used as the bag material although Nomex fabric is also used. A 10 percent Teflon B coating is the most commonly specified with acid resistant coating also used.

The bag sizes differ substantially for the two types of filters. Reverse air filters generally employ eight inch diameter by up to 24 feet long bags. Pulse jet bags are usually six inch diameter by 12 to 14 feet long. However, some vendors offer a low pressure pulse filter with up to 24 feet long bags. The biggest differences in operating parameters are in the air to cloth ratio and system pressure drop. Pulse jet filters generally operate at double the air to cloth ratio as reverse air filters and nearly double the pressure drop. This results in more frequent bag cleaning and a substantially shorter bag life.

The main advantages of a pulse jet fabric filter are a lower capital cost and a smaller footprint. However, because of the shorter bag life and higher pressure drop, the pulse jet filter generally has a higher total evaluated cost for plants exceeding 15 years of life. A reverse air filter typically has lower particulate emissions when compared to a pulse jet filter.

The majority of fabric filter applications are as a part of an acid gas cleaning system and incorporate specific design features for operating after a spray dryer. The flue gas after a spray dryer has been cooled (240-300°F), has a high moisture content (12-20 percent), is closer to the dew point (80-160°F) and may have a higher particulate loading. These flue gas conditions can lead to severe corrosion and baghouse plugging.

Corrosion control is accomplished by: insulation design; control of air in-leakage into the filter; hopper heating; and, in some instances, coating of the fabric filter internals with an acid resistant material. Insulation specifications usually require a minimum of four inches with double lapping on side panels and with the insulation extending into the hopper crotch areas. Air in-leakage is controlled by good quality control during erection and by minimizing the number of openings into the filter. Hopper heating is used to maintain the hopper skin temperature at the flue gas temperature to prevent cold spots and aid in maintaining product flowability.

As part of an acid gas cleaning system, the fabric filter also acts as a reactor to aid in acid gas absorption, especially for sulfur dioxide. Sulfur dioxide in the flue gas is absorbed by alkaline material in the filter cake on the bags. Therefore when a bag is freshly cleaned, SO₂ absorption decreases. In order to minimize this impact on overall absorption, the number of bags being simultaneously cleaned should be minimized. This can be accomplished by increasing the number of compartments. A minimum of six compartments is generally specified for acid gas cleaning systems.

Wet Scrubbers

Wet scrubbers are typically employed as part of a two stage flue gas cleaning system downstream of an electrostatic precipitator where they function as a particulate removal polishing stage and as an acid gas absorber. A venturi scrubber followed by a packed or tray tower is

commonly used, however, other types of wet scrubbers such as charged droplet scrubbers are also used. Figure 2. shows a typical wet scrubber design used for both particulate and acid gas control.

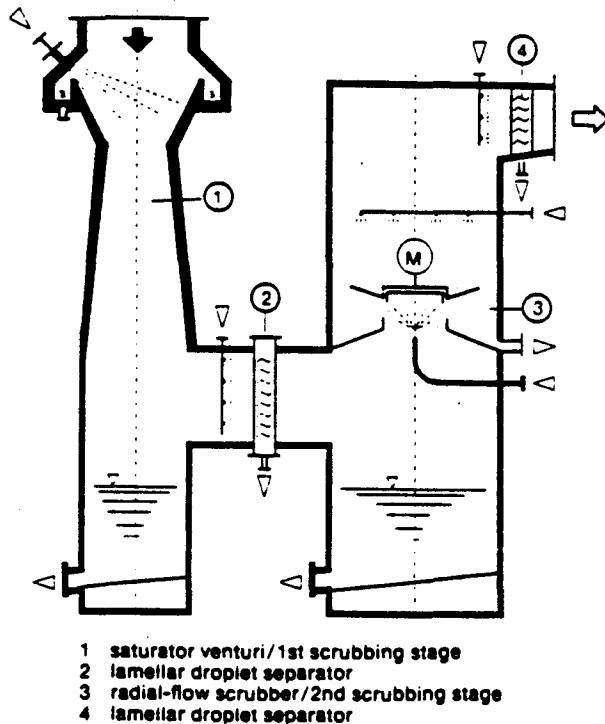


Figure 2. Saturator Venturi with Radial-Flow Scrubber.
(Courtesy Lurgi Corporation)

Typically, water is recycled in the venturi stage to achieve particulate removal. Hydrogen chloride present in the gas would also be removed in this stage. Additional particulate and acid gas removal can take place in the second scrubbing stage. Absorption of SO₂ is enhanced in this stage by maintaining a recirculating solution pH in the range of about 6.5 to 9 through addition of caustic (sodium hydroxide). A blow down stream is maintained for each stage to control the recirculating solution solids content. Typical design parameters for refuse incinerator wet scrubber applications are presented in Table 6.

Table 6. Wet Scrubber Design Parameters.

<u>Venturi Stage</u>	<u>Absorber Stage</u>
Gas Velocity, Ft/Sec	90 - 150
Pressure Drop, Inches W.C.	40 - 70
L/G, Gal/Kacf m	10 - 20
Scrubbing Media	Water
Solution pH	< 1 - 2
	6 - 10
	4 - 8
	20 - 40
	Caustic
	6.5 - 9

Materials of Construction	High Alloy Steel (eg. Inconel, Hastelloy)	FRP Lined Carbon Steel
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The venturi section is subjected to severe corrosive conditions due to the low circulating solution pH, high hydrochloric acid concentration and the presence of small amounts of sulfuric, nitric and hydrofluoric acids. The scrubber inlet temperature may be as high as 450°F which precludes the use of corrosion resistant resins, therefore, high alloy steels are typically specified as the materials of construction. In cases where the inlet flue gas contains high levels of particulate matter, the venturi section may be lined with a corrosion resistant materials such as bricks. The venturi section typically is equipped with a set of emergency quench nozzles to ensure that the flue gas temperature leaving the venturi is maintained at an acceptable level for the absorber stage materials of construction.

The absorber stage may be a packed tower, a tray tower or a radial flow tower as shown in Figure 2. Materials of construction for the absorber are typically fiberglass reinforced plastics (FRP) although carbon steel vessels lined with rubber or a corrosion resistant resin material, are also used.

ACID GAS CONTROLS ⁽⁸⁾

Control of refuse incinerator acid gas (HCl, SO₂, SO₃, and HF) emissions is achieved by dry sorbent injection, spray dryer absorption or wet scrubbing. Each of these types of technologies has been successfully applied to meet existing emissions regulations, however, as emissions limitations become more stringent, the trend is toward spray dryer absorption and wet scrubbing.

Dry Sorbent Injection, DSI

Dry sorbent injection involves the addition of an alkaline material, usually hydrated lime, Ca(OH)₂ or soda ash, Na₂(CO₃), into the gas stream to react with acid gases present thus producing a salt which is collected in a particulate collection device. This very simple process can capture up to 90% of the HCl present in the flue gas and about 50% of the SO₂. However, stoichiometric ratios (equivalents of alkali added per equivalents of acid in the flue gas) are high, typically on the order of 2 to 4. Therefore, simple DSI applications are normally limited to small facilities with moderate emissions control requirements.

The overall acid gas control efficiency of DSI can be improved and reagent consumption decreased by:

- Increasing flue gas humidity
- Recycling reaction products into the flue gas stream

Increasing the flue gas relative humidity can be accomplished by cooling the flue gas using heat exchangers or by quenching the flue gas using water sprays. Both approaches are commercially applied however, the use of a quench chamber predominates.

Typically flue gas from the incinerator enters a 3 to 5 second retention time cooling tower (or dry quench chamber) where water is sprayed into the gas to lower the temperature. The flue gas temperature leaving the cooling tower is maintained at a temperature high enough to ensure that all water droplets evaporate (300-350°F). Dry reagent is then mixed with the flue gas via pneumatic transport systems or eductor venturis. The reagent reacts with acid gases prior to removal in a dust collector (typically a fabric filter). A portion of the collected reaction products in some cases is re-injected to increase acid gas removal and decrease reagent consumption. Humidification and reagent injection steps can also be carried out together in specially designed reactors. This type of process can achieve greater than 95% HCl removal and 90% SO₂ removal at stoichiometric ratios between 1 and 2.

Spray Dryer Absorption SDA

Spray dryer absorption has been widely applied for refuse incinerator emissions control and has been specified as Best Available Control Technology (BACT) in a number of air permits. The SDA process combines a spray dryer with a dust collector. Reagent addition, flue gas humidification and some acid gas absorption takes place in the spray dryer. Additional acid gas absorption and collection of the dry fly ash reaction products mixture takes place in the dust collector. The SDA process is capable of achieving very high removal efficiencies for all acid gases (99+%HCl, 95%SO₂, 99+%SO₃, 95%HF) as well as for the removal of trace metals and organic compounds at stoichiometric ratios between 1 and about 1.8. Figure 3. is a simplified flow diagram for the SDA process.

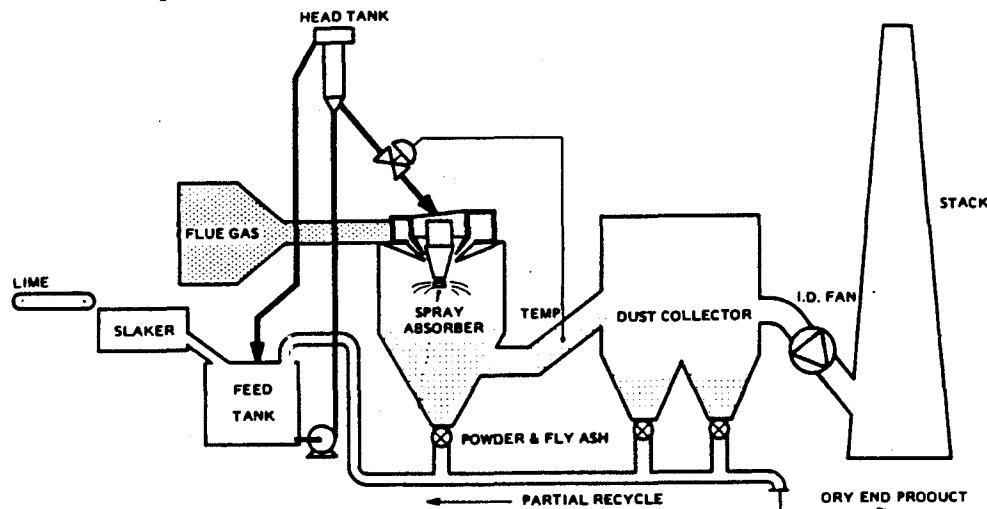


Figure 3. Spray Dryer Absorption Process.
(Courtesy of Niro Atomizer)

Incinerator flue gas enters the spray dryer where it is contacted by a cloud of finely atomized droplets of reagent (typically a hydrated lime slurry). The flue gas temperature is decreased and the flue gas humidity is increased as the reagent slurry simultaneously reacts with acid gases present and evaporates to dryness. In some systems, a portion of the dried product is removed from the bottom of the spray dryer while in others it is carried over to the duct collector. Collected reaction products are sometimes recycled to the feed system to reduce reagent consumption.

Several different spray dryer design concepts have been employed for incinerator SDA applications. These include; single rotary, multiple rotary and multiple dual fluid nozzle atomization; down flow, up flow and up flow with a cyclone pre-collector spray dryers; and single and multiple gas inlets. Flue gas retention times range from 10 to 18 seconds and flue gas temperatures leaving the spray dryers range from 230°F up to 300°F.

Generally the lower the spray dryer outlet temperature, the more efficient the acid gas absorption. The minimum reliable operating outlet temperature is a function of the spray dryer and dust collector design and the composition of the dry fly ash reaction product mixture. The spray dryer outlet temperature must be maintained high enough to ensure complete reagent evaporation and the production of a free flowing product. Low outlet temperature operation requires; efficient reagent atomization, good gas dispersion and mixing, adequate residence time for drying and design of the dust collector to minimize heat loss and air in-leakage.

The dust collector downstream of the spray dryer may be an electrostatic precipitator, a reverse-air baghouse or a pulse-jet type baghouse. The selection of a specific type of dust collector is dependent on site specific factors such as particulate emission limits, overall acid gas removal requirements and project economics. Each of these dust collection devices offers process advantages and disadvantages that are evaluated on a site specific basis. Generally where high acid gas control is required (95+%HCl, 85+%SO₂) a baghouse is utilized, as it is a better reactor than an electrostatic precipitator.

Whether a fabric filter or ESP is selected as the dust collector, minimization of heat loss from the dust collector to avoid corrosion and increased product stickiness is a prime design consideration. Four methods employed to achieve this, are as follows:

- Insulation, to control heat loss
- Control of air in-leakage, to minimize cold spots
- Hopper heating, to maintain product temperature
- Operating procedures to maintain product flowability and minimize cold areas

The end product from the SDA process is a fine hygroscopic material with a significant soluble fraction. The end product tends to be stickier than MSW fly ash and more difficult to convey and store. Major end product constituents include:

- | | |
|---------------------|-------------------|
| ◦ Fly Ash | ◦ Calcium Sulfite |
| ◦ Calcium Hydroxide | ◦ Calcium Sulfate |

- Calcium Chloride
- Calcium Carbonate
- Calcium Fluoride
- Moisture

The calcium chloride formed at typical spray dryer outlet temperatures is a mixture of mono and dehydrates ($\text{CaCl}_2\text{H}_2\text{O}$ and $\text{CaCl}_2\text{H}_2\text{O}$) and at lower temperatures will absorb moisture until it reaches the hexahydrate form ($\text{CaCl}_2\text{6H}_2\text{O}$) and melts. Therefore, it is necessary to keep the product from being exposed to cold and/or moist air. This is accomplished by proper design of the product conveying and storage systems.

Wet Scrubbing

Wet scrubbing systems are capable of achieving high acid gas removal efficiencies and have been applied to a large number of installations in Europe. Typical wet scrubbing applications included two-stage scrubbers located downstream of an electrostatic precipitator. The first stage is used for HCl removal and the second for SO_2 removal. Water is used to capture the HCl and either caustic or hydrated lime is used for SO_2 capture. Figure 2., shows a typical two-stage wet scrubber while Figure 4. shows a process flow diagram for an application of wet scrubbing with fly ash treatment.

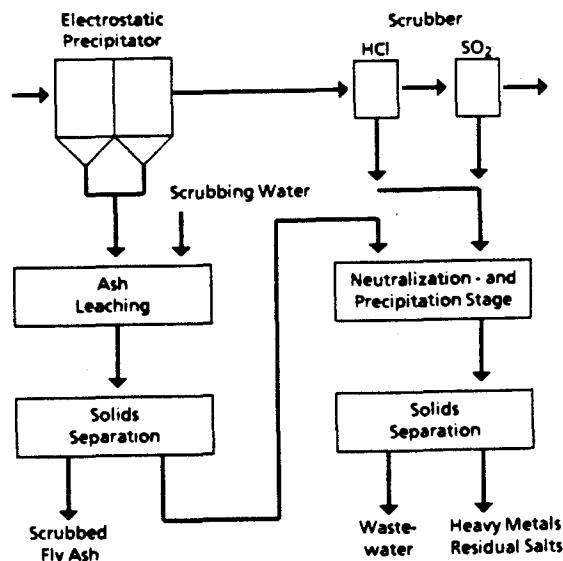


Figure 4. Wet Scrubbing With Ash Treatment.
Courtesy of Lurgi, Inc.)

In this process, the HCl stream from the first scrubbing stage is pumped to a fly ash leaching tank where it is used to leach out heavy metals from the fly ash collected in the dust collector. After leaching, residual fly ash solids are either disposed of or used in construction applications. The heavy metals bearing HCl stream is then treated alone or with the sodium sulfite/sulfate

solution from the second scrubber stage in a neutralization/precipitation stage to concentrate the heavy metals and produce salt-containing wastewater for disposal. When lime is used in the SO₂ absorption section of the scrubber, the calcium sulfite slurry can be oxidized to calcium sulfate (Gypsum) for utilization.

Wet scrubbers offer some advantages:

- They are relatively inexpensive to install and require relatively small plot space;
- They are capable of achieving very high removal efficiencies for acid gases (99+%HCl, 95+SO₂);
- They are capable of high removal efficiencies for many volatile trace compounds;
- They require the lowest reagent stoichiometrics (1.0 - 1.2) of any of the alternatives considered.

Wet scrubbers also have some disadvantages:

- They produce a wet effluent which requires additional treatment with complex effluent treatment systems, economics and space requirements are not as attractive as the other alternatives.
- Wet scrubbers are more prone to corrosion problems and may require expensive materials of construction.
- Historically, wet scrubbers have experienced more operating problems and higher maintenance requirements than the alternatives.

HEAVY METALS CONTROLS

The primary heavy metals of concern from refuse incinerators (arsenic, cadmium, lead, and mercury) are collected in the particulate control device or in the acid gas control system. The major fraction of these metals exist as solid particulates at incinerator exit flue gas temperatures and are collected as particulate matter. However, some arsenic, lead, and mercury compounds exist in the vapor state at incinerator flue gas exit temperatures and these compounds must be collected by condensation through cooling of the flue gas. This can be accomplished with either an SDA or wet scrubbing process.

In the SDA process, the flue gas cooling takes place rapidly in a cloud of finely atomized droplets. These droplets serve as sites for metals to condense or be absorbed onto. The condensed metal is then removed with the reaction products in the downstream dust collector. Collection efficiencies for arsenic and lead at typical SDA system operating temperatures are greater than 90 percent.

A significant fraction of mercury remains in the vapor phase even at SDA system outlet temperatures of 250°F. Addition of small amounts of powdered activated carbon or sodium

sulfide upstream of the spray dryer have been used to enhance mercury control and greater than 90% capture has been achieved.

Wet scrubbers following a dust collector, operate at saturated flue gas temperatures (150° - 180°F) and can achieve greater than 90% removal of mercury. They can also remove a major fraction of the other metals which may escape the particulate control device.

PCDD/PCDF CONTROL

PCDD/PCDF emissions are controlled by good combustion practices which inhibit their formations and by particulate and acid gas controls. Combustion temperature above 1800°F for greater than two seconds, are specified as a method of destroying PCDD/PCDF found in the waste stream and their precursors formed from the combustion of other organic and chlorine containing compounds. However, some PCDD/PCDF compounds may still form downstream of the incinerator on the surface of fly ash at temperatures from 500° - 700°F.

Control of PCDD/PCDF compounds found in the flue gas leaving the incinerator is achieved by electrostatic precipitators operating below 450°F or by acid gas control systems. Acid gas control system achieve a higher PCDD/PCDF capture efficiency because of their reduced outlet temperatures and the large droplet surface area available for adsorption to take place. PCDD/PCDF capture efficiencies up to 99% can be achieved and total emissions can be reduced to less than about 10 ng/nm³

CONCLUSIONS

Modern efficient incinerators are increasingly being used to simultaneously reduce municipal solid wastes volumes while recovering energy in the form of steam or electricity. As the fraction of MSW incinerated increases from today's 15% to about 25-30% in 1995, pressures will continue to ensure that these incinerators environmental impacts are minimized.

EPA has recently established New Source Performance Standards and Emissions Guidelines for existing facilities to reduce air pollution emissions. These regulations will require installation of new or more advanced air pollution control systems to meet these standards.

Air pollution control systems available today have demonstrated the ability to reduce flue gas emissions to below levels currently mandated. A wide range of manufacturers have experience with guaranteeing the emissions levels required.

The work described in this paper was not funded by the U.S. Environmental Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

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TOXIC METAL EMISSIONS FROM MWCs AND THEIR CONTROL

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ABSTRACT

Energy recovery in combustion facilities complements the volume reduction of waste for land disposal, but it also produces air polluting emissions and concentrates some pollutants in the ash or residue requiring disposal. Air pollutant emissions, such as acid gases, trace organics, trace heavy metals, and particulate matter, can be controlled by flue gas cleaning processes. These processes include both dry and wet scrubbing, with dry scrubbing being preferred for municipal waste combustors in the United States and wet scrubbing being extensively used in Europe.

Dry and wet acid gas scrubbing processes will be described and their effectiveness in controlling metal and related pollutant emissions will be presented. The control of metal emissions by these processes (particularly mercury by supplemental means) will be emphasized, and the treatment of scrubber wastes prior to disposal will be noted.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's administrative review policies and approved for presentation and publication.

INTRODUCTION

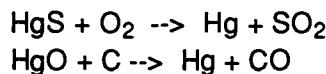
Waste combustion reduces the volume of waste requiring disposal, can thermally destroy toxic organic compounds present in the municipal solid waste (MSW) feed, and may be complemented by thermal energy recovery. However, combustion generates air polluting emissions, such as acid gases, trace organics [products of incomplete combustion including organics and carbon monoxide (CO)], trace metals, and particulate matter (PM), which depend on waste composition. Flue gas cleaning (FGC) processes to control these emissions transfer the reaction products or the pollutants to liquids or solids which may need treatment to remove components, such as heavy metals, or to stabilize the waste prior to its disposal or beneficial use.

The objectives here are to discuss potential ways of controlling metal emissions resulting from waste combustion. While fuel cleaning or materials separation may be a feasible approach for reducing selected air pollutant emissions, the focus here will be on controlling air pollutant emissions by FGC processes. Both wet and dry FGC processes will be discussed, but disposal of process waste will be noted only briefly. Generally, special landfills are used for waste requiring disposal while reuse is limited.

It should also be noted that Section 129 of the Clean Air Act Amendments of 1990 requires the U.S. Environmental Protection Agency to review and revise the promulgated standards and guidelines for municipal waste combustors (MWCs) within 1 year.¹ The Act stipulates that numerical emission limits be set for cadmium (Cd), lead (Pb), and mercury (Hg) by November 15, 1991. Thus, the control of these metals will be stressed. The standards and guidelines for MWCs are also to be broadened to apply to units of 225 tonnes/day (250 tons/day) or less within 2 years.

METAL EMISSIONS

The combustion of wastes containing metallic compounds usually leads to their thermal decomposition as temperatures above 700°C (1300°F) are present.² For example, the heating of compounds to over 700°C (1300°F) during combustion can lead to reduction processes such as:



where the mercuric sulfide (HgS) and mercuric oxide (HgO) in the waste feed react with oxygen (O_2) in combustion air and fuel carbon (C), respectively, to produce elemental Hg, sulfur dioxide (SO_2), and CO. On cooling of the combustion gases during energy recovery or prior to FGC, some Hg would be oxidized as Hg readily combines with O_2 at temperatures of 340 to 600°C (650 to 1100°F) to form HgO. Similarly, the presence of chlorine (Cl_2) in the combustion gases would result in mercuric chloride (HgCl_2) being formed as the gases cooled.

Metallic vapors also condense as the flue gases cool downstream of the combustion process. Condensation concentrates the volatile species on fine particles because of their high

surface areas (on a mass basis relative to large particles). Thus, the submicrometer fraction of the PM is enriched with condensable volatile species.³

Comparing data for MWCs having electrostatic precipitators (ESPs) for PM collection, Damle et al.⁴ concluded that the metallic species are collected primarily in the fine (submicrometer) PM fraction and that efficient collection of this fraction is essential to controlling the emission of semi-volatile species. They also observed that fine particles are collected less effectively than large particles in an ESP and that at stack conditions [~120 to 205°C (250 to 400°F)], the metallic species, except Hg, are mostly present on fine particles.

Figure 1 gives saturation curves for several metals and their compounds. Since the sampling and analytical methods (e.g., EPA's multimetals train and pertinent analytical methods for metals) determine the concentration of a metallic species regardless of its chemical form, it is not possible to compare the saturated vapor concentrations for specific metal species with their measured concentrations. Metal data, except for Hg, predominantly show over 90% of the metals analyzed to be in the solid phase (i.e., in particulate form) despite the high volatility of some of their chemical compounds. Elemental arsenic (As), Cd, Hg, and selenium (Se), as well as the chlorides of As, Hg, Se, and zinc (Zn), may be completely in the vapor phase leaving the combustor because of their relatively high volatilities.

In contrast to organic compounds, inorganic metal compounds have a low tendency for adsorption on PM. The high proportion of the total metallic species found in the particulate phase, based on flue gas sampling at 205°C (400°F) or lower, suggests that most metals were primarily in their less volatile chemical forms. Mercury, however, even at stack temperatures of 120 to 150°C (250 to 300°F), was in the vapor phase, since it was collected predominantly in the back half of the sampling train (i.e., after the PM filter).⁴

POST-COMBUSTION EMISSION CONTROL PROCESSES

As discussed earlier, air pollutant emissions requiring control include acid gases [mainly hydrogen chloride (HCl) and SO₂], trace organic compounds [polychlorinated dibenzodioxins and dibenzofurans (CDD/CDF)], trace metals (Cd, Hg, Pb,...), and PM. It has also been suggested that high PM control provides effective emission control of metals of concern, except Hg.⁵ However, Figure 2 suggests that Hg control is affected by inlet PM concentration (at least for dry scrubbers), with the lower Hg concentrations corresponding to higher PM concentrations entering dry scrubbing systems.⁶ It should be noted that the highest inlet PM concentrations corresponded to refuse-derived fuel (RDF) units (Biddeford and Mid-Connecticut) and the Quebec City mass burn unit (with a slipstream pilot spray dryer absorber/fabric filter system), which were believed to have higher C in their flyashes than other mass burn units represented in Figure 2. The use of acid gas control processes can complement the control of metal emissions through improved PM control as well as lowering the gas temperature which enhances condensation of some metal species (e.g., As, Hg, Se) and adsorption of both condensed metals and organics on particles.

Both wet and dry acid gas control processes are used to remove HCl and SO₂. Usually, HCl control is more of a concern than SO₂ when MSW is burned, but SO₂ is harder to control

than HCl although present at a significantly lower concentration than HCl. For small incinerators, wet acid gas scrubbers may be more economical than dry scrubbers. Dry scrubbers permit good acid gas and high PM control and may be less costly than wet scrubbers for moderate-to-large incinerators with low-to-moderate acid gas concentrations.

A two-stage wet scrubber is shown in Figure 3. In the first stage, the water venturi primarily effects PM control, accomplishes some HCl removal, and through gas cooling promotes condensation of vaporized species. The second stage removes SO₂ through the use of a sorbent, such as sodium hydroxide (NaOH), and also removes additional HCl and PM. Except for small MWCs, primary particulate collection is usually accomplished with an ESP preceding wet scrubbing. Since the flue gas is saturated with water vapor at 40 to 60°C (105 to 140°F) on leaving the scrubber, the flue gas may require heating to control corrosion of a metallic stack and/or preclude a vapor plume at the stack exit. Heating of the cleaned flue gas may also be required if additional gas treatment is needed after wet scrubbing, such as Hg removal via absorption filtration and nitrogen oxides (NO_x) control by selective catalytic reduction.

If the incinerator operates without energy recovery (i.e., without a boiler or heat exchangers), the flue gas from the combustor would require cooling from about 985°C (1800°F) to the acid gas scrubber temperature range. Flue gas cooling may be achieved using a spray dryer (SD) upstream of a wet acid gas scrubber, a heat exchanger or quench tower ahead of dry sorbent injection (DSI), or a spray dryer absorber (SDA). Both the DSI and SDA processes would be followed by a PM collector.

A dry acid gas scrubber [DSI or SDA plus PM collector] differs from a wet one in two ways: the waste discharged from a dry scrubber is a dry powder, not a liquid slurry, and the clean flue gas leaving the dry scrubber is not saturated with water vapor. While both dry and wet acid gas scrubbers require PM control components, PM removal follows acid gas neutralization in dry scrubbing and precedes it in wet scrubbing.

In both forms of dry scrubbing [DSI or SDA followed by either an ESP or a fabric filter (FF) for PM collection], calcium-based sorbents are generally used. With DSI, the sorbent, usually calcium hydroxide [Ca(OH)₂], is injected into flue gas which has been cooled to about 150°C (300°F) or less. The circulating bed (Figure 4) permits longer gas/sorbent contact time for the acid gas neutralization reaction to occur than does sorbent injection into the duct (Figure 5) where the gas velocity is higher than in the reactor. The solids entrained by the flue gas are removed in the PM collector, usually a FF (baghouse) because it enables additional acid gas removal by unreacted sorbent present in the dust cake on the bags.

While acid gas removals are 90 to 95% for HCl and 75 to 80% for SO₂ with the DSI/FF system, metals removal also is high because of the high collection of both total PM mass and fine particles. If Hg control is not adequate because of insufficient Hg in a collectible form (i.e., Hg species are not in the solid phase), it can be improved by injecting either sodium sulfide (Na₂S) or activated carbon (C) into the flue gas before Ca(OH)₂ addition. The elemental Hg is converted to HgS or adsorbed on the C particles, both of which are collected as PM. (As noted earlier, the suspected higher C content of flyashes in the inlet PM concentrations shown in Figure 2 may be partially responsible for the lower outlet Hg concentrations of the Biddeford, Mid-Connecticut,

and Quebec City units.) Figures 4, 5, and 6 show injection locations for these additives for supplementing Hg control.

The SDA/PM collection system, also referred to as a semi-dry scrubber, is shown in Figure 6. In this system, a $\text{Ca}(\text{OH})_2$ slurry is atomized into the surrounding dirty flue gas. As the gas cools to the 120 to 150°C (250 to 300°F) range, it evaporates the finely atomized droplets containing sorbent which reacts with the acid gases. The dry powdery solids formed contain calcium salts, flyash enriched with metals, and unreacted sorbent. Some of these solids may be collected in the bottom of the SDA, but most are entrained by the flue gas to the PM collector (either an ESP or a FF) for removal from the gas. HCl removals exceeding 95% and SO_2 removals over 90% can be attained with lime SDA/PM collection systems. However, dry systems require higher reagent-to-acid-gas ratios than do wet systems for comparable acid gas control when attainable.

Activated powdered C is also being applied at several incineration facilities in Europe primarily to improve CDD/CDF control, but the injected C is also enhancing Hg capture. Incineration plants in Germany are also using carbon beds after wet scrubbing to improve both CDD/CDF and Hg control in order to comply with tighter air emission regulations.

Another supplemental Hg control process uses a selenium (Se) filter as shown in Figure 7. This process, which was developed for the metal smelter industry in Sweden, is being applied to a MWC in Sweden after reheating the gas from a wet acid gas scrubber and just ahead of the stack.⁷ The Hg/Se reaction in the filter leads to the retention of the solid-phase product in the filter. Sizing of the filter permits effective operation for the desired period (~5 years) before its replacement. Operating limitations include an unsaturated (dry) flue gas at 60°C (140°F) or less and low particulate loading [preferably below 10 mg/Nm³ (0.005 gr/dscf)] to avoid premature cleaning of the porous Se-impregnated filter material. Hg concentrations of about 10 mg/Nm³ (referenced to 10% CO_2) at the outlet of the filter were reported.⁷

In Japan, Hg removals of 30 to 70% by a wet scrubber have led to several approaches for enhancing Hg capture.⁸ One method used with caustic-soda-based acid gas scrubbing injects a liquid chelating agent and cupric chloride into flue gas to absorb atomic Hg in the flue gas. Atomic Hg removal ranging from 65 to 85% over the increasing pH range of 2 to 12 in the absorbing solution was reported when the additive was injected into 600°C (1100°F) gas with 1500 ppm HCl. A second method involves sodium hypochlorite addition. This additive reacts with Hg to form HgCl_2 which is soluble in water. Mercury removals of 90 to 95% were achieved with this method. As reported earlier, this additive had been proposed for NO_x control by wet scrubbing.⁹ To achieve the concurrent removal of both Hg and NO_x , bromine has been added to reduce NO_x by 30 to 50%.

EFFLUENT/RESIDUE TREATMENT AND DISPOSAL

The wet acid gas scrubber generates a liquid effluent which may require treatment to remove metals prior to discharging blowdown to a sanitary sewer or water body, if permitted. If liquid discharges are not permitted or treatment costs are high, zero effluent discharge can be

achieved by a system such as shown in Figure 8. Hot flue gas enters the SD which receives blowdown after treatment to remove metals by precipitation and pH adjustment. While the SD functions primarily to evaporate the treated blowdown, it may also remove some acid gases. The cooled flue gas passes to a PM collector, such as an ESP, before entering the two-stage scrubber. If high PM and high fine particle (including aerosol) control is required, an ionizing wet scrubber can supplement wet acid gas scrubbing. If needed, the water-saturated flue gas can be reheated after leaving the ionizing wet scrubber and before entering the stack as unsaturated flue gas to address corrosion or vapor plume problems. This hybrid wet/dry scrubber enables high multipollutant control and discharges dry solids. The dry waste may require treatment to remove leachable metals, such as Cd and Pb, before the remaining waste is landfilled or reused where permitted. The concentrated metals may require disposal as hazardous waste.

Wet scrubber effluent treatment processes are used to concentrate and remove metal, such as Pb and Cd to preclude their leaching in landfills, prior to their disposal as hazardous wastes in Europe. The use of C beds following wet scrubbing to remove Hg and/or organic compounds or of the Se filter for Hg removal produces wastes which may need treatment or disposal of hazardous wastes.

Dry scrubber wastes are frequently landfilled as special wastes in the U.S., with the excess lime and pozzolanic character of the ash/residue aiding its stability. Monitoring of landfill leachate is also a usual regulatory requirement.

RESULTS

While Hg control information for the Se filter in Sweden and with wet acid gas scrubbing in Japan were mentioned earlier, test results, including limited data for Cd and Pb control, are presented here. High metal (except Hg) removal (>95%) has generally been achieved with both SDA/ESP and SDA/FF systems. The SDA/FF system has shown higher Hg capture (>90%) than the SDA/ESP system (35-70%), probably because of better fine particle removal. Tables 1, 2, and 3 show Cd, Hg, and Pb control results for dry acid gas scrubbers with and without supplemental Hg control processes.

Table 1 suggests good Cd and Pb control because of their low outlet concentrations and low PM emission, except for Unit 2, Dutchess County. Hg control for St. Croix appears to be high based on its outlet concentration of 35 µg/dscm and expected inlet concentrations for MWCs. Hg control at Springfield appears to be slight and nil for Unit 1 at Dutchess County, but good for Unit 2 at Dutchess County although it had a higher PM emission than Unit 1.

The metals data in Table 2 and 3 show very high removals of Cd and Pb, generally above 98% when dry scrubbers with either FFs or ESPs are used. Very high Hg control (>95%) has also been obtained with SDA/FF systems on RDF MWCs. Less effective Hg control has been seen with dry scrubbers on mass-burn units, possibly because of the apparent lower C in flyash from these combustors than in RDF units. Although no test data were found to support this theory, the effectiveness of C injection for improving Hg control has been demonstrated (see Table 3) and provides qualitative support for this theory. Very high Hg control in the February, 1989, Mid-Connecticut tests corresponded to loss-on-ignition (LOI) FF residue values as low as 4%. Assuming that water of hydration and C account for the LOI, these values

ranged from 4 to 10% for the Mid-Connecticut tests, while the Hg removal was over 95% for all 13 runs. Thus, the amount of C needed for high Hg control, if it improves Hg control, is small. This is consistent with the results of the activated C addition tests (Table 3) which required small addition rates to improve Hg removal significantly.

Table 2 indicates close agreement between PM removal and Cd and Pb capture for both ESPs and FFs and less effective Hg control with ESPs than with FFs. The Millbury outlet Hg data suggest little or no control (assuming a typical Hg inlet concentration between 500 and 1000 $\mu\text{g}/\text{Nm}^3$), while the SEMASS (which has five-field ESPs while Millbury has three-field ESPs) data imply at least moderate control.

Table 3 indicates that both Na_2S and C injection result in high Hg capture by dry scrubbers. Removals exceeding 85% seem feasible when these additives are used.

Table 4 shows Hg removal data for plants with wet scrubbers in Europe. It indicates that Hg captures of 85% or more were achieved with wet scrubbers. The results from Japan noted earlier indicated similar Hg removals when additives were used with wet scrubbers.

SUMMARY

Effective PM control is essential to control emissions of toxic metals from MWCs. High PM removal generally implies good metals control, with Hg being a possible exception. Additives to flue gas (Na_2S solution or activated powdered C) ahead of dry scrubbers improve Hg control, while C beds following wet scrubbing reduce air pollutant emissions to low levels. A Se filter for removing Hg from conventionally wet scrubbed flue gas followed by gas reheating before filtration has been proposed for MWC applications, but no performance data have yet been reported. Additives to enhance Hg control in wet scrubbers, such as cupric chloride with a chelating agent and sodium hypochlorite, are being successfully used in Japan. For high multipollutant emissions control, wet scrubbing is favored on MSW incinerators in Japan and Europe, while the semi-dry scrubber predominates in the U.S.

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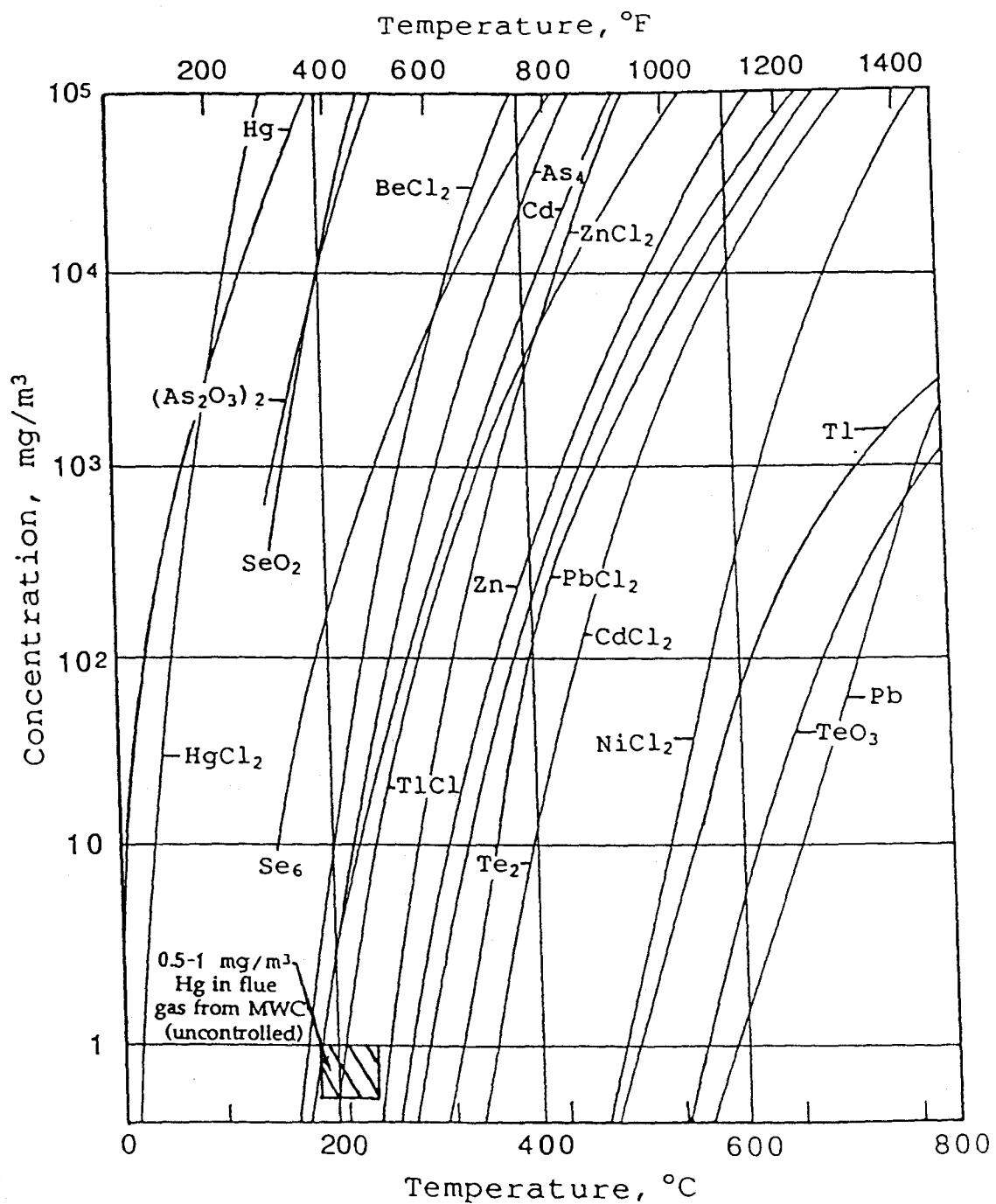


Figure 1. Saturation curves for selected metals and compounds.

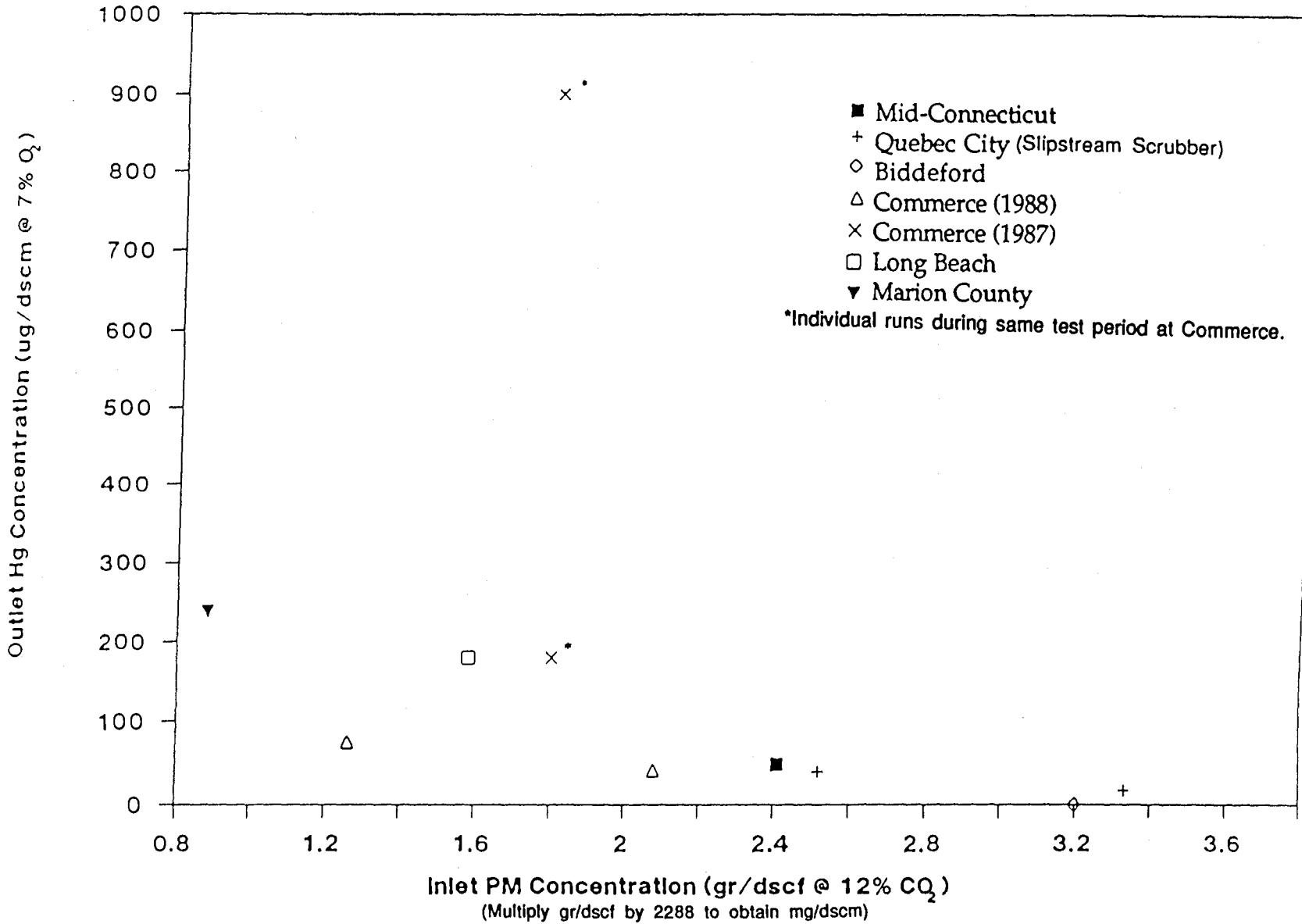


Figure 2. Relationship between outlet Hg and inlet PM concentrations for spray dryer/fabric filter systems.⁶

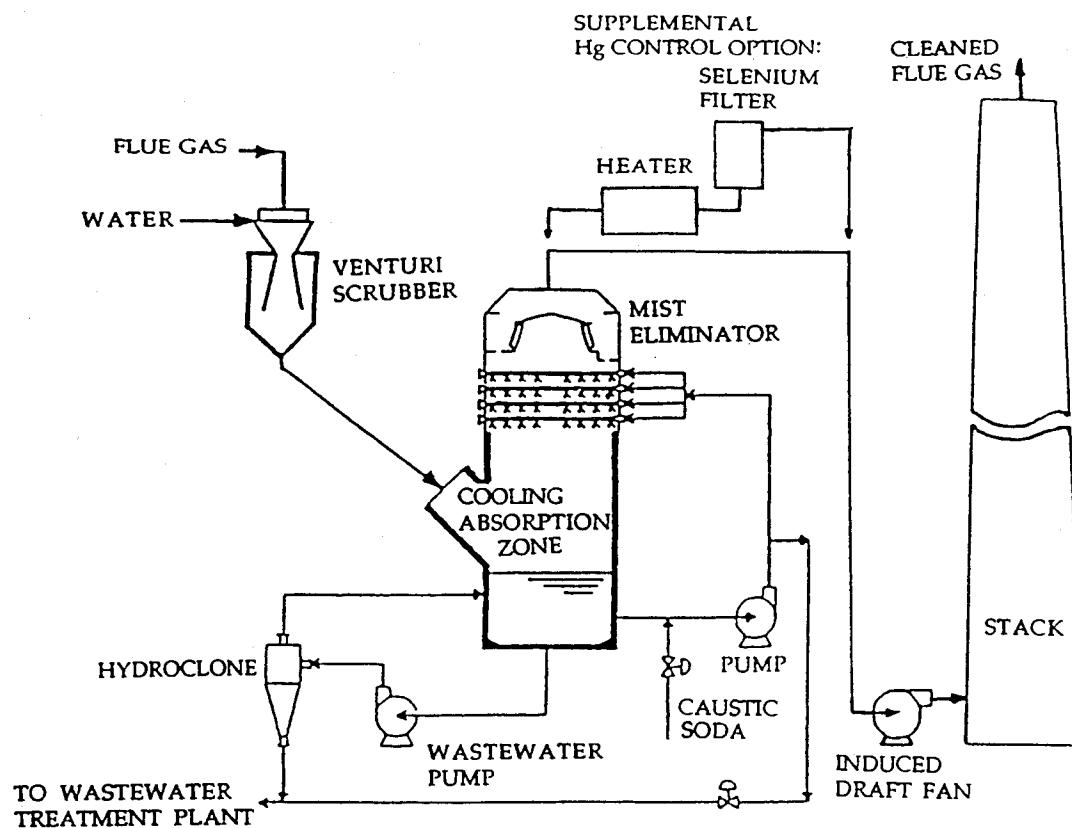


Figure 3. Wet flue gas scrubbing system.

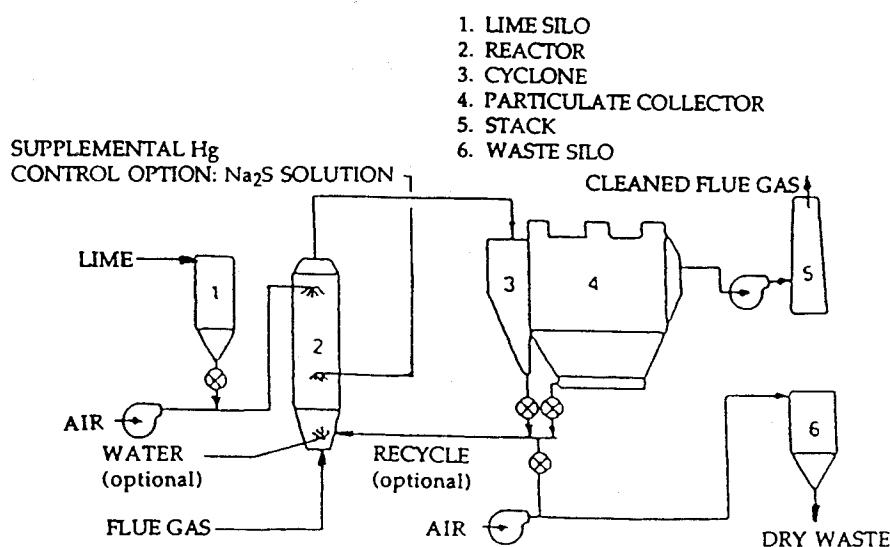


Figure 4. Dry sorbent injection into fluid bed reactor.

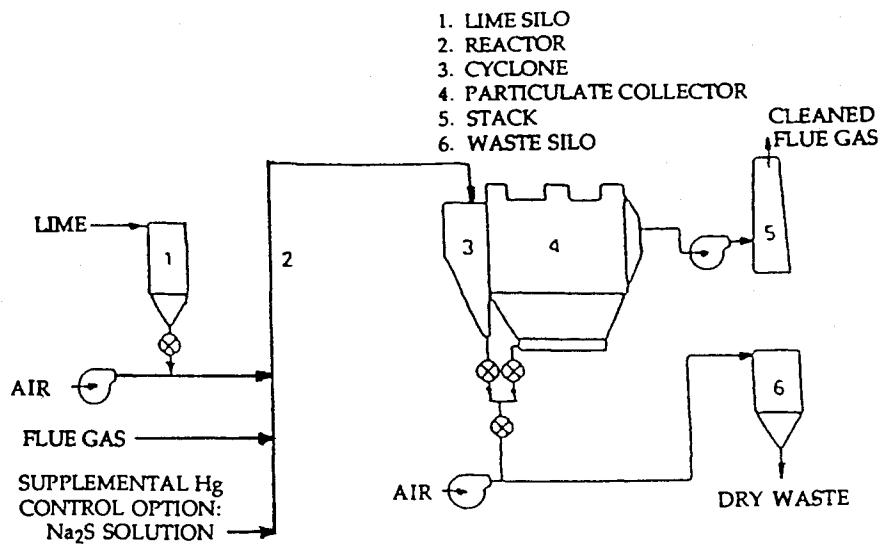


Figure 5. Dry sorbent injection process.

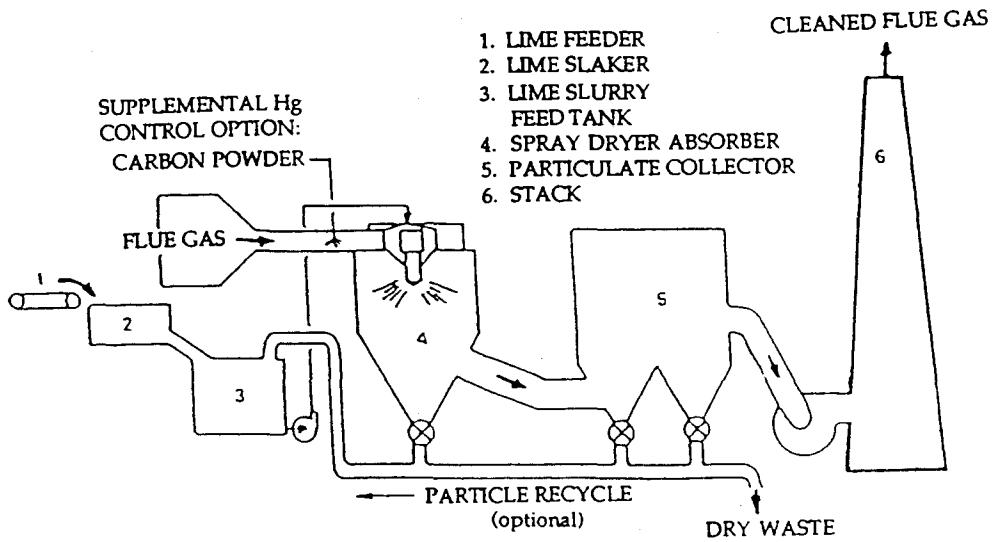


Figure 6. Spray dryer absorption (semi-dry) process.

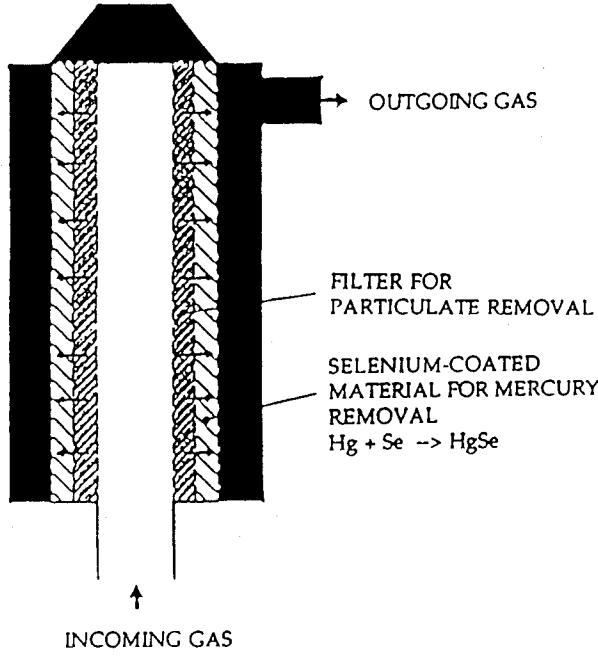


Figure 7. Selenium filter.⁷

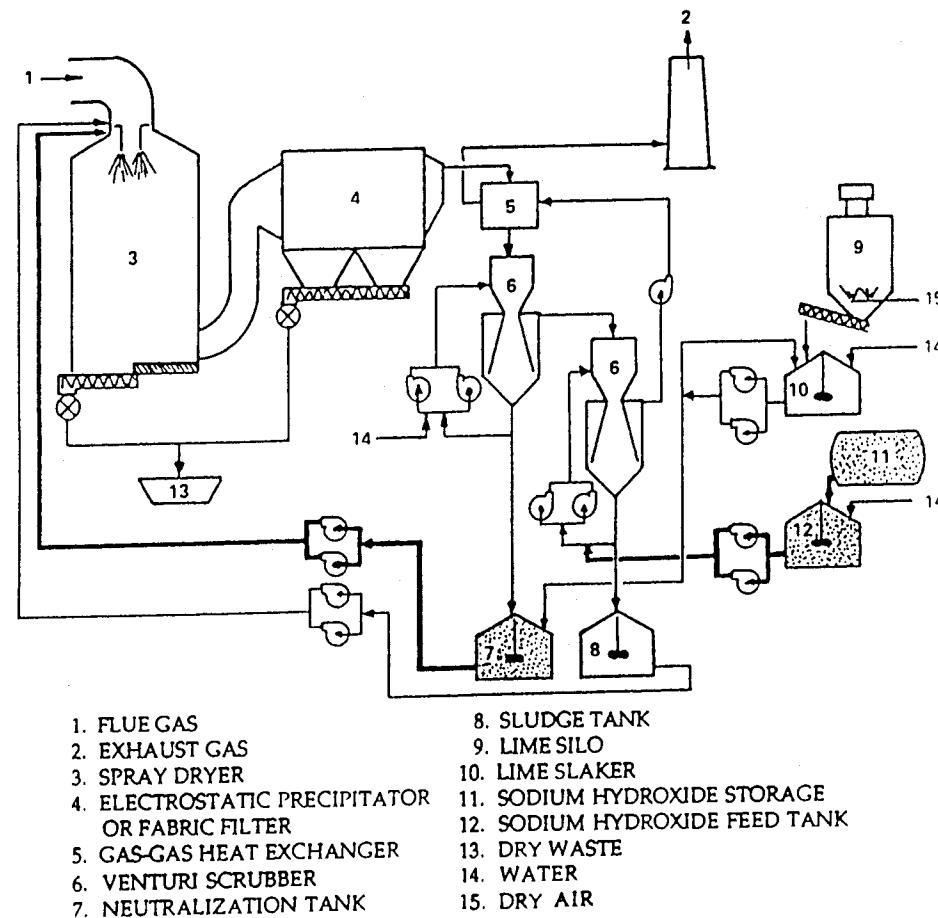


Figure 8. Wet scrubbing process with zero effluent discharge.

TABLE 1. CONTROL OF PARTICULATE MATTER (PM)
AND SELECTED HEAVY METALS WITH DRY LIME
INJECTION/FABRIC FILTER SYSTEMS

Location and Test Date	Average PM Concentration ^a gr/dscf @ 12% CO ₂	Average Concentration, µg/dscm @ 7% O ₂			Reference
	outlet	cadmium (Cd) outlet	lead (Pb) outlet	mercury (Hg) outlet	
•St. Croix, WI 6/88	0.015 ^b	2.3	18	35	6
•Springfield, MA ^c 7/88	0.0016	1	21	300	10
•Dutchess County, NY Unit 1, 2/89 Unit 2, 2/89	0.0097 0.035	2.72 3.03	38.9 49.1	1080 84.7	6

^aMultiply gr/dscf by 2288 to obtain mg/dscm.

^bNot measured simultaneously with metal, but is value from 5/88 tests.

^cAll concentrations are referenced to dry gas with 12% CO₂. Inlet PM concentration = 0.090 gr/dscf.

TABLE 2. CONTROL OF PARTICULATE MATTER (PM) AND SELECTED HEAVY METALS
WITH LIME SPRAY DRYER ABSORBER (SDA)/FABRIC FILTER (FF) OR
ELECTROSTATIC PRECIPITATOR (ESP) SYSTEMS

Location, Control System, and Test Date	Average PM Concentration ^a gr/dscf @ 12% CO ₂	Average Concentration µg/dscm @ 7% O ₂						Removal, %				Refs.
		cadmium (Cd)		lead (Pb)		mercury (Hg)		PM	Cd	Pb	Hg	
outlet	inlet	outlet	inlet	outlet	inlet	outlet	PM	Cd	Pb	Hg		
•Marion County, OR Unit 1, SDA/FF 9/86	0.0023	1,121	2.6	20,500	19	NA ^b	239	99.7	98.1	99.9	NA	6
	0.014	1,114	ND ^c	27,352	159	389	ND	99.5	NA	99.4	100	6
	0.0040	1068	NA	37,386	ND	884	50	99.8	NA	100	94.3	6
	0.0018	595	ND	7,513	52	646	8.7	99.9	100	99.9	98.7	11
	0.0018	NA	17.7	NA	278	NA	565 ^f	NA	NA	NA	NA	6
	0.0083	NA	21.5	NA	330	NA	954	NA	NA	NA	NA	12
•Biddeford, ME Unit A, SDA/FF 12/87	0.008	NA	9.53	NA	299	NA	59.1	99.8	NA	NA	NA	
	0.012	NA	6.74	NA	234	NA	105	99.6	NA	NA	NA	
•Mid-Conn. ^d Unit 11, SDA/FF 7/88 2/89 ^e	0.0018	NA	17.7	NA	278	NA	565 ^f	NA	NA	NA	NA	
	0.0083	NA	21.5	NA	330	NA	954	NA	NA	NA	NA	
•Millbury, MA Unit 1, SDA/ESP 2/88 Unit 2, SDA/ESP 2/88	0.0018	NA	17.7	NA	278	NA	565 ^f	NA	NA	NA	NA	
	0.0083	NA	21.5	NA	330	NA	954	NA	NA	NA	NA	
	0.008	NA	9.53	NA	299	NA	59.1	99.8	NA	NA	NA	
	0.012	NA	6.74	NA	234	NA	105	99.6	NA	NA	NA	
•SEMASS Unit 1, SDA/ESP 3/89 Unit 2, SDA/ESP 3/89	0.008	NA	9.53	NA	299	NA	59.1	99.8	NA	NA	NA	
	0.012	NA	6.74	NA	234	NA	105	99.6	NA	NA	NA	

^aMultiply gr/dscf by 2288 to obtain mg/dscm.

^bNot available or not measured.

^cNot detected.

^dAll concentrations are for dry gas referenced to 12% CO₂.

^eValues shown are averages for normal SDA/FF temperature operation (performance tests 6,8,12,13, and 14).

^fFrom May 1988 test.

TABLE 3. REMOVAL OF SELECTED METALS USING ADDITIVES WITH DRY SCRUBBERS

Additive: Na₂S Solution Before Dry Ca(OH)₂ Injection

Location	Date	Unit	Average Outlet Concentration, µg/Nm ³			Reduction, %			Reference
			Cadmium (Cd)	Lead (Pb)	Mercury (Hg)	Cd	Pb	Hg	
Burnaby Plant ^a Vancouver, British Columbia, Canada	1989-90	1	NA ^b	NA	117(3) ^c	NA	NA	87 ^d	13
	1989-90	2	NA	NA	127(3)	NA	NA	86 ^d	
	1989-90	3	NA	NA	155(2)	NA	NA	83 ^d	
Hogdalen Plant ^e Bandhagen, Sweden	1986	1	NA	NA	42(2)	NA	NA	89	13
	1987	1	NA	NA	26(3)	NA	NA	88	
	1988	1	NA	NA	16(3)	NA	NA	89	
	1989	1	NA	NA	4(1)	NA	NA	98	

Additive: Powdered Activated Carbon Before Lime Spray Dryer

Location	Date	Unit	Average Outlet Concentration, µg/Nm ³			Reduction, %			Reference
			Cadmium (Cd)	Lead (Pb)	Mercury (Hg)	Cd	Pb	Hg	
Josefstrasse Plant ^f Zurich, Switzerland (SDA/ESP)	1986	1	14	700 ^g	42	99	99	91	14
Range of Data ^h With Additive Without Additive	NA	1	NA	NA	20-50	NA	NA	85-93	13
NA	NA	1	NA	NA	100-250	NA	NA	20-70	13
Amagerforbraending I Amager, Denmark SDA/FF	NA	NA	NA	NA	15-25	NA	NA	90-95	13
Range of Data ^f With Additive Without Additive	NA	NA	NA	NA	<100	NA	NA	30-85	

^a Concentrations referenced to 7% O₂.

^b Not available or not measured.

^c Number of test runs shown in parentheses.

^d Inlet Hg concentration estimated at 900 µg/Nm³.

^e Concentrations referenced to 10% CO₂.

^f Concentrations referenced to 11% O₂.

^g Value for lead + zinc.

^h Concentrations believed referenced to 11% O₂.

TABLE 4. MERCURY REMOVAL WITH WET SCRUBBERS PRECEDED BY ESPs¹³

Location	Unit	Average Hg Concentration, µg/dscm @ 7% O ₂		Removal, %
		inlet	outlet	
Lyon-North Plant Lyon, France	1	370(3) ^a	<53 ^b (3)	>85
	2	177(3)	66(3)	63
Lyon-South Plant Lyon, France	1	550(2)	<65(2)	>88
	2	435(2)	<64(2)	>69
Basel Plant Basel, Switzerland	1	326(5)	19(5)	94
	2	222(1)	<19 ^c (11)	>91

^a Number of test runs shown in parentheses.^b Detection limit of 53 µg/dscm for the Lyon plants.^c Detection limit of 14 µg/dscm for the Basel plant.

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The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

Determination of efficiency of flue gas cleaning systems on Municipal Solid Waste Incinerators in Denmark.

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Abstract.

Flue gas cleaning equipment on waste incinerators to removal of acid gases, is a relative new technology in Denmark. This paper summarizes the investigations made on four different kind of equipment.

It is found that in general the plants are operating with acceptable removal efficiencies for acid gases, heavy metals and dioxins. To observe the regulation limits set up for hydrogen-chloride, some of the plants seems to have a rather high lime consumption.

Introduction.

A guideline from the Danish Environmental Protection Agency issued in 1986 requires a reduction of the emissions from municipal solid waste (MSW) incineration. The limit set for the flue gas concentration of hydrogenchloride (HCl), is at such a strict level, that most of the incinerators in Denmark have to be equipped with flue gas cleaning equipment to remove acid gases.

This type of equipment has not previously been used in Denmark and therefore we have carried out a number of investigations on the first 4 flue gas cleaning systems installed at Municipal Solid Waste incinerators in Denmark. The idea of the investigations was primarily to examine the acid gas removal efficiency when the flue gas cleaning systems were run under normal conditions.

In Denmark only a small amount (less than 10%) of the produced waste are landfilled, some waste are recycled or retrofitted, and most of the waste are burned in massburners. Therefore all MSW-incinerators in these investigations are mass-burners. The MSW-incinerators, that participated in the investigations were equipped with flue gas cleaning systems as described below.

Plant No. 1, Refa: Dry injection of lime in a simple reactor followed by an electrostatic precipitator (ESP).

MWC capacity: 3.5 t/h. Manuel regulation of lime consumption.

Plant No. 2, Kara: Injection of a limeslurry resulting in a dry residue (semi-dry process) followed by an ESP. Under normal conditions this plant are run with a certain amount of recycling of the flue gas cleaning residue to minimize the lime consumption.

MWC capacity: 7.0 t/h. Regulated by the outlet SO₂- and HCl-concentrations.

Plant No. 3, Nordforbrænding: Dry injection of lime in a reactor followed by a fabric filter (FF).

MWC capacity: 3.0 t/h. Manuel regulation of lime consumption.

Plant No. 4, Amagerforbrænding: Injection of limeslurry in a Spray Dryer Adsorber followed by a FF.

MWC capacity: 12.0 t/h. Regulated by the HCl-outlet concentration.

Test programme:

It has to be noted that different measuring programmes have been carried out at each plant which means that e.g. the conditions the plants were run under during sampling differs from plant to plant.

Plant No. 1: Acid gases (HCl, SO₂) and dioxins (PCDD + PCDF).

Plant No. 2: Acid gases (HCl, SO₂), dioxins and heavy metals (Hg, Pb and Cd).

Plant No. 3: Acid gases (HCl, SO₂) and heavy metals (Hg, Pb and Cd)

Plant No. 4: Acid gases (HCl, SO₂), dioxins and mercury.

Furthermore, samples have been extracted and analysed at plant No. 2 with the primary aim of establishing a total massbalance for heavy metals over the flue gas cleaning system.

RESULTS.

In the following, the test results are listed. Furthermore the emission values are compared to the Danish limits, set for flue gas concentrations for MWC's.

Acid gases.

Table 1 shows the result from the measurements for acid gases. It is seen that the regulation limits for emission of HCl and SO₂, set to 100 resp. 300 mg/m³(s,d), is not exceeded in any case.

The plants with the largest lime consumption are plant No. 1 and 3, which are equipped with the most simple flue gas cleaning systems. At the same time they are the smallest, and therefore a big lime consumption is not as critical as for the bigger plants, even though a stoichiometric ratio (SR) of 3-4 seems rather high.

Heavy metals.

Table 2 shows the result from measurements for lead, cadmium and mercury. The good removal efficiency (better than 90%) of lead and cadmium is due to a good removal efficiency of particulate. Analysis of the inlet measurements showed that most of the lead and cadmium are carried by the particulate.

The tests at plant No. 4 were performed with the aim to optimize the mercury absorption. It is shown that use of activated carbon as additive had a positive effect on mercury removal. Increasing amount of activated carbon resulted in decrease of mercury emission. A decrease in outlet temperature resulted in lower mercury emission both with and without additive.

It is seen that the regulation limits for emission of lead, cadmium and mercury, set to 1.4, 0.1 resp. 0.1 mg/m³(s,d) is only exceeded in one case, it is the mercury emission from plant No. 2. It seems to be due to the poorest removal efficiency.

Dioxin (Total Dioxins and Furans).

The removal efficiencies were in general good, e.g. plant No. 1: 85% removal, plant No. 4: 98% removal and Plant No. 3: no tests.

At plant No. 2 there were found a poorer efficiency (65% removal). The only condition that differs this plant from the others are the amount of recycling of the flue gas cleaning residue. This has not to be regarded as a proof for the poorer efficiency.

As well as for mercury, at plant No. 4, there were performed tests with the aim to optimize the dioxin absorption. It is seen that an outlet temperature at 127°C the outlet values seems to be lower than comparable tests with an outlet temperature at 140°C. The highest removal efficiencies were obtained with addition of additive (activated carbon), no significant influence of the amount added could be established.

Massbalance.

At plant No. 2 samples have been extracted in such way that it has been possible to establish massbalances for lead, cadmium and mercury. All massflow are determined by flue gas measurements and calculations, because of that it should be acceptable with a difference in the massbalance within 25%.

The massbalances are shown in table 3. The balances for cadmium and mercury are established within the acceptable difference. The reason why the difference in the massbalance for lead is as big as 88% has not been identified. It is important to notice that the 3 balances has been established with a negative difference, which might indicate a systematic but not identified error.

Conclusions.

It is found that the examined plants, which are the first of their kind in Denmark, in general are operating with acceptable removal efficiencies for acid gases, heavy metals and dioxins. To observe the regulation limits set for different emissions, some of the plants seems to have a rather high lime consumption. In general it is seen that the limits is not exceeded.

We have succeeded in establishing acceptable massbalances for cadmium and mercury at one of the plants. Of some not identified reasons the massbalance for lead is not acceptable.

References.

Kirsten Kragh Nielsen: Optimization of dioxin removal by semi-dry flue gas cleaning on full scale incinerator. A/S Niro Atimozer, Søborg, 1989.

Miljøstyrelsen: Dioxinemission from waste combustion (In Danish, English summary available), 1989. (Some of the results were presented on DIOXIN '89, Toronto).

Table 1: Values for efficiency, emission concentration and lime consumption (Stoichiometric Ratio) for acid gases.

Plant No.	Efficiency %		Emission mg/m³ (s,d)		S.R
	SO ₂	HCl	SO ₂	HCl	
1	-	83	-	50	3-4
2	80	96	40	22	0.9
3	47	90	68	26	~3
4	69	96	170	35	1.5

Table 2: Values for efficiency and emission concentration for heavy metals (Lead, Cadmium and Mercury).

Plant No.	Efficiency %			Emission mg/m³ (s,d)		
	Pb	Cd	Hg	Pb	Cd	Hg
1	-	-	-	-	-	-
2	92	90	54	0.9	0.078	0.054
3	>99	>90	44	<0.8	<0.022	0.13
4	-	-	66*	-	-	0.066*

*: Some tests were performed with an additive to the lime.

Table 3: Massbalance for Lead, Cadmium and Mercury. Performed at plant No. 2. Unit: g/h.

	Pb	Cd	Hg
Inlet			
Flue gas	464	33	5.0
Lime	1	~0	~0
Total inlet	465	33	5.0
Outlet			
Flue gas	40	2.6	2.1
Residue (from ESP)	836	37	3.4
Total outlet	876	40	5.5
Difference*	-88%	-21%	-10%

*: Difference = (Inlet + Outlet)/Inlet

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

TWO-AND-A-HALF YEARS OPERATING EXPERIENCE

AT THE

WARREN COUNTY ENERGY RESOURCE RECOVERY FACILITY

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ABSTRACT

The Blount Energy Resource Corporation's Municipal Waste Combustion Facility located in Warren County, New Jersey, consists of two 200 ton/day boiler units equipped with a spray dryer/baghouse system for acid gas and particulate control. This state-of-the-art resource recovery facility was the first of its kind to be built and started-up in New Jersey, and it has presently been operating for about two-and-a-half years. Design features and operational history of the air pollution control system supplied by Environmental Elements Corporation is described in this paper. Following a successful start-up of the facility the initial stack compliance and flue gas cleaning system performance tests for hydrogen chloride, hydrogen fluoride, sulfur dioxide, and particulate were conducted in November 1988. The test demonstrated that the system passed all emission and performance requirements. Two yearly compliance tests have been performed since this initial testing, demonstrating continued compliance of the system in terms of acid gas and particulate emissions. Also, a series of metals stack measurements have recently been performed aiming at evaluating the potential emissions of mercury and other metals from the facility. The test results are presented and discussed.

INTRODUCTION

The present paper describes the air pollution control (APC) system installed at the waste-to-energy facility located in Warren County, NJ. This state-of-the-art facility was the first of its kind to be built and started-up in New Jersey. The facility was also the first waste-to-energy plant to be awarded to Blount Energy Research Corporation (Montgomery, AL) in the United States. The air pollution control system comprising lime spray dryer and pulse-jet baghouse was awarded by Blount to Environmental Elements Corporation (EEC). This was EEC's first municipal solid waste (MSW) contract with total responsibility for acid gas and particulate control. EEC contracted with Komline-Sanderson Engineering Corporation, Peapack, NJ to supply the rotary atomization and spray drying technology essential for achieving acid gas control. Total process responsibility resided with EEC. Although EEC had experience for operating MSW facilities using electrostatic precipitators for particulate control, this was for EEC the first opportunity to use its established pulse-jet fabric filtration technology on this particular application. The waste-to-energy facility has now been operated by Blount Energy Resource Company for more than 2½ years and the APC system has shown very satisfactory performance. The design and the operating experience of the APC system is described in the following.

WASTE-TO-ENERGY FACILITY DESIGN

COMBUSTOR/BOILER

The Warren County waste-to-energy facility consists of two (2) 200-ton/day boiler trains equipped with Widmer+Ernst horizontal grates. Each boiler is sized for the production of 56,000 lb/h of steam which is used for the generation of 13 MW electricity. The facility uses 2 MW to support its own operation.

AIR POLLUTION CONTROL SYSTEM DESIGN CRITERIA

Each boiler is equipped with an APC system consisting of a lime spray dryer for acid gas removal followed by a pulse-jet baghouse for particulate control. A flow diagram of the APC system is shown in Figure 1. It is sized for a flue gas flow at maximum continuous rating (MCR) of 51,000 acfm (320°F), or 153,000 lb/h. The APC system is designed for boiler exit flue gas temperature excursions up to 500°F and will maintain stack temperatures at 265-285°F under all boiler operating conditions.

The expected acid gas concentrations in the flue gas exiting the boiler are 500-900 ppm hydrogen chloride (HCl), 40-50 ppm hydrogen fluoride (HF), and 150-450 ppm sulfur dioxide (SO₂) (all dry volume corrected to 7% O₂). The required removal performance of the APC systems is for HCl 95%, or a stack concentration of 25-45 ppm, whichever is less stringent; 95% HF removal; and 90% removal of SO₂, or a stack concentration of 40 ppm, whichever is less stringent. The required maximum particulate stack emission is 0.01 gr/dscf (7% O₂).

In addition to these emission guarantees three process performance guarantees were also provided by EEC. The lime consumption guarantee for the above specified conditions was typically in the range 295-480 lb/h (total for two boiler trains) corresponding to an equivalence ratio (ER) of 1.4.

The equivalence ratio, is here defined as

$$ER = \frac{2 \times (\text{lb-mol/h of CaO})}{\text{lb-mol/h of HCl} + \text{lb-mol/h of HF} + 2 \times (\text{lb-mol/h of SO}_2)}$$

A total APC system power consumption guarantee of about 85 kW, and a pressure drop guarantee of 10.0 in.WG were also offered.

As to specific equipment warranties it should be mentioned that a 24-month useful bag life guarantee and a 6 to 9-month useful life guarantee of the atomizer inserts (protecting against erosion by the abrasive slurry) were provided.

AIR POLLUTION CONTROL SYSTEM DESIGN FEATURES

The APC system can for clarity be divided into three major components, namely the spray dryer absorber (SDA) (including the rotary atomizer), the pulse-jet filter (PJF), and the lime storage and slurry preparation system. The SDA's and the rotary atomizers were designed and fabricated by Komline-Sanderson Engineering Corporation in Peapack, NJ. The PJF's (including associated ductwork, access, etc.) were designed and fabricated by EEC in Baltimore, MD. The common lime storage and slurry preparation equipment was supplied as a complete package by Chemco Equipment company in Pittsburgh, PA.

SPRAY DRYER ABSORBER

The spray dryer vessels are designed as downflow, single-rotary-atomizer units with a 22-ft diameter and a 28-ft cylindrical height section equipped with a 60° bottom cone. A schematic of the SDA is shown in Figure 2.

The hot flue gas exiting the boiler is ducted to the roof of the SDA and turned vertically downward along the centerline of the vessel, surrounding the approximately 18-inch diameter central tube enclosing the rotary atomizer assembly. Swirl vanes located immediately above the atomizer provide for some rotation of the flue gas as it exits this annular gas disperser and contacts the cloud of finely atomized slurry droplets. A uniform distribution of the flue gas around the atomizer as well as an adequate gas velocity and direction are essential features for achieving satisfactory initial drying conditions. The swirling flow of gas with entrained droplets continues down through the cylindrical vessel and is inverted in the cone section prior to the gas exiting via the single duct located in the side of the cone. The excellent conditions for simultaneous heat and mass transfer in the vessel result in the reaction between alkaline slurry droplets and acid components in the gas during the evaporative cooling process. The end result is that the cooled and dry flue gas (typically at a temperature of 265-285°F) with increased moisture content exits from the vessel, and a free-flowing, dry solid of flyash, salt (mainly calcium chloride and calcium sulfite/sulfate) and unused lime is generated.

Part of the dry solids is discharged from the spray dryer cone bottom, but most is entrained with the flue gas to the downstream located particulate collector. As the potential for wet wall deposits as a result of insufficient slurry drying was an occasional concern a motorized lump breaker was included at the cone discharge. This device would serve to break up any non-powdery product being discharged and avoid problems in the conveying system.

A schematic of Komline-Sanderson's rotary atomizer, Model 860 is shown in Figure 3. The rotary atomizer consists of a water-cooled variable-speed 60-HP-drive motor controlled by a frequency inverter, eliminating the need for a gear box. A fine mist of oil is carried on a stream of compressed air to the upper and lower bearings of the rotor assembly. Interlocks protect the assembly against loss of compressed air flow, low oil level in the mist generator, or loss of water flow to the water jacketed stator. All connections to the atomizer (oil mist, water, electricity) are through one central terminal stand which is located in the penthouse on top of the SDA roof. The speed of the atomizer is controlled by the frequency inverter with a thumbwheel adjustment for variation of the wheel speed. This feature provides for tuning for best system

performance and optimization of energy consumption. This adds process and operating flexibility that would be difficult to achieve with a constant-speed type of atomizer. Typical operating speed for the present process application is 14-15,000 rpm.

The atomization of the lime milk slurry in the atomizer unit is accomplished by its acceleration in the light-weight rotating 7.5-inch-diameter wheel (fabricated of titanium) to which the lime slurry is gravity fed from the head tank. The atomizer wheel is equipped with tungsten carbide inserts (for abrasion resistance) and is mounted on the "rigid" shaft (see Figure 3).

The atomizers were fitted with vibration monitors to provide an early warning system against imbalance. However, no significant potential for vibration problems are expected with this atomizer type. This is due to the unique feature of a "rigid" spindle shaft and a light-weight wheel body which makes the rotating assembly less prone to vibration than most other types of rotary atomizers. The wheel body is manufactured of titanium, as mentioned above, and the entire spindle shaft length is only 19 inches, of which less than 4-1/2 inches extends beyond the lower bearing. These two design considerations result in a rotating assembly which operates well below the first critical speed.

A hoist is provided inside the penthouse for removing or placing the atomizer in service. A spare atomizer assembly, common for both boiler trains, is also provided. This arrangement allows for easy replacement of an atomizer unit within a relatively short time period, i.e. approximately 20 minutes.

PULSE-JET FABRIC FILTER

Each boiler train is equipped with a four (4)-compartment PJF downstream of the SDA for particulate control. A schematic of the PJF is shown in Figure 4. Each compartment houses 210 woven fiberglass bags with Burlington-373 chemical resistant finish, each bag being 6 inches in diameter and 14 ft long. The PJF is designed for off-line cleaning, using a gross air-to-cloth ratio of 2.7 ft/min (all four compartments in service), and a net air-to-cloth ratio of 3.6 ft/min (one compartment in the cleaning mode). Each compartment consisting of housing with tube plate (separating dirty and clean gas side), pyramidal hopper and compressed air manifold and distribution system is shop assembled as an individual module (approximately 12 ft x 12 ft x 40 ft) and shipped to the jobsite for easy erection.

The four baghouse modules are connected to the inlet and outlet manifolds. The EEC baghouse design incorporates a patented stepped inlet manifold and a patented hopper vaning arrangement which assures improved flow balance and even dust distribution among compartments and among filter bags within each compartment (see Figure 4). The uniform gas distribution and low turbulence result in a low mechanical pressure loss (the mechanical pressure drop is less than 1.0 in.WG at all operating loads). Hopper vaning assures good gas and dust distribution to all the bags resulting in increased bag life by elimination of potentially damaging high local velocities and dust loadings.

While many different cleaning modes can be used, the recommended procedure is to clean the bags off-line. This mode of cleaning eliminates dust reintrainment and promotes longer bag life. Cleaning can be initiated manually, on a timed cycle basis, or by a preset pressure drop across the PJF.

Each compartment has 15 pulse pipes, each pipe cleaning a row of 14 bags by supplying a pulse of 60-80 psig compressed air from the compartment manifold via a solenoid-activated diaphragm valve. The entire cleaning sequence for one compartment (15 pipes) is of a 3-minutes duration.

The baghouse is of a walk-in plenum type of design, i.e. each clean-air plenum above the entire compartment tubesheet is tall enough to accommodate the full bag length (14 ft). This plenum is entered by a single door and bag removal, inspection and replacement can conveniently be done regardless of weather conditions. There is no reason to enter the dirty side of the compartment to replace bags. Once the pulse

pipe just above the tubesheet is disconnected each bag and cage assembly is inserted through the 6-inch diameter openings in the tube plate and retained by the top flange of the cage.

The 55°-valley-angle hoppers include electrical heaters (for maintaining up to 400°F inside surface temperature in the lower section), level detectors, vibrators, as well as poke holes and strike plates immediately above the 12-inch diameter hopper discharge flange. Rotary airlock valves are included between each hopper flange and the mechanical conveying system. The conveying system is conservatively designed (not EEC scope) and is not provided with heat tracing.

A flue gas bypass system is included for use during boiler start-up on No. 2 fuel oil. Also, a separate hydrated lime injection system consisting of a day bin, feeder, blower and piping to the PJF inlet manifolds, intended for pre-coating bags prior to garbage burning, was supplied.

LIME STORAGE AND SLAKING SYSTEM

The lime system was designed and shop assembled as a separate by Chemco. This approach allows for extensive shop testing of the separate components and easy field installation. This system measures 13 ft in diameter and has a total height of about 55 ft when installed in the field. The relative arrangement of equipment inside the lime system enclosure is indicated on Figure 1.

The quicklime storage silo is designed for truck delivery, and its 13 ft diameter and 14 ft cylindrical height provides a capacity of 60 ton, corresponding to an inventory of about 10 days of reagent at the maximum consumption rate. The silo has a 60° conical hopper equipped with a 5-ft bin activator for discharge into one slaker unit via a volumetric feeder. The slaker is a Wallace & Tiernan paste type unit with a capacity of 1000 lb/h, which is about 200% of the maximum process consumption rate. This unit is designed for slaking at a low water-to-lime ratio resulting in a high temperature (180-200°F) and efficient conversion of quicklime (CaO) to hydrate [Ca(OH)₂]. The slaker always operates at its rated capacity in an on/off type of mode responding to the process demand (see below). Well-water with no water pre-heating is used for slaking, and grit is removed immediately downstream of the unit by a 20-mesh Sweco screen discharging into a dump container via a 5-inch screw conveyor located inside the enclosure. The slaked and screened lime with a solids content of about 22% is stored in the 2,850 gallon agitated slurry tank providing a total supply of about 8 hours at maximum rated conditions. Low and high level switches at intermediate levels automatically start and stop the slaker, typically every one to two hours, to ensure that a reasonable inventory of slaked lime slurry is maintained.

A slurry bleed valve gravity feeds the 22% lime slurry to the lime dilution tank located at grade. Dilution of the lime slurry to the actual concentration level required by the flue gas cleaning process is done here, typically to 5-10% solids. This tank has a capacity of about 450 gallons of lime slurry to be fed to the two spray dryers, representing a slurry retention time of 15-60 minutes.

The diluted lime slurry is pumped from grade to the two head tanks located in the spray dryer penthouses. One pump for each spray dryer is transferring the lime slurry via 1-inch diameter steel pipes at typical velocities of 7-9 ft/sec, with an overflow return from the head tank to the diluted lime milk tank at grade. The 30-gallon head tank provides a small diluted lime inventory of about 2-8 minutes and primarily serves the purpose of ensuring a constant head to the feed control valve for gravity feeding the lime slurry to the atomizer.

PROCESS INSTRUMENTATION & CONTROL SYSTEM

The operation of the flue gas cleaning system is controlled and monitored by a Bailey Network 90 Distributed Control System. Local I/O panels & PLCs with residing control logic for the APC system were provided by EEC, and were tied in to the plant computer with terminals including monitors and keyboards located in the central control room. This provides for operation (start-up, shut-down, adjustment of setpoints, etc.) of the APC system from a central location with all required process readouts available.

The key operational parameter for the APC system is the flue gas outlet temperature from the SDA which normally is controlled in the range of 265-285°F. This temperature set-point is used for controlling the flow of lime slurry to the atomizer. A temperature lower than 265°F may lead to insufficient drying of the hygroscopic calcium chloride salt formed by the reaction between lime and HCl. Insufficient drying would result in solids deposits in the spray dryer vessel and/or build-up of moist powder in the baghouse, typically leading to high fabric pressure drops or product accumulation in the hoppers (moist product has poor flowability). On the other hand, a temperature higher than about 300°F may lead to insufficient acid gas control, specifically of the reactive SO₂, or to an excessive lime consumption rate when aiming at maintaining acid gas emission compliance.

The actual solids content of lime in the slurry to the atomizer is adjusted by the operator based on SO₂ data from the plant's Continuous Emission Monitoring (CEM) system. The acid gases HCl and HF are not monitored continuously as efficient control of SO₂ is known to result in even more efficient removal of these two gases.

Depending on the flue gas flow rate and available exit temperature from the boiler the water evaporation rate in the spray dryer may vary significantly, typically in the range from 3 to 15 gpm per unit. The rotary atomizer frequency inverter control system maintains constant wheel speed for all conditions, and changes in the lime slurry flowrate to the unit therefore results in proportional changes in the power consumption (kW). However, the specific power consumption (kW/lb slurry) remains constant, resulting in uniform atomization energy and uniform process performance throughout the operating range.

The control system gathers all relevant operational and emission performance data. A history capability for the last 26 hours of data exists which is a useful tool for following the most recent trends. All data is downloaded once a day on permanent storage for future reference.

OPERATIONAL HISTORY

SPECIFIC START-UP ISSUES

Initial start-up of the waste-to-energy boiler Unit #1 occurred on July 3, 1988. Detailed procedures for start-up of the flue gas cleaning system were developed and instituted. The boiler uses No. 2 fuel oil for start-up, but the fabric filter could not be by-passed during this initial phase as garbage would be introduced onto the grates as soon as a satisfactory furnace temperature was reached. To protect the filter bags against any acid gas attack, hydrated lime was pneumatically injected into the PJF inlet manifold during garbage combustion at the rate of 200 lb/h per unit from the installed precoat system. This was in addition to the approximately 2,000 lbs of hydrated lime which had been used for initial precoating. Once the SDA inlet temperature reached 320°F normal scrubbing using lime slurry spraying was initiated and the hydrated lime injection stopped.

Boiler Unit #2 was started-up a few weeks later.

A couple of upset conditions occurred during the initial weeks of operation which are worth discussing. During normal garbage combustion on July 12, the spray dryer outlet temperature was inadvertently lowered to 240°F by water spray only (no lime). This resulted in an increase in the tubesheet differential pressure of 3 to 4 in.WG which could not be reduced by the normal cleaning process of the PJF.

The filter bags were then individually air-lanced by manually inserting a section of copper tubing with radially drilled holes connected to a compressed air supply into each bag. The entire operation was carried out one module at a time while the remainder of the baghouse was operating. The PJF operation returned to normal conditions after completion of this procedure as evidenced by the establishment of the original pressure drop across the bags.

The second upset condition occurred on July 23. While the boiler was on fuel oil operation, the external economizer was brought in service for the first time. Lime slurry spray reduced the gas temperature across the SDA from 340°F to 300°F and the system operated in this mode for 16 hours. For reasons not completely understood an increase in differential pressure was observed , and again air-lancing was used to return the filter bags to normal conditions.

Selected filter bags from the facility start-up have been analyzed, including those which had gone through the described upset conditions. The results of this analysis are presented in Table 1.

It appears that the upset conditions described resulted in a quick loss of the fabric permeability. However, the permeability could be partly restored by the air-lancing operation (comparison of bags A and B in Table 1 - bag C's permeability cannot be directly compared as it has been in operation for 2-3 months). Somewhat surprisingly, the bag which experienced upset conditions, but was not air-lanced (bag A) seems to have less than a normal amount of attached dust, but a quite high moisture content. All these data seem to verify the hygroscopic nature of this product and particularly the impact of upset conditions. Also, it seems important to note that the adverse results of upset conditions on the fabric bags may be reversed such as by the manual air-lancing procedure described.

ROUTINE OPERATION

During the first year of operation the APC system operated with virtually 100% availability. Since then the system has shut down on 2 to 3 occasions due to electrical or control problems which appear to have been related to an incident when the plant was struck by lightning.

The current mode of operation of the APC system which has been selected by the plant is primarily aiming at maintaining compliance with an adequate margin of safety in SO₂ emission limits, and maintaining a fairly constant generation rate of waste product. This mode is characterized by the following two major points:

- The atomizer runs with a constant slurry density of 10% solids. The typical outlet temperature is 265-285°F. In the event of a spike in the inlet SO₂ concentration occurring, operators may lower the SDA outlet temperature in increments of 5°F. This provides additional lime slurry for scrubbing purposes.
- The baghouse cleaning cycle is operated on a time basis to maintain a fairly constant pressure drop across each module of 7 to 9 in.WG. This provides a uniform flow and composition of the waste product.

COMPONENT HISTORY

Lime Storage/Slaking System

Although somewhat plagued with problems that appear to be characteristic for these fairly compactly designed systems, such as high maintenance and dirty working conditions, the system continues to provide lime slurry at the required capacity with only minor equipment modifications.

Level indicators on the lime silo have had numerous problems, and the plant personnel maintain a visual inspection of the level of lime through the silo roof hatch. A fresh load of 20-22 tons of quicklime arrives approximately every three days. Problems with the opening of the silo relief valve during periods of loading with lime have been traced to improper operation of the exhaust on the bin vent filter.

The possible addition of a spare slaker is by the plant regarded as a desirable luxury for improving the maintenance situation, even though the existing single slaker is sufficient to meet the present consumption rate (even at higher than design usage rates). Good slaking operation has been partially attributed to a decision to switch to and maintain supply of a high-quality pebble lime shortly after start-up. Other areas of the slaking operation have, however, necessitated improvements. The slaker aspirator now uses air instead of water and further improvements are being considered relative to ventilation. The slaker is manually washed out after each slaking cycle to prevent build-ups of lime and grit. The grit screen has been replaced once in over two years of operation. Currently a 20-mesh screen is used. Additionally, 6"-donuts constructed of $\frac{1}{4}$ " rubber tubing are placed on top of screen to prevent build-up of solids.

The density monitors on the slurry feed tank have at times provided unreliable inputs, and operators now manually take two samples per shift to verify solids content of the slurry.

Slurry Pumps, Valves and Piping System

Pinch valves are used for slurry control and all original valves are still in service. Two slurry pumps have been replaced as this was determined to be more cost effective than rebuilding the old pumps.

The primary slurry handling problems are associated with pluggage of the lime slurry supply and return piping. Solids deposits in the piping became an apparent problem 1½ years after initial operation and the pipes now require close monitoring and cleaning with acetic acid during each outage.

A decision has been made to replace the normal slurry steel piping with heat-traced, impregnated hose within the near future. It is felt that maintenance will be easier and disassembly of the components will also be quicker, should replacement be necessary.

A cyclonic separator originally installed in the slurry supply line to the head tank never performed properly in terms of removing oversize particles and it has been replaced with a dual-basket strainer in the line between the head tank and rotary atomizer. A cross-over line between the two head tanks has also been added. This provides for additional redundancy if a sudden pluggage occurs in one of the supply lines, and also makes on-line maintenance of the individual supply and return lines possible.

Spray Dryer Absorber

There have been no deposits on the internal surfaces of the dryer vessels. An inspection after 2½ years operation revealed only a slight, uniform coating on the walls. In fact, the lump breaker originally installed at the hopper discharge has been removed. The dryers routinely operate with an outlet gas temperature as low as 260°F, and have exhibited no drying problems.

Rotary Atomizer

The atomizers have performed well albeit with a few modifications. Each atomizer wheel is water-flushed daily (on-line) and cleaned in a muriatic acid bath once per week (off-line). The spare wheel is put in service while the wheel is acid cleaned. The tungsten carbide inserts have performed consistently for one-year intervals before replacement is required. Likewise, the wheel bottom wear plates are replaced at one-year intervals. A maintenance agreement exists with Komline-Sanderson to replace all wear parts once each year and to perform general service on the atomizers.

The vibration detectors experienced interference as a result of external electrical noise and required adjustment. Early minor lubrication problems have been resolved with a slightly redesigned lubrication system.

Malfunctions associated with the frequency inverter are believed to be the result of an incident when the plant was struck by lightning as mentioned earlier. In one case the choke coil, which filters the incoming current into the DC bus, had been short-circuited and was replaced.

Pulse-Jet Fabric Filter

Initially the PJF used a batch cleaning method based on pressure drop. Once cleaning was initiated, individual modules were cleaned off-line and returned to service with only a 15-second delay before the next module was cleaned. The overall cleaning cycle would only be 12-15 minutes. The system now employed uses a 7-minute time delay between modules and a 15-minute delay between cycles, resulting in an overall cleaning cycle of 55-60 minutes. This time delay cycle maintains a fairly constant pressure drop of 7-9 in.WG across the PJF, and results in a quite uniform dry waste conveying rate.

The filter bags on Unit #2 were replaced in November 1990, while replacement of those on Unit #1 took place in March 1991. The original galvanized cages were not replaced. Both replacements were performed during a scheduled outage, but were not the result of bag failures. It was felt that the bags were near the end of their useful life, and there was concern about the shelf life of the spare bags which had been in storage since 1988.

The results of a recent analysis performed on filter bags removed from Unit #1 are listed in Table 2. The independent testing laboratory concluded that the analysis for strength retention (breaking strength, Mullen Burst, and flex cycles) show no evidence of either chemical or thermal degradation. There was no visible evidence of any internal migrated particulate into the inner fabric. Under pulse impact the bags demonstrated high discharge properties and good flow recovery, even though the residual dust did exhibit some moisture induced agglomerations. There was evidence of contact with corroded cages, however the level of damage was minimal. These bags were projected by the test laboratory to have 20 additional months of continuous service life.

The PJF on Unit #1 experienced one upset condition besides those reported during initial start-up. In June of 1989 a spike in opacity occurred and it was observed that one of the module hoppers had filled up with ash to the extent that the bags within that module became buried in dust to a level near the tubesheet. It was noted that the high opacity was due to holes in a bag near the gas inlet, presumably due to the high gas velocity caused by the restricted flow conditions.

There have been a total of 10 bag failures during 2½ years of operation on the two boiler trains. Good service life is believed attributable to a number of factors, such as:

- An excellent preventative maintenance program by plant personnel. Hopper poke holes are checked once per shift for draft, and corrective action is initiated immediately if a problem exists. There has been only one incident of an ash-filled hopper, as reported above.
- Good and consistent operating practices: Bags are precoated prior to each cold start, and hopper heater thermostats are set at 400°F.
- Close adherence to start-up procedures.
- A design using a quite tightly fit between bag and cage. Although the cleaning action may be less efficient with a tightly fitting bag, long bag life is achieved. It appears that this is accomplished with only a minor sacrifice in terms of slightly higher pressure drop.

GENERAL DESIGN ISSUES

A number of improvements have been incorporated into EEC's design of SDA systems for future waste-to-energy plants, largely as a result of operating experiences at Warren Energy Resource Company.

Dilution of the lime slurry in EEC's new design will take place in the head tank. This will provide a faster response to variation in inlet acid gas conditions. It is also anticipated that solids deposits in the slurry piping will be minimized, since the majority of the slurry piping will be handling a higher lime slurry solids content. Also, slurry piping less than 2½ inches will be avoided or minimized. Dual-basket strainers will always be included in the slurry lines between the head tank and the atomizer and in the slurry return lines.

The Komline-Sanderson rotary atomizer has incorporated only minimum basic design changes. However, an enhanced cooling system has been introduced thereby significantly improving motor efficiency and allowing for a 50% increase in atomization capacity. The bearing and motor winding temperatures have been lowered through a water purge to the shaft and wheel. Monitoring of the motor winding temperature has been added, along with a once-through, forced oil lubrication system, and a self-locking wheel-to-shaft assembly. A program to evaluate the performance of the new atomizer design at the Warren County Facility is planned for April, 1991.

Evaluation of the original filter bags is currently in progress. An analysis of the periodic fabric test reports demonstrates good service life of the bags and satisfactory ability to withstand upset conditions. The chemical resistant finish (Burlington-373) shows promise, although a direct comparison with bags provided with a typical Acid Resistant or a Teflon B finish has not been made. The collection efficiency of the fabric, as shown later by the emissions test in Section V, is excellent. Although the particulate generated from a municipal waste combustor followed by a lime spray dryer is very hygroscopic and appears to have a tendency to become agglomerated on the fabric, the fabric pressure loss is maintained at a constant level, albeit higher than most other applications.

TEST RESULTS AND EMISSION PERFORMANCE

PERFORMANCE TESTING OF APC SYSTEM

After successful start-up and initial operation of the waste-to-energy facility in the summer and fall of 1988 Environmental Elements conducted the APC system compliance and performance test program in

November of 1988. Clean Air Engineering (Palatine, IL) was contracted to do all field sampling and analysis. Blount operated the facility during the two days of testing with EEC representatives in an advisory capacity. All relevant operational data was collected, specifically flow rates, temperatures, pressures, and lime consumption rates and evaluated together with the analytical results of gas sampling (providing gas flowrates, composition, and pollutant concentrations), and slurry sampling (providing lime slurry composition). Three test runs were performed on both boiler Units #1 and #2, and the results averaged for each unit. The most important test results are presented in Table 3.

The equivalence ratio (ER), or the ratio between lime input and acid gases exiting the boiler, is a key parameter for the removal performance of the SDA/PJF system (see previous section for the definition of ER). HCl, the most significant of the acid gases, is not monitored continuously and the actual ER at any given time is therefore not available to the operator of the facility. A typical operational approach is to always add a comfortable margin of lime slurry in order to ensure compliance at all acid gas conditions.

About 238 lb/h quicklime was added to Unit #1 during performance testing. As the measured HCl inlet concentration was relatively low [about 450 ppmdv (7% O₂)] the actual ER exceeded 2 and resulted in significantly higher SO₂ removal than required for compliance (in excess of 99%, vs. 90% required). When testing on Unit #2 a clearly higher average HCl concentration into the spray dryer was measured. As the lime input was of the same order of magnitude as during testing on Unit #1 a lower actual ER resulted on Unit #2. The calculated ER of 1.4 is in line with the lime consumption guaranteed for this facility, and as Table 1 shows, all acid gas removal efficiencies meet the performance requirements (95% for HCl and HF, 90% for SO₂).

The measured particulate stack emissions of 0.0017-0.0031 gr/dscf (7% O₂) is comfortably below the maximum emission requirement of 0.01 gr/dscf. However, the measured pressure drop across the APC system of 9.8-10.4 in.WG is very close to the guaranteed value of 10 in.WG. It may be noted that the actual gas flow into the spray dryer appears to be 5-10% in excess of the MCR design value which would explain the slightly higher than predicted pressure loss.

All test results documented that the APC system had satisfied the performance guarantee which had been provided by EEC when supplying the system.

YEARLY COMPLIANCE TESTING AND EMISSION RECORDS

Acid gas and particulate emission data have been collected by independent stack sampling companies for Blount Energy Resource Corporation in 1988, 1989, and 1990 serving to verify continued emission compliance of the facility. These data are presented in Table 4. All reported data are the average of three test runs.

The particulate emission data from 1988 and 1989 were all taken when both units were operating with the originally installed bags and are all well below the contractual requirement of 0.01 gr/dscf (7% O₂). Even though the numbers from 1989 appear slightly higher than from 1988 there are hardly sufficient data to conclude that any slight deterioration of bags has resulted in higher emissions. Particulate emission compliance is also verified continuously at the facility by the opacity monitors typically showing between zero and two percent, as compared with the contractual limit of ten percent opacity.

Very high acid gas removal efficiencies have been achieved in these yearly compliance tests. In excess of 99% HCl removal and stack emissions of less than 5 ppmdv (7% O₂) were measured, which is exceeding the performance requirement of 95% HCl removal or maximum stack emissions of 25-45 ppmdv (7% O₂). The SO₂ removal/emission data has been continuously verified since 1989 by the CEM system. In excess of 90% SO₂ removal or 40 ppmdv (7% O₂) in the stack is typically demonstrated based on a 3-hr rolling average.

Normally, the operator will adjust the lime addition rate to aim at a minimum of 95% SO₂ removal in order to maintain some "buffer" capacity in the system should a peak of either HCl or SO₂ occur in the boiler exit gas due to changing chlorine or sulfur content in the garbage being burned. A recent (March 7, 1991) 2-hr history of SO₂ data from the CEM system on Unit #2 is shown in Figure 5. Typically the SO₂ is reduced from about 160 ppm at the boiler exit to less than 40 ppm in the stack. For a significant part of the time the SO₂ removal appears to be close to 100%, suggesting that an excess of lime is being introduced. As mentioned earlier, this mode of operation provides the plant with an adequate safety margin in maintaining compliance.

Obviously the excess lime results in the formation of a quite alkaline waste product. A high lime content of the APC waste may also have some beneficial impact on the characteristics of the final waste product (consisting of a mixture of boiler ash and APC waste). E.g., the leachability of certain metals contained in the boiler ash or in the APC ash can potentially be lowered by the increased alkalinity of the mixture, reducing the potential leachability impact of the disposed waste on the environment. This feature seems to suggest that adjustment and/or optimization of the operating conditions of the APC system downstream of a boiler burning a quite heterogenous municipal waste may be considered as one of the parameters used for controlling the final waste disposal options. However, the issue is complicated by the variation between various metals in the alkalinity reactions and a clear conclusion on the subject has not been reached.

METALS EMISSION TESTING

Sampling and analysis of the stack emissions of metals on a selected boiler train were done in both 1988 and 1989 as part of the yearly compliance verification program. The results of this testing are presented in Table 5 (all data are the average of three test runs). The boiler permit compliance number for each of the metals has also been indicated in this table. For all metals existing predominantly in particulate form at the stack gas temperature of about 265°F, i.e. lead (Pb), arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), and nickel (Ni), the measured emission numbers are well below the level set by the permit requirement. For many of the analyses the concentrations fall below the maximum detection limit used in these measurements. These low emissions are in large part due to the efficient particulate collection efficiency of the fabric filter.

For mercury (Hg), which is known to exist mostly in vapor form even at the relatively low stack gas temperature of 265°F, the measurement was below the permit level of 0.05 lb/h (the three test runs were in the range 0.013-0.030 lb/h) when tested in 1988 (see Table 5). However, the three test runs in 1989 showed an average emission of 0.10 lb/h, mainly due to one single test run showing a emission as high as 0.27 lb/h. It appeared unclear whether this measurement was a result of a temporary extremely high concentration of mercury in the garbage being burned during this test period or whether it truly reflected the potential for a higher-than-predicted general mercury emission level. In order to investigate this issue Blount Energy Resource Corporation embarked on a program aiming at reducing the amount of mercury-containing waste being fed to the boiler. Also, a commitment was made to gather more data by testing the stack emission of mercury at regular 3-month intervals for a one-year period starting in the fall of 1990. The result of the first test series is presented in Table 6. These data seem to verify that significant variation in the mercury emission (by a factor of 5) may occur during a time period of only a few hours. A each test run typically represents the average of a 2-hour period, even larger, but shorter-duration variations might also occur in the emission level than reflected by these data. This apparent fact certainly emphasizes that caution should be used when evaluating mercury emission numbers based on a limited number of test data and that averaging a large number of data is required in order to properly assess the mercury emission level. The average mercury emission of this first test series is 0.044 lb/h, which is below the permit compliance value of 0.05 lb/h. When expressed in concentration units a comparison of this average emission of 0.42 mg/Nm³ appear to be only slightly above the level which is typically seen from similar waste-to-energy facilities equipped with spray dryer/baghouses (1, 2). It is therefore believed that the above described efforts at Warren Energy Resource Company can be expected to result in compliance with the existing mercury emission standards for the facility.

CONCLUSIONS

- The Warren County waste-to-energy facility consisting of two 200 ton/day boilers has been in successful commercial operation for about two-and-a-half years.
- The APC system using spray dryer/pulse-jet filter technology was furnished by Environmental Elements Corporation. It was the company's first reference in the supply of this particular process technology.
- The APC system has demonstrated a very satisfactory operational history in terms of availability and process performance.
- No major mechanical problems associated with the APC system have been experienced at the waste-to-energy facility. Most operational problems appear fairly trivial and similar to what has been reported from other facilities, such as the high maintenance associated with the handling of lime slurry. Good operational practices and excellent maintenance programs at the facility have also significantly contributed to this favorable operational record.
- The APC system's guaranteed process performance in terms of acid gas removal (95% HCl and HF, 90% SO₂) has been satisfied at the guaranteed lime consumption rates.
- The baghouse has demonstrated particulate emissions well below the guarantee of 0.01 gr/dscf (7% O₂). Total pressure loss across the system is about 10 in.WG.
- Specific environmental concerns relating to the potential emissions of mercury initiated a regular stack sampling program in 1990 aiming at verifying that compliance with the permit emission limit of 0.05 lb/h per boiler can be documented.
- The system has also demonstrated compliance with all other metal emission limits, and in many cases showed emissions an order of magnitude less than the permitted values.

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- 1) P. C. Siebert: "Estimating Emissions from Municipal Solid Waste Incinerators". Paper presented at the Society for Risk Analysis 1989 Annual Meeting, San Francisco, CA, October 1989.
- 2) C. Jorgensen, J. G. Toher, J. L. Hahn, and P. F. Claerbout: "Stack Emission and Dry Scrubber Performance Testing at the 2362-TPD Indianapolis Resource Recovery Facility". Paper presented at the IGCI Forum '90: "Air Quality Control Systems for Today and Tomorrow", Baltimore, MD, March 1990.

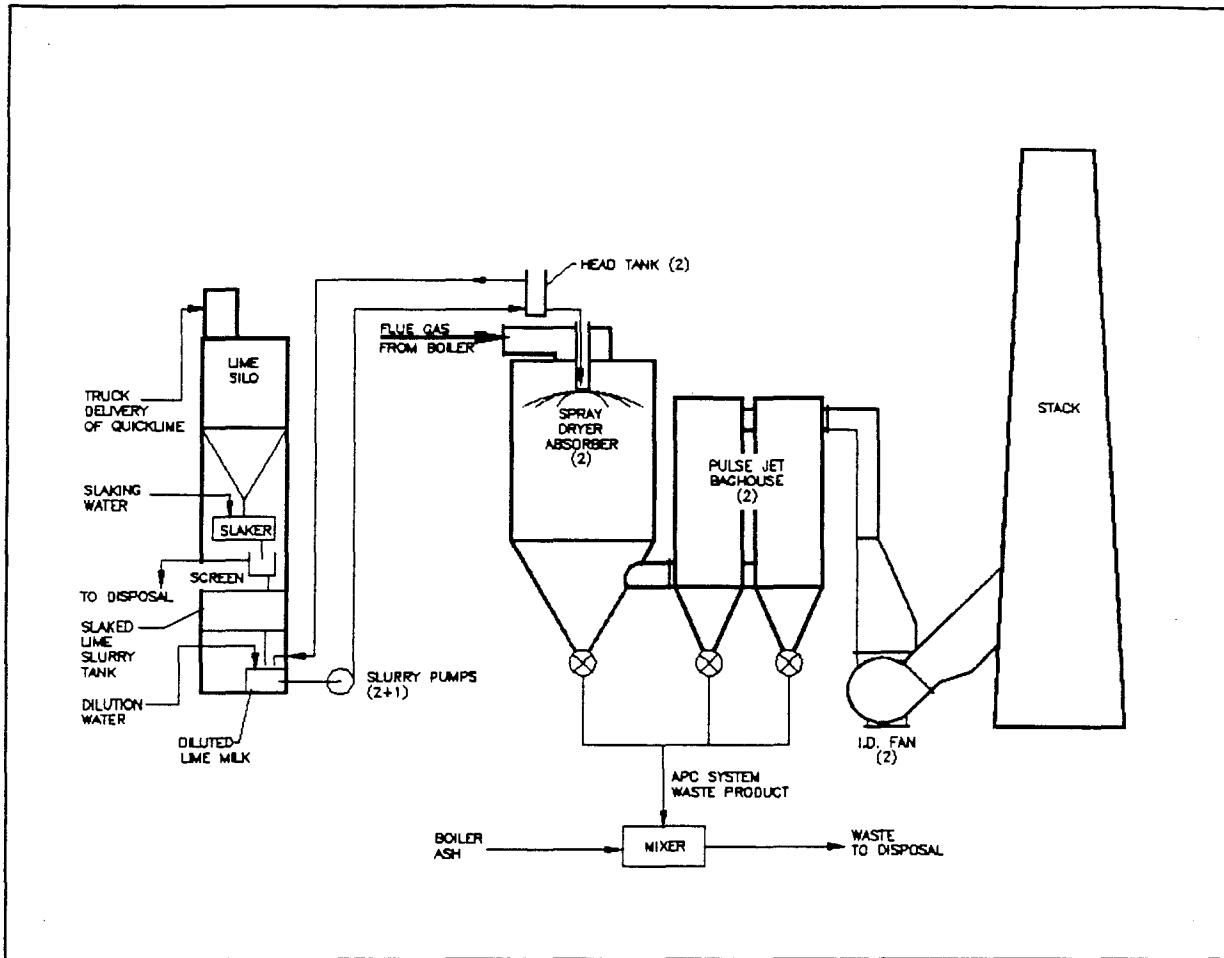


Figure 1. APC System Flow Sheet

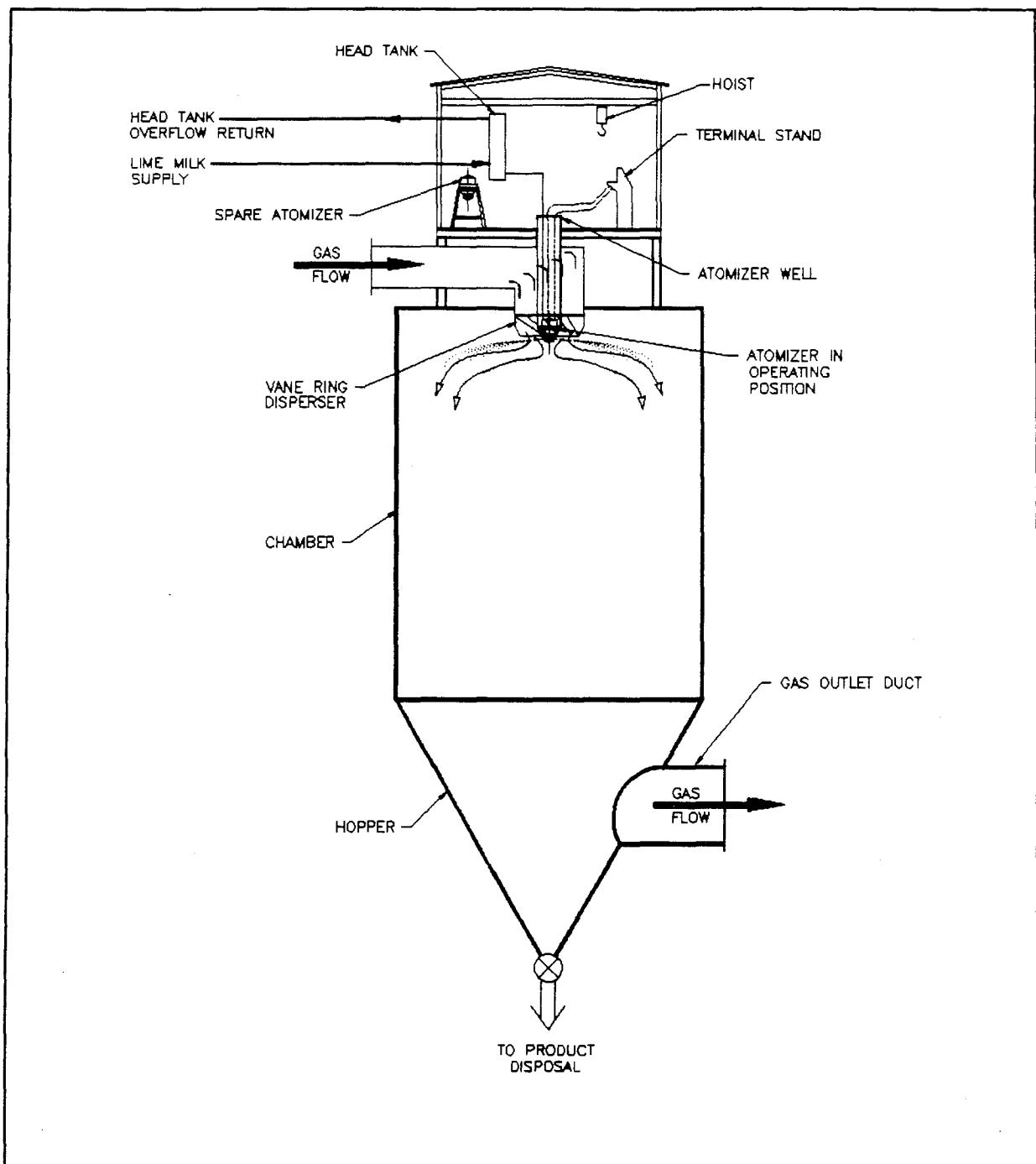


Figure 2. Spray Dryer Absorber

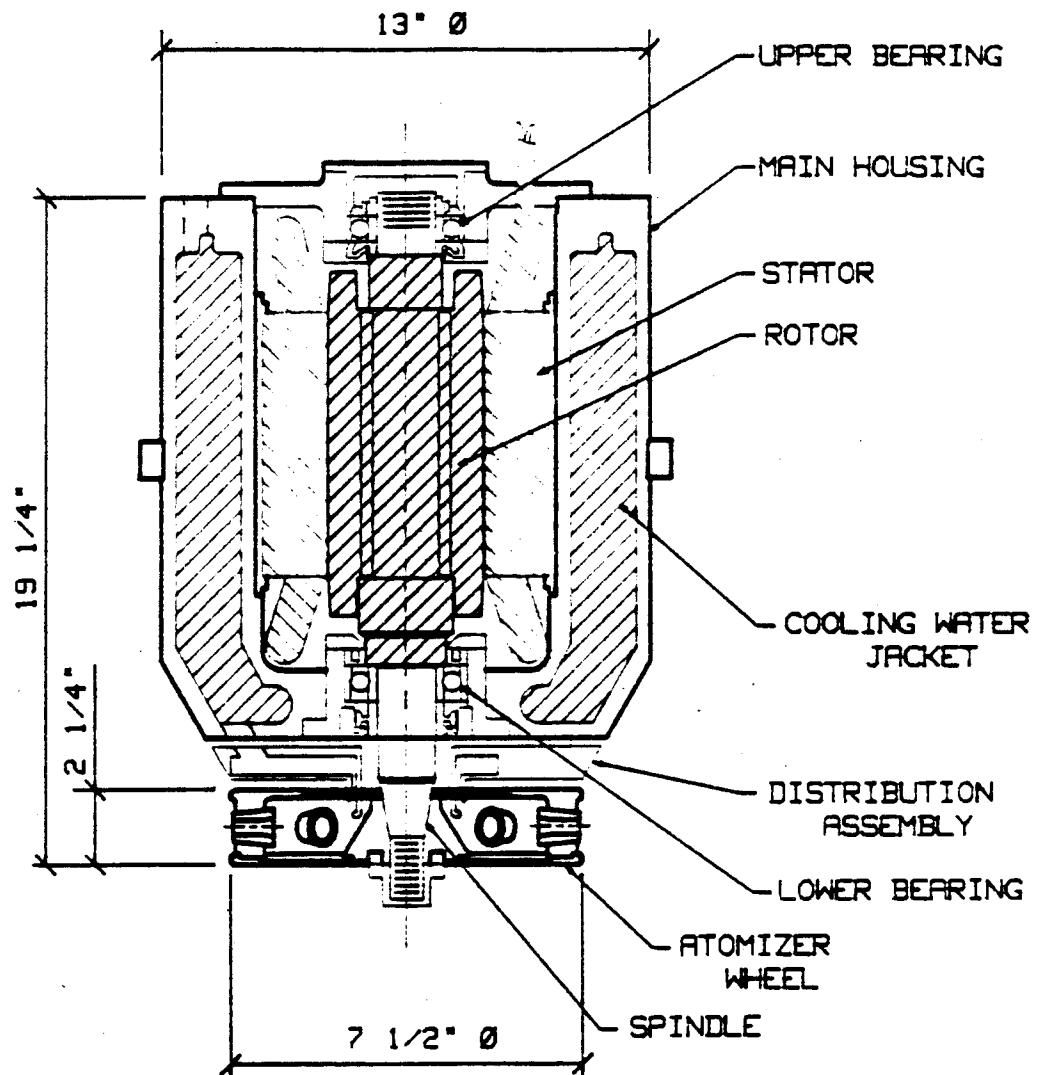


Figure 3. Komline-Sanderson Model 860 Rotary Atomizer

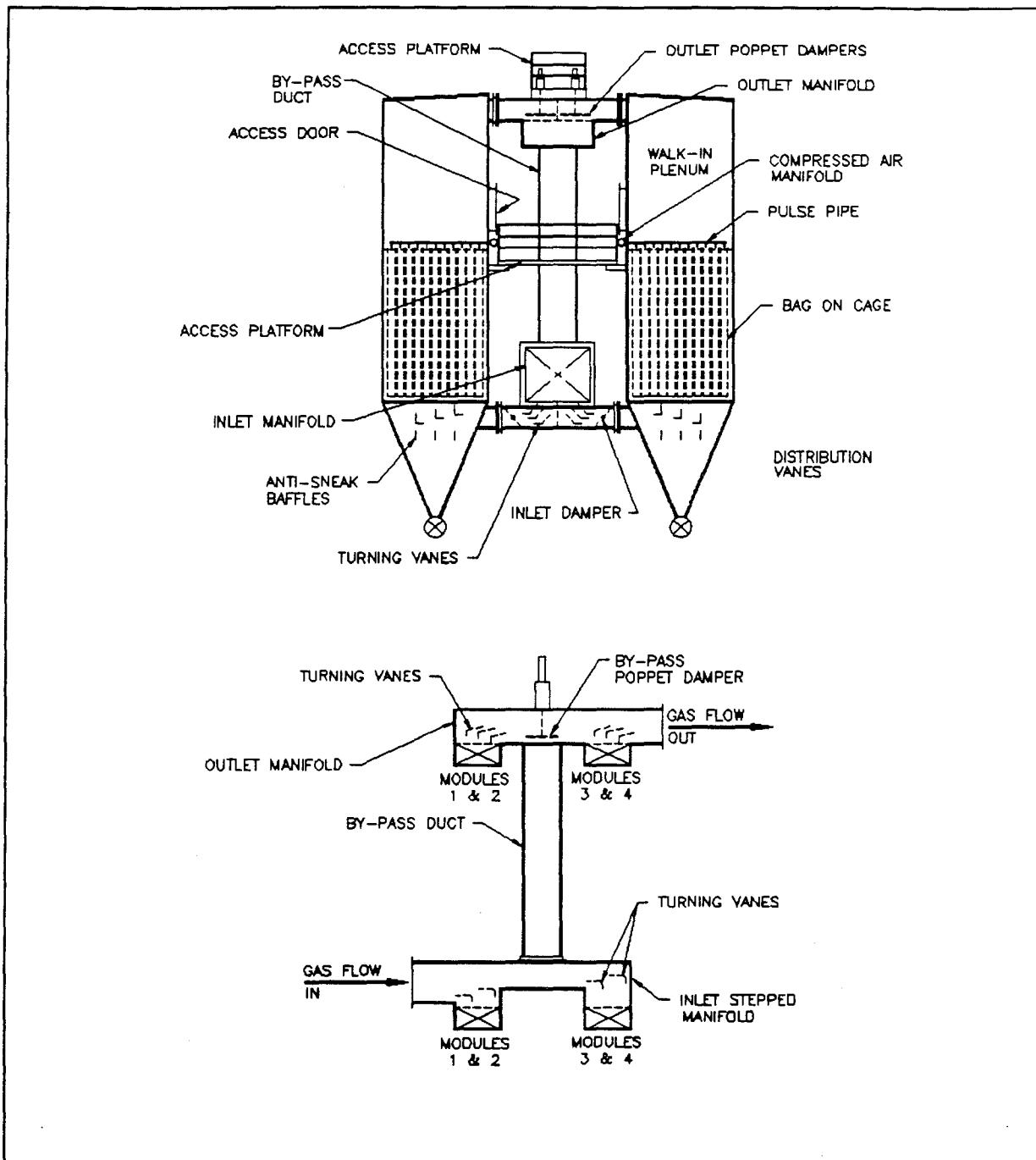


Figure 4. Pulse-Jet Fabric Filter

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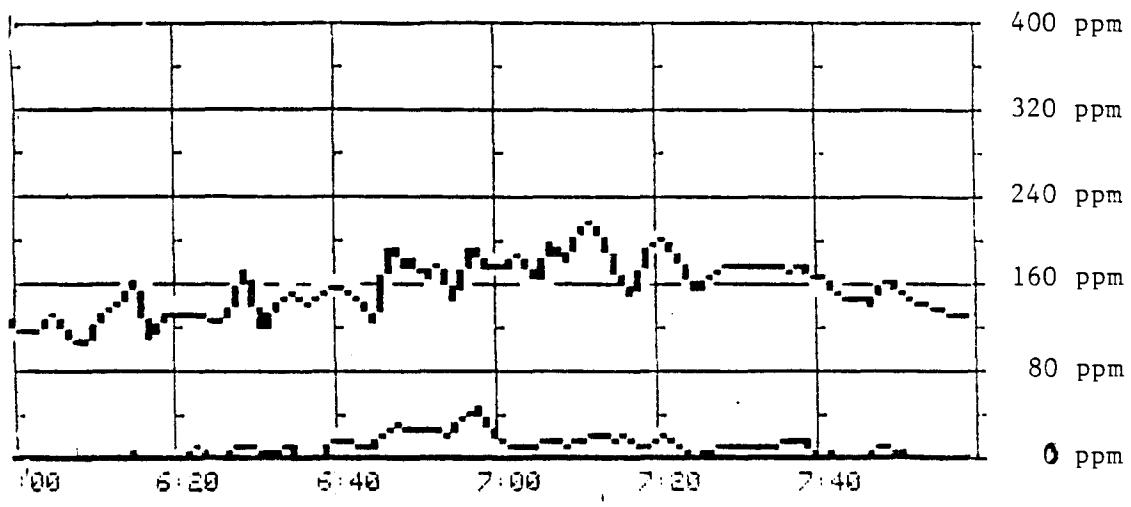


Figure 5. SO₂ Data From CEM System

TABLE 1. FILTER BAG TEST DATA (a)

BAG IDENTIFICATION (b)	A	B	C	D
PERMEABILITY (at 0.5"WG):				
-As received, cfm/sq.ft	7.52	12.60	2.78	20-40
-Vacuumed, cfm/sq.ft	9.60	14.60	7.64	N/A
WEIGHT:				
-As received, oz/sq.yd	25.7	22.9	30.3	21.6
-Washed, oz/sq.yd	21.7	22.3	22.3	N/A
MULLEN BURST, psig (avg)	1363	1477	1332	900 (c)
RESIDUAL DUST:				
-Moisture content, %	18.5		14.0	N/A
-Moisture regain:				
at ambient RH, %	22.6		16.3	N/A
at 100% RH, %	34.0		25.0	N/A

- (a) Grubb Filtration Testing Services, Inc - Report No. 342, Oct. 1988
Note: MIT Flex not performed as bags exhibited no physical wear
- (b) Bag A: Experienced low temperature excursions and "water spray only" operation. Tubesheet pressure drop 8-9 in.wg
Bag B: Experienced same conditions as Bag A, but was air-lanced and removed from service
Bag C: Experienced same conditions as Bags A and B, but was returned to normal SDA service
Bag D: Specifications for new bag
- (c) Specification lists minimum Mullen burst strength; however, tests routinely show results in excess of 1200-1400 psig

TABLE 2. FILTER BAG TEST DATA (a)

BAG IDENTIFICATION (b)	A	B	C
PERMEABILITY (at 0.5"WG):			
-As received, cfm/sq.ft	2.89	3.22	3.26
-Vacuumed, cfm/sq.ft	7.93	8.67	8.63
WEIGHT:			
-As received, oz/sq.yd	27.6	27.1	26.9
-Washed, oz/sq.yd	21.8	22.1	21.9
BREAKING STRENGTH, lbs/inch:			
-Warp (length)	460	463	468
-Fill (width)	421	142	145
BREAKING STRENGTH, % loss:			
-Warp (length)	38.7	38.9	37.6
-Fill (width)	59.9	59.5	58.7
MULLEN BURST, psig	617	619	622
MULLEN BURST, %loss	38.1	38.1	37.8
FLEX CYCLES (MIT Method):			
-Warp (length)	13642	13587	13965
-Fill (width)	4213	4154	4100
FLEX CYCLES, %loss:			
-Warp (length)	54.5	54.7	53.5
-Fill (width)	57.9	55.1	59.0

- (a) Environmental Consultant Company - Report No.TLN 8764, April 1991
- (b) Each bag sampled from different module

TABLE 3. RESULTS OF PERFORMANCE TESTS, NOVEMBER 1988

BOILER UNIT:	#1	#2	GUARANTEE:
SPRAY DRYER INLET CONDITIONS:			
Flue gas flow rate, ACFM	60,100	62,100	
Temperature, deg.F	366	365	
HCl conc, ppmdv (7%O ₂)	454	873	
HF conc, ppmdv (7%O ₂)	1.2	1.8	
SO ₂ conc, ppmdv (7%O ₂)	146	149	
STACK CONDITIONS:			
Flue gas flow rate, ACFM	57,900	59,800	
Temperature, deg.F	264	262	
HCl conc, ppmdv (7%O ₂)	21	29	
HF conc, ppmdv (7%O ₂)	0.09	0.08	
SO ₂ conc, ppmdv (7%O ₂)	0.48	14	
QUICKLIME FEED RATE, lb/h	238	215	
EQUIVALENCE RATIO (ER)	2.1	1.4	1.4
ACID GAS PERFORMANCE:			
HCl removal, %	95.4	96.6	95
HF removal, %	93	96	95
SO ₂ removal, %	99.7	90.4	90
PARTICULATE EMISSION:			
-gr/dscf (7%O ₂)	0.0017	0.0031	0.01
PRESSURE LOSS:			
-Total system, in.WG	9.8	10.4	10.0

TABLE 4. RESULTS OF YEARLY COMPLIANCE TESTS, 1988-1990

YEAR	1988	1989	1990			
BOILER UNIT	#1	#2	#1	#2	#1	#2
HCl INLET, ppmdv (7%O ₂)	840	718	466	182	(a)	(a)
HCl STACK, ppmdv (7%O ₂)	2.8	1.8	3.3	1.4	-	-
HCl-REMOVAL, %	99.7	99.7	99.3	99.3	-	-
SO ₂ INLET, ppmdv (7%O ₂)	170	199	(b)	(b)	(b)	(b)
SO ₂ STACK, ppmdv (7%O ₂)	1.2	0.23	-	-	-	-
SO ₂ -REMOVAL, %	99.3	99.9	-	-	-	-
PARTICULATES, gr/dscf(7%O ₂)	0.0036	0.0018	0.0048	0.0040	(a)	(a)

(a) Results not yet available

(b) Compliance verified by CEM data

TABLE 5. RESULTS OF METAL EMISSIONS TESTS, 1988-1989 (a)

YEAR	1988	1989	COMPLIANCE REQUIREMENT:
BOILER UNIT	#2	#2	
MERCURY (Hg)	0.022	0.101	0.05
LEAD (Pb)	< 0.0003	< 0.003	0.25
ARSENIC (As)	0.000087	< 0.0003	0.002
BERYLIUM (Be)	< 0.00015	< 0.0003	0.0004
CADMIUM (Cd)	< 0.0003	0.00040	0.03
CHROMIUM (Cr)	< 0.0005	< 0.0019	0.01
NICKEL (Ni)	< 0.0003	< 0.001	0.004

(a) All data in LB/H per boiler

TABLE 6. RESULTS OF MERCURY EMISSIONS TESTS, 1990 (a)

TEST	mg/Nm ³	LB/H
RUN #1	0.178	0.0185
RUN #2	0.893	0.0959
RUN #3	0.244	0.0427
RUN #4	0.417	0.0430
RUN #5	0.267	0.0293
RUN #6	0.495	0.0525
AVERAGE	0.416	0.0444

(a) All tests done on boiler unit #1

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SESSION 2C: RECENT DRY FLUE GAS CLEANING EXPERIENCE II

Co-Chairmen:

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The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

OPERATING EXPERIENCE AND EMISSION RATES OF
SCRUBBER BAGHOUSES, SCRUBBER ESP's AND FURNACE
INJECTION OF LIME AT RDF FACILITIES

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ABSTRACT

This paper will focus on operational, economic and environmental considerations of different air pollution control devices at three ABB Resource Recovery Systems (RRS) refuse derived fuel (RDF) facilities (Mid-Connecticut Facility in Hartford, CT, The Greater Detroit Resource Recovery Facility, the H-POWER Facility in Honolulu, HI.).

The air pollution control devices are: (1) a dry scrubber absorber followed by a fabric filter baghouse, (2) a dry scrubber absorber followed by a five field ESP, (3) lime injection to the furnace followed by a hot electrostatic precipitator.

Evaluating these three types of control devices is important because of new EPA emission guideline regulations that mandate restricted particulate, dioxin, and acid gas emission limits on municipal waste combustion facilities (MWC) greater than 250 tons per day combustion capacity. As a result of these new regulations, many existing MWC's will be faced with requirements to upgrade their air pollution control systems.

I. INTRODUCTION

This paper will summarize the operational experiences of three different air pollution control systems at three ABB Resource Recovery

Systems designed and operated RDF facilities in the United States.

The differing air pollution control systems are largely the result of differences in the air permitting process these facilities experienced, as will be explained later.

The three RDF facilities that will be compared are the Mid-Connecticut Resource Recovery Facility in Hartford Connecticut, the Greater Detroit Resource Recovery Facility in Detroit Michigan, and the H-POWER Facility in Honolulu Hawaii.

The summary of the key design features of these three facilities is shown in Table 1. The steam generators in each are waterwall spreader stokers with split traveling grates. Each uses three levels of tangential overfire air and an undergrate air system that is split into five compartments. The steam generator design is the basic Combustion Engineering VU-40 design. Mid-Connecticut is designed to be able to burn either coal or RDF, while the other two facilities are designed to burn only RDF, with oil as the startup and auxiliary fuel.

Permit applications to construct the Mid-Connecticut and Detroit facilities were submitted in the 1983-1984 time period. At that time, there were no Federal emission standards except for particulates. The permitting process was essentially controlled at the state level and was undergoing rapid change with no uniformity of emission standards. In Detroit, the state air permit was issued first in November 1984. The principal focus of pollution control in that permit was on good combustion conditions for control of organics and good control of particulates and metals by use of a high efficiency five-field hot ESP. There was no requirement in the Detroit permit for acid gas removal, although there were emission limits for SO₂ and HCl (see Table 2 for a listing of relevant air emission limits). There was a dioxin/furan limit, but there was no system included for control for dioxin other than good combustion conditions.

The Mid-Connecticut Facility, however, was required by the state permit process, when that air permit was issued in 1985, to add a scrubber/baghouse for control of acid gases as well as for dioxin and furan emissions.

The H-POWER project permit was issued in 1987 after the EPA Administrator issued a landmark "Remand Decision" which, for the first time, had the effect nationally of requiring scrubbers on all new municipal waste combustors. By this time, it was becoming better known in the scientific community that dry scrubber absorbers had a beneficial impact for a wide range of toxic metal and organic pollutants and was, in fact, a proven technology. Table 2 summarizes some relevant aspects of the H-POWER air permit for comparison to those of the Detroit and Mid-Connecticut facilities. This table does not contain all of the permit limits for these facilities, only the relevant ones that depend on an air pollution control system. Because work had already started on fabrication of an ESP for

H-POWER when the 1987 EPA Remand Decision came in, the facility retained its ESP's after the dry scrubber, although it was necessary to add an extra field to the ESP's.

All of these three facilities are now in operation and have had at least one set of air emission stack tests. These data will be summarized when the paper is presented. Because this paper is focused on the effect the air pollution control system has on conditions after the flue gas leaves the boiler, the pollutants that will be focused on will be particulates, acid gases (SO_2 and HCl), volatile trace metals (Pb, Hg, Cd, As) and dioxin/furan emissions after the particulate control device. The paper to be given at the conference will also discuss the mercury and HCl emission exceedance problems at the Detroit facility and the actions taken to install a furnace lime injection system.

To complete the paper, the operational experience for each of these back-end pollution control systems will be discussed. The discussion will identify and compare differences in labor needs, maintenance costs, lime usage, permit compliance experience and other relevant features.

TABLE 1

KEY DESIGN FEATURES

	<u>Mid-Conn.</u>	<u>Detroit</u>	<u>H-POWER</u>
MSW Throughput Design Capacity	2,000 TPD	3,300 TPD	2,160 TPD
Auxiliary/ Startup Fuel	Coal Natural Gas	Oil	Oil
Steam Generation Rate and # of Units	3 Units -- 231,000 lbs/hr each	3 Units -- 360,000 lbs/hr each	2 Units -- 250,000 lb/hr each
Energy Generation	68 MWe	65 MWe	57 MWe
Air Pollution Control System per Unit	Dry Scrubber absorber with 5 compartment bag- houses with 168 bags in each compartment, plus time, temperature and turbulence on combustion	Currently, lime furnace injec- tion with hot ESP. Dry scrubber absorber and baghouse in process of being retro- fitted, plus time, temperature and turbulence on combustion	Dry scrubber absorber with 5 field ESP, plus time, temperature and turbulence on combustion

TABLE 2
RELEVANT PERMIT LIMITS

POLLUTANT	MID-CONNECTICUT	DETROIT	H-POWER
PCDD/PCDF	1.95 ng/Nm ³ 2,3,7,8-TCDD Toxic Eq. @ 12% CO ₂	0.0043 lbs/hr ³ 7.767 ng/Nm ³ @ 12% CO ₂	None
PARTICULATE	0.015 gr/dscf @ 12% CO ₂	0.019 gr/dscf @ 12% CO ₂	0.015 gr/dscf
HC1	90% Control and 50 ppmv @ 12% CO ₂	294 lbs/hr 315 ppmv @ 12% CO ₂	None
SO ₂	0.32 lbs/10 ⁶ BTU 110 ppmv @ 12% CO ₂	457.1 lbs/hr 282 ppmv @ 12% CO ₂	30 ppmdv @ 12% CO ₂
Pb	700 ug/m ³ @ 12% CO ₂	1.37 lbs/hr ³ 2333 ug/m ³	0.0028 lbs per ton RDF 260 ug/m ³
Hg	240 ug/m ³ @ 12% CO ₂	0.07 lbs/hr ³ 120 ug/m ³	0.0022 lbs/ ton RDF 203 ug/m ³
Cd	None	0.085 lbs/hr ³ 143 ug/m ³	None

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REVIEW OF SD/FF VERSUS SD/ESP SYSTEM PERFORMANCE
FOR ACID GAS, PARTICULATE, AND CDD/CDF CONTROL

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ABSTRACT

Over the past five years, a number of new municipal waste combustors (MWC's) in the U.S. have installed spray dryer (SD) systems followed by either a fabric filter (FF) or an electrostatic precipitator (ESP). Initial performance data indicated that SD/FF systems were capable of achieving lower emission levels of sulfur dioxide (SO_2), hydrogen chloride (HCl), particulate matter (PM), and chlorinated dioxins and furans (CDD/CDF) than SD/ESP systems. Review of additional data from several recent SD/ESP systems suggests that these differences are smaller than the initial data indicated. This paper reviews the available emissions data from several existing SD/FF and SD/ESP systems and compares the emission reduction potential of both types of systems. This paper is of relevance to existing MWC's that may be considering retrofit of a SD system upstream of an existing ESP.

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

BACKGROUND

The first SD/FF system on an MWC in the U.S. began operating in Marion County, Oregon in 1986, and the first SD/ESP system began operating in 1988 at Millbury, Massachusetts. Based on the anticipated emissions control performance of SD/FF and SD/ESP systems and on the number of permits issued for such systems, the U.S. Environmental Protection Agency (EPA) issued operational guidance to permit writers on June 26, 1987, indicating that a SD followed by either a FF or an ESP was "best available control technology" (BACT) for MWC's under EPA's prevention of significant deterioration (PSD) program. Also in 1987, EPA initiated development of emission standards for new and existing MWC's. These standards were proposed in December 1989 (54 FR 52251) and were promulgated in February 1991 (56 FR 5488). This paper reviews acid gas, PM, and CDD/CDF emissions data associated with these two control technologies.

REVIEW OF AVAILABLE EMISSIONS DATA

As of the end of 1990, there were an estimated 66 MWC units in the U.S. operating with either SD/FF or SD/ESP systems. These units account for a combined waste combustion capacity of 39,000 tons/day (tpd). As shown in Table 1, these include 48 units equipped with SD/FF systems and 18 units with SD/ESP systems. The caustic used by all these units to control acid gas emissions is a lime-based (i.e., calcium) slurry. The information presented in this paper is based on compliance test and continuous emission monitor (CEM) data collected from the MWC's noted by asterisks (*) in the four right-hand columns of Table 1.

ACID GASES

The primary acid gases emitted by MWC's are SO₂ and HCl. Of these two acids, HCl has a stronger affinity for reaction with lime at typical SD operating temperatures (250-300°F). As a result, removal efficiencies for HCl across the SD/FF or SD/ESP system are always higher than for SO₂. Typical SO₂ and HCl emissions and reduction efficiencies measured during compliance testing are presented in Table 2. The data presented in Table 2 typically reflects the arithmetic average of measurements made during three separate test runs, each of which generally lasted three hours or less. Note that both SD/FF and SD/ESP systems achieved stack HCl emissions of less than 30 ppmv¹ and greater than 97 percent HCl reductions during compliance testing. SO₂ emissions, however, showed greater variability, with stack concentrations ranging up to 70 ppmv and emission reductions on a plant-wide basis of 73 to 97 percent. In most cases, the SO₂ control efficiency is higher for SD/FF systems than for SD/ESP systems.

Compliance test data indicate the level of emission reduction that a control system is capable of achieving. To ensure that a control system is operated to continuously achieve high levels of emissions reduction, however, it is necessary to continuously monitor system performance. Both SO₂ and HCl CEM systems are commercially available. However, HCl monitors are more expensive than SO₂ monitors and do not have the level of demonstrated reliability that has been achieved with SO₂ monitors. Based on the limitations on HCl CEM systems and on the ability to achieve high levels of HCl removal even at relatively low levels of SO₂ control, EPA based the demonstration of continuous acid gas emission reductions on the use of SO₂ monitors alone.

¹All emissions concentrations reported in this paper are at either 7% O₂ or 12% CO₂ and are on a dry-basis at standard temperature (68°F).

To confirm the SO₂ reduction capability of SD/FF and SD/ESP systems applied to MWC's, EPA obtained SO₂ CEM data from four commercial MWC's. Three of the facilities were equipped with SD/FF systems (York County, Pennsylvania; Stanislaus County, California; and Bridgeport, Connecticut) and one was equipped with an SD/ESP system (Millbury, Massachusetts).² The data indicated that short-term (e.g., hourly) concentrations of SO₂ measured before and after the SD/FF or SD/ESP can be much higher than weekly or monthly averages due to the heterogeneity of municipal waste and short-term variability in control system performance. The median (i.e., 50th percentile), minimum, and maximum hourly average inlet and stack SO₂ levels measured at each of these facilities are listed in Table 3 (inlet SO₂ levels were not monitored at Stanislaus County). Note that the maximum inlet SO₂ levels at the three MWC's with data are over three times the median value, and that the maximum outlet concentrations are 4 to 70 times higher than the median values. The higher median outlet level at Bridgeport, compared to Stanislaus County and York County, reflects Bridgeport's less stringent SO₂ emission limit.

As shown in Figure 1 (based on inlet data collected at the Bridgeport MWC), the hourly average SD inlet SO₂ data from all of the facilities were found to be lognormally distributed. Analysis of hourly average SO₂ levels measured after the control system found that stack emissions of SO₂ were also lognormally distributed. Because of the lognormality of the SO₂ CEM data, a geometric mean is statistically appropriate for estimating expected levels for longer time periods. Analysis of geometric means derived from inlet and stack SO₂ CEM data, for averaging periods of 3 hours to 7 days, found that a 24-hour averaging period was sufficient to account for most of the short-term "spikes" in SO₂, while being short enough to require operating personnel to carefully monitor control system performance.

Analysis of the CEM data from York County and Millbury indicate that carefully operated SD/FF systems are capable of continuously achieving greater than 80 percent SO₂ reductions and that carefully operated SD/ESP systems can continuously achieve greater than 70 percent SO₂ reductions. To continuously achieve these levels of SO₂ reduction, however, it will be necessary to operate with a system SO₂ control setpoint that will result in annual average SO₂ reductions of over 90 percent for SD/FF systems and over 80 percent for SD/ESP systems. The higher level of SO₂ reduction by SD/FF systems reflects the additional SO₂ reduction achieved by the filter cake on the FF bags.

PARTICULATE MATTER

Table 4 summarizes PM compliance test data collected during individual runs at several representative SD/FF and SD/ESP systems. In most instances, the PM emission rate measured during individual runs from both types of systems were less than 0.015 gr/dscf. The only exceptions were during single runs at Biddeford and Marion County, both of which are equipped with SD/FF systems, and at SEMASS and Millbury, both of which are equipped with SD/ESP systems. Except for one of the eight compliance tests conducted at Marion County, PM emission rates based on the average of three individual runs were less than 0.015 gr/dscf in all cases.

Based on review of the data from individual runs, elevated PM emissions during a compliance test can occur either as the result of higher emissions during all runs or during a single run. For example, above average PM emissions were measured during each of the runs at Biddeford and during each of the runs associated with the above compliance test at Marion County. The

²HCl CEM data were also collected at the Millbury MWC. These data indicated HCl reductions were almost always greater than 97 percent, except during periods when high inlet concentrations of HCl or SO₂ caused HCl reductions to decrease to 90-97 percent (based on an 8-hour averaging period).

attributable to the relatively high design net air-to-cloth ratio (5.2 acfm/ft²) of the unit's pulse-jet FF. The higher PM emission rate (averaging 0.016 gr/dscf) during one of eight Marion County tests may indicate a bag leak during this test. On the other hand, the higher PM emission rate (0.020 gr/dscf) measured during the single run at Millbury may have been due to an upset condition in the ESP or combustor during this run. During 20 other test runs conducted at Millbury, the next highest PM emission rate was 0.005 gr/dscf.

At the other end of the spectrum, PM emissions of less than 0.003 gr/dscf have been measured at SD/FF systems and at several new SD/ESP systems (e.g., the 5-field ESP in Honolulu and 4-field ESP in West Palm Beach) that are equipped with large ESP's able to collect fine PM and to minimize PM reentrainment and bypass. Based on these data, the PM control performance of SD/FF and SD/ESP units depends on system design and operation. As a result, there is no clear distinction in the ability of recently built SD/FF and SD/ESP systems to control total PM.

DIOXINS AND FURANS

Table 5 summarizes the CDD/CDF data collected from several SD/FF and SD/ESP systems. Both SD/FF and SD/ESP systems have demonstrated the ability to achieve CDD/CDF emissions of less than 30 ng/dscm, with several facilities achieving emissions of less than 10 ng/dscm. However, two of the MWC's equipped with SD/ESP systems (Millbury and SEMASS) have experienced relatively large variations in CDD/CDF emissions between individual test runs. For example, the SEMASS MWC had CDD/CDF emissions between 5 and 18 ng/dscm during five of six runs, but measured 907 ng/dscm on the sixth run. At Millbury, five of the six runs were between 40 and 70 ng/dscm, while the sixth run was 103 ng/dscm. Based on available data, it is not possible to determine whether the higher CDD/CDF level measured during these individual runs are caused by an upset condition in the combustor (causing higher CDD/CDF levels at the combustor exit) or in the SD/ESP system (resulting in reduced CDD/CDF collection efficiency). Similar large variations in stack concentrations of CDD/CDF have not been identified at MWC's using SD/FF systems, however. This suggests that the filter cake on FF bags may enhance the ability of SD/FF systems to handle upset operating conditions in the combustor and SD system.

Based on CDD/CDF levels measured at the combustor outlet at Commerce, Marion County, Mid-Connecticut, and the Quebec City pilot-scale tests, SD/FF systems have been able to reduce CDD/CDF emissions by more than 95 percent, and are frequently in excess of 99 percent. The only MWC with a SD/ESP that has simultaneously measured both inlet and outlet CDD/CDF levels is Millbury. During testing at Millbury, CDD/CDF reductions were between roughly 50 and 70 percent, with an average of approximately 65 percent. Based on these data, it appeared that SD/ESP systems were less efficient at CDD/CDF collection than SD/FF systems. However, subsequent testing conducted at several RDF-fired MWC's with SD/ESP systems having 4 or 5 fields (versus Millbury which has 3 fields) measured lower CDD/CDF emissions, suggesting that removal efficiencies from properly designed and carefully operated SD/ESP units can approach levels achieved by SD/FF systems.

CONCLUSIONS

The emissions control performance of both SD/FF and SD/ESP systems depends on proper design and operation. Based on compliance test data collected from recently built MWC's with SD/FF or SD/ESP systems, the PM and CDD/CDF control performance of both systems can be comparable. However, SD/ESP systems appear to be more sensitive to upsets in operating conditions than SD/FF systems, and may experience noticeable increases in PM and CDD/CDF emissions during these upsets. The failure to detect similar "spikes" in PM and CDD/CDF emissions from SD/FF systems may reflect the ability of the FF

filter cake to moderate short-term duration increases in the two pollutants.

Because most of the reaction between HCl and sorbent occurs before the flue gas enters the PM control device, HCl removal efficiencies by SD/FF and SD/ESP systems appear to be similar. However, a significant fraction of SO₂ removal occurs in the PM control device. Because of the SO₂ removal by the filter cake in a FF, the SO₂ emissions from a SD/FF are roughly one-half those associated with a SD/ESP.

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Sussman, D. B. (Ogden Martin Systems). Testimony Before the National Air Pollution Control Techniques Advisory Committee. Research Triangle Park, North Carolina. January 31, 1991.

TABLE 1. EXISTING U.S. MWC'S EQUIPPED WITH SD/FF OR SD/ESP SYSTEMS

Location	State	Control Type	No. of Units	Capacity Per Unit (tpd)	Startup Date	Compliance Test Data-			SO ₂ CEM Data
						Acid Gases	PM	CDD/CDF	
Marion County	OR	SD/FF	2	275	1986	*	*	*	
Biddeford	ME	SD/FF	2	350	1987	*	*	*	
Commerce	CA	SD/FF	1	300	1987	*	*	*	
Bridgeport	CT	SD/FF	3	750	1988		*		*
Bristol	CT	SD/FF	2	325	1988		*		
Mid-Connecticut	CT	SD/FF	3	667	1988	*	*	*	
Indianapolis	IN	SD/FF	3	787	1988	*	*	*	
Long Beach (SERRF)	CA	SD/FF	3	460	1988	*	*	*	
Penobscot	ME	SD/FF	2	360	1988	*	*	*	
Stanislaus County	CA	SD/FF	2	400	1988	*	*	*	*
Babylon	NY	SD/FF	2	375	1989	*	*	*	
Hennepin County	MN	SD/FF	2	600	1989				
Broward County (North)	FL	SD/FF	3	750	1990				
Broward County (South)	FL	SD/FF	3	750	1990				
Fairfax County	VA	SD/FF	4	750	1990		*		
Gloucester County	NJ	SD/FF	1	575	1990		*		
Hempstead	NY	SD/FF	3	773	1990	*	*	*	
Huntsville	AL	SD/FF	2	345	1990		*		
Kent County	MI	SD/FF	2	312	1990		*		
York County	PA	SD/FF	3	448	1990				*
			48	26714					
Millbury	MA	SD/ESP	2	750	1988	*	*	*	*
Portland	ME	SD/ESP	2	250	1988	*	*	*	
Charleston	SC	SD/ESP	2	350	1989	*	*	*	
Haverhill	MA	SD/ESP	3	550	1989		*		
SEMASS	MA	SD/ESP	2	950	1989	*	*	*	
West Palm Beach	FL	SD/ESP	2	1000	1989	*	*		
Essex County	NJ	SD/ESP	3	750	1990				
Honolulu	HI	SD/ESP	2	900	1990	*	*	*	
			18	12300					

TABLE 2. SELECTED ACID GAS COMPLIANCE TEST DATA

Location	Control Type	Stack Conc. (ppmv)		% Reduction	
		SO ₂	HCl	SO ₂	HCl
Marion County	SD/FF	31	18	85	97
Biddeford	SD/FF	22	6	76	99
Commerce	SD/FF	3	6	97	99
Mid-Connecticut	SD/FF	32	12	83	97
Stanislaus County	SD/FF	4	2	90	--
Millbury	SD/ESP	58	15	76	98
Portland	SD/ESP	40	--	87	--
SEMASS	SD/ESP	61	--	65	--
West Palm Beach	SD/ESP	33	16	73	97

TABLE 3. SUMMARY SO₂ CEM STATISTICS

Location	Control Type	Sampling Location	1-Hour Average (ppmv)		
			Median	Minimum	Maximum
Bridgeport	SD/FF	Inlet	155	50	617
		Outlet	33	11	286
Stanislaus County	SD/FF	Outlet	5	0	169
		Inlet	102	3	381
York County	SD/FF	Outlet	9	1	377
		Inlet	173	55	547
Millbury	SD/ESP	Outlet	35	2	227

TABLE 4. SELECTED PM COMPLIANCE TEST DATA

Location	Control Type	Sampling Location	Run Average	Average (gr/dscf)	Minimum	Maximum
Biddeford	SD/FF	Outlet	0.0140	0.0095	0.0190	
Bridgeport	SD/FF	Outlet	0.0022	0.0004	0.0130	
Marion County	SD/FF	Outlet	0.0073	0.0030	0.0211	
Mid-Connecticut	SD/FF	Outlet	0.0030	0.0017	0.0059	
Stanislaus County	SD/FF	Outlet	0.0039	0.0011	0.0086	
Honolulu	SD/ESP	Outlet	0.0016	0.0007	0.0027	
Millbury	SD/ESP	Outlet	0.0045	0.0004	0.0201	
SEMASS	SD/ESP	Outlet	0.0100	0.0070	0.0170	
West Palm Beach	SD/ESP	Outlet	0.0013	0.0003	0.0028	

TABLE 5. SELECTED CDD/CDF COMPLIANCE TEST DATA

Location	Control Type	Sampling Location	Run Average	Average (ng/dscm)	Minimum	Maximum
Babylon	SD/FF	Outlet	21.9	12.6	27.2	
Biddeford	SD/FF	Outlet	4.4	3.5	5.2	
Mid-Connecticut	SD/FF	Outlet	0.7	ND ^a	1.4	
Stanislaus Co. #1	SD/FF	Outlet	6.3	4.6	8.9	
Stanislaus Co. #2	SD/FF	Outlet	6.5	5.0	8.5	
Honolulu #1	SD/ESP	Outlet	9.9	4.1	16.7	
Honolulu #2	SD/ESP	Outlet	2.9	1.5	3.8	
Millbury	SD/ESP	Outlet	59.2	40.4	103.0	
SEMASS #1	SD/ESP	Outlet	9.3	5.1	13.6	
SEMASS #2	SD/ESP	Outlet	311.0	6.6	907.0	

^aNot detected

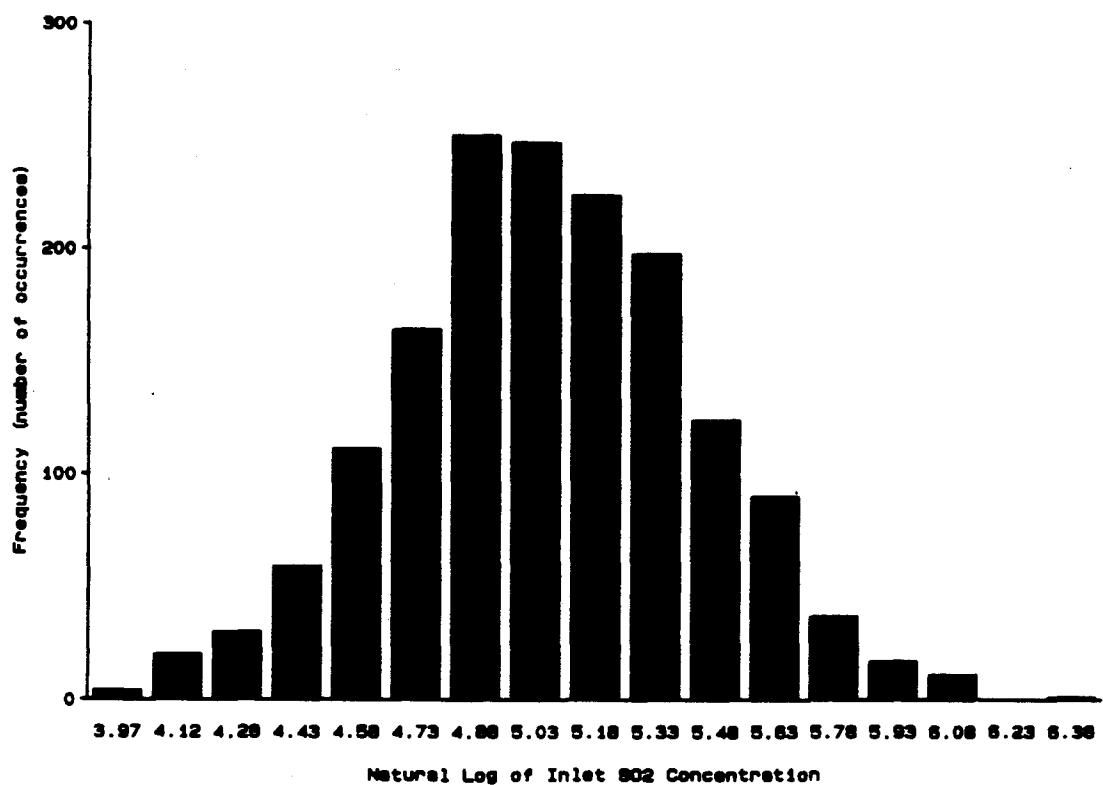
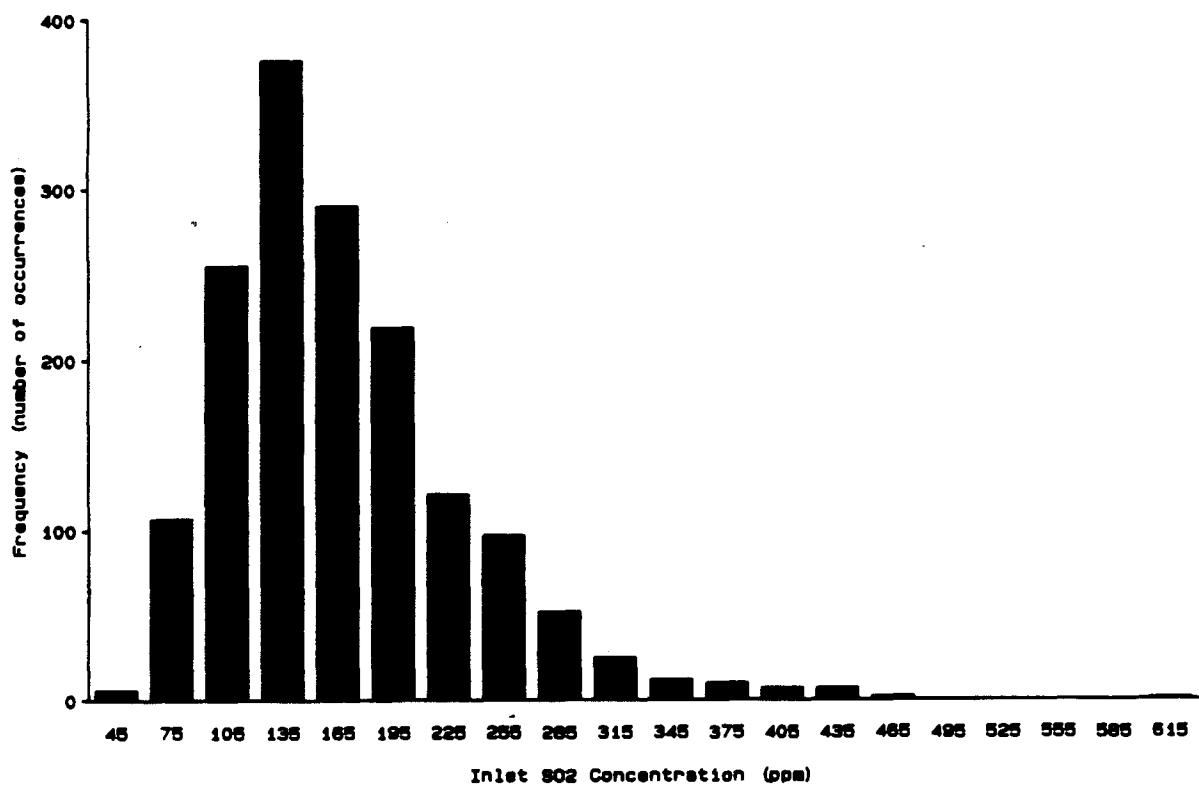


Figure 1. Distribution of Hourly Average Inlet SO₂ Concentrations at Bridgeport

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The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

REDUCTION OF DIOXIN AND HEAVY METALS
BY SEMI-DRY SCRUBBER AND BAGHOUSE FROM MSW INCINERATOR

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ABSTRACT

This paper presents the result of investigations about PCDDs/PCDFs and heavy metals discharged from MSW incineration plants.

As to the PCDDs/PCDFs, inlet temperature of the baghouse appeared to be most important parameter. To control the PCDDs/PCDFs, lower temperature is better. And dust load on the fabric filter is important parameter too. The heavier dust load on the fabric filter, the better the removal of the PCDDs/PCDFs.

As to the heavy metals, Pb, Cd, Zn, are removed well at the baghouse and the removal of them depends on the dust load on the fabric filter same as PCDDs and PCDFs. However, it is difficult to remove Hg at baghouse in spite of low temperature and heavy dust load on the fabric filter.

INTRODUCTION

The problem of dioxin discharged from refuse incinerators is attracting attention on a global scale. The refuse incineration rate in Japan is high at 72 percent in 1989. The development of technologies for controlling dioxins is a matter of utmost urgency.

With this background, research is under way on two items, namely, technologies for controlling the generation of dioxins in the incinerator and technologies for removing dioxins. This paper presents removal efficiency of dioxins and heavy metals by the semi-dry scrubber and baghouse.

EXPERIMENT CONDITIONS

The dioxins and heavy metal contents were investigated at the inlet and outlet of a semi-dry scrubber and baghouse installed in stoker type incinerator. Two refuse incineration plants A and B were selected as objectives of the investigation.

- (1) Refuse incineration plant A is made up of two continuous operating incinerators each having an incinerating capacity of 150 t/d. This plant is equipped with semi-dry scrubbers and electric precipitators. One of the two incinerators is so arranged that a fullscale baghouse, exhaust gases flowing is 10000 Nm³/H , is installed in parallel along ESP flow .
- (2) Waste incineration plant B is made up of one continuous operating incinerator with an incinerating capacity of 150 t/d. This plant is equipped with semi-dry scrubbers and baghouse.

A simplified flow is shown in Fig.1.

PCDDs/PCDFs ANALYTICAL METHODS

Flue gas samples were taken from the duct isokinetically using the 5-train-method modified US EPA with the dust collector settled outside of the duct. The sample preparation consist of matrix-specific extraction (Soxhlet for solid samples after 2N-HCl treatment of particulate, liquid-liquid for aqueous samples by toluene), acid-base partitioning followed by silicagel and basic alumina column chromatography. ¹³C₁₂-2,3,7,8-TCDD, ¹³C₁₂-2,3,7,8-TCDF, ¹³C₁₂-OCDD, ¹³C₁₂-OCDF were added to samples after the extraction as the recoverey standards during the analytical procedure. PCDDs/PCDFs isomer specific analysis was performed on SIM by HRGC/MRMS with a DB-5 and SP-2331 fused-silica capillary columns.

For quantification of PCDDs/PCDFs, the two most abundant ions were monitored, and the peaks in sample chromatograms where the isotopic ratios of each twoions are closed to that in native 2,3,7,8-substituted PCDDs/PCDFs standard, were identified and quantified as PCDDs/PCDFs by comparison ofpeak area.

RESULTS AND CONSIDERATIONS

DIOXINS

Bag filter temperature and dioxins

It has been reported by Yamagishi...(1),(2)that there is a close relationship between the bagfilter inlet temperature and dioxins. The relationship of baghouse inlet temperature to outlet PCDDs/PCDFs(2,3,7,8-

TCDDeq, Internatinal TEF) is shown in Fig.2. As can be seen in Fig.2, the lower the baghouse inlet temperature, the lower the dioxins . The relationship between dioxins removal rate and baghouse inlet temperature is shown in Fig.3.

$$\text{Dioxin removal rate} = \frac{\text{DXNin} - \text{DXNout}}{\text{DXNin}} \times 100 (\%)$$

DXNin : PCDD/PCDF at inlet of bag filter (Hg/Nm³)
 DXNout: PCDD/PCDF at outlet of bag filter (Hg/Nm³)

As can be seen in Fig.3, the lower the baghouse inlet temperature, the higher the removal rate. The reason is given as the lower the temperature, the higher the susceptibility of dioxins to adsorb on the dust layer.

The relationship of PCDDs/PCDFs(2,3,7,8-TCDDeq, Internatinal TEF) in fly ash to baghouse inlet temperature is shown in Fig.4. The figure shows that the lower the temperature, the higher the dioxins concentration. This indicates that the lower the temperature, dioxins contained in the exhaust gas is easier to remove and it is further considered that the shift into the dust is also made easier. Several papers (1),(2) have already reported that production of dioxins takes place in dust collectors as the dust collector temperature rises to the 300 C level and the dioxins concentration rises. Accordingly, Fig.4 will also show that the dioxin concentration rises when the baghouse inlet temperature is raised near the 300 C.

Dust load and dioxins

Dust load is indicated by the amount of dust layer accumulated on the baghouse and expressed by the following equation.

$$\text{Dust load} = C \times 10^{-3} \times Q \times \frac{1}{A} \times \frac{1}{60} \times T \quad (\text{kg/cm}^2)$$

C : Dust concentration (g/Nm³)
 Q : Exhaust gas volume (Nm³/h)
 A : Area of filter cloth (m²)
 T : Back wash interval (min)

The comparatively large particles contained in dust descends in the baghouse by gravitation. Therefore, the dust load obtained by the equation given above does not express the accurate amount of dust caught by the fabric filter, but it is capable of indicating the extent of dust layer. The relationship of dioxins removal to dust load is shown in Fig.5. The figure shows that the larger the accumulation of dust load, that is, the more dust accumulated on the fabric filter, the higher the dioxins removal rate.

The relationship between dust load and PCDD/PCDF(2,3,7,8-TCDDeq, International TEF) in fly ash is shown in Fig.6. It can be seen that the higher the accumulation of dust load, the higher dioxin concentration in dust. This indicates that the dust layer has become thicker and has raised the possibility of catching and adsorbing particles of dioxins or gaseous dioxins in exhaust gas.

HEAVY METALS

Pb, Zn, and Cd

The relationship of Pb, Zn, and Cd removal efficiency to baghouse inlet temperature is shown in Fig.7 to 9. The removal efficiency mentioned here is referred to as the extent of removal of heavy metals at the inlet and outlet of semi-dry scrubber. The lower the baghouse inlet temperature, the removal efficiency of Pb and Zn tends become higher. However, Cd, irrespective of temperature, indicates a high removal efficiency of not less than 90 percent.

The relationship between the removal efficiency of Pb, Zn, and Cd and dust load is shown in Fig.10 to 12. As the figures show, the higher the dust load, the higher the removal efficiency. However, the removal efficiency of Cd, irrespective of dust load, is greater than 90 percent.

Hg

The relationship between Hg removal efficiency, baghouse inlet temperature, and dust load is shown in Fig.13 and 14. The figures show large fluctuations in Hg removal efficiency values. The burning of refuse in incinerators causes the Hg concentration in exhaust gas to fluctuate sharply, but the fluctuations may have been amplified since the measurements were taken in this experiment in batches instead of using a continuous meter.

CONCLUSION

The experimental results indicated that the following items were found to be important in inhibiting the generation of dioxins and heavy metals.

- 1) Maintaining the exhaust gas temperature at the inlet of baghouse as low as possible.
- 2) Maintaining the dust load as high as possible.

However, removal efficiency of not less than 90 percent can be obtained for Cd without observing the conditions of 1) and 2) given above.

Since there are sharp fluctuations in the Hg data, definite conclusions could not be obtained from the experiment.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

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1. Yamagishi,M.,Shibuya,E., "Conyrol of PCDD/PCDF Emissions from Waste to Energy Plant", 9th International Symposium on Chlorinated Dioxins and Related Compound, 1989
2. Yamagishi,M.,Shibuya,E., "Simultaneous Control of Dioxins and NO_x in Municipal Waste Incinerator", 10th International Symposium on Chlorinated Dioxins and Related Compound, 1990

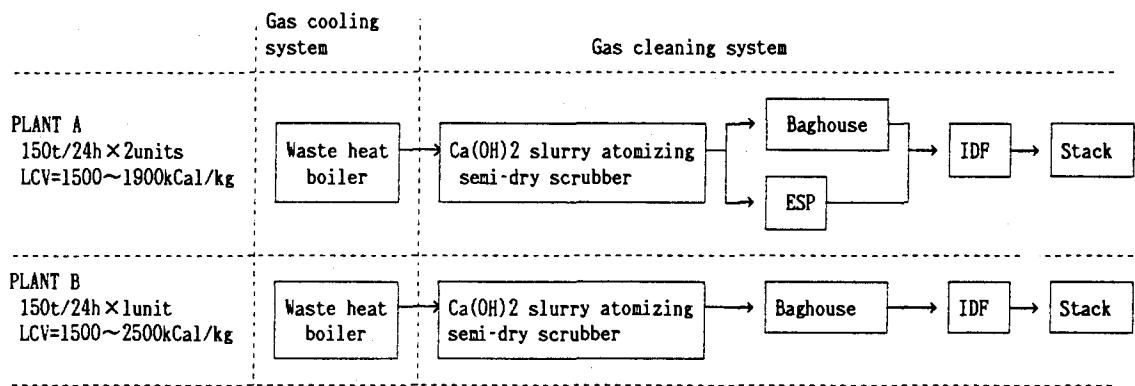


Fig.1 Plant flow diagram

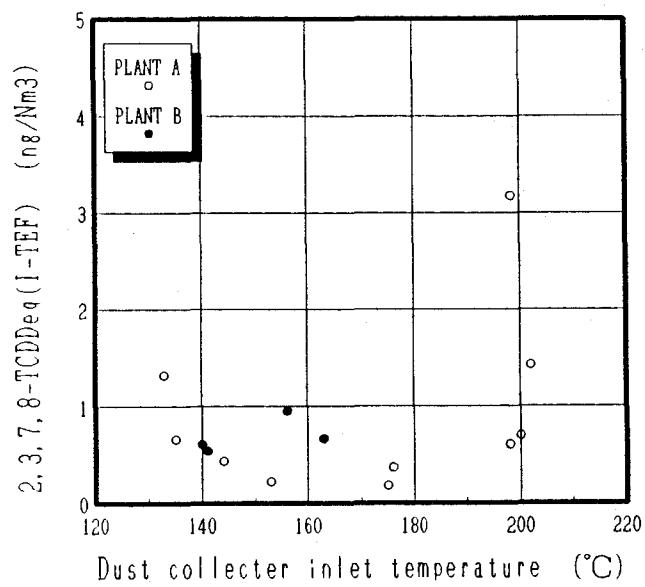


Fig.2 Dioxins VS dust collector inlet temp.

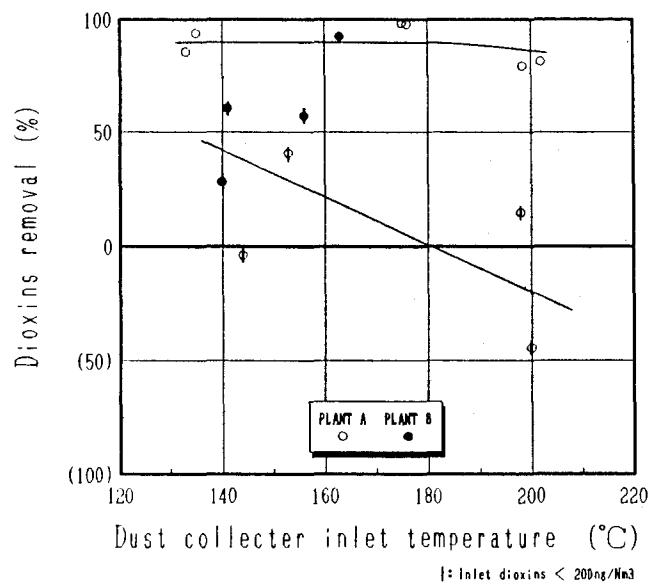


Fig.3 Dioxins removal VS dust collector inlet temp.

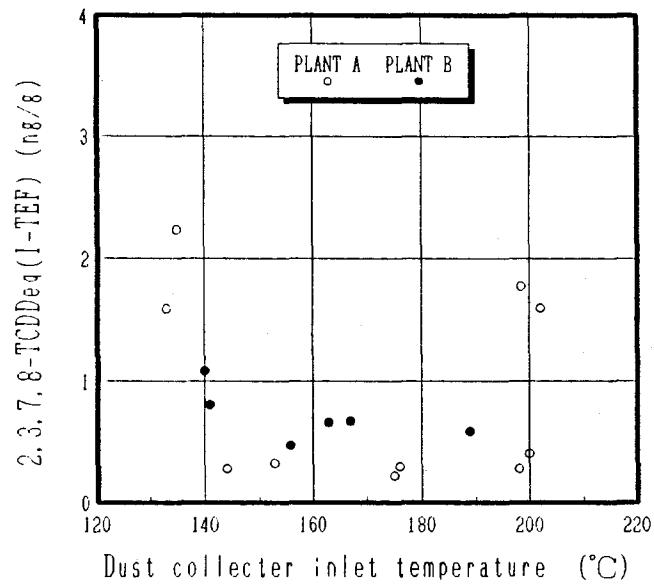


Fig.4 Dioxins in fly ash VS dust collector inlet temp.

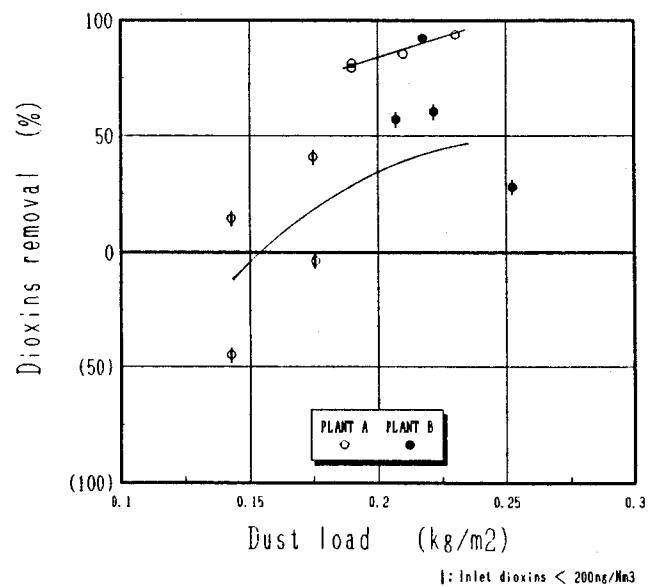


Fig.5 Dioxins removal VS dust load

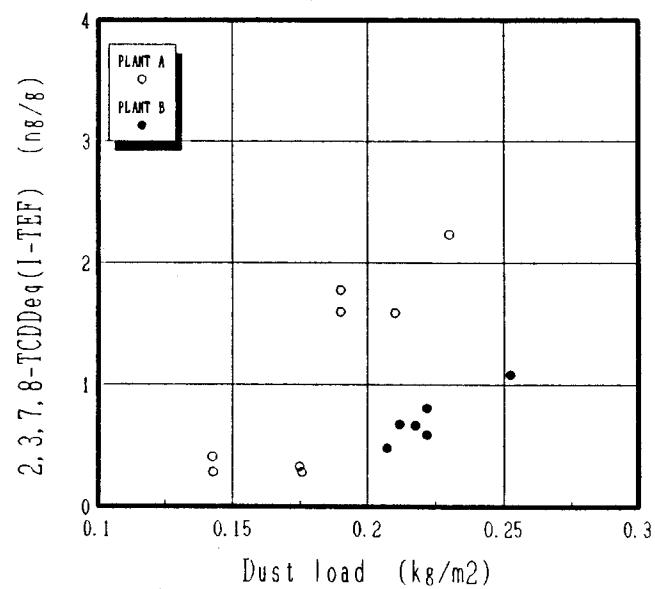


Fig.6 Dioxins in fly ash VS dust load

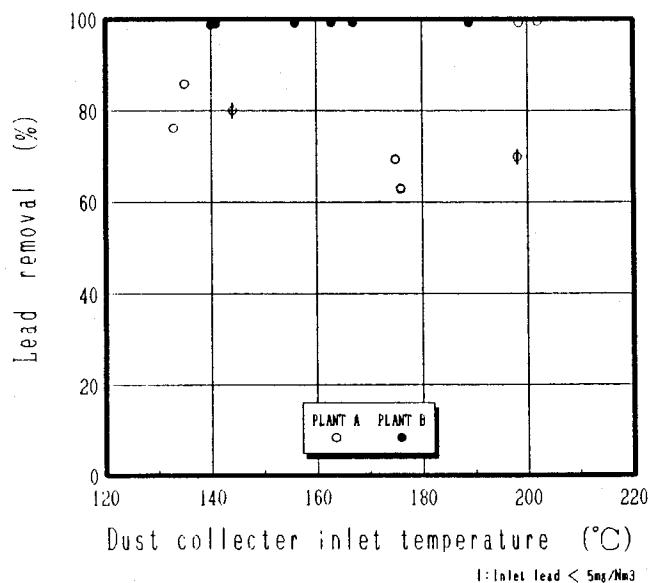


Fig.7 Lead removal VS dust collector inlet temp.

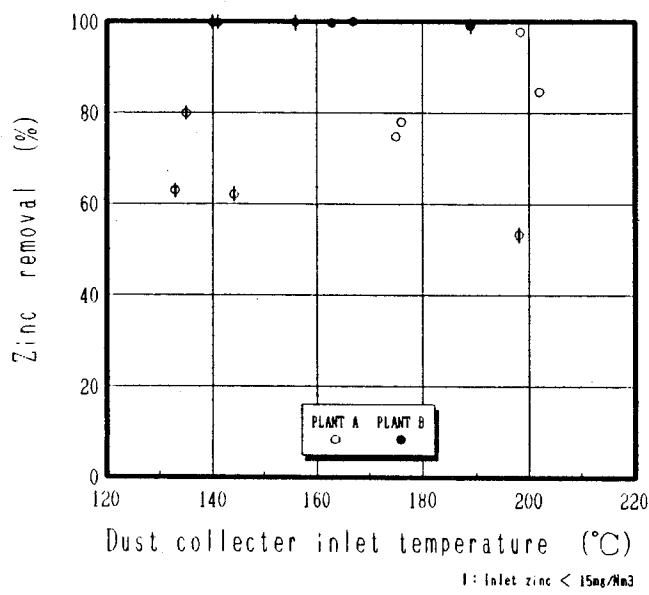


Fig.8 Zinc removal VS dust collector inlet temp.

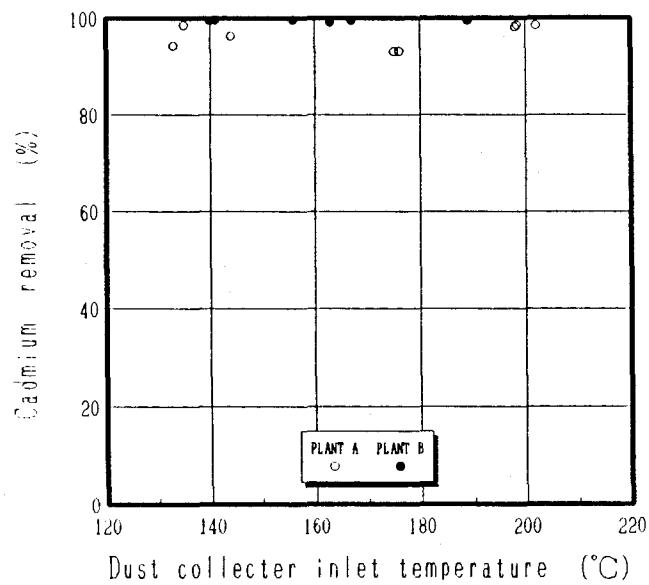


Fig.9 Cadmium removal VS dust collector inlet temp.

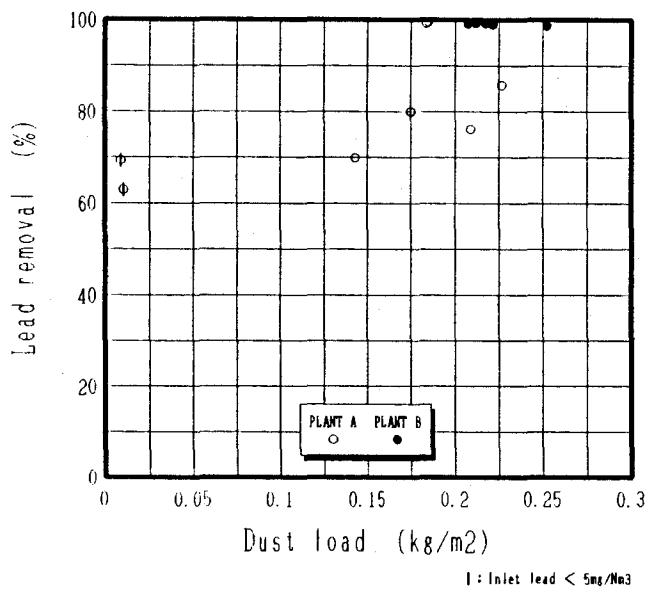


Fig.10 Lead removal VS dust load

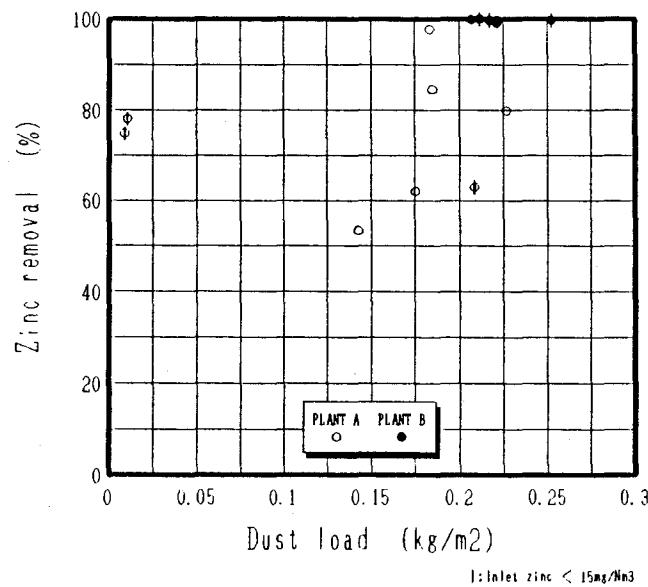


Fig.11 Zinc removal VS dust load

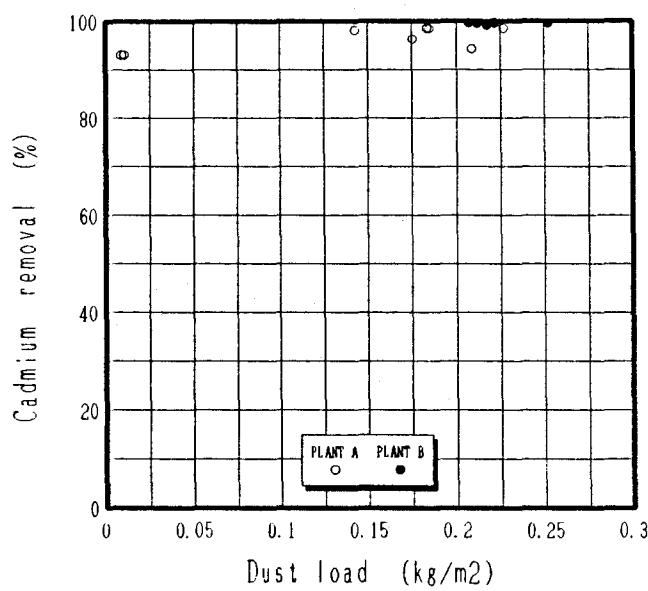


Fig.12 Cadmium removal VS dust load

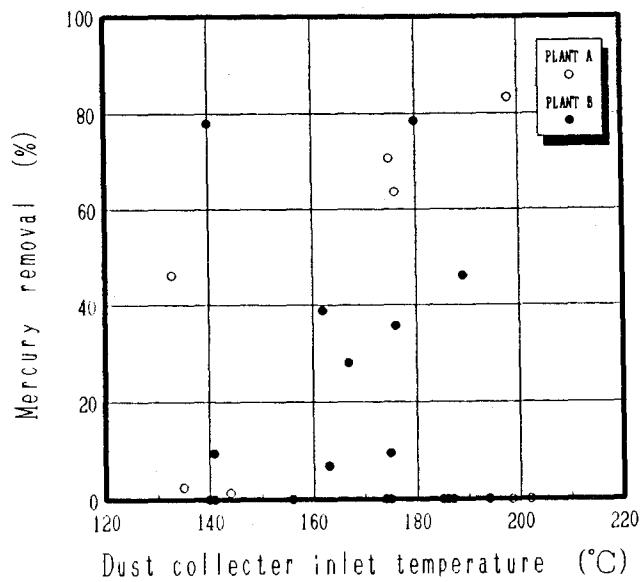


Fig.13 Mercury removal VS dust collector inlet temp.

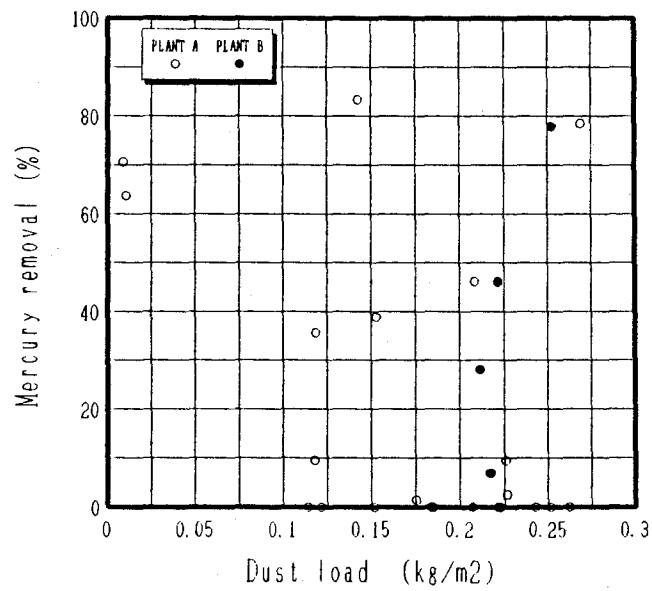


Fig.14 Mercury removal VS dust load

SESSION 3C: WET AND DRY FLUE GAS CLEANING EXPERIENCE

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GAS CLEANING IN CONNECTION WITH WASTE INCINERATION

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ABSTRACT

The Boliden process for gas treatment after waste incineration is based upon general experience in treating smelter and roaster gases and industrial waste waters at the Boliden smelters in Sweden, and is adapted to the specific conditions by waste incineration.

The Boliden technique is worked out to give:

- low emissions to air and water
- products that can be easily handled, stored or utilised
- high reliability
- minimum service demand
- easy operation and maintenance
- low consumption of energy and chemicals

These demands are fulfilled in the Boliden wet gas treatment process which consists of gas washing in a scrubber, separating the fine dust and aerosols in the wet electrostatic precipitators, and eliminating mercury in a selenium filter.

The fly ash which is collected in the scrubber is leached in the scrubber liquid and separated in a filter, and the water bleed is purified in a waste water treatment plant.

BASIC CONDITIONS

The Boliden process for gas treatment after waste incineration is based upon general experience in treating smelter and roaster gases and industrial waste waters at the Boliden smelters in Sweden. The process has been introduced at other sites. The system is adapted to the specific conditions encountered when gases emanate from such an inhomogenous source as waste incineration.

This process, wet gas treatment according to the Boliden system, consists of units designed in order to meet the environmental demands for dust, hydrochloric acid and other acidic compounds, dioxins and mercury in the gas leaving the plant; for heavy metals and other contaminants in the effluent water; and for composition and stability of the solid waste products.

Our technique is worked out to give:

- low emissions to air and water
- products that can be easily handled, stored or utilised
- high reliability
- minimum service demand
- easy operation and maintenance
- low consumption of energy and chemicals

These demands are fulfilled in our wet gas treatment process which consists of gas washing in a scrubber, separating the fine dust and aerosols in the wet electrostatic precipitators, and eliminating mercury in a selenium filter. The fly ash which is collected in the scrubber is leached in the scrubber liquid and separated in a filter, and the water bleed is purified in a waste water treatment plant.

We deliver complete turn-key plants including design, fabrication, delivery, erection, commissioning, start-up, and initial operation of the plant, including documentation and education of operators and maintenance personnel. In the plant there are systems for cooling and purification of the incoming waste gas; for handling of chemicals and waste products, for water and effluent water; electricity; process control; insulation and surface treatment.

PROCESS DESCRIPTION

A flow sheet of the process is shown in figure 1.

The gases from the incineration furnace pass a waste heat boiler and an economizer before they enter the scrubber through the central gas inlet nozzle.

In the scrubber most of the solid impurities and the acidic compounds are removed from the gas. The pH of the scrubber liquid is automatically controlled by addition of limestone from silo into the pump tank.

Since the dust load is very high, scrubber liquid is bled from the system in order to avoid too high slurry concentrations. This bleed goes to a reaction tank where it is mixed with fly ash collected in the boiler and economizer. The soluble compounds are dissolved in the acidic liquid, and then the solids are removed in a filter. The leached fly ash, which is returned to the furnace, has a low content of zinc, cadmium and other noxious metals. A part of the filtrate is taken as a bleed to the water treatment, while the rest is returned to the scrubber.

The gases from the scrubber continue to the Editube wet electrostatic precipitators, where aerosol and very fine dust particles, containing noxious matters such as hydrochloric acid, dioxins and other chlorinated organic compounds, are removed from the gas. The precipitator consists of a GRP inlet chamber and a stainless steel tube bundle with negatively charged needle point emission electrodes concentric in each tube. The dust and aerosol particles are charged by corona emissions and collected at the tube surfaces.

The precipitator also acts like a gas cooler, and the low steel temperature together with the dilution of the impurities by the condensate forming inside the precipitator tubes, ensures that metal corrosion is kept at a minimum. The clean gas leaves the precipitator by way of the upper chamber and the gas outlet nozzle. The dirty condensate collects in the bottom cone and drains out through the condensate nozzle. The Editube precipitator may be integrated with a heat recovery system: cooled by having a closed circuit that in its turn is cooled by sea water or cooled with water which is cooled by air in cooling towers.

After reheating the gas in order to avoid condensation, elemental mercury is removed in a selenium filter, and the purified gas is led to the stack.

The water bleed is treated in two steps in a water treatment plant. In the first step, sodium sulphide is added and the heavy metals are precipitated as sulphides and removed from the system in a centrifuge. Either sodium sulphide solution may be delivered in sufficient quantities from a nearby pulp mill to a storage tank, or the solution is prepared from a solid product. The sulphide sludge may be processed for recovery of its metal values.

In the second step ferrous hydroxide is precipitated by increasing the pH to between 7 and 8, and this precipitation removes the rest of the contaminants not 100% removed to the first step where the iron goes into solution again, and therefore only the iron losses from the system have to be compensated.

The offgas will have the following maximum concentrations based upon a dry gas with 10% CO₂:

TABLE 1. EMISSION TO AIR

Dust content	10 mg/Nm ³
HCl	10 mg/Nm ³
Hg total	10 µg/Nm ³
Dioxins	0.1 ng/Nm ³

The purified gases are reheated in order to avoid condensation in the selenium filter and in the stack.

The waste water will be treated in a multi-stage process. The effluent water will contain the following maximum concentrations:

TABLE 2. EMISSION TO WATER

Zn	0.1 mg/l
Pb	0.01 mg/l
Hg	2 µg/l
F	30 mg/l
CaCl ₂	10-100 g/l
pH	7-9

REMOVAL OF FINE DUST, MIST AND DIOXINS

Removal of these impurities is done in the Editube wet electrostatic precipitator.

MATERIAL CHOICE

The standard material chosen in the Editube wet electrostatic precipitator is the stainless steel Avesta 254 SMO which has excellent corrosion properties in chloride containing acidic solutions. If corrosion tests indicate that other metallic materials (for instance Sandvik Sanicro 28 or Titanium grade 2) may be more suitable, we will deliver the units accordingly.

BASIC DESIGN

In order to get a low-cost, easy transportable precipitator, it was chosen to produce it as a modular-shaped unit. If a higher gas capacity is needed that can be handled in one unit, the required number of units are put in parallel.

Each precipitator unit consists of gas inlet and outlet chambers, put together by a shell-and-tube bundle, see figure 2. Each chamber has a gas nozzle fitted with built-in shut-off damper. The lower (inlet) chamber is also equipped with a perforated plate in order to get a uniform distribution of the gas into the tubes. This plate also acts as a floor for personnel entering the precipitator.

The gas passes 90 grounded tubes (in the standard unit) which act as collecting surfaces for the impurities to be separated. The tube bundles are made of stainless steel or titanium, while the chambers may be in other materials as glass-reinforced plastics. In the case that the chambers are in other materials than the tube bundles, the parts are fitted with flanges and bolted together, otherwise the construction is all-welded.

The tube bundle is surrounded by a shell of the same material, and when cooling water is connected at the shell side, the unit is also acting as a shell-and-tube heat exchanger. Besides that this gives the unit a gas cooling capacity, it also has the advantage that the metal surface in contact with the gas is kept at a low temperature and is wetted with a condensate film which dilutes and continuously washes away the impurities that are collected on the surface, and this keeps the corrosion rate at a minimum. As an extra safety, the unit is equipped with an automatic flushing system. The flushing intervals can be adjusted by a timer.

Concentric in each circular tube there are negatively charged emission electrodes of a particular design which creates higher current density than conventional discharge electrodes. The electrodes are made of the same material as the tube bundle.

The emission electrodes are positioned by upper and lower frame-works. The upper frame is supported by beams which are introduced into the upper chamber through gas-tight, electrically heated, insulator compartments.

The high-voltage current to the electrodes comes from a rectifier-transformer unit placed at the top of the precipitator. The local control cabinet is equipped with a kV-panel, a mA-panel, a spark-counter and an operating-timer.

CAPACITY

The Editube wet electrostatic precipitator is designed as a standard unit, and is capable of cleaning gas flows between 20-40 000 Nm³/h on the gas composition. Only one purification step is necessary, while conventional precipitators operate two in series for the same duty. The clean gas has a dust content of 10 mg/Nm³ or lower.

The cooling capacity of the unit is about 0.8 MV.

DELIVERY

The Editube wet electrostatic precipitator is delivered by road or rail to the customer as a complete, workshop-fabricated and tested unit which is ready for operation after only a few days for erection and connection to the gas, cooling water, flushing water and electric systems.

DIOXIN REMOVAL EFFICIENCY

Measurements with dioxin removal in the Editube wet electrostatic precipitator has given the following results:

TABLE 3. DIOXIN REMOVAL EFFICIENCY

Inlet conc. ng/Nm ³ TCDD-equiv.	Outlet conc. (N)	Separation %
46.23	0.07	99.85
56.0	0.17	99.7
19.7	0.06	99.7

The over-all aerosol removal efficiency was 98.9%, which surprisingly is lower than the dioxin removal efficiency.

More than 98% of the aerosol particles which remain in the gas after treatment have diameters >15 µm. The removal efficiency of the particles >15 µm is only about 75% in the wet electrostatic precipitator, while there is an almost complete removal of the smaller particles. However, the concentration of dioxins is lower on the >15 µm particles than on the very small particles, which explains why the dioxin removal is higher than the general particle removal.

If all particles >15 µm are already removed from the gas in an efficient scrubber system or in a vane separator, this gives a total aerosol removal efficiency, and consequently dioxin removal efficiency, which is much higher than in the table above. It is therefore possible to guarantee a maximum dioxin content of 0.1 ng/Nm³ in the gas after treatment.

MERCURY REMOVAL AND RECOVERY

The growing use of mercury-based batteries, e.g. in personal electronic equipment, will inevitable increase the residual Hg content of municipal wastes. This is catered for in the Boliden plant, which incorporates a reactive filter first developed for and now widely used in metallurgical smelting operations. This consists of a cylindrical shell containing graded porous material impregnated with selenium, which has a strong affinity for mercury, see figure 3. In waste-gas cleaning practise, gas from the electrostatic precipitator - reheated to avoid dewpoint effects - passes through the selenium filters before being discharged to the stack. The filter cartridges have lives of several decades in municipal systems and, when spent, are replaced on a favourable exchange basis.

ASH TREATMENT

Most of the flue dust from the furnace off-gas is retained in the waste-heat boiler/precipitator/economizer system which forms part of a normal waste-incineration plant. Any dust still entrained in the gas leaving the economizer is removed as it passes through the scrubber and wet electrostatic precipitator.

It is not possible to recycle the generated flue-dust directly to the incineration furnace, because it contains such heavy metals as zinc and cadmium; or, for environmental reasons, is disposal of the dust to land-fill a viable alternative.

Boliden has therefore developed a system whereby the dust is leached of heavy metals, leaving only the residue to be recycled to the furnace. Leach residue is separated out by a band filter. The filtrate is treated with sodium sulphide, and sludge with a high heavy-metal content is formed which is removed by a centrifuge. This sludge, which represents only 2% by weight of the flue dust, can be re-utilized in a metal-processing plant such as a zinc or copper smelter. As a result there is no flue dust remaining to be disposed of.

UTILITIES DEMANDS

The following approximate figures will apply for a plant treating 50 000 Nm³/h:

TABLE 4. UTILITIES DEMANDS

Electric power	300 kW
Limestone 1-100 µm	400 tons per year
Sodium sulphide (60%)	100 tons per year
Polymer	0.8 tons per year
Iron sulphate (18% Fe)	2 tons per year
Sodium hydroxide (50%)	30 m ³ per year
Sodium hydroxide (100%)	20 tons per year

OPERATING ECONOMICS

The Boliden system has such a high flexibility to take care of pollutants that no previous sorting of the domestic waste is necessary. Also, as the amount of dust formed is so small compared with other systems, the costs for storage of flue ash are more or less eliminated.

The surplus of energy generated from the incineration make the total plant in many cases profitable at the same time as the world's most stringent environmental demands can be fulfilled.

REFERENCE LIST FOR BOLIDEN GAS CLEANING PROCESSES (JAN. 1991)

Client	Location	Product	Process	Capacity (gas)	Year compl./ status
Kemira Kemi*	Helsingborg Sweden	Sulphuric acid	Thiosulphate Mercury Removal	50 000 Nm ³ /h	1969
Kemira Kemi*	Helsingborg Sweden	Sulphuric acid	Wet Arsenic Separation	50 000 Nm ³ /h	1971
Boliden Mineral	Skelleftehamn Sweden	Liquid sulphur dioxide	Mercury Separation in Selenium Filters	60 000 Nm ³ /h	1972
Boliden Mineral	Skelleftehamn Sweden	Liquid sulphur dioxide	Mercury Separation in Selenium Filters	100 000 Nm ³ /h	1976
Boliden Mineral	Skelleftehamn Sweden	Copper, lead, sulphuric acid, liquid SO ₂	Wet Gas Treatment	300 000 Nm ³ /h	1978
Preussag	Nordenham Germany	Lead	Thiosulphate Mercury Removal	30 000 Nm ³ /h	1980
New Consort	Barberton RSA	Gold	Dry Arsenic Separation	10 000 Nm ³ /h	1982
Boliden Mineral	Skelleftehamn Sweden	Sulphuric acid	Wet Electrostatic Precipitators	100 000 Nm ³ /h	1986- -87
Arzberg	Germany	Power plant	Wet Arsenic Sep./ Mercury Removal Processes	2x3 000 Nm ³ /h	1987
Nuova Samim	Porto Vesme Italy	Lead	Wet Arsenic Separation	16 000 Nm ³ /h	1987
Ronte Adle	Bilbao Spain	Sulphuric acid	Wet Arsenic Separation	60 000 Nm ³ /h	1987
Scandust	Landskrona Sweden	Alloy metals from dust	Mercury Separation in Selenium Filters	20 000 Nm ³ /h	1987
Scharin	Urviken	Wood chip	Wet Electrostatic	70 000 Nm ³ /h	1988

Client	Location	Product	Process	Capacity (gas)	Year compl./ status
Unitex AB	Sweden	boiler	Precipitators		
Hoechst	Frankfurt/Main Germany	Power plant	Wet Arsenic Sep./ Mercury Removal Processes	1 500 Nm ³ /h	1989
Cominco	Trail Canada	Lead	Wet Arsenic Sep./ Cadmium Separation	16 000 Nm ³ /h	1990
Enami	Santiago Chile	Copper	Wet Arsenic Sep./ Thiosulphate Mercury Removal	88 000 Nm ³ /h	1990
Norsk Hydro	Porsgrunn Norway	Chlorine	Wet Electrostatic Precipitators	2 300 Nm ³ /h	1990
Norsk Hydro	Porsgrunn Norway	Magnesium	Dioxine Removal by Wet Electrostatic Precipitators	70 000 Nm ³ /h	1990
Chematur Internat.	Karlskoga Sweden	Municipal Waste Incineration	Flue Gas Treatment	35 000 Nm ³ /h	1991
Outo- kumpu	Harjavalta Finland	Sulphuric acid	Thiosulphate Mercury Removal	69 000 Nm ³ /h	1990

* Boliden Kemi before 1989

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

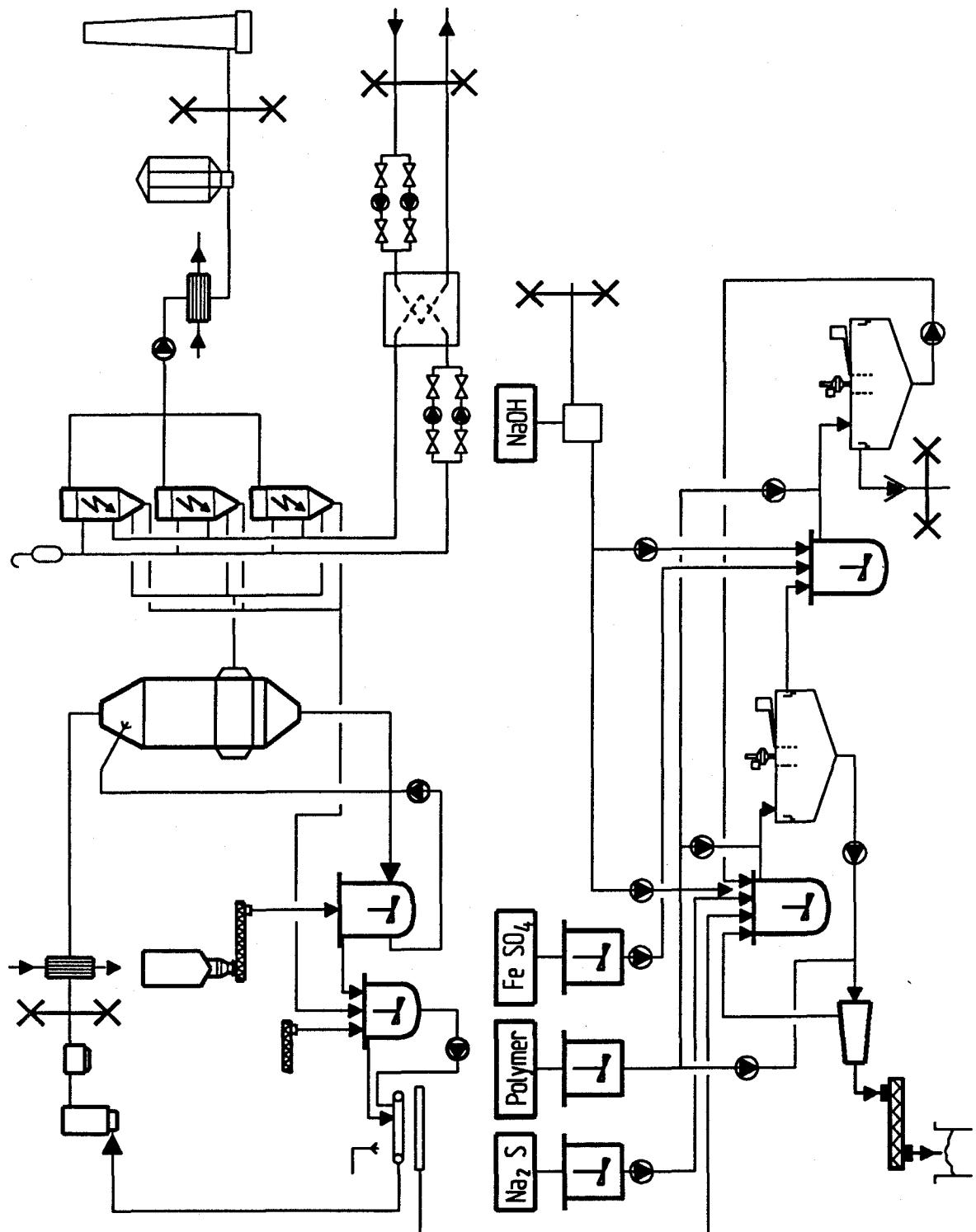


Figure 1. Flow-sheet; Treatment of gases from waste incineration

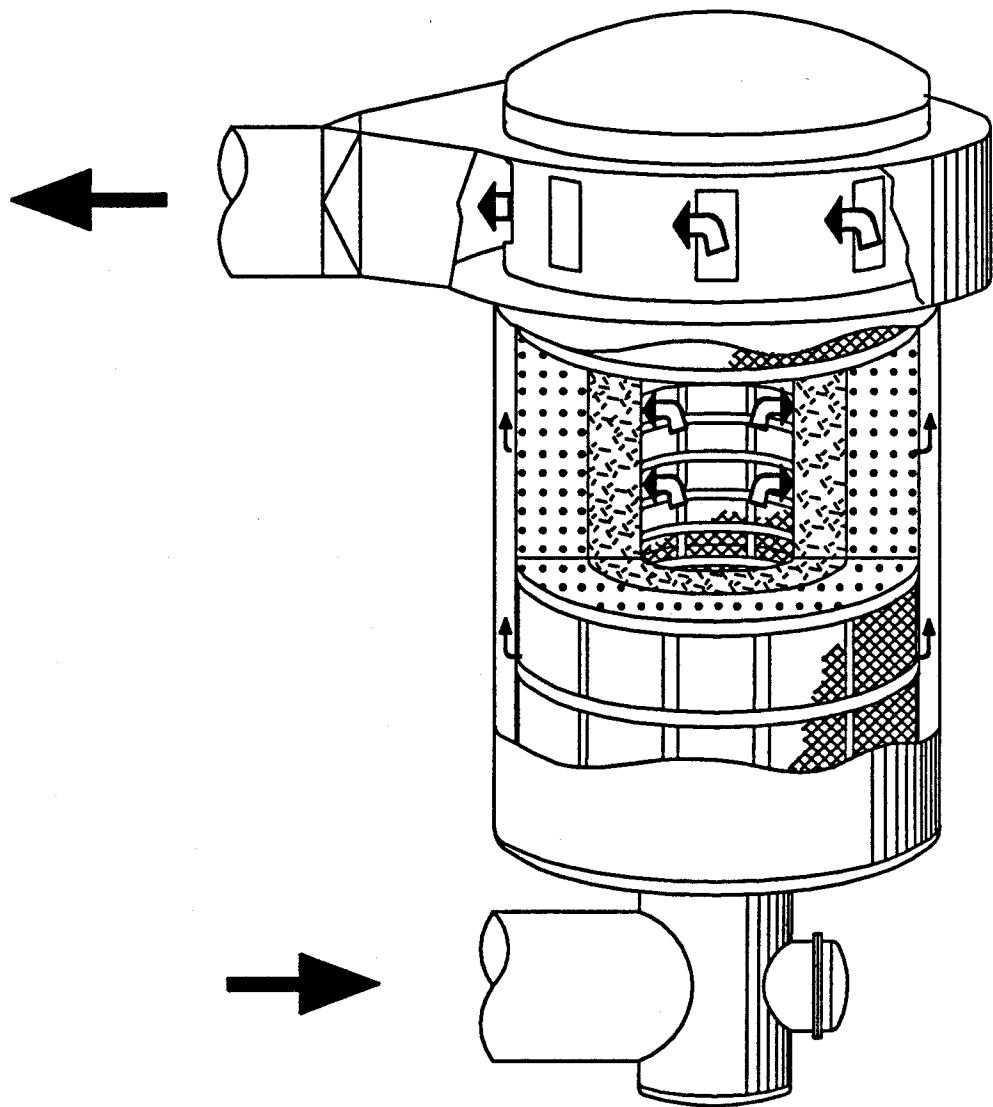


Figure 2. Selenium Filter; $Hg + Se \rightarrow HgSe$

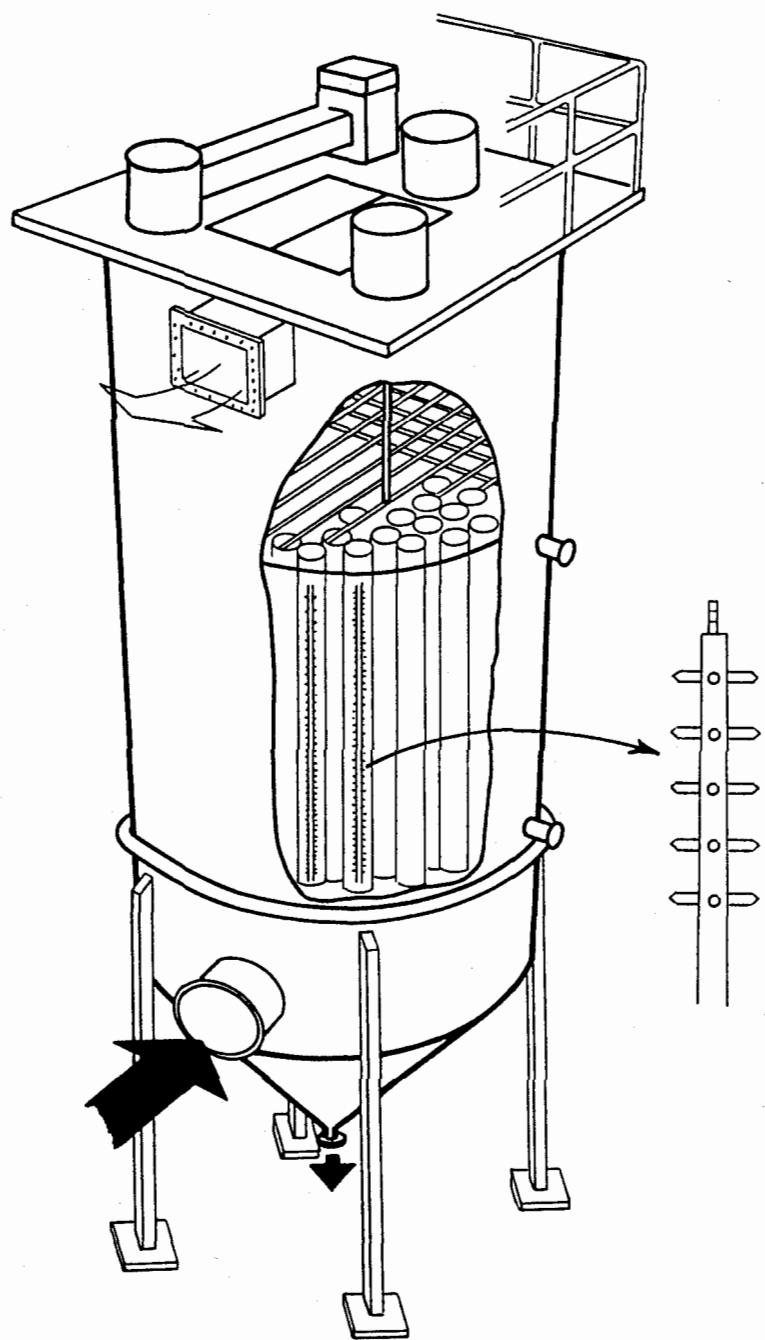


Figure 3. EDITUBE Wet Electrostatic Precipitator

THE JOINT EC/EPA MID-CONNECTICUT TEST PROGRAM: A SUMMARY

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ABSTRACT

In early 1989, Environment Canada and the U.S. Environmental Protection Agency sponsored a comprehensive test program on a refuse-derived fuel (RDF) unit of the Mid-Connecticut facility in Hartford. The program, conducted in cooperation with the Connecticut Resource Recovery Authority, the facility's owner, and ABB Resource Recovery Systems, the operator, included characterization and performance test phases. The results of the characterization tests were used in defining both the combustion and flue gas cleaning system operating conditions for the performance tests.

The results of the performance tests are emphasized here and will be summarized in three parts. First, the combustion tests results will be addressed and related to good combustion practice for RDF combustors. Then, the performance of the lime spray dryer absorber/fabric filter system in controlling acid gas (hydrogen chloride, sulfur dioxide), trace organic (polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran), trace metal (arsenic, cadmium, chromium, lead, and mercury), and particulate matter emissions will be discussed. Finally, the results of ash/residue analyses will be presented.

This paper has been reviewed in accordance with the administrative review policies of the U.S. Environmental Protection Agency and approved for presentation and publication.

INTRODUCTION

The joint Environment Canada (EC)/U.S. Environmental Protection Agency (EPA) program to evaluate the combustion and air pollution control systems for a modern refuse-derived fuel (RDF) combustor was performed on Unit 11 at the Mid-Connecticut facility (Mid-Conn) in Hartford. The test program, conducted with the cooperation and assistance of the owner, Connecticut Resource Recovery Authority (CRRA), and the operator, ABB Resource Recovery Systems (ABBRRS) - - formerly Combustion Engineering, Inc. (CE) - - involved two phases: characterization and performance. Since the results of the 28 characterization tests were reported earlier,^{1,2} the emphasis here will be on the 13 valid performance tests made during February 14-March 1, 1989. These results will be discussed in three parts: combustion, flue gas cleaning, and ash/residue, with emphasis on these topics in the order listed.

A major objective of the test program was to study the impact of combustor operation on the control of organic emissions. Another objective was determining the effect of flue gas system variables (temperature and sorbent/acid gas ratio) on the control of acid gases as well as organic, trace metal, and particulate matter emissions. Since the air pollutants from combustion gases are converted to solids by dry flue gas cleaning or are in particulate carryover, the third test program objective discussed here concerns organics and metals contained in the fabric filter ash/residue.

TEST FACILITY DESCRIPTION

The facility contains a processing plant and a RDF power plant.¹ The power plant contains three CE steam generating units, each consisting of a RDF spreader stoker, a natural circulation welded-wall boiler, a superheater, an economizer, and a tubular combustion air preheater. All tests were conducted on Unit 11, which is designed to produce 105 tonnes/hr (231,000 lb/hr) of steam at full load. Figure 1 provides a schematic of the unit.

The fuel burning system for each unit consists of a RDF injection system, a traveling grate stoker, and a combustion air system (see Figure 2). RDF is pneumatically injected through four ports in the front face of each combustor. The lighter fraction burns "in suspension" and the heavier falls onto the stoker where combustion is completed. Underfire air is provided at controlled rates to 10 zones under the grate. There are two separate overfire air (OFA) systems: a tangential system and a wall system. The tangential system has four tangential overfire air (TOFA) windbox assemblies in each furnace corner. Each TOFA assembly contains three elevations of nozzles which can be manually adjusted in the horizontal plane. The wall system contains one row of OFA ports on the front wall and two rows on the rear wall.

The flue gas cleaning (FGC) system consists of a lime-based spray dryer absorber (SDA) followed by a reverse-air-cleaned fabric filter (FF) or baghouse. This system is capable of controlling the gas temperature at the SDA outlet and the sulfur dioxide (SO_2) concentration at the FF outlet. The SDA outlet temperature is controlled by the lime slurry flow rate to the SDA, while the SO_2 removal rate is controlled by adjusting the lime concentration in the feed. The baghouse has 12 compartments, each with 168 Teflon-coated glass fiber bags.

TEST CONDITIONS, MEASUREMENT METHODS, AND TEST RESULTS

All performance tests were run at slightly de-rated load conditions because of unusually wet RDF being fired and insufficient combustion air fan capacity.² Combustion and FGC process conditions for the performance tests were based on the results of 28 characterization tests conducted in January 1989.^{2,3} During the performance tests, a computerized data acquisition system continuously recorded combustion and FGC process conditions. Continuous emission monitors (CEMs) measured the concentration of oxygen (O_2), carbon monoxide (CO), carbon dioxide (CO_2), total hydrocarbons (THCs), hydrogen chloride (HCl), and SO_2 at the SDA inlet and FF outlet. Nitrogen oxides (NO_x) were monitored at the SDA inlet. CEMs also measured the concentration of CO, HCl, and SO_2 at the "mid-point" between the SDA and FF. Modified Method 5 (MM-5) sampling trains were used to collect organic samples at the SDA inlet and FF outlet during all tests. Organic samples were also taken at the air heater inlet during four tests (PT07, PT08, PT09, and PT10). Method 5 (M-5) sampling trains collected total particulate samples at the SDA inlet and FF outlet. All sampling and analysis were done in accordance with protocols approved by EC and EPA. Figure 1 indicates sampling locations.

The duration of each test was from 4 to 6 hours to ensure that sufficient volumes of samples had passed through the MM-5 sampling trains. Combustion and FGC process conditions were set and the test was begun after stable operating conditions were obtained.

All polychlorinated dibenzo-p-dioxin and dibenzofuran (PCDD/PCDF), CO, NO_x , SO_2 , HCl, and other air pollutant data presented here have been corrected to 12% CO_2 . All PCDD/PCDF data are given in nanograms per standard cubic meter [25°C, 101.3 kPa(77°F, 1 atm)], denoted by ng/ Sm^3 .

Fourteen performance tests were conducted; however, since performance test 1 (PT01) did not meet all sampling requirements, its results are not given. Combustion and FGC process conditions were varied independently. The combustion tests were structured to evaluate the effects of good and poor combustion conditions on organic concentrations at the SDA inlet.

The primary combustion test variables were boiler steam load, underfire-to-overfire air ratio, and OFA distribution. During testing, the criterion for judging good or

poor combustion conditions was the CO concentration at the SDA inlet. The effects of load were evaluated by conducting tests at low (L), intermediate (I), normal (N), and high (H) boiler steam flow rates. Underfire-to-overfire air ratios, which influence the relative amount of RDF burned in suspension and the entrainment of particulate matter in the flue gases (particulate matter carryover), were controlled by changing the number of levels of OFA. Distributional mixing effects were evaluated by changes in the underfire-to-overfire air ratio and by using rear-wall overfire air (ROFA) in combination with different levels of TOFA.

Combustion test conditions, in order of increasing load, and the resultant average CO and PCDD/PCDF concentrations are summarized in Table 1. The CO values are averages based on measured values at the SDA inlet and FF outlet. The NO_x and PCDD/PCDF values are from the SDA inlet.

DISCUSSION

Combustion Tests

Test results were evaluated to assess the effects of combustion conditions on furnace emission of organics, NO_x, and metals using concentrations of these air pollutants at the SDA inlet.

Although organic compounds (such as PCDD/PCDF) may be in the waste feed, it is unlikely that they will pass through the combustor undestroyed.⁴ They may also be formed in high temperature regions of the furnace from the thermal decomposition products which are incompletely oxidized due to insufficient combustion air, mixing, temperature, or residence time. They may also originate from catalytic reactions on the surface of flyash downstream of the combustion chamber.

Multiple regression analyses show that PCDD, PCDF, chlorophenol (CP), chlorobenzene (CB), and polynuclear aromatic hydrocarbon (PAH) concentrations at the SDA inlet can best be correlated with two or more of the following easily monitored furnace/flue gas properties:

- a) CO concentration
- b) THC concentration
- c) NO_x concentration
- d) Moisture (H₂O) concentration
- e) Temperature in the furnace or at the economizer outlet

For example, the best correlation for PCDD concentrations at the SDA inlet ($R^2=0.9$)^{*} is based on the CO, NO_x, and H₂O concentrations at this location.

* R² is the correlation coefficient with R²=1.0 indicating a perfect (exact) correlation.

Multiple regression analyses provide correlations which indicate that the combustor operating variables (steam load, combustion air flows, RDF moisture content, etc.) can be used to control PCDD, PCDF, CP, CB, and PAH concentrations at the SDA inlet. These operating variables control combustion in the furnace by impacting the fundamental combustion parameters: time, temperature, air/fuel ratio, and mixing.

Multiple regression analyses based on easily monitored flue gas properties provide for better correlations of organics ($R^2=0.8$ to 0.98) than combustor operating variables ($R^2=0.6$ to 0.8). Optimum control systems for limiting the furnace emission of organics will probably require both flue gas property measurements and combustion operating variables as inputs.

Single parameter regression analyses using average test values show that either CO or THC tracks the furnace destruction of organics. Moderate correlations between CO (or THC) and PCDD/PCDF at the SDA inlet [$R^2=0.70$ (or 0.68)] were obtained when the entire data set (13 tests) was considered (see Figures 3 and 4). An excellent correlation ($R^2=0.95$) occurred for CO versus PCDD/PCDF under poor combustion ($CO>200$ ppm). No statistically significant correlation was found between CO and PCDD/PCDF for tests with good combustion conditions ($CO<200$ ppm). Tests with average THC concentrations greater than 7 ppm provided excellent correlations between THC and PCDD/PCDF emissions, but tests with less than 7 ppm showed no significant correlation.

Single parameter correlations between average CO (or THC) concentrations and CP, CB, or PAH concentrations at the SDA inlet provided better correlations [$R^2= 0.88$ (0.92), 0.83 (0.87), and 0.83 (0.85), respectively] than those for PCCD or PCDF. There were no significant correlations between average CO (or THC) and PCB at the SDA inlet. Thus, CO or THC concentration at the SDA inlet appears to be a good indicator for the furnace emission of most trace organics of concern.

Previous field tests have shown a strong positive correlation between the amount of PM entrained in flue gas (PM carryover) and emissions of PCDD/PCDF.⁵ The Mid-Conn data show a fair correlation ($R^2=0.61$) between PCDD/PCDF and PM concentrations at the SDA inlet for good combustion conditions ($CO<200$ ppm); yet, no significant correlation between these variables was seen for all combustion conditions. Possibly for good combustion, the emission rate of PM (as PM is postulated to provide reaction sites where PCDD/PCDF are formed) is the principal variable affecting the furnace PCDD/PCDF emission rate, while for poor combustion the effects of other parameters obscure the relationship between PM and PCDD/PCDF.

PCDD/PCDF and other chloro-organic compounds can be formed downstream of the furnace by de novo synthesis reactions on the surface of flyash.^{6,7,8} The amount formed is believed to be proportional to the amount of flyash and the time individual particles with reaction sites exist in the temperature range of about 450 to

150°C (750 to 300°F). Mid-Conn has an air heater just upstream of each SDA with flue gas in the upper end of this range. Thus, an increase in PCDD/PCDF concentrations across the air heater due to de novo synthesis was expected. The flue gas temperature at the economizer outlet (which approximates that at the air heater inlet) typically ranges from 343 to 388°C (650 to 730°F), while the temperature at the outlet of the air heater ranges from 177 to 210°C (350 to 410°F). To evaluate the hypothesis that PCDD/PCDF form on particulate deposits within the air heater, PCDD/PCDF measurements were made during four test runs just upstream of the air heater inlet simultaneously with those at the SDA inlet (air heater outlet). Contrary to expectations, a comparison of measurements at the inlet and outlet of the air heater indicated a reduction of PCDD/PCDF concentrations during three of four runs. No explanation for these unexpected results is presently available.

Average NO_x emissions ranged from 149 to 193 ppm. Generally, NO_x emissions increase with increased combustion temperatures and improved mixing. Accordingly, low CO emissions corresponded with high NO_x emissions. Conversely, the lowest NO_x emissions were associated with high concentrations of CO, THC, and organics at the SDA inlet. An evaluation of 30-second emission averages from the CEM data indicates that, to obtain a NO_x emission less than 180 ppm (the new U.S. New Source Performance Standard requirement for large municipal waste combustors), the Mid-Connecticut units would have to operate at a CO emission concentration of 71 ppm or higher.

There were no apparent correlations between combustion conditions and the concentration of metals in flyash at the SDA inlet.

Flue Gas Cleaning System Tests

As noted earlier, Unit 11 has a lime SDA/FF system for acid gas and PM control. Lime is slaked and the resultant calcium hydroxide slurry is diluted with water from the facility's surface water runoff/coal pile drainage pond, or Connecticut River water when pond water is unavailable, prior to being fed to the SDA's atomizer. During the performance tests, dilution water was mainly from the pond. As reported earlier,² the SDA outlet temperature was used as a surrogate for the approach to saturation temperature since it was directly measurable, and the SO₂ concentration at the FF outlet served as the on-line indicator of sorbent-to-acid gas ratio (or lime stoichiometry). Because the plant's measuring instrument for slurry density was inoperative and dilution water composition varied during the test program, the lime stoichiometry could only be estimated; thus, it is not quantitatively noted here. When stoichiometry is used here, it refers to lime stoichiometry; high, moderate (or medium), and low stoichiometry correspond to low, medium, and high FF outlet SO₂ concentration, respectively.

The HCl and SO₂ concentrations were monitored continuously, and their averaged values along with removals for each test run are shown in Table 2. Note that the data for PT02 and PT05, PT03 and PT11, and PT12, PT13, and PT14 have been

grouped, since the FGC system set points (SDA gas outlet temperature and FF outlet SO₂ concentration) were the same. Table 2 shows that the HCl and SO₂ values at the SDA inlet averaged 445 and 185 ppm, respectively, over all tests, with the individual test average values being $\pm 10\%$ of these averages, except that for PT08 when the HCl concentration was about 20% higher.

As expected the HCl and SO₂ removals increased with decreasing SDA outlet gas temperature (approach to saturation temperature) and increasing lime stoichiometry. The HCl removal averaged 95% or more and the SO₂ removal over 83% when the lime stoichiometry was high (low FF outlet SO₂ concentration), such as during normal FGC system operation, and showed only a slight decrease with temperature as the average SDA outlet temperature increased from 122 to 166°C (252 to 330°F). The HCl removal was above 92% for all temperature and stoichiometry combinations tested, except for high temperature (171°C or 339°F) and high stoichiometry when it was about 77%. The SO₂ removal was more sensitive to the change in stoichiometry than to temperature, being 83 to 95% for high stoichiometry and ranging from 62 to 76% for medium stoichiometry over the tested SDA outlet temperature range [122 to 171°C (252 to 339°F)]. At low stoichiometry, the SO₂ removal unexpectedly rose from 30 to 32% as the SDA outlet gas temperature increased from 122 to 142°C (252 to 287°F); however, the SO₂ removal was -6% at 171°C (339°F) (i.e., the SO₂ concentration at the FF outlet was greater than at the SDA inlet), suggesting that SO₂ was being desorbed in the filter cake. This suspected desorption was similar to that observed in the Mid-Conn characterization test series,² is consistent with pilot study findings,⁹ and is likely due to HCl's being more reactive than SO₂ with the calcium-based compounds in the filter cake. These results suggest that "normal" operation of the SDA/FF system [140°C (285°F), moderate stoichiometry] would be expected to yield 95% or more HCl removal and about 70% SO₂ removal.

Table 3 provides inlet concentrations and removal efficiencies for selected organics. With the exception of PT09 (highest SDA outlet temperature and low stoichiometry), the PCDD removal was at least 99.8% for SDA inlet concentrations ranging from 95 to 397 ng/Sm³. For PT09, the inlet PCDD concentration was 71 ng/Sm³ and the removal was 99.2%. Since the SDA outlet temperature, stoichiometry, and inlet PCDD concentration may affect PCDD removal, the specific reason for the relatively low removal during PT09 is not evident. All three variables had values suggesting low control (i.e., high temperature, low stoichiometry, and low inlet concentration). The PCDF removal was 99.9% or greater for all tests, although the SDA inlet PCDF concentration changed almost three-fold from 341 to 1007 ng/Sm³. CP control was usually slightly better than CB control, with CP control generally being 97% or more and CB control being 95% or more. The CP inlet concentration ranged from 11,329 to 62,938 ng/Sm³, more than double that for CB. The PAH removal generally increased with inlet concentration, ranging from 58.6 to 97.7% as the concentration rose from 6,289 to 88,626 ng/Sm³. The lowest PAH removals in the FGC system correspond to the lowest inlet

concentrations and occurred during good combustion (low CO). However, the PAH (as well as other organic) emissions varied with flue gas cleaning system variables. Generally, organics removal was high (over 95%), except PAH removal which was usually moderately high (over 92%), for all tests and conditions so that changes in the FGC process variables had little effect over the range evaluated. For example, the removal of combined PCDD and PCDF was 99.7% or higher for all tests.

As shown in Table 4, the PM concentration in the flue gas at the SDA inlet ranged from 3,274 to 4,949 mg/Sm³, while the outlet concentration ranged from 2.68 to 7.62 mg/Sm³. The corresponding PM removal was 99.8% or more. Because of the high PM removals, the effect of process changes could not be reliably distinguished.

Table 4 also presents selected metals control data, with complete removal of As and Cd being indicated for all tests. The removal of Pb followed very closely the removal of PM, usually being above 99%, despite a five-fold ratio of the maximum to minimum inlet concentration for the tests. Surprisingly, Hg control was over 96% for all the tests. The Cr removal was high and paralleled that of Hg.

While high C content in flyash, which is characteristic of RDF combustors, may be a factor in the observed high control of Hg emissions, conclusive test data were not obtained on C content during the test program. However, the loss-on-ignition data in Table 5 range from 4.26 to 10.45% and suggest high C content, since these values are believed representative of the C plus water of hydration content of the fabric filter ash. Since the flyash from highly efficient mass burn combustors is from 1 to 2%, the values in Table 5 suggest C values greater than this range even for water of hydration contents as high as 50%. However, PM loading may also be a factor affecting Hg control, since condensable metals are believed to enrich particles, especially small ones, because of the relatively high surface area on a mass basis. Other variables considered in studying the Hg removal were flue gas temperatures and lime stoichiometry. Hg removal decreased slightly with increasing temperature, probably due to decreasing condensation or adsorption on PM as the temperature rose. Using outlet SO₂ concentration as a surrogate for lime stoichiometry (note that the average inlet SO₂ values varied by less than 7% from 185 ppm, the average of all test averages), Hg removal decreased with increasing stoichiometry. Possibly a reaction between mercuric chloride and (excess) calcium hydroxide in the filter cake led to the liberation of Hg²⁺ ions and the increased Hg emission. Thus, operation at high lime stoichiometry to ensure high acid gas removal can be accompanied by increased Hg emission relative to low or moderate stoichiometry.

Ash/Residue Results

During the test program, RDF and ash/residue samples were collected. RDF was collected from the conveyor serving the combustor. Ash/residue were collected from the economizer, fabric filter, and grate (siftings). In addition, the ash from the

grate's surface was collected, after quenching, as bottom ash, and the flyash at the SDA inlet and FF outlet was collected using sampling trains. The distribution of metals in the ash streams is discussed elsewhere,¹⁰ as are the physical and chemical properties of the noted ash/residue.¹¹ The results to be discussed here concern the metals and organics collected in the FF ash (or residue).

While the FGC system data indicate complete removal of As and Cd, the concentrations of these metals in Table 5 suggest otherwise. This premise is based on the lime slurry's (slaked lime plus dilution water) not being a significant source of these elements. The Pb concentration in the FF ash was the highest of the metals shown in Table 5 and was expected as it had the highest flue gas concentrations at the SDA inlet and was removed very effectively (generally, over 99%) in the FGC system. While the SDA inlet concentrations and removals of Cr and Hg were quite similar, the Cr transferred to the FF was 4 to 20 times as great. Possibly the high volatility of Hg during collection and storage of the samples prior to their analyses may have affected the concentrations of Hg in the FF ash.

Considering the minimum and maximum PM emission rates of 2.68 (PT06) and 7.62 mg/Sm³ (PT04), the calculated Hg transfer rates to the FF ash for these runs are 44.57 and 66.48 g/hr, respectively. The Hg removal rates, based on flue gas sampling, are 90.32 and 92.98 g/hr, respectively, for the tests. Thus, the calculated Hg transfer rates to the FF ash for these tests are about 50 to 70% of those determined from flue gas data. For a less volatile metal, such as Pb, the calculated rates are 4,538 and 4,727 g/hr for PT06 and PT04, while removals in the FGC system are 1,120 and 1,549 g/hr, respectively, about 30% of the calculated values. These examples suggest that the input-output method is, at best, a crude check on gas sampling and analytical measurements.

Comparison of PCDD removal rates by the FGC system with values observed in the FF ash yields results similar to those noted for the metals above. For example, the PCDD removal rate by the FGC system ranged from 10.12 (PT09) to 57.57 mg/hr (average of PT02 and PT05), while the corresponding FF ash gained PCDD at the calculated rates of 147.5 and 41.18 mg/hr for these tests. Thus, the calculated PCDD transfer rate for PT09 was almost 15 times that of the FGC system, while for combined PT02 and PT05, the calculated rate reasonably approximates the PCDD removal from the flue gas, about 30% below the flue gas removal rate. Similar results would be expected from the input-out analyses for other organics.

SUMMARY

The comprehensive 1989 test program on an RDF municipal waste combustion unit at the Mid-Conn facility obtained combustion and FGC performance data useful for the design and operation of similar systems. The jointly sponsored EC/EPA effort also analyzed ash/residue for organic and metal contents as well as generation rates.

Multiple regression analyses show that organic concentrations at the spray dryer inlet can be best correlated by two or more of the following easily monitored flue gas properties: CO, THC, NO_x, moisture, and temperature at the economizer outlet (or in the furnace). Similar analyses indicate that combustion operating variables (steam load, air flows, RDF moisture content, etc.) can be used to control organic emissions, including PCDD, PCDF, CP, CB, and PAH emissions. For tracking the furnace destruction of organics, CO or THC is useful. CO is an excellent indicator of PCDD/PCDF for poor combustion (CO>200ppm), but not for good combustion (CO<200 ppm). PCDD/PCDF formation via de novo synthesis was not observed as expected in the air heater where the temperature supported their net production.

The FGC system demonstrated high removals of acid gases, organics, metals, and PM. HCl removals above 95% and SO₂ removals over 90% were achieved with high lime slurry flows (high lime stoichiometry) and flue gas temperatures at the SDA outlet as high as 166°C (330°F). PCDD and PCDF removals exceeded 99% under all test conditions and appeared to be independent of combustion conditions. Lime stoichiometry had a greater effect on acid gas removal than did SDA outlet temperature. Metal removals were very high: 100% for As and Cd, 98.5% or more for Pb, 96.9% or greater for Hg, and 96.4% or more for Cr for all tests. PM control was 99.8% or greater, and the removal of Pb, Hg, and Cr was only slightly less.

Generally, the organics in the FF ash were higher for poor combustion than for good combustion. The PCDD/PCDF ranged from 74 to 509 ng/g for the tests. Pb was the predominant metal in the ash, while As was the least prominent. Both were similarly ranked in the flue gas at the SDA inlet.

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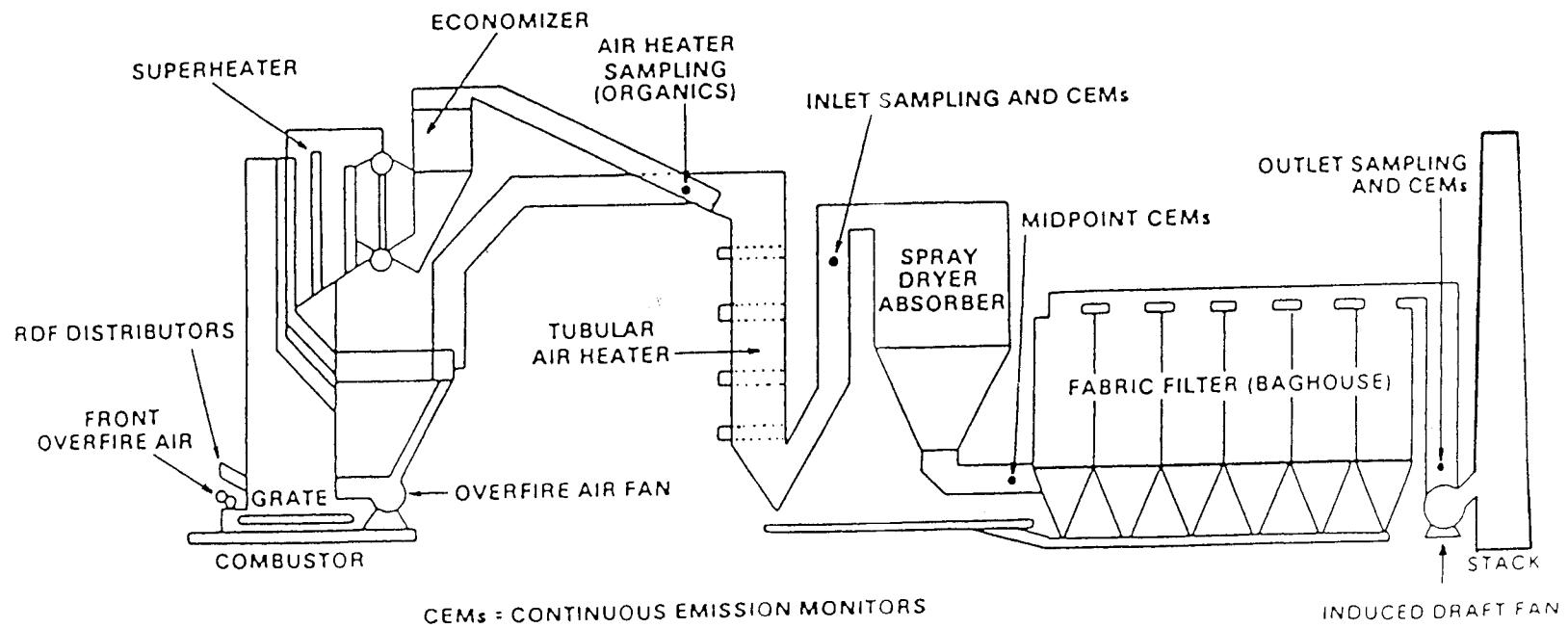


Figure 1. RDF traveling grate stoker boiler with spray dryer absorber/fabric filter (Combustion Engineering).

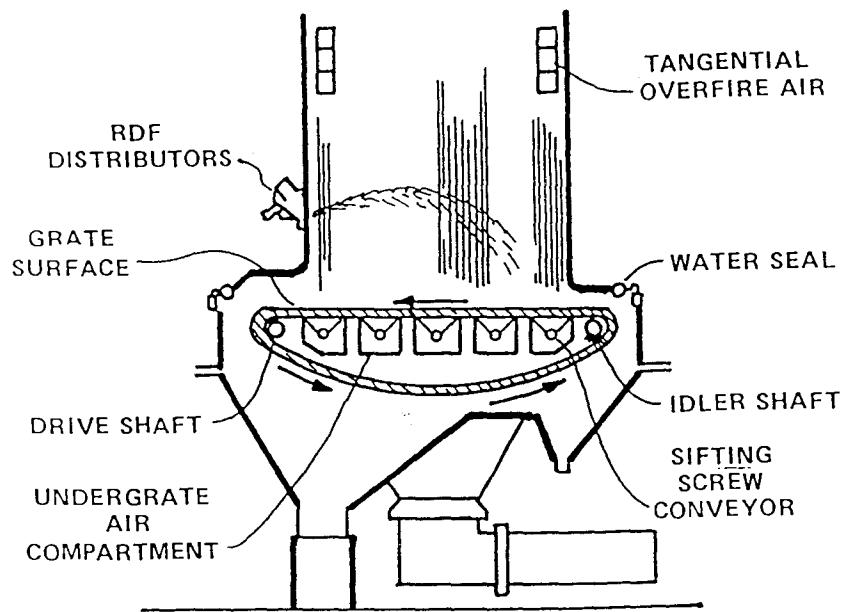


Figure 2. RDF traveling grate stoker boiler (Combustion Engineering).

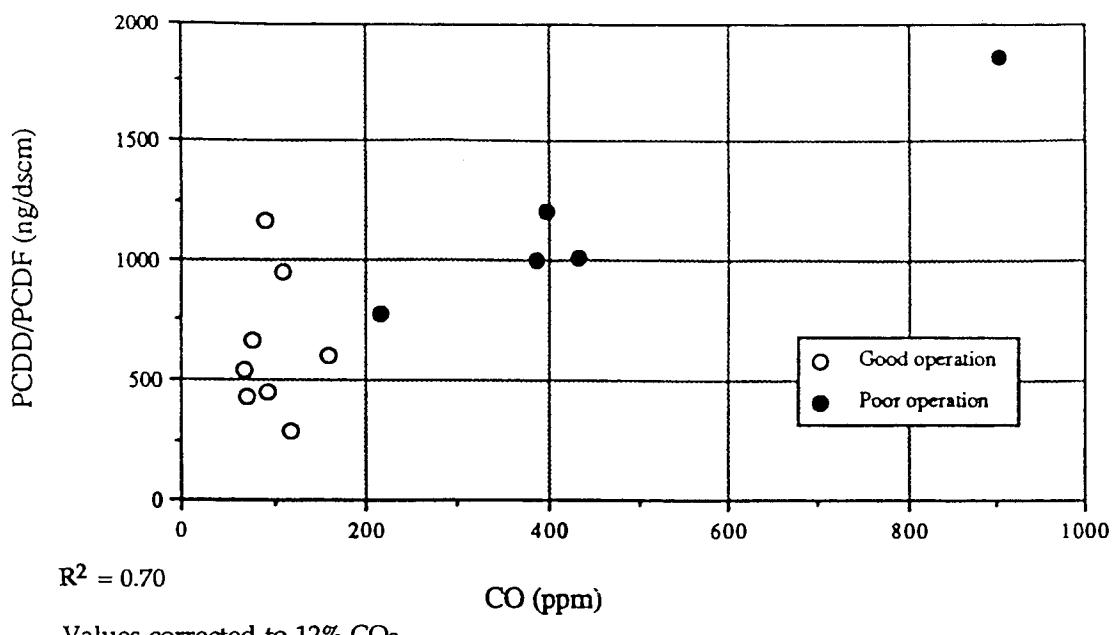


Figure 3. Dependence of uncontrolled PCDD/PCDF on CO emissions.

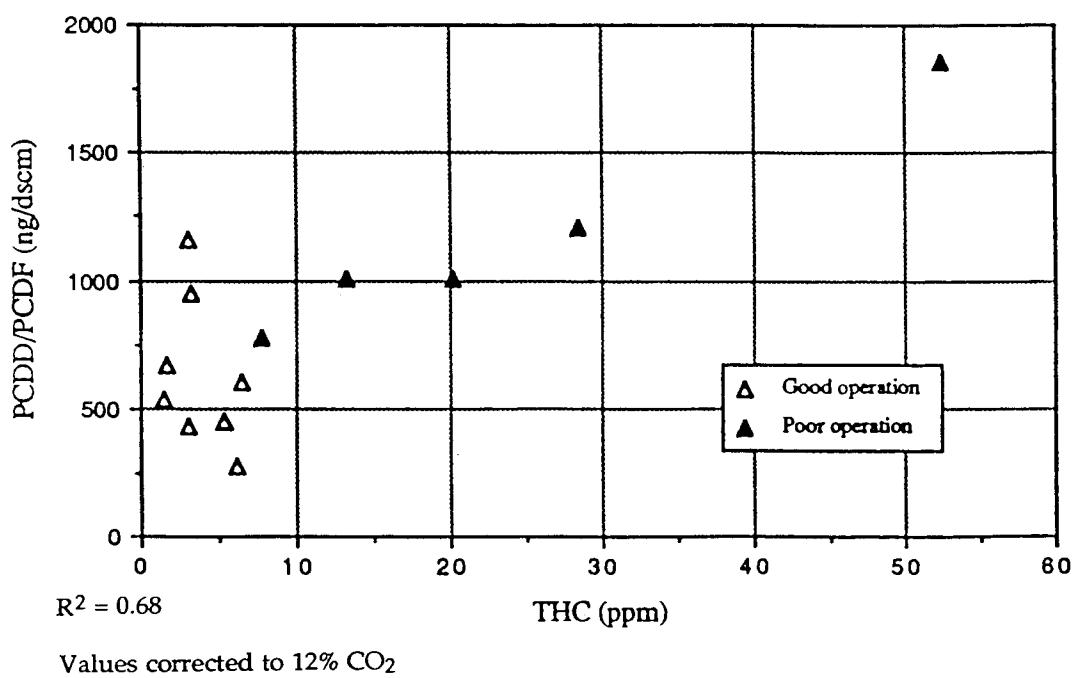


Figure 4. Dependence of uncontrolled PCDD/PCDF on THC at SDA inlet.

TABLE 1. COMBUSTION CONDITIONS AND RESULTS AT SDA INLET

Test No. (PT)	Load 1000 kg/hr	Comb. Cond. ^a	Overfire Air			CO ppm	NO _x ppm	PCDD/PCDF ng/m ³ ^e
			TOFA ^b	ROFA ^c	OFA ^d			
13	71 (L)	G	2	nil	47	158	157	599
14	74 (L)	G	2	nil	49	70	177	428
10	87 (I)	G	2	nil	52	77	186	667
02	88 (I)	G	2	nil	52	108	184	946
05	84 (I)	P	1	65	38	903	149	1861
09	95 (N)	G	2	65	51	92	188	449
08	96 (N)	G	2	65	48	89	193	1162
11	96 (N)	G	2	65	52	68	175	536
07	101 (N)	P	3	nil	51	387	172	1003
04	98 (N)	P	3	nil	54	214	172	774
03	99 (N)	P	1	65	44	432	160	1008
12	117 (H)	G	2	65	53	116	180	282
06	118 (H)	P	2	nil	57	397	157	1202

^a Good (G) or poor (P) combustion conditions^b Number of levels of TOFA^c Pressure in ROFA plenum, mm Hg^d OFA as a percentage of total combustion air^e Standard conditions: 25°C, 101.3 kPa

TABLE 2. FLUE GAS CLEANING (FGC) SYSTEM PERFORMANCE: ACID GASES

Test No. (PT) ^a	FGC Cond. Temp./SO ₂ ^b	Concentrations, ppm				Removal, %	
		Inlet	Outlet	HCl	SO ₂		
02,05	L/H	470	173	20	121	95.7	30.1
03,11	H/L	416	187	20	17	95.2	90.9
04	H/M	471	186	31	44	93.4	76.3
06	M/L	404	192	10	32	97.5	83.3
07	L/L	399	183	8	17	98.0	90.7
08	M/H	538	184	41	126	92.4	31.5
09	H/H	432	178	98	189	77.3	-6.2 ^c
10	L/M	429	194	19	74	95.6	61.9
12,13,14	M/M	444	187	18	59	95.9	68.4

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^a Values are averaged for multiple runs.^b High temperatures (H) ranged from 166 to 171°C (330 to 339°F), medium temperatures (M) from 141 to 142°C (285 to 287°F), and low (L) temperatures from 122 to 124°C (252 to 255°F) for the spray dryer outlet gas. Fabric filter SO₂ outlet concentrations were above 100 ppm for high (H) concentration, between 21 and 100 ppm for medium (M) concentration, and 20 ppm or less for low (L) concentration. All concentrations are referenced to 12% CO₂ in dry gas [25°C (77°F), 101.3 kPa (1 atm)].^c Desorption of SO₂ in the filter cake is suspected for low lime stoichiometry and relatively high HCl concentration.

TABLE 3. FLUE GAS CLEANING (FGC) SYSTEM PERFORMANCE: ORGANICS

Test No. (PT) ^b	FGC Cond. Temp./SO ₂ ^c	Inlet Concentrations, ng/Sm ³ ^a					Removal, %				
		PCDD	PCDF	CB	CP	PAH	PCDD	PCDF	CB	CP	PAH
02,05	L/H	397	1,007	10,860	62,938	60,176	99.9	99.9	96.2	97.4	92.0
03,11	H/L	161	611	6,159	20,798	46,976	99.8	100 ^d	95.2	99.1	92.2
04	H/M	151	623	5,964	16,964	25,519	99.8	99.9	98.4	99.0	92.2
06	M/L	317	885	9,403	41,588	88,626	99.9	100 ^d	94.3	96.9	97.7
07	L/L	207	796	7,074	25,168	51,774	99.9	100 ^d	98.5	99.1	97.3
08	M/H	211	951	7,071	20,226	10,259	99.9	100 ^d	98.4	99.1	76.7
09	H/H	71	378	4,848	11,329	32,421	99.2	99.9	97.7	96.5	92.5
10	L/M	243	424	6,170	16,198	6,289	99.9	100 ^d	99.3	99.9	58.6
12,13,14	M/M	95	341	4,647	14,419	7,747	99.6	100 ^d	99.1	99.4	63.2

^a Organics are: polychlorinated dibenz-p-dioxins (PCDD) and dibenzofurans (PCDF), chlorobenzenes (CB), chlorophenols (CP), and polynuclear aromatic hydrocarbons (PAH).

^b Values are averaged for multiple runs.

^c High temperatures (H) ranged from 166 to 171°C (330 to 339°F), medium temperatures (M) from 141 to 142°C (285 to 287°F), and low temperatures (L) from 122 to 124°C (252 to 255°F) for the spray dryer outlet gas. Fabric filter outlet SO₂ concentrations were above 100 ppm for high (H) concentration, between 21 and 100 ppm for moderate (M) concentration, and 20 ppm or less for low (L) concentration. All concentrations are referenced to 12% CO₂ in dry gas [25°C (77°F), 101.3 kPa (1 atm)].

^d Value is based on rounding off to three significant figures.

TABLE 4. FLUE GAS CLEANING (FGC) SYSTEM PERFORMANCE:
PARTICULATE MATTER AND SELECTED METALS

Test No. (PT) ^a	FGC Cond. Temp./SO ₂ ^b	Particulate Matter (PM) mg/Sm ³		Inlet Concentration, µg/Sm ³					Removal, %					
		Inlet	Outlet	As	Cd	Cr	Pb	Hg	PM	As ^c	Cd ^c	Cr	Pb	Hg
02,05	L/H	4,949	4.83	250	548	859	13,472	680	99.9	100	100	98.3	99.7	99.0
03,11	H/L	4,313	5.60	214	594	579	11,479	622	99.9	100	100	98.6	99.6	96.8
04	H/M	3,274	7.62	168	536	538	10,050	614	99.8	100	100	98.1	99.6	97.8
06	M/L	3,308	2.68	194	437	353	7,229	583	99.9	100	100	97.7	99.5	98.0
07	L/L	4,230	4.39	176	515	520	5,877	584	99.9	100	100	98.5	99.5	98.7
08	M/H	4,745	3.88	224	832	862	4,649	646	99.9	100	100	96.4	99.1	99.3
09	H/H	3,894	5.79	196	668	1,491	2,592	644	99.9	100	100	99.3	98.5	97.8
10	L/M	4,531	4.09	210	599	871	4,770	718	99.9	100	100	99.0	99.1	98.8
12,13,14	M/M	3,433	5.46	219	569	949	8,563	668	99.8	100	100	98.2	99.3	98.6

^a Values are averaged for multiple runs.

^b High temperatures (H) ranged from 166 to 171°C (330 to 339°F), medium temperatures from 141 to 142°C (285 to 287°F), low temperatures (L) from 122 to 124°C (252 to 255°F) for the spray dryer outlet gas. Fabric filter SO₂ outlet concentrations were above 100 ppm for high (H) concentration, between 21 and 100 ppm for medium (M) concentration, and 20 ppm or less for low concentration. All concentrations are referenced to 12% CO₂ in dry gas [25°C (77°F), 101.3 kPa (1 atm)].

^c All outlet concentrations were nondetectable and assigned zero values for calculating removal.

TABLE 5. FABRIC FILTER ASH CONTENT: ORGANICS AND SELECTED METALS

Test No. (PT) ^a	FGC Cond. Temp./SO ₂ ^b	Ash Rate kg/hr	Concentration, ng/g					Concentration, µg/g					LOI ^c %
			PCDD	PCDF	CB	CP	PAH	As	Cd	Cr	Pb	Hg	
02,05 ^d	L/H	429	96	71	1,085	2,870	9,437	15	70	264	1,987	25	6.52
03,11 ^e	H/L	2,140	49	100	704	2,225	1,087	18	97	240	2,405	30	4.50
04	H/M	1,385	84	172	1,059	3,320	1,806	20	96	179	3,413	48	8.15
06	M/L	1,239	227	282	1,684	6,095	7,431	19	96	154	3,666	36	10.45
07	L/L	550	154	271	941	4,997	1,992	17	90	147	3,051	37	9.97
08	M/H	434	62	96	729	1,636	2,905	22	62	210	2,439	25	5.00
09	H/H	1,317	112	222	1,266	4,336	4,780	21	119	287	4,545	37	9.30
10	L/M	1,166	27	47	684	1,924	1,402	19	87	274	2,352	27	4.26
12,13,14 ^f	M/M	707	102	111	1,218	1,832	4,093	19	118	207	2,812	39	8.89

^a Values are averaged for multiple runs.

^b High temperatures (H) ranged from 166 to 171°C (330 to 339°F), medium temperatures (M) from 141 to 142°C (285 to 287°F), and low temperatures (L) from 122 to 124°C (252 to 255°F) for the spray dryer outlet gas. Fabric Filter SO₂ outlet concentrations were above 100 ppm for high(H) concentration, between 21 and 100 ppm for medium (M) concentration, and 20 ppm or less for low(L) concentration. All concentrations are referenced to 12% CO₂ in dry gas [25°C (77°F), 101.3 kPa (1 atm)].

^c LOI is loss on ignition.

^d Data shown are based solely on PT05.

^e Data shown are based solely on PT11.

^f Data shown are based on PT12 and PT14.

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EFFECTIVE CONTROL OF MERCURY AND OTHER POLLUTANTS
FROM MWC FACILITIES BY EDV TECHNOLOGY

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ABSTRACT

The paper describes with several performance case histories operating experience of EDV gas cleaning technology for controlling particulate matter, heavy metals including mercury, acid gases and PCDD/PCDF emissions from both new and retrofitted MWC and waste water sludge incinerator facilities. Recent developments realized in EDV technology aimed at recovering new materials from waste streams are also reported. In addition, a status update of supplementary pollutant controls demonstrated on a 330 TPD MWC is presented.

Introduction

Thermal processing of municipal and hazardous wastes are two of the most closely and severely environmentally regulated operations in the U.S. today. As a consequence, these industries have become prime examples of community and commercial services that are dependent on the performance of pollution control technologies. In this environment, municipal agencies and operator managements need to re-evaluate the influence of pollution and pollution control on plant economics. In a growing number of situations there are compelling economic reasons why the control of pollution should be recognized as a legitimate part of the production process. As the influence of pollution control increases so should the priority allocated to assessing technology and equipment. A global cost-benefit perspective is therefore becoming an essential complementary evaluation process to the best available control technology approach.

Concerns over the fate of heavy metals contained in wastes processed by municipal solid waste combustion (MWC) continue to impact on air pollution control technology and residue management. Residues from current BACT MWC air pollution control systems operating in the U.S. contain heavy metals, excess lime and exhibit poor recycle properties. Alternate air pollution control technology extensively used in other countries, e.g. EDV, provide means for the controlled extraction and recovery of heavy metals and the production of inert residue suitable for commercial use.

Achieving effective control of pollution is dependent on understanding the nature of the problem. The formation mechanisms, the influence of combustion variables, the profile of individual pollutants, adaptability to future regulations are some of the parameters that should be addressed in the technology selection process. Impact of the growing application of continuous emission monitors for an ever widening range of pollutants and shorter averaging times will likely fuel reassessment of air pollution technologies applied to many thermal processes.

EDV Technology

EDV technology has been developed to provide a versatile range of gas cleaning systems to suit a wide variety of applications and performance requirements. Emissions of particulate matter, PM 2.5, acid gases, PCDD/PCDF, heavy metals, can be effectively and efficiently controlled by EDV gas cleaning systems.

The EDV concept consists of a sequence of fundamental functions namely saturation, expansion, condensation, ionization and filtration.

Saturation of the gas takes place in an open spray tower by means of proprietary LAB-G nozzles. For high temperature applications, quenching of the gas is a necessary prerequisite and the tower is designed accordingly. The turbulent contact produced by the LAB-G nozzles between the scrubbing liquor and the gas achieves a large degree of particulate removal as well as establishing the saturation condition. For applications where gas absorption of acid gases is required, this turbulent contact zone is used.

On leaving the spray tower, the saturated gas enters a tubular module(s). As the gas traverses the converging/diverging section; adiabatic expansion takes place, which is accompanied by a change of energy state.

The adiabatic expansion of a gas saturated with water vapor produces a state of supersaturation. Particulate matter suspended in the gas acts as condensation nuclei and a film of water is formed on the surface of the dust particles. The encapsulated fine dust particles achieve growth in both size and mass which will significantly improve the effectiveness of the subsequent particulate removal mechanisms. The presence of the water film also ensures that the particle is capable of receiving and retaining an electric charge regardless of the dielectric nature of the core material.

The divergent pressure recovery section of the module is designed to minimize pressure loss and ensures suitable ionization conditions. An electrode, mounted on the axial centerline of the module, creates a corona within the gas flow path. As the water-encapsulated particles traverse the ionizing zone, they become negatively charged. The electrical energy expended in ionization is nominal in comparison with the energy levels used in conventional electrostatic precipitation devices.

The filtering device developed for the EDV concept provides for a near absolute removal of particles/mist from the flue gas. Two separate contact mechanisms are integrated in the design, namely physical impaction and electrostatic attraction. A centrally mounted hollow cone spray nozzle is positioned adjacent to, and facing, the pressure recovery exit section of the module. The proximity of this nozzle to the polarizing tip of the electrode ensures that the water curtain created by the nozzle is positively charged under the influence of the electric field generated by the electrode. Since the filtering nozzle and feed pipe are earthed, there is a migration of electrons from the water curtain which results in the subsequently formed filtering spray curtain to retain a positive electrical charge.

The charged (negative) particles/mist are removed from the gas stream by the filtering spray curtain.

Collision capture by the large filtering spray droplets is boosted by the electrostatic attraction effect. The ELECTRO-DYNAMIC FILTRATION approximates a total removal of particles/mist from the gas stream which affords important benefits to plant operation.

Since the virtual elimination of dust bearing droplets from the gas stream can be assured, the hydraulic circuit of the EDV can be engineered to operate at a high suspended/dissolved solids level with the result that the associated materials recovery/effluent treatment plant is of a much reduced size and cost.

Mercury Capture

Mercury emissions from MWC have been studied by laboratory synthesis and a measurement program of over 4000 hours using a continuous emission monitor (CEM). Table 1 illustrates the primary findings of this research. Figure 1 shows the influence of temperature on mercuric chloride formation. The concentration of hydrogen chloride present in the flue gas further influences the speciation of mercury. Extensive test data from multiple MWC and other incineration processes show mercuric chloride as the dominant species present in the flue gas. Thus a controlled washout of this water soluble compound is readily achieved in the EDV system.

Figure 2 shows a CEM trace of total mercury from a MWC that serves a community that practices source separation of batteries. Correlation between the mercury CEM and standard measurement methodology is shown in Figure 3.

EDV performance for the control of MWC mercury emissions shown in Table 2 (Basle, Switzerland) were made at the flue gas adiabatic saturation temperature of 56/57°C (133/135°F). Subcooling of the flue gas to 35°C (94°F) improved capture beyond the detection limits of the test method (see Table 3). The stability of the captured mercury in the solid EDV cake residue is illustrated by lixiviation results by Swiss, Japanese and U.S. (TCLP) test methods shown in Table 4.

Typical EDV performance on other heavy metals is illustrated in Table 5.

PCDD-PCDF Suppression - Capture - Destruction

The majority of MWC facilities in the USA are of modern design and employ good combustion practices. As a consequence, the generation of PCDD/PCDF precursors is curtailed which results in a comparatively low level of PCDD/PCDF formation. The thermal designs of MWC facilities built in the 1950s, 60s and 70s frequently support formation of substantial quantities of PCDD/PCDF precursors.

Incinerator-heat recovery boiler-electrostatic precipitator is typically the process train of many of these earlier facilities. Temperatures in the range of 400°- 650°F are usual for flue gas exiting the heat recovery boiler. This temperature range and the presence of catalysts in the flyash have been found to promote the rapid formation of PCDD/PCDF in MWC flue gases.

A diagrammatic illustration of the effect of temperature-residence time on PCDD/PCDF formation is shown in Figure 4. The residence time is measured from the time that the flue gas exits the heat recovery boiler. The 220°C (428°F) inclined line represents the rapid rate of formation of PCDD/PCDF during passage of the flue gas through the electrostatic precipitator. After the facility had been retrofitted with an EDV gas cleaning system, the rate of PCDD/PCDF formation collapsed as represented by the line 61°C. When an EDV system is used as a stand-alone gas cleaning system, PCDD/PCDF formation follows the "dash 61°C" line, i.e. maximum suppression, minimum formation.

Condensation, and hence capture, of PCDD/PCDF is temperature dependent. This is illustrated in Figure 5. EDV systems typically operate in a temperature range of 55-65°C (131-149°F) as against 132-160°C (270-320°F) in spray dryer-fabric filter systems which can be important for retrofits of earlier generation (pre-1984) of incinerators.

EDV technology has been developed to achieve +99% capture of PCDD/PCDF. To alleviate possible future concerns over deposits of contaminated residues, the destruction of PCDD/PCDF has been integrated into EDV technology. Test data from commercial MWC shows that the destruction of captured PCDD/PCDF achieved in Phase I of the development program is already at a 90% level.

CEM

The introduction of continuous emission monitoring of pollutants and the steady reduction in averaging time imposes a new threshold of regulatory responsibility onto incinerator plant operators. Variable feedstocks and feedback control systems typically employed by spray-dryer-fabric filter systems aggravate an already sensitive operational situation.

Figures 6,7, and 8 show simultaneous inlet/outlet CEM strip chart records of SO₂, HCl and NOX across an EDV system installed on a MWC. The heavy line trace in each chart highlights the specified pollutant. The buffering capacity of the EDV system for acid gases is well illustrated in their CEM strip chart records.

The MWC at which the NOX strip chart (Figure 8) was recorded operates a THERMAL DeNOX system for controlling the emissions of nitrogen oxides. The EDV controls the ammonia slip and ammonium compounds produced. In addition, the EDV produces a further significant reduction in NOX emissions. This supplementary DeNOX capability has been complemented by the development of a wet DeNOX concept. The performance and long term efficiency of this wet DeNOX as an integral feature of an EDV system has been demonstrated on a 330 TPD MWC. The performance of the wet EDV achieved by DeNOX concept is shown in Figure 9.

Conclusion

In order to achieve maximum environmental and economic benefits from municipal services, a comprehensive perspective is an essential first step.

An integrated approach that embraces source separation, recycling of marketable materials and the thermal processing of residuals is applicable to the disposal of municipal solid wastes. Thermal treatment ought to be viewed not only for energy recovery but as an intermediate stage to the recovery of construction materials and heavy metals from ash residues. Realization of such objectives requires that the selection of technologies, especially gas cleaning technology, be made on site-specific global environmental-economic criteria rather than on institutionalized procedures. Environmental and economic objectives have been demonstrated to be compatible and mutually beneficial.

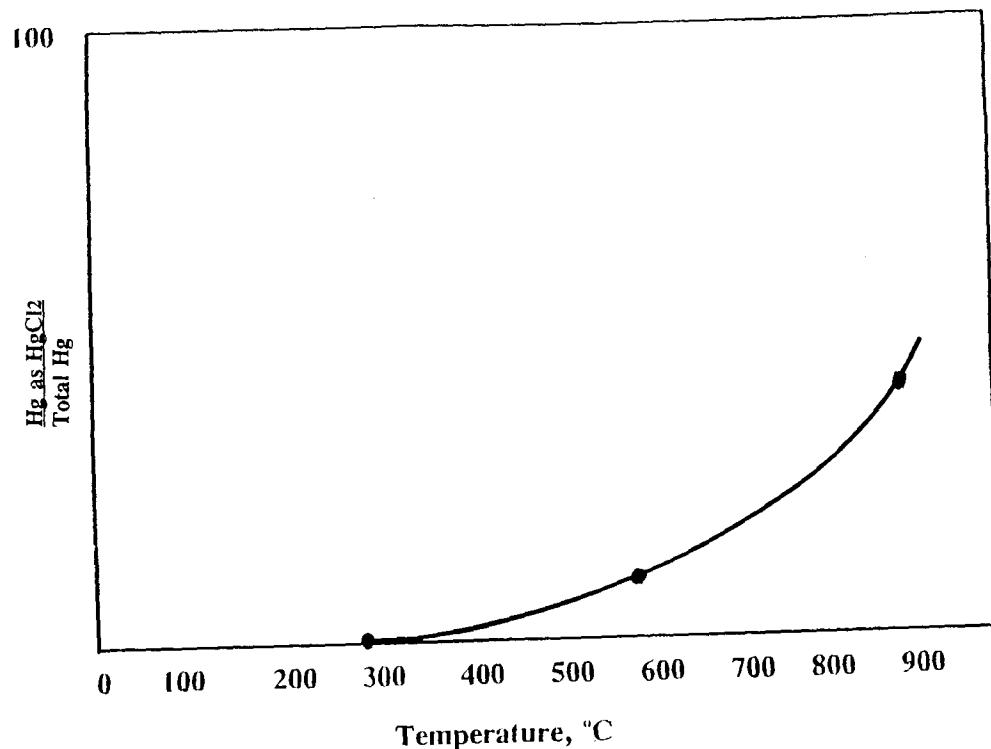


FIGURE 1 - MERCURIC CHLORIDE FORMATION

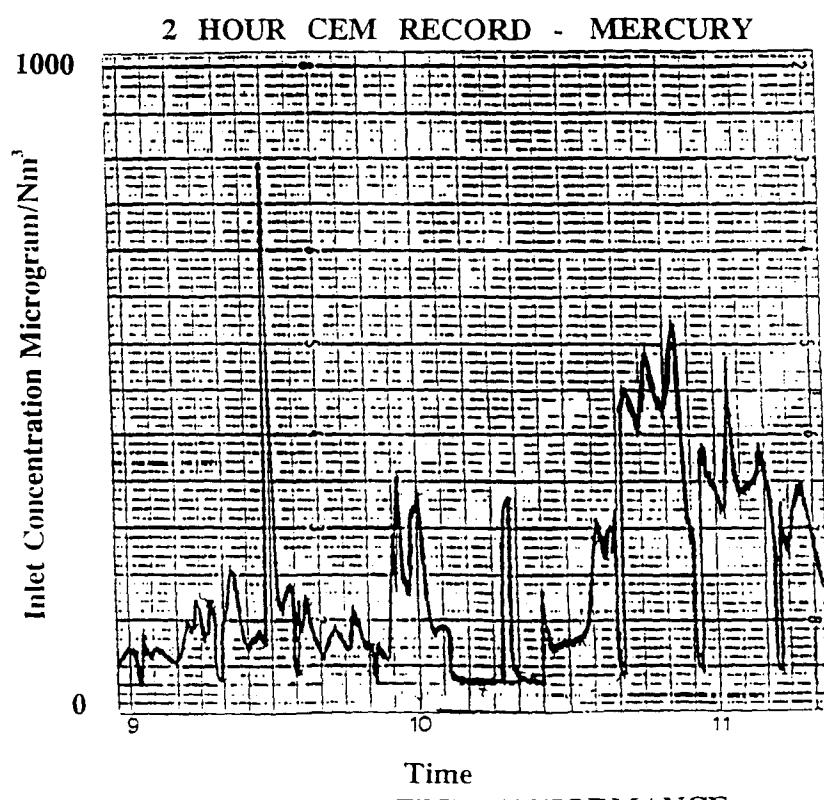


FIGURE 2 - EDV PERFORMANCE

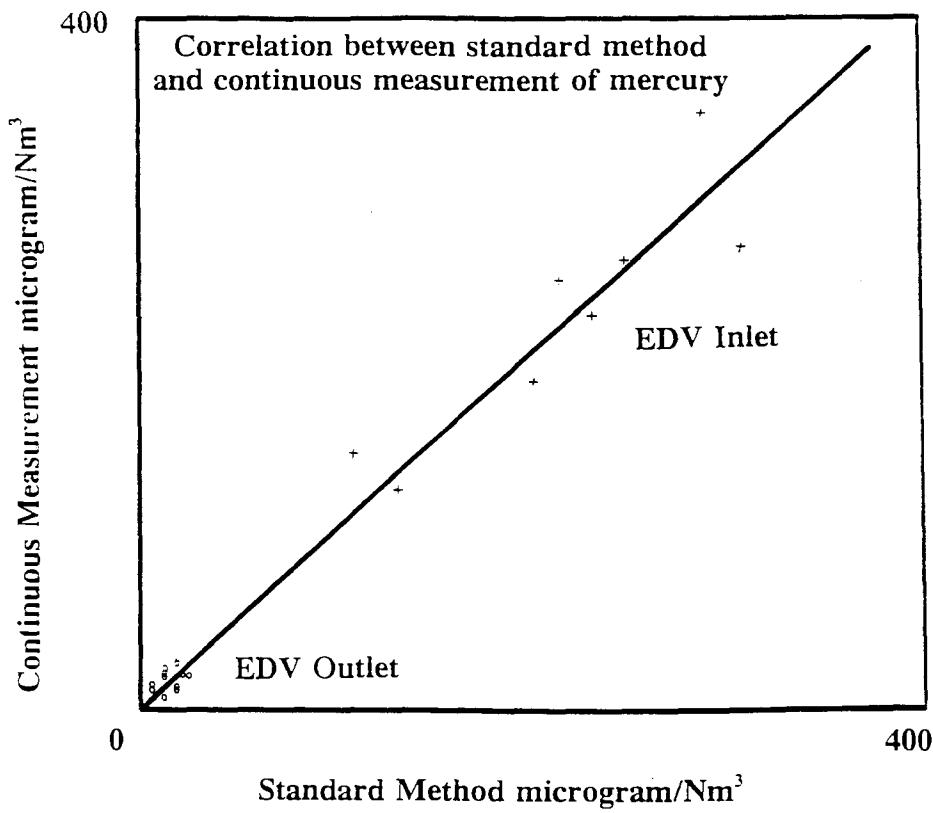


FIGURE 3 - EDV PERFORMANCE

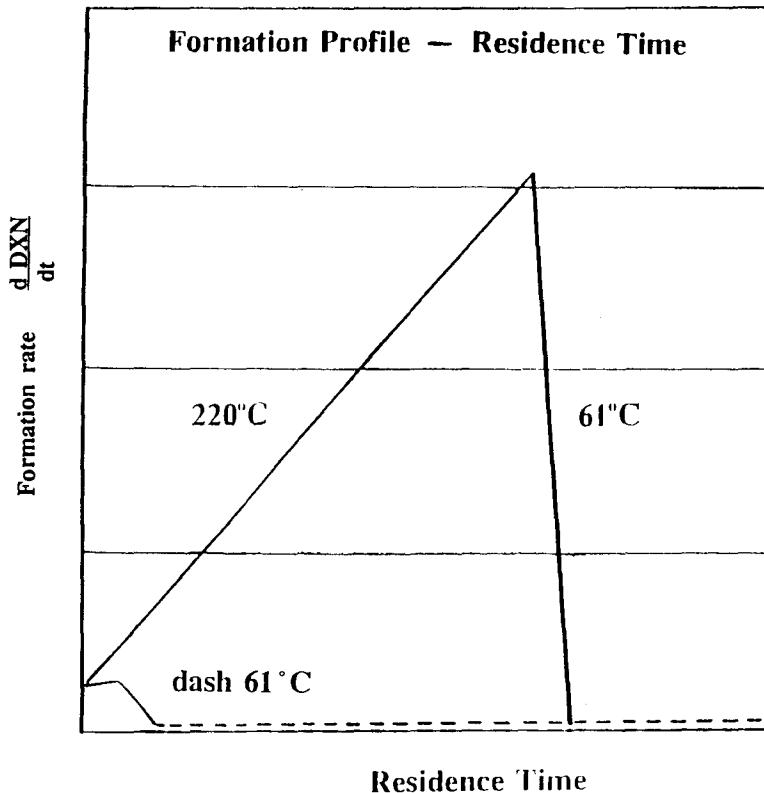


FIGURE 4 - PCDD - PCDF

Vapor Pressure - Temperature

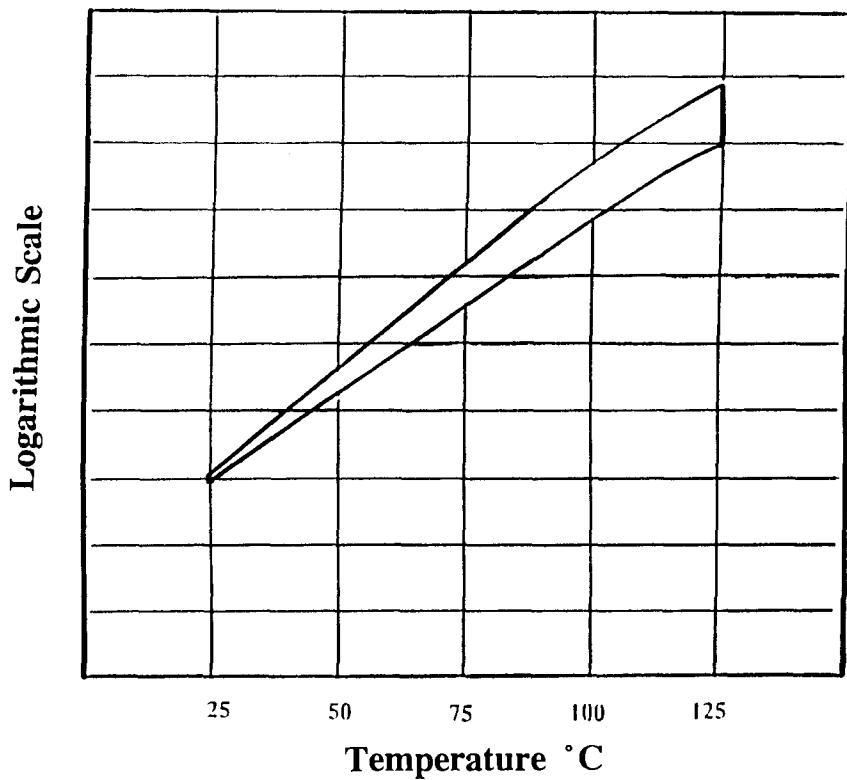


FIGURE 5 - PCDD - PCDF

12 HOUR CEM RECORD - SO₂ ppm

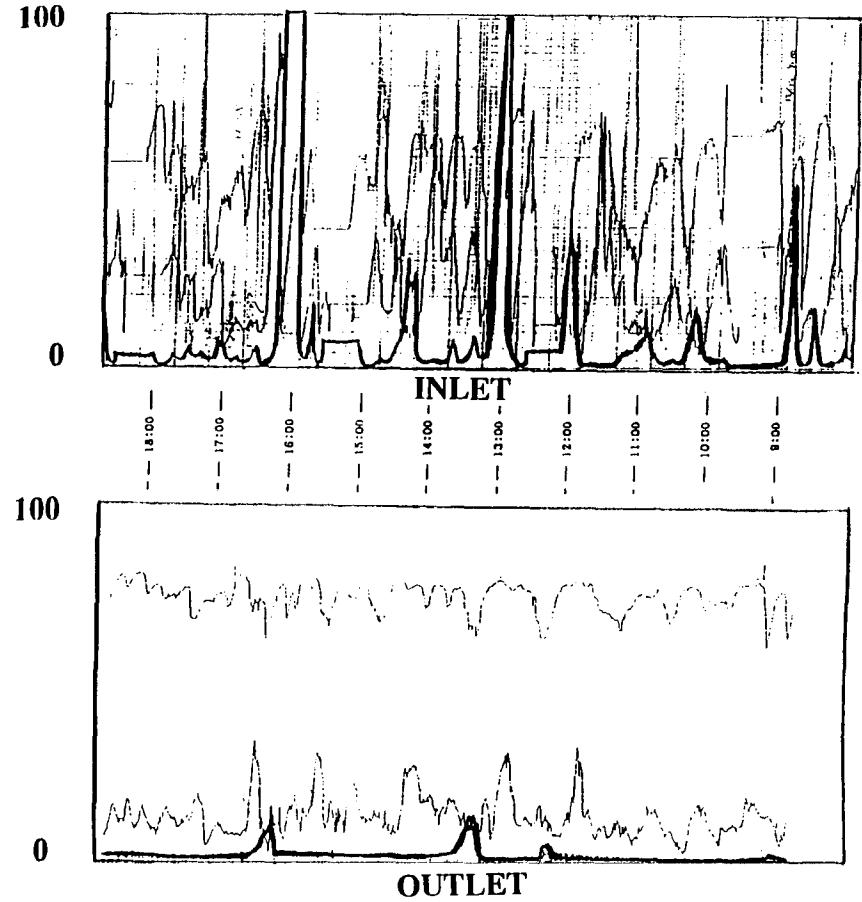


FIGURE 6 - EDV PERFORMANCE

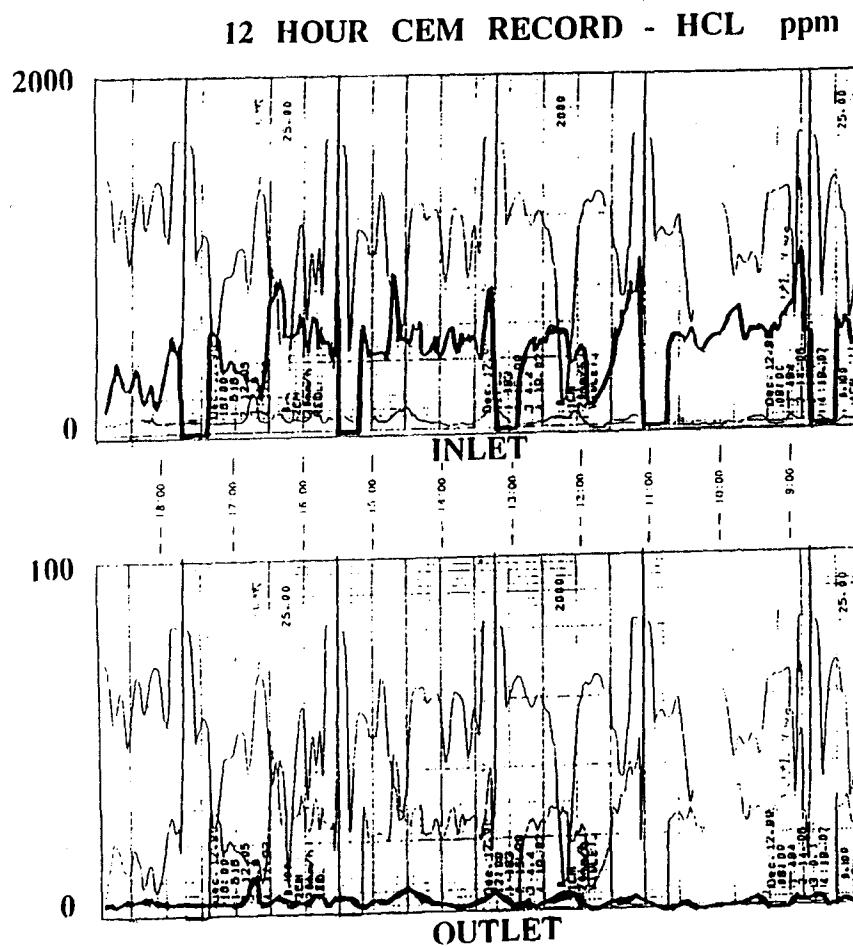


FIGURE 7 - EDV PERFORMANCE

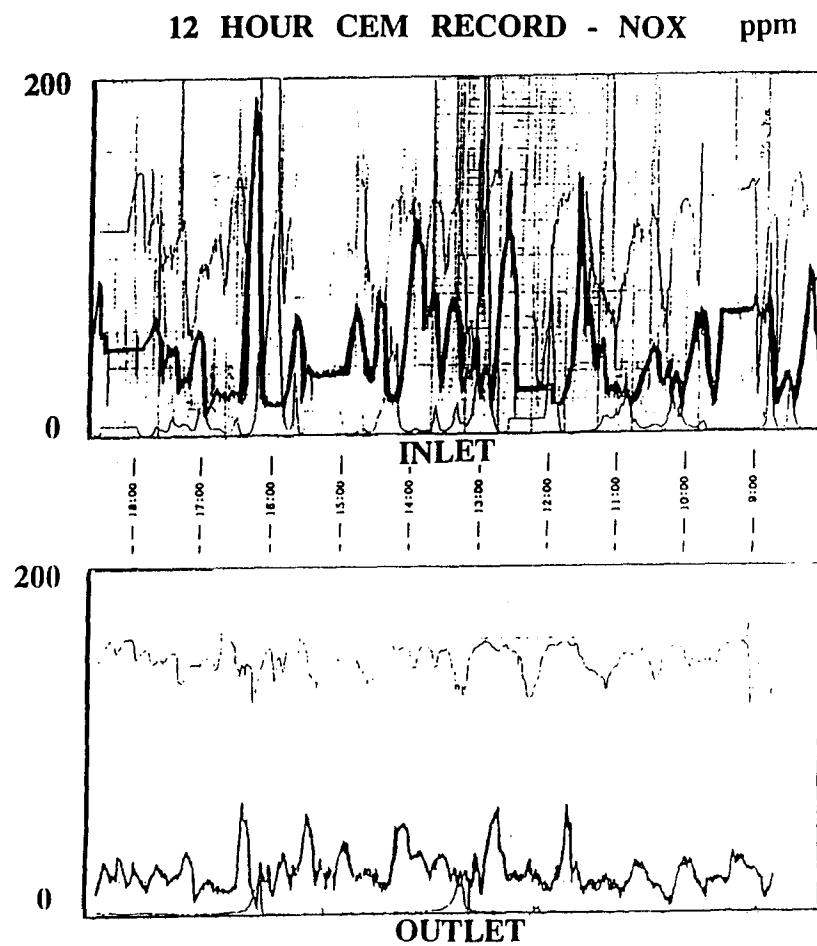
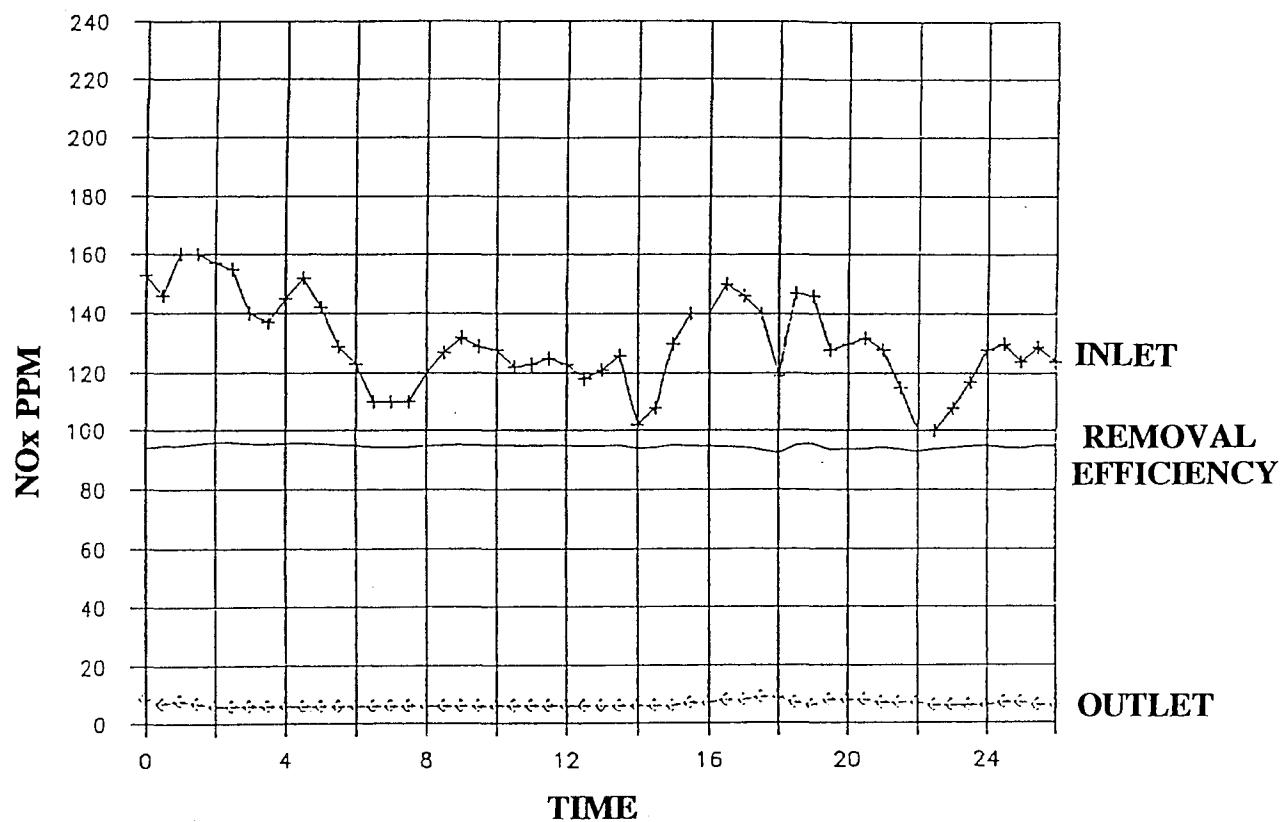


FIGURE 8 - EDV PERFORMANCE

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**FIGURE 9 - EDV DeNOX DEMONSTRATION
330 TPD MWC 01/11/90**

TABLE 1 MERCURY CAPTURE

1. Mercury reacts with hydrogen chloride (HCl) to form mercuric chloride (HgCl_2) at temperatures above 300°C.
2. Higher temperatures and higher HCl concentrations result in higher production rate of mercuric chloride.
3. Mercuric chloride is water soluble.
4. Oxidation of mercuric chloride in low pH solution promotes formation of stable compounds.
5. EDV absorption zone operates below pH2.
6. Metallic (atomic) mercury reacts with mercuric chloride to form insoluble mercurous chloride (Hg_2Cl_2).
7. Lower flue gas temperature promotes higher mercury removal.
8. EDV system operates below 66°C (150°F).

TABLE 2 EDV PERFORMANCE DATA - BASEL

Test Run	1	2	3	4
Unit No.	1	1	2	2
<u>Boiler Outlet</u>				
Gas flow Nm ³ /h wet	84800	84800	89100	76800
Gas Temp. °C	182	180	183	181
HCl	1170	1800	550	740
SO ₂	110	150	130	150
Hg	0.193	0.128	0.166	0.126
<u>EDV Outlet</u>				
Gas Temp. °C	57	56	57	57
Particulate	0.9	0.5	0.6	1.5
HCl	<1 DL	<1 DL	<1 DL	<1 DL
SO ₂	<11 DL	<13 DL	<24 DL	<13 DL
Hg	0.012	0.013	0.005	0.016

Note: 1. Values in mg/Nm³ dry corrected 11% O₂.
 2. DL - detection limit for SO₂ determined by sampling duration.

TABLE 3 SAMPLE BLANKS FOR MERCURY
AT BASEL MSW INCINERATION PLANT (SWITZERLAND)

MSW TRAIN #	1	1	2	1	2
Date	03/20/90	04/04/90	04/06/90	03/20/90	04/06/90
Test Run no.	7A	13A	23A	7B	23B
Hg sampled in micrograms	1.8	2.0	0.6	0.3	0.5
Volume sampled in Nl dry (2 hrs)	200	200	200	200	200
Hg sample blank concentration mg/Nm ³ dry	0.009	0.010	0.003	0.002	0.003

TABLE 4
TABLE 4 EDV PERFORMANCE
MERCURY LIXIVIATION TEST DATA

	<u>CH</u> <u>BUS 88</u>	<u>J</u> <u>KK 13</u>	<u>USA</u> <u>TCLP</u>
Residue mg/kg	126	126	126
Leachate Concentration mg/l	0.002	0.0005	0.002
Regulatory Limit (maximum) mg/l	0.01	0.005	0.2

TABLE 5 EDV PERFORMANCE DATA

HEAVY METALS

	5/18/88		5/20/88	
	<u>Inlet</u>	<u>Outlet</u>	<u>Inlet</u>	<u>Outlet</u>
Zn	0.406	0.004	0.42	0.007
Cd	0.0084	< 0.001	0.0038	< 0.001
Ni	0.009	0.002	0.074	< 0.005
Pb	0.21	< 0.001	0.144	0.005
Cu	0.154	< 0.001	0.116	< 0.001
Cr	0.098	< 0.001	0.108	< 0.0017
As	0.004	< 0.001	0.006	< 0.001

Data as mg/Nm³ to 7% O₂ dry.

< means under detection limit

TABLE 6 PCDD - PCDF CAPTURE

1. PCDD - PCDF formation is temperature dependent.
2. PCDD - PCDF condensation is strongly temperature dependent.
3. The presence of carbon in scrubbing liquid accentuates PCDD - PCDF capture.
4. PCDD - PCDF are destroyed in the scrubbing liquid.

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SESSION 4C: FLUE GAS CLEANING: PCDD/PCDF CONTROL

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The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

APPLICATION OF DeNO_x-CATALYSTS FOR THE REDUCTION OF
PCDD/PCDF AND OTHER PICs FROM WASTE INCINERATION FACILITIES
BY CATALYTIC OXIDATION

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ABSTRACT

In laboratory experiments it was demonstrated that PCDD/PCDF can be decomposed catalytically in the presence of oxygen in the temperature range of 150 - 500°C. Several commercially available oxidation catalysts and other catalysts on the basis of metals and metal oxides were tested. It was found that catalysts produced for the selective catalytic reduction of nitrogen oxides in the presence of ammonia (SCR-catalysts) exhibit some unexpected properties as oxidation catalysts for the decomposition of organohalogen compounds in general and of PCDD/PCDF in particular. While most recognized oxidation catalysts did not exhibit any activity below 300°C under the conditions of our laboratory experiments, SCR catalysts on the basis of TiO₂ showed under otherwise identical conditions high activity as oxidation catalysts for organochlorine compounds at temperatures of 250 - 350°C. Under appropriate conditions, organochlorine compounds could be decomposed by catalytic oxidation without PCDD/PCDF formation. In pilot plant studies at municipal waste incinerators we were able to demonstrate that catalysts originally developed for selective reduction of nitrogen oxide are capable of reducing the PCDD/PCDF emissions to levels below 0.1 ng TCDD-equivalents (I-TEQ) per m³. Other products of incomplete combustion (PICs) are reduced simultaneously. Prerequisites for this PCDD/PCDF reduction are residence times in the range of 0.3 to 0.7 seconds and (either the absence of ammonia or) ammonia concentrations of less than 10 ppm. When run in the temperature range of 250 - 350°C, these catalysts can be used either solely as oxidation

catalysts to lower the PCDD/PCDF emission, or as combined catalysts to also simultaneously reduce nitrogen oxides and oxidise halogenated compounds. In the latter case the catalyst volume has to be increased accordingly.

Since SCR catalysts are already in use in power stations and municipal waste combustors (MWCs) and have proven their resistance against catalyst poisoning, this technique for the reduction of PCDD/PCDF emissions from MWCs can be easily applied on a full technical scale. This full scale applicability has recently been demonstrated by measurements at the municipal waste incinerator at Vienna, Austria.

INTRODUCTION

At the 6th International Dioxin Symposium at Fukouka we reported upon the catalytic effects of filter ash on the decomposition of PCDD/PCDF /1,2/. Subsequently we investigated the source of this catalytic activity in filter ash. We found that every metal and metal oxide tested exhibited some catalytic activity in the decomposition of PCDD/PCDF in the temperature range of 250 to 350°C. In extensive laboratory tests we evaluated the conditions under which not only PCDD/PCDF could be decomposed by oxidation catalysts in the presence of oxygen, but also organochlorine compounds in general without the formation of PCDD/PCDF /3/. In order to apply these findings to the reduction of PCDD/PCDF emissions from waste incineration facilities effective PCDD/PCDF decomposition in the temperature range of 250 to 350°C appeared to be essential since this catalytic oxidation is best installed as the final gas cleaning device. We found in our laboratory tests that SCR catalysts of the titanium oxide, ferric oxide and zeolithe type in combination with the usual additions of other metal oxides are also very good oxidation catalysts for organochlorine compounds when applied in the absence of ammonia or at low ammonia concentrations. Some of these catalysts exhibit this property very efficiently at the desired temperature range of 250 to 350°C.

We therefore tested such catalysts in pilot plant studies at municipal waste incinerators.

LABORATORY EXPERIMENTS

With the model compounds hexachlorobenzene, 2,4,8-trichlorodibenzofuran and tetrachloroethene, the efficiency of decomposition with oxidation catalysts was tested in laboratory experiments. It could be demonstrated that in the temperature range of 200-500°C and space velocities of about 2000 h⁻¹ these compounds can be successfully decomposed in the presence of oxygen (air) and water without the formation of PCDD/PCDF /3/. We could also demonstrate that PCDD/PCDF are much more readily decomposed than hexachlorobenzene or terachloroethene.

Tetrachloroethene therefore proved to be a very good model compound in laboratory tests of the temperature dependence of the decomposition efficiency of oxidation catalysts for organochlorine compounds. While most of the commercially available oxidation catalysts tested show only limited efficiency below 350°C, the SCR catalysts on titanium oxide basis with dotaions of vanadium oxide exhibit good efficiencies at temperatures as low as 250°C. This is shown in Figure 1. Here three different "low dust" deNOx catalysts are compared with one "high dust" deNOx catalyst. While at high temperature (>400°C) there is little difference in the decomposition efficiency of the four catalysts, distinct differences are apparent at temperatures below 300°C.

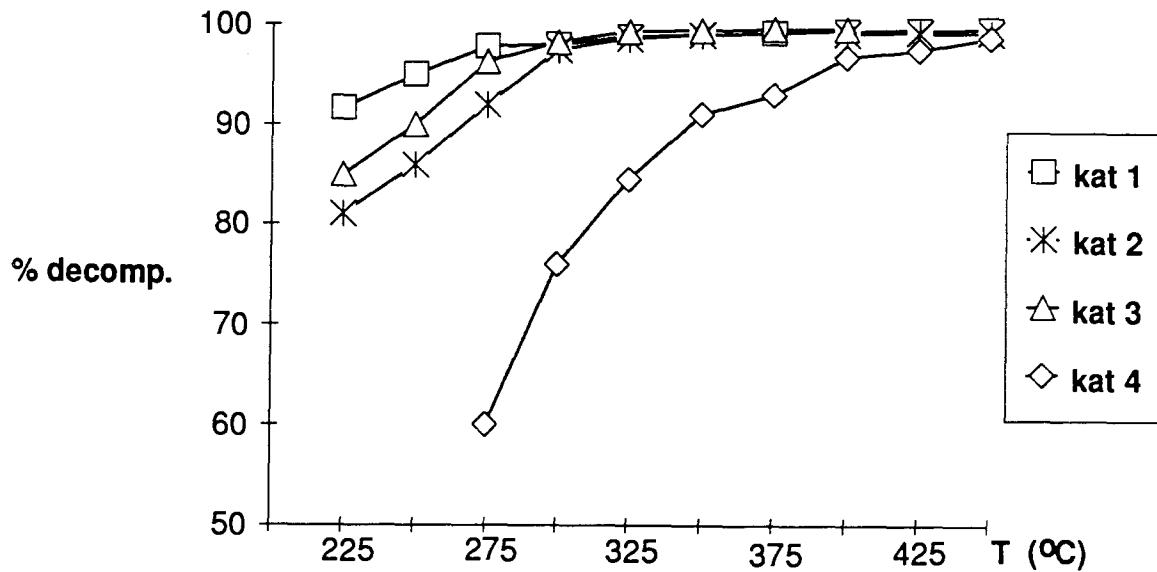


Figure 1: Temperature dependence of hexachloroethene decomposition by catalytic oxidation on deNOx catalysts. Kat 1 to Kat 3 "low dust"-type on TiO₂ basis. Kat 4 "high dust"-type on TiO₂ basis. Air/20% H₂O with 300 ppm hexachloroethene; space velocities 2000 h⁻¹.

It has been shown that there also exists a good correlation between the SO₂ oxidation rates of individual catalysts and their efficiency in PCDD/PCDF decomposition /4/. Therefore the SO₂ to SO₃ conversion factor of the individual catalyst is also a good indicator for its efficiency in PCDD/PCDF decomposition.

PILOT PLANT STUDIES

The laboratory experiments suggested that oxidation catalysts of the SCR type could be successfully used for the reduction of stack gas emissions of PCDD/PCDF and related compounds in waste incineration plants. Thus at three different waste incinerators pilot facilities, originally installed for the test of SCR catalysts with regard to NO_x reduction, were used to test the reduction of PCDD/PCDF and related compounds. A side stream of the off-gas in the range of 100 to 250 m³/ h was diverted through the catalytic reactor after preheating to the desired test temperature. The catalyst volume was divided into various parts, so that the influence of the catalyst volume could be evaluated in addition to temperature, catalyst configuration and NH₃-addition to the flue gas. In case of small catalyst volumes (high space velocities) and addition of NH₃ just the denox reaction took place while the decomposition of PCDD/PCDF was suppressed. In the absence of NH₃ or at NH₃ concentrations of a few ppm, under otherwise identical conditions, the PCDD/PCDF reduction was >95% /4/.

This means that in order to obtain the necessary reduction in PCDD/PCDF emissions by catalytic oxidation in combination with NO_x reduction one has to increase the volume of the catalytic reactor to obtain sufficient catalytic volume for the oxidation reaction.

Representative results for different starting concentrations of PCDD/PCDF are shown in detail in Table 1. The test IIIb shows that even under very low starting concentrations a reduction of PCDD/PCDF concentration was obtained. This demonstrates that under the conditions of catalytic oxidation in the temperature range of 250 to 350°C no relevant PCDD/PCDF de novo synthesis had occurred.

Examples from	Test II		Test IIIa		Test IIIb	
	in ng/cbm	out ng/cbm	in ng/cbm	out ng/cbm	in ng/cbm	out ng/cbm
Tetrachlordibenzodioxins	23.9	0.19	0.07	0.03	0.023	n.d.
Pentachlordibenzodioxins	25.2	0.37	1.09	0.05	0.029	n.d.
Hexachlordibenzodioxins	27.2	0.55	3.66	0.06	0.068	0.032
Heptachlordibenzodioxins	18.4	0.44	2.68	0.09	0.056	0.038
Octachlordibenzodioxin	8.3	0.41	1.20	0.06	0.113	0.031
Total PCDD	103.0	1.96	8.70	0.29	0.289	0.101
Tetrachlordibenzofurans	28.8	0.36	1.65	0.62	0.353	0.087
Pentachlordibenzofurans	20.4	0.53	5.08	0.45	0.384	0.074
Hexachlordibenzofurans	9.6	0.35	6.21	0.16	0.503	0.033
Heptachlordibenzofurans	5.1	0.24	3.09	0.14	0.258	0.013
Octachlordibenzofuran	0.5	0.10	0.69	n.d.	0.041	n.d.
Total PCDF	64.4	1.58	16.72	1.37	1.539	0.207
2,3,7,8-Tetrachlordibenzodioxin	0.17	n.d.	n.d.	n.d.	n.d.	n.d.
1,2,3,7,8-Pentachlordibenzodioxin	0.47	0.005	0.039	n.d.	n.d.	n.d.
1,2,3,4,7,8-Hexachlordibenzodioxin	0.58	0.011	0.039	n.d.	0.007	0.004
1,2,3,6,7,8-Hexachlordibenzodioxin	1.24	0.036	0.184	0.002	0.008	0.006
1,2,3,7,8,9-Hexachlordibenzodioxin	0.68	0.025	0.123	0.002	0.006	n.d.
1,2,3,4,6,7,8-Heptachlordibenzodioxin	9.67	0.250	0.878	0.048	0.029	0.051
2,3,7,8-Tetrachlordibenzofuran	0.63	0.018	0.106	0.013	0.012	0.006
1,2,3,7,8-Pentachlordibenzofuran	1.53	0.035	0.167	0.033	0.052	0.007
2,3,4,7,8-Pentachlordibenzofuran	1.17	0.023	0.233	0.024	0.038	0.005
1,2,3,4,7,8-Hexachlordibenzofuran	0.97	0.037	0.495	0.014	0.073	0.005
1,2,3,6,7,8-Hexachlordibenzofuran	1.09	0.041	0.800	0.030	0.089	0.005
1,2,3,7,8,9-Hexachlordibenzofuran	0.06	0.004	0.038	0.003	n.d.	n.d.
2,3,4,6,7,8-Hexachlordibenzofuran	0.73	0.030	0.953	0.013	0.053	0.003
1,2,3,4,6,7,8-Heptachlordibenzofuran	3.96	0.210	1.820	0.090	0.204	0.013
1,2,3,4,7,8,9-Heptachlordibenzofuran	0.13	0.006	0.370	0.008	0.016	n.d.
I/TEQ (NATO/CCMS)	1.81	0.041	0.451	0.023	0.049	0.006
% reduction in I/TEQ		97.70		94.90		86.90

Table 1. PCDD/PCDF-analyses of waste incinerator off-gases before (in) and after (out) catalytic oxidation. Examples from test series with a range of initial concentrations.

In Figure 2 residual PCDD/PCDF concentrations after catalytic oxidation from a range of initial concentrations in relation to the catalyst volume are shown. In the concentration range of interest the relative reduction in PCDD/PCDF concentration under comparable conditions was slightly dependent on the initial concentration. This means that in order to obtain a final concentration of <0.1 ng TEQ/m³, the surface of the catalytic reactor has to be adjusted according to the expected initial concentration range. Further optimization appears possible by

adjusting the catalyst configuration and/or the reaction temperature.

Under comparable conditions no substantial difference in the degree of PCDD/PCDF reduction could be detected between new catalysts and those which had been used for 6000 h under both denox conditions and oxidation conditions. This already indicates that the reduction of PCDD/PCDF is due to catalytic oxidation and not due to adsorptive effects. Analyses of catalyst material after use for more than 6000 h in the pilot facility did also not show any accumulation of PCDD/PCDF by adsorption.

PCBs, chlorobenzenes and chlorophenols were shown to be reduced by catalytic oxidation to the same extent as reported here for PCDD/PCDF.

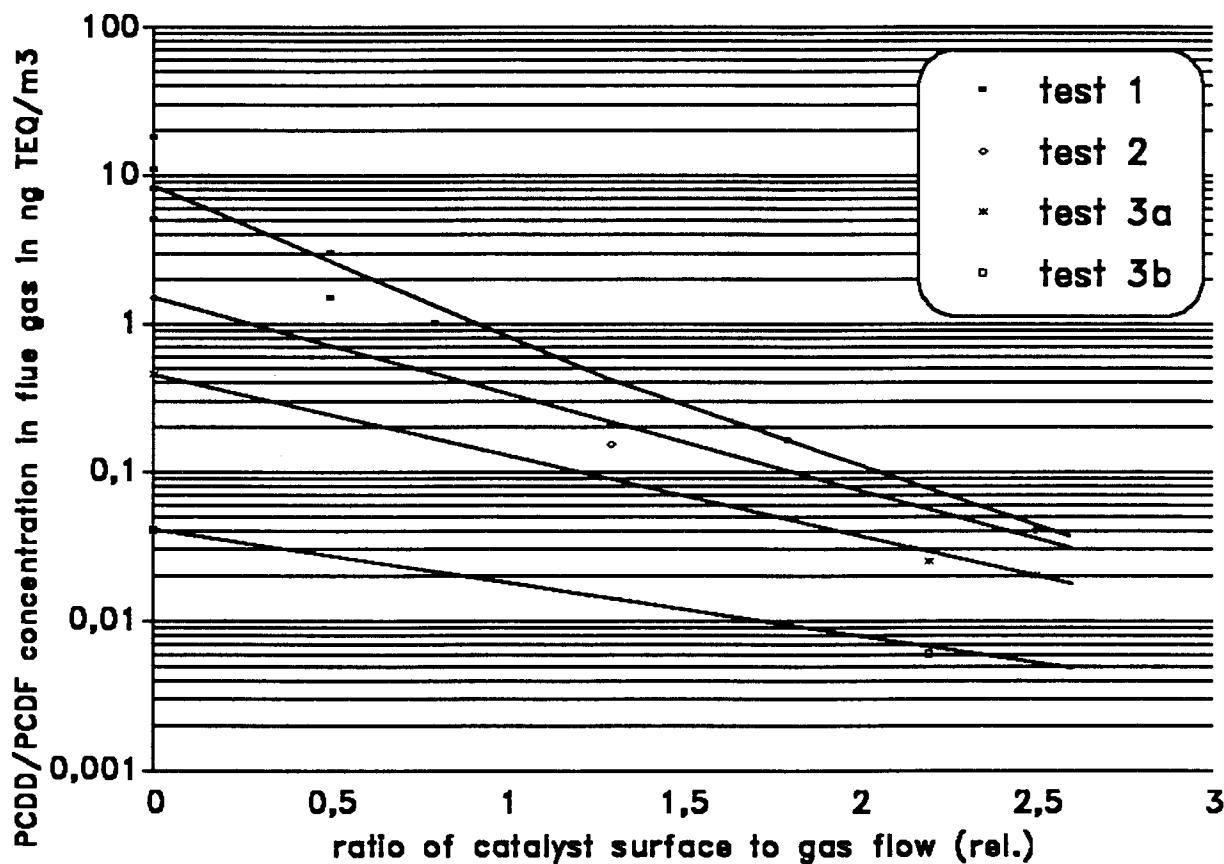


Figure 2. Residual concentrations after catalytic oxidation in relation to the outer catalyst surface. The inlet concentrations of PCDD/PCDF are the values at catalyst volume zero, the outlet concentrations are correlated to different catalyst sizes.

Recently a full scale deNOx-unit at the MWC Spittelau/Vienna was tested with regard to its capacity in lowering PCDD/PCDF emissions /6/. With a catalyst volume designed for deNOx function only, Reduction of PCDD/PCDF of 90 to 95% could be obtained under deNOx conditons. With increased catalyst volume further reduction can be expected.

CONCLUSIONS

Laboratory tests and pilot studies at waste incinerators have shown that catalysts of the SCR type, especially those on TiO₂ basis, are also excellent oxidation catalysts for the decomposition of PCDD/PCDF and related compounds.

PCDD/PCDF levels <0.1 ng TEQ/m³ in stack gas were obtained in pilot plant studies using SCR catalysts.

Simultaneous reduction of NOx and PCDD/PCDF requires additional catalyst volume either before or after the denox reaction.

No de novo synthesis of PCDD/PCDF and no accumulation of PCDD/PCDF in the catalytic reactor was observed under the conditions employed.

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The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

TECHNIQUES FOR DIOXIN EMISSION CONTROL

by

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ABSTRACT

Only several years ago it was generally thought that PCDD/F were either formed and/or not destroyed in the combustion of municipal solid waste (MSW). Today it is generally accepted that they are formed by the de-novo synthesis downstream from the combustion chamber at a temperature of about 300°C.

Fly ash, specifically copper, acts as a catalyst for the formation of free chlorine which chlorinates the aromatic structures through a Deacon like process. The transition of unburned carbon through a mesophase may play an important role in the formation of precursors.

The de-novo synthesis of PCDD/F homologues and isomers can be best postulated as the unimolecular reactions involving an activated complex. Once the PCDDs/Fs are formed, they are partitioned between gas, liquid, and solid phases depending on the spatial and temporal temperature profile in the flue gas.

A correlation between PCDD/F emissions from MSW incinerators and flue gas temperatures was quantified from data in the Danish Ministry of Environment study. An important practical implication of this correlation is that exit flue gas temperature can serve as a surrogate for estimating PCDD/F emissions.

An understanding of chemico-physical behavior of PCDD/F in MSW combustion allows the optimization of operating conditions to minimize their emissions.

The techniques for controlling PCDD/F emissions can be divided into three categories:

- o Minimization of precursors for PCDD/F formation
- o Prevention or reduction of PCDD/F formation
- o Post formation emission control and destruction

Vølund Miljøteknik A/S has implemented several mitigative techniques for the reduction of PCDD/F emissions in the design of MSW combustion plants.

INTRODUCTION

Ever since the discovery of emission of polychlorinated dibenzodioxins and dibenzofurans, PCDD/F, commonly referred to as dioxins, from the waste incineration facilities in the 1970s, they have been a hot topic of discussion. Both the scientific community and the general public are still involved in the controversy over their environmental impact, and specifically their health risk. The wide implementation of solid waste incineration, in spite of the landfill shortage situation, has been frequently opposed by the general public. One of the major arguments against incineration has been the health risk associated with the emissions of dioxins.

It has been discovered in recent years that the formation/emission of dioxins is a general phenomenon associated with combustion. Dioxins have been detected in the exhausts from automobiles, power plants, petroleum refineries, pulp and paper mills, etc. They are also generated in the everyday human activities like grilling of meats, dry cleaning, and burning logs in the fire places.

DIOXIN REGULATIONS

The future trends in the regulation of MSW incinerator emissions will be dictated by health risk standards. Dioxins, specifically TCDD, are the most toxic chemicals known to mankind. Until a couple of years ago, dioxin formation and/or not destruction was thought to take place in the combustion zone and therefore, remedial actions revolved around the three Ts of combustion.

Consequently, in the past, several European countries adopted regulations specifying furnace operating conditions such as temperature, residence time, and turbulence, while at the same time no specific emissions limits were mandated. Now, however, most European regulations call for a dioxin limit of 0.1 ng/m³ based on the toxic equivalents (TCDD).

Recent U.S. regulations for the dioxin emissions from MSW combustion plants distinguish between new and existing facilities and their capacity.

For new facilities total dioxin/furans emission limits are 75 ng/m³ for installations under 250 tons/day capacity and 5-30 ng/m³ for larger units.

For the existing facilities, the regulations limit total TCDD/F emissions to 500 ng/m³ for plants under 250 tons/day, 125 ng/m³ for plants between 250-2200 tons/day and 5-30 ng/m³ for the larger facilities.

FORMATION OF DIOXINS IN WASTE INCINERATION

The formation/emission of dioxins in the waste incineration has been extensively studied, resulting in a better understanding of their formation and reduced emissions.

In recent years it has been shown conclusively that dioxins are destroyed in the combustion zone but are formed downstream from the furnace at a temperature of about 300°C. The exact mechanism(s) of formation are not yet fully understood, but it appears that at least two mechanisms pertain. Chlorine donors and ring donors react in at least two different ways, and the dioxin products reach equilibrium, resulting in predictable isomer ratios.

COPPER CATALYTIC ACTION

Copper present on the fly ash particles from waste combustion plays an important role in a dioxin formation. An important step is the formation of free chlorine through a Deacon-like reaction.

The overall reaction in the Deacon process is:



This reaction is catalyzed by CuCl₂/CuCl and proceeds in three consecutive steps.

The chlorine radical Cl· formed through cleavage of chlorine is essential for chlorination of aromatic structures in dioxin formation.

The oxidative cyclization of the aromatic structures is also catalyzed by copper.

The catalytic activity of copper in PCDD/F formation indicates one way for their reduction. Vogg (1) and Naikwadi (2) have demonstrated through laboratory tests with fly ash that a reduction in PCDD/F formation can be accomplished by the inhibition of fly ash catalytic activity. Vogg demonstrated about 85% reduction in the dioxin formation when ammonia was present in the flue gas. Without the presence of ammonia, dioxin concentration was 6,197 ng/g in fly ash while in the presence of 300 mg NH₃/m³ only 914 ng/g were measured in the fly ash.

Naikwadi showed that both triethyl amine and CaO inhibit dioxin formation. Of more practical significance is the six fold reduction accomplished when 2% CaO is mixed with fly ash.

Vikelsoe (3) also showed the beneficial effect of CaO in the full scale incineration tests, but to a lesser degree.

An obvious, but impractical technique for dioxin reduction would be the elimination of copper from wastes.

THE ROLE OF CARBON IN DIOXIN FORMATION

The combustion of refuse takes place within luminous diffusion flames, luminosity resulting from the radiation of carbon in the yellow spectral region. The carbon structures formed in the flames consist of a number of roughly spherical particles strung together like pearls on a necklace. As the thermal transformation of carbon proceeds, the lower molecular weight components like benzene or phenol are vaporized while the higher molecular weight aromatic structures polymerize forming a pitch.

The basic organic molecules like benzene and phenol are readily chemisorbed on the fly ash metallic surfaces. Ordered structures of adsorbed benzene have been observed on several metallic surfaces. The optimal structure of benzene adsorbed on rhodium is shown in the top middle of Figure 1 (4). It shows that four benzene molecules form a rectangular unit cell, but the molecules are distorted and show losses of some vibrational frequencies.

FORMATION OF DIOXINS THROUGH AN ACTIVATED COMPLEX

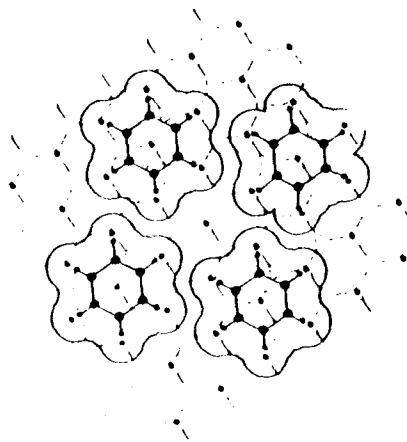
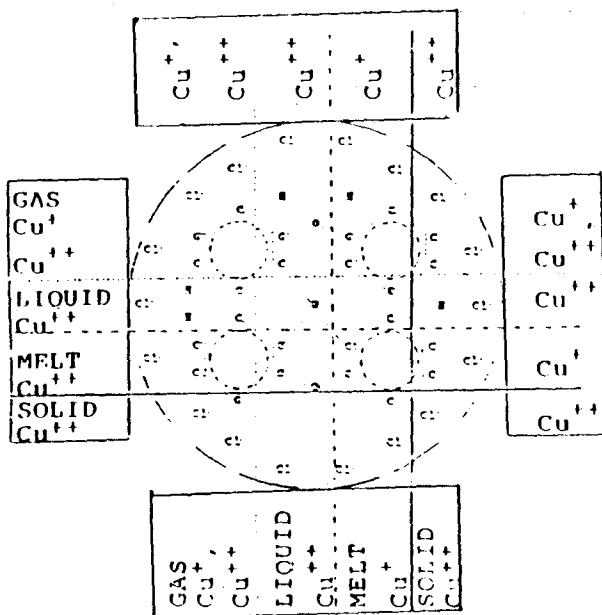
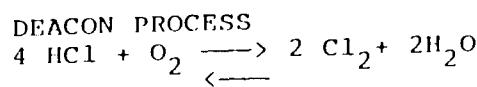
The formation of dioxins and furans (PCDD/F) in refuse incineration from aromatic structures, chlorine, oxygen, and hydrogen under copper catalytic action through an activated complex was proposed by Bosak (5).

Figure 1 illustrates the transition of aduct benzene molecules into an activated complex where chlorination and oxidative cyclization takes place.

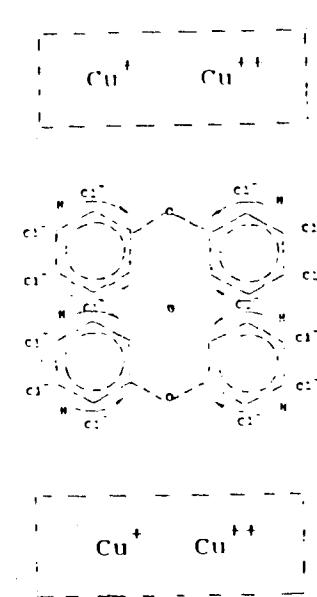
The energy of an activated complex is distributed among all its internal degrees of freedom. Some degrees of vibrational freedom are replaced by translational motion along the reaction coordinates. This part of energy gives rise to the transition of the activated complex either in the direction toward the products (PCDD/F) or back to the aduct molecules.

If dioxins are indeed formed from the aromatic structures on metallic surfaces, the obvious technique for their reduction is the complete combustion of carbon in the combustion zone.

Good mixing of refuse with primary combustion air and introduction of secondary air into the flame zone to create a turbulent premixed flame is an important technique for the reduction of soot (particulate carbon) formation.



OPTIMAL STRUCTURE
OF BENZENE ON
METALLIC SURFACE (4)



ACTIVATED COMPLEX

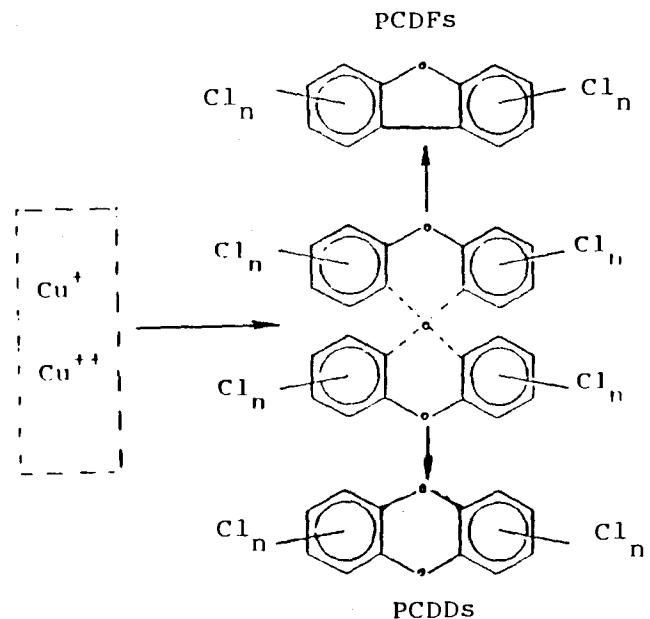


Figure 1 Formation of PCDD/F through an activated complex

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The presence of calcium, barium, strontium, and lithium salts has a strong inhibiting effect on soot formation. On the other hand, presence of sodium, potassium, and cesium salts increases soot formation.

OTHER COMBUSTION CONDITIONS

Oxygen concentration in the flue gas plays an important role in PCDD/F formation. The increase of O₂ content (high excess air) increases PCDD/F formation drastically with an especially pronounced formation of hepta and octa congeners.

The presence of water vapor is also important. While the "dry" conditions result in the formation of higher homologues, the "moist" conditions produce a maximum of the hexa isomers with increased penta and tetra isomers.

In general, good combustion i.e. high temperature, flame oxidative state, low CO content, etc. results in a trend toward higher chlorinated homologues. With poor combustion, low temperature, and high CO content more low chlorinated homologues are formed.

PHASE EQUILIBRIA

Once the dioxins are formed they are partitioned between the vapor, liquid, or solid phase depending on the spatial and temporal temperature profile within the flue gas stream.

The fugacity calculations by Schramm et al. (6) showed that the emission of PCDD/F from incinerators depends on the partition of these compounds between stack gas (gas phase) and fly ash (solid phase). The calculations showed that the separation of fly ash at low temperatures should decrease the total emissions up to a factor of one hundred. Increased fly ash concentrations would also enforce the separation effect, whereas low particle concentrations in the gas phase lead to high relative amounts of PCDD/F in the gas phase.

PCDD/F present in the gas phase can, upon temperature reduction, either condense on the fly ash or undergo homogeneous nucleation.

Since the aerosols formed through the homogeneous nucleation of PCDDs/Fs would be in the submicron range, they would be very difficult to collect in the particulate control equipment.

The presence of PCDD/F aerosols in the flue gas and the problems with their collection in the sampling train have been reported by Fängmark et al. (7). The result of the study showed that an aerosol filter has to be introduced after the condenser to collect particle-bound PCDD/F efficiently.

The PCDD/F condensed on the fly ash are readily collected in the particulate control equipment and can be subsequently destroyed via thermal treatment.

THE DANISH STUDY ON DIOXIN EMISSIONS

An important study on dioxin emissions from the waste incineration plants was carried out in Denmark from 1986 until 1989. The Danish Ministry of the Environment issued the report on the study showing that emissions are much lower than expected, and provided the data correlating the emissions with the operating parameters (8). Several correlations between dioxin emission and operating parameters were seen. It should especially be noticed that the emissions of dioxins increase with decreasing combustion temperature, increasing exit gas temperature, and increasing content of carbon monoxide.

One interesting but unexplained finding was that dioxin emissions varied significantly at the same plant when measured at different times.

In order to explain the variation in dioxin emissions at various times an attempt was made by the author to correlate the incinerator load and the exit gas temperature since the incinerator load was one of the test parameters. This correlation for the two plants where tests were conducted on several occasions is shown in Figure 2.

It can be seen that the incinerator load and the exit gas temperature do not have a singular functional relationship. The correlation is noticeable only if one correlates the data for each test period.

CORRELATION BETWEEN EXIT GAS TEMPERATURE AND PCDD/F EMISSIONS

The significance of the different exit gas temperature regimes during different testing periods is that it clearly correlates with the PCDD/F emissions: the higher the exit gas temperature the higher are the PCDD/F emissions.

The correlation between exit gas temperature and PCDD/F emissions at 100% incinerator loads for all 5 tests is shown in Figure 3 (9). The plot shows a clear exponential dependency between exit gas temperature and PCDD/F emissions. While the total PCDD/F emissions are about 100 ng/m^3 at a flue gas temperature of approximately 200°C it increases to about 1000 ng/m^3 at a flue gas temperature of approximately 240°C .

The simple explanation of this correlation is the vapor phase - solid phase partition of PCDD/F which depends on the temperature.

An important practical implication of this correlation is that the exit gas temperature can serve as a surrogate for PCDD/F emissions with several advantages including simplicity and measurement in real time.

The most important and easiest technique to implement for dioxin emissions control is to keep exit gas temperature low. This can be accomplished by several means like use of an economizer in the boilers, cooling

Figure 2 Correlation between exit gas temperature and load

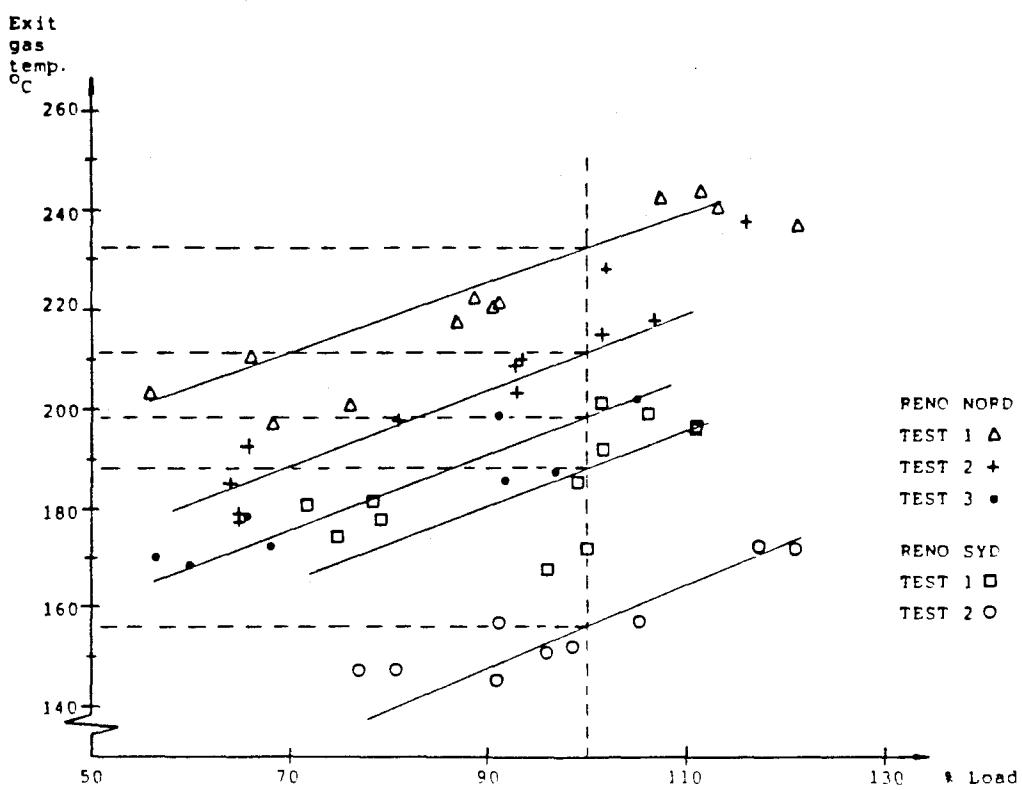
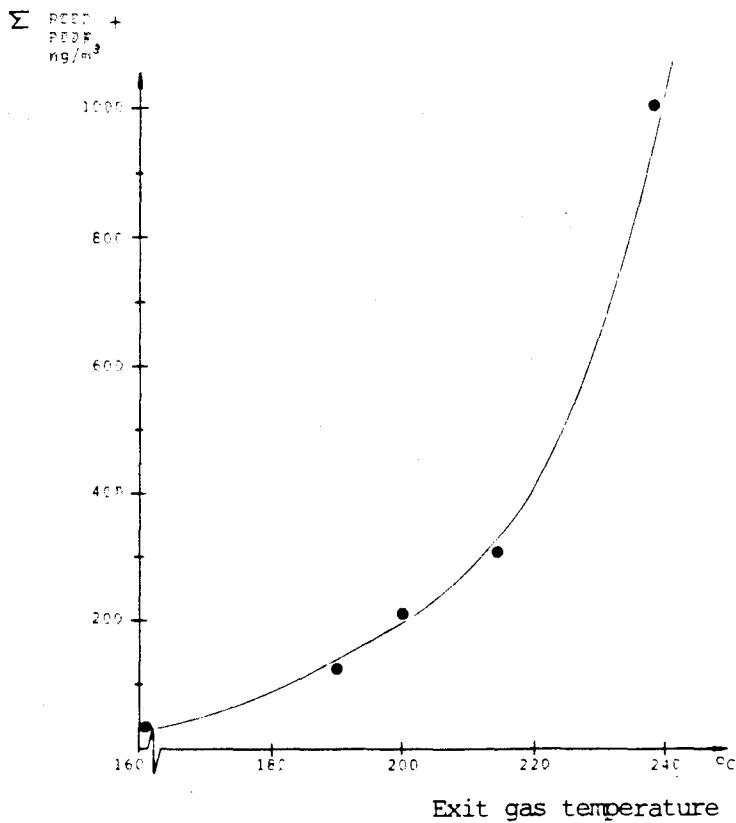


Figure 3 Correlation between PCDD/F emissions and exit gas temperature



of the flue gas either by heat exchangers or water injection, wet or semi-dry flue gas treatment etc. Most of the modern waste-to-energy plants designed by Vølund have low exit gas temperatures, because they are equipped with semi-dry flue gas treatment systems.

THE ROLE OF BOILER CLEANING INTERVALS

The different functional relationships between boiler load and exit gas temperature can be easily explained by the boiler cleaning intervals.

As the time after a manual boiler cleaning elapses, more and more fly ash accumulates on the boiler tubes. The fly ash and scale on the boiler tubes serve as an insulation reducing the heat transfer rate from the bulk gas to the boiler tubes. The consequence is a higher exit gas temperature and corresponding higher PCDD/F emissions.

The discussion with plant personnel at the Reno-Nord facility confirmed that in the tests with higher emissions more time had elapsed between the manual boiler cleaning and the testing.

An interesting phenomenon regarding dioxin emissions was observed during an incinerator test in Denmark (3). After a manual boiler cleaning, the dioxin emissions rose dramatically, but returned to normal after two days. The researchers speculated that possibly the cleaning had temporarily changed the chemical properties of the boiler surfaces, thereby introducing enhanced catalytic dioxin generating activity or previously formed dioxins were exposed.

High PCDD/F emissions during boiler cleaning by steam soot blowing was reported by Vogg (4). They concluded that the high emissions were probably due to the increased moisture content in the flue gas.

One technique for reducing of dioxin emissions is therefore to optimize the cleaning of boilers. Boilers should be cleaned continuously with as little steam as possible when steam soot blowing is used. Switching to cleaning with compressed air or mechanical rappers should also be considered. Most modern waste-to-energy plants designed by Vølund use either steel shots or mechanical rappers to clean the boiler tubes as required.

DIOXIN EMISSION TESTS AT AMAGERFORBRÄNDING

The Danish Ministry of Energy sponsored a study on the influence of flue gas cleaning system operating parameters on the removal of dioxins (10). The investigation was carried out on the fourth incineration line at Amagerforbrænding supplied by Vølund Miljøteknik as shown in Figure 4. This line uses a combination of grates and a rotary kiln for the complete combustion of refuse. The boiler is cleaned by a mechanical rapping system used in the recent Vølund installations. The Vølund-Limar flue gas cleaning system consists of a spray dryer absorber with a rotary atomizer followed by a pulse-jet fabric filter. The process flow diagram of the Vølund-Limar system is shown in Figure 5. The system treats 70,000-95,000 Nm³/h of flue

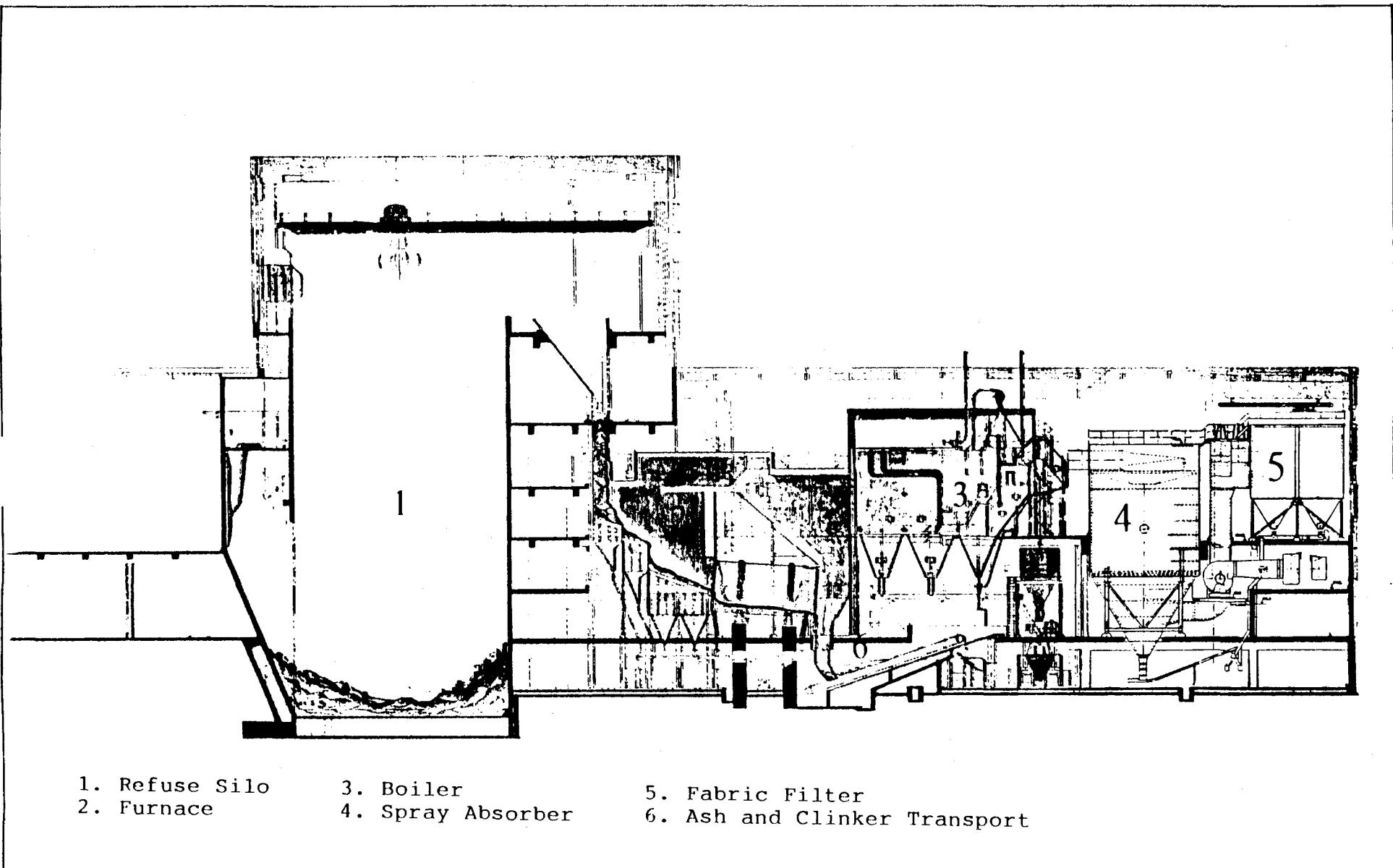
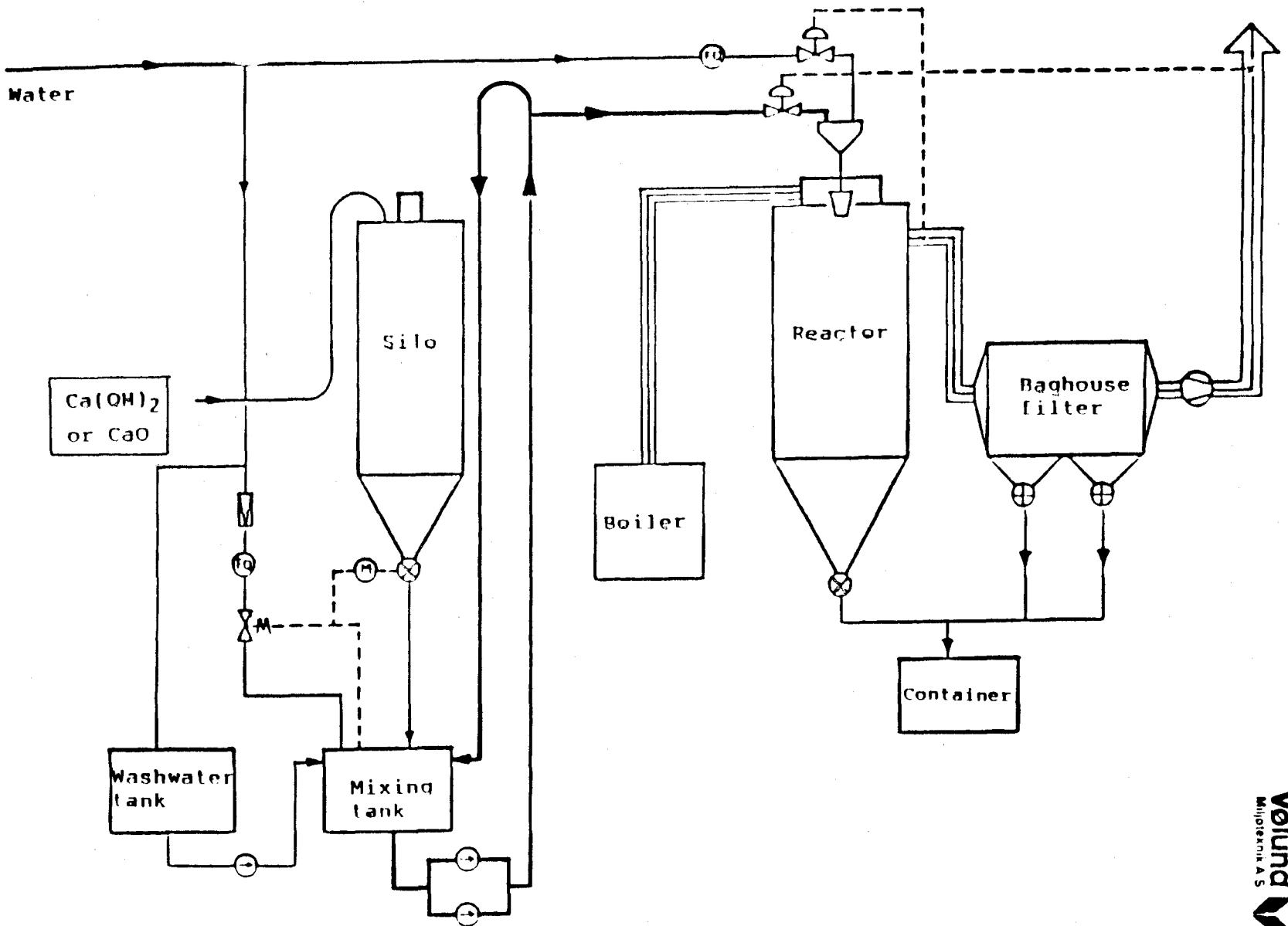


Figure 4 Sideview of the fourth incineration line at Amagerforbrænding

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Figure 5 Semi-dry absorption system Vølund-Limar

gas at a spray dryer absorber temperature of 140°C. The system operates in a single pass mode and uses a suspension of hydrated lime as the absorbent.

The test program was designed to investigate the effect of the spray dryer absorber outlet temperature as well as the use of activated carbon and active lime on dioxin removal.

Results of PCDD/F emissions and calculated Nordic toxic equivalents for the different tests are shown in Table 1 as reported by Nielsen et al. (10). Reduction of total PCDD/F is higher than 98% and for Nordic toxic equivalents higher than 99.5% in all cases. Outlet values are in all cases significantly below the 0.1 ng Nordic toxic equivalents/Nm³ at 10% O₂. Neither addition of activated carbon nor of active hydrated lime seems to have any effect on PCDD/F removal.

Figure 6 shows the correlation between exit gas temperature and dioxin emission for three plants including Amagerforbranding. Good exponential dependency of dioxin emissions on temperature is noticeable through the four orders of magnitude of dioxin concentrations.

The conclusion of this study was that using a spray dryer absorber followed by a fabric filter requires no modification in normal operation to secure an emission level of 0.1 ng Nordic toxic equivalents/Nm³ at 10% O₂. Even during start-up conditions, where an inlet level of 50 ng Nordic toxic equivalents/Nm³ was measured, the outlet level was below the 0.1 ng limit.

SUMMARY OF TECHNIQUES FOR DIOXIN EMISSIONS CONTROL

The techniques for PCDD/F emissions control can be divided into three categories:

1. Minimization of precursors for PCDD/F formation

Good combustion is essential for the minimization of reactive aromatic species which generate the precursors such as benzene, phenol etc. for PCDD/F formation. The keys to good combustion are the three Ts of combustion with the mixing of fuel and combustion air (both primary and secondary) being the most important. Reduction of copper in refuse is beneficial though that may not be practical. A low oxygen content in the flue gas will result in a reduction of PCDD/F formation.

2. Prevention or reduction of PCDD/F formation

The inhibition of copper catalytic activity in PCDD/F formation can be accomplished in the presence of ammonia, lime, etc. The continuous cleaning of boiler tubes and avoidance of steam use will reduce PCDD/F formation. The removal of fly ash from flue gas at temperatures above 300°C will reduce fly ash (copper) catalytic action.

TABLE 1: SPRAY DRYER ABSORBER (SDA) AND PULSE JET FABRIC FILTER (PJF)
OPERATING PARAMETERS AND RESULTS (10)

SDA Temperature	140 °C						127 °C			
Additive										
Carbon kg/h	4.5* 0.5 1.5 4.5						1.5 4.5			
Active lime kg/h							14			
SDA _{in} PCDD+PCDF	132	2170	283	276	201	278	254	154	154	307
PJF _{out} PCDD+PCDF	2.1	3.2	1.2	2.4	1.1	3.5	1.3	0.37	0.65	2.8
% Rem. PCDD/PCDF	98.4	99.9	99.6	99.2	99.5	98.8	Average (2.25)	Average (1.3)		
SDA _{in} N.t.e. TCDD	2.8	50	4.8	8.3	4.0	7.6	7.7	5.0	4.5	4.9
PJF _{out} N.t.e. TCDD	.0076	.050	.0075	.045	.035	.015	.0047	N.D.	.002	.043
% Rem. N.t.e. TCDD	99.7	99.9	99.8	99.5	99.1	99.8	99.9	=100	=100	99.1
PJF _{out} N.t.e. max. TCDD										
	.027	.079	.022	.060	.052	.033	.020	.016	.026	.056

All numbers in ng/Nm³ dry at 10% O₂

N.t.e. = Nordic toxic equivalents

N.D. = Non detectable

* = Simulated start-up

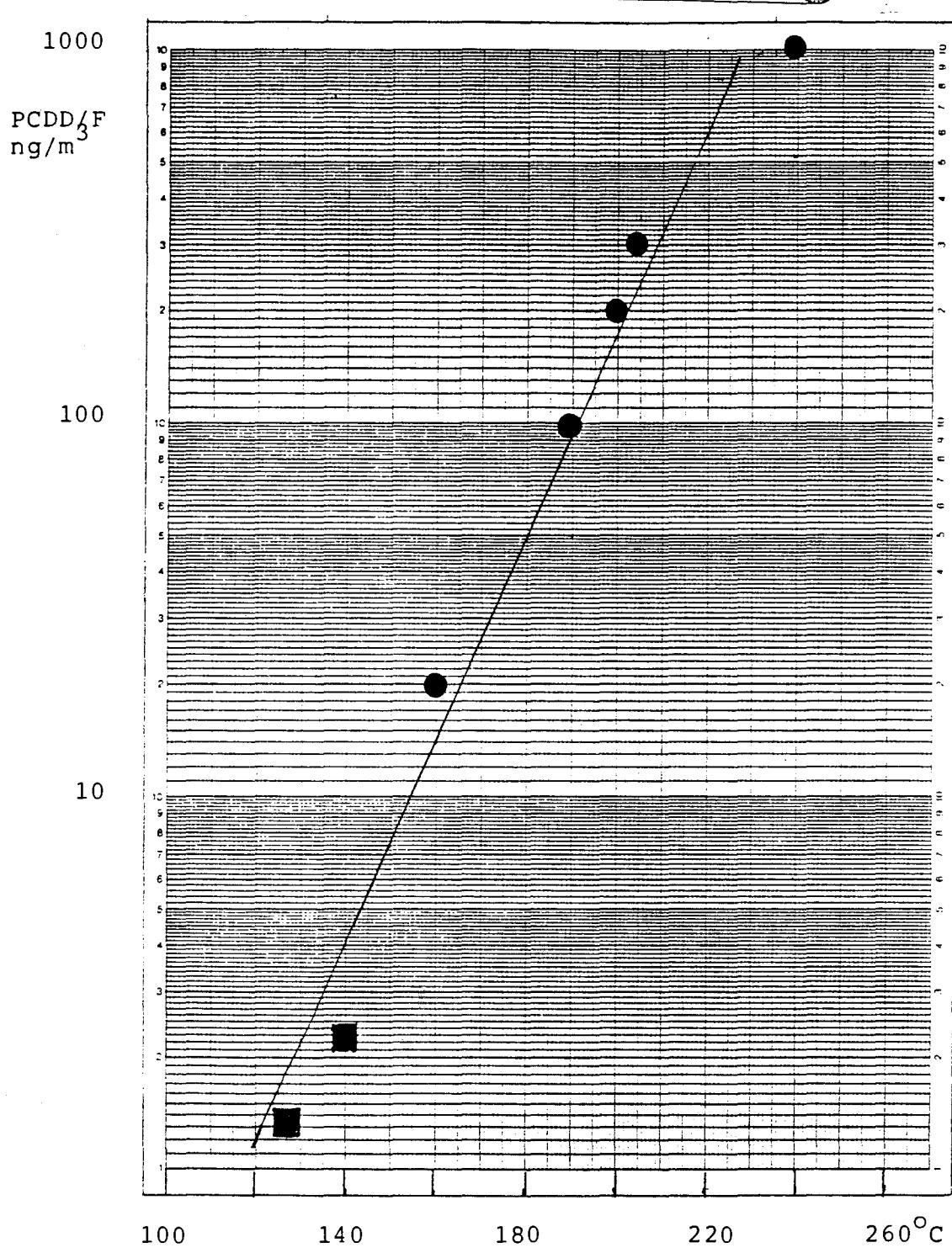


Figure 6 Correlation between exit gas temperature and PCDD/F emissions

● Reno-Nord and Syd plants
■ Amager plant

3. Post-formation emission control and destruction

Low exit flue gas exit temperature and high degree of particulate (fly ash with condensed PCDD/F) removal is essential for prevention of releases of PCDD/F to the atmosphere. The exit gas temperature can serve as a surrogate for PCDD/F emissions measurement. Adsorption of PCDD/F on filter cake or an activated carbon bed will also reduce the emissions. PCDD/F adsorbed on fly ash can be destroyed by reburning or alternative thermal or catalytic treatments.

The implementation of fully automatic computer operated incineration line controls, continuous mechanical boiler cleaning and use of a semi-dry flue gas treatment system (consisting of spray dryer absorber and fabric filter) at Amagerforbrænding (supplied by Vølund Miljøteknik) has demonstrated that dioxin emissions can be kept below the 0.1 ng Nordic toxic equivalents/Nm³.

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The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

REDUCTION OF DIOXINS-FURANS

FORMED IN COMBUSTION AND DE NOVO SYNTHESIS

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The acceptance that Denovo synthesis of dioxins and furans occurs on the surface of flyash particles in the temperature range of 200°C-400°C, establishes that post combustion formation of dioxins must be addressed. Dioxin-furan emission reduction can be achieved by addition of synthesis inhibitors, adsorbers, catalytic destruction, or utilization of the inherent capability of silica-alumina for chemisorption of the dioxins and furans within appropriate temperature ranges.

The chemisorption procedure, as applied to commercial incinerator operation adds no additional equipment or capital and operating costs to the system. The equilibria rather kinetics controls the absorption. Thus, wide variation in inlets are accepted by the system with no externally induced system response required.

Experience at the Commerce, California waste to energy system established reductions of total dioxin and furan cogeners to 1.9 ng/Nm³ from inlet concentrations ranging from 28 to 735 ng/Nm³, within the existing acid gas-particulate-heavy metal removal system, using only temperature control to affect the removal by chemisorption.

The increase in dioxin emissions present in the flue gas after the boiler occurred during a period of 18 months. During this period there was no change in the combustion conditions of time-temperature and carbon monoxide outlet concentrations. The significant increase in emissions dioxin-furan cogeners is attributed to Denovo synthesis on the boiler tubes.

The system consists of a Quench Reactor™-Dry Venturi™-and Baghouse. The baghouse operating temperature is maintained at 115-135°C to optimize the chemisorptive removal mechanism. The baghouse cake thickness is maintained in the range of 5 to 15 mm, at a pressure drop of about 100 mm aq., with a 6 hour cleaning cycle. The achievement of the thick fixed bed in the baghouse, resulting from the Dry Venturi™ action, provides for equilibrium control of the adsorption of the dioxins and furans as well as acid gas reductions of 99%, heavy metal reduction of 99.5%, and particulate emissions of less than 0.004 gr/dscf.

INTRODUCTION

The concern with emissions of dioxins and furans from municipal waste incineration processes has intensified, resulting in the emergence of regulations in Europe, Japan, and North America. The general target is 0.1 to 0.2 ng/Nm³ toxic equivalent in the stack gas.

The mode of control of these emissions has gone through an evolutionary period with the present consensus developing that dioxins and furans are formed both in the combustion zone and in the gas cooling zone. Thus, control of the emissions of dioxins and furans require more than control of combustion conditions.

In the 1970's and 1980's, theoretical and laboratory studies, such as conducted by Rordorf (8), Bozeka (1), and Tsang (16), indicated that both dioxin and furan emissions from the combustion process could be limited to close to zero if combustion temperatures were maintained in the range of 1000°C for 1 to 2 seconds. The ASME Solid Waste Committee and many regulatory agencies recommended this practice.

The achievement of this condition on a continuous basis was found to be difficult because of the heterogeneity of the waste fed to the incinerator. Clarke (2) reported high dioxin and furan emissions, up to 700 ng/Nm³ where a furnace operated at an average temperature of 1065°C.

A phenomenon apparently creating dioxins and furans downstream of the combustion zone became evident at the PEI tests on an incinerator provided with an afterburner. In this case, the dioxin-furan emission from the combustion zone were essentially zero, but the stack emissions contained significant quantities of dioxins and furans (3).

It was proposed by Teller (12, 14) that formation of the dioxins and furans were most probably occurring in the window of 200°C to 500°C in the boiler region, catalyzed by flyash and that effective control would be achieved by treatment of the gas downstream of the boiler.

The confirmation of dioxin-furan formation downstream of the combustion zone was presented by Hiraoka (5, 6), Naikwadi (7), and Stieglitz (10) in 1990.

The data presented by Hiraoka (5) indicated significant formation of dioxins in the gas/air heat exchanger operating in the temperature range 270°C to 400°C. Data presented by the authors are as follows:

	T°C	T ₄ CDD	P ₅ CDD	H ₆ CDD	H ₇ CDD	Q ₈ CDD
Inlet Gas/Air Heat Exchange	400	13.1	<0.25	21.2	50.5	19.1
Inlet of EP	270	29.6	33.7	84.3	132	141

A further study by Hiroaka et.al. (6) indicated that formation of dioxins in an electrostatic precipitator represented by the concentration of toxic equivalent 2, 3, 7, 8 TCDD, as a function of the operating temperature of the precipitator, with a ten-fold increase from 250°C to 290°C operating temperature.

Naikwadi (7) indicated that the temperature range for formation of the dioxins and furans, post combustion was 200°C to 400°C and that flyash appeared to be the catalyst.

Stieglitz (10) indicated that the denovo synthesis of dioxins and furans from preformed aromatic structures in a flyash environment.

The synthesis of dioxins and furans, catalyzed by flyash, from aromatic structures, that are more refractory than the dioxins, formed during the thermal destruction of dioxins in the furnace, is another potential component of the denovo synthesis.

The now confirmed formation of dioxins and furans downstream of the combustion zone requires reduction of these compounds in a flue gas emission control system.

TECHNOLOGY

In anticipation of the confirmation of the denovo synthesis of dioxins and furans downstream of the combustion zone, a technology for the recovery of these compounds including all congeners, was proposed in 1984 (13). It established the pseudo vapor pressure of the dioxin congeners in contact with flyash as 10⁻⁷ times the true vapor pressure proposed by Schroy (9), Figure 1. It further established the degree of chemisorption on flyash as a function of Temperature (13). The process, integrated with the Quench Reactor-Dry Venturi-Baghouse system, with specific temperature control requirements, now generally referred to as the RC/Teller system was patented in 1985 (12).

The process is now operational at MWS Resource Recovery systems in the U.S., Japan, and Italy. The data included are those from the Commerce, California facility.

The system (Figure 2), consists of the upflow Quench Reactor, Dry Venturi, ad Baghouse (17). Inasmuch as the thickness of the cake providing for fixed bed adsorption

and contact with the resident flyash is critical in the effectiveness of the chemisorptive process, the contribution of the Dry Venturi is significant.

The Dry Venturi action changes the characteristic of the baghouse cake, permitting a buildup of thickness to the range of 5mm with no significant increase in pressure drop. Thus a cake buildup of 4 to 8 hours between cleaning, at a maximum pressure drop of 4-5 in. w.g., is a normal operating condition.

The efficiency of recovery of acid gas as measured and that of TCDD as calculated for 120°C-130°C operation, based on HCD and SO₂ data approaches 96% in the baghouse as a function of the moving wave front number (Figure 3).

SYSTEM DATA

The system performance, TABLE I, was essentially constant over the 15-month period occurring between tests. The outlet levels and efficiencies of recoveries for particulate, acid gases, and non-volatile heavy metals were the same within the reproducibility of sampling and analysis.

The significant changes were improvement of recovery of mercury and the radical change in the inlet levels of dioxins and furans (Tables II, III, and IV). The total PCDD/PCDF at the boiler exit increased from 28.5 ng/Nm³ to 739 ng/Nm³. The CO level remained essentially the same.

If, indeed, CO concentrations are an indicator of the PCDD formed in the combustion chamber, the relationship observed by several investigators, then the significant increase is reflection of denovo synthesis.

It is believed that this increase is reflective of the seasoning of boiler tubes with the continuous deposition of flyash. Stieglitz (10) and others have demonstrated this phenomenon in controlled tests.

Significantly the performance of the emission control system produced final exhausts essentially the same as when the inlet PCDD/PCDF levels were 25 times the levels observed soon after startup. This behavior implies confirmation of the theoretical projections (13) that the vapor phase concentrations of the PCDD/PCDF were temperature related provided adequate thickness of the adsorbent were available.

Even where the toxic equivalents for inlet and outlet PCDD/PCDF concentrations were calculated (TABLE IV), the exit toxic equivalents were <0.113 ng/Nm³ (12% CO₂) for an inlet of 42.26 ng/Nm³ for an inlet of 2.15 ng/Nm³.

The only significant change is an increase in removal efficiencies as the inlet concentration increased.

The data further confirm the occurrence of denovo synthesis of dioxins and furans downstream of the combustion zone, and that these compounds in the vapor phase can be reduced by chemisorption on flyash and other silica-alumina compounds utilizing temperature control and adequate depth of adsorbent.

TABLE I
SYSTEM PERFORMANCE
COMMERCE REFUSE TO ENERGY FACILITY

	1987		1988	
	Conc. at Stack	Percent Removal	Conc. At Stack	Percent Removal
TOTAL PARTICULATE mg/Nm ³ (12% CO ₂)	9.8	99.9	11.4	99.8
HCl (ppm at 3% O ₂)	11.4	99.0	9.4	98.9
SO ₂ (ppm at 3% O ₂)	1.56	99.5	1.6	98.3
HF (ppm at 3% O ₂)	0.05	99.7	1.2	98.8
TOTAL PCDD/PCDF ng/Nm ³ (12% CO ₂)	<0.79	>97.3	<1.21	>99.7
TOTAL PAH mg/Nm ³ (12% CO ₂)			<0.15* <0.47**	>99.4
METALS mg/Nm ³ (12% CO ₂)				
Arsenic	<2.0	>98.1	<0.16	>99.8
Beryllium	<0.7	>90.0	<0.19	>97.2
Cadmium	<3.4	>99.9	2.0	99.9
Chromium	<0.7	>99.9	2.4	99.9
Lead	3.1	>99.9	2.0	>99.9
Mercury	270	0-20	41	91.3
Nickel	<28.0	>99.6	6.3	99.9

* excluding naphthalene

** including naphthalene

TABLE II
PCDD MISSIONS FROM COMMERCE
RESPONSE TO ENERGY FACILITY

Concentration ng/Nm³ at 12% CO₂
(< is below detectable limit)

	Boiler Exhaust (<50 PPM CO)	Stack	Boiler Exhaust (Test 8DF) (<50 PPM CO)	Stack (Test 8-DF)	Efficiency	
					1987	1988
2,3,7,8 TCDD	<0.097	<0.003	1.16	<0.007	96.9	>99.4
Total TCDD	0.865	0.112	91.90	0.063	88.1	99.9
1.2.3.7.8 PCDD	0.097	<0.003	4.31	<0.014	>96.9	>99.9
Total	0.448	0.051	100.77	0.142	88.6	99.9
123478 H _x CDD	0.078	<0.003	2.52	<0.004	>99.6	>99.8
123678	0.124	<0.011	4.58	<0.005	>91.1	>99.9
123789	0.124	<0.011	13.49	<0.012	>91.1	>99.9
Total H _x CDD	1.126	0.102	73.58	0.026	92.0	>99.9
1234678 H _p CDD	1.067	<0.058	13.53	<0.012	>94.6	>99.9
Total H _p CDD	2.160	0.062	29.73	0.055	97.1	99.8
OCDD	3.470	0.153	12.43	<0.037	95.6	>99.9
Total PCDD	8.200	<0.314	308.4 ⁽¹⁾	<0.308 ⁽¹⁾	>96.2	>99.9
Total PCDD			326.3 ⁽²⁾	<3.04 ⁽²⁾		>99.0

(1) Only run, stable operation, absent of interferences, and less than 50 PPM CO

(2) Average of 3 runs -- 1 unstable operation of incinerator
 1 interference in analysis

TABLE III
PCDF EMISSIONS FROM COMMERCE
REFUSE TO ENERGY FACILITY

Concentration ng/NM³ at 12% CO₂
(< is below detectable limit)

	Boiler Exhaust (<50 ppm CO)	Stack	Boiler Exhaust (Test 8DF) (<50 PPM CO)	Stack (Test 8-DF)	Efficiency	
					1987	1988
2,3,7,8 TCDD	<0.59	<0.028	13.78	<0.033	96.6	>99.8
Total TCDF	11.5	0.227	252.62	0.666	98.0	99.7
12378 PCDF	0.78	<0.003	4.66	<0.024	>99.6	>99.5
23478 PCDF	0.51	<0.015	15.04	<0.033	>97.1	>99.8
Total PCDF	2.83	0.059	70.18	0.163	98.0	99.8
123478 H _x CDD	0.64	<0.03	28.75	<0.003	95.3	>99.9
123678 H _x CDF	0.37	<0.012	8.10	<0.010	>96.8	>99.9
234678 H _x CDF	0.03	<0.015	15.49	<0.007	50.0	>99.9
123789 H _x CDF	<0.006	<0.001	3.39	<0.005	84.0	>99.9
Total H _x CDF	2.91	0.077	75.94	0.040	97.4	>99.9
1234678 H _p CDF	<0.0006	<0.001	18.53	<0.007	84.0	>99.9
1234789 H _p CDF	0.156	<0.001	2.06	<0.009	99.4	>99.6
Total H _p CDF	2.18	0.086	28.42	0.007	96.1	99.9
OCDF	0.88	0.032	3.36	<0.025	96.4	>99.3
Total PCDF	20.3	<0.480	430.6 ⁽¹⁾	0.901 ⁽¹⁾	97.6	99.8
Total PCDD			1219.5 ⁽²⁾	7.65 ⁽²⁾		99.4

(1) Only run, stable, absent of interferences, and less than 50 PPM CO.

(2) Average of 3 runs -- 1 unstable operation of incinerator
 1 interferences in analysis

TABLE IV

COMPARISON OF PCDD/PCDF TOXIC EQUIVALENTS

THREE MONTHS AFTER STARTUP -- EIGHTEEN MONTHS AFTER STARTUP
 Concentration in ng/Nm³ (12% CO₂)

Toxic Factor	Wt.	1987		1988	
		Boiler Exhaust	Stack	Boiler Exhaust	Stack
2378 TCDD	1.00	<0.097	<0.003	1.16	<0.007
12378 PCDD	1.00	0.097	0.003	4.31	<0.014
123478 H _x CDD	0.03	0.002	<0.003	0.077	<0.0001
123678 H _x CDD	0.03	0.004	<0.0003	0.137	<0.0002
123789 H _x CDD	0.03	0.004	<0.0003	0.405	<0.0004
1234678 H _x CDD	0.03	0.032	<0.0024	0.406	<0.0004
OCDD					
TOTAL PCDD		0.2361	<0.011	6.495	<0.022
2378 TCDF	1.00	0.59	<0.028	13.78	<0.033
12378 PCDF	1.00	0.78	<0.003	4.66	0.024
23478 PCDF	1.00	0.59	0.027	15.04	<0.033
123478 H _x CDF	0.03	0.019	0.001	0.163	<0.0001
123678 H _x CDF	0.03	0.011	0.0016	0.243	<0.0003
234678 H _x CDF	0.03	0.001	0.0006	0.465	<0.0002
123789 H _x CDF	0.03	0.000	0.000	0.102	<0.0002
1234678 H _x CDF	0.03	0.000	0.0016	0.556	<0.0002
1234789 H _x CDF	0.03	0.005	0.0001	0.062	<0.0003
OCDF	0.00	0.0	0.0	0.0	0.0
TOTAL PCDF		1.916	<0.063	35.77	<0.091

FIGURE 1: PSEUDO-VAPOR PRESSURE OF 4 CDD

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EMISSIONS FROM COMBUSTION PROCESSES

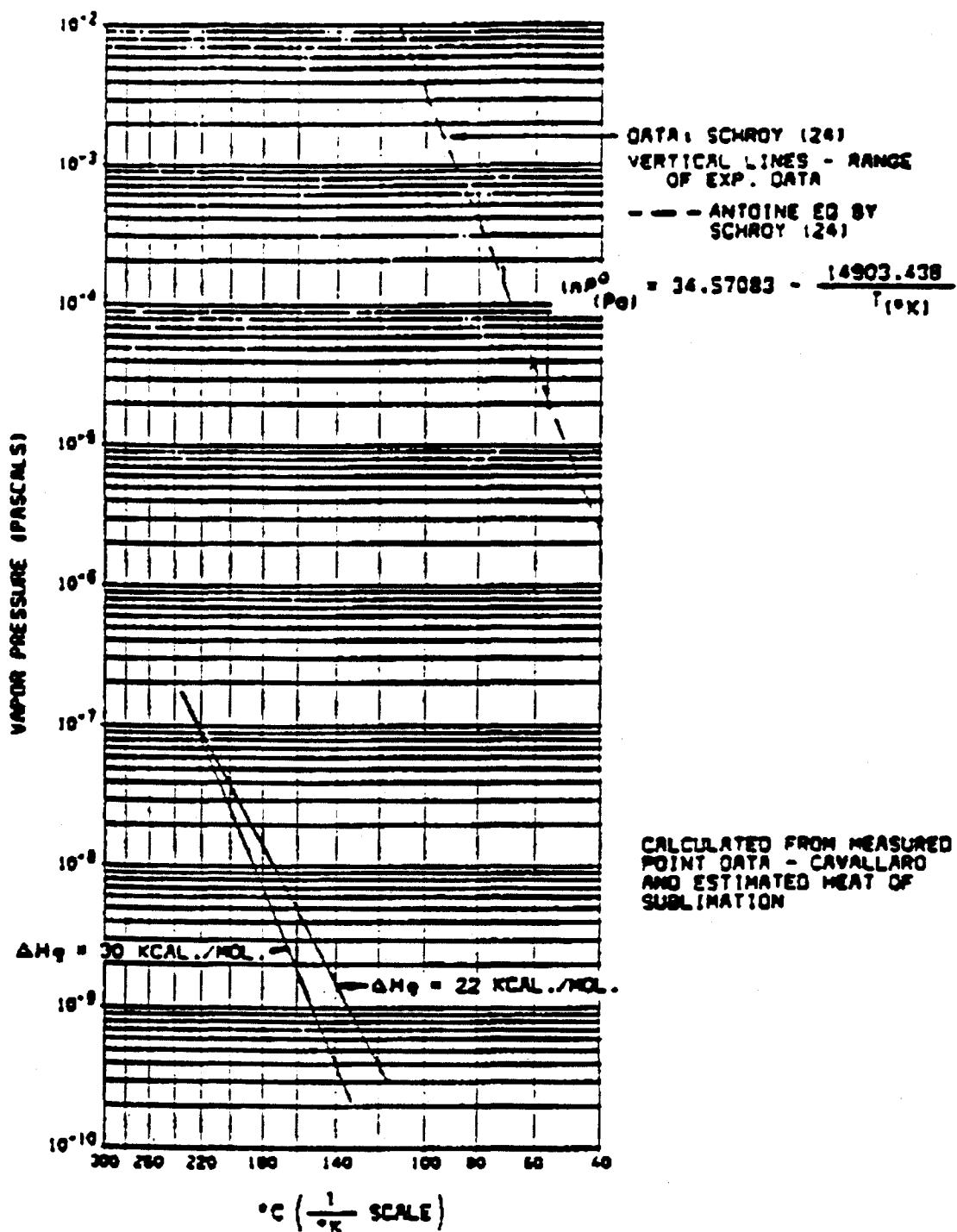


FIGURE 2: TELLER SEMI-DRY SYSTEM

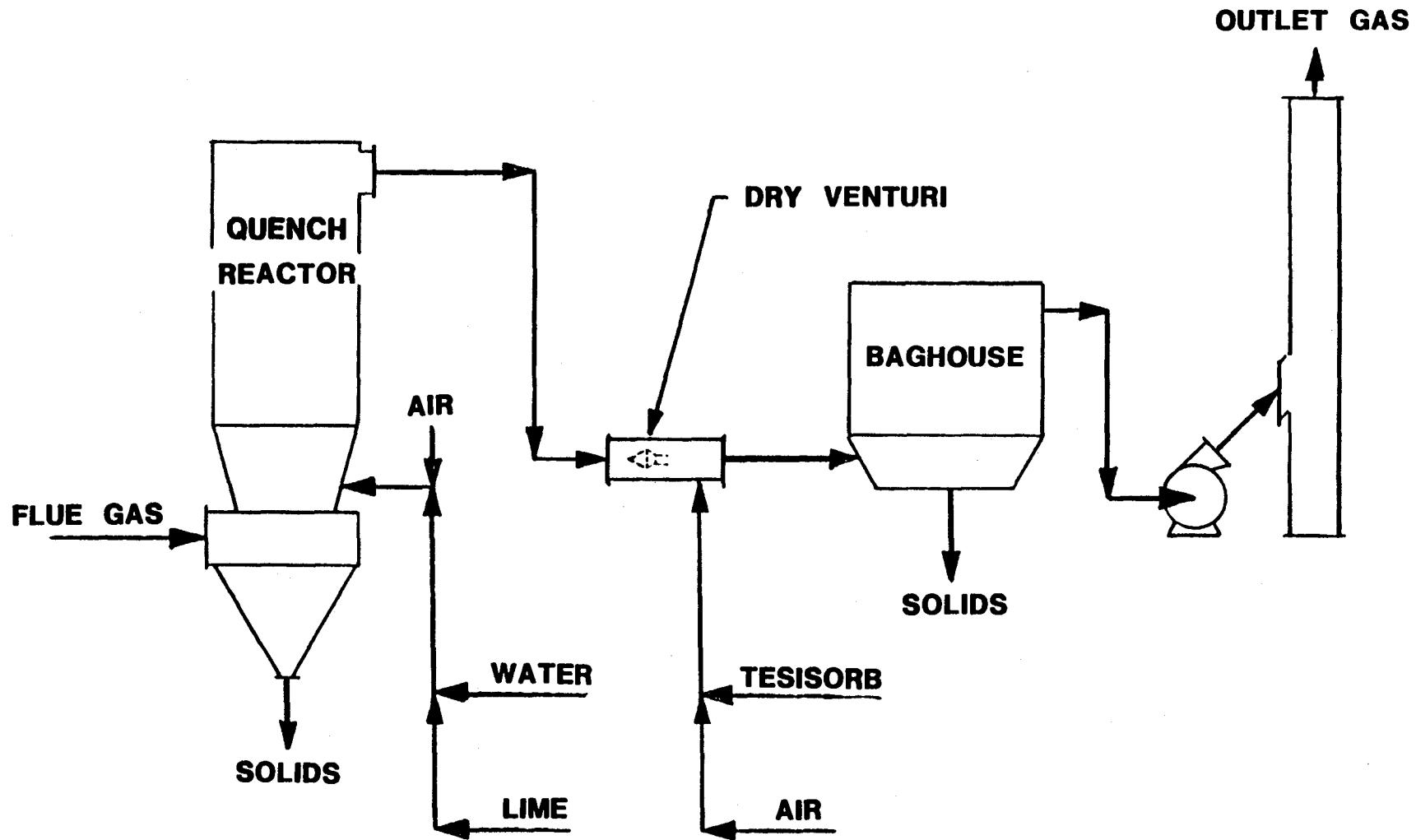
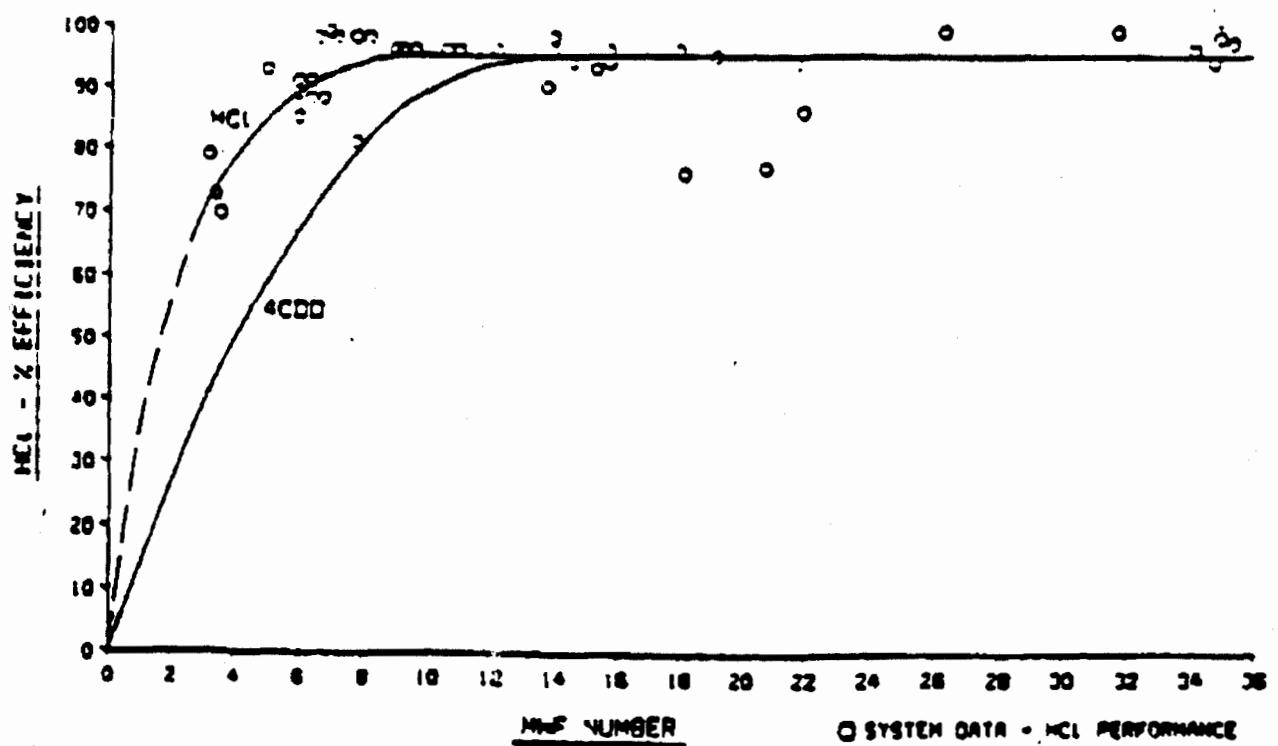


FIGURE 3: MOVING WAVE FRONT -- EFFICIENCY OF RECOVERY -- BAGHOUSE CAKE ADSORPTION

DIOXIN RECOVERY BY CHEMISORPTION

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SESSION 6C: NOVEL/EMERGING FLUE GAS CLEANING TECHNOLOGY I

Co-Chairmen:

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San Ramon, CA

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The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

PILOT-SCALE TESTING OF THE AMMONIA INJECTION TECHNOLOGY FOR SIMULTANEOUS CONTROL OF PCDD/PCDF, HCl AND NO_x EMISSIONS FROM MUNICIPAL SOLID WASTE INCINERATORS

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ABSTRACT

This paper describes the pilot-scale phase of a project for the development of a technology to simultaneously control emissions of PCDD/PCDF (polychlorinated dibenzodioxins/polychlorinated dibenzofurans), acid gases (hydrochloric acid (HCl) and sulfur oxides (SO_x)) and nitrogen oxides (NO_x) from municipal solid waste (MSW) incinerators. The technology utilizes ammonia (NH₃) as the control agent for all species of concern.

Previous work with a bench scale test system indicated that ammonia was effective both in suppressing low-temperature (<800 °F) PCDD/PCDF formation and in controlling HCl emissions when combined with a suitable particulate removal device. This technology promises to have many advantages over currently used alternative technologies. Mainly, this Ammonia Injection Technology (AIT) inhibits PCDD/PCDF formation rather than removing it after it formed. Therefore, AIT mitigates both air pollution and solid waste disposal concerns.

In this article, the theoretical basis for controlling all species, the previous experimental work and the currently ongoing pilot-scale ammonia injection experiment are described. In this current phase of the project, a pilot-scale economizer is used to simulate the behavior of the actual MSW economizer and to demonstrate the effectiveness of ammonia in suppressing PCDD/PCDF formation. A pilot-scale particulate control device is used to condense and to remove ammonium chloride and other ammonium salts in order to reduce HCl and SO₂ emissions.

After successful completion of the current phase of the pilot-scale study, additional project phases are planned. During the subsequent phases, the

effectiveness of ammonia in suppressing PCDD/PCDF formation at higher temperature (>800 °F), will be investigated and the optional NO_x reduction capability utilizing the demonstrated THERMAL DeNO_x technology will be incorporated into AIT.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

INTRODUCTION

THE TEST FACILITY

Occidental Chemical Corporation (OxyChem) operates one of the world's largest Refuse Derived Fuel (RDF) burning municipal solid waste incinerators in Niagara Falls, New York (Figure 1). This facility has a capacity of burning 2200 tons of RDF per day. The two boilers generate up to 270,000 pounds per hour steam (750 °F and 1250 psig). The steam is supplied to the adjacent chemical complex and/or to the two 25 MW turbine/generators. The basic features of each unit includes waterwall furnace enclosure, air-sweep stoker feed system, convective superheater, boiler bank, and economizer section. The OxyChem incinerators are equipped with highly efficient dry electrostatic precipitators for particulate control. They do not have acid gas control. As with other units using RDF technology, the Occidental incinerators have relatively high PCDD/PCDF emissions⁽¹⁾. Occidental has been investigating ways to retrofit its units to control these compounds.

THE CONCEPT OF MULTI-SPECIES CONTROL VIA AMMONIA INJECTION

PCDD/PCDF and HCl acid gas are two important species emitted from MSW combustion. In addition, emissions of NO_x and SO_x are also of concern. During Occidental's investigation of control options the concept of multi-species emission control utilizing a single reagent was considered. It was conceptualized that ammonia had the potential to simultaneously control emissions of several pollutants of concern: PCDD/PCDF, HCl and NO_x - and even SO_x, to some degree.

This concept was based on various degrees of previous knowledge. In 1987, Vogg and Stieglitz published results of laboratory furnace treatment of fly ash from MSW combustion in an air stream showing that NH₃ addition to the air stream suppressed PCDD/PCDF formation in the ash at the optimal temperature of 572 °F⁽²⁾.

In addition, it is known that in the presence of gas phase HCl, NH₃ will form NH₄Cl, which will condense out as a solid particle as the temperature falls. Also, the reduction of NO_x via gas phase NH₃ injection around the optimum temperature of 1750 °F via the THERMAL DeNO_x reaction is well proven and commercialized.

This multi-species control concept was first researched and studied "on paper". It was then concluded that there was opportunity for successful application of the Ammonia Injection Technology. However, several issues and unknowns were identified which were deemed to be resolvable only by experimental means.

OVERVIEW OF THE PROJECT

Based upon the favorable feedback from the "paper study", OxyChem initiated a four-stage project to develop the Ammonia Injection Technology. First, available background information and theories would be thoroughly researched. Second, a pilot-scale test program would be undertaken to verify that PCDD/PCDF is indeed formed at the lower temperature regions (<800 °F) of the incinerator and to investigate the degree of PCDD/PCDF formation suppression by ammonia. Also in this stage, the formation and capture of NH₄Cl would be demonstrated. Third, the entire AIT would be piloted. This would include the simulation of the equipment down-stream of the superheater, the investigation of the PCDD/PCDF formation/suppression by ammonia on a relatively larger scale, and the incorporation of the THERMAL DeNO_x process. Also in the third stage, the treatment of the generated waste water and solid waste would be studied. Finally, in the fourth stage, the full scale AIT would be installed on the Occidental facility. It was decided at the onset of the project that each subsequent stage would be executed only if the previous stage proved to be successful. The project was initiated in 1989 and now it is in its third stage.

BACKGROUND

THEORETICAL BASIS OF THE AMMONIA INJECTION TECHNOLOGY

PCDD/PCDF Control

The key to the Ammonia Injection Technology is the possibility that ammonia could prevent the formation of PCDD/PCDF. It is generally thought that PCDD/PCDF is formed either directly in the combustion chamber as a result of incomplete combustion (primary formation), or in the equipment downstream from the combustion chamber from unburned hydrocarbon precursors and chlorine/HCl (secondary formation). In reality, PCDD/PCDF is probably formed in both the combustion and the cooler downstream zones. According to prevailing theories^(2,3), the secondary formation of PCDD/PCDF is most prevalent in the 550-650 °F temperature range.

There are actually several theories as to why ammonia would prevent the formation of PCDD/PCDF. We suggest that the ammonia in the combustion gases competes with the hydrocarbon precursors present for the available chlorine (chloride). Since ammonia is more reactive with chloride than hydrocarbons are, ammonium chloride is more likely to form than chlorinated organics such as PCDD/PCDF. Others theorize that PCDD/PCDF is formed from chloride and hydrocarbon precursors by a catalytic reaction taking place on the surface of

the fly ash (4,5,6). Heavy metals, namely copper, may act as catalysts. It is thought that the catalytic action can be slowed down, or stopped entirely, by poisoning the catalyst. Various catalyst poisons have been tried and certain organic amines have been found to be effective⁽³⁾. We can then hypothesize that whatever an organic amine does in this regard, ammonia should react similarly. At a high injection temperature, the amines dissociate into NH₂ radicals and subsequently NH₄⁺ ions are formed. At the proper temperature, ammonia forms the same radical. Yet others⁽⁷⁾ further hold that an electrophilic mechanism is likely to be responsible for the chlorination of the organics. According to this theory, the fly ash surface functions as a stoichiometric oxidant, and not a catalyst, in promoting the chlorination of aromatics by HCl. Reaction of HCl with iron(3+) on the fly ash produces surface-bound iron(3+) chloride species that are the actual chlorinating agents. We again suggest that by tying up the HCl with ammonia, the chlorination of the aromatics can be minimized.

Therefore, if either (or all) of the above theories is true, the result is a reduction in PCDD/PCDF formation.

HCl Control

As for HCl control, it is well known that at the proper temperature ammonia and hydrochloric acid readily react to form ammonium chloride. The pure NH₄Cl would de-sublimate at 635 °F. However, in boiler operation, ammonium chloride is not likely to be in the solid phase until the flue gas temperature is much lower, perhaps after the particulate matter control device. If it condenses in the stack, or in the atmosphere outside the stack, it creates an unacceptable dense white cloud. Thus the challenge, regarding HCl control with ammonia, is to find the proper reaction temperature, to condense the vapor to a solid, and then capture the resulting sub-micron particulates in the appropriate control device. SO_x would behave with ammonia similarly, although the reaction would be somewhat slower (and less complete) and the resulting ammonium salt would be more difficult to handle.

NO_x Control

NO_x control is not a primary concern in this project. However, when controlling PCDD/PCDF and acid gases with ammonia, the control of NO_x would be an economically achievable added benefit. The control of NO_x with ammonia, either by the "THERMAL DeNOx" system⁽⁸⁾, or by the "Selective Catalytic Reduction" system⁽⁹⁾, is well-known technology. Therefore, it is not detailed here. However, it is included in the proposed technology in order to take full advantage of the use of ammonia.

SUMMARY OF BENCH-SCALE EXPERIMENT

Bench-scale test system description

In order to validate the above theories, and to establish the feasibility of ammonia injection as a potential emission control technology, a series of

bench-scale experiments were conducted at Occidental Chemical Corporation's MSW facility.

In the bench-scale experiment, a portion of the ash-containing flue gas from the boiler outlet was diverted isokinetically into the experimental apparatus (Figure 2). The system consisted of an 8 foot long (3" I.D.) sample probe inserted into the boiler outlet just before the economizer. The approximately 800 °F flue gas sidestream was pulled (via a jet pump) through an insulated, 10 feet long (3" I.D.) sample section. The sample section had six ports along its length which were used to sample and/or to monitor emissions or to inject ammonia (port # 3). The sidestream of flue gas was sampled to determine both the initial background PCDD/PCDF level (port #1) and the HCl concentration (port #2). A standard EPA train was used to sample the background PCDD/PCDF concentration.

A portion of the sidestream was diverted isokinetically into a PCDD/PCDF "reactor" consisting of thimble filters inside an isothermal oven (Figure 3). Downstream of the reactor, the back half of a standard EPA PCDD/PCDF sampling train was used to measure the PCDD/PCDF content of the filtered flue gas. The ash captured in the temperature-controlled thimble filters was also analyzed for PCDD/PCDF.

In selected experiments, ammonia was injected upstream of the PCDD/PCDF reactor. The flue gas exiting the reactor was sent to an NH_4Cl condensation system. This condensation system consisted of a condenser/filter assembly in a constant-temperature oven, followed by a standard HCl sampling train (Figure 4).

Bench-scale experiment design

Experiments on the bench-scale apparatus had three primary objectives: first, the verification of the secondary PCDD/PCDF formation at approximately 572 °F; second, the determination of the extent of ammonia suppression of this formation; third, the confirmation of the removal of HCl via formation and condensation of NH_4Cl .

A factorial experimental design was developed to investigate the effects of the key parameters. These included: ammonia stoichiometry, PCDD/PCDF reactor temperature, reactor residence time and ammonium chloride condensation temperature.

Bench-scale test results

This phase of the project was developed in 1989 and completed in 1990. The bench-scale test results are detailed in another paper⁽¹⁰⁾ and are only briefly summarized here. The bench-scale experiments demonstrated that:

- a. Substantial amounts of PCDD/PCDF formed, relative to background levels, in the "reactor" at 572 °F. (The average ash residence time in the reactor, which was equal to 1/2 the sampling time, varied between 30 and 60 minutes.)

- b. Ammonia injection virtually completely suppressed the PCDD/PCDF formation. In the presence of ammonia, the total PCDD and total PCDF concentrations in the reactor remained at approximately background levels.
- c. Greater than 97 percent reduction in HCl emissions was achieved with the NH₄Cl condensation/removal system.
- d. Excess ammonia concentration, over the stoichiometric amount, had no effect on NH₄Cl condensation and removal efficiency (in the range 260 °F to 180 °F).

PILOT-SCALE PROJECT

PILOT-SCALE PROJECT OBJECTIVES

Due to the encouraging results of the bench-scale tests, an expanded project at the pilot-scale size was approved and is currently in progress. This stage of the project itself is executed in three phases.

Phase 1

The objective of Phase 1 is to confirm the mechanism of PCDD/PCDF suppression with ammonia as found in the bench-scale tests. In addition, more detailed and expanded tests, focused on the NH₄Cl condensation temperature window and the NH₄Cl particle capture alternatives, are also targeted. For this, a pilot-scale test system simulating the PCDD/PCDF formation characteristics of the actual (full-size) economizer and dry electrostatic precipitator (ESP), a pilot-scale ammonia storage, supply, and injection system were designed and constructed.

Phase 2

Utilizing the experimental data obtained in Phase 1, Phase 2 expands the pilot system to test candidate NH₄Cl particulate control equipment and to upgrade the pilot system allowing enhanced and long term operation. In this phase, the issues of liquid and solid waste treatment, handling and disposal is also addressed.

Phase 3

The objective of Phase 3 is to further expand the pilot system to investigate PCDD/PCDF suppression at higher temperatures (in the combustion chamber) and to incorporate the NO_x control technology. In this Phase, the entire system will be optimized as to the number and locations of the ammonia injection ports, and the quantities of ammonia injected at those ports. Finally, the waste handling system will be refined and also optimized.

DESCRIPTION OF PILOT-SCALE TEST SYSTEM

Phase 1 Pilot-scale test system description

Table 1 presents a comparison of the key design values between the actual MSW system, the previous bench-scale system and the current pilot-scale system.

TABLE 1. COMPARISON OF THE KEY DESIGN PARAMETERS FOR THE ACTUAL MSW, THE PILOT-SCALE AND THE BENCH-SCALE UNITS

Parameter	Units	Actual Economizer	Pilot-scale Economizer	Bench-Scale Test System
Economizer Inlet Gas Flowrate	DSCFM WACFM	200,000 540,000	4,000 10,800	20 54
Economizer Inlet Gas Velocity	ft/s	22.5	22.5	22.5
Economizer Area	ft ²	400	8	0.04
Flue gas HCl concen- tration on dry basis	ppm @ 7% O ₂ ppm @ 14% O ₂	640 360	640 360	640 360
Stoichio- metric NH ₃ flowrate	lb/hr	200	4	0.02

Figure 5 presents a schematic of the Phase 1 experimental system. A flue gas stream of approximately 4000 DSCFM at approximately 800 °F will be withdrawn isokinetically from the boiler outlet duct through an inserted 7 foot long (3' I.D.) "probe". An isolation damper is installed between the probe and pilot system just outside the boiler duct wall. Next to the damper, a long horizontal section of insulated 3' I.D. duct is installed. The background PCDD/PCDF sample station is located on this section of the duct.

The flue gas will pass through additional insulated ducting to the ammonia injection station. The ammonia injection station has provisions for the continuous introduction and thorough mixing of ammonia over a wide range of stoichiometric ratios.

Down stream of the ammonia injection station the hot flue gas continues into the pilot-scale economizer, where the gas will be cooled to approximately 500 °F or lower. At the outlet of the pilot-scale economizer, the gas stream will pass through a dry ESP simulator (not energized) and then be drawn through a cyclone separator to remove large-size particulate matter. Finally, after passing through the fan, the stream is re-injected into the main flue gas stream at the inlet of the MSW's dry electrostatic precipitator unit.

Phase 2 Pilot-scale test system description

In the second phase of the pilot-scale experiments the economizer and dry ESP simulators from the Phase 1 experiments will be re-used and combined with additional equipment for NH_4Cl condensation and removal. Figure 6 presents the Phase 2 equipment. The gas stream at 500 °F or less from the pilot-scale economizer outlet will be directed into a transition duct, where provision will be made for secondary ammonia injection (as required). Next, the stream enters the flue gas precooler or quench chamber. Following the quench chamber, the gas passes into a pilot-scale particulate control device (PCD). Finally, through the ID fan, the stream is exhausted to the atmosphere through a short stack.

Various PCDs are being considered for investigation: a baghouse, a wet electrostatic precipitator (WESP) and scrubber/demisters of different designs. The device(s) for actual testing will be selected after completion of Phase 1.

Depending on the PCD employed, solid waste or wastewater in various quantities will be generated. Provisions will be made to treat and properly dispose of this waste. If the ammonia salts are collected as solid material, they might be disposed of as solid waste. If the ammonia salts are collected in solution, the options for treatment are wide open. These options include the simple disposal of the waste water with the ash (as a wetting agent). If the water balance dictates, the waste water might be evaporated (the vapors condensed and recycled) and the ammonium salt crystallized. Alternatively, the waste water can be reacted with caustic soda or soda ash. The resulting sodium chloride solution might be recycled to the chlorine/caustic soda manufacturing process of the adjacent chemical complex. The waste water can also be reacted with lime. The calcium sulfite/sulfate would be separated and disposed of as solid waste. The calcium chloride solution would be discharged. In both the caustic and lime treatment options, the ammonia would be purged from the waste water and recycled to the ammonia injection ports, resulting in a closed ammonia cycle. It is expected that a wet option (WESP or scrubber/demister) would also be beneficial in controlling the emissions of certain heavy metals, mainly of mercury.

During Phase 2, the pilot-scale process control and monitoring system will also be upgraded to ensure continuous operation for extended periods.

Phase 3 Pilot-scale test system description

In the Phase 3 experiments, the equipment from Phases 1 and 2 (pilot scale economizer, pilot-scale PCD and primary and secondary ammonia injection systems) will be re-used and combined with equipment for the determination of

high-temperature PCDD/PCDF formation/suppression and for the THERMAL DeNOx process. This expanded system is presented in Figure 7.

A gas stream at a temperature of 1800 °F, or higher, will be withdrawn from the incinerator furnace and sent through a pre-cooler into an insulated duct where tertiary ammonia injection will take place. The stream then would enter into a post-cooler, where the gas temperature will be reduced to approximately 800 °F. The temperature drop will be adjusted to give the temperature downstream of the ammonia injection point appropriate for the THERMAL DeNOx reaction. The outlet of the post-cooler will be connected to the inlet duct of the pilot-scale economizer previously described.

CURRENT PROJECT STATUS

Phase 1 Pilot-scale project experimental design

The Phase 1 tests will serve two purposes. First, they will demonstrate PCDD/PCDF formation in the pilot-scale economizer and its suppression by ammonia injection over a wide range of process conditions. This will include the evaluation of the extent of PCDD/PCDF formation suppression at very low ammonia stoichiometries, where NH_4Cl formation is relatively minor. Second, they will be used to make a preliminary determination of the conditions under which NH_4Cl condensation and removal occurs, such that the appropriate particulate control device can be selected for subsequent testing. To make this preliminary determination, some additional ammonium chloride condensation experiments, similar to those conducted in the bench-scale project in early 1990, will be performed.

As in the bench-scale test series, a factorial experimental design has been developed. Variables include: ammonia stoichiometry, pilot scale economizer/dry ESP simulator temperature, ammonium chloride condenser temperature, and pilot-scale economizer/dry ESP simulator residence time. Sampling and measurement requirements include: background PCDD/PCDF, inlet HCl concentration, inlet and outlet ammonia concentrations, pilot-scale test system outlet PCDD/PCDF, as well as flue gas flowrate, moisture content, oxygen, CO_2 , percent and CO concentrations. The PCDD/PCDF analysis will utilize High Resolution Gas chromatography/High Resolution Mass Spectrography (HRGC/HRMS) with quantification of the tetra - octa PCDD/PCDF isomers. Standard EPA methods will be used for sampling and analyses.

Phase 1 Pilot-scale project work in progress

Phase 1 began in the fall of 1990. The pilot-scale system design, engineering, equipment procurement and installation have been completed. Testing is currently underway. Phase 1 is scheduled to be completed by May 1991. If Phase 1 results are positive, then Phase 2 will commence immediately and be completed by November 1991.

As issues become positively resolved, Occidental will continue to expand the scale and scope of this project, up to and including a full scale demonstration of the Ammonia Injection Technology.

SUMMARY

The Ammonia Injection Technology offers an opportunity to simultaneously control PCDD/PCDF, acid gases and NO_x emissions from MSW incinerators. Since the process uses a gaseous control media, it is relatively simple and requires less space to install than technologies handling solids, such as the lime injection system. The main advantage of the AIT is, however, that it suppresses the formation of PCDD/PCDF, as opposed to control systems which transfer them to another media.

Occidental Chemical Corporation committed significant resources to develop this technology. A series of bench-scale experiments completed on its MSW unit were very encouraging. Based upon these results, a pilot-scale system has been designed and installed to develop the AIT further. Testing on this system is currently ongoing and is scheduled for completion by mid 1992.

It is intended that, after successful completion of the development project, the technology will be installed at OxyChem's Niagara Falls, NY MSW facility.

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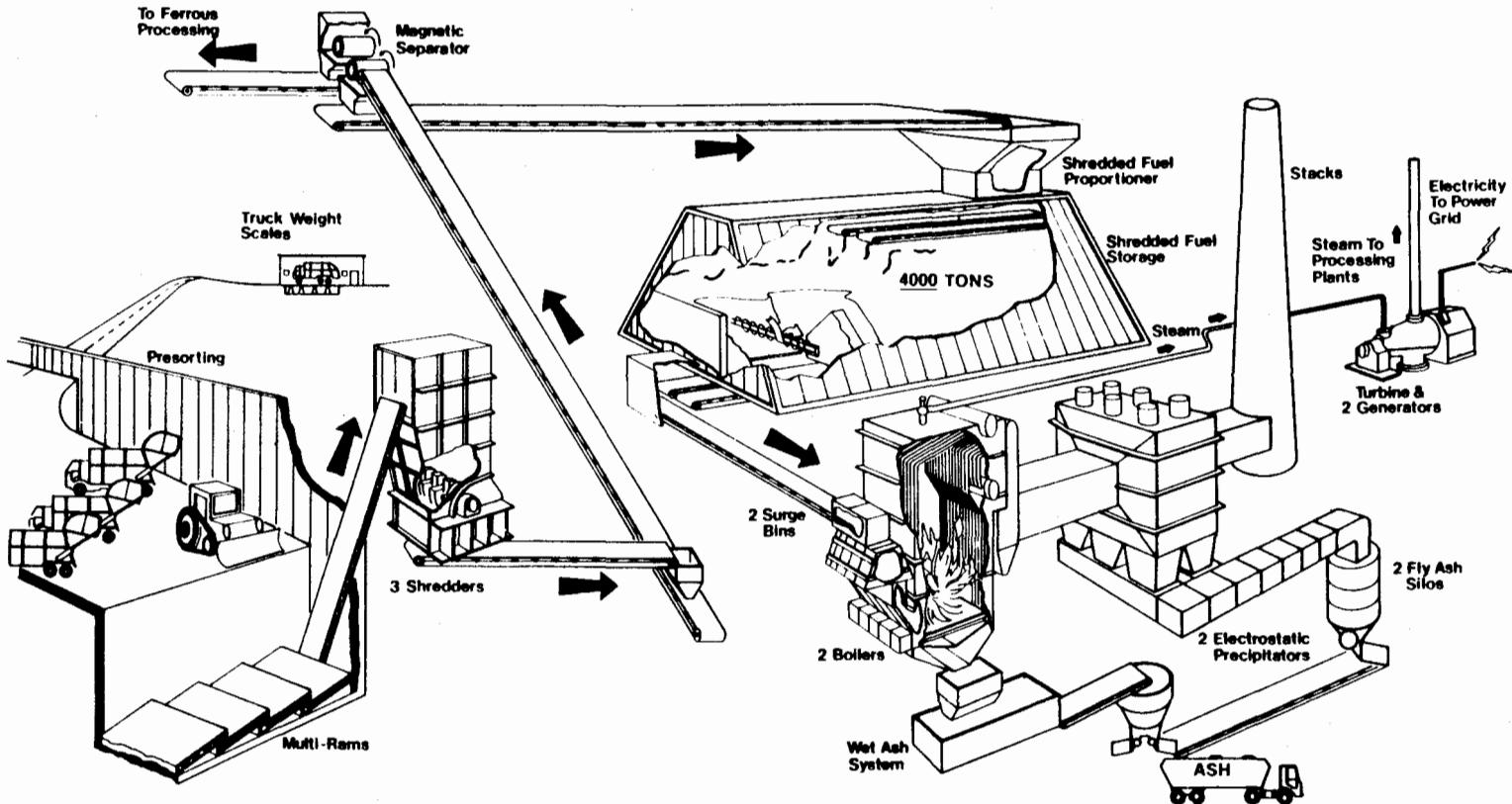


Figure 1. Schematic of OxyChem's MSW Facility

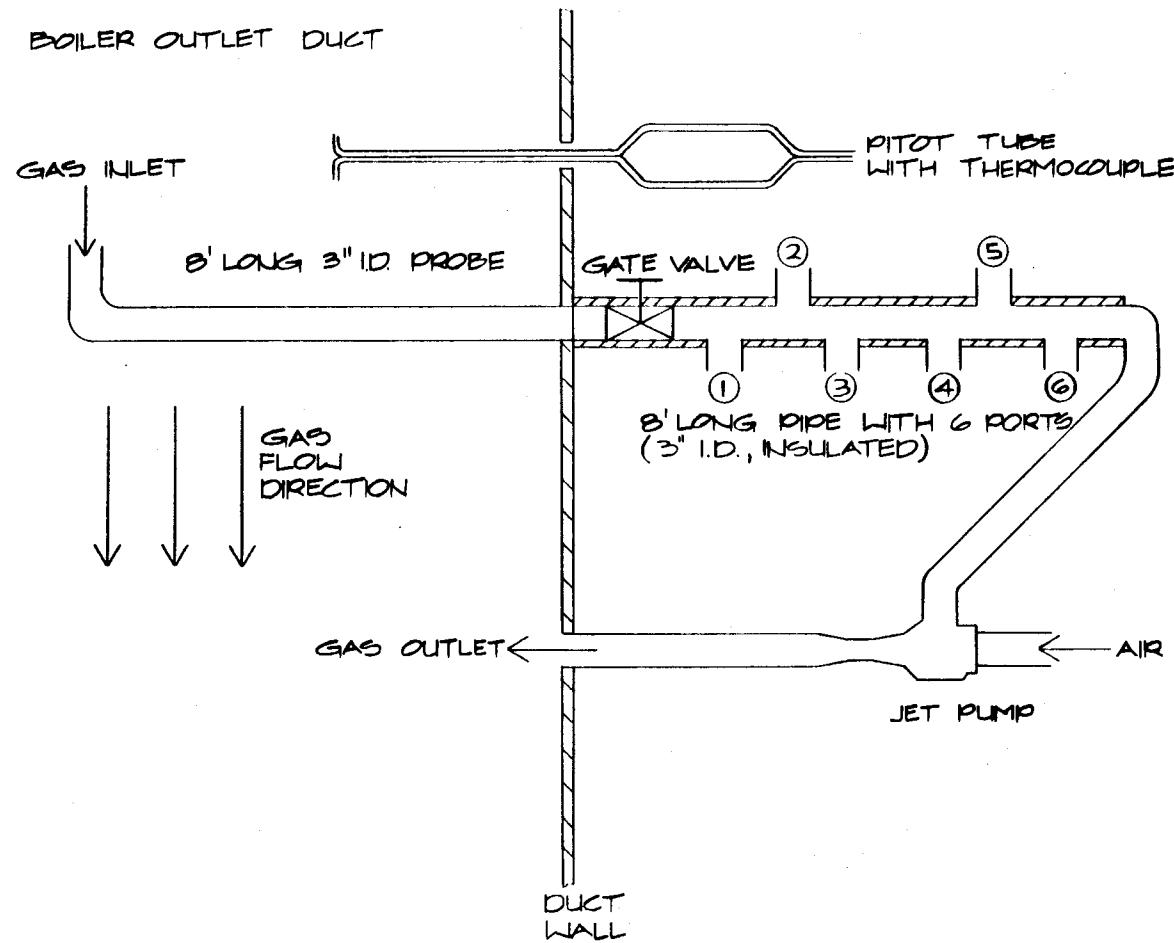


Figure 2. Bench-scale Test System

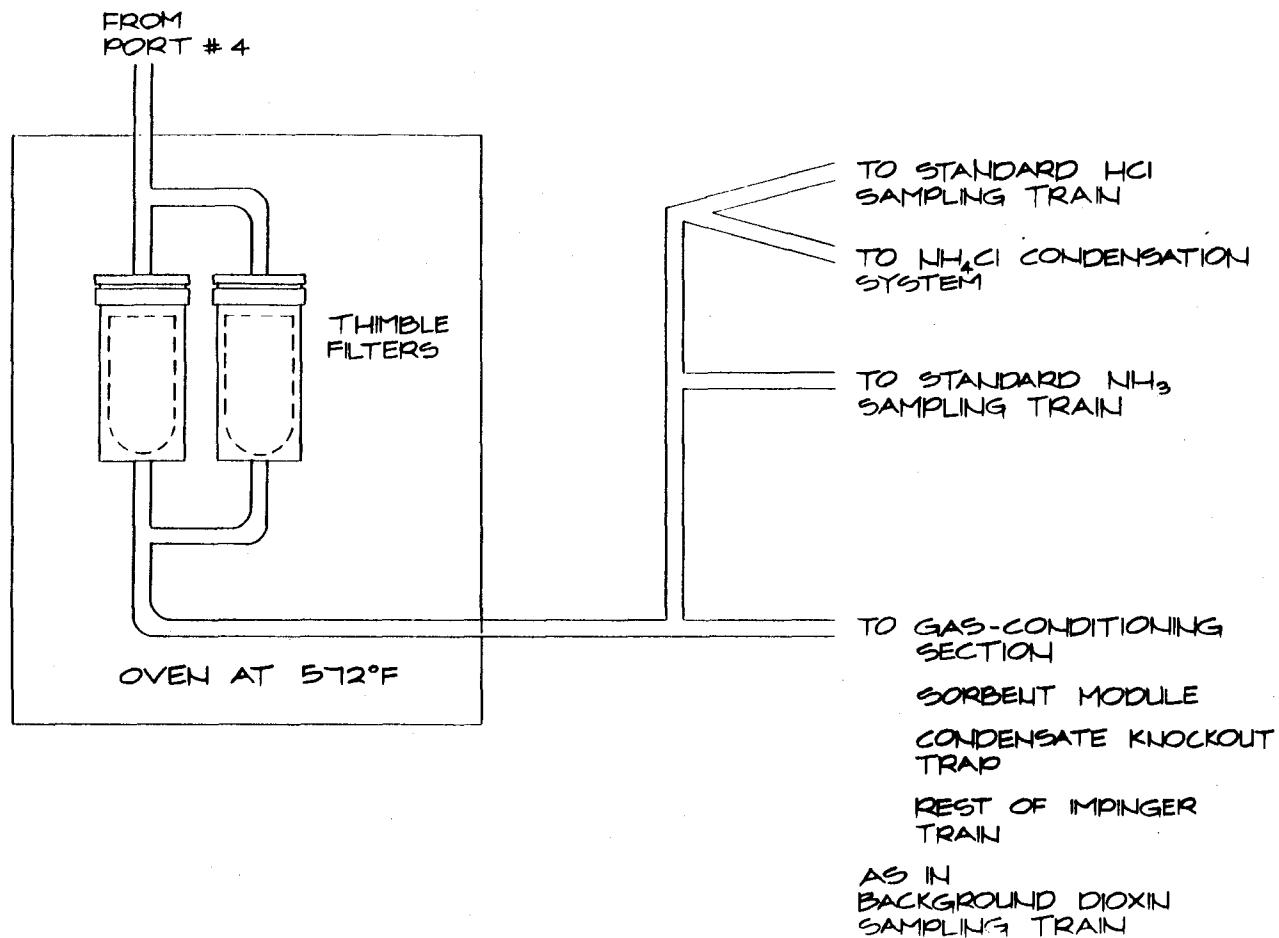


Figure 3. PCDD/PCDF "Reactor"

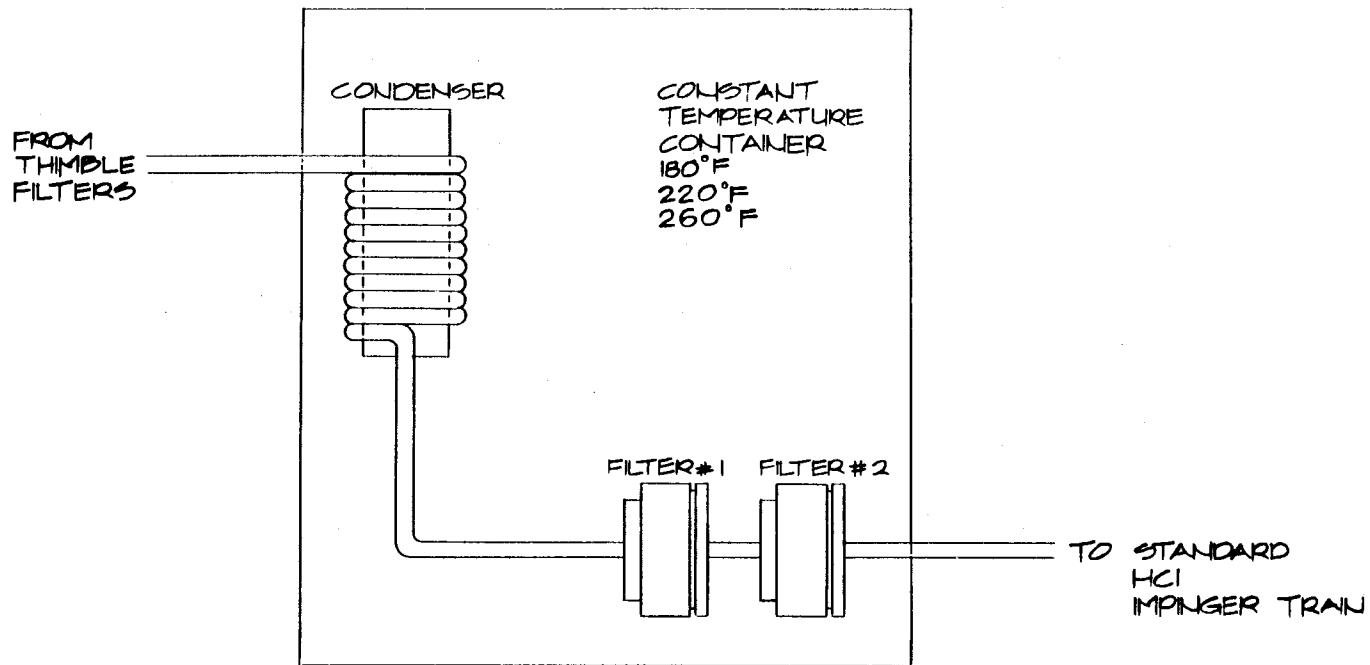


Figure 4. Ammonium Chloride Condensation System

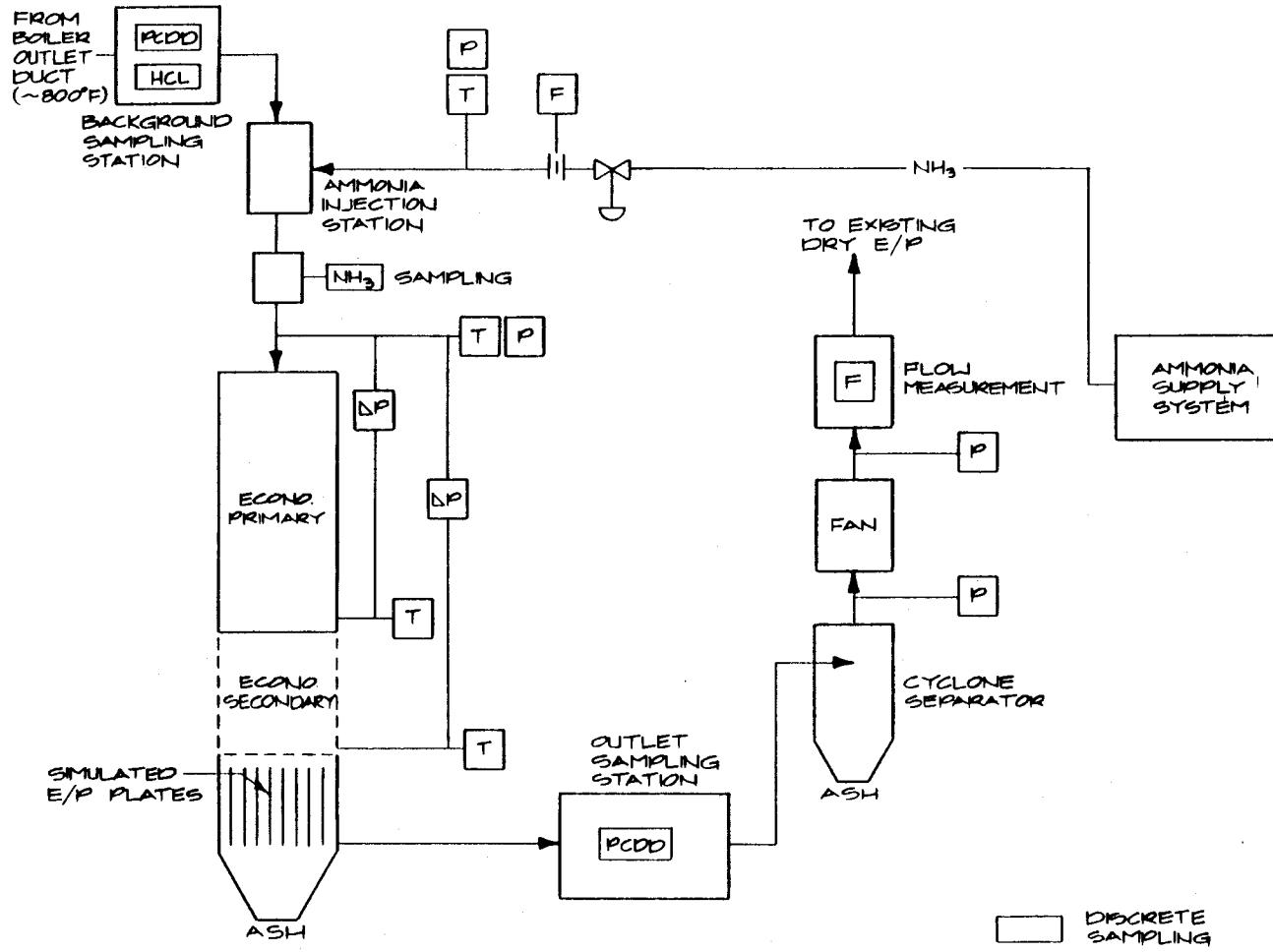


Figure 5. Phase 1 Pilot-scale Experimental System

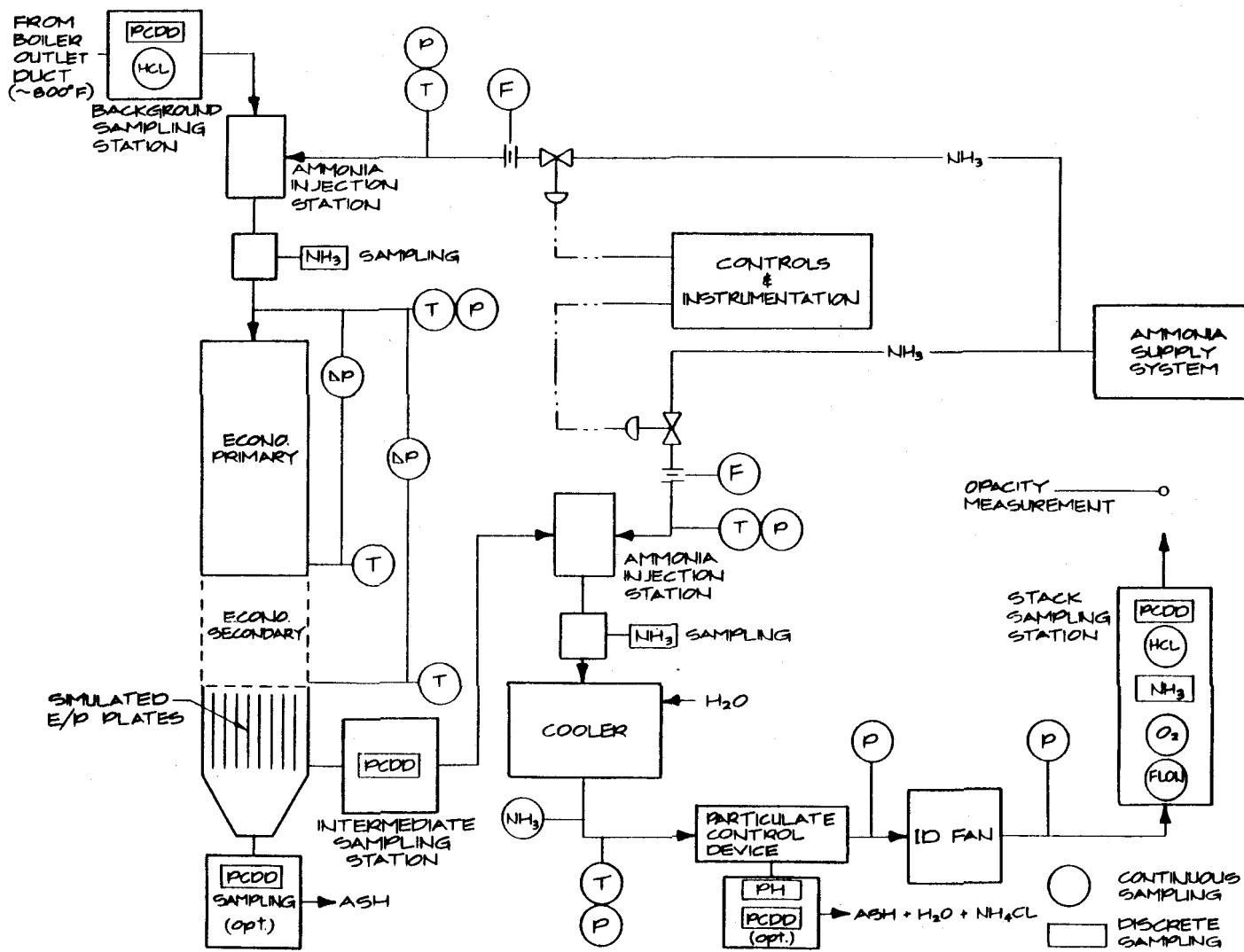


Figure 6. Phase 2 Pilot-scale Experimental System

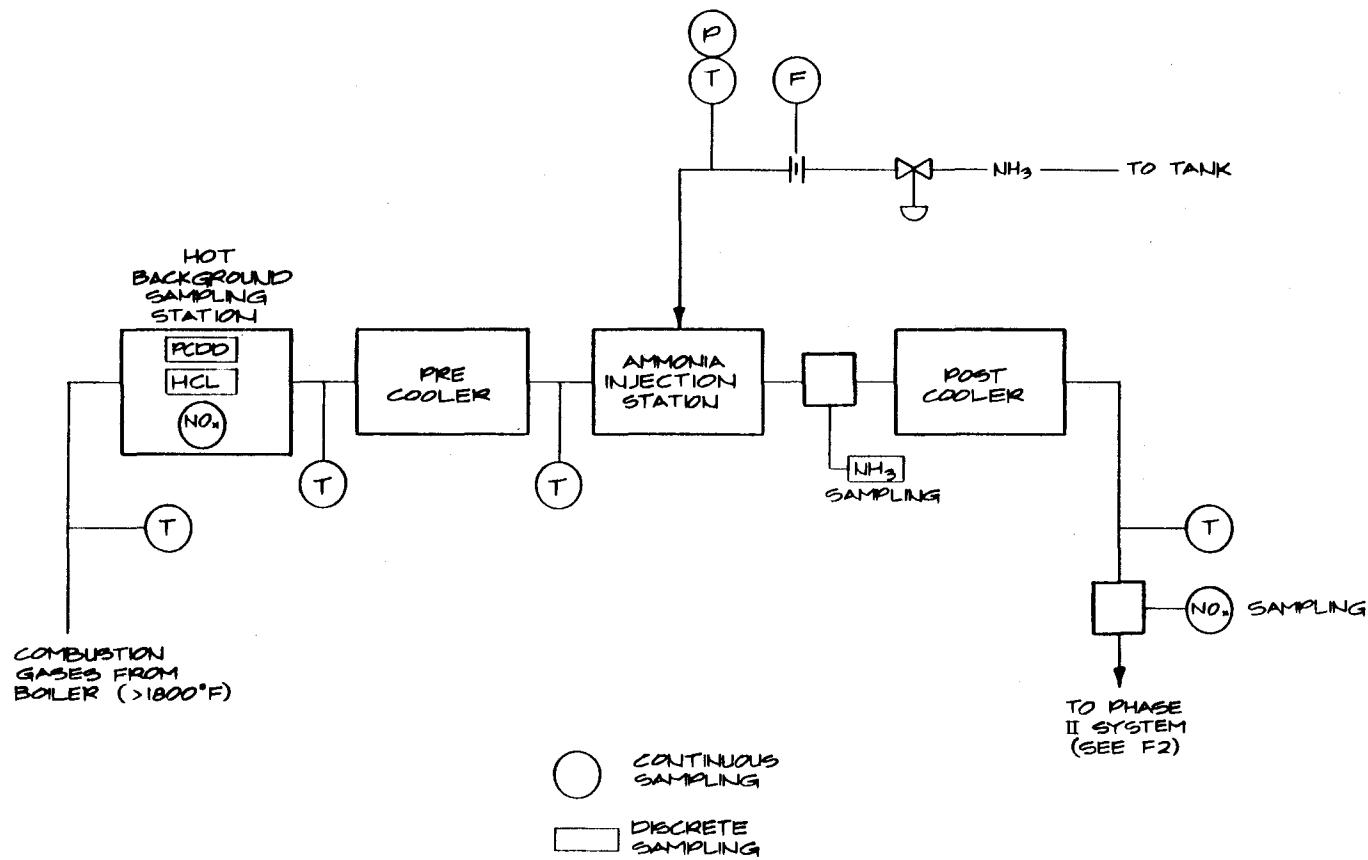


Figure 7. Phase 3 Pilot-scale Experimental System

A NOVEL CALCIUM-BASED SORBENT FOR THE REMOVAL OF FLUE GAS HCl
BY DRY INJECTION

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ABSTRACT

A novel calcium-based sorbent for HCl control in municipal waste combustor flue gas was produced by slurring waste bottle glass with Ca(OH)₂. The reactivity of the sorbent with HCl was measured in a fixed bed reactor simulating conditions for dry sorbent injection at economizer temperatures (~500 °C, 1,000 ppm HCl, and 3 s contact time). The novel sorbent has achieved reactivity levels over three times that of its base Ca(OH)₂ under similar conditions.

The sorbent is produced by slurring crushed waste bottle glass with Ca(OH)₂ at elevated temperatures for extended periods of time. The glass-to-Ca(OH)₂ weight ratio (GCWR) was varied from 1:1 to 4:1, slurring temperature from 25 to 90 °C, and slurring time from 0.25 to 5 h. The median particle size of glass used for the production of sorbent varied from 1.3 to 84.5 µm. The dried sorbent had a surface area up to 119 m²/g, depending on the GCWR, the slurring conditions, and the size of substrate glass particles. X-ray diffraction analyses of the sorbent revealed the formation of calcium silicate hydrate.

The reactivity of selected glass/Ca(OH)₂ sorbents was tested from 200 to 700 °C in the fixed bed reactor. Based on findings from the current program, some implications for large-scale process configurations for HCl/SO₂ control are discussed.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication. Reference in this paper to any specific commercial product is to facilitate understanding and does not imply endorsement or favoring by the U.S. Environmental Protection Agency.

For presentation at the Second International Conference on Municipal Waste Combustion, Tampa, FL,
April 16-19, 1991.

INTRODUCTION

Municipal solid waste (MSW) incineration produces numerous pollutants in the form of particulate matter, gases [hydrogen chloride (HCl), hydrogen fluoride (HF), sulfur dioxide (SO_2)], volatile organic compounds (VOCs), and heavy metals. Wet, semi-dry, and dry processes are considered for the removal of acid gases from MSW incineration. Dry sorbent injection offers the possibility of a technically simple and low cost alternative. Typically, the dry calcium-based sorbent is injected into the incinerator, economizer, or downstream flue gas duct (1,2) regions where it reacts with hot combustion, post-combustion, or cooled post-combustion gases, respectively. In the process of dry sorbent injection into the duct, the flue gas is humidified to a close approach to adiabatic saturation, either upstream or downstream of the sorbent injection point. Humidification can significantly increase reactivity of a dry sorbent with SO_2 (3). However, in the presence of HCl, drying difficulties may be encountered due to the strong water retaining properties of absorbed HCl and calcium chloride (CaCl_2) (4). These wet solids, with a decreased rate of drying, can cause wet wall deposits and operational problems with the particulate control device. To decrease the likelihood of the above adverse effects of CaCl_2 , the approach to adiabatic saturation is often widened (5), decreasing the reactivity of the sorbent with SO_2 .

Two contradicting trends described above (minimized approach to saturation for SO_2 removal and maximized approach to saturation for system reliability) indicate the need for a very reactive sorbent for simultaneous control of HCl and SO_2 from MSW incinerators.

This paper describes the bench scale development and testing under economizer conditions of such a novel, calcium-based sorbent for HCl removal. Based on findings from the current program and previous experience (3), some implications for the control of HCl/ SO_2 from MSW incinerators are discussed.

EXPERIMENTAL

REACTOR

Sorbent reactivity tests with HCl were run in a fixed bed, short time reactor (STR) presented in Figure 1. In this reactor, sorbent dispersed on a quartz wool bed is rapidly moved into the process gas stream and then extracted after a preset exposure time. To activate the sample bed holder, the start button is pushed, which simultaneously activates the air cylinder and starts the timer. This results in positioning the sample bed holder under the reactive process gas. The flow of gas in the air cylinder is reversed which drives the bed holder out from under the reactive process gas after the preset time expires. The sample is loaded into the STR via the sample loading port in the slider assembly and dispersed into a thin layer of quartz wool. Process gas, preheated to the desired temperature, enters the slider assembly via the process gas inlet and, after contacting the sorbent dispersed on the quartz wool, exits to the hood through the process gas outlet. A more detailed description of the reactor is given elsewhere (6).

The STR was operated at temperatures ranging from 200 to 700 °C, and most often at 500 °C. The residence time of the sorbent in the process gas stream was 3 s. The volumetric gas flow rate was 22 L/min (at standard temperature and pressure). The composition of the process gas was 5 volume percent oxygen (O_2), 1,000 ppm HCl, and the balance nitrogen (N_2). The concentration of HCl was measured with a Thermolectron HCl analyzer.

SORBENTS

Calcium Hydroxide

Reagent grade calcium hydroxide [Ca(OH)₂] from Fisher (Fisher C-97) was selected as a baseline sorbent. It was determined by a thermogravimetric analyzer (TGA) to be 93 percent Ca(OH)₂ (the remaining 7 percent was surface water, calcium carbonate, and impurities). Three other commercially available Ca(OH)₂ sorbents were used: Limwood, Marblehead, and Tenn-Luttrell. Structural properties of commercial Ca(OH)₂ and reagent grade Ca(OH)₂ are given in Table 1.

Glass/Ca(OH)₂

Novel sorbents were produced during the course of this work with the intended application for HCl removal from a simulated MSW incinerator flue gas. These novel sorbents were produced by slurring crushed waste glass with reagent grade Ca(OH)₂. Previously (7), sorbents that were several times as reactive with SO₂ under duct injection conditions as reagent grade Ca(OH)₂ were produced by slurring fly ash from coal-fired power plants with Ca(OH)₂. The increased reactivity of these sorbents was attributed to dramatically increased surface area and moisture carrying capabilities. Both properties were developed following a reaction between silica digested from fly ash and calcium. In the course of this reaction, amorphous, hydrated calcium silicates were formed. Crushed waste glass of a clear grade was used as a source of silica (as opposed to colored grade glass). The glass-to-Ca(OH)₂ weight ratio (GCWR) was varied from 1:1 to 4:1. Slurrying time varied from 0.25 to 5 h and slurrying temperatures from 25 to 90 °C. The water-to-solids ratio during slurring was 15:1, which corresponded to an approximately 6 percent solids slurry. Following slurring, solids were vacuum filtered and microwave dried for 6 min to rapidly stop the reaction between the silica and calcium.

Waste glass was crushed to a desired fineness using a bench scale attritor from Union Process. By varying the intensity and time of crushing, glass substrate of divergent structural properties was produced. The properties of ground glass are given in Table 2. As can be seen from Table 2, both surface area and pore volume of crushed glass substrate increased as median particle size decreased. Ground glass substrate, with a nominal particle size of 2 µm, is shown in a scanning electron microscope (SEM) photomicrograph in Figure 2. Irregularly shaped particles with smooth surfaces can be observed.

Analytical Techniques

Sorbents produced for this study were characterized rather extensively using a variety of analytical techniques. Specific surface area, pore volume, and median pore size were determined by N₂ adsorption/desorption (Micromeritics ASAP 2400). The amount of Ca(OH)₂ in a sorbent sample was detected by TGA (Perkin Elmer TGA7) and defined based on the TGA weight loss between 375 and 545 °C for a heating rate of 10 °C/min. Median particle size measurement was based on x-ray sedimentation (Micromeritics Sedigraph). Qualitative assessment of phases produced as a result of slurring of crushed glass and Ca(OH)₂ was done by x-ray diffraction (Siemens D-500). Spectra were identified by computer comparative analysis with the Joint Committee for Powder Diffraction Spectra (JCPDS) spectral file. The morphology of samples was characterized by SEM (Amray SEM). Conversion following the exposure of solids to HCl was determined by Ca⁺⁺ analysis by atomic absorption spectrophotometry (Perkin Elmer AA) and Cl⁻ analysis by ion chromatography (Dionex IC). Conversion percentage is described here as a ratio of half the number of Cl⁻ moles to the number of Ca⁺⁺ moles multiplied by 100.

RESULTS

SORBENT STRUCTURE DEVELOPMENT

Time/Temperature of Sorbent Preparation

Crushed glass substrate with a nominal median particle size of 2 μm was used during this part of the work. The combined effect of slurring time/temperature on the development of sorbent structure was investigated first at a GCWR of 3:1. Slurring time was varied from 0.25 to 5 h and temperatures tested were 25, 60, and 90 °C. The results are shown in Figures 3 and 4 giving surface areas and pore volumes, respectively. Both surface area and pore volume of the sorbent increased with longer slurring time. The rate of increase was higher for higher temperatures. For any given slurring time, the surface area and pore volume increased with increasing temperature. Only limited structural enhancement took place during slurring at 25 °C. Short slurring times of 0.25 and 0.5 h at 90 °C were tested because of the high rate of structural enhancement at this temperature. Following 1 h slurring at 90 °C, the sorbent developed 33 m^2/g surface area. It took 5 h slurring at 60 °C for sorbent to develop 32 m^2/g surface area.

GCWR

In the next series of experiments, the effect of varying GCWR on the development of structure was tested. The results for GCWR from 1:1 to 4:1 are given in Figures 5 and 6 for surface area and pore volume, respectively. Slurring conditions of 90 °C for 1 h and of 90 °C for 5 h were selected to represent what was thought to be an early and an advanced sorbent development stage, respectively. For 90 °C, 1 h slurring conditions, the surface area and pore volume developed by the sorbent were practically independent of the GCWR used for its production. Following 90 °C, 5 h slurring conditions, surface area and pore volume decreased somewhat as the GCWR increased. This is contrary to trends observed earlier (8,9) for slurring fly ash from coal-fired power plants with Ca(OH)_2 , when the sorbent's surface area increased with increasing fly-ash-to- Ca(OH)_2 weight ratio. However, glass—due to its amorphous structure—would be expected to dissolve considerably higher amounts of silica per unit of mass than was the case with fly ash. As a result of this overly increased supply, the excess silica may blind the reactive surface of calcium silicates and/or result in formation of calcium-lean calcium silicates. Calcium-lean calcium silicates would be expected to be less reactive than calcium-rich samples (10). It is not clear at this point why the structural development was independent of GCWS at the 90 °C, 1 h conditions tested. Perhaps the supply of dissolved silica was too low for the extensive formation of calcium silicates following slurring at 90 °C for 1 h.

Glass Fineness

Following the above structure development tests, testing of crushed glass substrates of varying degrees of fineness was done. The nominal sizes produced varied from 1 to 100 μm . Properties of sorbents produced by slurring these substrates at GCWR of 1:1 at 90 °C for 1 h are shown in Figures 7 and 8, giving surface area and pore volume, respectively. Both surface area and pore volume of sorbents increased with increasing fineness (decreasing median particle size) of glass substrate used to produce them. A surface area as high as 119 m^2/g was developed following slurring of 1 μm (nominal) glass substrate. Structural properties of all glass/ Ca(OH)_2 sorbents produced are given in Table 3.

CONVERSION

Ca(OH)₂ Source

Conversion of sorbents with HCl was measured in the STR operated at 500 °C (occasionally from 200 to 700 °C) with a 3 s residence time. The concentration of HCl was 1,000 ppm during all tests. Conversion of reagent grade Ca(OH)₂ and of Ca(OH)₂ from three commercial sources was measured first and it was approximately 14 percent, regardless of Ca(OH)₂ source. The initial glass/Ca(OH)₂ sorbent produced at a GCWR of 3:1, and slurried at 90 °C for 3 h reached a conversion of 39 percent. Lowering the slurring temperature to 25 °C and slurring glass and Ca(OH)₂ at the GCWR rate of 3:1 for 3 h produced sorbent which yielded 33 percent conversion when exposed to HCl. This comparison is shown in Figure 9 and clearly demonstrates superior conversion levels achieved by glass/Ca(OH)₂ sorbents, compared with Ca(OH)₂.

Time/Temperature of Sorbent Preparation

Following the above initial experiments, the combined effect of slurring time/temperature on sorbent conversion with HCl was investigated. Crushed glass substrate of nominal size 2 μm was used and the GCWR was set at 3:1. Three slurring temperatures were tested and the results are shown in Figure 10. The STR conditions were 500 °C, 1,000 ppm HCl, and 3 s residence time. There was no significant effect of slurring time on conversion with HCl for 25 °C slurring temperature. Conversion of sorbents prepared at 90 °C decreased sharply with increases in the slurring time, whereas conversion of sorbents prepared at 60 °C initially increased slightly (1 to 3 h) and then decreased with longer slurring time (3 to 5 h).

GCWR

Conversion of sorbents prepared by slurring crushed glass substrate with Ca(OH)₂ at GCWR ranging from 1:1 to 4:1 is shown in Figure 11. The STR conditions were 500 °C, 1,000 ppm HCl, and 3 s residence time. There was no significant effect of GCWR (except for GCWR of 3:1; it is not clear what caused this apparent anomaly) on the conversion of sorbents slurried at 90 °C for 5 h. Conversion of sorbents slurried at 90 °C for 1 h was increased with increasing GCWR from 1:1 to 3:1. No increase of conversion was measured following the increase of GCWR from 3:1 to 4:1.

GLASS/Ca(OH)₂ INJECTION PROCESS

Experimental results suggest the potential application of the glass/Ca(OH)₂ sorbent in a sorbent injection into the furnace or, more likely, into the economizer region where a large fraction of HCl would be removed from the flue gas. Since the preferred reaction temperature would allow HCl capture well upstream of the particulate collector, this should allow a number of options to be explored, including operation of the particulate collector at lower temperatures for better SO₂, metals, and VOC capture.

The results of preliminary tests investigating the temperature window for glass/Ca(OH)₂ sorbent injection are shown in Figure 12. Sorbent produced by slurring crushed waste glass with Ca(OH)₂ at GCWR of 3:1 and at 90 °C for 1 h was used. The conditions in the STR were 1000 ppm HCl and 3 s residence time. Temperature was varied from 200 to 700 °C. Based on results presented in Figure 12, the recommended reaction temperature would be approximately 500 °C. Due to the STR temperature limitations, the actual quenched temperature regime in an MSW incinerator has not been tested. However, based on data in Figure 12, the conversion would decrease dramatically for reaction temperatures significantly higher than 500 °C. This suggests that sorbent injection in a quenched

system at temperatures in excess of 500 °C, but below the melting point of the probable CaCl₂ product (782 °C), would be optimum. It appears, therefore, that the economizer would be a desired location for the injection.

To facilitate operation of the particle control device, coarse solids should be used during the primary injection. However, the reactivity of sorbents is known to decrease with increasing particle size. To test the effect of sorbent particle size (sorbent particle size was approximated here by crushed glass nominal size), glass was crushed to varying degrees of fineness. The nominal median particle size was varied from 1 to 100 µm and complete structural data were given in Table 2. Crushed glass was slurried with Ca(OH)₂ at a GCWR of 1:1 at 90 °C for 1 h. Dried sorbents were exposed to HCl in the STR operated at 500 °C, 3 s residence time, and with 1,000 ppm HCl. Results presented in Figure 13 indicate decreasing conversion with increasing particle size of crushed glass substrate. Increasing the nominal particle size of crushed glass substrate from 1 to 100 µm resulted in conversion decreases from 23 to 17 percent. The conversion measured for sorbent produced with glass of a nominal size of 50 µm was 21 percent. While these results are preliminary, they indicate a potential tradeoff between the coarseness of glass substrate used for production of the sorbent and sorbent reactivity. It appears that crushed glass as coarse as 50 or 100 µm could be used for sorbent injection.

DISCUSSION

Glass/Ca(OH)₂ sorbents were produced, their structural properties analyzed, and reactivity tested for the removal of HCl from MSW incinerator flue gas. All glass/Ca(OH)₂ sorbents tested were more reactive (yielded higher conversion) than Ca(OH)₂ alone. When exposed to HCl under conditions representative of those encountered during dry sorbent injection into the economizer (11): 500 °C, 3 s residence time, and 1000 ppm HCl.

Sorbents produced during the course of work described here were characterized by a variety of analytical techniques in order to better understand how structural properties relate to sorbent reactivity with SO₂. Surface area was found not to be a unique indicator of reactivity. For example, comparison of Figures 3 and 10 indicates that, for a sorbent produced at a GCWR of 3:1 by slurring at 25 °C, both conversion and surface area were weakly affected by increasing the slurring time. SEM examination of morphology indicated that particles with two different types of surface features were formed. Figure 14 is an SEM photomicrograph of a glass/Ca(OH)₂ sorbent produced by slurring at 25 °C for 1 h at a GCWR of 3:1. Particles with smooth surfaces typical for glass substrate (see Figure 2) can be seen, indicating the lack of extensive reaction between glass and Ca(OH)₂.

Figure 15 is an SEM photomicrograph of sorbent produced at a GCWR of 3:1, slurried at 90 °C for 1 h. This sorbent had considerably higher surface area than the one slurried at 25 °C (33 versus 15 m²/g, respectively). The microscope field, shown in Figure 15, reveals particles coated with amorphous-looking deposits without clearly defined morphological surface features. Increasing the 90 °C slurring time to 5 h resulted in sorbent with a surface area of 67 m²/g. However, despite the increased surface area, the conversion decreased compared with sorbent prepared by 1 h slurring at 90 °C. As can be seen in Figure 16, sorbent slurried at 90 °C for 5 h had particles coated with deposits. The appearance of these deposits is different from that observed in Figure 15. Small, µm-sized ridges are visible and they may indicate higher crystallinity of sorbent produced at 90 °C, 5 h than that of sorbent produced at 90 °C, 1 h. Previously (12), sorbents with high surface area, but with crystalline morphology, were shown to be less reactive with SO₂ than ones with amorphous morphology.

X-ray diffraction (XRD) studies indicated decreased amounts of $\text{Ca}(\text{OH})_2$ in sorbents that developed increased surface area. Formation of hydrated calcium silicates was detected by XRD (JCPDS File No. 33-306). However, the XRD results are not fully conclusive.

Decreasing amounts of $\text{Ca}(\text{OH})_2$ in samples which developed increased surface area were detected by a TGA method that measures the TGA weight loss corresponding to temperature increases from 375 to 545 °C [the decomposition temperature of $\text{Ca}(\text{OH})_2$]. This weight loss would be 24.3 and 12.15 percent for pure $\text{Ca}(\text{OH})_2$ and glass/ $\text{Ca}(\text{OH})_2$ sorbent prepared at a GCWR of 1:1, respectively. A family of glass/ $\text{Ca}(\text{OH})_2$ sorbents prepared by slurring at 90 °C for 1 h at a GCWR of 1:1, but using glass substrate of varying fineness, was examined and results are shown in Table 4. The amount of $\text{Ca}(\text{OH})_2$ —as detected by TGA—decreased with decreasing particle size of a glass substrate. Sorbent reactivity with HCl increased with decreasing amounts of $\text{Ca}(\text{OH})_2$ in the sample. Also shown in Table 4 are TGA weight losses for the temperature ranges from ambient to 125 °C, 125 to 375 °C, and 375 to 545 °C. The first corresponds to the surface moisture, the second may be attributed to hydrate decomposition, and the third may be attributed to calcium silicate hydrate decomposition (13). Both the amount of surface water and of calcium silicate hydrates increased with decreasing particle size of glass substrate used for the production of a sorbent. Conversion with HCl (Figure 13) could be correlated with TGA weight losses described above. However, it should be emphasized that this correlation was not valid for the whole family of sorbents produced throughout this study. A series of results presented in Table 4 for sorbents produced at a fixed GCWR, the same slurring conditions, yet having dissimilar structural properties and reactivity with HCl, were used here only to demonstrate structure-reactivity trends. It should be pointed out that the glass/ $\text{Ca}(\text{OH})_2$ sorbents used for primary injection (~500 °C) will be subjected to decomposition/sintering in this temperature region. The effect of decomposition on structural properties of glass/ $\text{Ca}(\text{OH})_2$ sorbents is unknown. One of the products of decomposition will be water vapor, which is known to promote sintering (14). Correlations need to be developed between the amount of calcium silicate hydrate produced, its crystallinity, the amount of surface water, the decomposition/sintering properties, and the sorbents' reactivity.

CONCLUSIONS

Novel sorbents produced by slurring crushed waste glass with $\text{Ca}(\text{OH})_2$ were demonstrated to be up to three times as reactive with HCl as $\text{Ca}(\text{OH})_2$ under conditions typical for economizer injection of dry sorbent for the control of HCl from MSW incineration. The structure and reactivity of sorbents varied with slurring conditions (GCWR, temperature, time). The amount of $\text{Ca}(\text{OH})_2$ detected by TGA in prepared sorbents was lower than theoretically expected and SEM examination indicated changes of sorbent morphology as a result of slurring.

A novel process was described for the removal of MSW incinerator HCl with glass/ $\text{Ca}(\text{OH})_2$ sorbents. Laboratory tests indicated approximately 500 °C as a preferred reaction temperature and potential for use of coarse (50-100 μm) glass substrate for the production of the sorbent.

ACKNOWLEDGEMENTS

The authors wish to recognize the assistance of Frank E. Briden and George R. Gillis of the U.S. Environmental Protection Agency and Monsie M. Gillis and Wojciech Kozlowski of Acurex Corporation. This work was supported by the U.S. Environmental Protection Agency's Air and Energy Engineering Research Laboratory (EPA Contract 68-DO-0141) located in Research Triangle Park, NC, USA.

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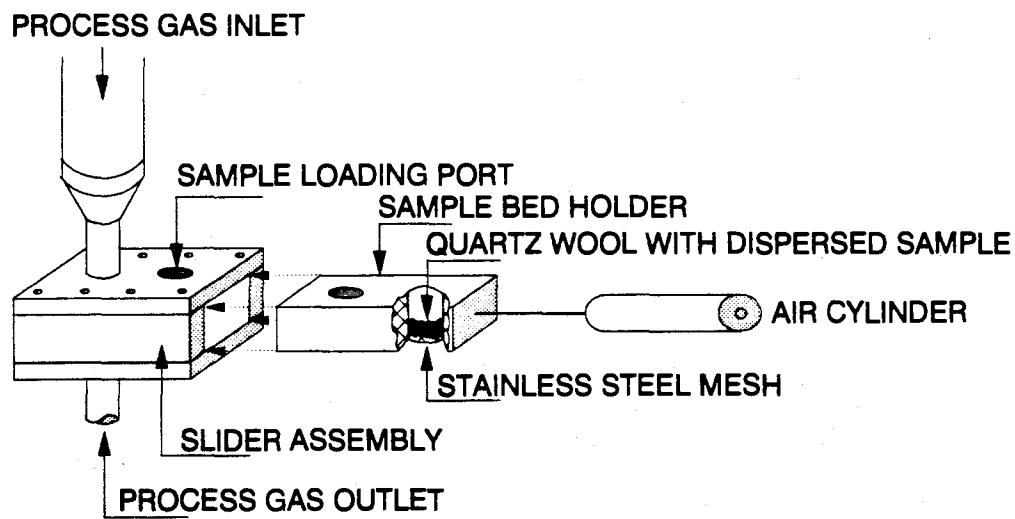


Figure 1. Schematic and cutaway of the short time reactor (STR).



Figure 2. SEM photomicrograph of a crushed glass substrate. Nominal size 2 μm (x5,000).

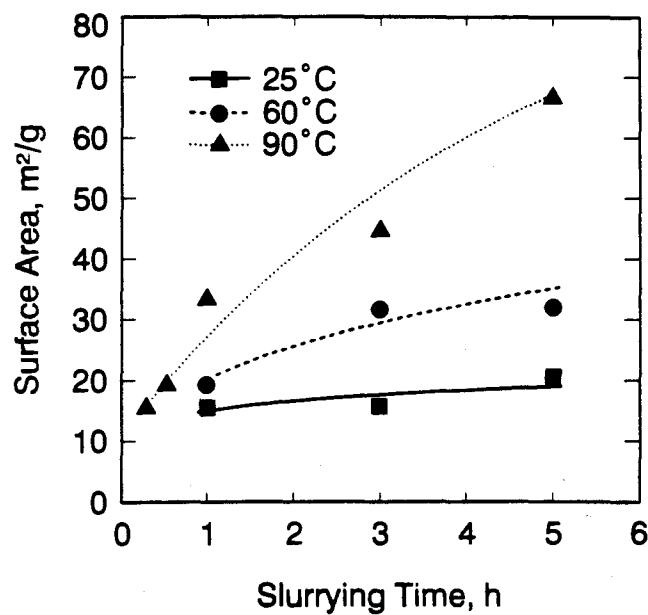


Figure 3. Combined effect of slurring time/temperature on the development of surface area by glass/Ca(OH)₂ sorbents (GCWR=3:1, nominal glass size 2 μm).

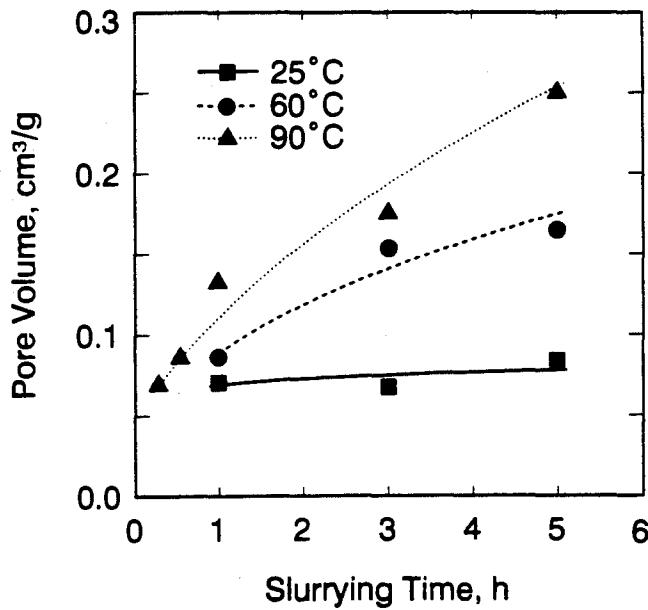


Figure 4. Combined effect of slurring time/temperature on the development of pore volume by glass/Ca(OH)₂ sorbents (GCWR=3:1, nominal glass size 2 μm).

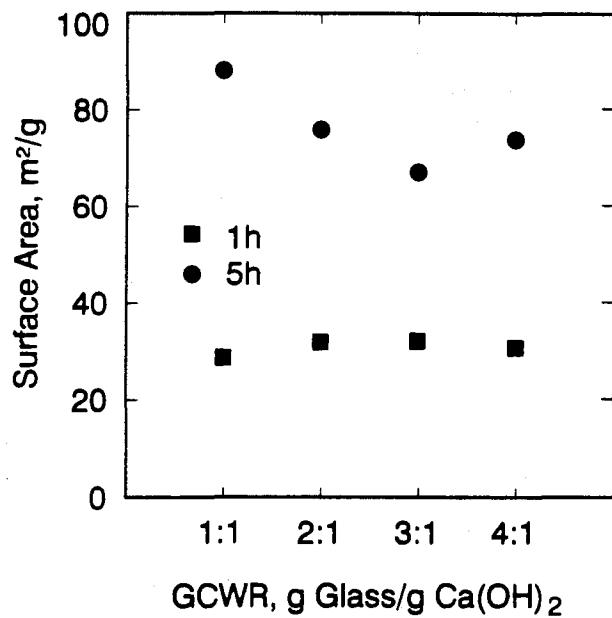


Figure 5. The effect of GCWR and slurring time on the development of surface area by glass/ Ca(OH)_2 sorbents slurried at 90 °C (nominal glass size 2 μm).

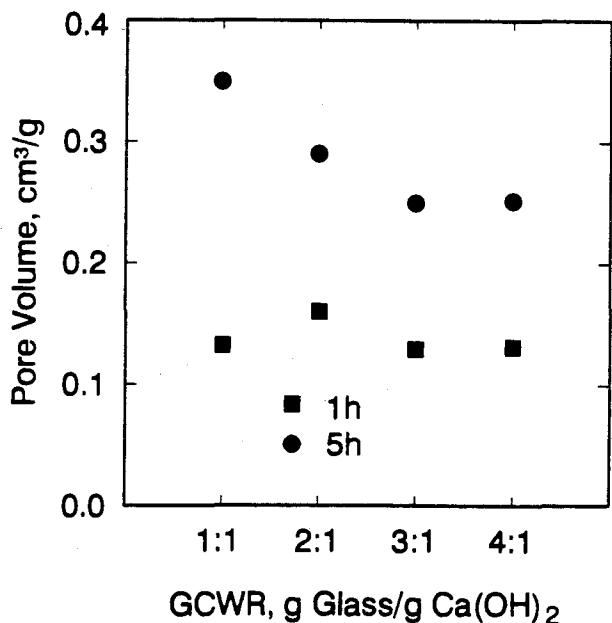


Figure 6. The effect of GCWR and slurring time on the development of pore volume by glass/ Ca(OH)_2 sorbents slurried at 90 °C (nominal glass size 2 μm).

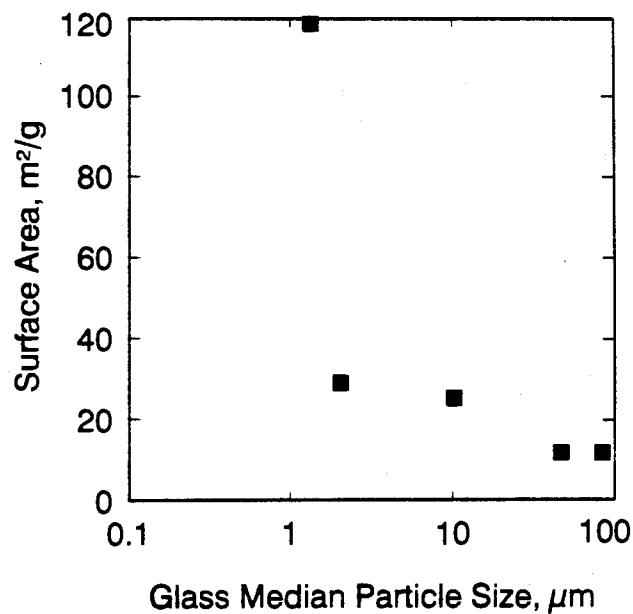


Figure 7. The effect of crushed glass size on the development of surface area by glass/Ca(OH)₂ sorbents (90 °C, 1 h slurring time, GCWR=1:1).

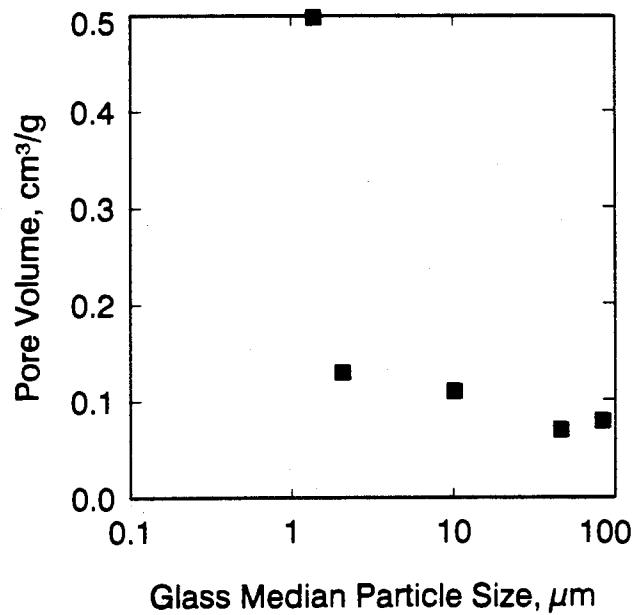


Figure 8. The effect of crushed glass size on the development of pore volume by glass/Ca(OH)₂ sorbents (90 °C, 1 h slurring time, GCWR=1:1).

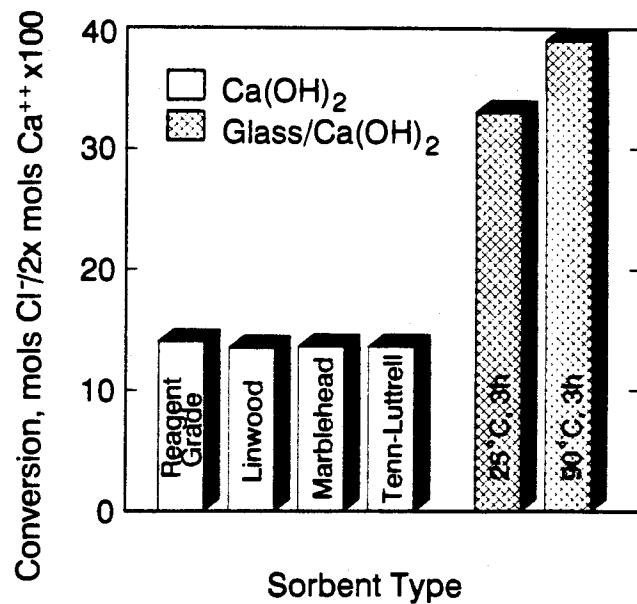


Figure 9. Comparison of STR conversion of $\text{Ca}(\text{OH})_2$ and glass/ $\text{Ca}(\text{OH})_2$ sorbents (500 °C, 1,000 ppm HCl, 3 s).

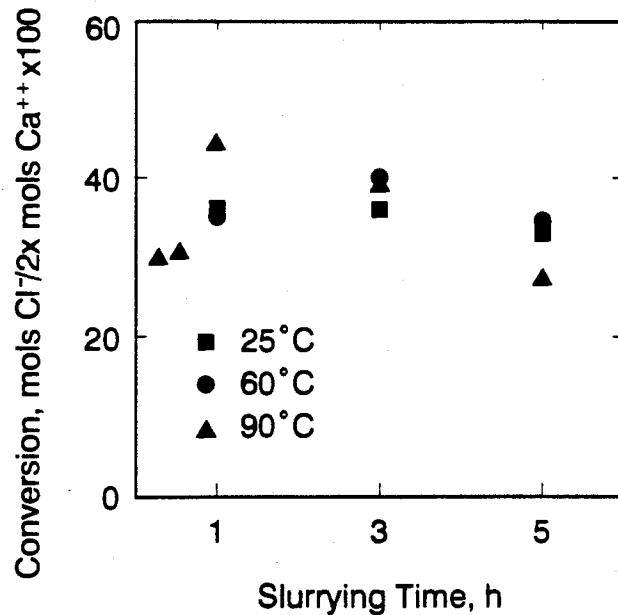


Figure 10. Combined effect of slurring time/temperature on the reactivity of glass/ $\text{Ca}(\text{OH})_2$ sorbents with HCl (sorbents: GCWR=3:1, nominal glass size 2 μm ; reactor: 500 °C, 1000 ppm HCl, 3 s).

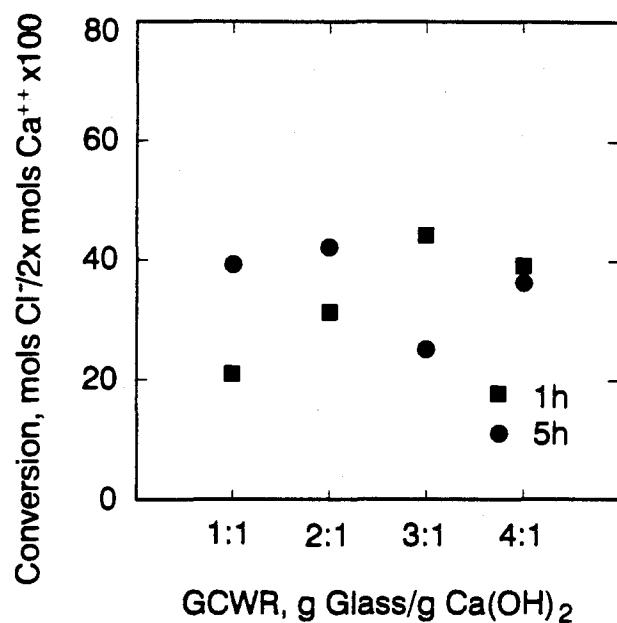


Figure 11. The effect of GCWR on the reactivity of glass/Ca(OH)₂ sorbents with HCl (sorbents: 90 °C, nominal glass size 2 µm; reactor: 500 °C, 1000 ppm HCl, 3 s).

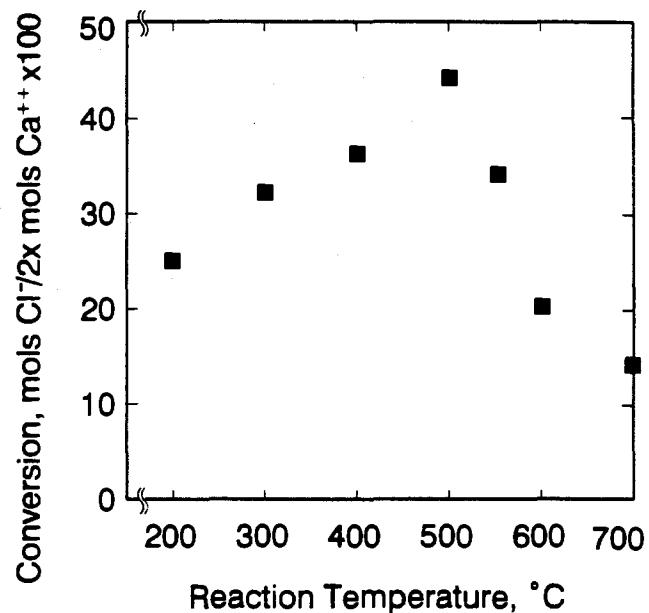


Figure 12. The effect of STR temperature on reactivity of glass/Ca(OH)₂ sorbent (sorbent: 90 °C, 1 h slurring time, GCWR=3:1; reactor: 1000 ppm HCl, 3 s).

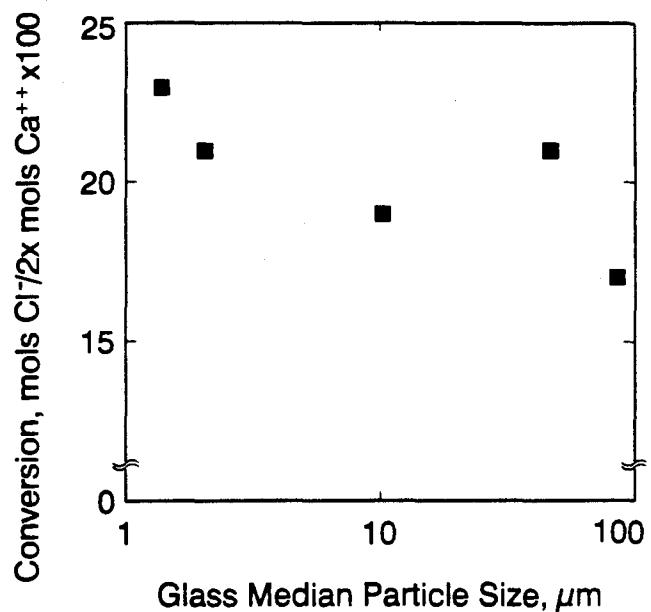


Figure 13. The effect of crushed glass size on sorbent reactivity with HCl (sorbents: 90 °C, 1 h slurring time, GCWR=1:1; reactor: 500 °C, 1000 ppm HCl, 3 s).



Figure 14. SEM photomicrograph of a sorbent prepared by slurring glass/Ca(OH)₂ at GCWR=3:1, 25 °C, 1 h (x 10,000).



Figure 15. SEM photomicrograph of a sorbent prepared by slurring glass/Ca(OH)₂ at GCWR=3:1, 90 °C, 1 h (x 5,000).

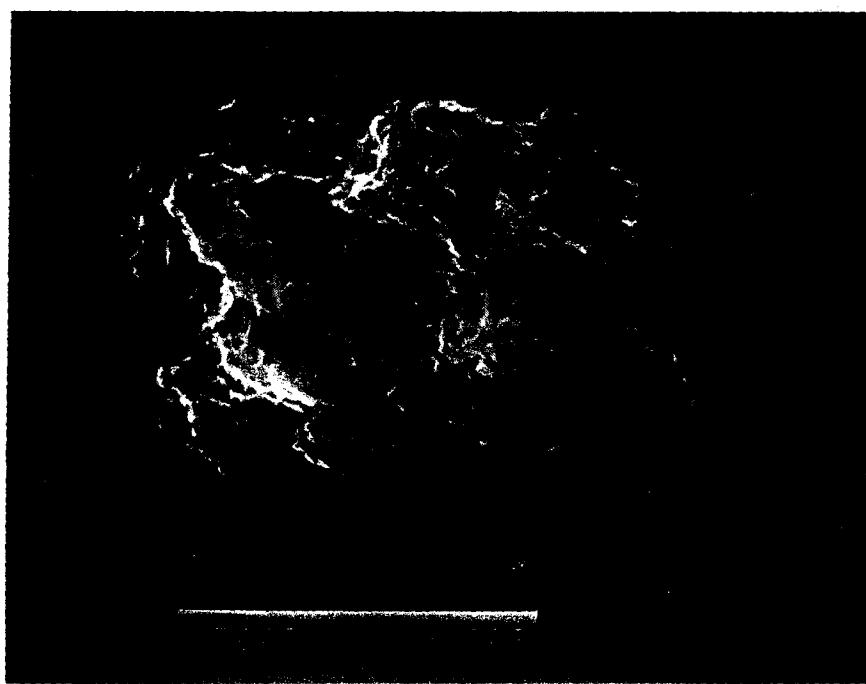


Figure 16. SEM photomicrograph of a sorbent prepared by slurring glass/Ca(OH)₂ at GCWR=3:1, 90 °C, 5 h (x 5,000).

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TABLE 1. STRUCTURAL PROPERTIES OF Ca(OH)₂ SORBENTS

Ca(OH) ₂ Source	Surface Area [m ² /g]	Pore Volume [cm ³ /g]	Median Particle Size [μm] ^a	Ca(OH) ₂ Content [percent] ^b
Reagent Grade	15.4	0.081	5.6	93
Linwood	13.7	0.066	3.5	87
Marblehead	18.6	0.082	4.3	86
Tenn-Luttrell	18.9	0.102	2.6	90

^a by gravity sedimentation

^b by TGA, weight loss between 375 and 545 °C

TABLE 2. STRUCTURAL PROPERTIES OF GROUND GLASS

Nominal Size [μm]	Median Particle Size [μm]	Surface Area [m ² /g]	Pore Volume [cm ³ /g]	Median Pore Size [Å]
1	1.4	25.0	0.104	166
2	2.1	9.8	0.034	138
10	10.3	1.2	0.003	115
50	47.7	0.5	0.001	107
100	84.6	0.3	0.001	136

TABLE 3. STRUCTURAL PROPERTIES OF GLASS/Ca(OH)₂ SORBENTS
 (Clear Glass and Reagent Grade Ca(OH)₂, 6 Percent Solids Slurry)

Glass Nominal Size [μm]	GCWR [g Glass/g Ca(OH) ₂]	Slurrying Time [h]	Temperature [°C]	Surface Area [m ² /g]	Pore Volume [cm ³ /g]
2	3:1	1	25	15	0.071
2	3:1	3	25	16	0.068
2	3:1	5	25	20	0.083
2	3:1	1	60	19	0.086
2	3:1	3	60	31	0.150
2	3:1	5	60	32	0.165
2	3:1	1	90	33	0.130
2	3:1	3	90	45	0.175
2	3:1	5	90	67	0.249
2	1:1	1	90	30	0.126
2	2:1	1	90	32	0.159
2	4:1	1	90	29	0.132
2	1:1	5	90	74	0.247
2	2:1	5	90	76	0.290
2	4:1	5	90	88	0.350
2	3:1	0.25	90	16	0.069
2	3:1	0.5	90	19	0.086
1	1:1	1	90	119	0.505
10	1:1	1	90	25	0.114
50	1:1	1	90	12	0.066
100	1:1	1	90	12	0.076
1	1:1	5	90	102	0.448
10	1:1	5	90	40	0.179
50	1:1	5	90	34	0.124
100	1:1	5	90	20	0.088

TABLE 4. CHARACTERIZATION OF A SERIES OF GLASS/Ca(OH)₂ SORBENTS
 (All Slurried at GCWR=1:1, 90 °C, 1 h)

Glass Nominal Size [μm]	TGA Weight Loss [percent] ^a			Conversion with HCl ^b [percent]
	ambient-125 °C	125-375 °C	375-545 °C	
1	4.31	5.27	7.47	23
2	1.85	2.19	8.60	21
10	0.71	1.11	9.35	19
50	0.44	0.64	10.32	21
100	0.43	0.50	10.28	17

^a10 °C/min heating rate

^bIn STR, 500 °C, 3 s, 1000 ppm HCl (see also Figure 13)

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

RESULTS OF FULL SCALE DRY INJECTION TESTS AT MSW INCINERATORS USING A NEW ACTIVE ABSORBENT

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ABSTRACT

Worldwide incineration of municipal solid waste (MSW) has been utilized to reduce the volume of waste to be disposed of. Increasing environmental concerns over the potential air pollution impacts have led to emission limits for pollutants such as HCl, SO₂, particulate, and more recently also for mercury and dioxins. For a certain size of incinerators, dry sorbent injection is the preferred technology for air pollution control.

This paper describes the development of a new active sorbent, Scansorb, which is particularly suited for use in dry injection processes. The new sorbent is a lime based product with adjustable properties. Scansorb can be produced with a specific surface area of 30 to 100 m²/g.

Pilot plant development work has shown that a considerable reduction in the absorbent quantity can be achieved when Scansorb is used instead of commercial hydrated lime. Full scale tests performed at four different MSW incinerators have confirmed the viability of the new active absorbent. The full scale tests have demonstrated that more than 50% SO₂ removal can be achieved with Scansorb at quantities much less than with commercial hydrated lime.

The potential savings in absorbent and disposal costs might be a major incentive for MSW operators to use Scansorb for air pollution control.

INTRODUCTION

For many years, incineration of municipal solid waste (MSW) has been utilized in Europe to reduce the volume of waste to be disposed of, while at the same time producing energy for district heating or in some instances electricity. In the 1960's, concerns were raised over the potential air pollution impacts from MSW incineration. Hence, emission limits were promulgated for pollutants such as HCl and particulate emission.

In the last two decades, technology has been developed to control HCl and other pollutants as the emission regulations became more and more stringent. These technologies include wet scrubbers, spray dryer absorbers, and dry sorbent injection. Based on state-of-the-art scrubbing technology, the European Economic Community (EEC) has promulgated emission requirements for MSW plants in Europe (Table 1). Emission limitations are set for particulate, HCl, SO₂, as well as trace metals.

Competition among European countries has led to more and more stringent emission requirements (Table 2). Pollutants such as SO₂, NOx, mercury, and dioxins are now being regulated (1). As a result of the strict competition for more stringent emission limits, the costs of cleaning up the flue gases from MSW incinerators are sky rocketing.

In the U.S. new standards have been proposed (2) which regulate the HCl and SO₂ emission from new and existing facilities according to size (Table 3). Spray dryer absorption is recommended for most stringent requirement (95% HCl reduction, and 85% SO₂ reduction), whereas, dry sorbent injection is recommended for the less stringent requirement (80% HCl, and 50% SO₂).

SCANSORB - A NEW ACTIVE ABSORBENT

In the early eighties, Niro Atomizer developed and patented a lime based dry active sorbent for use in dry injection processes. However, it was not until later that the industry showed interest for dry injection processes.

Niro Atomizer continued the development of lime based dry sorbents with the purpose to:

1. Save Capital Investment
2. Save Operating and Disposal Costs

The basic idea was to develop dry active absorbents with such a high reactivity, that the required HCl and SO₂ removal could be achieved by a simple dry injection into the duct work ahead of the existing electrostatic

TABLE 1. EMISSION LIMITS (MG/NM³) FOR MSW INCINERATORS ACCORDING TO EEC DIRECTIVE (JUNE 1990)

	MSW Capacity < 72 TPD > 72 TPD	
Particulate	100	30
HCl	100	50
SO ₂	300	300
Cd + Hg	0.2	0.2
Ni + As	0.5	0.5
Pb + Cr + Cu + Mn	5	5

TABLE 2. EMISSION LIMITS (MG/NM³) FROM EUROPEAN MSW INCINERATORS (NOVEMBER, 1990)

	Austria	Germany	Holland	Italy	Switzerland	Sweden
Particulate	15	10	5	30	50	50
HCl	10	10	10	50	30	200
SO ₂	50	50	40	300	500	-
NO _x	100	100	70	-	500	-
Hg	0.05	0.1	0.05	0.1	0.1	0.08
Dioxins - Equivalents (ng/Nm ³)	0.1	0.1	0.1	-	-	0.1

Note: TPD denotes Tons of waste per day.

TABLE 3. PROPOSED EMISSION STANDARD FOR MSW INCINERATORS IN THE U.S.

	New facilities	Existing facilities
HCl Reduction	95% or 25 ppm ^a 80% or 25 ppm ^b	None ^c 50% ^d 95% ^e
SO ₂ Reduction	85% or 30 ppm 50% or 30 ppm	None 50% 85%

a - >250 TPD

b - <250 TPD

c - <250 TPD

d - >250 to 2200 TPD

e - >2200 TPD

]recipitator or baghouse. In this case, capital investment would be minimized to an absorbent receiving silo and some simple injection and distribution equipment. Further, it was the purpose to accomplish this emission reduction with absorbent quantities much less than by using commercial hydrated lime, whereby disposal costs could be reduced. Disposal costs in Europe range from \$20.00 to \$70.00/ton and in the U.S. disposal costs can be as high as \$130.00/ton.

As described in this paper, a new lime based dry active absorbent, called Scansorb, was successfully developed. A production facility for the production of 10,000 ton/yr. of Scansorb has been built in Denmark. This facility which starts production in April 1991, will cover the need for dry sorbent in the northern part of Germany, Denmark, and the southern part of Sweden. The production process is proprietary (patent pending) and cannot be disclosed at this point. However, the product is lime based with certain additives added, which do not impair the waste disposal properties of the product.

RESULTS OF PILOT PLANT DEVELOPMENT

The pilot plant development work showed that, by carefully adjusting the parameters in the production process, Scansorb can be produced with a surface area (BET) ranging from 25 to 120 m^2/g . In the initial development phase, Scansorb products with different surface area were produced and used in dry injection pilot tests to compare their performance.

Not surprisingly an increase in HCl and SO_2 absorption was achieved by increasing specific surface areas. Figure 1 shows the correlation between specific surface area and HCl and SO_2 absorption respectively. The results are from a 1500 Nm^3/h pilot plant, where the Scansorb was injected into the ductwork upstream of a pulse jet fabric filter. The temperature was 170° C and the stoichiometry was approximately 1.2.

The improved performance of the Scansorb products were further demonstrated in pilot plant tests, in which the Scansorb performance was compared with commercial hydrated lime with a surface area of 15 m^2/g . Figure 2 and 3 show the comparable HCl and SO_2 efficiency of Scansorb 100, Scansorb 35, and commercial hydrated lime.

The influence of higher specific surface area on HCl and SO_2 absorption has been verified by other investigators (3).

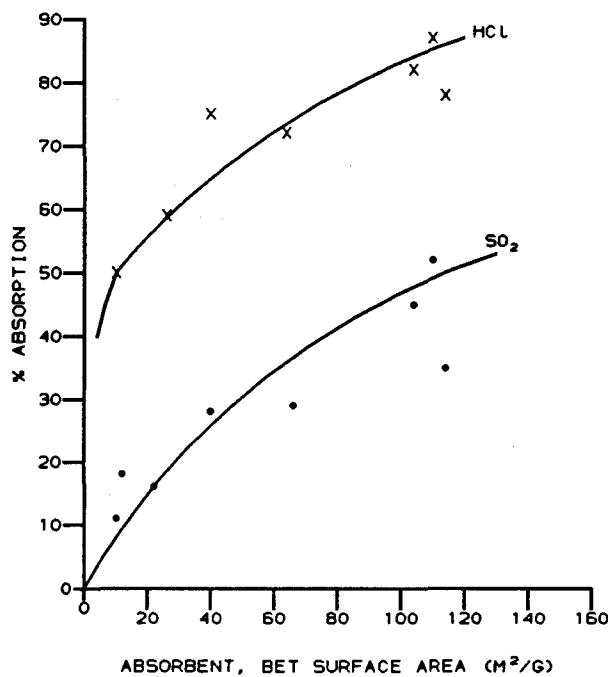
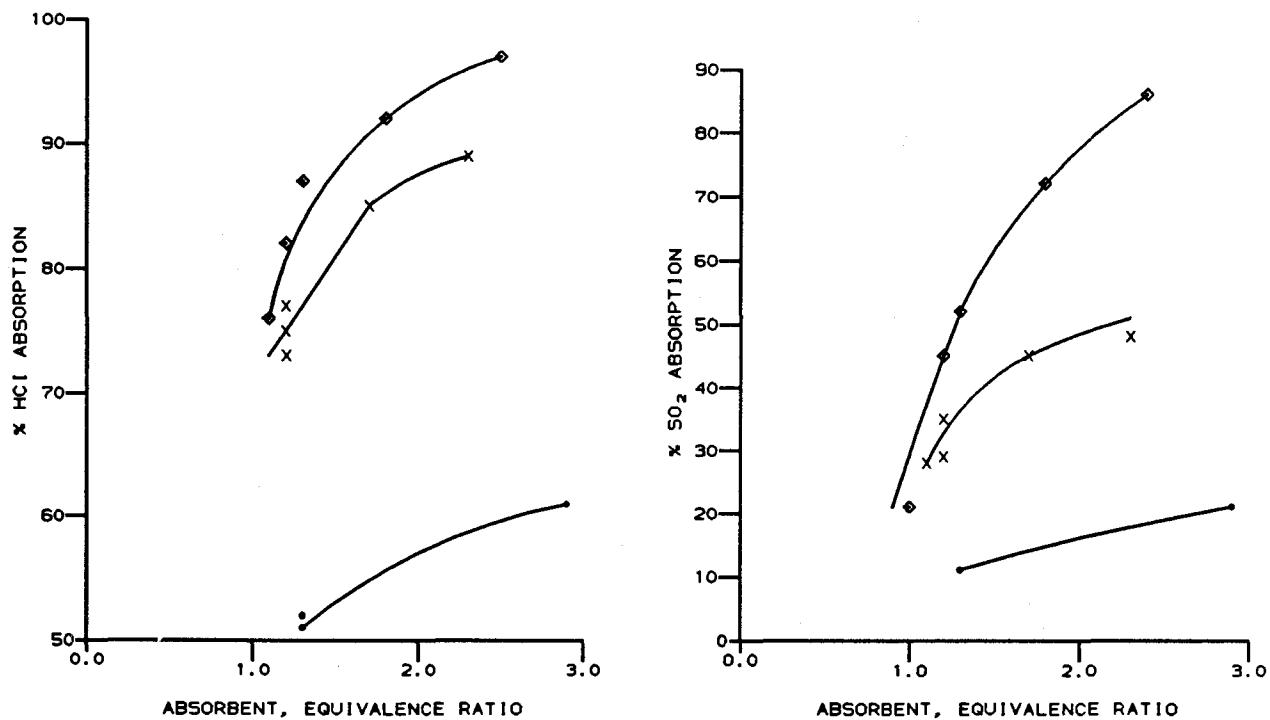


Figure 1. Pilot plant results with Scansorb



• Commercial Hydrated Lime X Scansorb 35 ♦ Scansorb 100 • Commercial Hydrated Lime X Scansorb 35 ♦ Scansorb 100

Figure 2. Pilot plant results with Scansorb and Hydrated Lime Figure 3. Pilot plant results with Scansorb and Hydrated Lime

FULL SCALE TEST RESULTS

DESCRIPTION OF MSW FACILITIES

Full scale dry injection tests with Scansorb were carried out at four different MSW incinerators in Denmark and Sweden. Table 4 indicates the location and capacity of the incinerators. They are all traveling grate incinerators, two of them equipped with electrostatic precipitators as the only air pollution control equipment, one plant has installed a dry injection system consisting of a reactor in combination with an electrostatic precipitator, and the last plant has a reactor followed by a pulse jet fabric filter. The last two installations currently use commercial hydrated lime as absorbent. Figure 4 shows the Sonderborg MSW incinerator equipped with electrostatic precipitators. Figure 5 is a close-up of the ducts into which Scansorb was injected. Figure 6 shows the big bag with Scansorb and the variable speed screw conveyor used for injection of the product. Characteristics of the Scansorb and commercial hydrated lime used is shown in table 5.

A typical test which lasted up to four hours, was carried out as follows. Absorbent injection was started and the absorbent rate was measured by the weight loss of the big bag. HCl, SO₂, O₂, and moisture content, were measured continuously before the injection point and after the filter. Before the tests, the delta-T over a pitot-tube installed in the stack, was correlated with the incinerator flue gas flow. Furthermore, the flue gas temperature and in some cases the stack opacity was continuously monitored. All measurements were continuously fed to a data logging system, which allowed an on-line calculation of removal efficiency and absorbent usage.

The incinerators were burning a typical municipal solid waste. The pollutant concentrations that were experienced during the Scansorb dry injection tests described below are shown in table 6.

TESTS WITH ELECTROSTATIC PRECIPITATOR AS DUST COLLECTOR

The incinerator at Kolding is equipped with a small two field electrostatic precipitator as dust collector. Scansorb and hydrated lime were injected five meters upstream of the ESP giving a maximum reaction time in the duct of 1/2 second. The temperature of the flue gas was in average 190° C and the moisture content of the flue gas was only approximately 10%. Figure 7 and 8 show the achieved HCl and SO₂ removal efficiencies using Scansorb 30, Scansorb 100, and commercial hydrated lime. It can be seen that for a given HCl and SO₂ removal efficiency, a considerable reduction of the quantity of absorbent is achieved when using Scansorb instead of commercial hydrated lime.

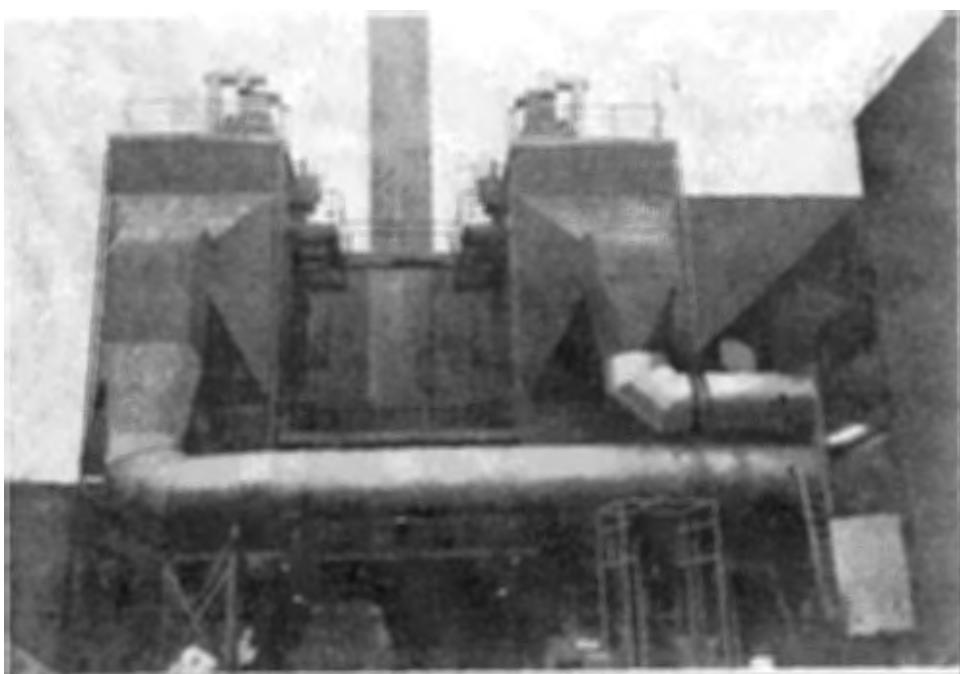


Figure 4. Sonderborg Incinerator

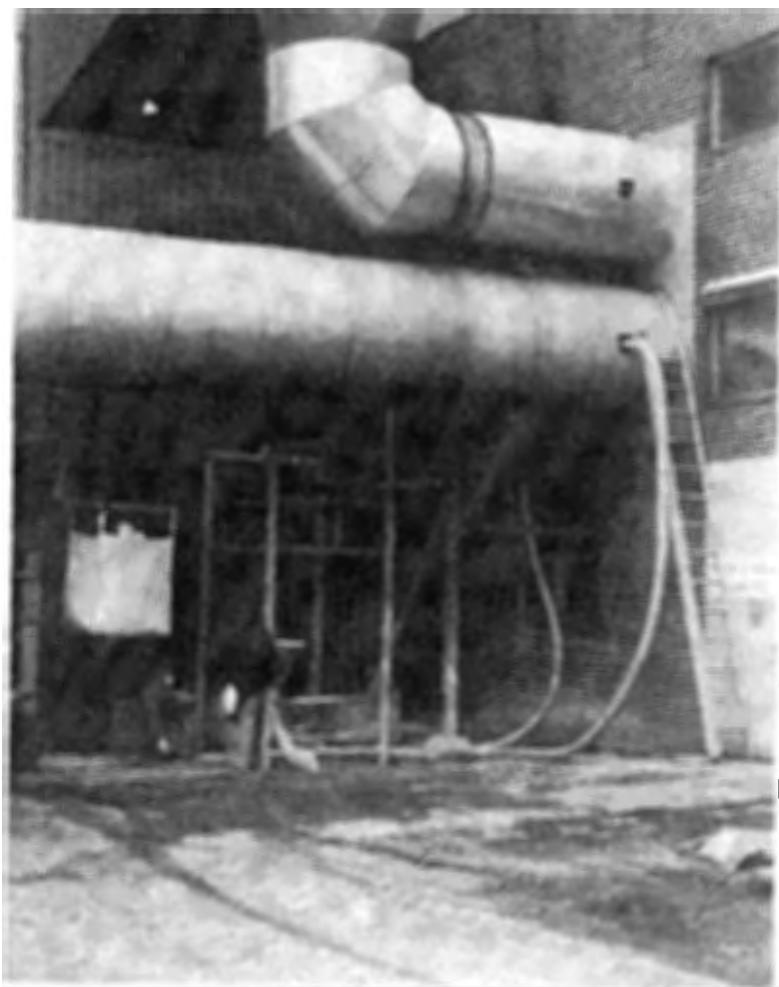


Figure 5. Dry Injection
Set-up

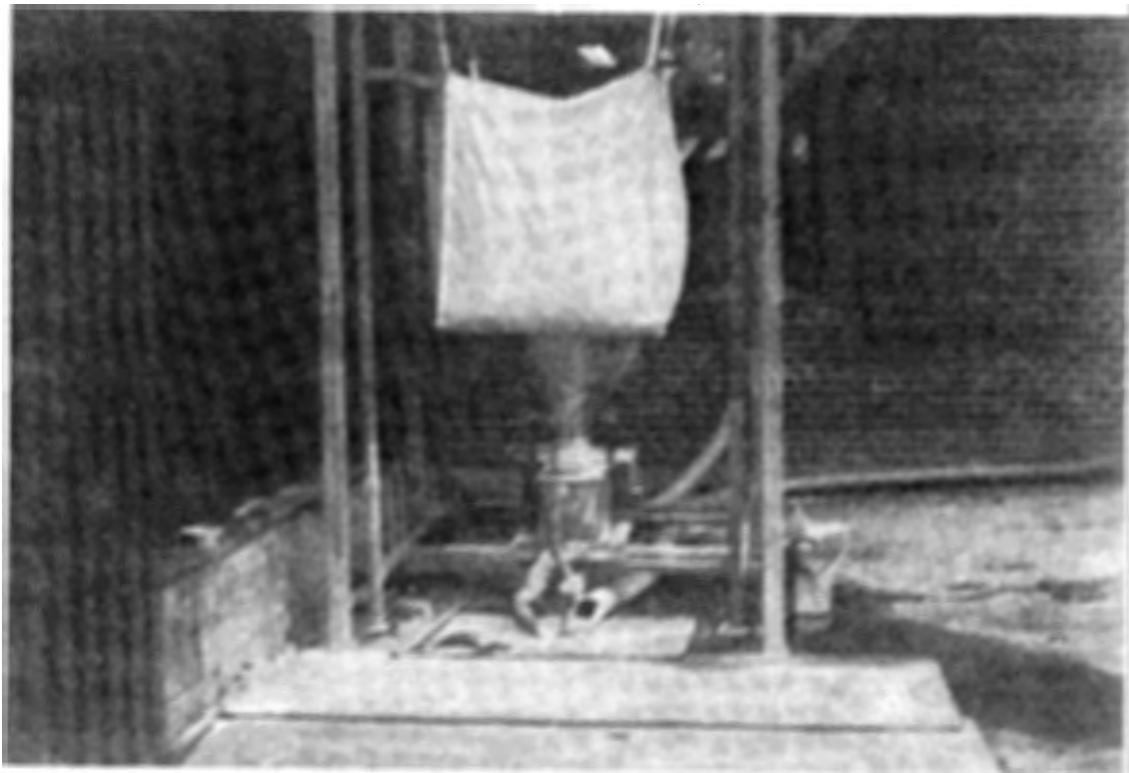


Figure 6. Big bag with Scansorb and screw feeder for absorbent flow control.

TABLE 4. MSW PLANT DATA

Name and plant location	Capacity (TPD)	Air pollution control ^a
Kolding, Denmark	2 x 100	ESP
Sonderborg, Denmark	2 x 120	ESP
Nykobing, Denmark	2 x 100	Reactor + ESP
Sysav, Sweden	2 x 300	Reactor + FF

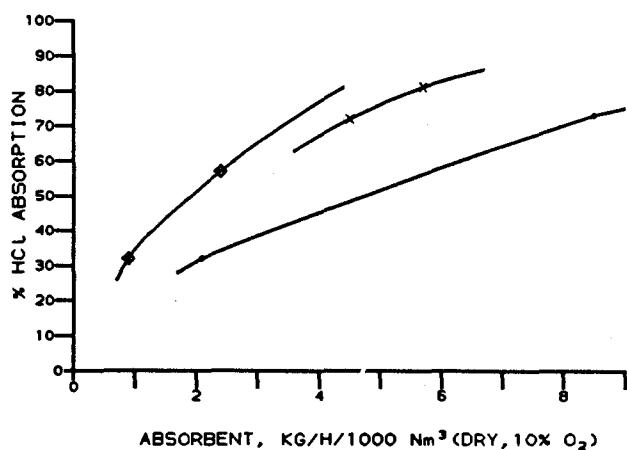
^a ESP = Electrostatic precipitator
FF = Fabric filter

TABLE 5. CHARACTERISTICS OF USED ABSORBENTS

Product	BET - Surface Area (m ² /g)	Bulk Density (g/cm ³)
Commercial Hydrate	12-18	0.60
Scansorb 35	27-43	0.37
Scansorb 100	54-93	0.25

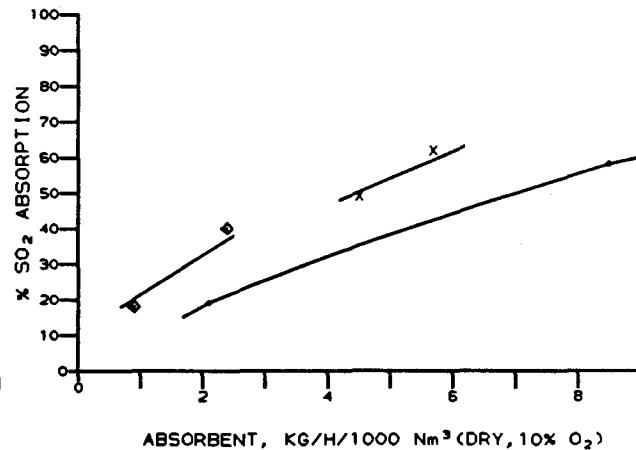
TABLE 6. POLLUTANT CONCENTRATION DURING FULL-SCALE DRY INJECTION TESTS

	Range	Average
HCl, mg/Nm ³	500-1200	800
SO ₂ , mg/Nm ³	200-500	300
H ₂ O, Vol. %	8-17	14
O ₂ , Vol. %	10-15	13



• Commercial Hydrated Lime X Scansorb 35 ♦ Scansorb 100 • Commercial Hydrated Lime X Scansorb 35 ♦ Scansorb 100

Figure 7. HCl Removal - Kolding

Figure 8. SO₂ Removal - Kolding

This difference in absorbent quantity was again verified at the Nykobing incinerator. This incinerator is equipped with a dry injection system consisting of a reactor and a downstream electrostatic precipitator. Residence time in the reactor is approximately 2 seconds. Figure 9 and 10 show the results of the full scale dry injection tests with Scansorb 35 and commercial hydrated lime. The tests were performed at 170° C at a moisture content of 15%.

Moisture content of flue gas has a significant influence on the performance of dry injection systems. This was verified at yet another full scale test carried out at the Sonderborg incinerator in Denmark. This incinerator is equipped with a two field large electrostatic precipitator and one of the units has a rather long duct upstream the ESP. This allows for 1 - 1.5 seconds residence time in the duct before entering the ESP.

The moisture content in the flue gas is to a great extent a function of how well the operators run the incinerator. The better they can control the excess air, the higher the moisture content in the flue gas. Figure 11 shows the correlation between moisture content and oxygen content of the flue gas as developed at the Sonderborg incinerator. Rules for good combustion practice specifies 10% oxygen in the flue gas, which will increase the moisture content to a reasonable level. Figure 12 and 13 are showing the influence of the flue gas moisture content on the performance of Scansorb 100. By increasing the moisture content from 10 to 17%, considerable savings in the absorbent usage can be achieved.

RESULTS OF TESTS USING FABRIC FILTER AS DUST COLLECTOR

The reaction and contact time achieved by dry injection into a duct upstream of an electrostatic precipitator is not very high. In contrary, a fabric filter allows for a more intimate contact between the flue gas and the collected active absorbent. This was verified by dry injection tests performed at the Kolding incinerator where a pilot fabric filter was installed. The results (figure 14, 15) show a considerable reduction in absorbent usage for a given removal efficiency. Furthermore, the figures show the influence of the flue gas temperature on the consumption.

The improved performance by using a fabric filter as dust collector were also confirmed by dry injection tests carried out at the Sysav incinerator in Sweden. This incinerator is equipped with a dry injection system incorporating a reactor and downstream fabric filter. The temperature of the flue gas was 140° C and the moisture content was 16%. Results of the tests are shown in figure 16 and 17.

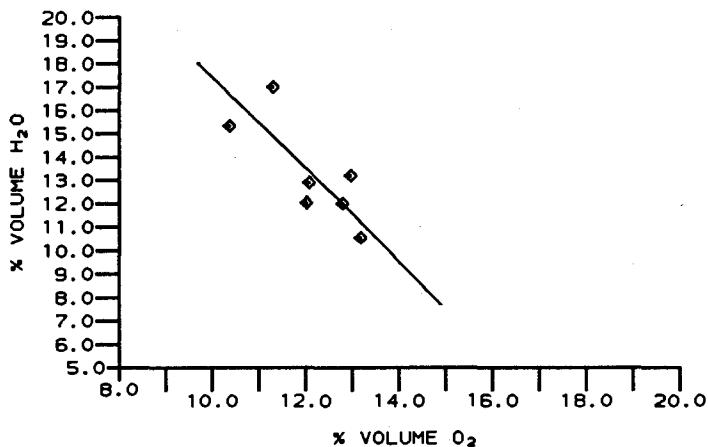
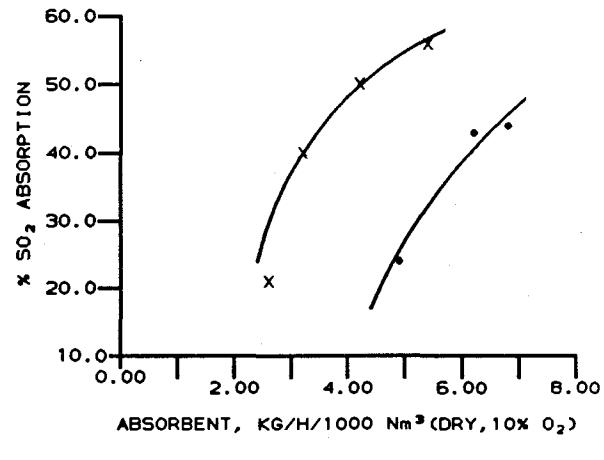
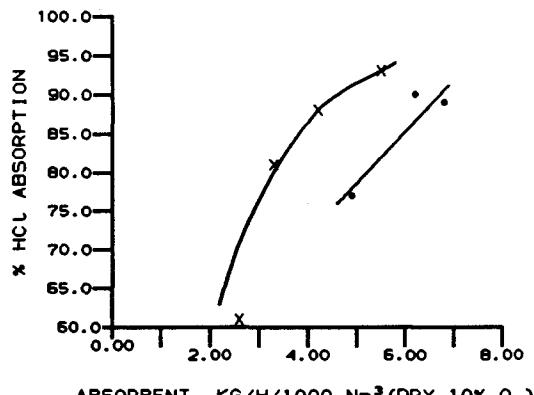
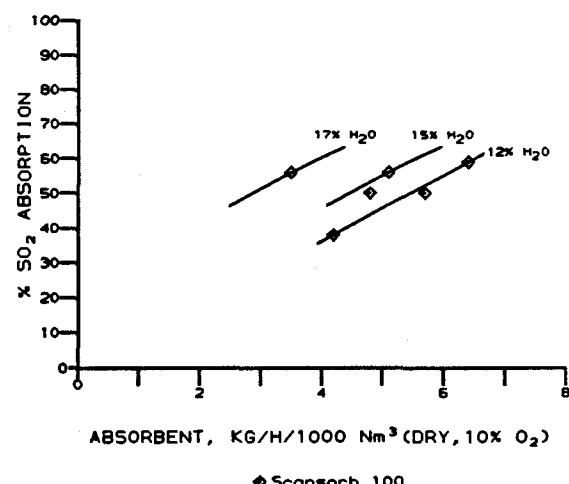
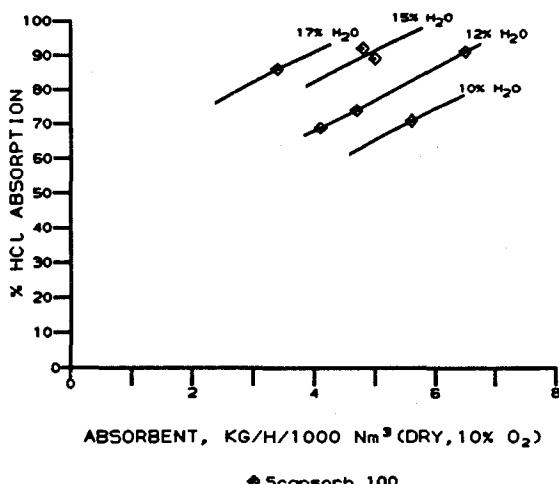


Figure 11. Correlation between moisture and oxygen



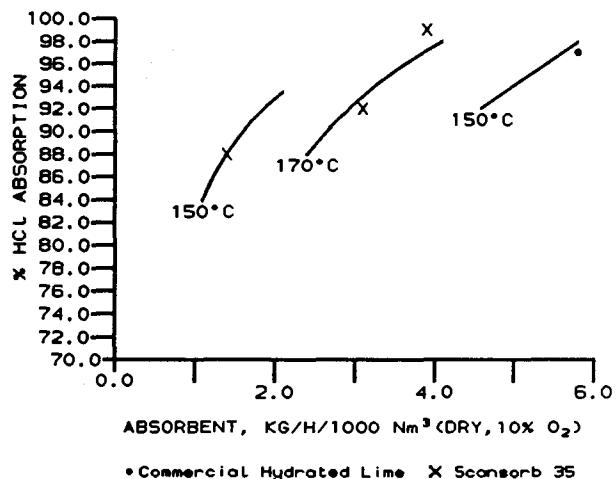


Figure 14. HCl Removal - Kolding, Pilot

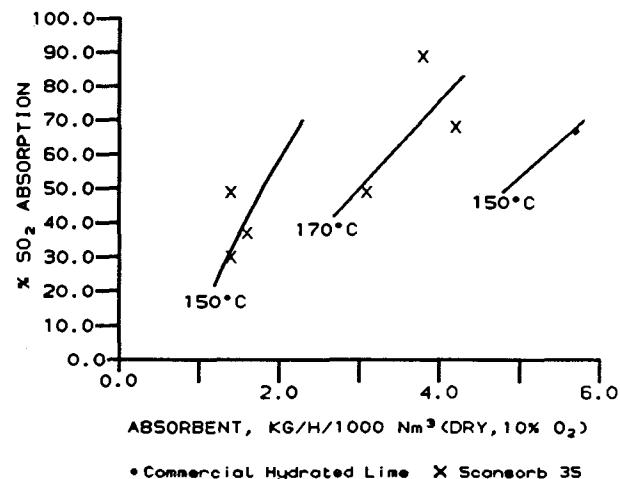


Figure 15. SO₂ Removal - Kolding, Pilot

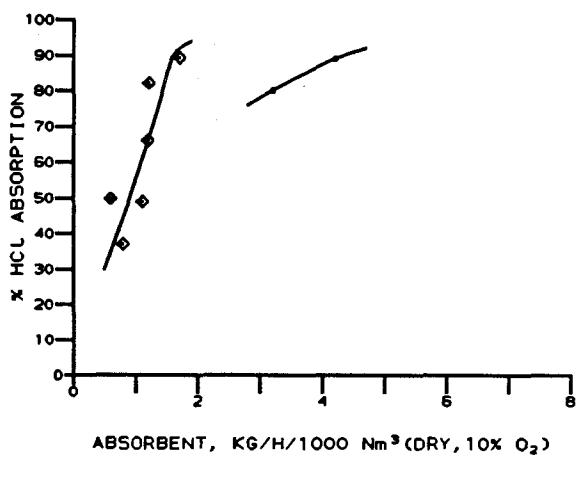


Figure 16. HCl Removal - Sysav

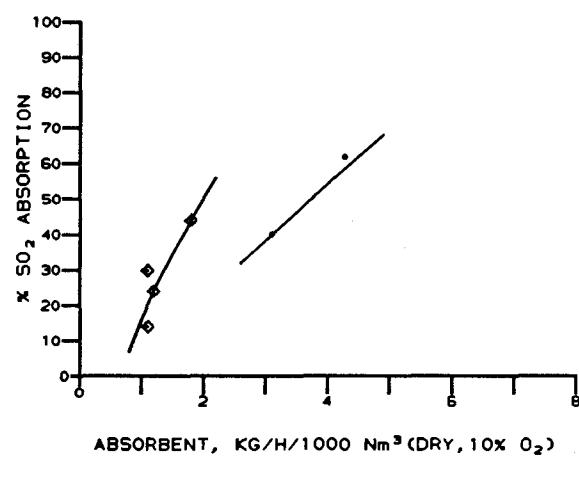


Figure 17. SO₂ Removal - Sysav

MERCURY REMOVAL

Mercury removal efficiency was measured at the Sysav incinerator. As it appears from table 7, an average of 82% mercury removal was achieved by Scansorb injection. Table 8 shows mercury removal efficiency measured at the Kolding plant. As this plant was operating at a much higher flue gas temperature and is using an electrostatic precipitator, only a marginal mercury removal was achieved. Although the mercury removal during these tests were marginal, later development has shown that a significant mercury removal can be achieved by modification of the Scansorb product.

CONCLUSION

The full scale test program has successfully demonstrated the viability of the new active absorbent Scansorb. The required outlet emission of SO₂ and HCl on existing, as well as new incinerators, can be met with a simple dry injection system using Scansorb as absorbent.

In table 9 the required amount of Scansorb for 50% SO₂ removal is summarized. It appears that when commercially hydrated lime is used the quantity required to achieve 50% SO₂ removal is increased with 60 to more than 100% compared with Scansorb. Also, it is significant that the quantities of absorbent required for 50% SO₂ removal when an electrostatic precipitator is used, is considerably higher than when a fabric filter is used as a dust collector. The potential savings in absorbent and disposal costs might be a major incentive for MSW operators to add a new fabric filter or rebuild the existing electrostatic precipitator into a pulse jet fabric filter.

TABLE 7. MERCURY REMOVAL BY SCANSORB INJECTION AT SYSAV, SWEDEN

Mercury Concentrations (ug/Nm ³)			
Test #	Inlet	Outlet	% Removal
3A	15	4	73
3B	26	2	92
4A	15	2	87
4B	8	2	75
		Average:	82%

TABLE 8. MERCURY REMOVAL BY SCANSORB INJECTION AT KOLDING, DENMARK

Mercury Concentrations (ug/Nm ³)			
Test #	Inlet	Outlet	% Removal
3A	116	97	17%
3B	44	45	0

TABLE 9. ABSORBENT USAGE (Kg/1000 Nm³) FOR 50% SO₂ REMOVAL

Plant	Temp. °C	% H ₂ O	ESP ^b	R + ESP	FF	R + FF
Kolding	190	10	4.3(7.0) ^a			
Nykobing	170	15		4.2(7.5)		
Sonderborg	155	15	4.8			
		17	3.0			
Kolding	150	14			1.9(4.8)	
	170				2.8	
Sysav	140	16				1.9(3.8)

^a - Scansorb (Hydrated lime)^b - R = Reactor

ESP = Electrostatic precipitator

FF = Fabric filter

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SESSION 7C: MERCURY CONTROL

Co-Chairmen:

**Karsten S. Felsvang
Niro Atomizer, Inc.
Columbia, MD**

**James R. Donnelly
Davy McKee Corporation
San Ramon, CA**

MUNICIPAL WASTE COMBUSTORS:
A SURVEY OF MERCURY EMISSIONS
AND APPLICABLE CONTROL TECHNOLOGIES

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ABSTRACT

Measured mercury emissions from municipal waste combustors (MWC's) are highly variable. Measured emission reductions from MWC's with acid gas controls indicate that factors other than air pollution control device (APCD) operating conditions play a significant role in determining potential emission reductions. This paper reviews mercury emissions data from MWC's located in the U. S. that are equipped with spray dryer/electrostatic precipitators (SD/ESP's) or SD/fabric filters (SD/FF's). Key operating variables examined include combustor type, APCD, flue gas temperature, and organics emission levels. The performance of add-on mercury control technologies (sodium sulfide [Na₂S] injection, activated carbon injection) and wet scrubbing are also discussed.

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

INTRODUCTION

As part of Section 129 of the Clean Air Act (CAA) Amendments of 1990, the U. S. Environmental Protection Agency (EPA) must revise the MWC standards and guidelines that were promulgated on February 11, 1991. These revisions must include, among other things, the addition of mercury emission limits for MWC's.

This paper provides information on mercury emissions from MWC's and examines how mercury removal relates to various parameters such as APCD inlet temperature and levels of carbon in the fly ash. Further, this paper discusses applicable mercury control techniques that could be used to reduce mercury emissions.

EXISTING MERCURY DATA

Table 1 presents mercury emissions data from 25 MWC units (located at 16 plants) that are equipped with either SD/ESP's or SD/FF's (1). Available inlet and outlet emissions data, along with combustor type, APCD type, APCD inlet temperature, and inlet dioxin/furan (CDD/CDF) levels are listed. The APCD inlet temperature is important because mercury exists in a vaporous form and does not effectively condense onto particulate matter (PM) at temperatures greater than roughly 300°F. Inlet CDD/CDF levels serve as a surrogate for estimating residual carbon in the fly ash, which may enhance mercury removal due to the adsorption of mercury onto carbon.

UNCONTROLLED EMISSIONS

Uncontrolled mercury levels from eight MWC's (four of which are listed in Table 1) that range from roughly 200 to 1,400 micrograms per dry standard cubic meter ($\mu\text{g/dscm}$) at 7 percent O_2 are reported (1).¹ Based on these data, there is no clear distinction between inlet mercury levels at mass burn plants and at refuse-derived fuel (RDF) plants.

CONTROLLED EMISSIONS

For the 12 SD/ESP-equipped MWC's listed in Table 1, outlet mercury emissions range from 5 to 950 $\mu\text{g/dscm}$, with the lower emission rates occurring at RDF plants. Due to the suspension feeding of fuel into the combustor, RDF units are believed to have higher PM loadings and carbon contents at the combustor exit than many mass burn units. The data support the theory that increased levels of carbon in the fly ash enhance mercury removal, since mercury adsorbs onto carbon. Inlet APCD temperatures during all of the tests at these units were less than approximately 300°F.

The 13 SD/FF-equipped MWC's listed in Table 1 have outlet mercury emissions levels ranging from below detection to 570 $\mu\text{g/dscm}$. Flue gas temperatures entering the APCD's were less than 300°F at all of the facilities. Additional data provided by Ogden Martin Systems indicate outlet mercury emissions for individual runs from SD/FF systems that are higher than those listed in Table 1 (2). Average outlet emissions, however, are similar to those listed in Table 1. As with the SD/ESP data, the lowest mercury outlet levels and highest removal efficiencies occurred at the two RDF plants, Biddeford and Mid-Connecticut. The reported inlet CDD/CDF levels at these two plants were 903 nanograms per dscm (ng/dscm) and 436 ng/dscm, respectively.

¹All emissions results reported in this paper are at 7 percent O_2 and are on a dry-basis at standard temperature (68°F).

The highest outlet mercury level for the SD/FF-equipped MWC's listed in Table 1 was during the 1987 testing at the Commerce MWC. During this testing, inlet CDD/CDF levels were very low, averaging 28 ng/dscm. During subsequent testing the following year, average mercury outlet levels were approximately 40 µg/dscm and 70 µg/dscm. The inlet CDD/CDF levels during the 1988 testing were much higher than during the 1987 testing, averaging roughly 450 ng/dscm and 780 ng/dscm. This data further supports the theory that increased levels of carbon in the fly ash enhance mercury removal.

It should be noted that the Hempstead facility, which is a mass burn MWC, also had low mercury emissions -- 25 µg/dscm or less. Inlet CDD/CDF levels were not reported.

Although not as apparent with the SD/ESP and SD/FF data since all of the systems operated at flue gas temperatures less than 300°F, reduced temperature entering the APCD also enhances the adsorption of mercury onto PM. As discussed previously, the condensation temperature of mercury is around 300°F. Therefore, at temperatures at or below 300°F, mercury can condense onto PM. Data from the Quebec City pilot plant which was tested with a dry sorbent injection/FF (DSI/FF) system demonstrated this trend (1). With an APCD inlet temperature of 400°F and an inlet CDD/CDF level of roughly 1600 ng/dscm, Quebec City reported an average outlet mercury emission level over 600 µg/dscm, corresponding to essentially no mercury removal. At APCD inlet temperatures between 230°F and 285°F and inlet CDD/CDF levels between approximately 900 and 2400 ng/dscm, average outlet mercury levels were less than 40 µg/dscm and removal efficiencies were between 91 and 97 percent.

Based on the available mercury emissions data, it can be observed that mechanisms of mercury removal are related to carbon levels in the fly ash, reduced temperature entering the APCD, and effective collection of PM.

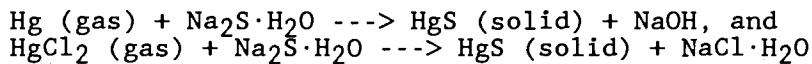
MERCURY CONTROL TECHNIQUES

Supplemental mercury control techniques include the injection of Na₂S or activated carbon into the combustion flue gas, and wet scrubbing. None of these technologies are currently in use at MWC's in the U. S., but have been applied to MWC's in Canada and Europe. Brief discussions of these technologies are presented below.

SODIUM SULFIDE INJECTION (1)

Background

Sodium sulfide is a crystalline solid that dissolves in water. The resulting Na₂S solution is sprayed into the flue gas prior to the acid gas control device. The specific reactions of Na₂S and mercury are not totally clear, but appear to be:



The effect of (a) flue gas temperature or (b) lime or ammonia injection for acid gas or NO_x control on these mercury reactions is uncertain.

Sodium sulfide is currently used for mercury control by MWC's in Avesta, Kopings, and Hogdalen, Sweden; Kempten, Germany; and Burnaby, British Columbia. Injection of Na₂S has been used at the Hogdalen MWC since 1986. The other three plants in Europe began Na₂S injection in 1989. The Burnaby MWC began testing of Na₂S in 1989 and began continuous operation with a temporary system in December 1989.

All of these facilities use DSI/FF systems supplied by Fläkt for acid gas and PM control. Injection of Na₂S occurs prior to the DSI system at flue gas temperatures of 260-300°F. Hogdalen reduces flue gas temperatures prior to Na₂S injection with a heat exchanger which provides hot water for district space heating. The Burnaby MWC uses a water quench tower for flue gas cooling. Flue gas temperatures at the stack normally range from 260-300°F.

Fläkt reports that Na₂S feed rates vary from 0.1 to 1 lb/ton (0.05 to 0.5 kg/Mg) of MSW, depending on site-specific conditions such as the amount of mercury in the flue gas, the level of control required, and the amount of carbon present in the fly ash. If a plant has little carbon in its fly ash, it may be necessary to increase the amount of Na₂S injected.

Performance

Mercury control performance data with Na₂S injection are shown in Table 2. The data has been compiled from information provided by Fläkt, the Burnaby MWC facility owner (the Greater Vancouver Regional District (GVRD)), and from trip reports to the Hogdalen and Burnaby MWC's.

Mercury levels prior to Na₂S injection at the Burnaby MWC (400-1400 µg/dscm) are higher than general inlet values reported at European MWC's (55-560 µg/dscm) (1). The objective of the initial testing conducted at the Burnaby MWC was to evaluate key system parameters. During these tests, 2 to 7 lb/hr (1 to 3 kg/hr) of Na₂S was fed as 10-15 percent concentration solutions and achieved mercury reductions of 50-65 percent. Subsequent tests conducted at a feed rate of 4 to 13 lb/hr (2 to 6 kg/hr) of Na₂S and a solution concentration of 2-4 percent achieved average mercury reductions of 86 percent and outlet mercury concentrations between 84 and 103 µg/dscm. Testing conducted at a Na₂S feed rate of 9 lb/hr (4 kg/hr) and a solution concentration of 2 percent achieved average outlet mercury concentrations between 117 and 155 µg/dscm; inlet mercury concentrations were not measured during these tests, therefore percent reductions could not be calculated. The improved mercury reduction at lower Na₂S concentrations is believed to be the result of improved atomization and mixing when feeding higher volumes of low concentration solution versus lower volumes of high concentration solutions.

Test results from the European facilities show mercury emissions ranging from 40 to 70 µg/dscm, with average levels of approximately 60 µg/dscm. Inlet mercury levels measured at Hogdalen indicate mercury removal efficiencies greater than 85 percent. The outlet levels at Kempten of less than 56 µg/dscm correspond to an estimated removal efficiency between 65 and 90 percent.

All of the existing MWC's using Na₂S injection are equipped with DSI/FF systems. As a result, some uncertainty exists regarding the applicability of Na₂S injection to other APCD configurations, such as spray drying. Fläkt indicated that they do not believe this will be a problem, but do not have any actual operating experience with application of Na₂S injection to spray drying systems. Fläkt did indicate, however, that it would probably be necessary to have separate Na₂S and calcium sorbent feed and injection systems to avoid CaS scaling of the sorbent feed line.

Cost Estimates

Available cost data for Na₂S injection systems are based on estimates from Fläkt, information provided for the Burnaby plant, and chemical costs from PPG. The Burnaby MWC operator estimated capital costs for a Na₂S system for the Burnaby plant, which has a capacity of 800 TPD, at \$150,000-\$250,000. The chemical costs for the sodium sulfide, as quoted by Fläkt, range from \$0.10-0.50/ton of MSW. This cost is dependent upon the uncontrolled mercury level and the level of reduction required. The chemical cost reported for the Burnaby MWC is \$0.50/ton of MSW, and the chemical cost (without shipping) reported by PPG is \$0.30/ton of MSW, both of which are consistent with Fläkt's estimate. Based on this information, annualized costs (based on a capital

recovery factor of 0.1315 and 8,000 hours of operation per year) for Burnaby are estimated at \$0.50-1.00/ton of MSW.

ACTIVATED CARBON INJECTION

Another mercury control technology used in Europe is the injection of powdered activated carbon prior to the APCD. This technology has been used commercially on two MWC's, one located in Zurich, Switzerland, and one in Geiselbullach, Germany. Additionally, activated carbon injection has been used during a test program at an MWC in Amager, Denmark.

The Zurich MWC is equipped with an SD/ESP system, the Geiselbullach MWC is equipped with a DSI/FF system, and the Amager MWC is equipped with a SD/FF system. At the Zurich plant, powdered activated carbon is injected into the flue gas, ahead of the SD, at a rate of 2 to 3 kg/hr (4 to 7 lb/hr). The temperature entering the SD is between 430 and 540°F. Test results from the Zurich plant show an increase in mercury reduction from 70 percent without activated carbon injection, to 90 percent with activated carbon injection (3).

At the Geiselbullach plant, solids recirculation is used to improve sorbent and additive utilization, and a heat exchanger is used to cool the flue gas prior to its entering the DSI. A powdered mixture of calcium hydroxide [Ca(OH)₂] and coke is then injected into the upward-flowing cooled and humidified flue gas. Test data and operational features are not available for the Geiselbullach plant (3).

The Amager MWC operates similarly to the Zurich plant. Testing was conducted with temperatures at the SD exit of 284°F and at 260°F. As shown in Table 3, results from the testing with activated carbon injection at the higher temperature indicate outlet mercury levels between 23 and 77 µg/dscm, corresponding to removal efficiencies between 82 and 95 percent. Without activated carbon injection, outlet mercury emissions were between 67 and 195 µg/dscm, with removal efficiencies between 15 and 65 percent. The highest removal efficiencies when using activated carbon occurred with increased additive levels (70 mg/dscm vs. 7 mg/dscm) (4).

Testing at the lower APCD inlet temperature shows greater control of mercury, especially when activated carbon injection was not used. With activated carbon, outlet mercury levels ranged from 6 to 24 µg/dscm (88 to 97 percent removal), and without activated carbon the outlet levels were between 30 and 53 µg/dscm (72 to 92 percent removal) (4).

No cost data are available for activated carbon injection. However, the costs are expected to be low, similar to Na₂S injection. One of the criteria for selecting the additive used at the Zurich MWC was its low cost (3).

WET SCRUBBING

Wet scrubbing is a form of acid gas control that has primarily been used in Europe and Japan. Wet scrubbing involves passing the flue gas through an ESP to reduce PM, followed by an absorber where flue gas is contacted with an alkaline solution to saturate the gas stream and reduces flue gas temperatures to as low as 130°F. The alkaline solution, typically containing calcium hydroxide [Ca(OH)₂], reacts with the acid gas to form salts, which are generally insoluble and may be removed by sequential clarifying, thickening, and vacuum filtering. The dewatered salts or sludges are then landfilled.

The wet scrubbing technology results in increased mercury reduction relative to SD/FF control without supplemental mercury control due to the lower operating temperature that increases mercury condensation. As a result, the collection of mercury improves and mercury can be reduced by up to 90 percent. Disadvantages to wet scrubbing, however, include the quantity of water required and potential difficulties with waste handling. Further, control of organics may be less than with dry acid gas controls.

Test results from two MWC's located in France and one MWC located in Switzerland are available (5). The two French plants, Lyon-Nord and Lyon-Sud began commercial operation in 1989 and 1990, respectively, and they are equipped with ESP's followed by wet scrubbers. Mercury emissions results from these plants are shown in Table 4. Average mercury outlet emissions at Lyon-Nord were under 50 $\mu\text{g}/\text{dscm}$ for Unit 1 and 62 $\mu\text{g}/\text{dscm}$ for Unit 2. Average removal efficiencies were greater than 82 percent for Unit 1 and 62 percent for Unit 2. At Lyon-Sud, average mercury outlet emissions were less than approximately 60 $\mu\text{g}/\text{dscm}$ for both units, and average removal efficiencies were greater than 86 percent.

The Basel, Switzerland MWC, which was equipped with only ESP's, was retrofitted with wet scrubbing systems in 1989. Mercury outlet emissions, listed in Table 4, ranged from 16 $\mu\text{g}/\text{dscm}$ to 20 $\mu\text{g}/\text{dscm}$ at Unit 1, and from less than 13 $\mu\text{g}/\text{dscm}$ to 34 $\mu\text{g}/\text{dscm}$ at Unit 2. This corresponds to average removal efficiencies between 90 and 96 percent for Unit 1, and between 82 and 96 percent for Unit 2.

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TABLE 1. EXISTING MERCURY EMISSIONS DATA FROM SD/ESP'S AND SD/FF'S

MWC NAME	RUN NUMBERS	COMBUSTOR TYPE	APCD TYPE	APCD TEMP. (F)	INLET CDD/CDFa (ng/dscm)	INLET Hg AVERAGEa (ug/dscm)	OUTLET Hg AVERAGEa (ug/dscm)	REMOVAL EFFICIENCY (%)
Charleston, Units A & B	1-3	MB/WW	SD/ESP	--	-- b	--	723	--
Honolulu, Unit 1	1-3	RDF	SD/ESP	300	-- c	--	5	--
Honolulu, Unit 2	1-3	RDF	SD/ESP	293	-- c	--	7	--
Millbury, Unit 1	1-6	MB/WW	SD/ESP	249	--	--	565	--
Millbury, Unit 2	1-3	MB/WW	SD/ESP	240	170 d	--	954	--
Portland, Unit 1 (12/89)	4-6	MB/WW	SD/ESP	308	-- e	--	550	--
Portland, Unit 2 (12/89)	1-3	MB/WW	SD/ESP	285	-- e	--	382	--
SEMASS, Unit 1	1-3	RDF	SD/ESP	287	-- f	--	59	--
SEMASS, Unit 2	2-4	RDF	SD/ESP	293	-- f	--	105	--
West Palm Beach, Unit 1	3 tests	RDF	SD/ESP	275	--	--	56	--
West Palm Beach, Unit 2	3 tests	RDF	SD/ESP	278	--	--	23	--
Babylon, Unit 2	1-3	MB/WW	SD/FF	331	--	--	451	--
Biddeford	1-3	RDF	SD/FF	278	903	389	ND g	>99
Commerce (1987)	11,13,14	MB/WW	SD/FF	270 h	28	450	570	-26.7
Commerce (1988)	3,5,9	MB/WW	SD/FF	290 h	446 d	453	39	91.4
Commerce (1988)	13,16,18,29	MB/WW	SD/FF	290 h	783 d	261	68	74.0
Hempstead, Unit 1 (9/89)	1-3	MB/WW	SD/FF	310 h	--	--	9	--
Hempstead, Unit 2 (9/89)	1-3	MB/WW	SD/FF	310 h	--	--	25	--
Hempstead, Unit 3 (10/89)	1-3	MB/WW	SD/FF	310 h	--	--	25	--
Indianapolis, Unit 1	1-3	MB/WW	SD/FF	307	--	--	283	--
Long Beach	1-3	MB/WW	SD/FF	298	305	--	180	--
Marion County	4-6	MB/WW	SD/FF	272	43 d	--	239	--
Mid-Connecticut (7/88)	1-3	RDF	SD/FF	276	1019	1008	--	--
Mid-Connecticut (7/88)	1-3 i	RDF	SD/FF	284	--	884	50	94.3
Mid-Connecticut (2/89)	12-14	RDF	SD/FF	--	436	668	9	98.7
Quebec City - Pilot	7-8	MB/WW	SD/FF	282	1764	187	10	94.7
Quebec City - Pilot	9-10	MB/WW	SD/FF	284	2157	360	19	94.7
Stanislaus County, Unit 1	14,16,19	MB/WW	SD/FF	295	--	--	499	--
Stanislaus County, Unit 2	38,40,42	MB/WW	SD/FF	290	--	--	462	--

M/E - Modular/Excess Air
M/S - Modular Starved Air
MB/R - Mass Burn/Refractory
MB/WW - Mass Burn/Waterwall
RDF - Refuse Derived Fuel

- a Results reported at 7% O₂.
- b Outlet CDD/CDF values: Unit B - 44.2 ng/dscm (average of three runs conducted during same test campaign).
- c Outlet CDD/CDF values: Unit 1 - 6.3 ng/dscm; Unit 2 - 3.8 ng/dscm.
- d Inlet CDD/CDF samples collected during separate runs from Hg, but during same test campaign and at similar operating conditions.
- e Outlet CDD/CDF values: Unit 1 - 36.5 ng/dscm; Unit 2 - 43.6 ng/dscm.
- f Outlet CDD/CDF values: Unit 1 - 9.3 ng/dscm; Unit 2 - 12.3 ng/dscm.
- g Not detected.
- h Temperatures not reported for Hg runs; temperatures estimated based on other runs during same test campaign.
- i Additional inlet and outlet mercury samples were collected by Method 101A. Not measured simultaneously with other metals.

TABLE 2. MERCURY EMISSIONS DATA WITH Na₂S INJECTION

MWC PLANT	WASTE TPD	APCD TYPE	Na ₂ S FEED RATE (kg/hr)	TESTED Hg INLET (ug/dscm)	EMISSIONS ^a OUTLET (ug/dscm)	REDUCTION EFFICIENCY (%)
Burnaby Unit ?, 3/89 (10% Na ₂ S)	265	DSI/FF	Run 1 = 1.0 Run 2 = 2.0 Run 3 = 2.0	1465 993 1151	570 407 393	
			Avg	1203	Avg 457	Avg 62
Unit 1, 4/89 (15% Na ₂ S)		All runs =	3.0	1423 1443 1205	670 750 473	
			Avg	1357	Avg 632	Avg 53
Unit ?, 8/89 (2-4% Na ₂ S)		Run 1 = 2.5 Run 2 = 6.0 Run 3 = 2.0 Run 4 = 3.0 Run 5 = 6.0		406 775 670 793 661	98 91 84 101 103	
			Avg	661	Avg 95	Avg 86
Unit 1, 12/89 (2% Na ₂ S)		All runs =	4.0	NR NR NR	138 67 146	
			Avg	117	NA	
Unit 2, 12/89 (2% Na ₂ S)		All runs =	4.0	NR NR NR	149 115 118	
			Avg	127	NA	
Unit 3, 12/89 (2% Na ₂ S)		All runs =	4.0	NR NR Avg	152 159 155	NA
Hogdalen - 3 Units Unit 3, 8/86-9/86	400	DSI/FF	1.24 1.05 1.4 0.89	NR 370 497 NR	70 40 61 55	
			Avg	57		
Kempten (Germany)	210	DSI/FF	NR	NR	<56	65-90 b

NR - Not reported; NA - Not applicable

a Results reported at 12% CO₂ (assumed to be equal to 7% O₂).

b Based on general inlet values at German MSW plants ranging from 170-560 ug/dscm.

TABLE 3. MERCURY EMISSIONS DATA FROM THE AMAGER MWC

ADDITIVE (mg/dscm)	SD OUTLET TEMPERATURE (F)	INLET MERCURY (ug/dscm)	OUTLET MERCURY (ug/dscm)	REMOVAL EFFICIENCY (%)
0	284	203	154	24
		229	195	15
		219	86	61
		202	74	64
		165	67	59
7	284	378	58	85
		227	40	82
20	284	214	31	86
		248	35	86
		336	36	89
70	284	1516	77	95
		318	23	93
0	260	421	32	92
		196	48	76
		163	30	82
		189	54	71
23	260	201	24	88
83	260	198	6	97
		220	7	97

*All concentrations are at 7 percent O₂.

TABLE 4. MERCURY EMISSIONS DATA FROM WET SCRUBBING SYSTEMS

MWC NAME	UNIT	RUN NUMBER	INLET (ug/dscm)	OUTLET (ug/dscm)	REMOVAL EFFICIENCY (%)
LYON-NORD, FRANCE	1	1	168	<49	>71
		2	289	<50	>83
		3	578	<49	>91
		AVERAGE	345	<49	>82
	2	4	177	49	72
		5	177	76	57
		6	140	60	57
		AVERAGE	165	62	62
LYON-SUD, FRANCE	1	3	457	72	84
		4	568	<49	>91
		AVERAGE	513	<61	>88
	2	1	438	69	84
		2	373	<49	>87
		AVERAGE	406	<59	>86
BASEL, SWITZERLAND	1	1	252	16	94
		2	168	17	90
		4	401	17	96
		7	513	20	96
		8	187	19	90
	2	1	186	<13	>93
		2	224	<14	>94
		3	261	32	88
		4	224	<13	>94
		5	168	<13	>92
		6	168	21	88
		7	140	<13	>91
		20	363	13	96
		21	270	33	88
		23	75	<13	>82
		24	196	<13	>93

*All concentrations are at 7 percent O₂.

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The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

CONTROLLING MERCURY EMISSIONS FROM RDF FACILITIES

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ABSTRACT

Concern over the potential effects of mercury on food chains, public health, and sport fisheries is resulting in close examination of sources of mercury in the environment, in particular municipal waste combustors (MWC's). Mercury emissions data from MWC's, mercury emission test methods and the potential health effects of mercury are being scrutinized. The U.S. EPA is studying potential mercury emission control technologies and developing specific mercury emission standards for MWC's.

The potential air emissions of mercury from the processing of municipal solid waste (MSW) at refuse derived fuel (RDF) facilities are effectively minimized. The combination of processing MSW to remove noncombustibles in the production of RDF, and the use of spray dryer/electrostatic precipitator (SD/ESP) or spray dryer/fabric filter (SD/FF) technology to control emissions from RDF-fired boilers, results in extremely high reductions of potential mercury emissions.

Tests conducted at the Greater Detroit Resource Recovery Facility (GDRRF) and at the Mid-Connecticut Resource Recovery Facility (MID-CT) in Hartford, CT, each employing the ABB waste processing technology, indicate that a significant portion of the mercury-bearing components are removed from MSW through magnetic separation and subsequent processing steps prior to combustion of the resultant RDF. High mercury removal efficiencies were achieved at the RDF facilities in Biddeford, Maine (> 99 percent) and at MID-CT (98.3 percent), both of which are equipped with SD/FF. Outlet flue gas mercury concentrations recorded at the RDF facility in Honolulu, Hawaii, and other RDF facilities equipped with SD/ESP, are among the lowest values reported.

Statistical analysis of the data from the U.S. EPA/Environment Canada (U.S.EPA/EC) test program conducted at MID-CT indicates a good correlation between mercury removal by the flue gas cleaning system and decreasing flue gas temperature (spray dryer outlet) and increasing carbon content of the fabric filter ash. Increased sorbent-to-acid-gas ratio (stoichiometric ratio) tended to result in increased mercury emissions. Questionable validity of the percent carbon in flyash data from the test program dictates that additional research into the mechanisms of mercury removal is necessary.

MERCURY EMISSIONS FROM MWC's

Mercury is emitted to the atmosphere from natural (non-anthropogenic) sources and from human (anthropogenic) sources. Non-anthropogenic sources include oceans, volcanoes, forest fires and terrestrial mineral deposits. Fossil fuel combustion, the manufacturing and application of paints and pesticides, the manufacturing and disposal of batteries and fluorescent lamps, and municipal solid waste incineration are human activities which generate mercury emissions. Mercury is also used in the manufacturing of chlorine and caustic as well as in non-household consumer batteries used for medical, industrial, and military purposes.

Based on published estimates, mercury emissions from MWC's in the United States represent a small percentage of the annual global atmospheric mercury burden. The Electric Power Research Institute (EPRI) estimates total annual global emissions of mercury to be between 5 and 6 million kilograms, about 30 to 55 percent of which is derived from anthropogenic sources.¹ EPRI's estimate that fossil fuel combustion by utilities in the United States amounts to approximately 75,000 kilograms of mercury annually agrees with an estimate published by the New Jersey Chapter of the Clean Water Action/Clean Water Fund.² The latter source also contains an estimate that 34,000 kilograms of mercury were emitted from MWC's in the United States in 1989. If these estimates are correct, mercury emissions from MWC's in the United States accounted for from 0.6 to 0.7 percent of the global total in 1989.

Mercury emissions from MWC's are directly related to the presence of mercury-bearing components in the MSW stream during combustion. According to a recent study by Franklin Associates, approximately 88 percent of the mercury contained in MSW comes from household batteries, primarily alkaline and mercuric zinc "button" batteries. This study also estimates that electric lighting components contribute 5 percent, thermometers 2 percent, thermostats 2 percent, pigments 2 percent, and other components, which include dental uses, special paper coating, mercury light switches, and film pack batteries, approximately 1 percent of the total amount of mercury. It is estimated that the mercury content of MSW is on the order of approximately 0.003 to 0.004 pounds per ton of MSW.² Efforts are underway to reduce this concentration by the reformulation of consumer products.

METHODS OF MINIMIZING MERCURY EMISSIONS FROM MWC's

There are four potential means of minimizing mercury air emissions from MWC's. These methods are identified as follows:

1. The removal of mercury from consumer products which ultimately are disposed of and contained in the incoming MSW stream.
2. The removal of mercury-bearing components from the MSW stream prior to reaching the MWC (i.e. source separation).
3. The removal of mercury-bearing components from the MSW stream at the MWC.
4. The use of post-combustion air pollution control technology at MWC's to remove mercury compounds from the flue gas.

Brief discussions of the first two methods are presented below, followed by a discussion of the effectiveness of RDF technology in controlling mercury emission by the latter two means.

REMOVAL OF MERCURY FROM CONSUMER PRODUCTS

Substantial progress is being made to reduce the amount of mercury discarded into MSW. The National Electrical Manufacturer's Association has announced its intent by 1993 to substantially reduce the mercury content of alkaline batteries to 0.025 percent by weight.⁴ Such batteries are currently available on the market in some areas. Mercury zinc "button" batteries, which each contain approximately 50 percent mercury by weight, are being replaced to some degree by silver oxide and zinc air batteries which contain less mercury. In August 1990, the U.S. EPA banned the use of mercury from all new interior latex house paints. Mercury discarded from dental uses, paper coating, and film pack batteries is also projected to decline rapidly or be eliminated. According to the Franklin Associates study, the amount of mercury discarded in MSW will decrease by approximately 65 percent between the years 1990 and 1995.³

REMOVAL OF MERCURY BY SOURCE SEPARATION

Efforts to remove mercury-bearing components from the MSW stream prior to reaching MWC's have almost exclusively consisted of household battery recycling programs. Such programs associated with the Hennepin County, MN; New Hampshire/Vermont Solid Waste Project; and the GDRRF have met with limited success. While large quantities of batteries have been collected, some of them have a limited mercury content, and most of them are not being recycled. Rather, the majority are being stored, or disposed of in sanitary or hazardous waste landfills.⁴ The U.S. EPA did not adopt a proposed requirement to remove mercury-bearing household batteries from the incoming MSW stream to an MWC in adopting the New Source Performance

Standards for MWC's on January 11, 1991. The Franklin Associates study assumed that only 5 percent of the mercury in batteries in 1995 and 20₃ percent in the year 2,000 will be recovered through source separation.

CONTROL OF MERCURY EMISSIONS AT RDF FACILITIES

Evidence indicates that RDF technology is effective in minimizing potential air emissions of mercury which are generated as a result of mercury contained in the incoming MSW stream. Such facilities differ from more common mass burning MWC's by processing MSW to remove noncombustibles before burning, and by injecting the RDF into a boiler so that approximately 50 percent of the fuel burns in suspension instead of all the MSW burning on a grate. Research and developmental testing at the GDRRF and the MID-CT Facility indicates that front-end processing of MSW to produce RDF results in the removal of a significant percentage of the mercury in the incoming MSW stream. Mercury emissions test data demonstrates that the mercury content of the flue gas which is generated by the combustion of RDF can be reduced by greater than 96 percent using SD/FF technology. Low stack gas mercury concentrations have also been recorded at RDF facilities equipped with DS/ESP technology.

REMOVAL OF MERCURY FROM MSW

ABB Resource Recovery Systems (ABB-RRS) is the leader in the design, construction and operation of RDF facilities. Currently, ABB-RRS has three operating RDF facilities employing essentially identical front-end processing technology and boiler design features, but each with different air pollution control technology. These facilities are the MID-CT in Hartford, CT with DS/FF technology; the GDRRF in Detroit, MI with lime addition and ESP technology; and the Honolulu Resource Recovery Venture Facility in Honolulu, HI with DS/ESP technology.

The flow of waste through the waste processing system at an ABB process facility is shown on Figure 1. The design includes complete residue conveying and materials load-out systems. The process equipment is arranged to minimize changes in flow direction and material transfer points.

Incoming trucks are weighed and then directed to the MSW receiving area where the waste is discharged on the receiving building floor. The waste is spread and compacted in the storage area with large sized front-end loaders and inspected for the presence of non-processible items which are separated for removal from the facility.

Processible waste is loaded onto a feed conveyor by front-end loaders. The solid waste is metered by the feed conveyor onto an inclined steel pan conveyor for leveling. The inclined conveyor carries the waste onto a horizontal, steel infeed conveyor which feeds the primary shredder. Prior to the shredder, a picking station is located alongside each horizontal feed conveyor to allow the operator to inspect the waste being carried to

the primary shredder and to stop the conveyor and remove non-processible items. Non-processible items are picked using a hydraulic grapple controlled from the picking station control booth.

The primary shredder is a flail mill which performs coarse shredding of the waste stream. Closed bags are opened, ferrous metal is exposed, and glass containers are broken. Each primary shredder is enclosed in a reinforced concrete room and equipped with a dedicated dust control system consisting of an exhaust fan and fabric filter.

Upon completion of primary shredding, the waste is conveyed to the ferrous separation system which consists of a primary electromagnetic drum and a secondary drum type transfer magnet.

After the ferrous separation point, the waste is conveyed to the primary separation unit which is a totally enclosed trommel rotary screen. Two discharge streams are conveyed from the trommel. One of the streams is a sized fraction consisting of small combustible products, aluminum cans, and medium sized non-combustibles. This stream is transported to the secondary separation system. The second stream is an oversized fraction consisting primarily of paper and plastic which is conveyed to the secondary shredder for size reduction.

The secondary separation unit consists of a totally enclosed, two-staged trommel rotary screen which further separates the sized fraction received from the primary separation units. The discharge undersized streams consist of:

1. Process residue consisting of fine sand, glass, dirt, etc., which is conveyed directly to the residue load-out area where further recovery of combustibles may be provided; and
2. A sized fraction which is conveyed to the RDF collection conveyor.

The oversized fraction from the secondary separation unit is conveyed to the RDF storage area.

The oversized fraction from the primary separation unit is conveyed to the secondary shredder. The secondary shredder is a high horsepower, horizontal shaft machine with hammers and grates arranged and sized to produce the desired RDF particle size. Hammer and grate shape and size are changeable to control top size and optimum particle size for boiler performance and to accommodate seasonal variations in waste composition. RDF is conveyed to the RDF storage building where a front-end loader distributes and stockpiles the RDF.

On a weight basis, the following approximate materials distributions exist at an RDF facility during normal operations:

1. Ferrous - 5 percent
2. Primary Trommel Overs (RDF stream) - 60 percent
3. Primary Trommel Unders (Residue stream) - 6 percent
4. Secondary Trommel Overs (RDF stream) - 23 percent
5. Secondary Trommel Unders (Residue stream) - 6 percent

Thus, waste processing converts approximately 83 percent of the processible MSW stream to RDF, with the remainder removed as ferrous material (5 percent) and residue (12 percent).

Data from studies conducted at both the GDRRF and the MID-CT facilities indicate that waste processing to produce RDF results in the removal of mercury-bearing components and, hence, mercury from processible MSW prior to combustion. This, in turn, results in a reduction in potential mercury air emissions generated by combustion, as compared to levels which would have occurred in the absence of processing.

MAGNETIC SEPARATION OF BATTERIES

ABB-RRS has conducted testing at the GDRRF to assess the fate of mercury-bearing household batteries as a result of processing the incoming MSW stream. Data was obtained during six days of field testing at the facility during the week of February 5, 1990.

A test plan was carried out which involved placing color-coded batteries into the processible MSW stream prior to processing. Annual national sales information was used to determine the number and types of batteries with which to "spike" a known weight of processible MSW. Having spiked a 14.63-ton sample of waste with 221 batteries prior to processing, each of the three resultant process streams (ferrous, residue and RDF) could be collected and sorted to determine the number of batteries. Color-coded batteries, along with any additional batteries originally in the waste material, were recovered and their size and type recorded.

The results of the test program indicated that 31 of the 221 color-coded batteries (14 percent) were magnetically separated from the MSW sample during processing. These batteries were almost exclusively steel-jacketed alkaline batteries. Based on the reported mercury content of all of the color-coded batteries, the mercury content of the magnetically separated batteries was calculated to equal approximately 17.6 percent of the total amount of mercury contained in all of the batteries.

In a perceived effort to minimize mercury emissions, the facility was mandated in November 1989 to operate in a bypass configuration whereby all of the material which falls through the primary trommel is diverted to landfill, rather than directed to the secondary trommels for normal processing. Because of this operating requirement, useful data on battery removal other than by the drum magnet system during normal operation of the facility could not be obtained during the test program.

PARTITIONING OF ELEMENTS BY PROCESSING MSW

The MID-CT Resource Recovery Facility, located in Hartford, Connecticut, was recently tested to study the partitioning of elements in MSW and the advancement of methods for processing refuse. The study was conducted for ABB-RRS by the University of Wisconsin-Madison with funding supplied by ABB Resource Recovery Systems.⁵ The research was conducted from the summer of 1988 through the end of 1989.

A portion of the research involved an examination of twenty-seven (27 elements) in MSW and in the end products (i.e. ferrous, residue, and RDF) of the MSW processing system at the facility. Composite samples of the streams for a five-day production period were reduced following a protocol developed by the research team and then analyzed.

The results from the MID-CT portion of the test are presented in Table I. The distribution analyses indicate that approximately 53 percent of the mercury in the processible MSW stream was diverted from the RDF which was combusted at the facility. The majority of this amount was removed via the drum magnet system.

Because of the nature of the sampling methods and variability of MSW and the process streams, the results of this study should be viewed in relative rather than precise quantitative terms. Nonetheless, the research supports the findings at the GDRRF in that a significant portion of the mercury contained in the incoming MSW stream to an RDF facility is magnetically removed prior to combustion of the RDF product.

POST COMBUSTION CONTROL OF MERCURY EMISSIONS

Emissions data from MWC's indicate that mercury levels in the flue gas from RDF MWC's can be efficiently controlled using DS/FF or DS/ESP post-combustion control technology. The U.S. EPA recently published a mercury emissions database which covered 40 MWC units at 28 different plants in North America.⁶ Outlet flue gas mercury concentrations, type of combustor, type of air pollution control technology, control device operating temperature, and inlet dioxin/furan concentration were reported. Where available, control device inlet flue gas mercury concentrations were reported, and mercury removal efficiencies were calculated.

Mercury emissions data from ten MWC's (13 units) equipped with SD/FF technology were contained in the U.S. EPA's database. The highest mercury removal efficiencies were detected at the only two listed RDF facilities. Mercury removal efficiencies at the Biddeford, ME facility were greater than 99 percent and averaged 98.3 percent at MID-CT. The mercury emissions data from the 13 performance tests of the U.S. EPA/EC test program at MID-CT, for which the mercury removal efficiency averaged 98.3 percent, are presented in Table II. The average inlet flue gas mercury concentration of 659 ug/dscm at 7 percent O₂ is approximately equal to the average of the entire database. The outlet flue gas mercury concentrations at these two

RDF facilities were among the lowest values reported, and much lower than the average outlet concentrations for similarly equipped mass burn MWC's.

Outlet mercury emissions data were reported for six MWC facilities (12 units) equipped with DS/ESP technology. Three of the six MWC's were mass burn facilities, and the other three were RDF facilities. Similar control device operating temperatures were reported for all six facilities. Outlet flue gas mercury concentrations at the mass burn MWC's ranged from approximately 380 to 950 ug/dscm at 7 percent O₂. Mercury emission data from the three RDF MWC's (6 units) is presented in Table III. Outlet flue gas mercury concentrations for these RDF facilities ranged from 5 to 105 ug/dscm at 7 percent O₂, well below the range reported for the mass burn MWC's. No inlet flue gas mercury concentration data were available for any of the six facilities; hence, no mercury removal efficiencies could be calculated.

OPERATIONAL FACTORS RELATED TO MERCURY EMISSIONS CONTROL

The primary purpose of the U.S. EPA/EC test program conducted at MID-CT was to aid both agencies in the development of regulations for MWC facilities. In addition to establishing an emissions baseline for a new RDF-fired facility, the goals of the test program included evaluation of design and operating parameters, and the establishment of design and operating criteria for combustion and flue gas cleaning systems. MID-CT was the third MWC selected for evaluation under EC's National Incinerator Testing and Evaluation Program (NITEP), which had previously examined the two-stage combustion facility in Parksdale, Prince Edward Island, Canada and the moving grate mass-burn facility in Quebec City, Canada. The U.S. EPA had previously analyzed data from the mass burn MWC's in Marion County, OR and Millbury, MA, as well as the RDF MWC in Biddeford, ME.

A two-phased approach was used in the NITEP testing program at MID-CT. Twenty-eight characterization tests were conducted in January 1989 to provide information on an RDF MWC under a wide range of operating conditions. These data were then used in the process of selecting process scenarios to be examined during the performance testing phase. A total of 13 valid performance test runs were conducted during the period of February 13 to March 1, 1989. During some of the performance tests, the combustion and air pollution control systems at the facility were deliberately operated under "poor" conditions in order to assess the effect of various parameters upon emission levels.

Streams and locations sampled during testing included the RDF feed, pond water, lime slurry feed, grate siftings, economizer ash, dry and wet bottom ash, fabric filter ash, air preheater inlet, spray dryer inlet and fabric filter outlet. Concurrent with the sampling, a data acquisition system was used to record process data and continuous emission monitoring data from the spray dryer inlet, spray dryer outlet and fabric filter outlet locations. The large volume of data collected was statistically analyzed using single linear regression and multiple linear regression to

develop coefficients of correlation and determination between emission and process parameters. These data and determinations were used in the development of the New Source Performance Standards (NSPS) and emission guidelines for new and existing RDF MWC's, respectively, which were adopted by the U.S. EPA on January 11, 1991.

In accordance with the Clean Air Act Amendments of 1990, the U.S. EPA must adopt specific mercury emission standards for new and existing MWC's by mid-November of 1991. The U.S. EPA is currently studying mercury emissions data and potential mercury emission control technologies, such as the injection of sodium sulfide or activated carbon into the combustion flue gas. None of these technologies are currently being used at an MWC in the United States and they have only been used at a limited number of MWC's in Europe and Canada. Also under study are the factors which affect mercury removal and explain the apparently enhanced mercury removal at RDF MWC's as compared to mass burn MWC's.

Although stating that their exact effects are unclear, it is asserted by the U.S. EPA that factors such as combustion efficiency and the type and operation of air pollution control equipment affect mercury removal. It is purported that good particulate matter control, low temperatures in the control system, and the level of carbon in the flyash are associated with enhanced mercury removal efficiency. It is reasoned that a combination of low operating temperature of the particulate matter control device and higher levels of carbon in the flyash enhance mercury adsorption onto the particulate matter which is then removed from the flue gas by the particulate matter control device. This theory would support the higher mercury control efficiencies noted at RDF MWC's, as compared to mass burn MWC's, in that suspension firing of RDF results in slightly greater amounts of flyash containing higher levels of carbon than at mass burn MWC's. However, the concentration of flyash in the uncontrolled flue gas stream at RDF MWC's is significantly greater than at mass burn MWC's because of the reduced excess air levels at which RDF MWC's are typically operated. Most of the unburned carbon remaining at mass burn MWC's is contained in the bottom ash stream and is unavailable for functioning in an adsorptive capacity.

Data collected during the NITEP test program at MID-CT partially supports the U.S. EPA's theory of mercury removal from MWC flue gas. Data relevant to this discussion is presented in Table IV. The flue gas carbon content data presented in Column 4 of Table IV for each performance test was calculated by multiplying the tested values of percent carbon in flyash by the measured rates of flyash produced during each test run. Measurements of percent carbon in the ash were based on loss-on-ignition measurements and ranged from 4.26 to 10.45 percent. It has been noted by Radian Corporation that much of loss-on-ignition is suspected to be water of hydration in the collected slurry solids and, therefore, using these ash samples to estimate percent carbon in the ash may cause an overestimate.

The carbon content of the ash collected in the boiler economizer, prior to the introduction of lime slurry in the spray dryer, ranged from 0.96 to 4.39 percent.

Statistical analysis of the NITEP data from MID-CT using single regression analysis indicated that the only individual operating variables which showed a good correlation with mercury emissions removal were decreasing operating temperatures of the air pollution control system, both DS outlet ($R^2 = 0.550$) and FF outlet ($R^2 = 0.525$) and the fabric filter ash rate ($R^2 = 0.687$). The correlation between mercury removal and DS outlet temperature is pictured in Figure 2.

Mercury removal did not correlate with percent carbon in flyash. As previously mentioned, the data on percent carbon in flyash is suspect because of potential interferences associated with the test method. It is interesting to note that the calculated flue gas carbon content values presented in Column 4 of Table IV are significantly higher than the rates of carbon injection (6 to 105 mg/Nm³) used at mass burn MWC's in Europe to demonstrate the effectiveness of carbon injection as a post-combustion control technology. This fact may help explain the consistently high mercury removal efficiencies achieved at MID-CT.

Multiple regression analysis of the NITEP data from MID-CT showed a very good correlation ($R^2 = 0.89$) between mercury removal and decreasing flue gas temperature (spray dryer outlet), increasing percent carbon in flyash, and decreasing stoichiometric ratio. Stoichiometric ratio is believed to affect mercury emissions in that calcium contained in excess amounts of lime may react with mercuric chloride ($HgCl_2$) and form calcium chloride ($CaCl_2$), thus liberating mercury vapor. Although the results of the multiple regression analysis tend to support the U. S. EPA's hypothesis on the mechanism of mercury removal from the flue gas from MWC's, the questionable validity of the percent carbon in flyash data does not permit a firm conclusion to be reached. Additional research is clearly necessary to gain a more thorough understanding of the operating variables which affect the control of mercury at MWC's.

CONCLUSION

The control of mercury emissions from MWC's is an issue of considerable debate. Although mercury emissions from MWC's represent a small fraction of the global annual mercury emissions into the environment, a great deal of focus is being placed on minimizing mercury emissions from MWC's by reformulating consumer products which contain mercury and source separation of household batteries. The U. S. EPA is evaluating mercury emissions data and potential mercury emission control technologies in view of a mandate to adopt mercury emission standards for MWC's by mid-November 1991.

Data indicate that potential air emissions of mercury at RDF MWC's are effectively minimized. Effective control of mercury is being accomplished by a combination of processing MSW to remove mercury-bearing noncombustibles and efficiently removing mercury from the MWC flue gas. Although the precise mechanisms for mercury removal from MWC's is not clear, it appears that good particulate removal, reduced control system operating temperature, carbon level in flyash, and stoichiometric ratio of scrubber reagent are factors which affect mercury removal. Additional research is necessary to better understand the control of mercury emissions from MWC's.

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FIGURE 1

Municipal Solid Waste Processing - Single Line

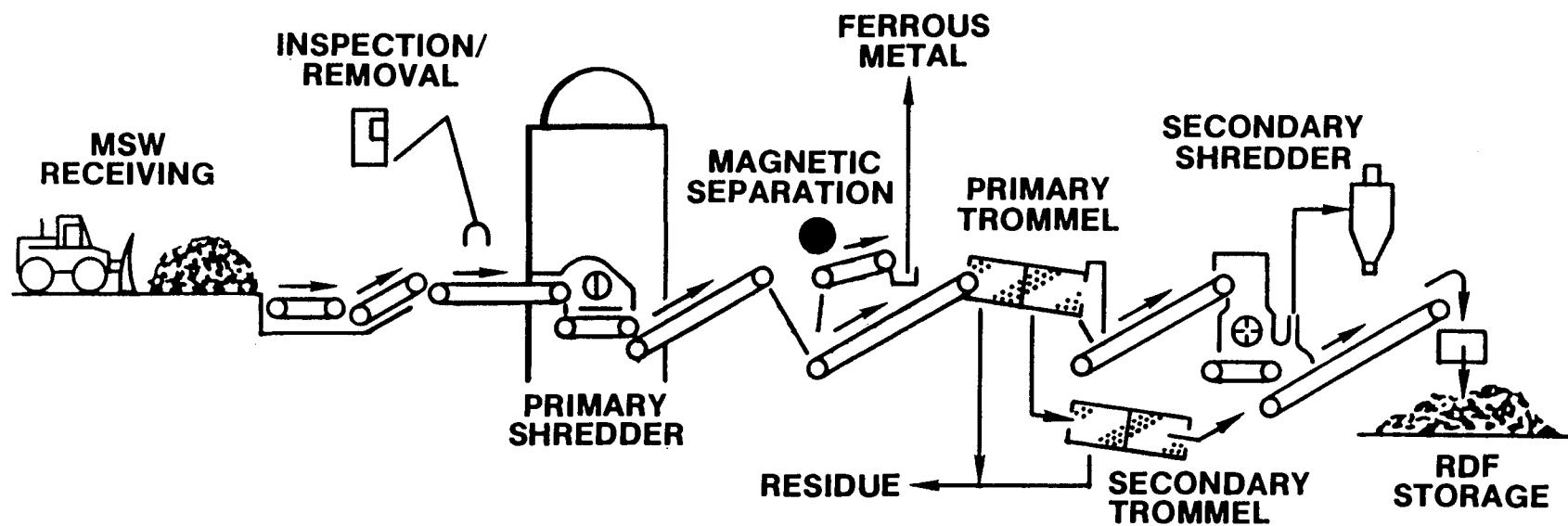


FIGURE 2

Mercury Removal Efficiency vs Temperature At SDA Outlet

LZ1

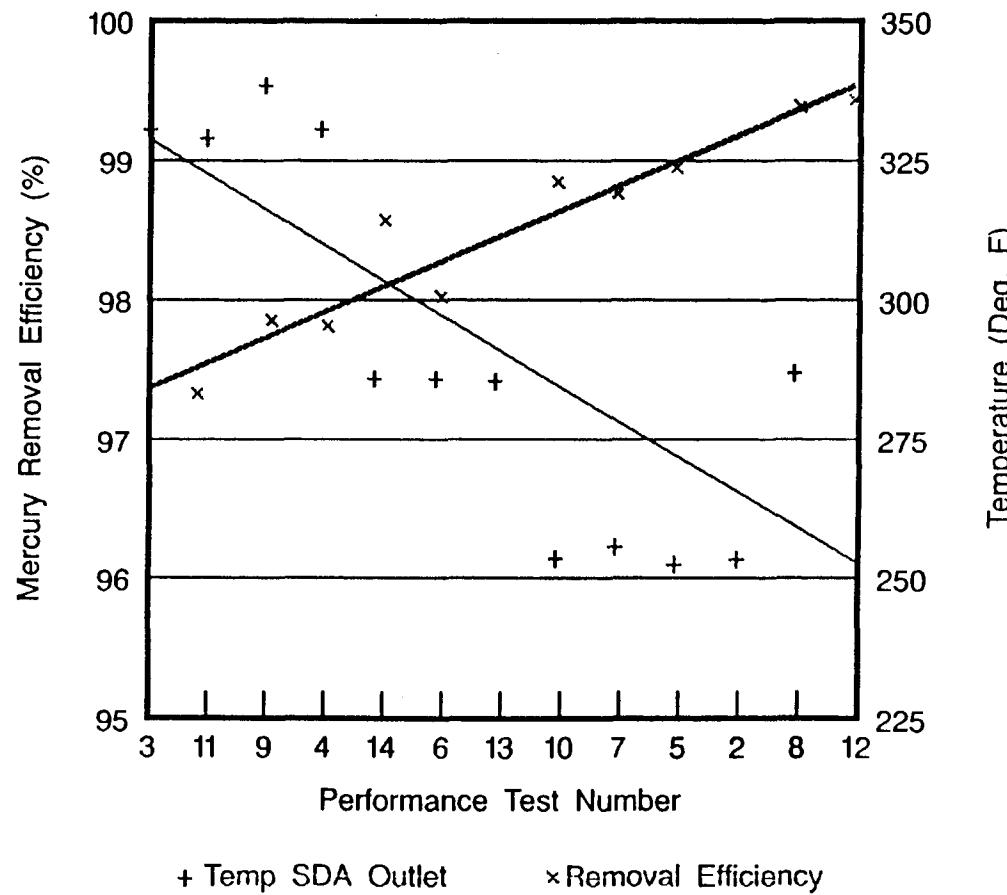


TABLE I MERCURY DISTRIBUTION AT MID-CT FACILITY

MSW	2.4 LB/1,000 TON MSW
FERROUS METAL	49%
PROCESS RESIDUE	4%
RDF	47%

TABLE II MERCURY EMISSIONS DATA FROM EPA/EC
TEST PROGRAM AT MID-CONNECTICUT FACILITY (2/89)

TEST RUN	INLET MERCURY* (ug/dscm)	OUTLET MERCURY* (ug/dscm)	REMOVAL EFFICIENCY (%)
PT-02	740	6.9	99.1
PT-03	579	22.7	96.1
PT-04	636	14.7	97.7
PT-05	661	7.1	98.9
PT-06	597	12.2	98.0
PT-07	597	7.7	98.7
PT-08	659	4.5	99.3
PT-09	667	15.1	97.7
PT-10	745	8.8	98.8
PT-11	683	18.9	97.2
PT-12	498	3.5	99.3
PT-13	557	11.7	97.9
PT-14	<u>945</u>	<u>14.2</u>	<u>98.5</u>
AVERAGE	659	11.4	98.3

* CORRECTED TO 7% O₂

TABLE III MERCURY EMISSIONS DATA
FROM RDF MWC's WITH DS/ESP

FACILITY	NUMBER OF TESTS	OUTLET MERCURY ⁺ (ug/dscm)
HONOLULU, UNIT 1	3	5
HONOLULU, UNIT 2	3	7
SEMASS, UNIT 1	3	59
SEMASS, UNIT 2	3	105
WEST PALM BEACH, UNIT 1	3	56
WEST PALM BEACH, UNIT 2	3	23

* CORRECTED TO 7% O₂

TABLE IV OPERATING DATA FROM EPA/EC
TEST PROGRAM AT MID-CONNECTICUT FACILITY

TEST RUN	Hg REMOVAL (%)	FABRIC FILTER OUTLET TEMPERATURE (°F)	FLUE GAS CARBON CONTENT (mg/Nm ³)	STOICHIOMETRIC RATIO
PT-02	99.1	225	NC	0.81
PT-03	96.1	282	NC	2.47
PT-04	97.7	287	735	1.81
PT-05	98.9	220	194	0.18
PT-06	98.0	253	810	2.50
PT-07	98.7	223	378	1.44
PT-08	99.3	245	143	0.65
PT-09	97.7	284	803	0.67
PT-10	98.8	223	321	0.66
PT-11	97.2	285	640	2.64
PT-12	99.3	247	148	0.74
PT-13	97.9	233	NC	1.13
PT-14	98.5	247	782	0.81

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

MERCURY EMISSION CONTROL

SODIUM SULPHIDE DOSING AT THE HÖGDALEN PLANT IN STOCKHOLM

By: Christer Andersson, Högdalen Plant
Bengt Weimer, Högdalen Plant

ABSTRACT

Sodium sulphide dosing is employed at the Högdalen Plant in Stockholm with the aim of minimizing mercury emissions. Dosing has been in progress since 1986, and has been employed continuously since the beginning of 1988. The following typical problems were initially encountered

- Working environment
- Various handling problems
- Sludge precipitation
- Deposition at the dosing point

During 1988 - 1989, sodium sulphide was used for all three lines. However, due to the low emission values on the two older lines (P1/P2, VKW/Deutsche Babcock), even without sodium sulphide, dosing of sodium sulphide is now employed only on line 3 (Martin/Werkle-Werk). The mercury emission values are usually below 30 µm/mm³ of dry gas at 10% CO, and at a collecting efficiency of approximately 80%. The annual cost of sodium sulphide dosing is approximately SEK 4.60 per tonne of refuse burned (including capital cost).

BACKGROUND

The first plant for domestic refuse incineration in Sweden and Stockholm was built at the beginning of the century in Lövsta, north-west of central Stockholm. The plant was a pure incineration plant. New furnaces were successively built as the quantities of refuse increased. By the early 1960s, the quantities of refuse had increased so much that a new plant had to be built to meet the need for incineration capacity. For transport reasons, the new plant was to be sited south of central Stockholm.

Construction of the Högdalen Plant began during the latter part of the 1960s and was ready for commissioning in the summer of 1970. The plant consisted of two boilers (VWK/Deutsche Babcock), each with a capacity of 11 tonnes of refuse per hour or 125 000 tonnes annually. The boilers generated superheated steam (at 36 bar and 360°C) which was supplied to a 24 MW turbo-generator. A two-stage electrostatic precipitator, with cyclone batteries downstream of it, was installed for flue gas treatment. The buildings and turbine were designed to enable two additional boilers to be installed.

The plant was taken over by Stockholm Energi AB in the mid-1970s, and was converted for simultaneous generation of electric power and heat for district heating. Stockholm Energi AB is Sweden's third largest energy utility, and owns hydro-electric power stations, fossil-fired power plants, heat pump plants and shares in a nuclear power plant. The company is wholly owned by Stockholm City and supplies Stockholm with electric power, heat for district heating and town gas. The company has around 2500 employees and the turnover in 1989 was SEK 4 billion. In 1985, a third refuse-fired steam boiler (Martin/Werle-Werk) with a capacity of 15 tonnes of refuse per hour and generating steam at 36 bar and 360°C was built in Högdalen. As a result, the capacity of the plant increased to 250 000 tonnes annually. A system employing dry injection of sodium hydroxide and a fabric barrier filter (Fläkt Industri AB) downstream of it were installed for flue gas treatment as shown in Fig. 1.

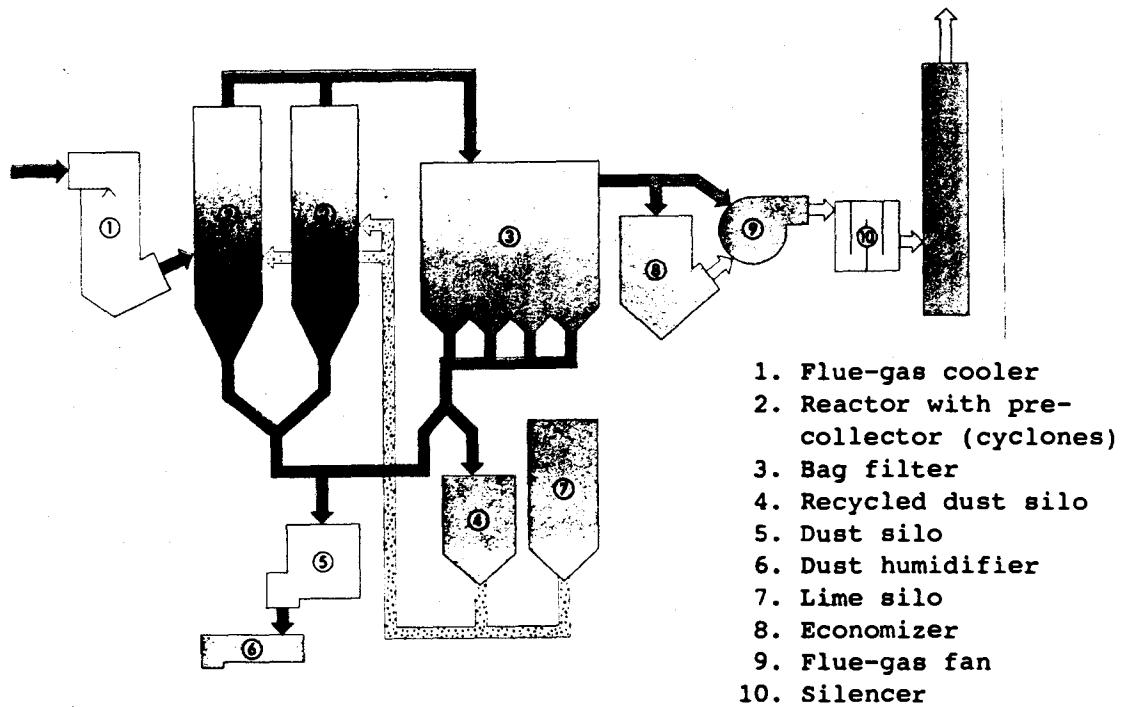


Fig. 1. Flow diagram for the flue-gas treatment system.

MERCURY EMISSION CONTROL

In conjunction with the first emission measurements in the spring of 1986, it was found that the mercury emissions exceeded the guaranteed values (50 µg/m³ of dry gas at s.t.p. at 10% CO₂). The supplier, Fläkt Industri AB, carried out tests on employing almost 10 different additives. Two of these - pulverized activated charcoal and sodium sulphide in a water solution - were selected for further full-scale trials. Activated charcoal was added to the flue gases upstream of the cooling tower, and sodium sulphide solution was dosed into the cooling water in the cooling tower. The results of the trials (Table 1) and commercial considerations led to the installation of a system for the preparation and dosing and sodium sulphide solution at the Högdalen Plant.

Type	Additives Rate, l/h	Average outlet concentration of total mercury in mg/m ³ at s.t.p.	
		t = 170 °C	t = 150 °C
Na ₂ S solution	10	90	370
	20	45	10
	40	15	5
Pulverized activated charcoal	5	120	55
	15	10*	5*

Table 1. Results of testing various additives.

The originally low or insignificant collection of mercury was considered to be due to the low content of unburned carbon in the fly ash from the boiler.

STAGE 1. SYSTEM DESCRIPTION:

Sodium sulphide is supplied to the plant in the form of flakes (approx. 40% bound crystal water) in 25 kg plastic bags. The bags are cut open with a knife and the sodium sulphide flakes are conveyed by a pneumatic system (vacuum) to the storage silo.

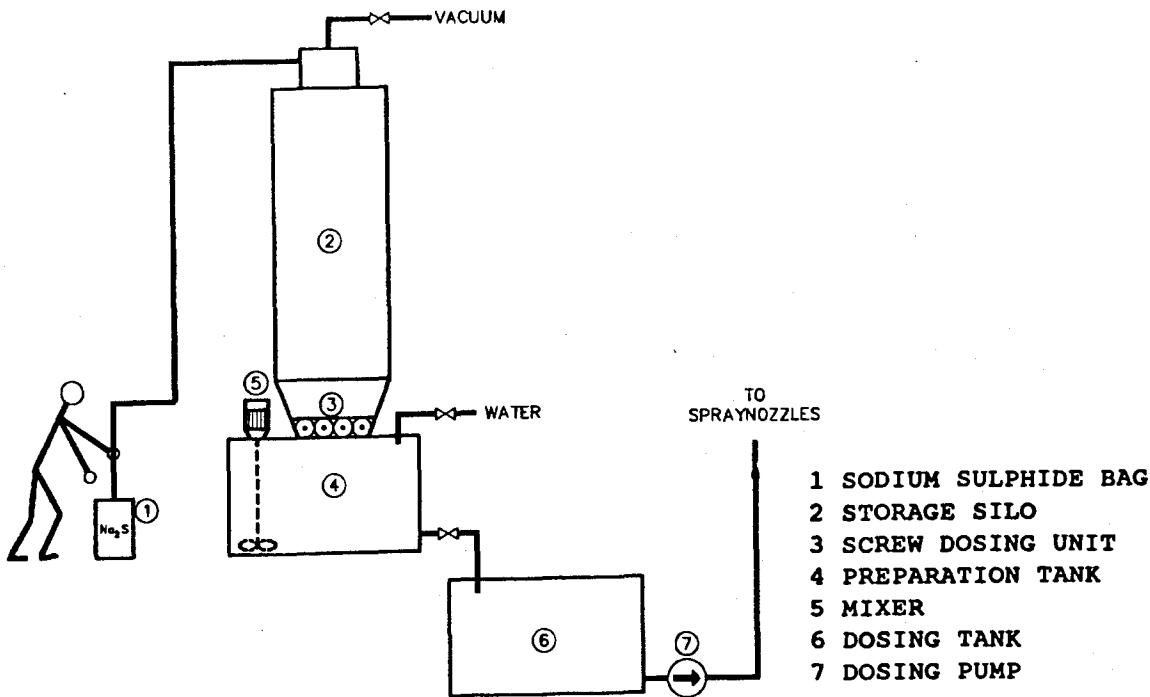


Fig. 2. Flow diagram showing the Na₂S plant

From the storage silo, the flakes are metered in batches by a screw dosing unit to the mixing tank, in which the flakes are dissolved in water with the assistance of a mixer to produce a solution with a concentration of approx. 6%. After mixing to ensure that the flakes are dissolved, the solution is discharged to a dosing tank. From the dosing tank, the solution is delivered by a steel centrifugal pump to the injection nozzles in the cooling tower. The pump capacity is controlled by a mechanical variator. The injection nozzles are of two-media type, in which the solution is atomized by means of compressed air. The nozzles are made of stainless steel. The solution is sprayed into the upper part of the evaporative flue-gas cooler. The temperature at the dosing point is 190 - 225°C, depending on the load and the degree of boiler fouling. Dosing is normally carried out at the rate of 20 litres of solution per hour.

DESCRIPTION OF PROBLEMS:

Hydrogen sulphide is emitted when the sodium sulphide bags are cut open, which is perceived as a working environment problem. To eliminate this, an agreement was concluded with the chemicals supplier that the sodium sulphide would be delivered in 500 kg safe-bin containers. From the container, the flakes are conveyed to the storage silo in an enclosed pneumatic system. A vacuum pump (central vacuum-cleaning system) raises a vacuum in the system and also in the storage silo, and the conveying air is drawn in at the container. This system also gave rise to problems, since

the pressure reduction caused the hygroscopic sulphide to absorb some water from the conveying air, and the flakes were then "cemented together" into large lumps. The screw dosing unit also gave rise to problems caused by clogging by humid sulphide flakes. Due to the above problems, the operating time of the system was very short. When a new flue gas treatment system was purchased from Fläkt Industri AB for the two older boilers (Fig. 3) of basically the same design as the existing system, it was decided that an entirely new sodium sulphide system which is common to all three lines would be installed.

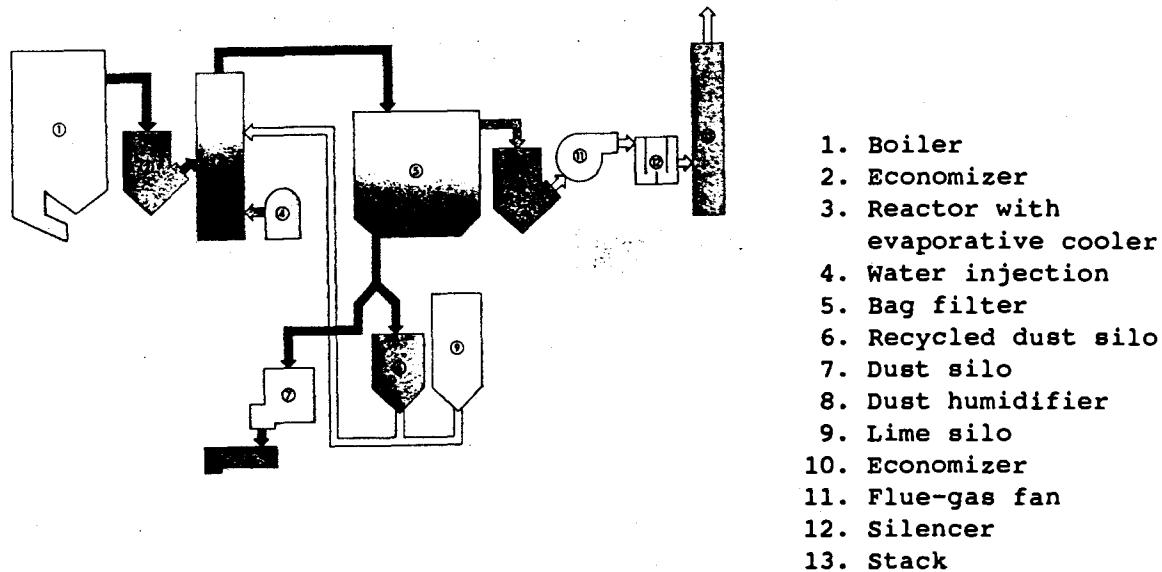


Fig. 3. Flow diagram for the flue-gas treatment system on P1/P2

STAGE 2. SYSTEM DESCRIPTION:

The preparation and dosing system is accommodated in a separate part of the building, with its own comfort ventilation system (Fig. 4).

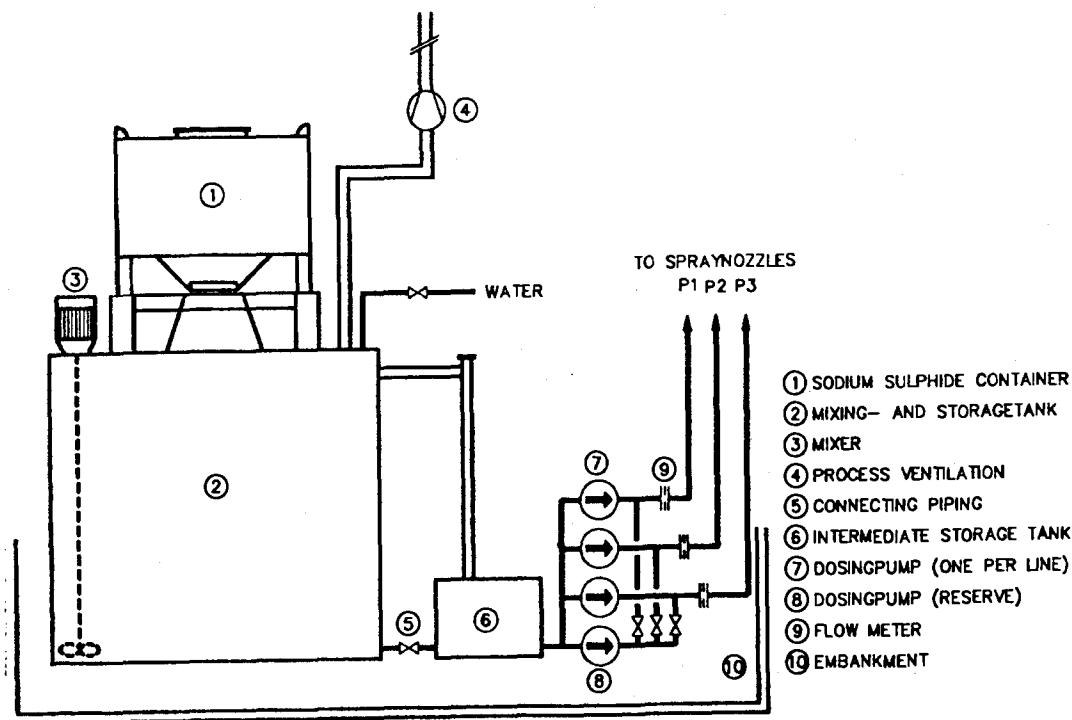


Fig. 4. Flow diagram for stage 2 of the Na₂S plant.

The plant is controlled from a control desk located outside the building, with a window provided for supervision. The full container is placed on top of the mixing and storage tank by means of the overhead travelling crane. The slide damper at the bottom of the container is opened by means of a pneumatic actuator, and the container contents drop into the tank. At the same time, a water valve is opened, and a valve is used to separate the mixing tank from the intermediate storage tank, in order to prevent undissolved sodium sulphide from being drawn into the pumps. The mixing tank is equipped with a continuous mixer in the form of a propeller. The mixing tank is provided with separate process ventilation in order to eliminate the problem of smell. When the liquid level in the mixing tank is normal, the water supply is shut off, and after 30 minutes of continued mixing, the communicating line between the mixing and intermediate storage tanks is opened. The pumps - one per boiler plus one on stand-by - are of steel centrifugal type, with a mechanical variator for flow control. The entire system, including tanks, pipes and valves, is made of stainless steel. The sodium sulphide solution which is dosed to lines 1 and 2 (VKW/Deutsche Babcock, 1970) is mixed with additional water and is sprayed into the combined conditioning towers/reactors by means of a nozzle lance equipped with two spray nozzles. The inlet flue gas temperature is around 140°C, and when the water is sprayed in, the temperature drops to around 125°C. Since 1988, the evaporative cooler of line 3 (Martin/Werle-Werk, 1985) has been replaced by a heat exchanger (recovery boiler) to enable all energy to be utilized and to allow the flue gases to be treated at as low a temperature as possible. The sodium sulphide solution is sprayed in by two nozzle lances equipped with two-media nozzles and located in a horizontal

flue-gas duct between the heat exchanger and the reactors. The temperature at this point is around 140°C. Compressed air is used for atomization. The nozzles are made of Hastalloy C, and the nozzle lance is made of conventional stainless steel.

DESCRIPTION OF PROBLEMS:

The first major problem that occurred on the new plant was that a relatively large amount of sludge occurred when the sodium sulphide was dissolved. The sludge originated from impurities in the sodium sulphide flakes and also from metal ions that were precipitated out of the water. This sludge clogged the pumps and nozzles. Although change-over to a better quality of sodium sulphide reduced the problem, it did not solve it entirely. To reduce further the risk of sludge formation, the water was replaced by partially demineralized water. The flow rate from the dosing pumps was difficult to adjust and was very sensitive to pressure changes. To ensure more uniform dosing, the pumps were replaced by piston pumps. To reduce the pressure variations from these pumps, the connections to the pumps were changed to rubber hoses. In conjunction with the delivery tests on the flue gas treatment system for lines 1 and 2 (VKW, Deutsche Babcock), measurements were carried out with and without the addition of sodium sulphide. In all cases, the mercury emissions proved to be very low (Table 2). For particulars of the measurement method, see Appendix 1.

Date	Boiler no:	Raw gas Hg total, ug/m ³ of dry gas at s.t.p.	Clean gas	Sulphide dosing	Filter temp.	Boiler load tonne of steam/h
				l/h	°C	
890420	2	200	1	20	125	31
890424	1	250	1	20	125	31
890511	2	190	2	20	142	31
890516	2	290	3	0	142	30
890519	2	180	2	0	125	31

Table 2. Mercury emission on P1/P2

In view of these results, and similar results from other plants in Sweden, the dosing of sodium sulphide into these boilers was abandoned. The high collection of mercury is due to the relatively high content of unburned carbon in the flue gases. On boiler 3, a further problem of deposition on nozzles and surrounding flue gas duct persisted. In order to solve these problems, the nozzle lances were modified so that they were supplied with preheated flushing air in order to prevent the condensation of flue gas on the nozzle lances, with resulting dust deposition which, in turn, disturbed the flow around the nozzle and led to further deposition in the flue gas duct. In addition, the concentration of the sodium sulphide solution was increased to around 10%. As a result, less water need be evaporated and, by using a higher compressed air pressure, quick evaporation of the liquid droplets is achieved.

RESULTS

The data from all mercury measurements carried out on P3 is shown in Table 3.

**SUMMARY OF Hg MEASUREMENTS ON BOILER 3
AT THE HÖGDALEN PLANT**

DATE	RAW GAS	CLEAN GAS	SULPHIDE DOSING	FILTER TEMP.	BOILER LOAD
	Hg total, ug/m ³ of dry gas at s.t.p.		l/h	°C	Boiler load, tonne of steam/h
860211	-	86	-	173	52
860528	162	150	-	158	52
860825	-	58	20	151	54
860827	308	33	20	173	55
860829	414	51	20	174	54
860901	-	46	15	151	53
861216	-	25	20	168	55
870226	277	3	20	123	55
870309	111	94	-	168	55
870428	185	48	20	168	55
870915	327	27	20	169	55
871221	-	124	-	169	55
880412	238	122	-	169	55
880518	330	20	20	163	55
880824	108	16	20	155	55
880825	-	7	20	155	55
880825	-	20	-	155	55
881004	91	12	30	144	49
891018	141	127	20	132	39
891122	172	4	40	138	53
900206	-	8	20	138	55
900207	-	7	20	128	35
900208	-	5	40	127	35
900628	-	23	40	130	50

Table 3. Mercury emissions on P3.

High emission values were found in all cases of high flue-gas temperature (above 155°C) and without sulphide addition. Reading 880825 without sulphide dosing was taken immediately after a measurement with sulphide dosing, and the results are therefore uncertain. The results of reading 891018 deviate substantially from other comparable readings. While these readings were being taken, the boiler load was increased from minimum load (approx. 30 t/h of steam) to full load (approx. 55 t/h of steam), which resulted in a temperature increase. This may possibly be responsible for the high emission value. For particulars of the measurement method, see Appendix 1. In addition to the equipment at the Högdalen Plant, other equipment for the preparation and dosing of sodium sulphide solution has

been installed in Sweden in Köping, Avesta and Umeå. All plants are equipped with dry flue-gas treatment systems (in Avesta, followed by a condensation stage).

ECONOMICS

The cost of the existing plant in the Högdalen Plant, including the building, is estimated to be SEK 2 million. Apart from the problems mentioned earlier, the maintenance requirements are very low. The time that the operations personnel have to devote to the plant is confined to the mixing of new solution and the cleaning of nozzles and nozzle lances twice a week. The costs are summarized in Table 4. The total cost is SEK 4.60 per tonne of fuel incinerated. This figure is based on the entire capital cost being allocated to one line (P3). If sodium sulphide were dosed to the other two lines, the cost would drop to SEK 3.20 per tonne of refuse incinerated.

Capa- city	Mainten- ance	Opera- tion	Na ₂ S	Water	Total	Gross refuse, tonnes	Cost, SEK/tonne
300	50	50	150	2	552	120 000	4.60

Table 4. Summary of costs (SEK x 1000, unless otherwise specified).

2.5 Mercury

The mercury in the flue gases is mainly in gaseous form. During sampling, part of the mercury is bound to the dust. The determination of total mercury content involves adding the dust-bound mercury to the gaseous mercury.

The gaseous mercury in the flue gases is determined in a sampled flow from dust sampling. The gas sample is taken from the dust-free gas at the outlet from the filter holder. The gas sample flow rate is 2 - 3 l/min. The gas sample passes through three absorption flasks connected in series. The first flask contains 10% by weight of sodium carbonate (soda) in distilled water. The water-soluble mercury is absorbed here. The other two flasks contain sulphuric-acid acidified sodium permanganate solution (6 g KMnO₄ in 10% by volume of H₂SO₄). Water-insoluble mercury is absorbed in these two flasks.

All test flasks are treated at around 450°C and the purity of the absorption solutions is checked before they leave our analysis laboratory.

Tests on metallic mercury in the sampling equipment used have revealed that Hg⁰ is not absorbed to any significant extent in the soda solution. On the other hand, more than 98% of the Hg⁰ is normally absorbed in the first permanganate flask. The second absorption flask serves only as a safety and monitoring unit.

The absorption flasks are sealed off by means of ground glass stoppers immediately after sampling, and are transported to the analysis laboratory.

Mercury bound to the dust is collected on a quartz-fibre flat filter. Before sampling, the filters are treated at 300°C, conditioned in a desiccator and weighed. After sampling, the filters are conditioned only in the desiccator and are weighed, so that the mercury retained will not be liberated.

The mercury bound during dust sampling is determined by the composition of the sample of dust and filter material. The entire sample of dust and filter material from the filter container is crushed to a homogeneous powder sample before analysis. Carefully weighed analysis samples are treated in a teflon bomb at 160°C for one hour with 50 ml of H₂O and 5 ml of HNO₃. The quantity of mercury in the solutions from the decomposition of the solid materials and the absorption solutions from the gaseous phase sampling are determined by flameless atom absorption. The mercury is driven out of the solution with nitrogen after reduction with boron hydride.

The mercury in the flue gas is reported in three fractions:

Hg_s is the mercury bound to the dust during sampling.

Hg_{aq} is the water-soluble mercury which has been absorbed in the soda solution.

Hg^0 is the mercury which has been absorbed in the permanganate solution during sampling.

Hg^+ is the calculated sum of Hg_s and Hg_{aq} . Hg^+ is a measure of the reactive quantity of mercury in the flue gas.

Hg_{tot} is the sum of Hg^0 and Hg^+ in the flue gas. This sum should represent a measure of how much mercury leaves with the flue gases from combustion, even though it is distributed differently due to reactions in the plant and during sampling.

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The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

CONTROL OF MERCURY AND DIOXIN EMISSIONS
FROM UNITED STATES AND EUROPEAN
MUNICIPAL SOLID WASTE INCINERATORS
BY SPRAY DRYER ABSORPTION SYSTEMS

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ABSTRACT

Incineration of Municipal Solids Waste (MSW) as a method of reducing disposal volume requirements and recovery of energy has been practiced extensively for many years in Europe and more recently in North America. Concerns of potential air pollution from this incineration have resulted in the promulgation of emission standards for a wide range of pollutants and the subsequent application of Spray Dryer Absorption (SDA) flue gas cleaning systems to control incinerator emissions. In Europe, where emission standards were adapted several years ago, SDA systems have been installed using both fabric filters or existing electrostatic precipitators as dust collectors. Emission standards have required stringent control of acid gases (HCl, HF, SO₂), particulate matter, trace metals (in particular mercury) and dioxins. SDA systems in operation have demonstrated the ability to achieve the required levels of control when either an electrostatic precipitator or fabric filter has been used as dust collector.

The paper will focus on the mercury and dioxin emissions, which have been achieved at three European and two United States SDA systems. The operating experience has shown that the SDA systems equipped with a single rotary atomizer per absorber can achieve high removal efficiencies of mercury and dioxins by proper control of spray dryer outlet temperature and by using a patented dry additive injection system.

ABSTRACT

Incineration of Municipal Solids Waste (MSW) as a method of reducing disposal volume requirements and recovery of energy has been practiced extensively for many years in Europe and more recently in North America. Concerns of potential air pollution from this incineration have resulted in the promulgation of emission standards for a wide range of pollutants and the subsequent application of Spray Dryer Absorption (SDA) flue gas cleaning systems to control incinerator emissions. In Europe, where emission standards were adapted several years ago, SDA systems have been installed using both fabric filters or existing electrostatic precipitators as dust collectors. Emission standards have required stringent control of acid gases (HCl, HF, SO₂), particulate matter, trace metals (in particular mercury) and dioxins. SDA systems in operation have demonstrated the ability to achieve the required levels of control when either an electrostatic precipitator or fabric filter has been used as dust collector.

The paper will focus on the mercury and dioxin emissions, which have been achieved at three European and two United States SDA systems. The operating experience has shown that the SDA systems equipped with a single rotary atomizer per absorber can achieve high removal efficiencies of mercury and dioxins by proper control of spray dryer outlet temperature and by using a patented dry additive injection system.

INTRODUCTION

Incineration of municipal solid waste (MSW) has been utilized for many years in Europe and more recently in North America to substantially reduce the volume of waste to be disposed of while at the same time producing energy in the form of steam or electricity. As the application of incinerators has increased, concerns have been raised over potential air pollution impacts associated from their use. This has led to the promulgation of emissions limits and control requirements for a wide range of pollutants, first in the European countries, and more recently in the states and provinces in North America. Spray Dryer Absorption (SDA) flue gas cleaning systems have been successfully applied to control incinerator air pollutants.

Joy Environmental Equipment Company and A/S Niro Atomizer have been jointly developing SDA gas cleaning systems since 1977 and have successfully applied this technology for control of acid gases, particulates and trace element emissions from coal-fired boilers, mass-burn and RDF-fired MSW incinerators and hazardous waste incinerators. Today more than 24 MSW incinerator trains are in operation employing this technology with an additional 22 trains under construction. The majority of the operating units have successfully completed performance tests and operate reliably while maintaining the incinerators in compliance with local air pollution regulations. This success can be attributed to Niro's vast knowledge of spray drying and Joy's extensive experience in application of particulate control technologies to a wide range of processes.

The systems applied in Europe and North America, while utilizing the same basic technology, incorporate many different design features for each particular application. The majority of the systems installed in Europe were retrofitted to existing incinerators where increasingly more stringent air pollution regulations require acid gas and trace metal emission controls on both new and existing plants. These systems (where possible) utilize existing electrostatic precipitators either as the main dust collector downstream of the spray dryer or as a precollector upstream of the spray dryer. A few of the newer installations employ a fabric filter as the dust collector.

In North America the opposite is true. The majority of SDA applications are on new incinerators. Whereas the first four Joy/Niro systems to start-up in the United States have electrostatic precipitators as dust collectors, the remaining trains under construction are equipped with fabric filters.

This paper presents a description of the SDA process and addresses key design parameters for successful applications. Design parameters and emission requirements from three European and two North American installations are presented. Results of mercury and dioxin testing on the European and North American MSW incinerators

are being reported. Effects on the removal efficiency of mercury and dioxins of a dry additive injection system are documented.

SYSTEM DESCRIPTION

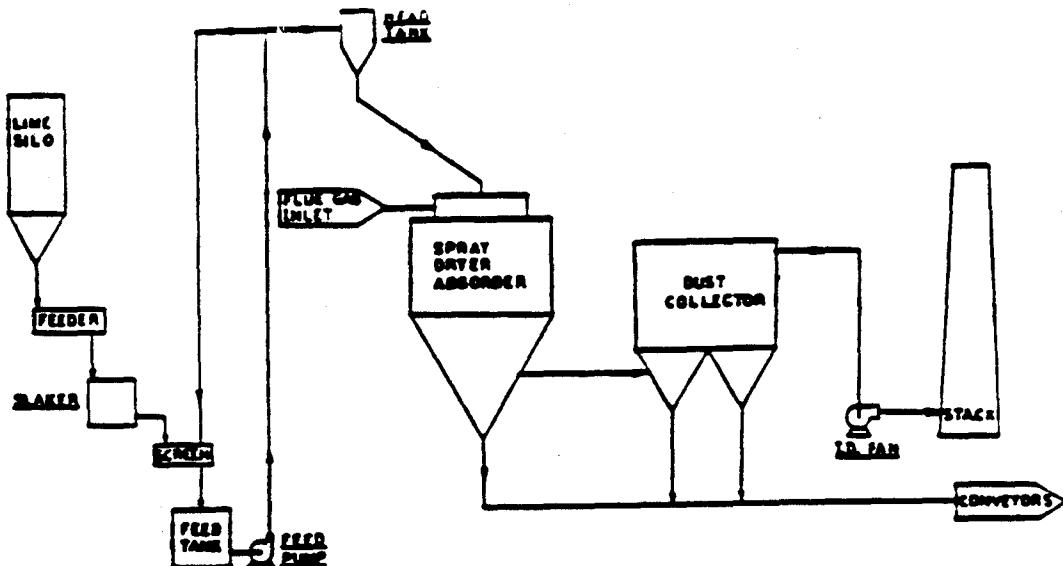
The Zurich, Amager and Kassel SDA systems are all retrofit applications while the Semass and Palm Beach are complete new incinerator installations. All plants incorporate design features common to Joy/Niro acid gas cleaning systems (1,2,3). These features include:

- Use of a single spray dryer per incinerator train.
- Use of a single rotary atomizer per spray dryer to produce a cloud of fine slurry droplets.
- Use of a single gas disperser to control the shape of the droplet cloud and achieve mixing between the gas and the slurry.
- Inclusion of a two-point product discharge design to ensure an open gas passage.
- Sufficient spray dryer gas residence time to ensure adequate product drying.
- Use of lime reagent to achieve acid gas removal.

The Zurich, Amager, Palm Beach and Semass plants are designed as single-pass systems, whereas the Kassel plant has the capability to operate in either the single-pass or partial-product recycle mode. The Zurich and Amager systems have retrofitted an additive system for mercury and dioxin control. Figure 1 shows a simplified flow sheet of the basic single-pass system.

The SDA flue gas cleaning system consists of a reagent preparation system, a spray dryer absorber, a dust collector and an ash transport system. Typically there is one spray dryer and dust collector per incinerator train and common reagent preparation and ash transport systems per multiple trains.

Quick lime is delivered by truck and conveyed pneumatically to the storage silo. From the storage silo the lime is sent to a paste or detention slaker, where a 20-30% lime slurry is prepared. The lime slurry is either stored in a lime milk tank or transferred directly to the feed tank. The final dilution of the lime slurry is accomplished either in a small dilution head tank located above the spray dryer absorber or in the rotary atomizer utilizing a unique dual-liquid distributor. By using the latter method, lime slurry and water are mixed directly in the atomizer wheel. The dilution in the European plants is controlled by a signal from the HCl-analyzer located in the stack, while the American plants use an SO₂ stack monitor for control.



*Figure 1
Simplified Process Flow Diagram*

From the head tank the lime slurry flows by gravity to the atomizer. Control of the total liquid flow to the atomizer is based on a spray dryer outlet temperature control. The atomized lime slurry enters the spray dryer where it mixes with the hot incoming gas, simultaneously reacts with acid gases present and prior to exiting the spray dryer absorber. A single rotary atomizer per absorber module makes the control of the process and the uniform mixing of the slurry droplets and flue gas extremely efficient. Operating experience has shown that SDA systems with a single rotary atomizer per module are able to control spray dryer absorber outlet temperatures to lower levels than systems with multiple atomizing devices, such as dual-fluid nozzles. The extremely good contact in the spray dryer absorber utilizing a rotary atomizer is of utmost importance for achieving high mercury and dioxin removal efficiencies.

A portion of the dry product is removed from the bottom of the spray dryer while the majority of the product is carried over to the dust collector. Additional acid gas absorption takes place in the dust collector and dust is removed from the flue gas. The dry product from the spray dryer absorber and the dust collector is conveyed either mechanically or pneumatically to a waste disposal silo.

For additional mercury and dioxin control, the SDA system can be retrofitted with an add-on control system. This consists of a patented, dry additive system (4) for injection of the additive upstream of the spray dryer absorber. The previously mentioned extremely efficient mixing of flue gas, additive and slurry droplets inside the spray dryer absorber provides optimum conditions for contact between the additive and the dioxins and mercury present in the flue gas.

As mentioned earlier in the system description, the unit at Kassel recycles a portion of the dry product back to the feed system to improve reagent consumption. The Amager system utilizes hydrated lime as reagent; however, they are presently retrofitting a slaking system utilizing powdered quicklime. The Kassel SDA is retrofitted downstream of existing electrostatic precipitators, the Zurich plant is utilizing the existing electrostatic precipitator (EP) for dust control, whereas the electrostatic precipitator at the Amager system was scrapped and replaced by a SDA and pulse-jet fabric filter (PJF). The Semass and Palm Beach systems utilize Joy/BSH rigid-frame precipitators downstream of the spray dryers.

Figure 2 presents design conditions for the various acid gas pollutants and the required removal efficiencies. The European plants are designed to achieve a set emission rate on a one-half hour averaging period for each pollutant, while the Semass plant is based on a three-hour averaging period. The Kassel SDA system has precollector and is utilizing dry product recycle which increases the chloride concentration in the feed slurry. Therefore, the spray dryer outlet temperature is controlled to a minimum of 275° F to ensure proper drying.

In addition to the acid gas and dust removal requirements, some regulatory agencies have placed limits on trace metal emissions from MSW incinerators. The approach in Europe has been to separate heavy metals in three major classes and set emission levels for each of these classes. In some cases, specific metal emission levels have also been set. The emission limits include both dust-bound and vapor-phase emissions. Furthermore, European regulatory agencies limit the emissions of dioxins from MSW incineration (6). Figure 3 presents the trace metal emission requirements of the European installations.

The permits for Semass and Palm Beach did not have specific stack emission requirements for metals and dioxins, but that does not mean these issues were not addressed. Semass has a 608 ng/NM³ stack emission limitation as well as an ambient air quality standard listed in its permit.

TEST RESULTS

Mercury

Zurich

After start-up, the SDA system in Zurich, Switzerland, was operated at various outlet temperatures to verify the impact of outlet temperature on efficiency of acid gas and mercury removal. These tests confirmed earlier work carried out at the pilot plant level; i.e., the lower the SDA outlet temperature, the higher the removal efficiency for acid gases and mercury. The system was successfully operated at SDA outlet temperatures as low as 230° F.

Project	Semass Rochester, Mass.	W. Palm Beach, Florida	Zurich Josephstr. Switzerland	Kassel City of Germany	Amager City of Denmark
Type Waste Size, TPD	RDF 2x900	RDF 2x1000	MSW 400	MSW 2x300	MSW 300
<u>Inlet Flue Gas Conditions</u>					
Flue Gas Flow (Nominal), acfm	212,000	197,000	103,000	2x67,000	1x82,000
Temperature, °F	350	350	430-570	460	356-446
Fly Ash, gr/scf	10.0	7.2	1.0	0.02	3.5
HCl					
Average, ppm	400	710	500	500	750
Maximum, ppm	1,000	1,290	700	1150	1150
SO ₂					
Average, ppm	110	240	--	200	--
Maximum, ppm	330	430	200	500	140
HF					
Maximum, ppm	--	40	15	10	--

Figure 2
Design Conditions

Project	Semass Rochester, Mass.	W. Palm Beach, Florida	Zurich Josephstr. Switzerland	Kassel City of Germany	Amager City of Denmark
Type Waste Size, TPD	RDF 2x900	RDF 2x1000	MSW 400	MSW 2x300	MSW 300
<u>Outlet Flue Gas Conditions</u>					
Reference Conditions	12% CO ₂ dry	12% CO ₂ dry	11% O ₂ dry	11% O ₂ dry	11% O ₂ dry
Temperature, °F	265	255	285	275	284
HCl,	ppm % removal	50 90	-- 90	20 87-96	12 97-99
SO ₂	ppm % removal	100 65	-- 70	75 50-75	30 79-94
HF,	ppm % removal	-- --	-- 93	5	5
Particulate,	gr/scf	0.03	.015	0.02	0.013
Dust Collector		EP	EP	EP Two- Field	Pulsejet Baghouse
Process Type	Single Pass	Single Pass	Single Pass	Recycle	Single Pass

Figure 2
Design Conditions
(Continued)

	<i>Zurich</i>	<i>Amager</i>	<i>Kassel</i>
<i>mg/Nm³, 11% O₂ dry</i>			
<i>Class I</i>	<0.1	<0.1	<0.1
<i>Class II</i>	<0.1	-	-
<i>Class III</i>	<5	-	<5
<i>Class I</i>	<i>Mercury, Cadmium, Thallium</i>		
<i>Class II</i>	<i>Arsenic, Cobalt, Nickel Selenium, Tellurium</i>		
<i>Class III</i>	<i>Antimony, Lead, Chromium Copper, Manganese, Vanadium Cyanides and Fluorides</i>		

Figure 3
Trace Metal Emission Requirements

Although a significant increase in mercury removal was achieved by lowering the outlet temperature of the SDA, this was not sufficient to meet the stringent requirements of 0.1 mg/Nm³ mercury outlet emission. In May 1986, a dry additive system developed and patented by Niro Atomizer (4) was retrofitted upstream the spray dryer absorber. The preferred additive is active carbon.

Figure 4 shows detailed results of the tests that were done with and without activated carbon at various SDA outlet temperatures. All mercury measurements were made simultaneously at the SDA inlet and the EP outlet. Both multi-point isokinetic traverses and single-point isokinetic samples were taken simultaneously over a four-hour period to determine if it was necessary to test with full duct traverses. The three single-point samples showed an average of 144 $\mu\text{g}/\text{Nm}^3$ compared to 145 $\mu\text{g}/\text{Nm}^3$ for the full traverse. Therefore, further tests were run on the carbon additive system using only single-point isokinetic sampling.

Figure 5 shows an averaged summary of the detailed results in Figure 4. The table shows the effect of lowering the SDA outlet temperature and also the pronounced effect of carbon additive. Note that even with fluctuating inlet mercury concentrations, the lower outlet temperature results in a mild improvement in efficiency, the use of carbon additive, roughly doubles the efficiency from the mid-40% to the high 80% range. To see the effect in more detail, the tests in Figure 4 at 239° F and 230° F SDA outlet temperatures show wide variations in inlet concentration. Without carbon addition, the outlet concentrations vary widely between 117 and 670 $\mu\text{g}/\text{Nm}^3$, while the outlet concentrations fall in a narrow range between 29-68 $\mu\text{g}/\text{Nm}^3$ when additive is injected.

Figure 6 shows tests in which the influence of additive injection rate on mercury removal was investigated. It is confirmed that low outlet mercury emissions are achieved regardless of inlet mercury level. Based on these tests, it appears the additive injection rate does not have a major impact on the outlet emission concentration or removal efficiency. We feel this is due in part to the fact the downstream particulate collector is a precipitator. Therefore it is concluded that the low and relatively uniform outlet Hg emission is due to the efficient control of the mixing of flue gas, additive and liquid in the SDA due to the single rotary atomizer concept. The absorber module can be compared with a fully back-mixed reactor with almost ideal mixing.

Amager

The Amager MSW incinerator is situated in the middle of Copenhagen. The retrofit SDA/BH system was brought into operation mid 1988. In August 1989, a test program was carried out to characterize the mercury emissions. Figure 7 shows the detailed mercury test results with the SDA operating at 284° and

Hg concentration µg/Nm³, dry

<i>SDA Outlet Temp. °F</i>	<i>Additive mg/Nm³</i>	<i>SDA</i>	<i>EP Outlet</i>	<i>% Removal</i>
284	0	537	390	27
		343	237	31
		680	417	39
		558	414	26
		406	335	17
		1072	769	28
248	30	539	39	93
		589	31	95
239	0	495	232	53
		643	207	68
		234	117	64
		949	670	29
		736	476	36
		401	250	38
	30	352	44	88
		353	44	88
		281	29	90
230	0	249	124	50
		224	132	41
		346	212	39
	30	486	68	86
		650	45	93
		131	44	66
		417	40	90
		269	51	81

*Figure 4
Zurich - Detailed Mercury Test Results
With Variable SDA Outlet Temperature*

<i>Hg concentration $\mu\text{g}/\text{Nm}^3$, dry</i>				
<i>SDA Outlet Temp. °F</i>	<i>Additive mg/Nm^3</i>	<i>SDA Inlet</i>	<i>EP Outlet</i>	<i>% Removal</i>
284	0	600	427	29
239	0	576	325	44
239	30	329	39	89
230	0	273	156	43
230	30	390	49	87

Figure 5
Zurich - Summary of Hg Test Results
Averages of Detailed Results (Figure 4)

Hg concentration $\mu\text{g}/\text{Nm}^3$, dry				
SDA Outlet Temp. °F	Additive mg/Nm^3	SDA Inlet	EP Outlet	% Removal
248	7	501 <u>439</u>	93 <u>47</u>	81 <u>89</u>
	Average	470	70	85
	15	229 176 <u>239</u>	33 11 <u>22</u>	86 94 <u>91</u>
	Average	215	22	90
248	30	539 589 154 <u>113</u>	39 31 20 <u>23</u>	93 94 87 <u>80</u>
	Average	349	28	92

Figure 6
Zurich - Hg Results
Influence of Additive Injection Rate

		Hg concentration $\mu\text{g}/\text{Nm}^3$, 10% O_2		
SDA Outlet	Temp. °F	Additive mg/Nm^3	SDA Inlet	PJF Outlet
				% Removal
284	0	171	130	15
		193	164	29
		184	72	61
		170	62	64
		139	56	59
	6	318	49	85
		191	34	82
	17	180	26	86
		209	29	86
		283	30	89
58	58	1276	65	95
		268	19	93
260	0	354	27	92
		165	40	76
		137	25	82
		159	45	72
	19	169	20	88
		167	5	97
	70	185	6	97

Figure 7
Amager - Detailed Mercury Test Results

260° F outlet temperature with a variation in the quantity of additive injected. In Figure 8 these results are averaged and summarized for clarity. Again with no additive injection, it is clear that reducing the SDA outlet temperature is effective in increasing mercury removal. With additive injection, mercury emissions can be controlled to values much lower than the required 100 $\mu\text{g}/\text{Nm}^3$.

Kassel

The SDA system at Kassel in West Germany differs from Zurich and Amager, because this system has incorporated a partial dry solids recycle system. Furthermore, the incinerator fly ash is precollected upstream of the SDA system. These factors will increase the chloride concentration in the feed slurry of the SDA system. Potentially a recycle system has a negative effect on mercury removal, as previously captured mercury will evaporate from the recycle solids after re-injection into the SDA system. This phenomenon has been confirmed by test work at the Leverkusen incinerator plant, where only 5-10% mercury removal was achieved. The Leverkusen system consists of a SDA and a downstream EP and is designed with recycle.

In Kassel the required outlet emission of 100 $\mu\text{g}/\text{Nm}^3$ of mercury can be achieved with dry additive injection upstream of the spray dryer absorber. Figure 9 shows results from recent measurements at the plant. By adding 20 mg/Nm^3 additive or more, the emission can be controlled to a safe value under 100 $\mu\text{g}/\text{Nm}^3$. Note that due to spray drying considerations with high chloride concentrations in the feed slurry, the SDA outlet temperature has to be kept at 279° F.

Semass

The Semass unit has been described in detail previously (12) and underwent emissions testing in April 1989 and September 1990. This plant differs slightly from the European installations because it used a prepared fuel as opposed to the mass burn principal. Unfortunately, SDA inlet concentrations were not measured so the efficiency of the SDA/EP system could not be calculated. The unit operates without carbon additive and achieves emission levels consistent with the European installations just described. The mercury emissions vary between 48-140 $\mu\text{g}/\text{Nm}^3$ and are detailed in Figure 10.

Palm Beach

The RDF plant at Palm Beach was started in late 1988 and is very similar to the configuration at Semass. Here again, SDA inlet mercury concentrations were not measured so the removal efficiency is not known. However, mercury emissions data taken at the stack are quite good. Unit 1 has an average emission of 50 $\mu\text{g}/\text{Nm}^3$ and Unit 2 was tested at 20 $\mu\text{g}/\text{Nm}^3$. Detailed results are available in Figure 11.

<i>Hg concentration $\mu\text{g}/\text{Nm}^3$, 10% O_2</i>				
<i>SDA Outlet Temp. °F</i>	<i>Additive mg/Nm^3</i>	<i>SDA Inlet</i>	<i>PJF Outlet</i>	<i>% Removal</i>
284	0	171	97	43
	6	255	42	84
	17	224	28	87
	58	633	37	94
	0	154	37	76
260	19	169	20	88
	70	176	5	97

Figure 8
Amager - Summary of Hg Test Results

		<i>Hg concentration $\mu\text{g}/\text{Nm}^3$, dry</i>		
<i>SDA Outlet Temp. °F</i>	<i>Additive mg/Nm^3</i>	<i>SDA Inlet</i>	<i>PJF Outlet</i>	<i>% Removal</i>
279	0	898	582	35
	9	336	175	48
	20	324	57	82
	47	179	19	89
	64	297	52	82

*Figure 9
Kassel - Summary of Hg Test Results*

		<i>Hg concentration</i> $\mu\text{g}/\text{Nm}^3$, dry, 12% CO_2	
<i>SDA Outlet</i>	<i>Temp. °F</i>	<i>April 1989</i>	<i>Sept. 1990</i>
	<i>Additive mg/Nm^3</i>	<i>EP Outlet</i>	<i>EP Outlet</i>
<u>Unit 1</u>			
270	0	57	--
270	0	42	--
270	0	<u>45</u>	--
	Average	48	
<u>Unit 2</u>			
270	0	96	162
270	0	68	119
270	0	<u>54</u>	<u>140</u>
	Average	73	140

Figure 10
Semass - Hg Emission Test

<i>SDA Outlet Temp. °F</i>	<i>Additive mg/Nm³</i>	<i>Hg concentration µg/Nm³, dry</i>	<i>SDA Inlet</i>	<i>EP Outlet</i>
<u><i>Unit 1</i></u>				
261	0	<i>Not Measured</i>		29
261	0	<i>Not Measured</i>		52
261	0	<i>Not Measured</i>		<u>69</u>
		<i>Average</i>		50
<u><i>Unit 2</i></u>				
261	0	<i>Not Measured</i>		23
261	0	<i>Not Measured</i>		15
261	0	<i>Not Measured</i>		<u>23</u>
		<i>Average</i>		20

*Figure 11
Palm Beach - Hg Emission*

The mercury emissions data from the five plants are summarized in Figure 12. Shown on the figure are SDA inlet concentrations, when measured, and the effect that treatment in the SDA system provides. The X axis shows the effect of carbon additive. Note that in all cases save one, the mercury emission level can be kept below 100 $\mu\text{g}/\text{Nm}^3$. The one exception is the unit at Kassel, which has a pulsejet baghouse recycle system.

Dioxins and Furans

There has been worldwide concern over dioxin and furan emissions from municipal solid-waste incinerators. For the last 20 years studies have been conducted to define the toxic effects of these compounds. Therefore, we have attempted to summarize the emissions levels and the efficiency of spray dryer absorption systems of these waste incinerators. The measurements presented include three European installations, as well as the Semass unit. Data was not available for the West Palm Beach installation. The emissions levels are expressed as totals of tetra through octa chlorinated dibenzo-p-dioxins and chlorinated dibenzofurans, as well as toxic equivalents appropriate to the country and time of test. EPA currently requires a limit of 30 ng/Nm³ dry at 7% O₂ to meet new source standards, while other authorities are interested in toxic equivalents. Although not in the scope of this paper, please refer to Figure 13 for a comparison of various toxicity equivalencies. This information plus a thorough description of the various toxic equivalent methods is contained in Reference (5).

Zurich

Dioxin and furan measurements at Zurich were performed by dk-Teknik of Denmark. Before performing tests at Zurich, they had been involved in test programs on Danish incinerators on behalf of the Danish Environmental Protection Agency (6, 7, and 8).

The tests were performed in accordance with procedures outlined by the Nordic Method. Simultaneous samples were collected isokinetically at the inlet to the spray dryer absorber and the outlet of the precipitator. The filter temperature was kept at a temperature of 248° F. The dioxin and furan content reported include that found in the condensate, the XAD2 column, the quartz wool filter and the methylenechloride rinsing liquid.

Sample preparation and isomer specific analyses were made by the Department of Organic Chemistry, Umeaa University, Sweden. The samples were analyzed for the 12 most toxic dioxins commonly known as the "dirty dozen". From this analysis an equivalent amount of 2,3,7,8 TCDD was computed according to the Eadon Method.

The plant was operated steady-state for an extended time for each test condition before measurements were carried out. The testing took place over four days. During sampling the incinerator was operated at steady load and with a low CO content of 20-30 ppm

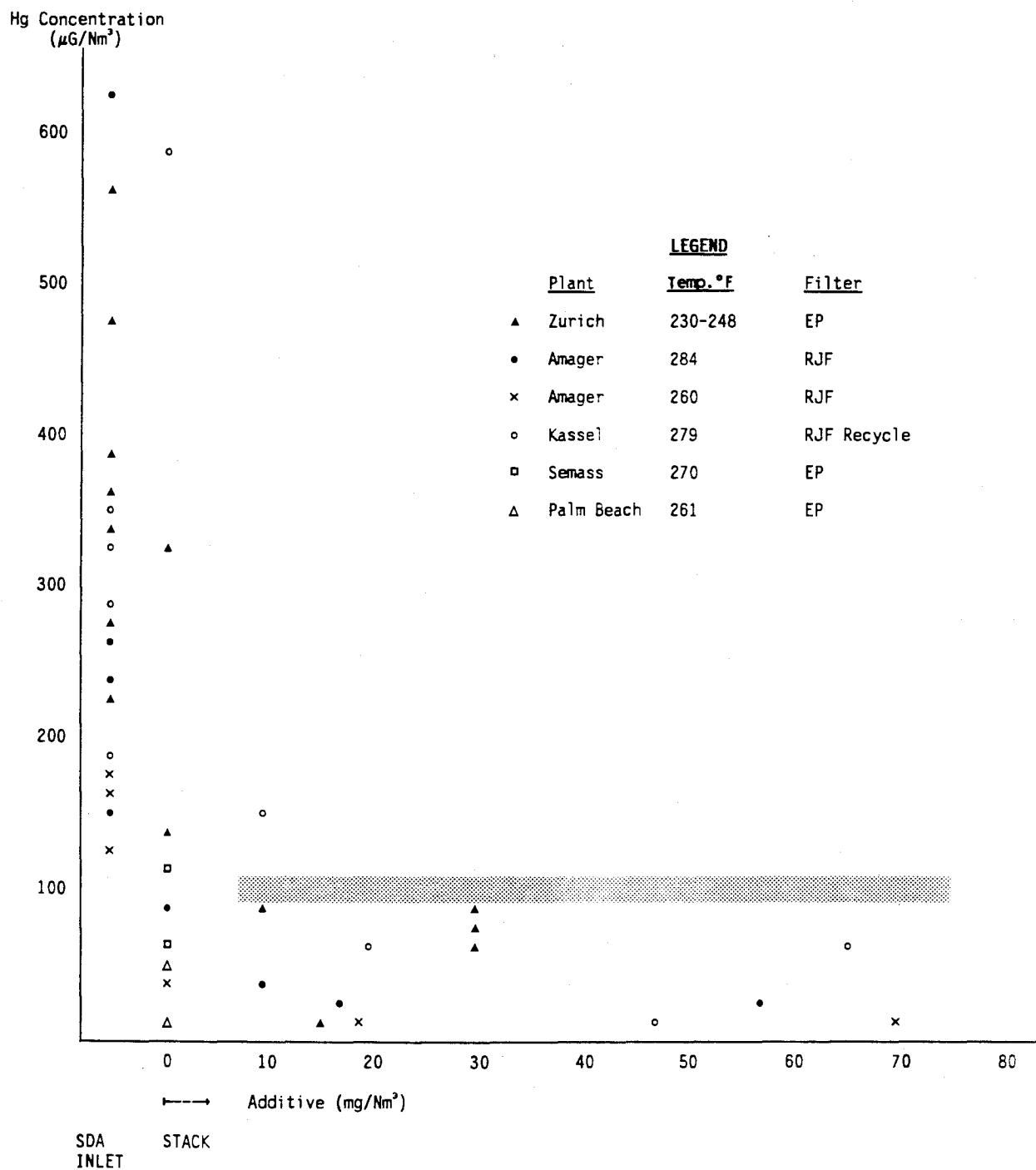
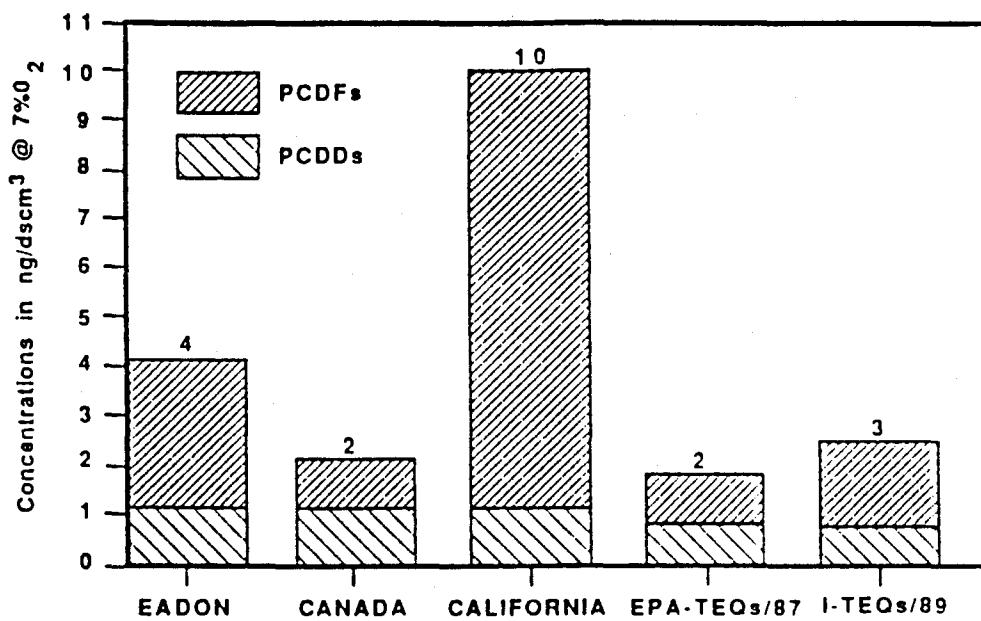


Figure 12
Control of Mercury Emissions by Additive Injection



Data for Above Figure (Concentrations in ng/dscm³ @ 7% O₂)

SPECIES	SOURCE DATA	TEF SCHEME				
		EADON	CANADA	CALIFORNIA	EPA-TEF/87	I-TEF/89
2378-TCDD	0.30	0.30	0.30	0.30	0.30	0.30
TCDDs (OTHER)	2.7	0	0.27	0	0.027	0
12378-PeCDD	0.79	0.79	0.39	0.79	0.39	0.39
PeCDDs (OTHER)	2.2	0	0.011	0	0.011	0
123478-HxCDD	0.16	0.0047	0.016	0.0047	0.0063	0.016
123678-HxCDD	0.39	0.012	0.039	0.012	0.015	0.039
123789-HxCDD	0.059	0.0018	0.0059	0.0018	0.0023	0.0059
HxCDDs (OTHER)	3.6	0	0.0036	0	0.0014	0
1234678-HpCDD	0	0	0	0	0	0
HpCDDs (OTHER)	5.9	0	0.00059	0	0.000059	0
OCDD	9.5	0	0.00095	0	0	0.00095
TOTAL CDDs		1.1	1.0	1.1	0.8	0.8
2378-TCDF	2.3	0.76	0.23	2.3	0.23	0.23
TCDFs (OTHER)	30	0	0.03	0	0.030	0
12378-PeCDF	4.2	1.4	0.42	4.2	0.42	0.21
23478-PeCDF	2.5	0.82	0.25	2.5	0.25	1.2
PeCDFs (OTHER)	1.2	0	0.012	0	0.012	0
123478-HxCDF	1.6	0.016	0.079	0.047	0.016	0.16
123678-HxCDF	0	0	0	0	0	0
234678-HxCDF	0.46	0.0046	0.023	0.014	0.0046	0.046
123789-HxCDF	0.0095	0.000095	0.00048	0.00029	0.000095	0.00095
HxCDFs (OTHER)	17	0	0.0086	0	0.0017	0
1234678-HpCDF	0	0	0	0	0	0
1234789-HpCDF	0	0	0	0	0	0
HpCDFs (OTHER)	11	0	0.011	0	0.011	0
OCDF	0.41	0	0.000041	0	0	0.00041
TOTAL CDFs		3.0	1.1	9.1	1.0	1.8
TOTAL TEQs		4	2	10	EPA-TEQs/87 = 2	I-TEQs/89 = 3
					15% Contributed by 2,3,7,8 - TCDD	10% Contributed by 2,3,7,8 - TCDD

Reference: Adapted from NATO/CCMS, 1988a.

Figure 13
Toxicity Equivalents in Emissions from a
Municipal Waste Incinerator

(dry), which indicated that the combustion conditions were good and stable.

The results of the dioxin testing are shown in Figure 14 and are reported as total PCDD and PCDF, as well as toxic equivalents according to the Eadon Method. The spray dryer was operated at inlet temperatures of 392-428° F and outlet temperatures of 248-284° F. The results show a significant reduction of approximately 75% when operating without carbon additive. This reduction is effected by the intimate contact of the dry solids and the treated gas in the spray dryer. We suspect the operation of the precipitator does not contribute much to the adsorption of dioxins. It should be noted that an additive injection rate of 18 mg/Nm³ increases the removal efficiency to 90% at 284° F and to 98.5% at 248° F with 59 mg/Nm³ additive injection rate.

Amager

The Amager system is similar to Zurich except the dust collector is a pulsejet fabric filter instead of a precipitator.

The sampling and measurement technique was the same as used for the Zurich testing. Results of the test work are shown in Figure 15. The test results are expressed as total PCDD and PCDF and as Nordic toxic equivalents, which in most cases are very similar to Eadon equivalents. The results confirm that a spray dryer absorber with fabric filter operating at low spray dryer absorber outlet temperature is highly efficient and could be considered best available control technology for dioxins. Comparing the outlet emissions without additive results in a reduction of dioxins by approximately 50% when lowering the outlet temperature from 284 to 260° F. Injection of additive at 260° F further reduces the dioxin emissions corresponding to almost complete removal on a Nordic toxic equivalent basis.

It is interesting to note that one test was done under simulated start-up conditions, where dioxin emissions from the incinerator were much higher than normal due to non-ideal burning conditions. It is significant in all cases, including the simulated start-up, very high removal efficiencies and Nordic toxic equivalents of less than 0.1 ng/Nm³ were achieved with carbon additive (10).

Kassel

Recent proposed German regulation requires a set limit of dioxin emission of less than 0.1 ng/Nm³ toxic equivalents according to the TE/NATO CCMS methods of August 1988 (5).

Figure 16 shows results of dioxin removal tests at the Kassel incinerator. With no additive injection, a dioxin removal efficiency of only 60-65% is achieved. The relatively low removal efficiency can be attributed to the absence of fly ash due to the fly ash precollector and to the recycling of the dry reaction product through the feed system. Earlier pilot plant

		Total PCDD + PCDF ng/Nm ³ , dry			Toxic Equivalents, Eadon ng/Nm ³ , dry			
SDA Outlet	Temp. °F	Additive mg/Nm ³	SDA Inlet	EP Outlet	% Removal	SDA Inlet	EP Outlet	% Removal
284	0	306	77	74.8	7.7	1.9	75.3	
	18	223	33	85.2	7.5	0.79	89.5	
248	0	277	69	75.1	6.9	1.8	73.9	
	59	455	5.0	98.9	6.0	0.09	98.5	

Figure 14
Zurich - Dioxin Removal Test Results

		Total PCDD + PCDF ng/Nm ³ , dry			Toxic Equivalents, Nordic ng/Nm ³ , dry		
SDA Outlet Temp. °F	Additive mg/Nm ³	SDA Inlet	PJF Outlet	% Removal	SDA Inlet	PJF Outlet	% Removal
284	0	132	2.1	98.4	2.8	0.076	99.7
	6	283	1.2	99.6	4.8	0.0075	99.8
	17	276	2.4	99.2	8.3	0.045	99.5
	58	201	1.1	99.5	4.0	0.035	99.1
	58	2170*	3.2	99.9	50.0	0.050	99.9
261	0	254	1.3	99.5	7.7	0.0047	99.9
	19	154	0.4	99.8	5.0	N.D.	100
	70	154	0.7	99.6	4.5	0.002	100

* Start-up Condition, Simulated

N.D. = Non Detectable

Figure 15
Amager - Dioxin Removal Test Results

		Total PCDD + PCDF ng/Nm ³ , dry			Toxic Equivalents TE/NATO/CCMS ng/Nm ³ , dry		
SDA Outlet Temp. °F	Additive mg/Nm ³	SDA Inlet	PJF Outlet	% Removal	SDA Inlet	PJF Outlet	% Removal
275	0	380	151	60	9.58	3.46	64
	19	134	12	91	3.21	0.19	94
	19	238	8	97	5.11	0.15	97
	47	298	9	97	5.53	0.13	98
	105	359	7	98	5.94	0.07	99

Figure 16
Kassel - Dioxin Removal Test Results

results at an incinerator in Denmark (8) showed that by operating a spray absorption system with bag filter in recirculation mode without precollection of fly ash, one could achieve approximately 90% dioxin removal at the same temperature level as in Kassel. It is therefore believed that the presence of fly ash plays a major role in dioxin removal in the SDA system. Figure 16 shows that injection of additive can compensate for the lack of fly ash and secure high removal efficiencies of dioxins and furans. The results also show the 0.1 ng/Nm³ toxic equivalent limit can be achieved.

Semass

The Semass plant has been tested three times in the last two years for a variety of pollutants, including dioxin and furan. The results of stack testing are shown on Figures 17 and 18. Note that results are given as a summation of total dioxin and furan or as toxic equivalents (EPA-TEF/87). As in the case of the mercury tests, the SDA inlet was not measured, so there is no indication of SDA/EP dioxin/furan removal efficiency. However, when compared to the Zurich installation (SDA/EP) with no additive, the Semass emission levels are quite similar with the exception of one test. The reason for the unusually high emission level of this one test is unknown at this time. Based on the test results at Zurich, it is safe to assume the use of carbon additive could improve the emission levels at Semass.

Comparing the dioxin and furan removal test results from Zurich, Amager, Kassel and Semass, it can be concluded that injection of additive can secure a very low dioxin emission regardless of operating mode (single pass vs. recirculation), type of filter (fabric filter vs. electrostatic precipitator), spray dryer outlet temperature and upset conditions.

CONCLUSIONS

The paper has described the mercury and dioxin removal efficiencies achieved at five full-scale operating SDA systems in Europe and the United States. The test results have clearly demonstrated the ability of the SDA system with a single rotary atomizer per absorber module to achieve outlet emission levels of mercury below 0.1 mg/Nm³ and outlet dioxin and furan emissions of less than 0.1 ng/Nm³ toxic equivalents when using a dry additive injection system.

SDA Outlet	Temp. °F	Additive mg/Nm ³	Total PCDD + PCDF ng/Nm ³ , dry		
			EP Outlet April '89	EP Outlet Jan. '90	EP Outlet Sept. '90
<u>Unit 1</u>					
270	0		4.2	--	--
270	0		11.6	--	--
270	0		<u>7.1</u>	--	--
		Average	7.6	17.3	
<u>Unit 2</u>					
270	0		12.7	--	12.2
270	0		5.2	--	12.4
270	0		<u>698.1</u>	--	<u>10.7</u>
		Average	238.7		11.8

Figure 17
Semass - Dioxin and Furan Test Results

Toxic Equivalent EPA/TEF (2,3,7,8 TCDD)

Test Averages (ng/Nm³ @ 12% CO₂)

<i>Test Date</i>	<i>April 1989</i>	<i>January 1990</i>	<i>September 1990</i>
<i>Unit 1</i>	--	2.469	--
<i>Unit 2</i>	2.320	--	1.0826

Figure 18
Semass - Dioxin and Furan Test Averages

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SESSION 8C: NOVEL/EMERGING FLUE GAS CLEANING TECHNOLOGY II

Co-Chairmen:

Charles B. Sedman
AEERL
U.S. EPA
Research Triangle Park, NC

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The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

RETROFIT ACID GAS EMISSIONS CONTROLS
FOR
MUNICIPAL WASTE INCINERATION:

AN APPLICATION OF DRY SORBENT INJECTION

by

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ABSTRACT

The EPA has developed revised emission standards for existing municipal solid waste incinerators. Compliance with these proposed standards will have a significant impact on operating incinerator facilities. Retrofit of acid gas emissions controls will be required for many of these units.

Dry sorbent injection has been successfully demonstrated on coal fired boiler applications as a means of reducing sulfur dioxide emissions. Recently, a Dense Phase Dry Sorbent Injection system was applied to an existing municipal waste incinerator to provide acid gas emission controls. The results obtained from the successful demonstration of the sorbent injection system on an existing municipal incinerator are presented. Removal efficiencies of compounds such as HCl, SO₂, SO₃, and others by the use of sorbent injection are shown.

An application case study will outline exhaust conditions, expected pollution reductions, and capital and operating costs for various types of sorbents for a typical municipal incinerator which will require acid gas emission controls.

INTRODUCTION

On November 15, 1990 the Clean Air Act Amendments of 1990 were signed into law by President Bush. The enactment of these Amendments has ushered in a new era of regulatory activity with the goal of improving the quality of the environment. The Amendments require the U.S. Environmental Protection Agency to develop regulations to control the emissions of a wide range of chemicals and compounds. These regulations will affect a broad range of industries, many of which have previously not been subject to stringent air emission controls. The EPA is also provided with enforcement powers to ensure that the regulations are followed by the affected industries.

One of the new provisions contained in the Amendments applies to Municipal Waste Combustion Facilities (MWC). These new provisions required that the EPA develop new emissions standards for these facilities. In fact, the first set of regulations which were developed by the EPA apply to the control of emissions from municipal waste combustion.

Two sets of regulations have been developed to control emissions from municipal waste combustion. These are (1) those that apply to new facilities, ie. revised New Source Performance Standards (NSPS) and (2) those which apply to existing sources, the "Emissions Guidelines." The regulations which apply to existing facilities are the focus of this paper.

Compliance with these proposed standards will have a significant impact on many operating incinerator facilities. Retrofit of acid gas emissions controls will be required for many of these units.

REGULATIONS

The new emissions guidelines proposed for existing facilities are the first issued under the new Clean Air Act Amendments. As presently developed, these "Guidelines" are only partially complete. The new emissions guidelines apply to all MWC units which have a capacity of greater than 250 tons per day (TPD), per combustor. Within two years, the EPA will issue additional regulations for combustors of 250 TPD, or less, capacity. Furthermore, within one year, the EPA is required to develop additional, specific numerical limits for mercury, cadmium, and lead emissions.

The Clean Air Act Amendments require that the emissions limits developed for municipal waste combustion reflect the "maximum degree of reduction in emissions of air pollutants ... that the Administrator, taking into account the cost of achieving such emission reduction, and any non-air quality health and environmental impacts and energy requirements, determines is achievable for new or existing units in each category."

The Amendments also state that the "emissions standards for existing units in a category ... shall not be less stringent than the average emission limitations achieved by the best performing 12 % of existing units in the category ...". This is referred to as the

Maximum Achievable Control Technology or MACT.

The new emissions levels specified in the guidelines are further based on the premise that the "best demonstrated technological basis" (BDT) for reducing emissions differs based on the aggregate size of each facility. (The BDT is considered to be that technology which achieves the greatest reduction in emissions, considering cost.) Consequently, the emissions guidelines are categorized by the size of the total facility (within which individual units of capacities greater than 250 ton/day are contained). For facilities in which the total aggregate capacity is less than or equal to 1,100 tons per day one set of regulations apply. Another set of regulations apply to plants with a total aggregate capacity greater than 1,100 tons/day.

Figure 1 summarizes the new emissions guidelines for municipal waste combustors which are greater than 250 ton per day per unit at facilities with an aggregate capacity of greater than 1,100 tons per day. This table shows that for facilities within this range, the required emission controls include 90 % reduction of HCl or 25 ppmdv, 70 % reduction of SO₂ or 30 ppmdv, and control of particulate emissions to 0.015 grains/dscf.

Figure 2 summarizes the emissions guidelines for municipal waste combustors which are greater than 250 tons per day per unit with an aggregate capacity which is equal to or less than 1,100 tons per day. For these facilities, less stringent requirements apply. These include 50 % reduction of HCl, 50 % reduction of SO₂, and control of particulate emissions to 0.03 grains/dscf.

Heavy metals for both size facilities are not individually regulated. It is believed that control of particulate matter would provide sufficient reduction of heavy metals emissions. Mercury, however, will be regulated in the future. Mercury requirements are to be promulgated by November 15, 1991. At present it is not clear what form these regulations will have.

The Guidelines also identify the best demonstrated technologies for reducing emissions. These technologies are not presented as the required control equipment but merely to serve as the technological and economic basis for the guidelines.

For facilities which have an aggregate capacity greater than 1,100 tons/day the BDT includes:

- Good combustion practice for control of organics.
- Spray dryer followed by an electrostatic precipitator for control of acid gas and metals.

For facilities with aggregate capacity less than or equal to 1,100 tons/day the BDT includes:

- Good combustion practice for control of organics.

- Dry sorbent injection followed by an existing electrostatic precipitator for control of acid gas and metals.

Recently Waste Age magazine published a report on the status of municipal waste combustion which included a survey of operational waste incinerator installations (both waste-to-energy plants and incinerators). According to this survey, there are 128 waste-to-energy facilities and 40 incinerator facilities in operation in the U.S. Of these, approximately 100 units fit the criteria established by the current regulations and require installation of emission controls. These facilities will have until 1996 to be in compliance with the emissions guidelines.

The EPA has until 1992 to establish comparable emissions standards for smaller combustors, those less than or equal to 250 tons/day per train.

An analysis of the operating waste incinerator installations which are rated at 250 tons/day or greater, at facilities which have a total operating capacity of less than 1,100 tons per day was made. Based on this survey, there are about 30 operating incinerator "trains", at roughly 15 plants, which do not have acid gas controls. However, these units all have existing particulate controls, primarily electrostatic precipitators.

These units would be likely candidates for retrofit dry sorbent injection technology.

DRY SORBENT INJECTION TECHNOLOGY OVERVIEW

Dry Sorbent Injection, or DSI, is a means of acid gas control in which a totally dry, highly pulverized reagent, or sorbent, is introduced into a flue gas stream containing acid gases. Dry sorbent technology has been applied for acid gas control in two fundamental forms. The first type utilizes the injection of a sorbent directly into the combustor or furnace, in a high temperature regime. This type is sometimes referred to as furnace sorbent injection, or FSI. The second type utilizes the injection of a dry sorbent into the flue gas downstream of the combustion chamber. This process is a post-combustion process and is sometimes referred to as duct sorbent injection. In this approach sorbent can be injected in the economizer region of a boiler at relatively high temperatures or in the flue gas duct upstream of the final particulate control device where the temperatures are much lower. In both control approaches the reaction products and any unreacted sorbent are captured in conventional particulate control equipment such as an electrostatic precipitator or fabric filter. Disposal of the waste products is accomplished in the same manner as existing fly ash disposal.

A brief discussion of these sorbent injection techniques will be provided below.

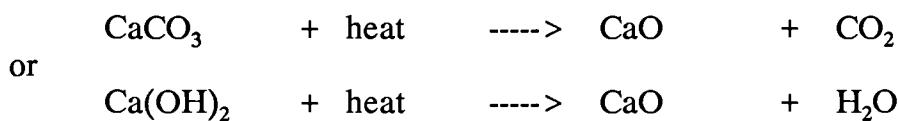
FURNACE SORBENT INJECTION

The technique of combustion zone injection for the control of acid gas emissions is shown in Figure 3. In this approach a dry sorbent such as limestone or hydrated lime

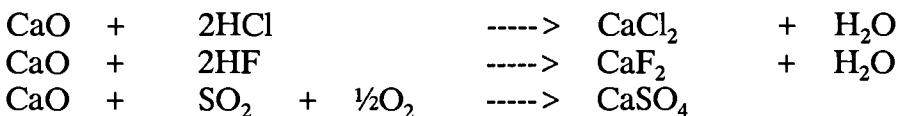
is injected into the combustor. Injection of the sorbent is accomplished in several different methods. These include adding the reagent with the waste charge to the furnace, pneumatically conveying the reagent with combustion air, or pneumatically injecting the reagent through nozzles in the combustion zone just above the fuel bed. Furnace sorbent injection has been utilized to control SO₂ emissions in utility and industrial coal fired boiler applications since the mid 1980's. Several furnace sorbent injection systems have been operating for over 5 years.

Limestone injected into the furnace at temperatures between 1,800 to 2,200 will calcine to produce lime. The lime (either from the calcined limestone or as directly injected) reacts with the acid gases.

The chemical reactions which occur include:



then:



Within the furnace there are several temperature zones which yield optimal removal efficiencies. The calcination of limestone to lime occurs in the 1,800 to 2,200 °F temperature window. SO₂ removal is also greatest in this high temperature zone as well as in a second zone of temperature between 900 to 1000 °F. HCl and HF, however, are more effectively removed at lower temperatures, downstream of the furnace. Figure 4 illustrates the removal efficiency of SO₂ as a function of temperature of the injection zone. The different zones of optimal efficiencies are clearly shown.

One criteria which is used to measure the effectiveness of dry sorbent injection system operation is the calcium to sulfur molar ratio. This ratio reflects the quantity of sorbent required to achieve acid gas removal. This ratio, also referred to as the stoichiometric ratio, is the moles of calcium injected divided by the moles of entering acid gases. Figure 4 illustrates sulfur dioxide capture at a stoichiometric ratio of 2.0.

Furnace sorbent injection of limestone has been demonstrated commercially on coal fired boiler applications for many years. This approach is considered to be commercially proven.

Furnace sorbent injection has several advantages, particularly as a retrofit control technology. These include:

- provides extended contact time for lime and acid gas reactions to occur

- from the furnace to the particulate control device.
- potential to reduce dioxin/furan formation by removing chlorine.
- provide some measure of corrosion prevention within furnace and heat recovery sections.
- relatively easy to retrofit.
- low capital cost.
- high reliability.
- commercially demonstrated technology.

The potential disadvantages of furnace sorbent injection include:

- possible fouling and erosion of convective heat transfer surfaces.
- low utilization of sorbent.
- limited removal capability.
- significant increase in particulate loading which may require modifications to existing electrostatic precipitators and ash handling equipment.

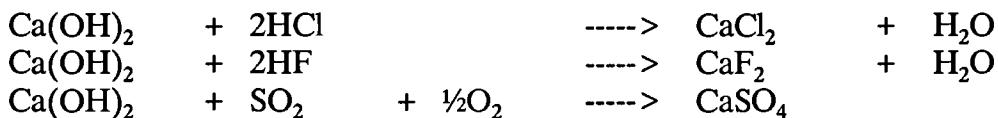
POST-COMBUSTION INJECTION

Post furnace sorbent injection involves the introduction of a dry sorbent material into the process after the combustion zone. Figure 5 shows a schematic of the various locations which can be utilized for post-furnace combustion controls. These include injection into the economizer region of the boiler or in the flue gas duct downstream of the boiler.

A number of different sorbents can also be utilized for this dry sorbent injection approach depending upon the location of the injection point. Each sorbent can provide a different degree of acid gas emission reduction.

Hydrated lime can be injected into the economizer zone at a temperature of approximately 800 to 1,000 °F. Hydrated lime can also be injected in the flue gas duct at a temperature of 350 °F.

The chemical reactions which occur include:



In addition to hydrated lime, several sodium based sorbents have been utilized for post-combustion injection. These include sodium bicarbonate and sodium sesquicarbonate, or trona. These materials would be injected downstream of the economizer, in the flue gas duct at a temperature of 350 °F.

The sodium reagents will not be discussed in this paper. It should be noted that these reagents have demonstrated higher removal efficiencies at lower "equivalent"

injection rates. However, the costs of these sorbents is substantially higher than those of the calcium based reagents, and in general, disposal of calcium based waste products is less difficult than disposal of sodium compounds.

In addition to reagent type and injection location, other factors which affect the performance of these dry sorbent injection systems include quantity of injected sorbent (stoichiometric ratio), contact time, flue gas moisture content, type of particulate control device, and acid gas concentration.

In some cases, the retrofit of post-combustion sorbent injection systems have included additional design features, some of which address the variables previously mentioned. One such modification is the use of flue gas humidification. Humidifying the flue gas enhances the collection efficiency of acid gases and conditions the flue gas to improve the capture of particulates in a downstream ESP. Downstream humidification is applicable for both calcium and sodium based sorbents.

Post-combustion sorbent injection also has a number of advantages as a retrofit control technology. These include:

- easy to retrofit.
- simple design and operation.
- low capital cost.
- commercially demonstrated technology.
- higher removal efficiencies and utilizations (compared to FSI).

Potential disadvantages include:

- utilization of sorbent is low.
- limited removal capability.
- significant increase in particulate load to existing particulate controls.

A dry sorbent injection system is a very simple system to retrofit. The equipment required includes a sorbent storage silo(s), feeder(s), compressed air system, pneumatic conveying piping, and miscellaneous valves and fittings. Other modifications may include upgrades to electrostatic precipitator ash handling equipment as well as possible improvements which may be required to the electrostatic precipitator to insure that existing particulate emissions standards are met, even with the increased dust loadings.

DENSE-PHASE DRY SORBENT INJECTION

One application of the dry sorbent injection system utilizes a dense-phase sorbent transport and injection system. The term "Dense-Phase" refers to the method of pneumatic transport of the reagent to the injection zones. Typical pneumatic conveying is accomplished using dilute phase conveying, ie. there is a large amount of transport air required to convey a specific mass rate of solids. In dense-phase transport, extremely low volumes of air are used to transport and inject the same mass rate of solids. Since

the volume of transport air is low, there are no impacts on the combustion process (temperatures, volumes, etc.).

The dense phase transport also provides greater transport distances, in smaller diameter pipe, as compared to typical pneumatic transport. This has two benefits. The first is that lower operating power consumption is required. The second benefit is that installation is simplified since the reagent storage equipment can be located at more remote locations where space limitations are less critical. Figure 6 compares dilute phase and dense phase pneumatic transport characteristics.

This process has successfully been applied to coal fired boiler applications with sorbent injection directly into the combustion zone of the boiler.

The dense phase dry injection system was retrofitted on a full scale municipal waste-to-energy facility for a program to demonstrate the feasibility of this technology for control of acid gases. The demonstration site has several operating combustor units, each greater than 250 tons/day. The total aggregate size of all of the operating combustor units would place the site in the "greater than 1,100 ton per day" category.

The demonstration dense phase dry sorbent injection system is designed to be a transportable system which can be moved to various sites as required. The mobile unit consists of a flatbed truck which contains a storage silo and silo fill system, dense-phase transporter, compressor with dryer and receiver, and a control panel. This system can be quickly and easily set up. Delivery of sorbent is accomplished with a 20 ton capacity tanker truck. This truck provides the sorbent to fill the silo as necessary using a remote transport system.

A sketch of the dense phase mobile demonstration unit is shown in Figure 7.

DENSE PHASE SORBENT INJECTION PERFORMANCE

A demonstration program of the dry sorbent injection system on a municipal waste combustor began in August 1990. The injection of sorbent was accomplished using a dense phase injection into multiple locations in the furnace. Hydrated lime was used as the sorbent. Figure 8 contains a summary of the chemical analysis of the hydrated lime used during the demonstration program.

The demonstration system was located approximately 350 feet from the furnace. Transport of the sorbent to the injection ports was via a 1 ½ " I.D. carbon steel pipe.

A preliminary evaluation of the performance of the incinerator facility was conducted to establish baseline information of acid gas emissions and to establish sorbent injection rates. Based on this evaluation, the dense phase sorbent injection system was sized to provide from 500 to 2,500 lb/hr of sorbent. However, for much of the demonstration period the unit was operated at about 1,000 lb/hr.

The uncontrolled emissions levels from the incinerator were determined to be:

HCl 700 ppmdv corrected to 7 % O₂

SO₂ 200 ppmdv corrected to 7 % O₂

In terms of mass rates, the uncontrolled emissions were determined to be 374 lbs/hr. for HCl and 175 lb/hr. for SO₂ for the baseline data.

Emissions data was obtained during various phases of the demonstration program. It should be pointed out that uncontrolled emissions data could not be obtained with the dense phase system in service. Consequently, the uncontrolled emissions data from the baseline evaluation was used to establish the performance of the dry sorbent injection system.

The results of the demonstration program showed that with an injection rate of 1,000 lbs/hr. of hydrated lime into the furnace the following emissions levels were achieved:

HCl 350 ppmdv corrected to 7 % O₂

SO₂ 80 ppmdv corrected to 7 % O₂

HCl mass emissions were 180 lb/hr., which represents a reduction of 53 % from uncontrolled levels. SO₂ mass emissions were 70 lb/hr., which represents a reduction of 60 % from the uncontrolled level. Again, the percentage reductions are based on emissions data taken from a different period of testing.

The injection rate of 1,000 lb/hr. of hydrated lime represents a normalized stoichiometric ratio of approximately 1.65 using the baseline uncontrolled acid gas emissions levels.

HCl emission reductions in excess of 75 % with SO₂ emission reductions in excess of 80 % were recorded during different phases of the demonstration program. Hydrated lime feed rates were not recorded during these tests. However, based on recorded operating parametric data, it is believed that the hydrated lime feed rate was approximately 1,200 lb/hr. This corresponds to a normalized stoichiometric ratio of about 2.1.

Still lower outlet emissions were obtained at higher hydrated lime feed rates. However, insufficient operating data was recorded to report these lower emissions now.

Particulate control for this incinerator is accomplished with an electrostatic precipitator. Specific tests of precipitator performance (inlet-outlet) were not conducted. However, an emissions monitor was used to track outlet opacity. No deterioration of precipitator performance was exhibited during the demonstration program.

No adverse effects were evident in the operation of the furnace or downstream equipment as a result of dense phase dry sorbent injection. The existing ash handling equipment was adequate to remove the additional dry waste products resulting from the sorbent injection system. This equipment showed no adverse effects. Overall combustor system reliability was maintained.

By way of comparison, data presented by Beckman and Spahn showed 70 % HCl and 80 % SO₂ reduction by use of a multiple-location dry sorbent injection system on a 400 ton/day facility. Injection of hydrated lime at this site is accomplished in three locations: at the furnace entrance, between the superheater and convection section, and in the ductwork between the convection zone and the economizer. The approach here is to take advantage of the acid gas removal efficiencies provided by the different temperature zones.

Insufficient data was recorded to allow us to present data on reductions of heavy metals or mercury at this time.

APPLICATION CASE STUDY

A typical municipal combustor can be used to illustrate the costs and operating requirements of a dense phase sorbent injection system. Figure 9 contains a summary of the performance variables associated with this "typical" 250 ton per day incinerator and the associated dry sorbent injection system. The system design is based on hydrated lime injection into the furnace. The equipment required for a dense phase sorbent injection system includes:

- reagent storage silo with bin activator and feeder
- pneumatic transport piping
- compressors for transport air
- injection ports

Figure 10 summarizes the sizes of this equipment for a 250 ton/day facility.

The economics of the dense phase system can be summarized as:

<u>Item</u>	<u>Annual Cost</u>
Equipment amortized (20 yrs)	\$ 50,000
Operation & Maintenance	\$ 65,000
Hydrated Lime @ \$80/ton	\$ 149,000
Waste disposal @ \$50/ton	<u>\$ 112,000</u>
	\$ 376,000

Our 250 ton per day plant, operating at 85 % capacity, would handle approximately 77,600 tons per year of waste. The annual incremental cost of the air pollution equipment, represented as annual cost per ton of waste would be \$ 4.85 per ton.

It should be noted that while the numbers used are fairly conservative, actual costs for a specific site could differ, particularly for facilities with multiple incinerator units.

CONCLUSIONS

The application of dry sorbent injection has been demonstrated to be a viable emissions control strategy for retrofit on existing municipal waste combustion units. Dry sorbent technology is simple to retrofit and has substantially lower capital costs as compared to installation of spray dryers. It is simple to operate. No liquids are circulated, all materials including the sorbent and waste products are dry.

In summary:

- dry sorbent injection is an effective means to achieve compliance for acid gases for municipal waste combustors which are larger than 250 TPD at facilities whose aggregate capacity is less than or equal to 1,100 TPD
- dry sorbent injection is easy to retrofit.
- dry sorbent injection is simple to operate.
- when combined with flue gas cooling and an ESP control of particulate matter, heavy metals, CDD/CDF, and acid gases can be achieved.
- dry sorbent injection is an economical, effective method to achieve compliance as required by the established EPA Emissions Guidelines.

The mobile dense-phase demonstration unit can be readily transported and set-up at an existing facility to demonstrate the suitability of this technology on a site-specific basis. The demonstration unit, coupled with a detailed analytical and operational test program is a cost effective means of demonstrating the effectiveness of dry sorbent injection technology and optimizing the design strategy for a particular municipal waste incinerator facility. The use of the demonstration unit will permit the identification of the impact of this type of acid gas control technology on the existing electrostatic precipitator and ash handling equipment.

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6. Beckman, Arthur and Spahn, David, "Dry Lime Injection for Acid Gas Control in Municipal Waste Incinerators," Presented at the 82nd Annual Meeting of the Air and Waste Management Association, June 25-30, 1989.

Figure 1

**Summary of Guidelines for Existing Facilities
Facility Aggregate Capacity: > 1,100 TPD**

HCl	90 % or 25 ppmv
SO ₂	70 % or 30 ppmv (24 hr.avg)
Particulates	0.015 grains/dscf
Opacity	10 % (6 minute average)
Organic emissions ¹	60 ng/dscm
Technology Basis:	Good combustion practice followed by a spray dryer and electrostatic precipitator

Notes:

1. Organic emissions are measured as total dioxin/furans.
2. All emission levels are at 7% O₂, dry basis.

Figure 2

**Summary of Guidelines for Existing Facilities
Facility Aggregate Capacity: ≤ 1,100 TPD**

HCl	50 % or 25 ppmv
SO ₂	50 % or 30 ppmv (24 hr.avg)
Particulates	0.03 grains/dscf
Opacity	10 % (6 minute average)
Organic emissions ¹	125 ng/dscm
Technology Basis:	Good combustion practice followed by dry sorbent injection and electrostatic precipitator

Notes:

1. Organic emissions are measured as total dioxin/furans.
2. All emission levels are at 7% O₂, dry basis.

Figure 3
Furnace Sorbent Injection

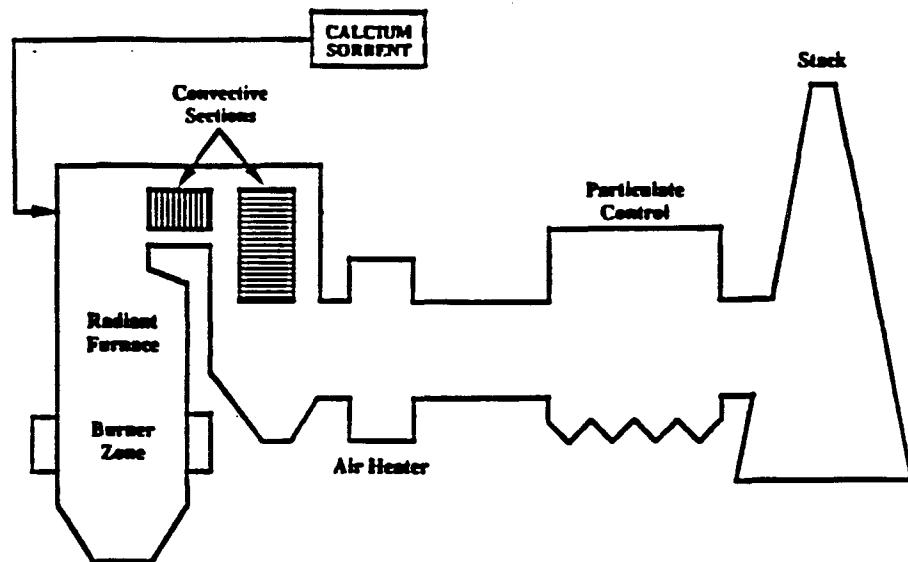


Figure 4
Temperature Effects On Removal Efficiency of Sulfur Dioxide

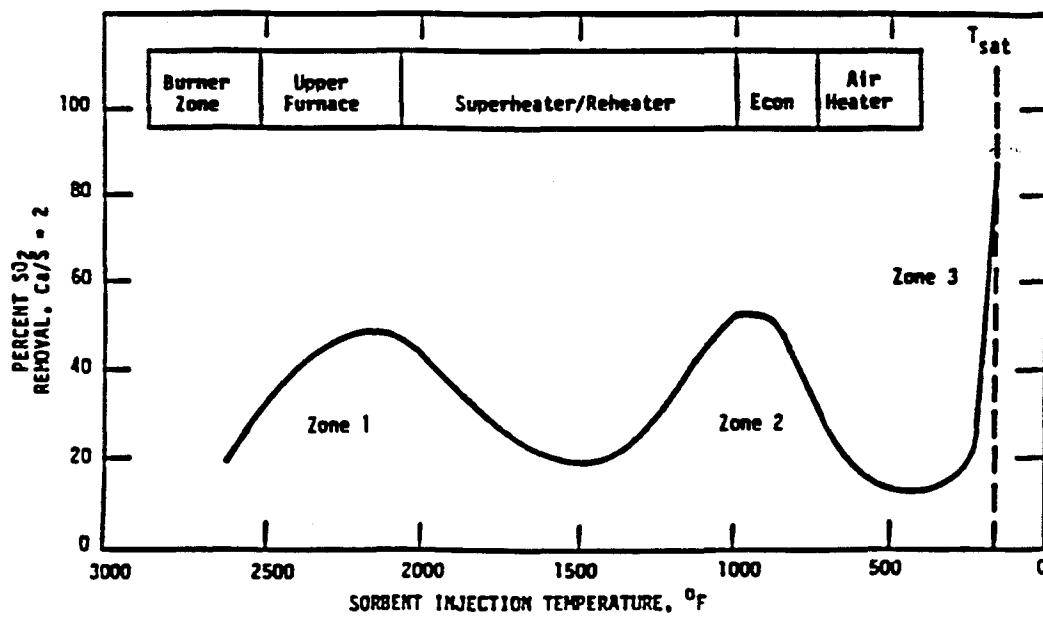


Figure 5
Post Combustion Sorbent Injection

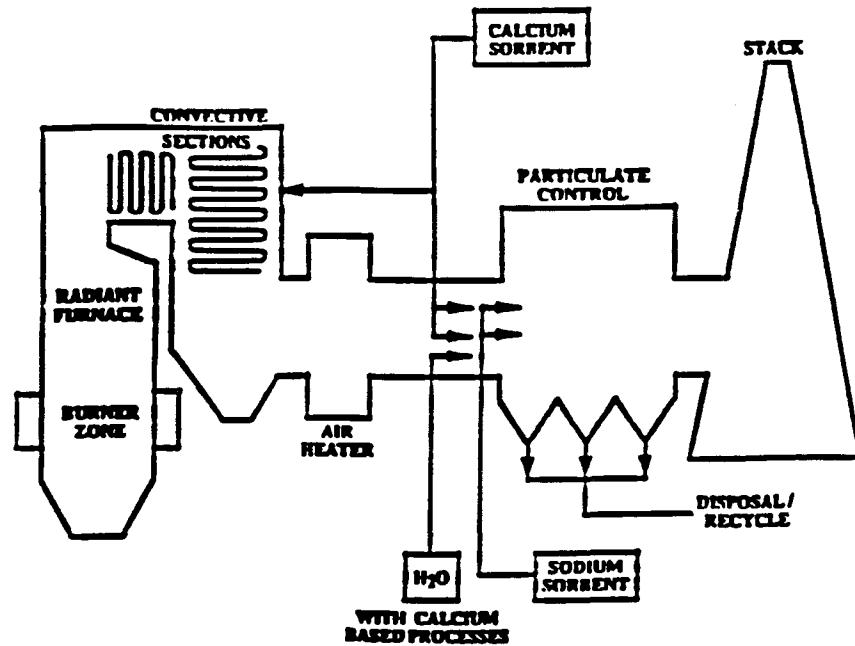


Figure 6
Dense Phase vs. Dilute Phase Characteristics

<u>Characteristics</u>	<u>Dense Phase</u>	<u>Dilute Phase</u>
Solids/Air Ratio	30+ : 1	5 : 1
Design Pressure, psig	40 - 100	5 - 10
Operating Pressure, psig	50	5
Pipe Velocity, ft/min.	300 - 500	3000 - 4000
Line size, ID	1 - 3	6 - 12
Horsepower	60	250
Conveying Distance, ft.	800 - 1000	200 - 300
Air Use, scfm	250	2000

Figure 7
Dense Phase Mobile Demonstration Unit

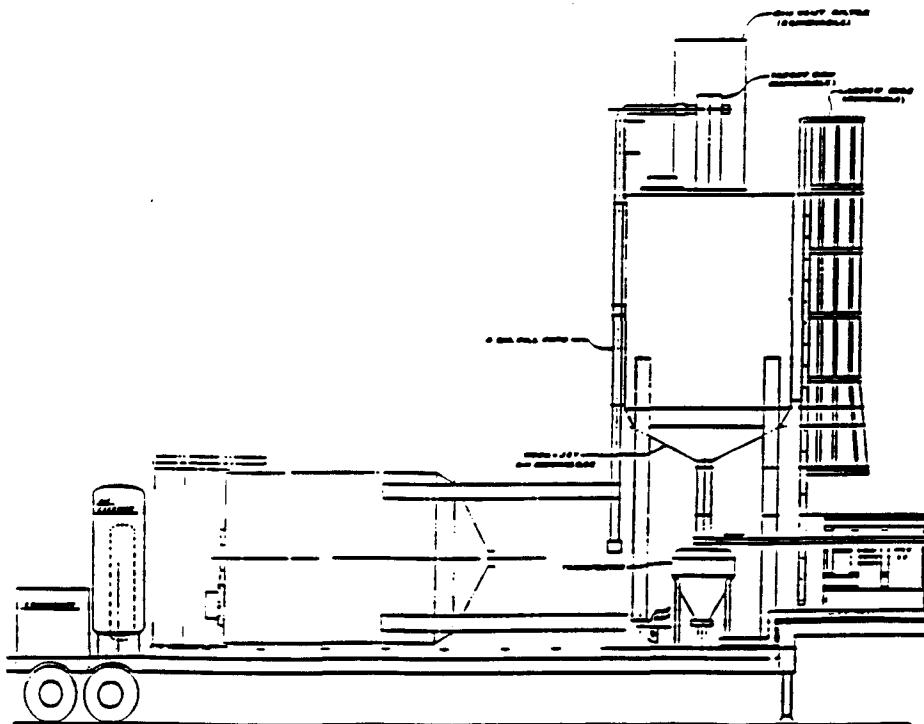


Figure 8
Hydrated Lime Chemical Analysis

<u>Component</u>	<u>% by weight</u>
Calcium Hydroxide, $\text{Ca}(\text{OH})_2$	90 - 95
Calcium Carbonate, CaCO_3	3 - 5
Magnesium Carbonate, MgCO_3	1.5 - 2.5
Silica, SiO_2	1.0 - 1.4
Iron, Fe_2O_3	0.2 - 0.4
Aluminum, Al_2O_3	0.3 - 0.6
Moisture, H_2O	0 - 2

Figure 9
Operating Conditions of a "Typical" Incinerator

Incinerator:

Capacity	250 tons/day (77,600 tons/year)
Capacity factor	85 % annual on-line operation
Flue gas	50,000 acfm @ 400 F
HCl	150 lb/hr.
SO ₂	75 lb/hr.

Sorbent Injection System:

Hydrated lime	500 lb/hr. at 95 % purity (1,860 tons/year)
Waste ash	600 lb/hr. additional waste (2,230 tons/year)

Figure 10
Dense Phase Dry Sorbent Injection System
Major Equipment List

<u>Equipment</u>	<u>Description</u>
Silo	30 tons capacity (> 5 days) 2,400 cu.ft. capacity
Transporter	2 @ 10 cu.ft. (one operating)
Compressor	2 @ 100 cfm (one operating, one standby) with receiver and dryer.
Transport pipe	1 ½ " I.D. carbon steel pipe.

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The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

PILOT PLANT TESTS TO OBTAIN HCl and Hg reduction in emissions produced by a Municipal and Hospital Solid Waste Combustor

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AMNIUP - Padua, Italy

INTRODUCTION

In July 1990 a Decree of Environment Ministry had fixed limits for the emissions of industrial plants in general and for MSW incinerators in particular. Each plant that does non comply with these limits has to present a treatment gas project to the Region administration to reach these limits within two years the end of 1992.

Padua Incinerator, that treats MSW together with Hospital Waste (25% of total amount) and expired medicines (2% of the total amount) complies the law for all parametrs except for Dust, Mercury and Hydrochloric Acid.

PLANT GENERAL DESCRIPTION

Combustion Chamber

Hospital waste are not dumped in the receiving bunker as municipal waste but, packed in a polietilene bag introduced in a cardboard box or in a polietilene drum, are directly put into the feed shaft with a conveyer belt.

Primary and secondary air of combustion may be conveniently adjusted and their distribution system is designed to create a good turbulence to realize an effective mixing between comburent and combustible to maintain a more uniform heat distribution all over the chamber.

Post-Combustion Chamber

The flue gas, coming from combustion chamber, passes in the post- combustion chamber that, according to italian law, must guarantee the follow operating conditions:

- O₂ free in wet fumes (downstream the chamber) : > 6% in vol.
- average gases velocity in chamber entrance section : >10 m/s

- contact time	: >2 s.
- temperature	: >950°C
- combustion efficiency	: > 99.9%

This chamber is provided with a burner that is automatically started as temperature of fumes goes under 950°C. In Padua incinerator temperature is normally around 1050-1100°C without the necessity of using the burner.

Heat recovery

Thermoelectric group consists of a vertical superheater working mainly by radiation. Vapour generator is a tube nest type, vertically disposed, operating by convection. Produced vapour is sended to a turbine to produce electric energy.

Dry Scrubbers

Flue gases coming from air mixer enter in the two reactors designed for dry adsorption of acid gases. Dry scrubbers are composed of two parallel units. Downstream each reactor is installed a cyclone for partial recycle of reagent. The gas control is obtained by injection of Calcium Hydroxide through nozzles that realize a chemi-adsorption of acid gases on line, giving as products salts as CaCl₂, CaF₂, CaSO₃, CaSO₄.

Adsorption efficiency is depending on: specific surface of the dry adsorbent per cubic meter of gas; concentration of polluting acid gases; contact time; homogeneity of mixing; temperature of reaction; water content of gases.

In our case temperature of reaction is in the range 250-300 °C too high to obtain good efficiencies of acid gases scrubbing.

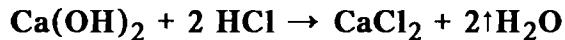
Since 1991 we started to use Sodium Bicarbonate. In Table 1 and 2 are summarized the removal efficiencies versus stoichiometric ratio for Sodium Bicarbonate and Calcium Hydroxide.

Tab. 1 - Calcium Hydroxide versus Sodium Bicarbonate HCl removal efficiencies

Reactive	Stoichiometric ratio	HCl removal efficiency %
Sodium Bicarbonate	1	80
	1.2	90
	1.5	97
Calcium Hydroxide	6.7	90

Tab. 2 - Calcium Hydroxide and Sodium Bicarbonate: chemical reactions for HCl removal and fly ash production.

Calcium Hydroxide



Stoichiometric calculations

$74/73 = 1.014$ kg di Ca(OH)_2 for 1 kg of HCl

1 kg of HCl \rightarrow 1.52 kg of CaCl_2

Fly ash produced for a 90% yield

1 kg of HCl \rightarrow 1.52 kg of CaCl_2 + 5.78 kg of Ca(OH)_2 = 7.3 kg of fly ash

Sodium Bicarbonate



Stoichiometric calculations

$84/36.5 = 2.301$ kg of NaHCO_3 for 1 kg of HCl

1 kg of HCl \rightarrow 1.6 kg of NaCl

Fly ash produced for a 97% yield

1 kg of HCl \rightarrow 1.6 kg of NaCl + 0.73 of Na_2CO_3 = 2.33 kg of fly ash

ESP

Solid particles - dust from combustion chamber, salts produced by reaction between acid gases and lime, and unreacted lime - are carried by the flue gas to an electrostatic precipitator.

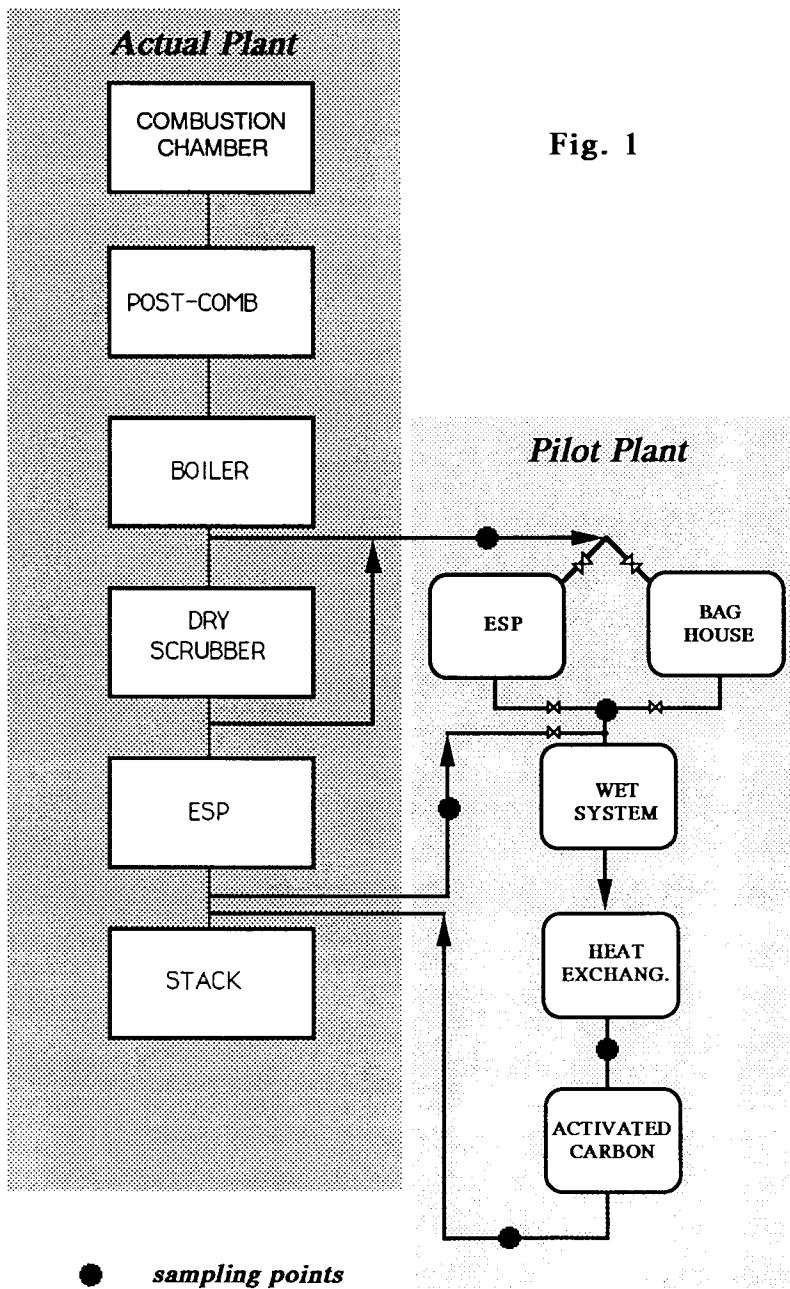
Fly ash, classified as a toxic waste by Italian law for the high content in Lead and Cadmium, is sent to a stabilization-solidification plant in Modena (Italy).

Pilot Plant

The pollutants that do not comply with Emission limits fixed by Italian normative are:

- particulate matter;
- Hydrochloric acid;
- Mercury.

Because of this, we realized a pilot plant consisting of a wet system, an ESP and a Baghouse. These three devices are connected to the actual plant as shown in Fig. 1.



Pilot Plant Description

The plant has been realized to treat a gas flow of 4000 Nm³/h.

Dedusted gas (by the ESP or the Baghouse) enter in a QUENCH to cool down the gas from 210 °C to 70 °C.

The Quench has an anti - acid heat shock resistance fettling.

The gas enters at the temperature of 70 °C in a wet scrubber divided into two stages (an acid washer stage and a basic washer stage).

The tower, containing special plates, has been realized in plastic material reinforced with glass fibre.

In the bottom stage water is used to obtain HCl adsorption. The solution is almost entirely recycled so that the pH is very low. A specific pH control system will provides to the automatic immission of fresh water to mantain HCl concentration constant.

A small amount of solution (5-10% of total amount in cycle) containg HCl, heavy metals his sended to existing water treatment plant.

Air, coming out from the bottom stage of the column, passes to the second washer stage in which a basic solution of water is used to get rid residual HCl and of SO₂.

The caustic soda solution leads to the formation of Na₂SO₃ (sodium sulphite).

The basic solution is sended to an oxidation tower in which air is injected for conversion of sulphite to sulphate.

The fue gas, after the exit of the column passes a dimister.

The saturated flue gas is than sended to an heat exchanger to bring temperature to 70 °C so that percentage relative humidity drops to 35-45% . Treatet gas are sended to the existing stack.

Some test will be conducted using an activated carbon adsorber.

The results of some of the tests are summarized in Fig. 2, 3 and 4.

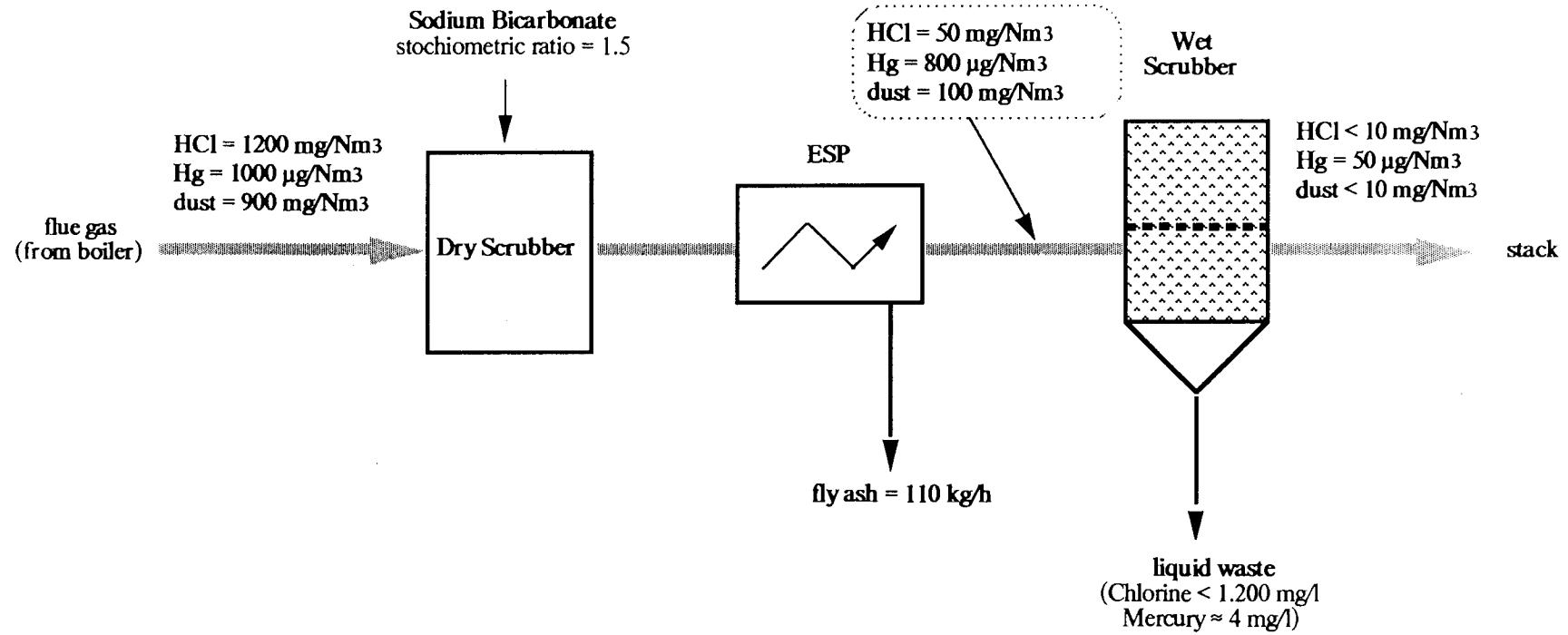


Fig. 2

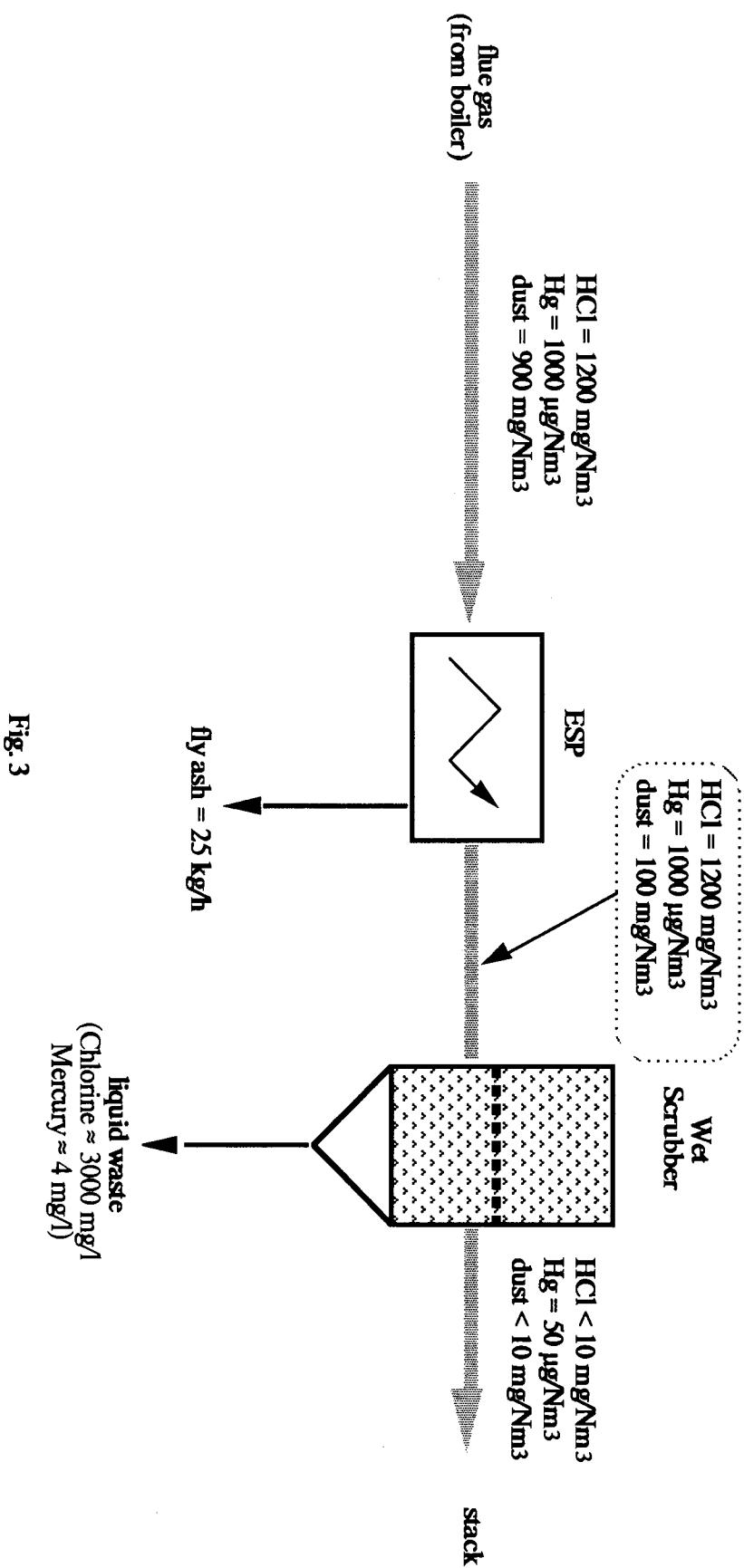


Fig. 3

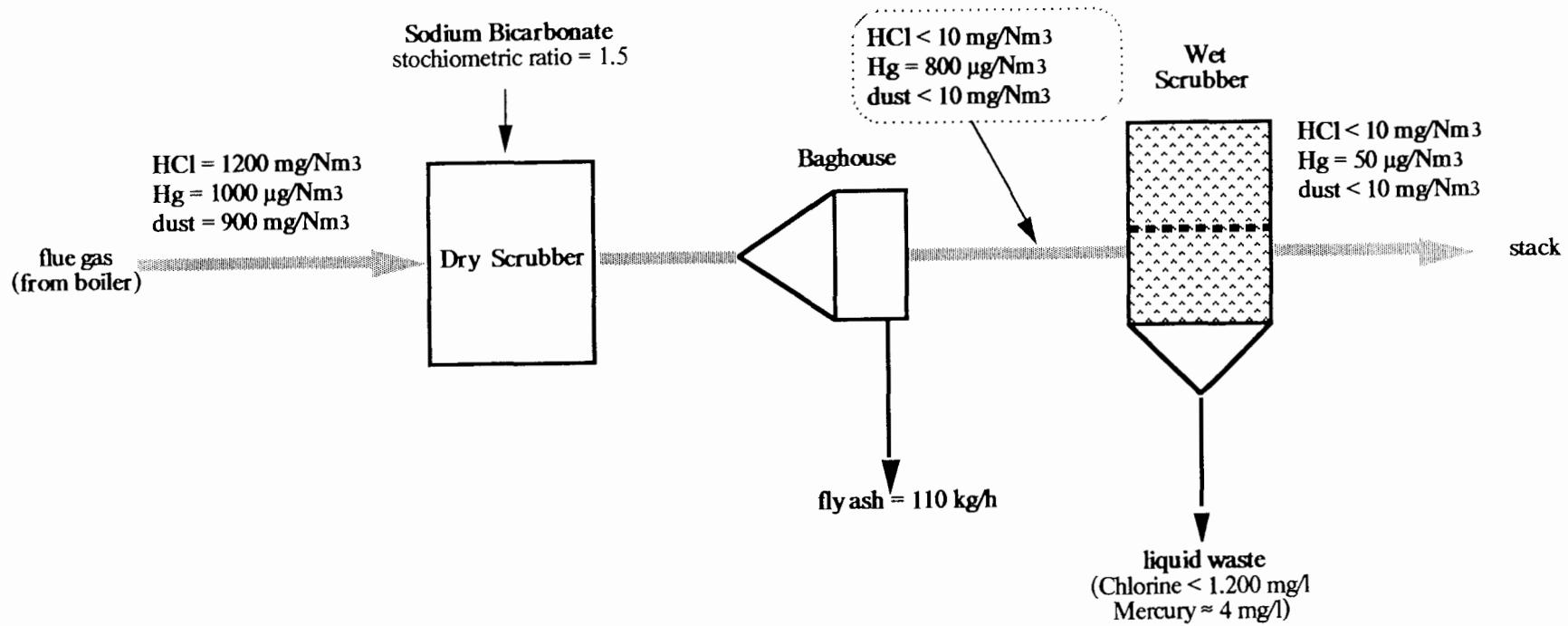


Fig. 4

Conclusions

The best configuration for Padua Plant are the one shown in Fig. 2 and 3.

Advantaged and disadvantages are summarized in the following Tables.

Boiler → ESP → Wet Scrubber → Stack	
Advantages	Disadvantages
- a low production of fly ashes; - no need for a chemical reactive for HCl removal;	- high concentrations of chlorine in waste waters (Italian law fixes a limit of 1200 mg/l)

Boiler → Dry Scrubber → ESP → Wet Scrubber → Stack	
Advantages	Disadvantages
- low concentrations of chlorine in waste waters (< 1200 mg/l)	- use of a chemical reactive - high production of fly ash

Probably the best configuration for Padua Plant is intermediate between the two shown above. That is, the quantity of Sodium Bicarbonate could be reduced to a quantity equal to 0.7 the stoichiometric value so that the Chlorine present in liquid waste could be kept lower than 1200 mg/l (limit fixed by Italian regulations) and the quantity of fly ashes produced could be kept to acceptable values.

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SESSION 9A : SAMPLING AND ANALYSIS I

Co-Chairmen:

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MERCURY EMISSION MONITORING
ON MUNICIPAL WASTE COMBUSTION

by

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ABSTRACT

In waste incineration, mercury is the only heavy metal to be released as a gas, mostly as mercury(II) chloride, because of its high volatility. Continuous emission monitoring is possible only when mercury occurs in its elemental form. Various possibilities of converting Hg(II) into Hg(0) have been studied and tested on a laboratory scale and in the TAMARA refuse incineration pilot facility. Continuous mercury emission measurement appears to be possible, provided mercury is converted in the flue gas condensate precipitated. The measuring results obtained on two municipal solid waste and on one sewage treatment sludge incineration plants show that the mercury monitor is a highly sensitive and selective continuously working instrument for mercury emission monitoring.

INTRODUCTION

In waste incineration, mercury is the only heavy metal to be released as a gas because of its high volatility. This makes it the real problem element in waste incineration. Elemental mercury, which constitutes the bulk occurring in waste, is oxidized quantitatively to mercury(II) chloride by the hydrogen chloride gas present; in the flue gas only this compound is to be found [1,2]. This fact is important in designing suitable offgas purification techniques. If the offgas is cleaned in scrubbers, it is possible that the plant will emit not only the Hg(II) component, which is not precipitated quantitatively, but also elemental mercury reconstituted as a result of reduction in the scrubbing water.

The mercury emission limits defined in the German Clean Air Regulations (TA Luft) cannot always be observed reliably, as the authors found in their measurements. However, today's sporadic sampling technique for mercury is unable to monitor the functioning capability of the flue gas purification equipment.

In addition, the amount of mercury on the input side and, consequently, also contained in the offgas is subject to major variations. Discontinuous measurements of the kind occasionally carried out by the monitoring agencies provide information only about the emission status while the sample is being taken. No satisfactory monitoring of the real emission situation is possible in this way. There is need for developing a continuous method of measurement allowing mercury emission and pollution to be monitored, independent of the type of mercury compound.

DISCONTINUOUS MERCURY MEASUREMENT TECHNIQUES

Continuous monitoring of the current emission and pollution limits with respect to mercury is not possible at the present time. Monitoring for these limits is done in the discontinuous mode by these two techniques [3]:

(1) Absorption in Solutions

Irrespective of the type of compound involved, mercury can be absorbed quantitatively from the offgas in strongly acid oxidizing scrubbing solutions. For this purpose, the sample gas flow is passed through two series-connected impingers filled with a peroxodisulfate solution

acidified with nitric acid, or a permanganate solution acidified with sulfuric acid. After the mercury content in the absorption solution has been analyzed, the corresponding mercury emission is calculated in the light of the gas volume.

(2) Adsorption onto Solids

Various solid adsorbers are available for the detection of elemental and bound mercury. Iodized activated carbon is particularly suitable for this purpose. The gas stream sampled is passed through an adsorber tube filled with iodized activated carbon. The adsorber is decomposed chemically, and the mercury emission is calculated from the amount of mercury adsorbed, with the gas volume being known. In addition, speciation of the mercury is possible if various adsorber tubes, those for mercury chloride and those for elemental mercury, are combined (see Fig. 1). Selective $HgCl_2$ separation can be achieved in a particularly effective way by a strongly basic anion exchange resin, such as Dowex 1X8. Dowex covered with chloride ions in an appropriate pretreatment step can be used to remove more than 98 % of $HgCl_2$ from a gas stream at sorption temperatures of 120 °C. $Hg(0)$ is practically unresorbable. Combining the two solid adsorbers, Dowex and iodized activated carbon, makes for an efficient speciation of the forms of mercury existing in the gas phase [3].

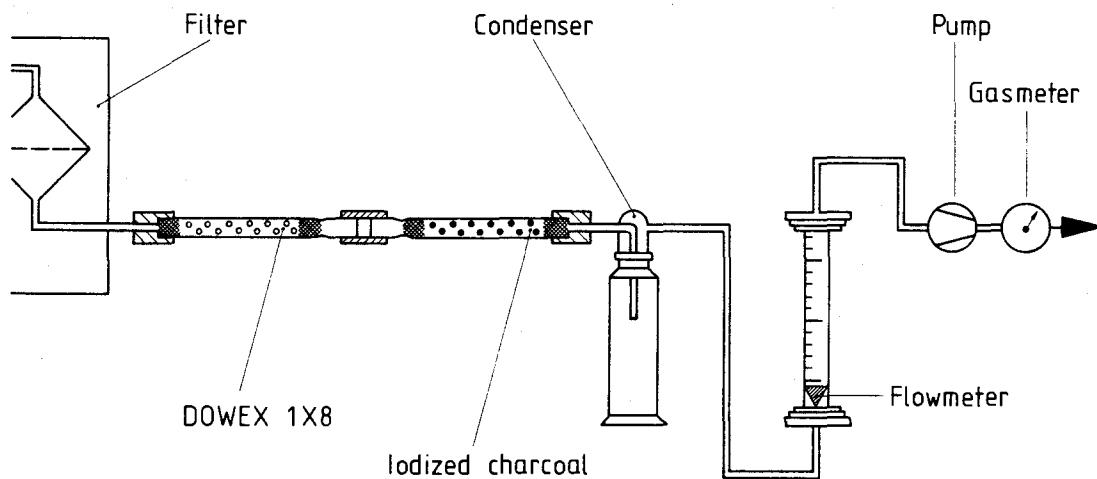


Figure 1. Measuring device for mercury speciation

The discontinuous measuring techniques referred to above can be carried out only at considerable expense. No analytical information can be obtained at the sampling point, as the samples can only be analyzed in a laboratory. And yet, there is need for these techniques, especially when balances must be established at various points in an offgas purification plant, or if it is a matter of speciation. In those cases, valuable information is obtained about the functions of various plant components in offgas purification.

CONTINUOUS METHODS OF MERCURY MEASUREMENT

Elemental mercury measurements representing the state of the art are carried out by means of resonance absorption at $\lambda = 253.7$ nm. This technique is used, e.g., in work place monitoring. However, no mercury compounds can be detected in this way.

In emission measurements conducted in incineration plants, i.e., in those cases in which mercury exists in a bound form, no direct determination is possible. Instead, the mercury compounds would have to be converted continuously into the elemental form if resonance absorption was to be used.

Various techniques of converting bound mercury into elemental mercury are known from measurements of mercury concentrations in the ambient air [e.g. 4,5]:

- (1) One technique, which is also customarily employed in laboratory analyses, is the addition of a reducing agent to a sample containing mercury, which reliably causes the reduction of Hg(II). This method lends itself well to monitoring liquid streams and is used for controlling scrubber circuits and the liquid effluent of refuse incineration plants.
- (2) Another method makes use of the reducing action of activated carbon for converting Hg(II) into Hg(0) at temperatures around 330 °C. In the presence of hydrogen chloride, which occurs in gaseous effluents especially of refuse incineration, lime may be added to stop any reverse reaction. The carbon converter can also be used to transform reliably into the elemental form the low mercury contents of the ambient air.

- (3) Another method operates at high temperatures of around 800 °C, which cause a direct conversion of Hg(II) into Hg(0). A reverse reaction with hydrogen chloride must be excluded. Thermal decomposition can be employed without any restrictions only if the existence of hydrogen chloride can be largely excluded. As a rule, this is true in environmental impact monitoring.

So far only the first method [6-9] has been used to measure mercury emissions downstream of power plants and refuse incineration plants. All these variants have some fundamental shortcomings:

- Method 1 suffers from the drawback of continuously consuming chemicals, which makes it expensive; the equipment needs permanent maintenance and supervision.
- Method 2 requires regular exchanges of the adsorber pipe as soon as the adsorber mix has been spent and, as a consequence, can be used meaningfully only in so-called clean gas at hydrogen chloride concentrations < 100 mg/m³.
- Because of a possible recombination with hydrogen chloride, method 3 works safely only in the absence of HCl. In addition, there are technical problems because of the high temperatures.

In our development of a mercury analyzer, a different possibility is utilized to convert the non-detectable molecular form into the detectable elemental form, namely the reaction of mercury bearing flue gas with its own condensate, which is obtained by cooling the sample gas stream to the required level. Naturally, this condensate contains reducing constituents, especially dissolved SO₂. The contact of mercury bearing offgases with the condensate causes Hg(II) to be directly reduced to Hg(0) and to be expelled with the gas stream. It can then be measured by means of resonance absorption.

EXPERIMENTAL INVESTIGATIONS OF MERCURY REDUCTION

VARIANT 1: Reduction with Stannous Chloride

Gas containing mercury must first be absorbed in a solution before being reduced to its elemental state by the addition of stannous chloride or borohydride solutions or sulfurous acid. The sample gas stream is passed through an impinger with an acid solution, which provokes the adsorption of Hg(II) in a first step; in a second step, Hg(0) is released after reduction. Within the framework of our development of a continuously measuring analyzer for mercury bearing solutions, fundamental studies were conducted in the laboratory. Experience has also been accumulated in practical application in refuse incineration plants [10].

VARIANT 2: Reduction with Carbon

Gases containing mercury(II) are completely reduced to their elemental form when passed through tempered carbon, e.g. in the form of activated carbon, and through carbon bearing solids, respectively, such as a lime-carbon mixture. The sample gas stream is drawn through such an adsorber tube and, after conversion, the mercury is detected by means of resonance absorption. The hydrogen chloride concentrations normally encountered in the gaseous effluents of refuse incineration plants affect the conversion reaction. A suitable adsorber must be used to separate the HCl. For this purpose, e.g., carbon may be mixed with an appropriate amount of lime and this mixture may be used simultaneously as an HCl adsorber and Hg converter.

VARIANT 3: Thermal Decomposition

The mercury(II) halides existing in the gaseous effluent or ambient air are decomposed completely, forming elemental mercury, when passed through a sufficiently heated temperature zone. Thermal decomposition can be felt already at temperatures around 600 °C. Complete decomposition occurs at reaction temperatures of 800 °C at gas retention times of only 0.4 s. The presence of hydrogen chloride counteracts the decomposition reaction. The mere presence of 100 mg of HCl/m³ more or less shifts the balance of formation back to the side of Hg(II). If HCl is assumed to be present, this component must be removed on all accounts. This can be achieved, e.g., by means of a tempered HCl adsorber, such as lime or silica gel, upstream. However, the adsorber efficiency needs to be monitored permanently.

Direct thermal decomposition in the heated absorption cell of a spectral photometer, while the unit is being used for measurement, is possible if sufficient retention times can be maintained and hydrogen chlorides can be safely excluded. However, this is difficult to achieve technically.

VARIANT 4: Reaction with the Condensate

This procedure is characterized by the conversion of Hg(II), brought about solely by the reducing components existing in the flue gas. These are, above all, sulfurous acid, but also certain substances contained in the dust [11]. Consequently, the reduction of Hg(II) can succeed only if the element is brought into close contact with a condensate of the flue gas. For this purpose, the sample gas stream is cooled down slightly, thus causing condensate to form. The sample gas stream is passed through the condensate, as in an impinger. The elemental mercury formed is directly expelled again with the sample gas stream, entering the absorption cell of the spectral photometer. The reactor is equipped with an overflow to discharge the spent condensate. This reactor design ensures that there is always fresh condensate to maintain the reducing effect. This makes for a strictly continuous mode of operation.

The reducing component(s) in the flue gas condensate, and their mechanisms of action, will not be discussed in this paper. Suffice it to say that this reducing property exists only in condensate *in statu nascendi*. In modern, smoothly functioning flue gas purification systems, the reducing effect of the clean gas may no longer be sufficient. In that case, adding a small amount of a reducing agent, such as a stannous chloride solution, is enough to make the conversion complete.

CONTINUOUS MERCURY MEASUREMENT IN TECHNICAL PLANTS

ANALYTICAL COMPARISON BETWEEN CONTINUOUS AND DISCONTINUOUS MEASUREMENTS

In a test setup in the TAMARA refuse incineration pilot plant of the Karlsruhe Nuclear Research Center, with a throughput of 200 kg of solid municipal waste/h, the mercury monitor has been tested. The sample gas stream was extracted through a heated quartz glass probe and passed into the cell of a commercial mercury analyzer (both after dust removal by means of

quartz filter and, alternatively, directly) through the reactor in which the condensate collects. For this purpose, the monitor developed for measurements of maximum permissible work place concentrations by Seefelder Mess-technik GmbH, with a measuring range between 0 and 1200 $\mu\text{g}/\text{m}^3$, was used. The signal generated by resonance absorption was recorded and stored in a computer. Figure 2 shows the test setup for continuous mercury measurement.

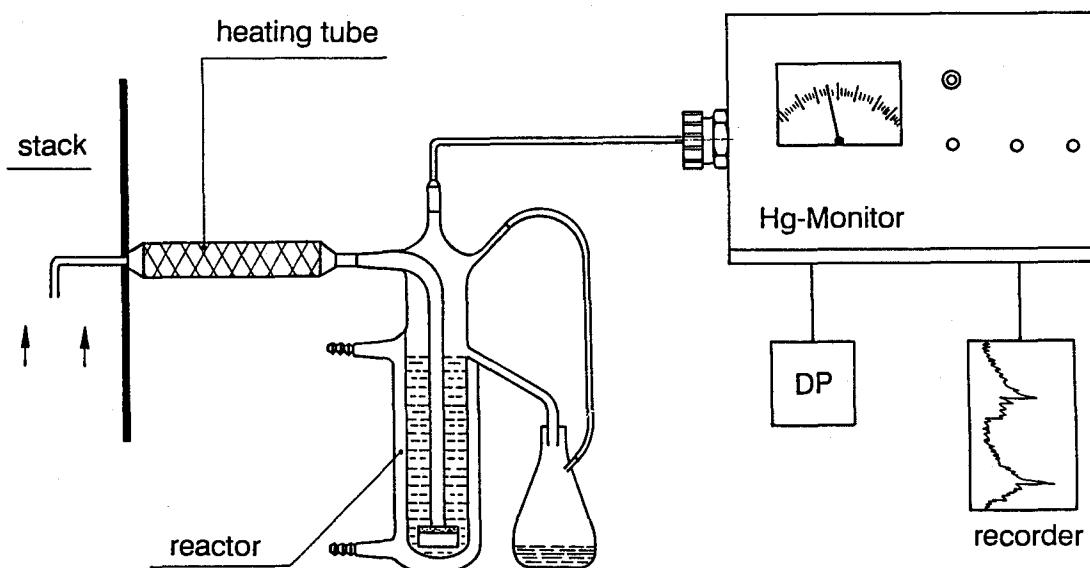


Figure 2. Test setup for continuous measurement

In parallel with this step, another partial gas stream was extracted for discontinuous sampling and passed through solid adsorbers ensuring precise speciation of the mercury as Hg(II) and Hg(0). The four-hour averages obtained in this way were to be used to monitor the concentrations obtained on line.

Table 1 contains a summary of the results both of the discontinuous measurements and of the data measured on-line as averaged by the computer. These results were obtained in various TAMARA measurement campaigns, in measurements in a sewage treatment sludge incineration plant, and in measurements conducted in a technical scale incineration plant for solid municipal waste. The good agreement between mercury concentrations in the flue gas obtained continuously and those determined discontinuously is evident. This proves that the conversion of Hg(II) to Hg(0) is complete during the continuous sampling process. Figure 3 is a graphic plot of the data obtained.

TABLE 1. COMPARISON OF MEASURED DATA (in $\mu\text{g}/\text{m}^3$)
 (discontinuous, Hg(II)/Hg(0) with Dowex/iodized
 activated carbon; continuous with Hg analyzer;
 T=TAMARA, S=sewage sludge, M=municipal waste)

Test No.	Date	Time	Hg discont. (II)	Hg cont. (0) total	Hg cont. mean
T49	19.09.89	11-15	8	1 9	8 \pm 15
	20.09.89	11-15	8	<1 9	10 \pm 16
	21.09.89	7-11	7	1 8	9 \pm 3
	22.09.89	9-13	8	1 9	9 \pm 2
T59	08.11.89	11-14	21	8 29	28 \pm 29
	09.11.89	13-16	8	3 11	9 \pm 11
	14.11.89	13-16	26	4 30	24 \pm 1
T10	27.03.90	7-9	8	7 15	18 \pm 4
	28.03.90	10-13	18	60 78	92 \pm 161
	29.03.90	11-14	14	28 42	49 \pm 55
	20.06.90	10-13	36	9 45	46 \pm 13
T30	21.06.90	10-13	16	6 22	38 \pm 10
	19.02.90	9-12	26	152 178	170
	20.02.90	9-13	26	139 165	170
	21.02.90	9-13	41	152 193	230
S01	01.03.90	9-13	57	145 202	180
	15.10.90	10-14	20	6 26	22
	17.10.90	10-14	17	10 27	40
	19.10.90	9-13	68	57 125	160
M01	30.10.90	10-14	170	19 189	190
	31.10.90	10-14	74	71 145	135

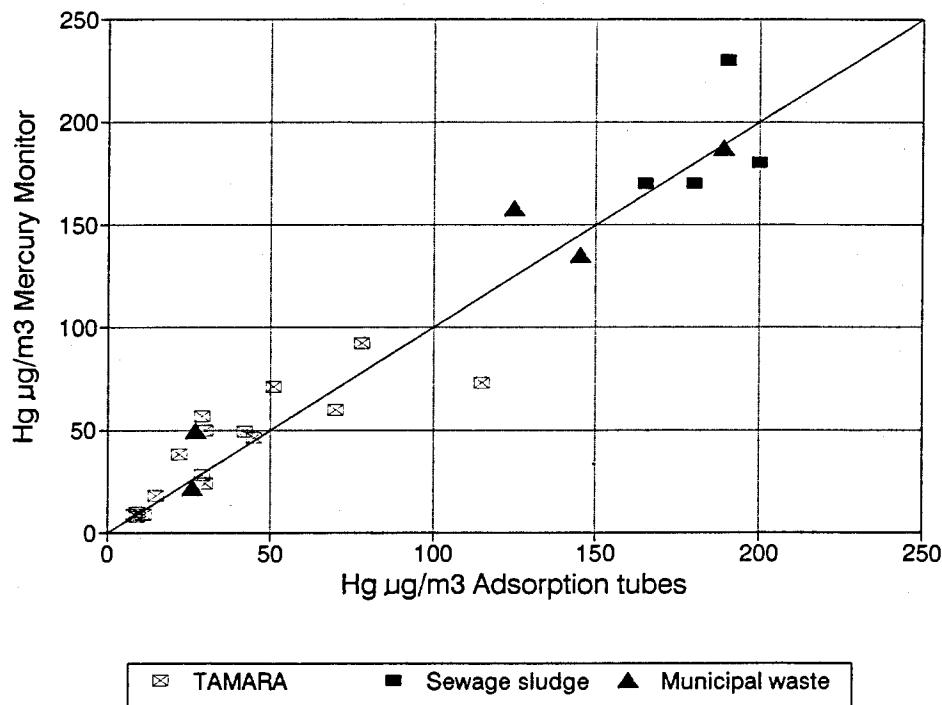


Figure 3. Analytical comparison of continuous versus discontinuous measurements

DISCUSSION OF THE CONTINUOUS MEASUREMENT SERIES

TAMARA Pilot Plant

Some typical series of clean gas measurements performed on the stack of the TAMARA plant will be shown below. The plots are the curves of on-line measurements of the flue gas scrubbing water in the first scrubber stage (Hg in mg/l , scale 10 times enlarged) and the curves of the flue gas measurement (Hg in $\mu g/m^3$). The time resolution is 5 minutes; the measured points represent averages over the past 5 minutes.

Figure 4 very impressively shows that mercury is not distributed homogeneously in the refuse, but is detected as a discrete event. This had been known from earlier continuous measurements in the flue gas scrubbing water

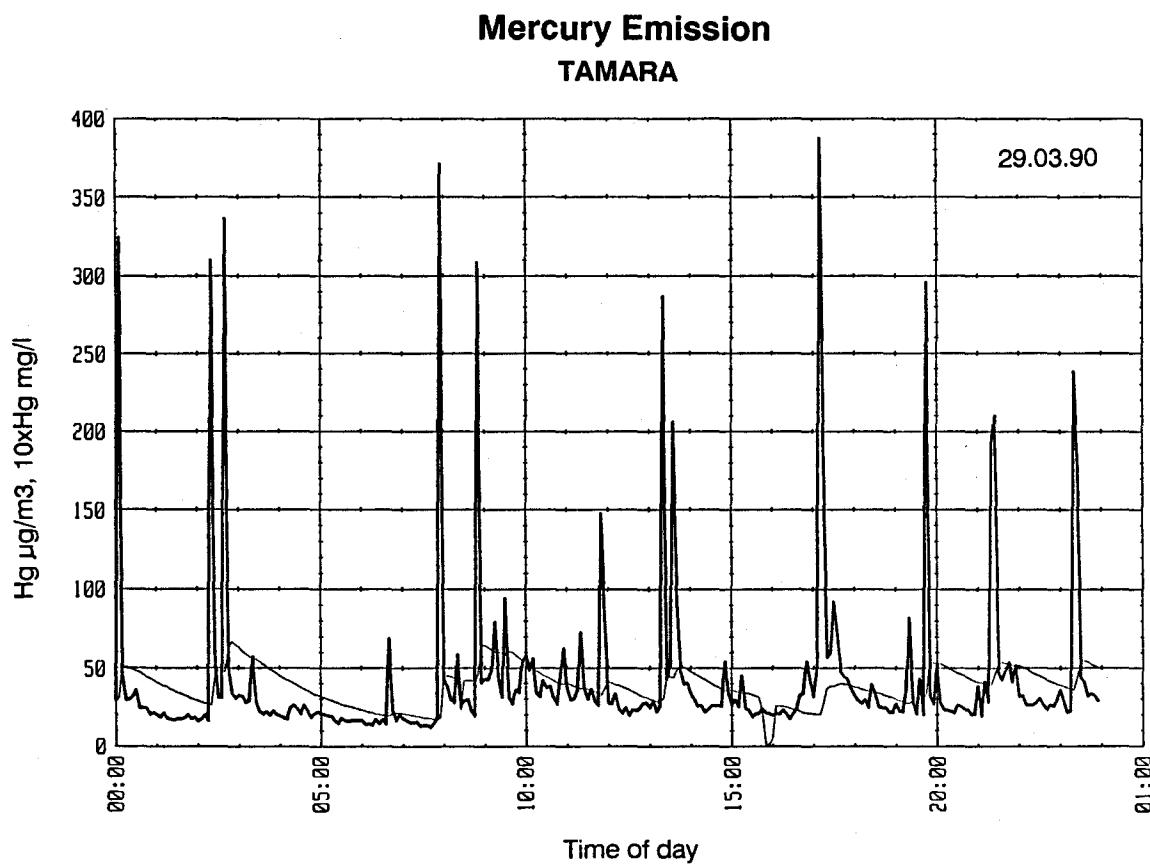


Figure 4. On-line measurement curves showing mercury concentrations in the scrubber and at the stack

Mercury Emission TAMARA

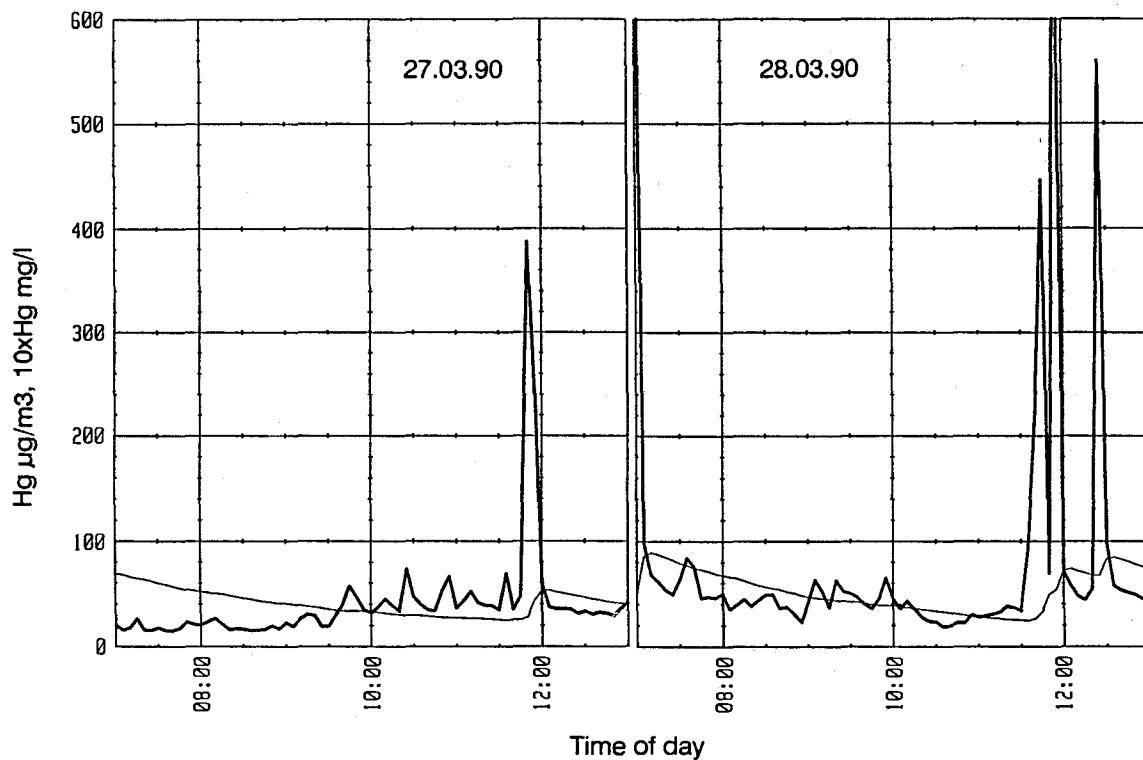


Figure 5. On-line measurement curves showing mercury concentrations in the scrubber and at the stack

of a refuse incineration plant [10]. However, the measurements performed in the flue gas show the mercury peaks even more clearly. Sometimes peak levels exceeding $500 \mu\text{g}/\text{m}^3$ were measured. Deflections of the scrubber signal follow, much broadened and with long decay times.

The example of two days of measurements is to show the doubtful nature of discontinuous random sample measurements. On March 27, 1990 (Fig. 5, measuring time 7 - 9 a.m.), a very low emission level (discontinuous) of $15 \mu\text{g}/\text{m}^3$ was obtained. It is obvious that a minimum emission level was sampled on that occasion. On the next day, March 28, 1990 (Fig. 5, measuring time 10 a.m. - 1 p.m.), the value measured of $78 \mu\text{g}/\text{m}^3$ turned out to be much higher. Continuous measurement in this case reveals peaks existing during the measuring period. So, discontinuous mercury measurements do not lend themselves to emission monitoring, nor to producing information about the effectiveness of flue gas purification equipment.

Mercury Emission
TAMARA

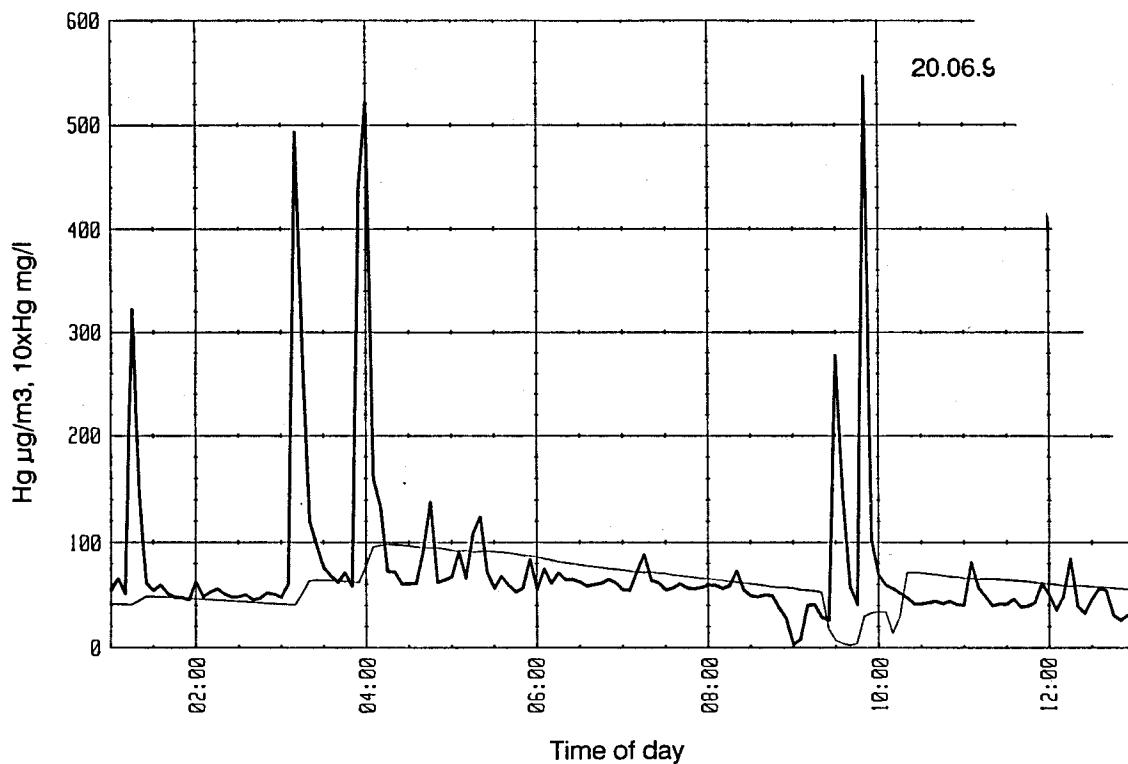


Figure 6. On-line measurement curves showing mercury concentrations in the scrubber and at the stack

The law prescribes mean values obtained over one half hour and two hours for assessing the emission situation. The effects of the peaks will be shown below, again by the example of one day of measurement. One June 20, 1990, the sampling period considered (Fig. 6, measuring time 9 - 11 a.m.) includes a five-minute mean of $550 \mu\text{g}/\text{m}^3$. The computer produces these half-hour mean values:

9:00- 9:30	60 ± 97
9:30-10:00	176 ± 187
10:00-10:30	52 ± 10
10:30-11:00	42 ± 2

This leads to a two-hour mean value of $77 \pm 112 \mu\text{g}/\text{m}^3$. The occurrence of high peak emissions for very short periods of time thus does not necessarily have to be a source of concern.

Sewage Treatment Sludge Incineration Plant

The findings made in emission measurements at an incineration plant of sewage treatment sludge are quite different (Fig. 7; the time resolution is 1 minute). Little had been known so far about mercury in connection with such plants. Our measurements indicate that mercury is present practically in a homogeneous distribution. The pronounced fluctuations, with peak emission levels, customarily found in the incineration plants of solid municipal waste do not exist in this case. The concentration level in the flue gas of incineration plants for sewage treatment sludge is equal to that found in incineration plants for solid municipal waste. Consequently, the flue gas purification systems must meet the same requirements. In contrast to solid municipal waste incineration plants, elemental mercury is detected already as a constituent of the unfiltered gas. This is due in particular to a different HCl/SO₂ ratio in the flue gas.

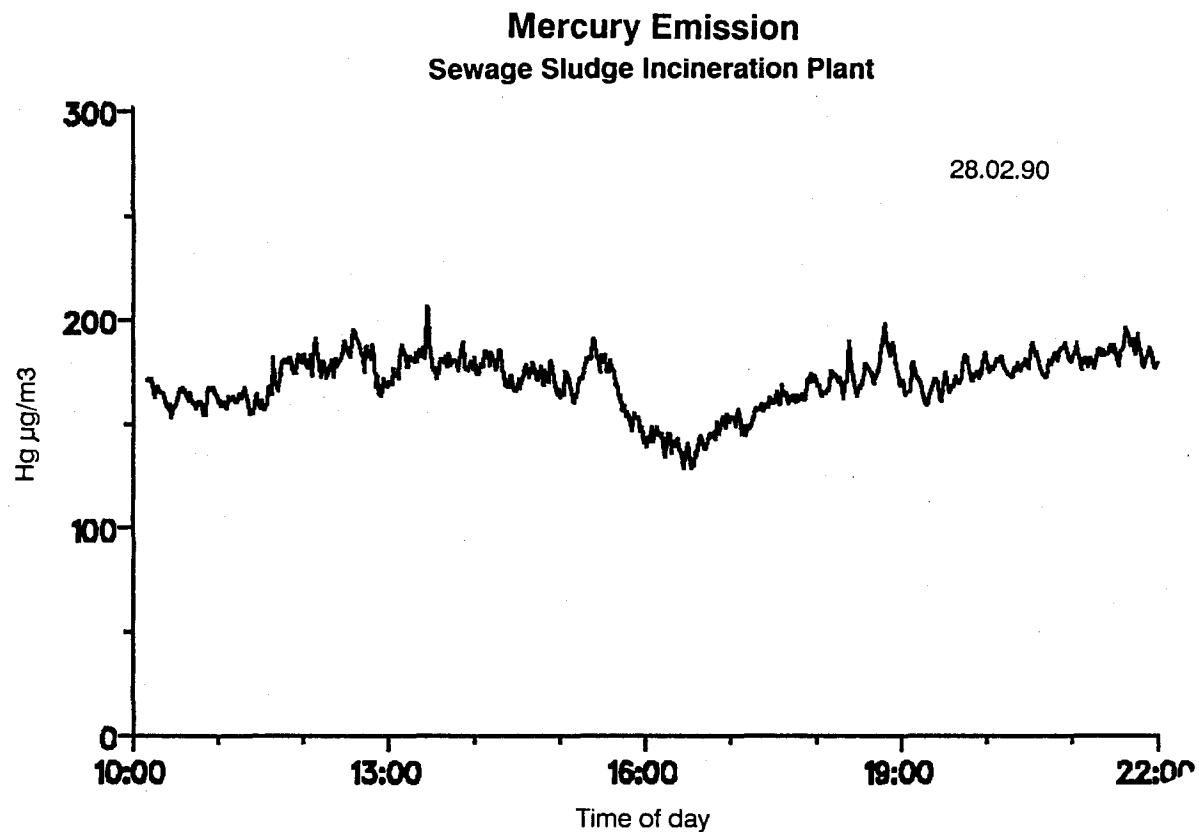


Figure 7. On-line measurement curves showing mercury concentrations at the stack

Solid Municipal Waste Incineration Plant

Our measurements performed in a technical scale plant proved for good that mercury emissions are detected completely by the mercury monitor. In the course of the measurement campaigns, the flue gas purification system was operated in two modes so as to allow the optimum setting for mercury removal in the scrubber to be found (see Fig. 3). Figure 8 shows the record of one day. The results indicate that the legal limits can be observed reliably provided that an instrument for continuous emission monitoring is available.

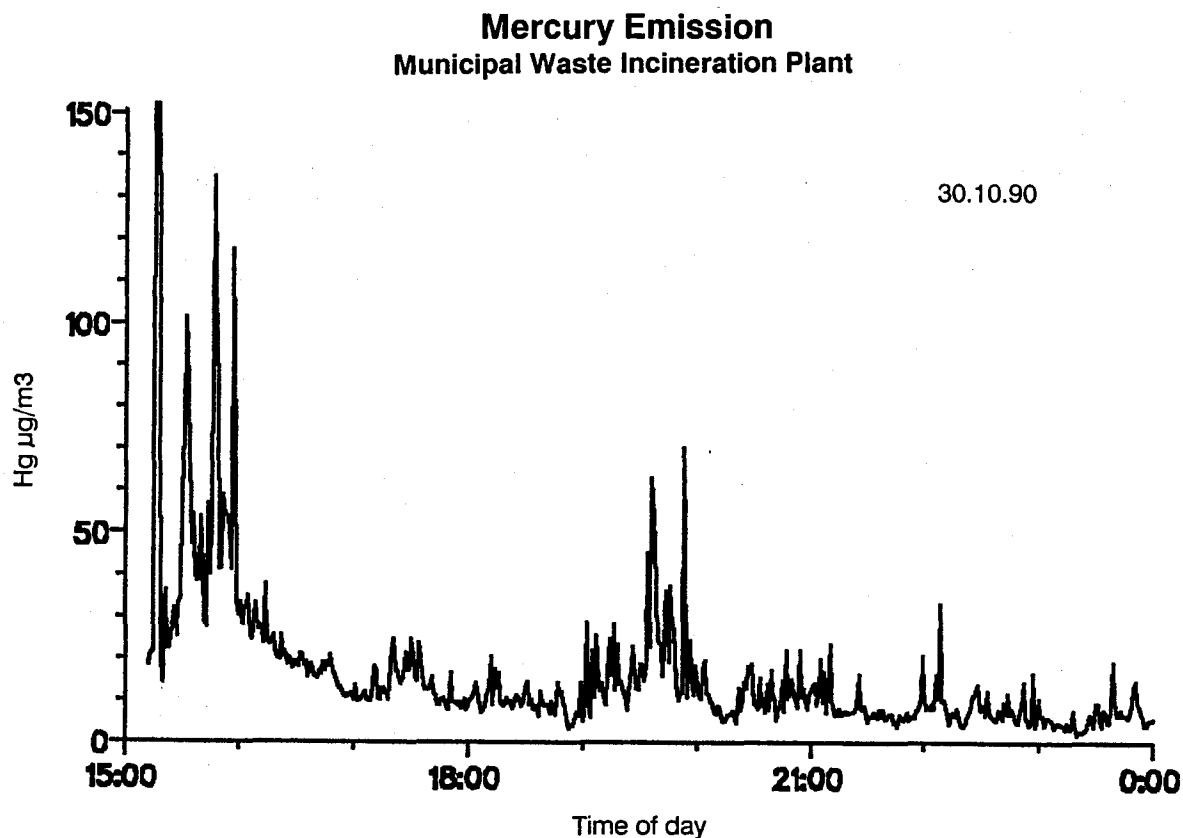


Figure 8. On-line measurement curves showing mercury concentrations at the stack

CONCLUSION

The measured results obtained so far allow the statement to be made that continuous measurement of mercury emissions in refuse incineration plants is possible. The conversion of mercury chloride into elemental mercury required for this purpose seems to be fully possible by passing the substance through flue gas condensate. The measuring results obtained on two municipal solid waste and on one sewage treatment sludge incineration plants show that the mercury monitor is a highly sensitive and selective continuously working instrument for mercury emission monitoring. A commercially viable piece of equipment is being developed jointly with the licensee.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

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A NEW METHOD FOR SAMPLING HALOGENATED DIOXINS
AND RELATED COMPOUNDS IN FLUE GASES.

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ABSTRACT

A new sampling method has been constructed that cools the flue gas directly in the stack to avoid chemical formation and/or degradation reactions. The sampling method is optimized for adsorption of organic micropollutants in gases, particulates and in aerosols. The sampler is simple and easy to handle. The cooled probe, the impinger system, and the aerosol trap are assembled on a trolley running on a rail. This means that it is very easy to use a traversing procedure on a cross-sectional area of the duct. The probe can be equipped with a built-in pitot. The sample velocity can be adjusted to equal the gas velocity in the duct during the whole sampling period and at every sampling point. Another advantage is the ability to measure hot gases. With a titanium probe and a quartz glass line flue gases with temperatures up to 1100°C can be sampled.

INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) as well as other chlorinated pollutants in stack emissions from municipal solid waste (MSW) incinerators have become a matter of scientific and public concern during the last years. The maximum emission of PCDDs and PCDFs from MSW incinerators in Sweden has been legislated to 0.1 ng/m³ (norm. d.g. 10% CO₂) based on International Toxicity Equivalents (I-TEQ). High requirements must be met during the flue gas sampling procedure and also by the analytical techniques used to measure each toxic PCDD/F isomer with high specificity and a

sensitivity, to a level below 10 pg/m³. Currently most countries use their sampling procedure for measuring PCDDs and PCDFs in flue gases from combustion sources. Data from different countries are therefore often compared without any consideration to different sampling, analytical, and calculation methods.

The partitioning of PCDDs and PCDFs between the vapor and the particle phase is very dynamical in nature. It depends on the partial pressure of the compounds, the temperature of the flue gas, the available surface area, and the nature, of the fly ash particles. Thus the partitioning ratio will shift toward more particle bound PCDDs and PCDFs in the cooling regions within the incinerator and smoke stack. The ratio is also changing when the temperature drops in the sampling train. A condensation aerosol is formed in the condenser when the equilibrium vapor concentration (EVC) at the temperature of the condenser is exceeded. This condensation aerosol is of physical dimension that most easily passes through sampling equipment (around 0.5 µm aerodynamic diameter). An efficient stack sampling method for PCDDs and PCDFs must collect both the vapor phase and the particle bound components, as well as the condensation aerosol, that could be formed in the sampling train. Failure to collect the particle bound PCDDs and PCDFs will result in an underestimation of the PCDD/F emission. Furthermore failure to retain pre-sampling spikes will have a negative effect on the method accuracy due to difficulties in correction of these losses.

Practical "in-the-field" experiments (1,2) have demonstrated the following weaknesses with the existing flue gas sampling methods:

1. High temperature at the filter house (as in the EPA sampling train 120-160°C). This can cause formation and/or degradation reactions of the native and labelled PCDDs and PCDFs isomers on the filter yielding erroneous results.
2. Very few sampling methods are optimized for collection of aerosols(3).
3. Sampling trains in which most of the PCDDs and PCDFs are found in the rinsing fraction (US-EPA method 23) had to be treated with extreme care, otherwise losses of sample during the rinsing procedure would occur.
4. Most sampling methods were unnecessarily complicated and difficult to use in practice.

METHODS

A new sampling apparatus with which most of the above problems are remedied has been constructed (3), and is shown in Figure 1.

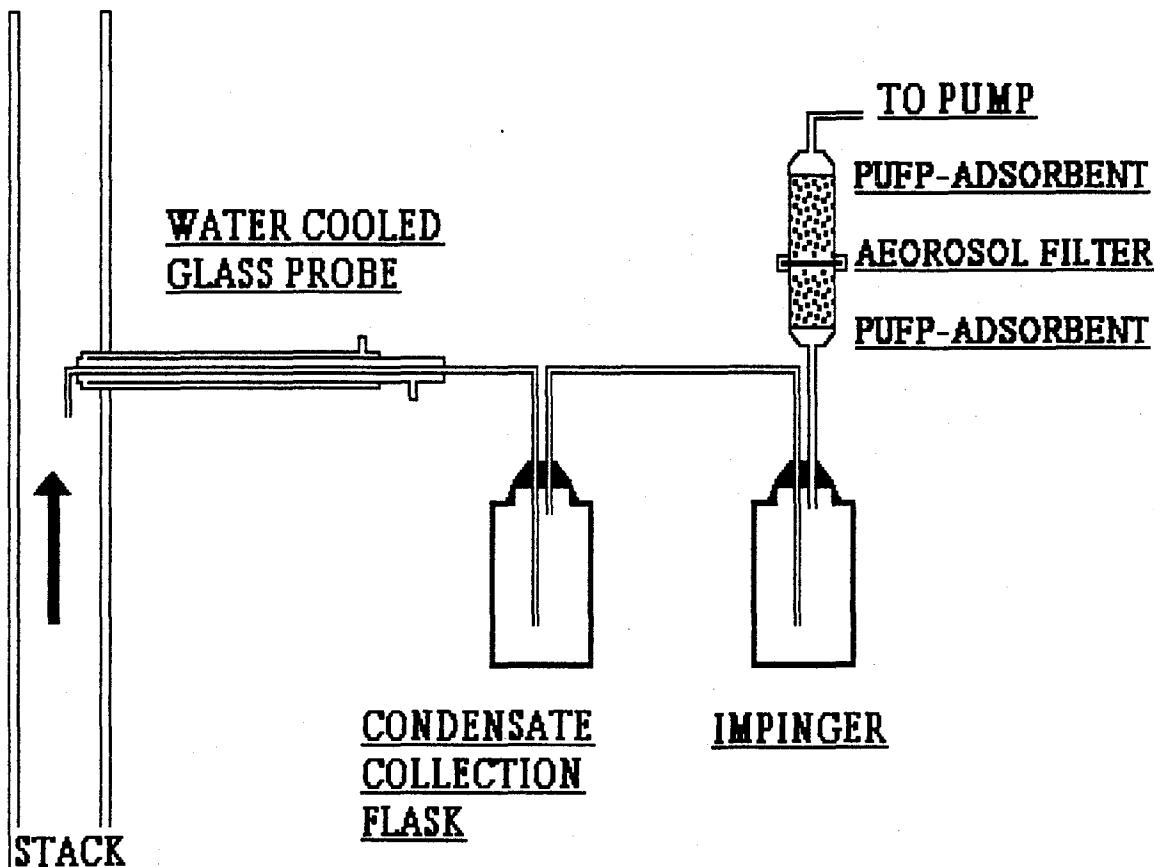


Figure 1. Schematic drawing of the modified sampling train.

The advantages of this sampling strategy include:

1. Rapidly cooling of the flue gas to 5°C in the front end of the probe. This eliminates formation/degradation reactions in the sampling train.
2. The probe can be equipped with a pitot that improves the ability for isokinetic sampling.
3. The sample train is assembled on a movable trolley which thereby makes it possible to sample from a multitude of points within the stack.

4. Optimization for aerosol adsorption. The second impinger has a nozzle and a water soluble solvent, ethylene glycol, which increases the adsorption of small particles. The combination adsorbent - aerosol filter - adsorbent also improves the collection of small volatile aerosols.
5. Easy in handling. The compartments are composed of four glass components: the glass probe, two impingers, and a glass housing for two polyurethane foam plugs with an aerosol filter between them.

TABLE 1 PROPOSED SPIKING PROTOCOL FOR SAMPLING OF PCDDs AND PCDFs IN STACKS, WITH EMISSION RESULTS COMPENSATED FOR INCOMPLETE SAMPLING RECOVERY.

Sample spike Internal standard	Clean up spike MS group 1	Syringe spike Recovery standard MS group 1
$^{13}\text{C}_{12}-2,3,7,8\text{-TCDD}$	$^{37}\text{Cl } 2,3,7,8\text{-TCDD}$	
$^{13}\text{C}_{12}-1,2,3,7,8\text{-PeCDD}$		
$^{13}\text{C}_{12}-1,2,3,6,7,8\text{-HxCDD}$	$^{13}\text{C}_{12}-1,2,3,7,8,9\text{-HxCDD}$	
$^{13}\text{C}_{12}-2,3,7,8\text{-TCDF}$		
$^{13}\text{C}_{12}-2,3,4,7,8\text{-PeCDF}$		$^{13}\text{C}_{12}-1,2,3,7,8\text{-PeCDF}$
$^{13}\text{C}_{12}-1,2,3,6,7,8\text{-HxCDF}$		
MS group 2	MS group 2	MS group 2
$^{13}\text{C}_{12}-1,2,3,4,6,7,8\text{-HpCDD}$		
$^{13}\text{C}_{12}-2,3,4,6,7,8\text{-HxCDF}$	$^{13}\text{C}_{12}-1,2,3,7,8,9\text{-HxCDF}$	
$^{13}\text{C}_{12}-1,2,3,4,6,7,8\text{-HpCDF}$		$^{13}\text{C}_{12}-1,2,3,4,7,8,9\text{-HpCDF}$
MS group 3	MS group 3	MS group 3
$^{13}\text{C}_{12}\text{-OCDD}$		$\text{Br}, \text{Cl-DD or -DF}$
$^{13}\text{C}_{12}\text{-OCDF}$		

CONCLUSIONS

Validation studies between this sampling method and other recommended sampling methods in Europe presented by Marklund et al(1,2) show comparable results both for PCDDs, PCDFs, and other chlorinated components. But the studies took place before the

sampling method was modified with the aerosol filter, so losses of small particles may have occurred in all sampling trains.

One important conclusion from the two validation studies of sampling techniques is identification of the need for an appropriate spiking protocol. If, as in the Scandinavian countries, the regulation prescribes emission data, compensated for sampling recoveries(4), as many labelled PCDD and PCDF congeners as possible, should be included in the sampling spike. Table 1 shows the spiking protocol used at the University of Umeå.

Another conclusion is that the sampling spike should be applied in the first cold region in the sampling train. Experience from the validation studies clearly demonstrates, that spikes added on the glasswall inside the cooled probe can vary largely and are not related to the losses of the sampling spike applied in the cold part of the sampling train, nor to the losses of native isomers. Explanations may be attributed to losses in the evaporation of the spike mixture solvent, irreversible adsorption onto the glass walls, or backflushing when the probe is introduced into the stack.

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SESSION 10A: SAMPLING AND ANALYSIS II

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The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

Assessment of an On-Line CI-Mass Spectrometer as a Continuous Emission Monitor for Sewage Sludge Incinerators

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ABSTRACT

ELI Eco Technologies Inc. tested two sewage sludge incinerators using regulatory methods and a V&F CIMS-500 chemical ionization mass spectrometer. Correlations between dioxins and dibenzofurans from the regulatory MM5 trains and the continuous readings from the CIMS-500 for chlorobenzenes and chlorophenols were noted. As well, correlations between chlorinated organics and other volatile organics were obvious under poor combustion conditions.

ELI Eco Technologies Inc. recently completed an extensive survey of organic chemical emissions including VOCs, chlorobenzenes, chlorophenols, chlorinated dioxins and dibenzofurans from two sewage sludge incinerators. The program was funded by the Municipality of Metro Toronto, Environment Ontario, and Environment Canada. Contaminants were measured by regulatory methods (ASME Modified Method 5) and simultaneously with the continuous mass spectrometer. The purpose of the study was to provide regulatory testing and at the same time evaluate the usefulness of the CIMS-500 mass spectrometer in assessing emissions.

Continuous monitoring of emission concentrations at two sewage slide incinerators with the V&F CIMS-500 mass spectrometer correlated well with data obtained using regulatory methods. The most important difference found between the regulatory method (ASME Modified Method 5) and measurement with the CIMS-500 was that the results were available immediately using the continuous mass spectrometer system, and the higher emissions from one day to the next were noted at the time, when some corrective action could have been taken.

The regulatory method requires triplicate sampling for day-long periods, lengthy delays for lab analysis, and yields only one number per test for each contaminant. With current regulatory testing, it is difficult to establish correlations between incinerator operating conditions and stack emissions, let alone attempt to correct them. Continuous emission monitoring with the CIMS-500 would make it possible to optimize combustion by measurement of various hydrocarbons, reduce dioxin and dibenzofuran emissions by monitoring chlorobenzene and chlorophenol emissions, and track emissions year-round.

Three days of testing at a sewage sludge incinerator in January 1990 showed chlorinated dioxin and dibenzofuran emissions that can respectively be called low, high and medium, relative to each other. The CIMS-500 data for both chlorobenzene and chlorophenol concentrations correlated well with that trend. Although the mass spectrometer system cannot measure the extremely low concentrations of dioxin and dibenzofuran emissions, it can measure the part per billion levels of chlorophenols that occur in conjunction with dioxins and dibenzofurans, thus providing an indirect measurement of dioxin and dibenzofuran emissions. Figure 1 shows correlations of dioxin and furan concentrations by ASME MM5 versus chlorophenol and chlorobenzene concentrations by CIMS-500. A slightly better correlation results using the chlorobenzene data. Although continuous data is available for the chlorobenzene and chlorophenol concentrations, the correlations are limited by the three data points available from the ASME MM5 trains for dioxins and dibenzofurans.

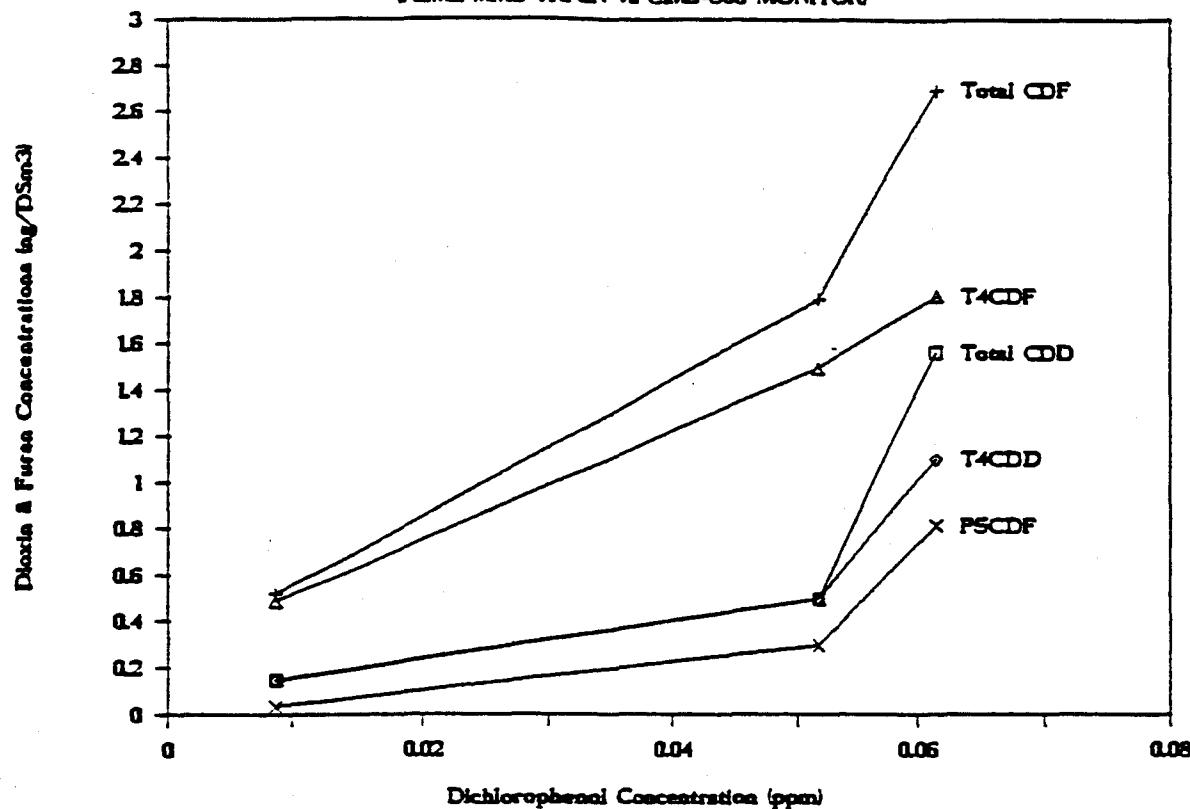
Other correlations were noted between chlorophenol and chlorobenzene concentrations and those for benzene, toluene, xylene, and phenol. These correlations reflect the poor combustion conditions that occurred on the test day with the highest dioxin emissions. The continuous analysis of organic emission with an installed mass spectrometer system would therefore allow the incinerator operator to optimize combustion using benzene, toluene, and xylene readouts, and further optimize to achieve the lowest dioxin and dibenzofuran emissions by measurement of chlorobenzenes and chlorophenols. As well, a continuous record of emission data would be produced all year, rather than three days per year.

Figure 2 shows the continuous monitoring of benzene, toluene and xylene, with dichlorophenol (DCP), trichlorophenol (TCP) and tetrachlorophenol (TeCP) on the first graph and with chlorobenzene (CB), dichlorobenzene (DCB) and trichlorobenzene (TCB) on the second graph. Note that the benzene, toluene and xylene concentrations are shown 10 times reduced. It is quite obvious from this graph that there are correlations between the compounds that were measured. Note that the feed to the incinerator was off at 12:10 and at a reduced rate at 13:30. Bringing the system back on line probably contributed to the high results obtained. Breaks in the continuous monitoring correspond to instrument calibration periods.

In summary, continuous emission monitoring using the CIMS-500 mass spectrometer has been successful in comparison with ASME MM5 sample train measurement and should be useful in optimizing combustion conditions, minimizing emissions of chlorinated dioxins and dibenzofurans, and providing continuous emission data for incinerators.

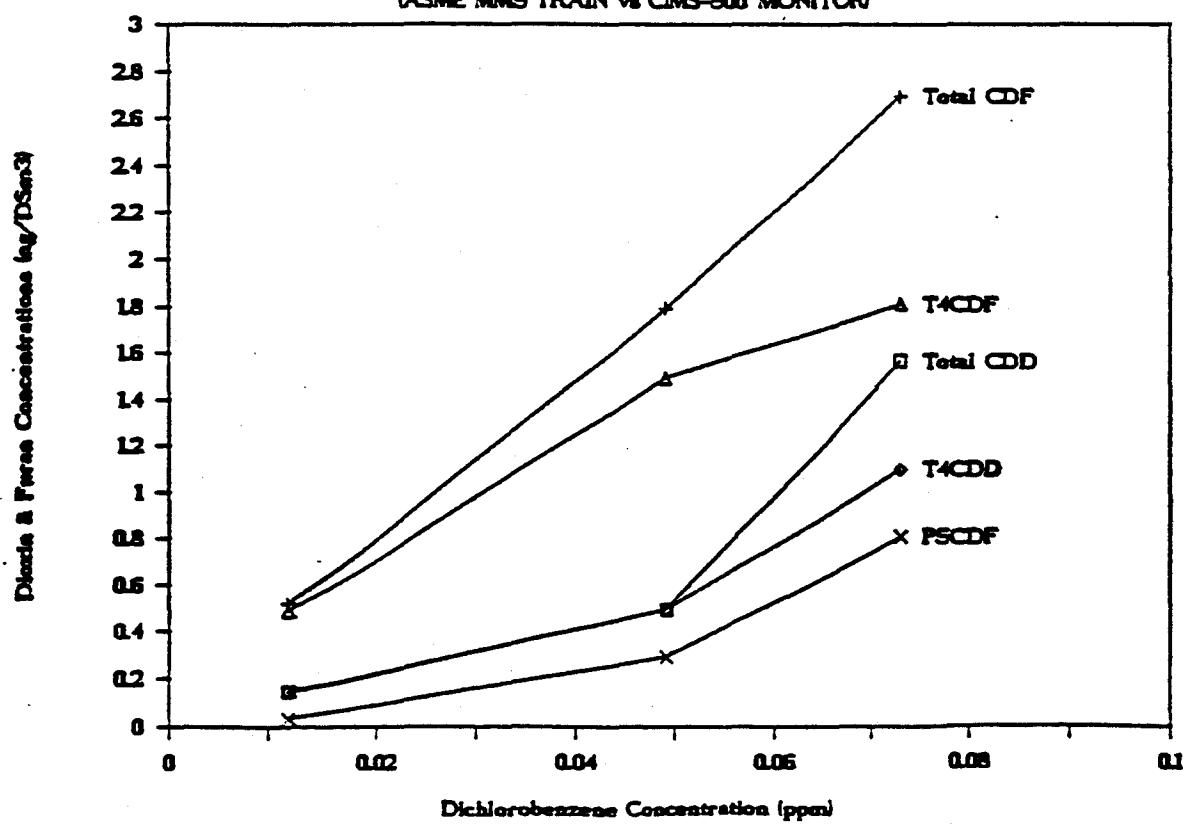
DIOXINS & FURANS vs DICHLOROPHENOL

(ASME MMS TRAIN vs CIMS-500 MONITOR)

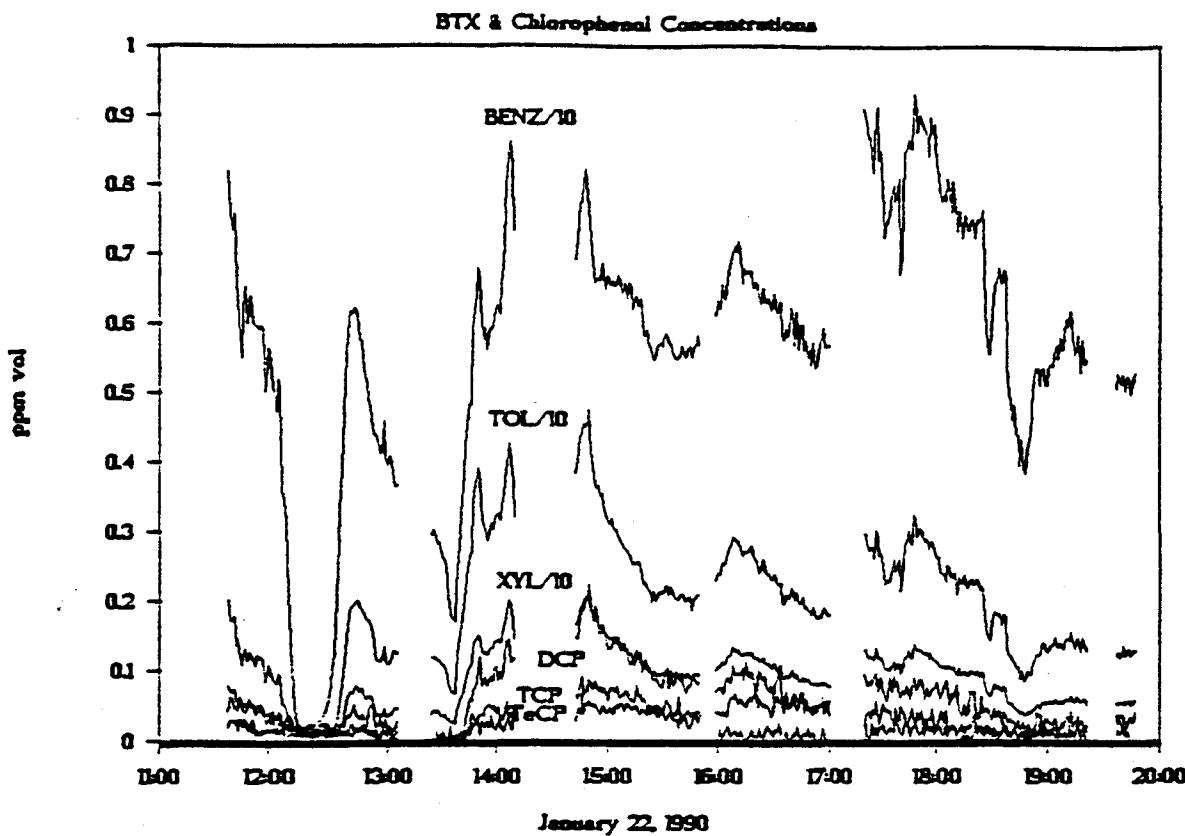


DIOXINS & FURANS vs DICHLOROBENZENE

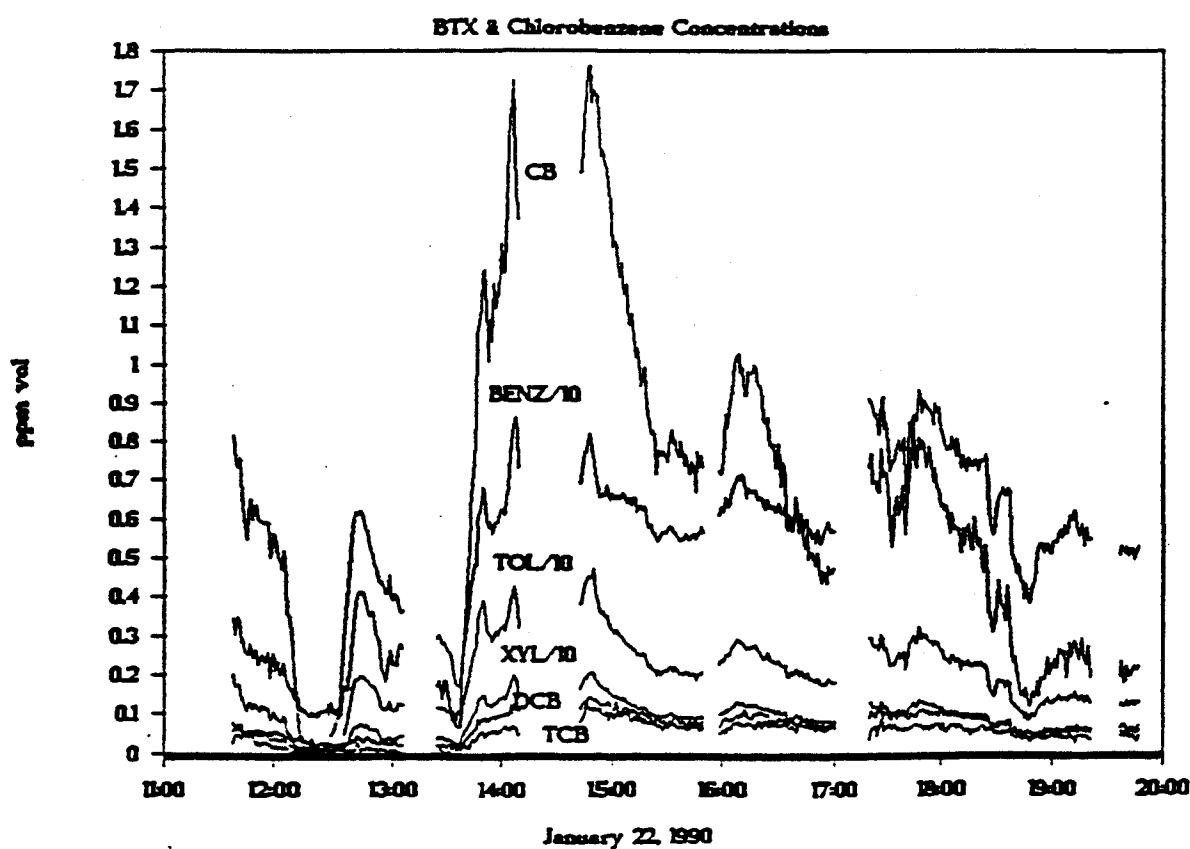
(ASME MMS TRAIN vs CIMS-500 MONITOR)



SEWAGE SLUDGE INCINERATOR CMS-500 DATA



SEWAGE SLUDGE INCINERATOR CMS-500 DATA



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SAMPLING AND ANALYSIS OF AIR TOXICS FROM MUNICIPAL WASTE COMBUSTORS

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ABSTRACT

The new federal rules addressing emissions from large municipal incinerators will significantly increase the scope and complexity of periodic emissions testing at these facilities. New and existing facilities with a capacity of more than 250 tons per day will be required to test for metals emissions, organics, and acid gases. Specific testing for mercury and other metals may be addressed in a forthcoming proposed rule for municipal waste combustors. This paper provides a brief introduction to the principal test methods which are currently available to meet the expanded emission measurement requirements. Test methods presented here include: EPA Method 5 (particulates), EPA Proposed Method 0012 (multiple metals), EPA Proposed Method 23 (PCDD/PCDF), EPA Proposed Method 26 (hydrochloric acid), and a brief summary of wet chemistry methods for oxides of sulfur and nitrogen.

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

INTRODUCTION

Traditional emission sampling (or stack testing) methods have long been an established fact of life for Municipal Waste Combustors (MWC). Stack testing has usually been the best means of verifying compliance with a variety of federal, state, and local regulations which stipulate maximum atmospheric emission levels from waste incineration facilities. Stack testing is also an important tool in assessing unit operating performance, control system performance, and efficiency and accuracy of continuous emission monitors.

New and forthcoming federal regulations will add substantially to the scope, frequency, and complexity of required testing. However, most of the emission tests which are "new" to municipal waste combustion are established test methods which have been previously developed and applied to the measurement of emissions from other sources. In some cases, these methods have been specifically modified for application to the testing of municipal

waste combustors. This presentation is intended to provide a brief introduction to the principal test methods currently available to meet the expanding emission measurement regulations applicable to municipal waste combustors.

Emissions from MWCs include a complex mixture of pollutants that can affect public health. The three general subclasses of pollutants within MWC emissions consist of metals, organics, and acid gases. In total, MWC emissions contain 100 or more pollutant components. Although it is theoretically possible to measure all of the components, such a task would be extremely burdensome, expensive, and quite impractical. EPA has determined that it is unnecessary to measure MWC emissions as an entity; it makes far more sense to develop standards for certain components of MWC emissions. The current list of regulated emissions from MWCs includes: particulates (PM), MWC metals, dioxin/furans, sulphur dioxide (SO_2), and hydrogen chloride (HCl). For new MWCs, emissions of oxides of nitrogen (NO_x) are also regulated. Of these substances, continuous emission monitors (CEMs) are recommended (and in some cases may be required) for SO_2 and NO_x . Forthcoming proposed regulations (MWCII) will address MWC metals and stipulate emissions testing methods, for mercury, cadmium, and lead. Control of MWC organics is demonstrated through the measurement of dioxin/furans and control of acid gases is demonstrated through the measurement of HCl and SO_2 . Standardized emission sampling methodologies exist for all of these pollutants.

A summary of available sampling procedures (including instrumental or CEM methods) are presented in Table 1. The measurement methods are primarily those in general use. Most are EPA methods from the *Federal Register*^{1,2}, or "Test Methods for Evaluation of Solid Waste," SW-846.³ It is important to note that, in practice, all sampling methods are in various stages of development and subject to processes of evaluation and refinement. In addition, state or local agencies may require specific procedures or modifications to established methods. Before undertaking or contracting for any type of emission testing, the current status of EPA methods, as well as local regulatory requirements, should be confirmed.

All EPA methods are published in the *Federal Register* (40 CFR Part 60, 61). Copies of individual methods are also available from the Emissions Measurement Branch, USEPA, Mail Drop 19, RTP, NC 27711. The contact person for Method 0012 (multiple metals) is Tom Ward, (919) 541-3788. For Method 23 (PCDD/PCDF), contact Gary McAlister at (919) 541-1062. For Method 26 (Hydrochloric Acid), contact Foston Curtis at (919) 541-1063.

TYPES OF TESTING

Stack testing can be divided into two categories: continuous testing and periodic testing. Generally, continuous testing is effective only for constituent gases and stack gas opacity, although some particulate matter samplers are available for specific processes and needs. Continuous emission monitoring systems (CEMS) are used as an operations tool to monitor or

TABLE 1. STACK SAMPLING METHODS

Pollutant	Principle	Procedure
Particulate	Isokinetic collection of a 1 hr sample on glass fiber filter at $120 \pm 14^{\circ}\text{C}$. Train includes: heated probe, optional cyclones, heated filter, impingers, flow control and gas volume metering system.	EPA Method 5, 17
	Visual determination of opacity.	EPA Method 9
	Instrumental measurement of opacity (optical density).	
Multiple Metals (cadmium, lead)	Collection on glass fiber filter, nitric acid/hydrogen peroxide and potassium permanganate impingers.	EPA Proposed Method 0012
Mercury	Collection in iodine monochloride or acidic permanganate impingers in M5-type train.	EPA Method 101A
PCDD/PCDF	Collection by sorption on XAD2 resin with MM5 train, analysis by GC/MS	EPA Proposed Method 23
Hydrochloric Acid	Collection in acidified water impinger solution in M5-type train or midget impingers.	EPA Proposed Method 26 SW-846 Methods 0050 or 0051
Sulfur Oxides	Instrumental using UV, NDIR, or fluorescence	EPA Method 6C
	Collection in isopropanol (SO_3) and hydrogen peroxide (SO_2) impingers of M5-type train.	EPA Method 6,8
Nitrogen Oxides	Instrumental using chemiluminescent analyzer.	EPA Method 7E
	Collection in evacuated flask containing sulfuric acid and hydrogen peroxide.	EPA Method 7,7A,7B
	Collection in impinger solutions of potassium permanganate.	EPA Method 7C,7D

maintain combustion air, ensure flue gas path integrity, and control stoichiometric ratios in control systems. As analytical instruments, CEMS provide a means of continuously determining the compliance status of the source. Under the new MWC standards, CEMS are to be utilized for the measurement of SO_2 and NO_x emissions as well as to monitor ongoing adherence to operating standards required of certain MWCs.

Periodic testing is conducted for regulatory compliance, unit performance testing, calibration and validation of CEMS accuracy, and research and development (R&D) studies. Periodic tests include both wet chemistry methods and instrumental techniques. Wet chemistry methods are essentially sample capture techniques which require off-site analysis and measurement of the pollutants of concern. Instrumental tests, if they are available or feasible, provide on-site analysis for target pollutants. For the pollutants discussed in this paper, most of the readily available methods are wet chemistry techniques.

METHOD 5: MEASUREMENT OF PARTICULATES

The basic method for measurement of particulate matter in stack gas, whether for compliance or performance testing, is that specified in EPA Method 5 and the associated Methods 1-4.¹ Moreover, Method 5 constitutes the basic equipment and sampling methodology on which many other sampling methods are based. Many of these tests can be described as a variation of Method 5 and, in some cases (such as multiple metals) the sampling objectives can be combined into a single, modified Method 5 which measures both particulates and the additional pollutants.

SAMPLING EQUIPMENT AND PREPARATION

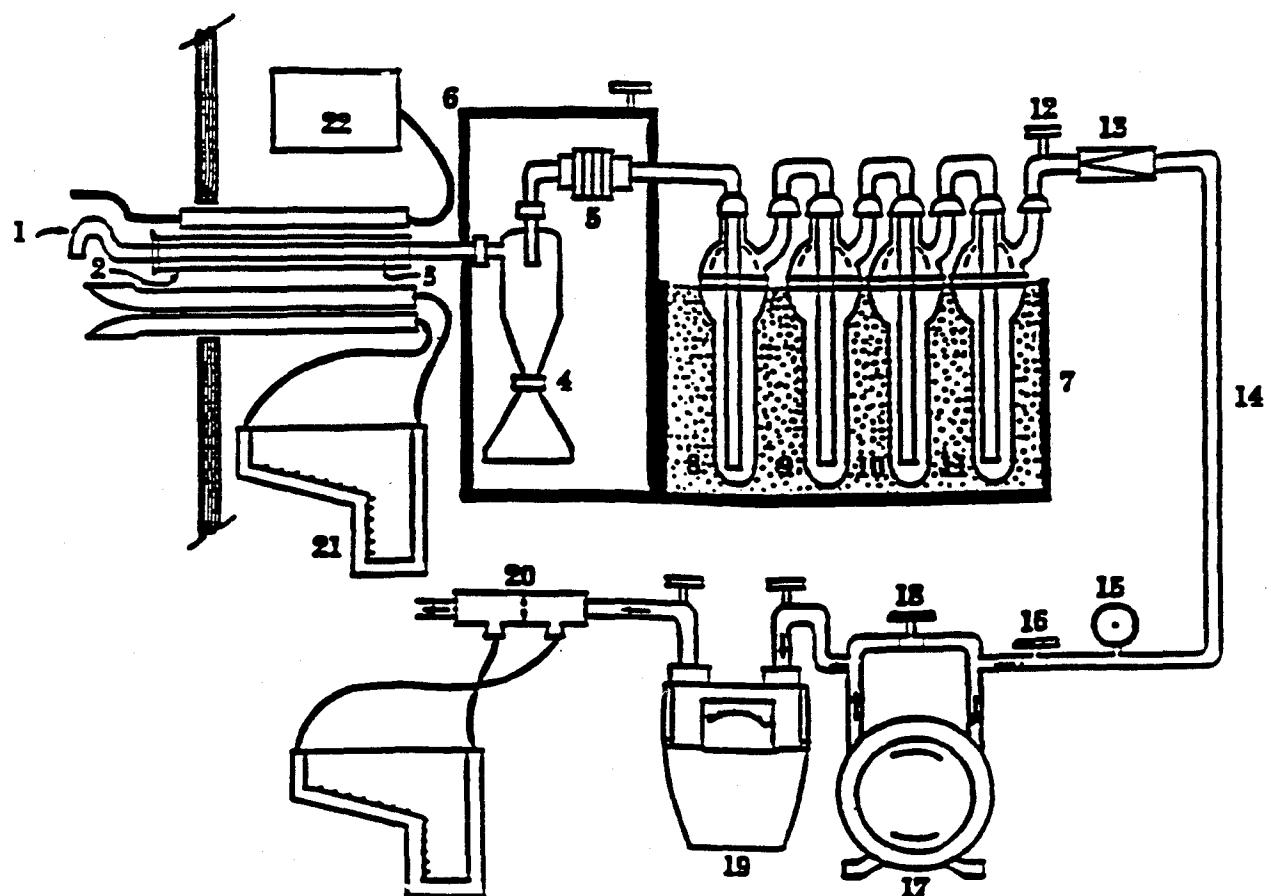
The Method 5 sampling train is shown schematically in Figure 1. The essential elements are: a borosilicate or quartz-lined, temperature-controlled probe equipped with a Pitot tube and thermocouple (for measuring stack gas flow rate); a sharp-edged button hook nozzle; a glass or quartz-fiber filter, supported in a glass or Teflon filter holder, inside an oven, and immediately at the outlet of the probe; an impinger train or condenser to remove water; and a pump and metering system.

Hardware suitable for use in EPA Method 5 is commercially available from a number of suppliers, and no reason exists to consider a nonstandard train configuration for compliance/performance measurement of particulate matter. Quartz glass probe liners can be used if the temperature does not exceed 900°C(1650°F). Water-cooled probes with quartz or borosilicate glass liners should be used if the stack temperature is expected to exceed 900°C; at temperatures below 480°C, borosilicate glass can be used without cooling. The metal probe option allowed in Method 5 is not recommended for MWC testing, due to the potential for corrosion.⁴

EPA Method 5 operationally defines particulate matter as any material that is collected on the filter when stack gas is withdrawn isokinetically through a temperature controlled, glass lined probe and high efficiency, glass-fiber filter. If the only purpose for which the sample is to be used is determination of particulate matter emissions, regular or quartz glass may be chosen as the fiber filter medium. Note, however, that if chemical analysis procedures, e.g., metals, are to be applied to the collected particulate material after its mass has been gravimetrically determined, the filter medium selected must be shown to be free of analytical interferences and/or background contamination. Component cleaning and system preparation is described in detail in Method 5.

SAMPLING/SAMPLE VOLUMES

Procedures for selecting sampling locations and for operation of the train are specified in detail in Method 5 and associated Methods 1-4. The procedure indicates a sampling rate of 0.5 to 1.0 cubic feet per minute (cfm) or 14 to 28 liters per minute (lpm) for a minimum of 1 hour total sampling time.¹ The



1. Sampling nozzle
2. Sampling probe sheath
3. Heated sample probe liner
4. Cyclone assembly (optional, for heavy particulate load situations)
5. Out of stack filter assembly
6. Heated filter compartment
7. Impinger case
8. First impinger filled with H₂O (100 ml)
9. Greenburg-Smith (or modified Greenburg-Smith) impinger filled with H₂O (100 ml)
10. Third impinger - dry
11. Fourth impinger - filled with H₂O absorption media (200-300 gm)
12. Impinger exit gas thermometer
13. Check valve to prevent back pressure
14. Umbilical cord - vacuum line
15. Pressure gage
16. Coarse adjustment valve
17. Leak free pump
18. By-pass valve
19. Dry gas meter with inlet and outlet dry gas meter thermometer
20. Orifice meter with manometer
21. Type S pitot tube with manometer
22. Stack temperature sensor

Figure 1. EPA Method 5 Particulate Sampling Train

minimum total sample size is, thus, 30 cubic feet (ft^3) or 0.85 cubic meters (m^3). Sampling is performed isokinetically.

Depending on the particulate matter emission standard with which a given facility must comply, a sampling period longer than the 1 hour indicated in the Method 5 protocol may be necessary. For example, at an emission rate of 0.03 grains per dry standard cubic foot (gr/dscf), the limit specified in some regulations,⁵ a larger sample of stack gas may be required to ensure that the precision of the compliance/performance determination is adequate. The necessary stack gas sample size (and sampling time) for a given test must be calculated by dividing the minimum weighable particulate mass (taking into account the filter tare weight) by the particulate mass emission rate specified in the permit. A rule-of-thumb is that the particulate weight should be at least 1% of the filter tare weight.

ANALYSIS

Analytical procedures for particulate analysis are described in detail in Method 5. The exposed filter is desiccated to dryness and weighed. The acetone probe/nozzle wash is transferred to a tared beaker, evaporated to dryness and weighed. The net weight gains of the filter and beaker are summed and divided by the sample volume to obtain a concentration. The emission rate is the product of the concentration and the stack gas flow rate. The standard expression of concentration is grains per dry standard cubic foot (gr/dscf) or milligrams per normal cubic meter (mg/Nm^3). Emission rates are reported as pounds per hour (lb/hr), kilograms per hour (kg/hr), or pounds per pound of throughput (lb/lb).

Some agency regulations may require analysis of the impinger contents for condensable particulates. Quantification of condensable vapors passing through the filter, or demonstration of the integrity of the filter during sampling may be possible with this analysis. Either an extractive procedure, to separate solids from crystallized compounds, or an evaporative routine may be required.

QUALITY ASSURANCE AND QUALITY CONTROL PROCEDURES

The comprehensive QA/QC procedures for Method 5 can be found in the USEPA "Quality Assurance Handbook for Air Pollution Measurement Systems: Volume III."⁶ Procedures are specified in Reference Method 5 that must be used to calibrate and leak check the sampling equipment. The analytical balance used for the gravimetric determinations also must be calibrated regularly.

In applying Method 5, a QC blank sample, consisting of an aliquot of the acetone solvent used for sample recovery, must be analyzed. The method does not require a blank filter QC sample. However, generation of a field blank filter is standard practice. To ensure comparability with the sample filters, this blank may be mounted in a filter holder and held at $120^\circ \pm 14^\circ\text{C}$ for a time equal to the total sampling run time. Although not stipulated in the Federal Register, standard practice is to perform Method 5 determinations in triplicate (three separate stack sampling runs).

The equations to be used to calculate the percent isokineticity and the particulate matter emission rate are presented in Method 5. Isokineticity must be in the range of 90% to 110%.¹ Some agencies require that this objective be met for each sampling point, or for a specified fraction (percent) of the sampling points, while others require that only the average isokineticity over each run meet the objective.

Data quality objectives for precision of replicate determinations are not included in Method 5. Usual practice is to compute the mean of the three separate determinations and compare this mean value with the emission limitations. Some agencies may require that each of the three measurements fall within the emission limitations.

LIMITATIONS OF THE TECHNIQUE

The greatest limitation of Method 5 is the batch nature of the sampling. Continuous sampling is impossible, and even frequent sampling is economically and logically prohibitive. In the case of performance and R&D testing, the time delay between sampling and analysis can create a problem, as a 24-48 hour minimum time lag occurs for results.

Some tests may require sampling upstream of control devices; consequently, additional considerations and method modifications may be necessary. If, for example, a Method 5 traverse is impossible, a traverse for velocity only may be made, and isokinetic sampling may be performed at a single representative point away from the duct walls. High temperatures and corrosivity can also be a problem. Water cooled probes or exotic metal probe liners, i.e. inconnel®, may be necessary. These options must be approved by the appropriate regulatory agency for compliance testing.

ALTERNATIVE TECHNIQUES

EPA Method 17¹ may be used as an alternative to Method 5 in some situations. The basic difference in the two methods is that the Method 17 filter is contained in a stainless steel holder, which is attached to the front of the probe. This places the filter in the stack and defines the particulates at stack conditions, i.e. temperature and pressure. Operating procedures are exactly the same as for Method 5.

No other alternative particulate evaluation methods will generate the precise information determined by Methods 5/17. However, some devices exist which enable the continuous monitoring of relative emissions. The most common of these is the opacity monitor. This instrument has a transmitter mounted on one side of the duct, and a photodetector or reflector on the opposite side. A light beam is projected between the two, and the diminished intensity of the beam reaching the photodetector determines the percent opacity of the stack gas. Applicable agency regulations may require an opacity monitor. A means of visually determining opacity is presented in EPA Method 9.¹

METHOD 0012: MULTIPLE METALS

DESCRIPTION OF METHOD

The most comprehensive means of sampling for metals is the USEPA proposed Method 0012, "Methodology for the Determination of Metals Emissions in Exhaust Gases from Hazardous Waste Incineration and Similar Combustion Processes."¹² This method is applicable for simultaneously determining emissions of: total chromium (Cr), cadmium (Cd), arsenic (As), nickel (Ni), manganese (Mn), beryllium (Be), copper (Cu), zinc (Zn), lead (Pb), selenium (Se), phosphorus (P), thallium (Tl), silver (Ag), antimony (Sb), barium (Ba), and mercury (Hg).

The basic sample system is a Method 5 particulate train operated in the same manner as for particulate determinations. The stack sample is extracted isokinetically through a glass lined probe, glass-fiber filter, absorbing solutions of dilute nitric acid in hydrogen peroxide (HNO_3/H_2O_2) in two impingers, and acidic potassium permanganate ($KMnO_4$) in one (or two) impingers. Particulate emissions can be determined by recovering the filter and front half of the sample train for gravimetric analysis. Metals are determined by laboratory analyses of the particulate catch and the impinger solutions, using appropriate detectors and analytical equipment.

SAMPLING EQUIPMENT AND PREPARATION

The sampling equipment is basically the same as for Method 5. The nozzle, probe, and filter holder are of borosilicate or quartz glass construction, and the filter is of quartz-or glass-fiber, supported in the holder by a Teflon frit. The condensing system consists of four to six impingers. When high moisture levels are expected, the first impinger will be empty and serve only as a knock-out for H_2O . The first two absorbing impingers contain a solution of 5% nitric acid (HNO_3) and 10% hydrogen peroxide (H_2O_2) in water. The following impingers (one or two) contain an absorbing solution of 4% potassium permanganate ($KMnO_4$) in 10% sulfuric acid (H_2SO_4). The $KMnO_4$ solution must not contact the glassware to be analyzed for Mn and the two absorbing solutions must not be mixed. The last impinger contains a drying agent to aid in determining moisture levels in the stack and to protect the sample pump and meter. A standard metals sampling train is shown in Figure 2.

Metals train glassware must be thoroughly washed and soaked in nitric acid before use. Detailed cleaning procedures are given in proposed Method 0012.⁷

SAMPLING/SAMPLE VOLUMES

The sample train should be operated exactly as a Method 5 particulate train.¹ Great care must be taken to ensure no mixing of the impinger solutions during the leak checks. The use of a glass nozzle also merits caution in handling the train, especially when changing ports. Sampling times should be sufficiently long to capture minimum amounts of the target metals. Generally, sampling for two (2) hours at a rate of 14 to 28 liters per minute is recommended. The metals and their in-stack detection limits are shown in

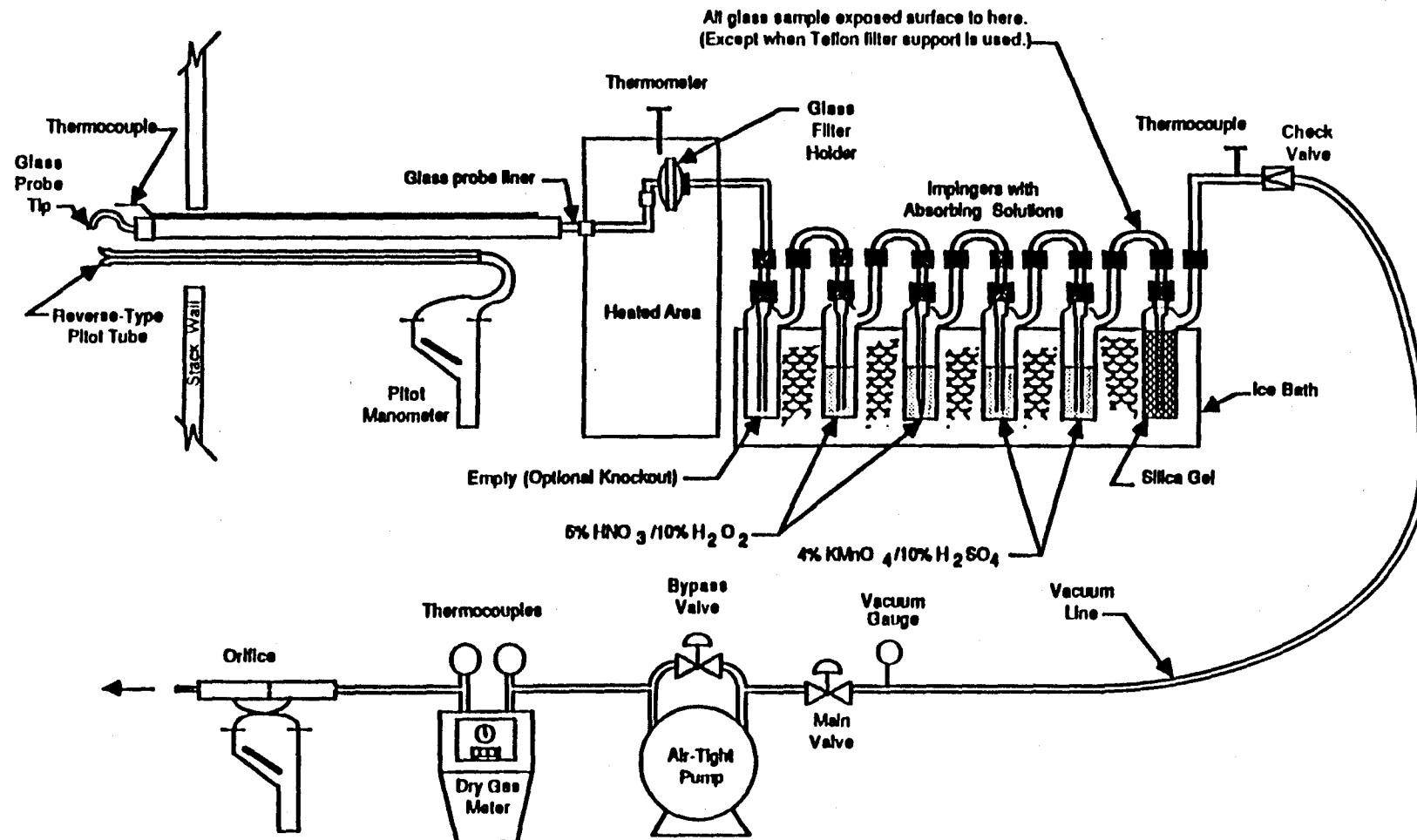


Figure 2. Standard Metals Sampling Train

Table 2. These should be used when calculating sample volumes, to ensure that the analytical limit is less than the emission limit.

The sample recovery procedures must be performed with care. Five individual samples are recovered:

1. Filter;
2. Acetone probe wash;
3. Front half rinse - front of the filter holder, the nozzle, probe, and any connecting glassware are rinsed with exactly 100 ml of 0.1N nitric acid;
4. Impingers 1 and 2 (and 3 if 1 is a knockout) and back half - recover and measure the contents of the impingers and rinse the back half of the filter holder, connecting glassware, and impingers with exactly 100 ml of 0.1N nitric acid.

TABLE 2. IN-STACK METHOD DETECTION LIMITS ($\mu\text{g}/\text{m}^3$)
FOR TRAIN FRACTIONS USING ICAP AND AAS

Metal	Front Half/Fraction 1 Probe and Filter	Back Half/Fraction 2 Impingers 1-3	Fraction 3 Impingers 4-5	Total Train
Antimony	7.7 (0.7)*	3.8 (0.4)*		11.5 (1.1)*
Arsenic	12.7 (0.3)*	6.4 (0.1)*		19.1 (0.4)*
Barium	0.5	0.3		0.8
Beryllium	0.07 (0.05)*	0.04 (0.03)*		0.11 (0.08)*
Cadmium	1.0 (0.02)*	0.5 (0.01)*		1.5 (0.03)*
Chromium	1.7 (0.2)*	0.8 (0.1)*		2.5 (0.3)*
Copper	1.4	0.7		2.1
Lead	10.1 (0.2)*	5.0 (0.1)*		15.1 (0.3)*
Manganese	0.5 (0.2)*	0.2 (0.1)*		0.7 (0.3)*
Mercury	0.05**	0.03**	0.03**	0.11**
Nickel	3.6	1.8		5.4
Phosphorus	18	9		27
Selenium	18 (0.5)*	9 (0.3)*		27 (0.8)*
Silver	1.7	0.9		2.6
Thallium	9.6 (0.2)*	4.8 (0.1)*		14.4 (0.3)*
Zinc	0.5	0.3		0.8

()* Detection limit when analyzed by GFAAS.

**Detection limit when analyzed by CVAAS.

5. Impingers 3 and 4 (or 4 and 5 if 1 is a knockout) - recover, measure the contents of, and rinse the impingers and connecting glassware with exactly 50 ml of 8N HCl.

Detailed recovery procedures are given in the EPA proposed Method 0012.⁷ All sample containers must be pre-cleaned, using the glassware cleaning procedure in the Method. Sample volumes should be marked and containers capped and sealed with Teflon tape for transport to the laboratory.

ANALYSIS

The filter and acetone probe wash may be gravimetrically analyzed to determine particulate emissions, as given in Method 5. Anything which contacts the filter (forceps, balance tray, etc.) must be free of possible metallic contamination.

The filter and probe wash residue are acid digested, using Parr Bomb or microwave digestion techniques. The HNO₃/H₂O₂ impinger solution, the KMnO₄ impinger solution, the digested filter, and the front half rinse are all analyzed for Hg by cold vapor atomic adsorption spectroscopy (CVAAS). Except for the KMnO₄ solution, the other samples are analyzed for Cr, Cd, Ni, Mn, Br, Cu, Zn, Pb, Se, P, Tl, Ag, Sb, Ba, and As by inductively coupled argon plasma emission spectroscopy (ICAP) or atomic adsorption spectroscopy (AAS). Graphite furnace atomic adsorption spectroscopy (GFAAS) may be used for Sb, As, Cd, Pb, Se and Tl if greater sensitivity is required. Detailed analytical procedures are presented in the draft Method 0012.

QUALITY ASSURANCE AND QUALITY CONTROL PROCEDURES

QA for the sampling train is the same as that for particulate sampling and is presented in the Method 5 procedures given in the Federal Register.¹ As with Method 5, triplicate measurement runs are standard practice. Method 5 calculations for isokineticity and emission rates are also used. During sampling, the KMnO₄ impingers must be monitored visually, as a change in color of the absorbing solution indicates exhaustion of the reagent.

Field blanks of the absorbing solutions, the recovery reagents and an unused filter are prepared. Measured volumes of blank solutions are required to perform blank analytical corrections on the samples. The filter blank is not required to be mounted in a holder or heated.

The ICAP, AAS, and GFAAS instruments must be calibrated according to manufacturers specifications. Mercury standards are prepared using procedures outlined in the "Standard Methods for Water and Wastewater," 15th Edition, Method 303F.² The other standards are prepared using procedures in the draft Method 0012.⁷ All samples are analyzed in duplicate, and matrix spikes are performed on one sample with each analytical procedure.

LIMITATIONS OF THE TECHNIQUE

Continuous analysis for metals is not possible with this method. The possibility of incomplete reaction in the impingers, as well as cross-contamination and introduction of other artifacts, is minimal if procedures are followed.

ALTERNATIVE TECHNIQUES

No single comprehensive alternative exists for the Draft Method. However, several Federal Register Methods exist, which can be used to measure emissions of individual metals or multiple metal combinations. All are configured from a Method 5 sample train, some without filters, but each with a unique combination of absorbing solutions. The Federal Register Methods and their respective target metals are: Method 12 - Lead¹; Method 101 and 101A - Mercury²; Method 104 - Beryllium²; and Method 108 - Arsenic². In the case of MWCs, the most important of these concerns the measurement of Mercury. While Method 101A is usually acceptable for testing incinerators, Method 101 is generally not recommended. If a separate test for Mercury is required, the Multiple Metals sample train can be greatly simplified by eliminating the KMnO₄ impingers.

METHOD 23: MEASUREMENT OF PCDD/PCDF

METHOD DESCRIPTION

USEPA Proposed Method 23, "Determination of PCDDs and PCDFs From Stationary Sources," is recommended as the most appropriate method for measuring tetrachloro- through octachloro-polychlorinated dibenzofurans (PCDFs). Example target PCDDs and PCDFs are listed in Table 3.⁴

Stack emissions are sampled isokinetically with a Method 5 train which has been modified by the addition of a condenser (to cool the gases) and a sorbent cartridge (to capture the gaseous organic compounds). Particulates are collected on an inert heated filter, and vaporous emissions are collected on the cooled sorbent material. Following sampling, the individual sample components (probe wash, filter and cartridge) are recovered and transferred to the laboratory for analysis. The samples are cleaned to remove potential interferences and analyzed for PCDDs and PCDFs by gas chromatography/high resolution mass spectrometry (GC/HRMS).

TABLE 3. PCDDs AND PCDFs ANALYZED FOR IN MWC STACK GASES⁴

DIOXINS

- 2,3,7,8 Tetrachlorodibenzo-p-dioxin (2,3,7,8 TCDD)
- Total Tetrachlorinated dibenzo-p-dioxins (TCDD)
- 1,2,3,7,8 Pentachlorodibenzo-p-dioxin (1,2,3,7,8 PCDD)
- Total Pentachlorinated dibenzo-p-dioxins (PCDD)
- 1,2,3,4,7,8 Hexachlorodibenzo-p-dioxin (1,2,3,4,7,8 HxCDD)

TABLE 3. (cont.)

DIOXINS (cont.)

1,2,3,6,7,8 Hexachlorodibenzo-p-dioxin (1,2,3,6,7,8 HxCDD)
1,2,3,7,8,9 Hexachlorodibenzo-p-dioxin (1,2,3,7,8,9 HxCDD)
Total Hexachlorinated dibenzo-p-dioxins (HxCDD)
Total Heptachlorinated dibenzo-p-dioxins (HpCDD)
Total Octachlorinated dibenzo-p-dioxins (OCDD)

FURANS

2,3,7,8 Tetrachlorodibenzofurans (2,3,7,8 TCDF)
Total Tetrachlorinated dibenzofurans (TCDF)
1,2,3,7,8 Pentachlorodibenzofuran (1,2,3,7,8 PCDF)
2,3,4,7,8 Pentachlorodibenzofuran (2,3,4,7,8 PCDF)
Total Pentachlorinated dibenzofurans (PCDF)
1,2,3,4,7,8 Hexachlorodibenzofuran (1,2,3,4,7,8 HxCDF)
1,2,3,6,7,8 Hexachlorodibenzofuran (1,2,3,6,7,8 HxCDF)
1,2,3,7,8,9 Hexachlorodibenzofuran (1,2,3,7,8,9 HxCDF)
Total Hexachlorinated dibenzofurans (HxCDF)
Total Heptachlorinated dibenzofurans (HpCDF)
Total Octachlorinated dibenzofurans (OCDF)

Proposed Method 23 has evolved primarily from Method 0010 of SW-846.³ Changes may have been made since publication of this paper. The entire method is continually being evaluated and revised, and changes have been made since the publication of this paper. The Emission Measurement Branch (MD-19), Technical Support Division, USEPA, Research Triangle Park, North Carolina 27711, should be contacted for current developments before commencing dioxin testing on MWCs.

SAMPLING EQUIPMENT AND PREPARATION

The MM5 sampling train is shown schematically in Figure 3. The components are essentially the same as for Method 5, except with the addition of a condenser and sorbent cartridge¹. The sorbent cartridge is filled with Amberlite XAD-2 resin, which has been thoroughly cleaned. Sorbent cartridge cleaning and preparation procedures are described in Method 0010.³ The condenser and sorbent cartridge may be constructed as a single unit (Figure 4) or as separate components (Figure 5). The preferred practice is to construct them as separate units to facilitate sample recovery.

The filter must be free of organic binders and cleaned with toluene. The nozzle is constructed of nickel, nickel plated stainless steel, or glass. Glass is recommended, in the presence of HCl, due to HCl's corrosive effect on metal nozzles. All components must be meticulously cleaned with solvent (e.g. acetone, methylene chloride), prior to testing, and sealed from contamination with Teflon tape or hexane cleaned aluminum foil. Detailed glassware cleaning procedures are described in Section 3A of "Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples" (see SW846).³

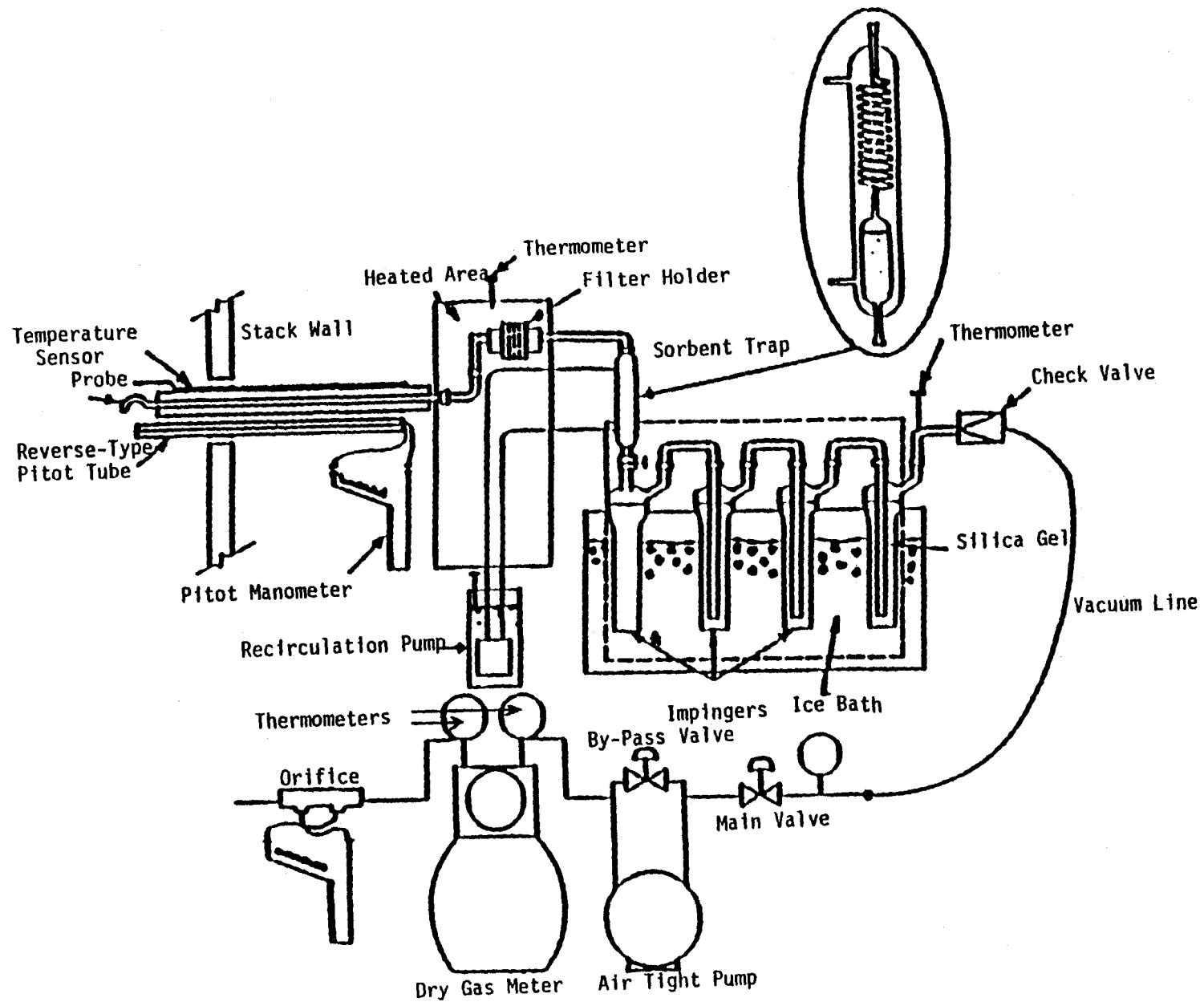


Figure 3. Modified EPA Method 5 Sampling Train

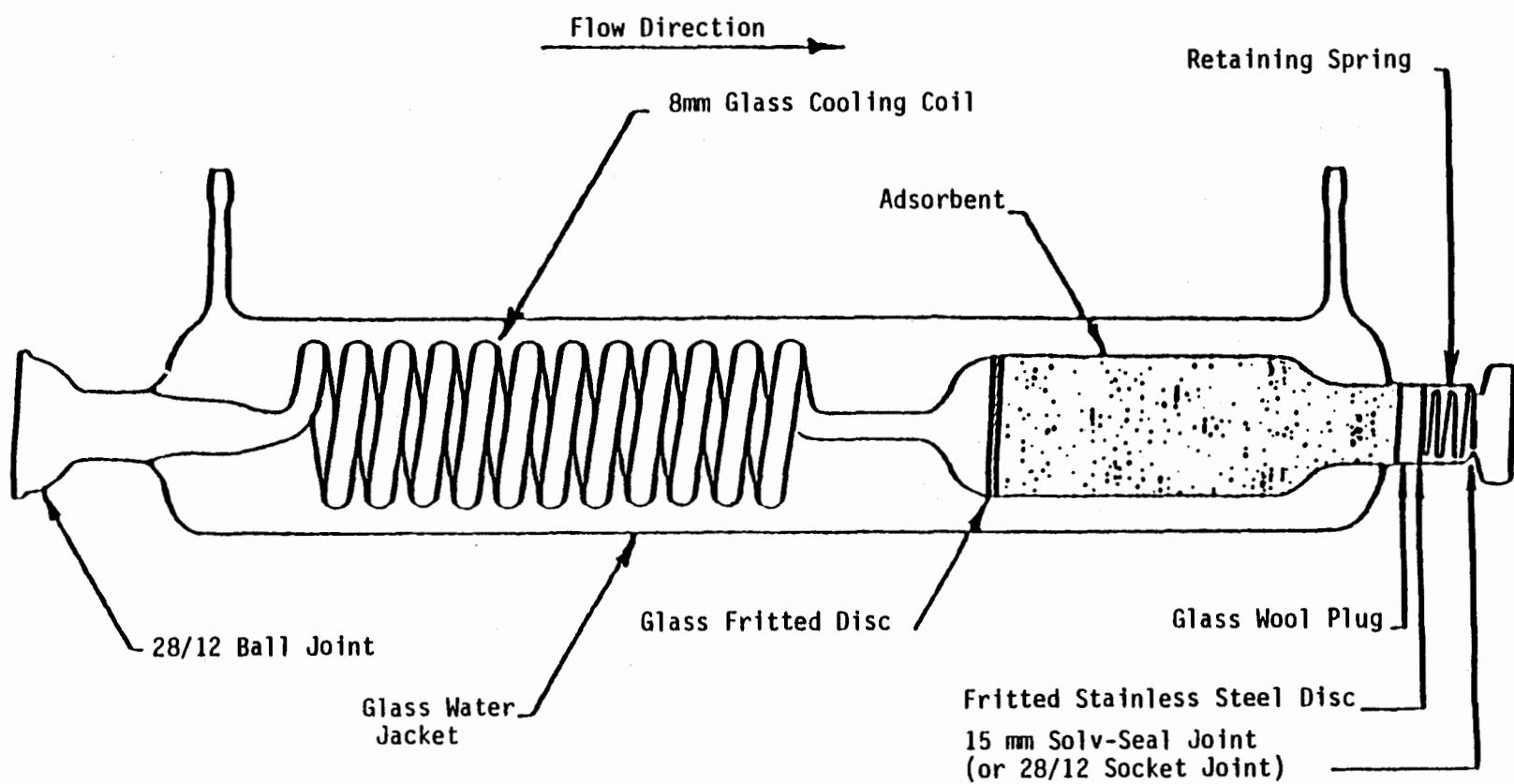


Figure 4. Combined Condenser - Adsorbent Cartridge Unit

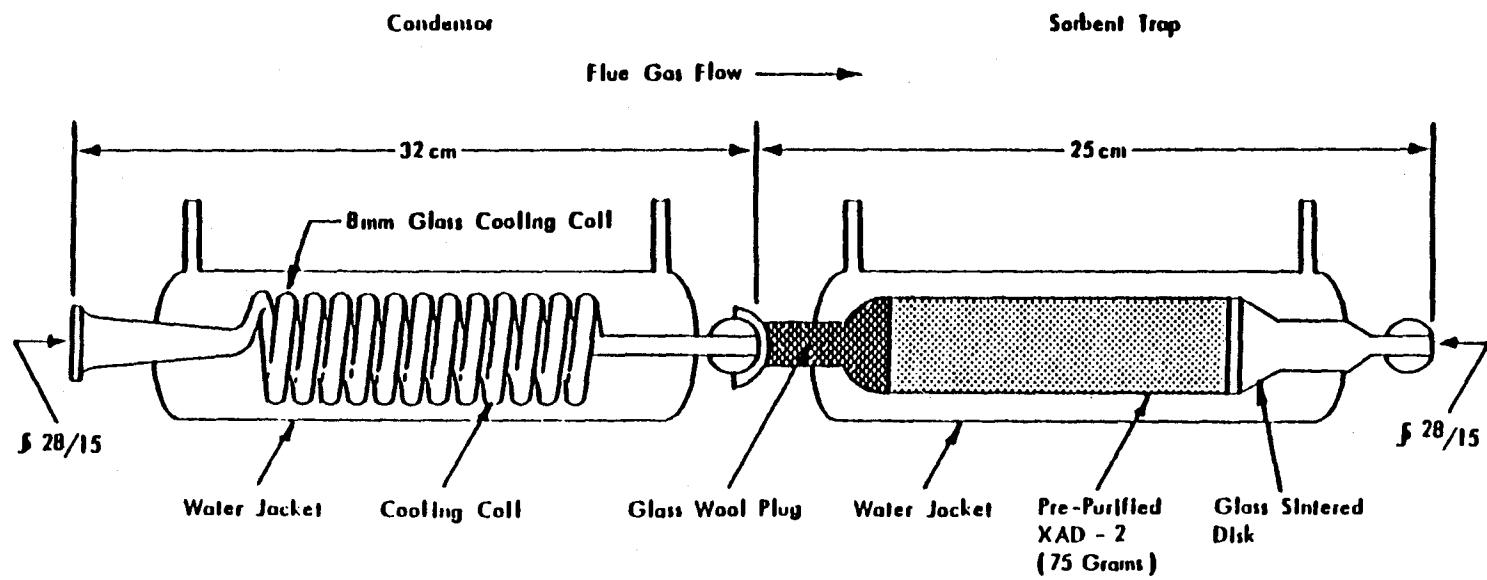


Figure 5. Separate Condenser and Adsorbent Trap Units Train

To avoid contamination, an enclosed clean area at the job site should be dedicated to assembly of the sample trains and recovery of the samples. During preparation, assembly, and disassembly of the sampling train, all component openings where contamination can occur must be sealed with Teflon, hexane rinsed aluminum foil, or ground glass caps. No sealant greases shall be used on the sampling train.

SAMPLING/SAMPLING VOLUMES

Sampling procedures are exactly the same as those for Method 5 particulate sampling.¹ The stack should be traversed and sampled isokinetically. Since the M23 train is very cumbersome and fragile, the sampling location must be carefully selected and prepared. Leak checks are performed in the same manner as for Method 5. During sampling, the XAD-2 resin should not exceed 20°C (68°F) to insure efficient capture of the PCDDs and PCDFs. The cartridge should be wrapped in foil to shield the resin from light.

A minimum sample volume of 3 dscm (105.9 dscf) is required for the determination of the destruction and removal efficiency (DRE) of PCDDs and PCDFs from incineration systems.⁴ Additional sample volumes may be necessary if, for example, unusually low concentrations are expected. Presented in Method 0010 are the calculations to determine specific sample volumes, based on refuse charging rates and expected DREs.³

Sample recovery is extremely critical. The entire train, or the individual components, should be sealed with hexane cleaned foil, ground glass caps, or Teflon tape before transporting to the recovery area. The individual samples to be recovered consist of the following:

- a. Sample train rinse - the solvent rinses of the probe, nozzle, cyclone (if used), connecting lines between probe and filter, the front half of the filter holder, the back half of the filter holder, and the connecting lines from the filter holder to the resin cartridge (including condenser, if separate). Each component is rinsed three times with acetone followed by three rinses of methylene chloride.
- b. Particulate catch - filter and cyclone catch (if used).
- c. Resin cartridge.
- d. Quality assurance rinse - all components mentioned in part a. (see above) are rinsed into one container with toluene and analyzed separately.

Detailed recovery procedures are presented in EPA Proposed Method 23.¹ Basically, all components, except the adsorbent cartridge, are recovered to precleaned amber glass bottles for transport to the lab. Liquid levels are noted, bottles are capped and sealed and chain of custody data sheets are prepared to accompany the samples. The resin cartridge is tightly sealed with Teflon tape or ground glass caps, wrapped in foil and stored on ice until

ready for analysis. Samples are carefully packed for shipment, as leakage or breakage may void the test.

ANALYSIS

In the laboratory, all samples are spiked with a solution of method internal standard (MIS) compounds prior to extraction. These MIS compounds contain standards to analytically quantitate the PCDD and PCDF concentrations. A typical set of calibration compounds is presented in Table 4.⁴ Samples are prepared for analysis using a Soxhlet extraction apparatus. A detailed procedure for sample preparation and extraction is given in EPA Proposed Method 23.¹

The primary analytical method for PCDDs and PCDFs, as specified in Proposed Method 23, is GC/MS, using fused-silica capillary columns. Samples are first analyzed, using a column coated with DB-5, to determine the concentration of each isomer of PCDDs and PCDFs. If tetra-chlorinated dibenzofurans (TCDFs) are detected, a separate analysis is performed with an SP2331 coated column to measure the 2,3,7,8-TCDF isomer.

The GC/MS system must provide sufficient response and chromatographic separation to achieve the minimum detection limits for the subject compounds. PCDD and PCDF levels are quantified using response factors generated by the standard compounds spiked prior to sample extractions. Proposed Method 23¹ contains detailed procedures for calibration and calculations.

TABLE 4. LIST OF ANALYTES, METHOD INTERNAL STANDARDS, SURROGATES, AND RECOVERY INTERNAL STANDARDS FOR DIOXIN/FURAN ANALYSIS

Analyte	Compounds In Calibration Standard	Method Internal Standard ^a	Recovery Internal Standard ^b
Tetra-CDD Tetra-CDF	2,3,7,8-TCDD 2,3,7,8-TCDF	$^{13}\text{C}_{12}$ -2,3,7,8-TCDD $^{13}\text{C}_{12}$ -2,3,7,8-TCDF	$^{37}\text{Cl}_4$ -2,3,7,8-TCDD or $^{37}\text{Cl}_4$ -1,2,3,4,-TCDD
Penta-CDD Penta-CDF Penta-CDF	1,2,3,7,8-PeCDD 1,2,3,8,9-PeCDF 2,3,4,7,8-PeCDF	$^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDD $^{13}\text{C}_{12}$ -1,2,3,8,9-PeCDF $^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDD	
Hexa-CDD Hexa-CDD Hexa-CDD Hexa-CDF Hexa-CDF Hexa-CDF Hexa-CDF	1,2,3,4,7,8-HxCDD 1,2,3,6,7,8-HxCDD 1,2,3,7,8,9-HxCDD 1,2,3,4,7,8-HxCDF 1,2,3,6,7,8-HxCDF 2,3,4,6,7,8-HxCDF 1,2,3,4,8,9-HxCDF	$^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDD $^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDD $^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDD $^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDD $^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDD $^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDD $^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDD	$^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDD
Hepta-CDD Hepta-CDF Hepta-CDF	1,2,3,4,6,7,8-HpCDD 1,2,3,4,6,7,8-HpCDF 1,2,3,4,7,8,9-HpCDF	$^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDD $^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDD $^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDD	
Octa-CDD Octa-CDF	OCDD OCDF	$^{13}\text{C}_{12}$ -OCDD $^{13}\text{C}_{12}$ -OCDF	

^aAdded to sample prior to extraction

^bAdded to sample at time of injection into GC/MS

QUALITY ASSURANCE AND QUALITY CONTROL TECHNIQUES

Sampling train calibrations and leak checks are the same as those given for Method 5. At least one blank sample train is required in the procedure. The blank train will be assembled in the recovery area and will accompany the working train to the sampling site. The probe and filter holder will be heated and maintained for the duration of the actual test, but no gas will be passed through the system. Leak checks will be performed concurrently with the actual sampling system, and recovery will be identical to that of the other MMS trains. In addition, field blanks of sample containers, filters, resin cartridges, and rinse solvents should be reserved for analysis, should the blank train become contaminated or be unacceptable.

Analytical blanks should include samples of all solvents and materials used in the extraction and preparation process. A quantity of XAD-2 resin from each lot should be reserved for analysis. Blind quality control standards in the expected range of the facility samples should be prepared and analyzed with the samples. A bias in the analysis is determined by comparing GC/MS results of the MIS surrogates to the known spiked concentrations.⁸

LIMITATIONS OF THE TECHNIQUE

The batch nature of this type of sampling limits actual emission determinations to the testing periods. Refuse feed rates and unit operating conditions during testing must be monitored closely and should be typical of actual process rates.⁹ Continuous process monitoring and periodic chemical analysis of the refuse can then be employed to demonstrate long term conformity to the operating conditions which were in effect during testing. Implementation of good combustion practices and operator training/certification programs can help reduce organic emissions (including emissions of dioxins/furans and their precursors) by promoting more thorough combustion of these pollutants.¹⁰ Continuous monitoring of carbon monoxide concentrations, maximum combustor load limits, and flue gas temperatures at the inlet to air pollution control devices, provides a means of documenting adherence to the desired operating conditions.

Most of the problems common to stack testing methodologies are magnified by the demands of testing for dioxins and furans. During sampling, the possibility of incomplete sorption exists if the XAD 2 resin is allowed to exceed 20°C. Another major problem is contamination. Total sample catches often weigh only a few nanograms, and such small sample quantities demand a much more rigorous approach than routine stack sampling.

ALTERNATIVE TECHNIQUES

No widely accepted alternatives to MM5 exist for the quantification of PCDDs and PCDFs in flue gas.

METHOD 26: MEASUREMENT OF HYDROCHLORIC ACID

METHOD DESCRIPTION

The collection of hydrogen chloride (HCl) in stack gas emission samples from municipal waste combustors is described in the EPA Proposed Method 0026.¹ This method represents a simplified alternative to the traditional M5 configuration which can be applied when the pollutants of concern are in a gaseous form. Smaller (midget) impingers are used and isokinetic sampling is not required. This method has been recently reviewed and modified and the USEPA Emissions Measurement Branch should be consulted before proceeding with testing for HCl.

SAMPLING EQUIPMENT AND PREPARATION

A schematic of the sampling train used in this method is shown in Figure 6. Stack gases are drawn through a borosilicate glass probe with a Teflon filter installed at the probe outlet. A borosilicate, three-way glass stopcock is connected directly to the outlet of the probe and inlet of the first impinger. The probe and stopcock are heated to prevent any condensation up to the inlet of the first impinger. Stack gases are then drawn through a sequence of 30 ml midget impingers. In the first two impingers, a 0.1N sulfuric acid (H_2SO_4) solution collects the HCl sample. This is followed by one impinger containing a 0.1N Sodium hydroxide (NaOH) solution, which protects the sampling system against corrosion by Cl_2 . Leak checks, pre-test calculations, and sampling parameters are all described in the proposed Method.

SAMPLING/SAMPLE VOLUMES

In the method, sampling is recommended at a rate of 2 liters/min. for a period of one hour. Shorter sampling times may introduce a significant negative bias in the HCl concentration. Sample recovery for HCl consists of combining the H_2SO_4 impinger solutions and rinses in a leak-free glass or polyethylene bottle, for transport or storage (refrigerated samples can be stored for up to four weeks before analysis). Bottles should be marked at liquid level and sealed to prevent contamination and leakage.

ANALYSIS

Analysis of samples is by ion chromatograph (IC) for Cl^- ions. The volume of each sample is determined or adjusted with distilled, deionized water (e.g., to 100 ml). An aliquot of each sample is then analyzed and a concentration in ug/ml is determined. Total ug/sample can then be ascertained, and the stack concentration can be calculated. Calculations are presented in the Method.

QUALITY ASSURANCE AND QUALITY CONTROL PROCEDURES

A set of two audit samples must be concurrently analyzed with the compliance samples to evaluate the technique of the analyst and the standards

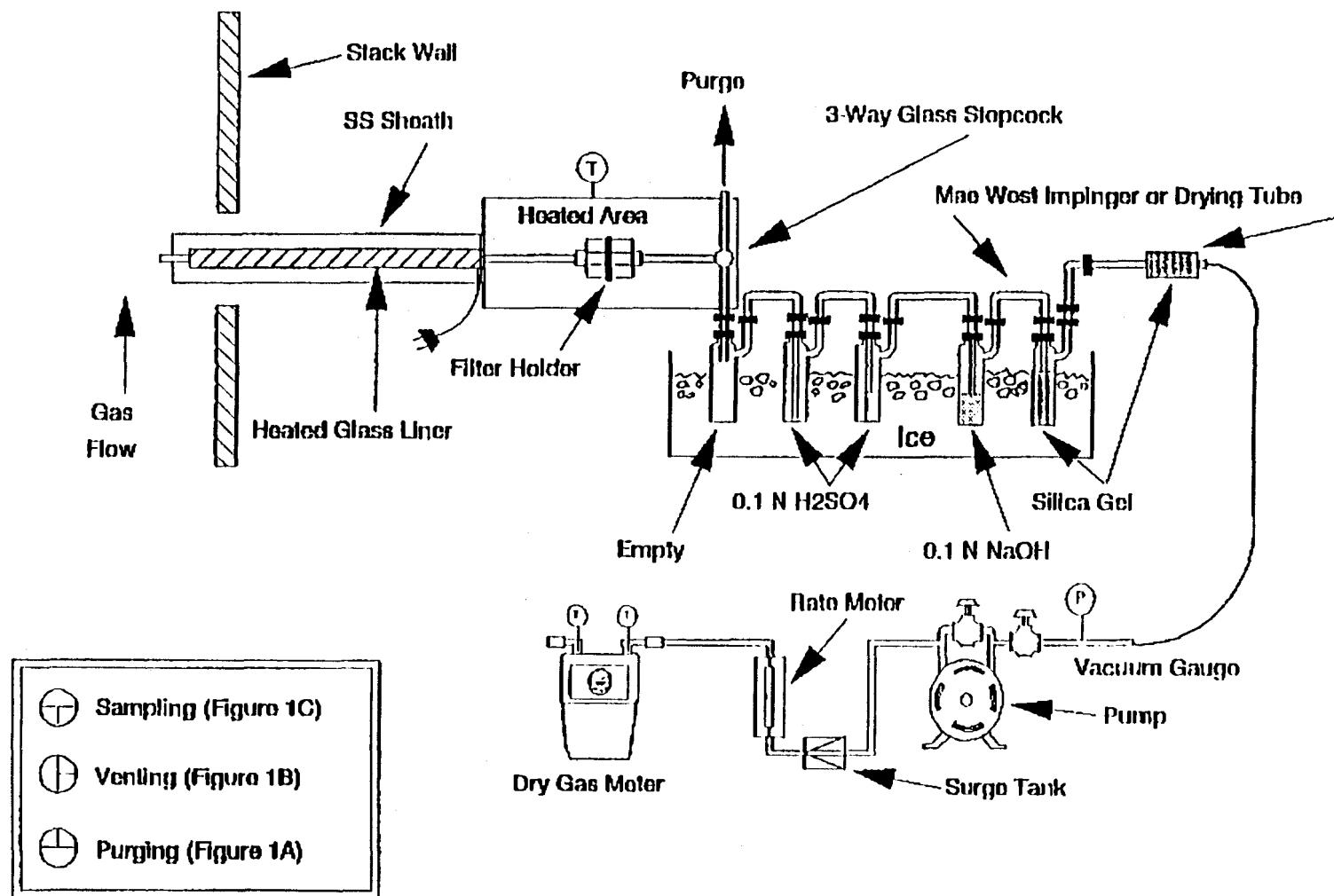


Figure 6. EPA Proposed Method 26 - HCl Sampling Train

preparation. Audit samples are available through written requests to EPA regional offices.

As is conventional with other sampling methods, tests should include triplicate measurement runs. The IC instrument must be calibrated according to manufacturers' specifications. Blank samples of the H_2SO_4 and rinse water must be generated during field testing to be analyzed with the stack samples.

LIMITATIONS OF TECHNIQUE

As with other stack sampling techniques, this approach provides a "snapshot" or short-term profile of emissions. However, triplicate replication of sampling runs is intended to address this concern. Proposed requirements for continuous monitoring of selected combustion parameters will further serve to demonstrate long term compliance with optimum combustion practices in effect during the test periods.¹⁰

This method is designed to minimize possible analytical interference of the HCl sample with Cl₂. However, it is possible that other volatile compounds in the stack gases may produce chlorine ions upon dissolution during sampling (after passing through the filter as a gas).

ALTERNATIVE TECHNIQUES

Proposed Methods 0050 and 0051 are available when more exacting measurements of HCl and Cl₂ are required. Method 0051 also utilizes midget impingers and is very similar to proposed Method 26. The addition of a second impinger containing NaOH permits measurement of both HCl and Cl₂.

Proposed Method 0050 utilizes conventional impingers in a Method 5 type sampling train. This method collects the sample isokinetically and is, therefore, particularly suited for sampling at sources (such as those controlled by wet scrubbers) emitting acid particulate matter (e.g., HCl dissolved in water droplets). This method is also designed for collection of both HCl and Cl₂.

Instrumental analyzers are available for HCl determinations and their practicality as a CEM has been demonstrated.¹¹ It is probable that they will be accepted in some states for MWC compliance testing.

SAMPLING METHODS FOR OXIDES OF SULFUR AND NITROGEN

Instrumental Methods are available for SO₂ (EPA Method 6C) and for NO_x (EPA Method 7E). These methods can be incorporated into CEMS which are now generally required for monitoring of SO₂ and NO_x emissions. However, chemistry methods may still be required from time to time for calibration or relative accuracy tests of the CEMS.

SULFUR OXIDES METHOD DESCRIPTION

Sampling methods are designed to address two sulfur oxides of primary concern: sulfur dioxide (SO_2) and sulfur trioxide (SO_3). SO_2 is, by far, the more prevalent of the two. Generally, most methods screen out SO_3 so as not to bias SO_2 determinations. The most commonly used method for SO_2 collection and analysis is EPA Method 6.

SAMPLING EQUIPMENT AND PREPARATION

The basic sampling train consists of a borosilicate glass or stainless steel probe with a glass wool plug, a series of midget impingers, and a pump and dry gas meter to control and measure sample flow rates. The first impinger contains isopropyl alcohol (IPA) and has a glass wool plug in the neck. The second and third impingers contain a solution of 3% hydrogen peroxide (H_2O_2). The fourth impinger is empty and is followed by a fifth impinger containing a drying agent or a drying tube. The resultant sampling train is shown on Figure 7.

SAMPLING/SAMPLING VOLUMES

A sample of stack gas is extracted at a constant rate, nominally 1 liter per minute for 20 minutes at a single representative point in the duct. The SO_3 is absorbed in the IPA, with the glass wool plug preventing carryover of any sulfuric acid mist. The SO_2 is oxidized to H_2SO_4 in the H_2O_2 impingers. Sample volumes are measured with the dry gas meter. Post test leak checks are mandatory, and care must be taken not to allow backflushing of the impingers, as this will void the test. The IPA is discarded, and the H_2O_2 impingers are recovered and rinsed into a single borosilicate glass bottle. Liquid level is marked, and the bottle is sealed for transport to the laboratory.

ANALYSIS

Analysis for SO_2 is colorimetric titration. In the lab, the sample is diluted to 100 ml, and a color change indicator (e.g., thorin) is added. Barium perchlorate ($\text{Ba}(\text{ClO}_4)_2$) is added via burette until a color change occurs. The SO_2 concentration is then calculated from the volume of titrant and volume of stack gas metered. Alternatively, the analysis may be performed by ion chromatograph (IC). SO_2 is most often reported as a concentration, ppm or mg/dscm, but may be converted to a rate, lb/hr. The complete sampling, analytical, and calculational procedures are presented in Method 6.¹

QUALITY ASSURANCE AND QUALITY CONTROL PROCEDURES

Method 6 tests are typically run in triplicate. Duplicate titrations, which must agree within $\pm 1\%$ or ± 0.2 ml, are performed on each sample. Audit samples are available from the EPA and must be analyzed concurrently with the stack samples.¹² The titrant must be normalized against a sulfuric acid solution which has been standardized against a primary standard. Calibration procedures for the metering system are given in the Method.

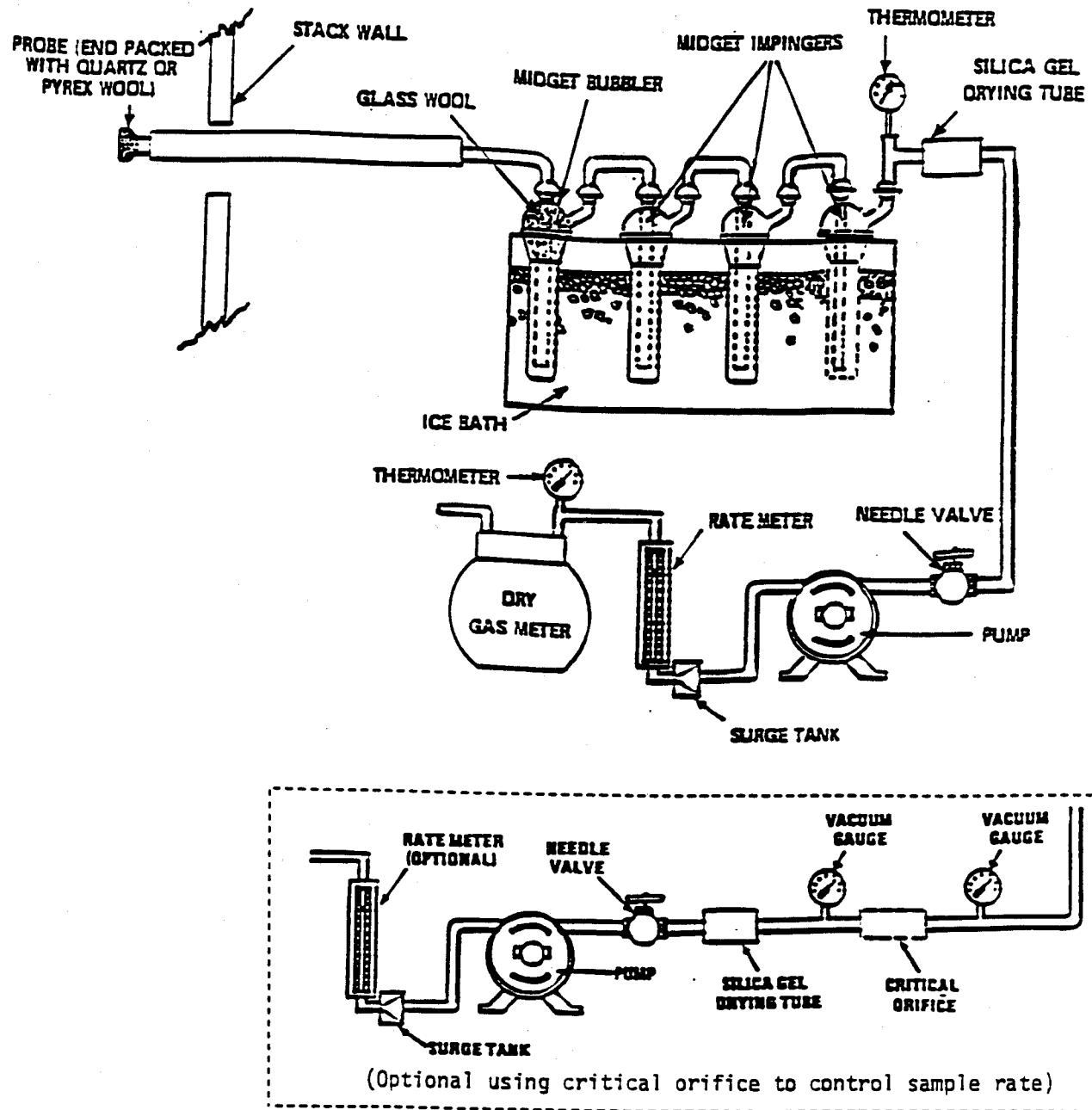


Figure 7. EPA Method 6 SO₂ Sampling Train

METHOD DESCRIPTION FOR OXIDES OF NITROGEN

EPA Method 7, 7A, 7B, 7C, and 7D are all applicable for determining NO_x emissions in incinerator stack gases. Methods 7, 7A, and 7B all involve extracting a gas sample with an evacuated flask containing a dilute sulfuric acid hydrogen peroxide absorbing solution.

The differences in the three methods are only in the preparation and laboratory analysis of the samples. Colorimetric titration is used for analysis in Method 7, while ion chromatograph (IC) and ultraviolet spectrophotometry (UVS) are used in Methods 7A and 7B respectively. Of these, Method 7A is the most widely employed.

The main disadvantage to Method 7, 7A or 7B sampling is the extremely short duration (typically less than 30 seconds) of individual tests. Several sets, of at least three (3) tests each, must be run to ensure determination of average emissions.

Methods 7C and 7D employ an impinger train to absorb NO_x compounds in an alkaline, potassium permanganate solution. The two methods differ only in analysis, which is colorimetric titration for Method 7C and IC for Method 7D. The gas sample is extracted through a glass lined probe and a series of restricted orifice impingers containing the KMnO₄ absorbing solution. A pump and dry gas meter are used to maintain and measure flow.

QUALITY ASSURANCE AND QUALITY CONTROL PROCEDURES

QA/QC procedures include calibration of sampling equipment prior to testing, generating blank samples, and the use of audit samples, which are available from the EPA.¹² IC and UVS calibration techniques are given in the appropriate Methods. Usual practice requires triplicate tests and replicate laboratory analyses.

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Development of Source Testing, Analytical and Mutagenicity Bioassay Procedures
for Evaluating Emissions from Municipal and Hospital Waste Combustors

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ABSTRACT

Incineration is currently being utilized for disposal of about 10 percent of the solid waste generated in this country, and this percentage will likely increase as land disposal declines. Siting of new incinerators, however, is often controversial because of concerns related to the possibility of adverse health effects and environmental contamination from long-term exposure to stack emissions. Specific concerns relate to the adequacies of a) stack emission testing protocols, b) existing regulations, and c) compliance monitoring and enforcement of regulations. These U.S. EPA Laboratories are cooperatively conducting research aimed at developing new testing equipment and procedures that will allow a more comprehensive assessment of the complex mixture of organics that is present in stack emissions. These efforts are directed specifically toward development of source testing equipment and procedures, analytical procedures, and bioassay procedures. The objectives of this study were to field test two types of high-volume source dilution samplers, collect stack samples for use in developing analytical and mutagenicity bioassay procedures, and determine mutagenicity of organics associated with emission particles from two municipal waste incinerators. Data are presented for particle concentrations and emission rates, extractable organic concentrations and emission rates, and Salmonella (Ames) mutagenic potency and emission rates. The mutagenic emission rates and emission factors are compared to other incinerators and combustion sources.

This document has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

INTRODUCTION

Solid waste management is increasingly becoming a public issue in many urban areas as city managers and engineers seek new ways of handling the nearly 250 million tons of trash that is generated in the U.S. each year. Approximately 160 million tons is produced by individual households and neighborhood businesses. Landfilling accounts for about 80 percent of solid waste disposal, and incineration and recycling each account for about 10 percent (1). Since 1979, however, 3500 landfills have been closed (2). Furthermore, the U.S. Environmental Protection Agency projects that more than 30 percent of the existing landfills will close within 5 years. This will result in an overall yearly capacity loss of 56 million tons. At current construction rates, additional landfill space will be available for only 20 million tons, resulting in a significant shortfall of disposal capacity (1). Alternative solutions to these problems will include concentrating more effort into source reduction and recycling and also increased utilization of incineration through expansion of existing municipal waste combustion (MWC) units and construction of new ones. This incineration option is further reinforced in many areas because of problems that have been encountered with soil and ground water contamination resulting from runoff and seepage from waste landfills.

The siting of new incinerators, however, is one of the most controversial environmental issues today. The adequacies of existing regulations, stack testing protocols, and compliance monitoring associated with incinerators are being challenged, especially in areas being considered for siting of new incinerator facilities. Of immediate concern to residents, of course, are stack emissions and their effect on air quality in nearby neighborhoods and areas downwind from the incinerator. The accompanying problems of disposal of bottom ash and precipitated fly ash in landfills are also a primary concern in many areas. The possibility of adverse health effects and environmental contamination that could result from long-term exposure to stack emissions has become an important issue. Research is needed to directly assess the potential health effects of incinerator emissions through biological studies of the complex mixtures that are emitted.

These U.S. EPA engineering and health Laboratories are cooperatively conducting research aimed at developing additional sampling and assay procedures for assessing possible health and environmental risks from MWC. This research includes developing MWC stack sampling equipment and analytical techniques that can be used to analyze the complex mixture of organics that is present in emissions. Stack emission samples are being analyzed by the Ames Salmonella typhimurium bacterial mutagenicity bioassay (3,4). These procedures represent simple, sensitive, rapid, and reliable screening tools for mutagenic substances. This approach, therefore, diverges from assessments which combine emission studies that determine individual compounds or a class of compounds (5-8) with toxicological data for those direct emissions. Analyses for specific organics (e.g., the chlorinated dibenzodioxins and dibenzofurans) will continue to be important in assessing potentially hazardous emissions. However, approaches that analyze incinerator emissions as a whole complex mixture by using assays (e.g., mutagenicity bioassay) that

are not compound specific but are targeted to specific health effects are needed. Such assays are especially relevant for combustion emissions, which include products of incomplete combustion and pyrolysis products, because these emissions contain thousands of compounds. The potential hazards associated with such a complex mixture might be underestimated if only a few species were included in a risk assessment determination. Mutagenicity bioassay was also chosen for this study because chemicals and mixtures recognized as human carcinogens are generally mutagenic in short-term tests (9), and combustion emissions from other sources have been shown to be both mutagenic in this assay and carcinogenic in rodents. It has also been reported that chemicals that are rodent carcinogens across several species and organ sites (trans-species carcinogens) are generally also mutagenic in Salmonella typhimurium (10). Other biological studies were planned, e.g., rodent cancer studies, and will be reported elsewhere.

A study using the Ames *Salmonella*/microsomal mutagenicity bioassay to analyze MWC stack emissions was reported by Kamiya and Ose in 1987 (11). These investigators used a small sampling apparatus to collect fine particles (<7 μm) and gaseous organics in 10-15 m^3 of stack gas emissions. They sampled a continuously operating modern incinerator with a complete combustion system and a discontinuous batch-type incinerator, where combustion was incomplete. Both incinerators were located in Aichi Prefecture, Japan. The authors found significant mutagenicity in the stack gas emissions from the latter MWC unit and, in fact, concluded "the emission gases from batch-type incinerators are mainly responsible for atmospheric pollution." They also identified and quantified 13 polynuclear aromatic hydrocarbon (PAH) compounds in the same emission gases and found a high correlation between mutagenic activity and PAH concentrations.

Ahlborg and Victorin (12) analyzed emission samples from four MWC sites using mutagenicity bioassay. Results were reported in revertants per megajoule of fuel and were compared to other Swedish combustion sources. These authors also concluded that MWC can cause relatively high emission of organic mutagens and potentially carcinogenic compounds if well controlled combustion conditions are not used.

More recent studies of incineration have also used Ames mutagenicity bioassay to characterize emissions. Driver, et al. (13) found that the mutagenic potencies of the stack fly ash from a medical pathological waste incinerator and from an adjacent industrial boiler were similar when both combustors were operated under "normal" conditions. This finding was unexpected considering the vastly different fuels for the medical waste incinerator and the industrial boiler burning No. 6 residual fuel oil. This assay was also able to determine significant increases in mutagenic emissions resulting from "upset" burn conditions caused by auxiliary burner failure. Linak et al. (14) and DeMarini et al. (15) determined mutagenicity emission factors for incineration experiments with the pesticide Dinoseb in a fuel-oil/xylene solvent. Results with either air staging or air staging and reburning were similar to those measured for the burning of fuel oil for residential heating.

The primary goal of the work reported here was to begin development of procedures to assess mutagenicity of emissions from municipal or hazardous waste incinerators. Specific objectives were to a) field test two types of high-volume source-dilution samplers, b) collect stack samples from three incinerator units for use in developing analytical and mutagenicity bioassay techniques required for analyses, c) determine the mutagenicity of organics associated with particle emissions, d) determine the stack emission rate for organic mutagens, and e) identify specific compounds/mutagens that are present in emission samples. This paper presents data on the mutagenic activity of stack gas emission samples and emission rates from a municipal waste incinerator, a municipal waste/hospital medical pathological waste incinerator and an incinerator dedicated to hospital medical pathological waste combustion (HMPWC). These data are compared to results from earlier MWC research and to other combustion sources (11,12,13,16). Details of the field sampling portion of this study will be described elsewhere (17).

EXPERIMENTAL

SAMPLE COLLECTION

Two prototype source dilution samplers were field tested at three sites in three USA states. These samplers, the 10 cfm ($0.28 \text{ m}^3/\text{min}$) Source Dilution Sampler (SDS)(18) and the 100 cfm ($2.83 \text{ m}^3/\text{min}$) Baghouse/Dilution Tunnel sampler (19), were designed to collect the large gram or even kilogram quantities of sample required for in vitro and in vivo toxicological studies including mutagenicity bioassay, animal carcinogenicity studies; and for identification of principal organic components responsible for mutagenic/carcinogenic activity. Both samplers bring outdoor air into a mixing chamber to dilute emission gases in a 10:1 ratio; i.e., 100:10 for the SDS sampler and 1000:100 for the baghouse sampler. This dilution process simulates the flue gas quenching that occurs upon emission from the stack to the atmosphere and was incorporated into the design to give organic vapors a sufficient sampler residence time to condense on fine particles prior to being collected on a particle filter or trapped in the baghouse. Both units also have the possibility of collecting semi-volatile organics on XAD-2 or other cartridge filters placed downstream from the particle filters, however, XAD-2 collections were not used in the present study.

In the SDS sampler, outdoor air was heated to approx. 75°F (24°C) and was HEPA (high efficiency particulate air filter) and charcoal filtered prior to entering the dilution chamber. Diluted particles were collected on round (approximately 26 in. [66 cm] diameter) Teflon-impregnated glass-fiber (TIGF) filters. A modified SASS cyclone used at the sampler inlet removed particles $>2.5 \mu\text{m}$ prior to dilution and collection.

The baghouse/dilution tunnel sampler was also designed to filter heated outdoor air through HEPA and charcoal filters prior to mixing with the stack gases in a mixing chamber. Mixed gases passed into a baghouse unit containing a felt filter cartridge. This filter fabric consisted of a Gore-Tex^R membrane backed with 100 percent Nomex^R fiber. Periodically, inlet gas flow was interrupted long enough to use a reverse pulse of high pressure nitrogen to

dislodge particles from the filter into a glass collection bulb positioned at the bottom of the unit.

Source samples were collected by the SDS sampler in two field studies during September and November 1988 from a MWC unit (site A) and during December of 1988 from a MWC/HMPWC at site B. The baghouse sampler was field tested for the first time during the second sampling study at site A and then tested again during the sampling study at site B. The baghouse heater for the dilution air was not installed prior to sampling at site A. A third sampling study, which utilized only the baghouse sampler, was conducted during August 1990 at the HMPWC unit located at site C. The baghouse sampler at this site C, with the dilution air heater installed, was primarily used to gain further experience with operation of this modified sampler and to attempt to collect sufficient sample size for mutagenicity and carcinogenicity determinations. An experimental sampler was also installed upstream from the baghouse at site C to draw a small portion of the sample/dilution air mixture through a 142 mm TIGF particle filter. This small sampler flow was approximately 300 percent of isokinetic. Sampling was not conducted at isokinetic rates at any of the three sites.

The incinerator at site A had two refuse-fired boilers, each with a capacity of 100 tons/day. Each combustion unit had a reciprocating stoker, an economizer, and an electrostatic precipitator (ESP). Combustion emissions were vented into a common stack. The sampling probe was inserted into the emission gases from one boiler just prior to their entrance to the base of the stack. Stack gas temperature measured after the ESP unit was 425°F (218°C).

The incinerator at site B consisted of two 50 ton/day Consumat starved-air combustors with a common ESP and stack. The unit burns primarily municipal waste and about 3-5 tons/day of hospital wastes. Stack gas temperature measured just after the ESP unit was 483°F (251°C). Sampling was conducted in the stack just downstream from the ESP outlet.

The HMPWC unit at site C consisted of a single 6.8 ton/day Consumat starved-air combustion system. No air pollution control devices were used on this unit. Stack gases leave the secondary chamber and are vented to the atmosphere through the stack. The incinerator is operated for an 8 h period and burns approximately 500-800 waste boxes/day with each weighing an average of 17.5 lb (7.9 kg). Sampling was performed with the baghouse sampler probe placed in the transfer duct between the secondary combustion chamber and the stack, where the gas temperature was approximately 1800°F (982°C). Stack emissions were sampled at a lower rate than used at sites A and B due to the requirement of maintaining a maximum dilution tunnel inlet temperature of 450°F (232°C) so as to avoid decomposition of Teflon parts in the sampler. Site C emissions were also diluted with outside air to a greater extent than at the other sites due to the lower sampling rate. In addition to the baghouse samples, experimental particle samplers were fitted to the dilution tunnel before and after the baghouse. These samplers pulled dilution tunnel gases through a 142 mm TIGF filter at rates of approx. 2.6 ft³/min (4.4 m³/h). The post-baghouse TIGF particle sampler pump failed, however, soon after start-up and did not collect a sample.

EXTRACTION AND FRACTIONATION

The SDS filters were cut into small pieces, placed in a glass or Teflon container along with 150 mL of dichloromethane (DCM) and sonicated (Branson 117 V 50/60 Hz Sonicator) for 10 min. at 77°F (25°C). This process was repeated two additional times. Combined extracts were filtered in an all-glass apparatus through a 0.45 µm Teflon filter. Extracts were concentrated by rotary vacuum evaporation at 95°F (35°C) and transferred to a volumetric flask where volumes were adjusted to 10 mL. Aliquots were removed for gravimetric determination of extractable organic mass (EOM) and for solvent exchange to dimethyl sulfoxide (DMSO) prior to bioassay (20). Gravimetric determinations of EOM for each sample extract were performed using two or three 0.5 mL aliquots from the known volume of extract. Aliquots were placed in tared aluminum weigh pans and solvent was evaporated in a hood. Sample pans were then equilibrated overnight in a desiccator prior to final weighing. Baghouse particles were Soxhlet extracted for 24 h with 850 mL of DCM. Solvent cycle time was 13.5 min. Extracts were filtered, concentrated, volume adjusted and aliquoted for gravimetric and bioassay determinations as above.

Aliquots representing specific amounts of EOM were solvent exchanged to DMSO and bioassayed whole or were fractionated on a nonaqueous ion-exchange column prior to DMSO solvent exchange and bioassay. The fractionation scheme utilized a quaternary ammonium styrene ion-exchange resin, Bio-Rad AGMP-1, to class fractionate DCM extracts of incineration samples. This solid phase extraction (SPE) procedure is described in more detail elsewhere (21) and is a modification of an earlier procedure (22). The modified procedure utilized 1 mL of washed and activated resin in a 1 cm i.d. column. Sample aliquots of <500 µL of DCM extracts were placed on the column and four 16 mL eluates were separately collected. The sequential elution solvents were: 1) DCM, 2) methanol, 3) methanol saturated with CO₂ and 4) 10 percent trifluoroacetic acid in methanol. Gravimetric analyses on aliquots of the four fractions showed that fraction 1 contained approximately 70 percent of the organic mass placed on the column. Fraction 1, utilized for determinations of mutagenic potency and emission rates, was concentrated and prepared for bioassay as previously described for whole sample extracts.

MUTAGENICITY TESTING

The Ames Salmonella typhimurium histidine reversion assay (3) with strain TA98 was used for mutagenicity bioassay. Samples having sufficient EOM to meet the minimum detectable limits of the assay were tested at a minimum of five doses using triplicate plates with and without Aroclor-induced rat liver S9 metabolic activation (+S9 and -S9) at each dose. Duplicate plates were used for samples with limited quantities. The minimum amount of sample for testing was approximately 0.5 mg. Sample extraction/elution solvents were exchanged to DMSO to make bioassay stock solution concentrations of 1 mg/mL. Spontaneous counts for TA98 were 25-50 colonies per plate after a 72-h incubation. Mutagenicities were confirmed by streaking revertant colonies onto minimal medium supplemented with biotin, but not histidine. A set of positive controls was incorporated in each experiment. These controls included 2-aminoanthracene (0.5 µg/plate) and 2-nitrofluorene (3.0 µg/plate).

with and without S9, respectively. A negative bioassay control utilized in each experiment consisted of a DMSO blank. Controls, consisting of blank filters and/or laboratory blanks, were extracted and analyzed in parallel with actual samples.

The revertant colony versus microgram of EOM data were plotted and analyzed by linear regression. The slope values (revertants/ μ g) from these dose-response determinations were used to calculate revertants/mg of particles, revertants/ μ g of EOM, revertants/ m^3 of emission gas, and stack emission rates in revertants/min.

RESULTS AND DISCUSSION

The mass burn municipal waste incinerator at site A was sampled in September 1988 with the SDS sampler and again in November of the same year with both the SDS and baghouse samplers. The SDS sampler collected five filter samples containing particle masses of 1.3 to 3.8 g during the first sampling study and one filter containing 3.4 g of particles during the second sampling trip. Collection periods were from approximately 1 to 4.5 h. Table 1 lists the volumes collected during each period and also shows particle concentrations of 35 to 102 mg/ m^3 of stack gas. The percent EOM values ranged from 0.26 to 1.72 percent with a mean of 0.77 percent. The EOM concentrations in stack gases were 0.16 to 1.61 mg/ m^3 . Particle and EOM emission rates were calculated for the six SDS samples collected during the two sampling periods at site A. Average emission rates were 359 mg/min for EOM and 41.4 g/min for particles. These rates were calculated with a stack gas emission rate of 644 wet std. m^3 /min.

The weather conditions and consequently the nature of the municipal waste being burned were quite different for the two sampling studies at site A. Rainy weather during the second sampling study resulted in wet trash being fed to the two MWC units and, consequently, emission gases contained a higher percentage of water. This burn condition plus intake of water saturated dilution air (10:1 ratio of air to sample) led to condensation of very corrosive gases that damaged the stainless steel transfer lines and sampler pumps. Condensation problems were also encountered inside the baghouse sampler which caused collection of a black liquid/particulate mixture in the sample jar. These liquid baghouse samples were deemed unuseable for mutagenicity analysis.

Three of the baghouse liquid condensate samples were subjected to ion speciation analyses. Atomic absorption (AA) was used for cations and ion chromatography (IC) for anions. Table 2 results of these analyses show a 3 percent chlorine content which would indicate corrosion problems resulted from formation of hydrochloric acid. Fluorine was present in concentrations of 88 - 207 ppm. Nitric and sulfuric acids were also indicated by the IC results of 200 and 450 ppm concentrations respectively for these anions. Chromium and nickel concentrations were each in excess of 1000 ppm. The presence of significant quantities of fluorine and chlorine indicates a high likelihood of finding halogenated organic species in stack emissions.

The SDS samples collected during the same second study at site A were also different in character from those collected during the September sampling study. Only one SDS sample (identified as 3/2 in Table 1) was suitable for analysis. The DCM extract of this filter was corrosive and mass determinations on aliquots of the extract resulted in aluminum weigh pans being corroded and mass determinations voided because of sample leakage. Polypropylene weigh pans, therefore, had to be utilized for these EOM analyses. A baghouse particle sample, which was obtained only after dismantling the filter housing assembly and physically rapping to dislodge particles, consisted of 102 g of wet filter cake. DCM extracts of this sample were also found to be corrosive. Mutagenicity assay of samples collected from both types of samplers failed because extracts proved to be too cytotoxic.

A sampling study at the site B MWC/HMPWC was initiated before analyses were completed for site A samples. Results for three SDS filters are reported in Table 1. Particle concentrations in stack emissions averaged 55 mg/m^3 . This value is a close comparison with the average particle concentration of 64 mg/m^3 found at site A. The percent EOM and EOM concentrations (mg/m^3) in the stack emissions were also similar to those from site A. The smaller particle and EOM emission rates are partly due to the lower stack emission rate of $393 \text{ std m}^3/\text{min}$. These Table 1 values from sites A and B, however, are all remarkably similar. Corrosion problems were again encountered while sampling with the SDS sampler, and extracts of the SDS filters from site B were also found to be cytotoxic. The baghouse sampler at site B failed to collect a sufficient amount of particles for bioassay analysis.

A non-aqueous solid phase extraction (SPE) scheme (21), which was developed to separate acidic fractions from neutral organics, was applied to selected extracts from sites A and B. These highly acidic fractions are often too cytotoxic to measure any mutagenic activity. The first SPE column fraction, the DCM neutral fraction, was found to contain approximately 70 percent of the organic mass placed on the column. Moreover, this fraction did not exhibit cytotoxicity in the Ames bioassay.

Table 1 also shows results for the HMPWC unit at site C. Four samples represent baghouse particles and one sample is a composite of three 142 mm TIGF filters collected by the experimental sampler with the intake positioned in the mixing chamber upstream from the baghouse sampler. The particle concentrations calculated for the baghouse samples at this site are approximately half of the amounts from sites A and B; however, the 59.7 mg/m^3 particle concentration determined for the composited TIGF particle filters is very similar to the 64 mg/m^3 average for site A and the 55 mg/m^3 average for site B. The 0.15 average percent EOM for the baghouse samples are also about half of the average value for site B (0.33) and one-fifth of the site A value (0.77). The TIGF percent EOM of 1.04 is again similar to that observed from site A. Additional testing of the baghouse sampler is being planned in order to make further comparisons between the particles collected by the baghouse and those collected on a particle filter; e.g., the TIGF filter media used in the SDS sampler.

Table 3 shows mutagenic measurements for emissions expressed as revertant colonies (rev)/mg of particles and rev/ μ g of EOM, mutagenicity concentrations (rev/ m^3) and emission rates (rev/min) for samples taken from incinerators at sites A and C. Results are shown for whole samples (unfractionated) and DCM neutral fractions (fraction 1) from SPE column separations. Three SDS filters (2, 3, and 4) from site A were composited prior to bioassay to provide sufficient sample size for further chemical characterization studies on high performance liquid chromatography (HPLC) subfractions of the first elution (neutral fraction) from the SPE column. This bioassay directed fractionation and chemical characterization work is a continuing effort to identify specific compounds and/or compound classes that are responsible for observed mutagenicity. The small (142 mm) TIGF filters from site C were also combined to provide sufficient sample size for bioassay. The mutagenic potency data for the site A filters show divergent values for the whole sample extracts. Filter 1 gave a +S9 value of 27 rev/ug compared to 0.95 rev/ug for the composite sample (filters 2, 3, and 4). The fractionated composite sample, however, shows a potent first (neutral) fraction from the SPE column, indicating the possibility that the 0.95 value for the whole sample was depressed due to the presence of acidic cytotoxic components that inhibit the expression of mutagenicity. This type of bioassay requires that the *Salmonella* cells remain viable during incubation. A fractionation step, therefore, may be necessary for some or all incinerator samples to remove such interferences prior to the mutagenicity assay. Site B whole samples were also cytotoxic, and analyses of SPE fractions failed to demonstrate mutagenicity.

The emission factors in Table 4 were developed to make comparisons with previous MWC studies and other combustion sources. The mutagenicity per hour values from site A closely match those reported for an incinerator in Aichi Prefecture, Japan (11). Better comparisons, however, can be made for emission results reported as revertants per kg of fuel. A study of four MWC units in Sweden reported approximately 10,000 to 100,000 revertants per megajoule (MJ) of fuel (12). Conversion of these values to rev/kg of fuel basis was made using the factor of 11.614 MJ/kg of municipal solid waste (MSW). These values ranged from $1-12 \times 10^5$ rev/kg, which compare with the $1.6-4.4 \times 10^5$ rev/kg values from the MWC at site A and 0.7×10^5 rev/kg from the HMPWC at site C. Data for industrial and utility boilers and power plants using oil, coal, and wood fuel (16) show emission factors ranging from $0.03-0.2 \times 10^5$ rev/kg of fuel. The similarity of these emission factors indicates that the mutagenic potency of emissions may not be greatly affected by the fuel source. The combustion condition or "completeness of combustion" combined with the effectiveness of pollution control equipment operating at the incinerator may be much more relevant factors to consider for controlling the mutagenicity of incinerator emissions.

Table 4 emission factors reported for gasoline and diesel vehicles range from $1-40 \times 10^5$ rev/kg of fuel (16). A comparison of the 0.5×10^6 rev/hour rate for a gasoline catalyst car (24) with 1000×10^6 rev/hour from a MWC unit (11) shows that MWC emission to be equivalent to approximately 2000 gasoline catalyst cars. However, it should be noted that comparisons between emission sources may be misleading. Automobile exhausts contain highly mutagenic, but not necessarily strongly carcinogenic species, and MWC emissions may contain

strongly carcinogenic species, i.e., chlorinated dibenzodioxins, that are not mutagenic (12).

The data reported here should be considered as pilot study information obtained during initial field testing of the SDS and baghouse/dilution tunnel samplers. Isokinetic sampling was not used at any of the incineration sites. Problems were encountered during each sampling event (e.g., condensation inside sampler housings and corrosion damage) which are currently being addressed. The analytical operations of sample extraction, gravimetric determinations, and bioassay also encountered problems related to the corrosive nature of extracts and to cytotoxic species that often prevented or otherwise affected mutagenic potency analyses on the whole or unfractionated extracts. A fractionation scheme had to be developed before bioassay could be successfully performed.

Engineering modifications have been made on the sampling equipment, and further field testing is needed in order to continue the development of incinerator emission samplers. The quality assurance aspects of field sampling, sample handling, and analytical procedures all need additional study. The SPE fractionation method used and perhaps other similar methods need to be further examined for their suitability in removing cytotoxic species and separating organics into class fractions. Additional bioassay-directed fractionation procedures (e.g., HPLC coupled with microsuspension bioassay (25)) are being used to subfractionate the neutral fraction for further examination by mass spectroscopy in order to identify and quantify the principal organic mutagens.

SUMMARY

Two types of incinerator stack samplers were field tested at three sites. Emission samples were collected from municipal waste and hospital medical pathological waste incinerators. Organics associated with emission particles were bioassayed for mutagenicity using the Ames plate incorporation assay. Stack emissions, which were characterized by particle concentration and percent extractable organic mass, were similar although there were large differences in the nature of the fuel materials consumed at the various sites. Emissions, characterized by mutagenicity emission factors, also were similar for these same sites and were similar to factors previously reported for a hospital medical pathological incinerator and for industrial and utility boilers burning coal, wood, and oil. The mutagenicity of incinerator emissions, therefore, may not be greatly affected by the fuel source. Burn conditions and pollution control devices are likely to be more important considerations for ensuring safest possible emissions.

Mutagenicity concentrations reported here for a MWC unit are also similar to those reported by other researchers. The mutagenicity of sample fractions from a MWC sample extract indicates the presence of potent organic mutagens associated with particle emissions. However, additional research is needed to identify such species and to determine their emission rates. Additional studies are also needed to further improve: sampling equipment, sampling and

sample handling procedures, analytical and sample preparation methods, and bioassay procedures.

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TABLE 1. PARTICLE AND EXTRACTABLE ORGANICS IN INCINERATOR EMISSIONS.

Filter No.	Site A, MWC (SDS filters.....)						Site B, MWC/HMPWC (SDS filters.....)			Site C, HMPWC (Baghouse samples.....)TIGF				
	1	2	3	4	5	3/2	7	21	23	1	2	3,4	5	1,3,4
3	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
std m collected	40.7	57.3	80.3	12.8	63.8	43.1	68.8	140.9	141.6	72.5	268.1	214.2	359.4	3.57
3	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
part. mg/m stack gas	93.4	34.9	41.1	101.6	36.1	78.9	78.5	52.5	33.2	33.1	16.2	62.8	8	59.7
% EOM 3	1.72	0.62	0.76	0.82	0.43	0.26	0.31	0.23	0.46	0.25	0.14	0.04	0.15	1.04
EOM mg/m stack gas	1.61	0.22	0.31	0.83	0.16	0.21	0.24	0.12	0.15	0.08	0.02	0.03	0.01	0.62
a EOM mg/min from stack	1037	142	200	535	103	135	94	47	59	9.8	2.7	3.1	1.4	75
part. g/min from stack	60.1	22.5	26.5	65.4	23.2	50.8	30.9	20.6	13.0	4.0	2.0	7.6	1.0	7.2

a

Stack gas emission rates (wet basis): site A = 644 std. cubic meters/min (flue gas temperature of 425 deg. F); site B = 393 std. cubic meters/min (flue gas temperature of 483 deg. F); and site C = 120.6 std. cubic meters/min (flue gas temperature of 1400 deg. F)

Table 2. CATIONIC AND ANIONIC SPECIATION RESULTS FOR BAGHOUSE LIQUID CONDENSATES COLLECTED FROM INCINERATOR A.

Sample	AA Results (ppm)					
	Cd	Cr	Pb	Zn	Cu	Ni
1	6	500-1000	~100	>50	25-50	~1000
2	9	>1000	>100	>50	25-50	>1000
3	5	>1000	50-100	>50	50-100	>1000

	IC Results (ppm)			
	F	Cl(%)	NO ₃	SO ₄
1	88	3	---	268
2	108	3	210	456
3	207	3.4	203	418

Table 3. MUTAGENIC POTENCY, CONCENTRATIONS, AND STACK EMISSION RATES.

Sample		Revertant colonies per.....					
Site No.	Fract.	+/-S9	mg part.	ug EOM	cubic m	a min	
A 1	whole	+	458	26.6	42800	276 x 10 ⁵	
A 1	whole	-	339	19.7	31700	204 x 10 ⁵	
A 2,3 & 4	whole	+	6.9	0.95	304	1.96 x 10 ⁵	
A 2,3 & 4	whole	-	25.4	3.48	1115	7.18 x 10 ⁵	
A 2,3 & 4	neutral	+	353	48.3	15479	100 x 10 ⁵	
A 2,3 & 4	neutral	-	351	48	15383	99 x 10 ⁵	
C BH 1	whole	+	2.95	1.2	98	0.12 x 10 ⁵	
C BH 1	whole	-	6.11	2.49	202	0.24 x 10 ⁵	
C BH 2	whole	+	1.41	1.03	23	0.03 x 10 ⁵	
C BH 2	whole	-	1.37	1	22	0.03 x 10 ⁵	
C BH 3&4	whole	+	0.44	1.07	27	0.03 x 10 ⁵	
C BH 3&4	whole	-	0.94	2.3	59	0.07 x 10 ⁵	
C BH 5	whole	+	2.69	1.82	21	0.03 x 10 ⁵	
C BH 5	whole	-	1.77	1.2	14	0.02 x 10 ⁵	
C TIGF 1,3&4 whole		+	7.78	0.75	465	0.56 x 10 ⁵	
C TIGF 1,3&4 whole		-	18.77	1.81	1121	1.35 x 10 ⁵	

a

Stack gas emission rates (std. cubic meters/min): site A = 644;
site C = 120.6

Table 4. TYPICAL MUTAGENIC EMISSION FACTORS FROM VARIOUS COMBUSTION SOURCES.

Source	Revertants per.....		
	hour	a kg fuel	b MJ
MWC; site A	6 1656×10	5 4.4×10	4 3.8×10
MWC; site A neutral fraction	6 600×10	5 1.6×10	4 1.4×10
HMPWC; site C	3.4 x 10 6	0.7 x 10	580
MWC (11)	1008 x 10	5	4
MWC (12)		1-12 x 10	1-10 x 10
Industrial and utility boilers and power plants (16)			
oil	0.03 x 10	70	5
coal	0.06 x 10	230	5
wood	0.20 x 10	1000	5
Automobiles and trucks (16)			
diesel vehicles	40 x 10	5	5
diesel trucks/buses	40 x 10	5	5
gasoline-noncatalyst	10 x 10	5	5
gasoline-catalyst	1 x 10	6	6
wood stove (23)	6 x 10	6	6
gasoline car (24)	0.5 x 10	6	6
diesel car (24)	6 x 10		

a

waste burn rates (kg/min): site A = 63; site C = 8.4

b

megajoule: literature value or calculated for MWC using 11.614 MJ/kg of
municipal solid waste (MSW)

c

calculated revertants/kg MSW using factor of 11.614 MJ/kg MSW

SESSION 10C: FLUE GAS CLEANING SYSTEM PERFORMANCE

Co-Chairmen:

**R. Michael Hartman
ABB Resource Recovery Systems
Windsor, CT**

**Charles B. Sedman
AEERL
U.S. EPA
Research Triangle Park, NC**

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The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

A REVIEW OF ACTIVATED CARBON TECHNOLOGIES FOR REDUCING MSW INCINERATOR EMISSIONS

by

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ABSTRACT

Though activated carbon is, by no means, a newcomer to the pollution control field, having been used as a water purifier and more recently demonstrated as a flue gas cleaner on power plants, it is now attracting considerable attention in Europe as a means to reduce further the quantity of toxic organic and metal emissions from new and existing municipal waste combustors. Since activated carbon is a potentially important future emissions control technology for MWCs in the US, particularly for removal of mercury and dioxin, this paper will discuss the impetus which has motivated the experimentation with various activated carbon technologies which is now taking place, will describe how some of the activated carbon systems (e.g., post-emissions control fixed carbon bed and injection of carbon with scrubber reagent) being tested now function and where they fit in existing pollution control trains, and will present available performance data and emissions reductions actually achieved for each system.

INTRODUCTION

Activated carbon technologies are, and have been for decades, commonly used as a method for filtering a wide variety of pollutants from both gaseous streams and effluent streams. In one database alone, EPA lists 171 oils and hazardous materials, including pesticides, oils, fuels, organics (including hexachlorobenzene and three chlorophenols), metallic compounds, radioactive compounds, and various halides (chlorides, sulfates, fluorides), for which activated carbon is listed as an appropriate adsorbent and control technology. (Ref. 27)

THE BASIS FOR ACTIVATED CARBON TECHNOLOGY

Activated carbon, or activated coke, functions as a very effective adsorbent due to the fact that its particles or fibers contain extraordinarily large internal pore surface area which can bond adsorptively to a very broad range of substances. The internal surface area of the active coke/carbon used on large-scale applications today are between 300 to 800 m^2 per gram of activated carbon. (Ref. 22) Grains having an internal surface area up to approximately 300 m^2/gram are referred to as activated cokes; above this value, and as high as 1500 m^2/g , the material is called activated carbon. (Ref. 3) For purposes of reference, the 800 square meters of pore space in one gram of activated carbon is equivalent to a tenth of a city block.

In addition to having large internal pore surface area on which to bond impurities in gases, some activated carbons also possess catalytic properties. For example, this effect has been used to achieve reduction of oxides of nitrogen by adding ammonia or ammonium hydroxide. (Ref. 22)

Once the activated carbon has been in place for a period of time it becomes saturated with the impurities it has been adsorbing. At this point, it becomes necessary to regenerate the carbon.

HISTORY AND USES OF ACTIVATED CARBON TECHNOLOGIES

The first use of activated carbon for extraction of harmful substances from flue gases and sewage occurred in 1909. Activated coke filters were first used in respirators to purify air in World War I. (Ref. 22) Since then much effort has been expended to develop more efficient and specialized activated carbon products for distinctive tasks. Such diverse tasks have included the purification of water for drinking water (Ref. 6), treatment of industrial effluents, (Ref. 9) and the treatment of landfill leachate (Ref. 8). Other research has involved the study of process kinetics and the development of models for predicting the removal efficiency of these materials. (See Refs. 4, 18, 21, and 29) Investigations have been pursued to determine the optimal configurations and methods of using activated carbons, (see Refs. 14, 15, 16), and optimal conditions under which these materials would produce the greatest removal efficiency. (see Ref. 12). Finally, still further research has concentrated on methods of regenerating the adsorbent (Refs. 20, 23, 24)

In the last decade activated coke has been demonstrated as an air pollution control device on various pilot and full-scale, large applications, most commonly for power stations. The first large-scale activated carbon bed using lignite coke was used on a power plant, located behind ten reactors, each of which has a throughput of 250,000 Nm³/hour, at Garath, near Duesseldorf. (Ref. 22) This pilot plant, with 65,000 m³/hr capacity was used for SO₂ adsorption and NOx reduction. (Ref. 3)

UPSURGE IN INTEREST IN ACTIVATED CARBON FOR MSW INCINERATORS -- REGULATIONS IN EUROPE

Why all the current interest in activated carbon to reduce emissions from incinerators? While it is true that advances over the last ten years in combustion efficiency, furnace design, operating techniques, and add-on emission control devices (e.g., multi-field ESP's, baghouses, and scrubbers) have improved the state-of-the-art as much as two orders of magnitude insofar as emissions are concerned, it is also true that the incineration industry is facing an increasing challenge from solid waste solutions that are more energy and natural resources-efficient and less environmentally deleterious on a process lifecycle basis, and which are now officially recognized by EPA and many states as superior: reduction, reuse, recycling, and organics composting.

In Europe these realities, combined with a heightened public awareness and concern about environmental issues in general, have contributed to the promulgation of increasingly more stringent standards, regulations, and goals for incinerator emissions. In Sweden and the Netherlands, increased standards were the direct result of findings of unacceptably high levels of dioxins, traced to MSW incinerator emissions, in the food chain. Thus, commencing with Sweden in 1986, the Netherlands, Austria, Denmark, Germany, and Sweden have adopted as either a standard or a goal a 0.1 ng/Nm³ dioxin toxic equivalent level.

More stringent standards for heavy metals have also been issued. Previous standards for mercury were as high as 130 ug/Nm³ for Austria, Switzerland, and Germany. However, at present the emission limit is 50 ug/Nm³ in Austria for mercury and for cadmium/thallium. (Ref. 11) The maximum emission limits during test sampling for new and existing incinerators set in the Netherlands in 1989 also included a level of 50 ug/m³ each for cadmium and for mercury. The Dutch government also set more stringent standards for NOx (70 mg/m³ or 52 ppm corrected to 7% O₂), SO₂ (40 mg/m³ or 21 ppm corrected), HCl (10 mg/m³ or 9.4 ppm) and particulates (5 mg/m³ or 0.003 gr/dscf). (Ref. 10)

In order for new and existing plants to meet these emission levels, the recent state-of-the-art practiced in the U.S. (the dry scrubber/baghouse) is not considered sufficiently reliable. Thus, various activated carbon and other emission control technologies are being examined for purposes of retrofitting older incinerators and complementing the conventional emissions control devices on new plants so as to achieve further reductions in mercury, dioxins, NOx, and other emissions of concern.

The most recent baseline regulations issued in Germany (the 17th regulation pertinent to the Bundes Emissionsschutz Gesetz -- their Clean Air Act), requires that new incinerators of municipal solid waste and similar materials must, under normal operation, meet a 0.1 ng/Nm³ dioxin toxic equivalent level and that they meet a level of 0.05 mg/Nm³ for Cadmium plus Thallium, and 0.05 mg/Nm³ for Mercury (all at 11% O₂ dry). The regulation for another group of metals (Sb, As, Cr, Pb, Co, Cu, Ni, Mn, V, and Sn) is 0.5 mg/Nm³, particulate, hydrocarbons, and HCl emissions are each limited to 10 mg/Nm³, the SO₂ limit is 50 mg/Nm³ and the HF limit is 1 mg/Nm³.

New plants (those with permits issued after December 1, 1990) will have to meet the regulation immediately. Older existing incinerators (those with permits issued under TA Luft 1974) will have to comply with these new regulations by March 1, 1994; those newer existing incinerators (with permits issued under TA Luft 1986 or those not issued permits prior to December 1, 1990) will have to comply by March 1, 1996. According to Bernd Johnke, an engineer with the German environmental research agency (UBA), the regulations were developed based on the information that sufficient technology exists now for new plants to meet the standards, and it is fully expected that all plants will be able to comply with the regulation.

A case in point is a newly constructed large-scale incinerator in Bonn, which was designed with an ESP and wet scrubber. Since the facility did not receive its permit before December 1, 1990, it is now being retrofit in order to achieve the mercury and dioxin limits. The new system positioned after the existing pollution control train involves a fabric filter (100°C inlet) into which activated carbon and lime will be injected. (Ref. 13)

By way of comparison, the New Source Performance Standards (NSPS) recently issued by USEPA are considerably higher for all pollutants of concern. For example, the final standards require only large plants to meet a total dioxin/furan limit of 30 ng/dscm. Though these units are not directly comparable to toxic equivalents, it is safe to say that this new U.S. limit is at least one and possibly two or more orders of magnitude higher than those currently in effect for all plants in several European countries based on data elsewhere in this paper.

The NSPS for specific heavy metals have not yet been established, but draft standards for mercury, cadmium, and lead are expected soon, since the new Clean Air Act requires that limits for these metals be promulgated by November 15, 1991. Some discussion has centered around setting the U.S. standard to equal the previous European standard of roughly 130 ug/dscm, a value over two and one-half times the current European standard. The NSPS for NOx is 180 ppmv (7% O₂) 24-hour block average. This level is over three times the Dutch limit.

A DESCRIPTION OF THE ACTIVATED CARBON TECHNOLOGIES

INJECTION OF ACTIVATED CARBON WITH LIME

This technology is essentially a hybrid of two emissions control mechanisms: alkaline absorption and activated carbon adsorption. After injection of Sorbalit and hydrated lime, dust collection onto the activated carbon begins in the scrubber and continues in the flue gases downstream. Of similar significance insofar as adsorption of pollutants is concerned, is the further adsorption which takes place on the cake which adheres to the fabric filter. Unfortunately, ESP's do not have the latter capability. After the carbon is injected, some is collected, some remains in circulation, allowing for fresh carbon to replace saturated carbon.

Well suited to retrofit into systems already possessing an acid gas scrubber, injection of activated carbon has been demonstrated on a number of pilot and existing full-scale plants. According to Flakt removal efficiency for dioxins and for mercury corresponds to that obtained with granular static bed filters of activated coke. In addition, Flakt contends that injection of activated carbon uses less activated carbon than the static carbon bed system.

FINAL STAGE ACTIVATED CARBON BED

Much of the experimentation with "back-end" activated carbon beds for MSW Incinerators has been in Germany and Austria. There are mainly two types of active coke/carbon on the market today having similar adsorptive capacity, but different catalytic activity. The formation coke, marketed by Mining Research, and based on mineral coal, has a higher catalytic activity and is also ten to twenty times as expensive as its chief competitor, the hearth-type furnace coke sold by Rheinbraun, which is based on lignite. This activated carbon bed system is positioned after all other add-on emissions control devices in a pollution control train.

Flue gas cleaning is accomplished by drawing the flue gas through the bed, whereupon the pollutants of concern accumulate on the abundant surfaces of the pore spaces. From investigations by the firm Hugo Petersen and the Technical University of Berlin it was found that mercury, other heavy metals, and large molecular hydrocarbons, such as dioxin and furan, are adsorbed in the first layers of the reactor. Sulfur dioxide is displaced by heavy metals in the coke pores and then redeposited in the following layers. HCl and HF are, in turn, displaced by SO₂ from the pores and are adsorbed in the following, unfilled layers of the bed. All pollutants are fully adsorbed when the filter is appropriately large. (Ref. 3)

One present potential drawback of upscaling the technology is the possibility of fires, particularly in a bed sized for a full-scale, large incinerator. Activated carbons are naturally flammable because of their high carbon content, and may tend to self-ignition at temperatures from 80 to 400°C when oxygen is present. (Ref. 3) According to Justus Engelfried of the EPEA Umwelt Institut in Hamburg, a large incinerator processing 300,000 TPY would require an activated carbon bed of 1000 square meters 40 meters high. However, the ignition point of the furnace coke is at least 390°C and of the

formation coke is roughly 350°C (Ref. 19), so in back-end installations, where the operating temperature of the bed is usually less than 140°C and sometimes as low as 110°C, the risk would seem to be small under normal operating conditions. In addition activated carbon beds can be monitored for temperature and the difference in CO before and after the reactor. However, in one case a fire in an activated carbon bed was reported after major upset conditions lasting 24 hours caused back-end temperatures to rise. (It was easily extinguished.) This experience underscores the need for well-trained, attentive operators. (Ref. 19)

REGENERATION/DISPOSAL OF ACTIVATED CARBON

Several alternatives are available for treating and/or disposing of saturated activated carbon. The total amount of charged or used-up coke represents about 1% in relation to the total amount of solid waste processed. One method of disposal involves depositing the saturated carbon in an incinerator. This is deemed economically advantageous and would result in a destruction of organics collected by the carbon. It is important, however, that sufficient emissions reduction potential exists in the incinerator's pollution control train to absorb the additional load represented by the disposed activated carbon. A method for regeneration involves separate thermal treatment in a moving bed desorber, where the carbon is brought into contact with a circulating gas whose temperature lies in the range of 350°C to 500°C. (Ref. 3) This process desorbs the mercury and catalytically reduces the dioxins, with subsequent condensation at 20°C at which point the mercury precipitates. (Ref. 22) A third method involves mechanical cleaning or desorption to regenerate the coke and retain its properties. (Ref. 19) A fourth alternative is to use the saturated carbon as an additive for converting flue dust into glass, for example, using the ABB process DEGLOR. (Ref. 2) Because the furnace coke is so inexpensive, it is usually incinerated, however, the formation coke is usually regenerated in a mechanical screening process. (Ref. 19)

A DESCRIPTION OF PILOT AND FULL-SCALE INVESTIGATIONS TO-DATE INJECTION OF ACTIVATED CARBON

NIRO Atomizer

One of the early innovators in applying activated carbon technology to MSW incineration was NIRO Atomizer. At the Zurich Josefstrasse plant, a full-scale plant with a large conventional ESP, later retrofitted with a NIRO spray dry scrubber, activated carbon injection testing began in 1987. Four sets of samples were collected at the inlet and outlet of the SDA system and analyzed for total dioxin content. Table 1 indicates the inlet, outlet, and removal efficiencies for the tests which measured the effectiveness of lowering outlet temperature from 285°F to 245°F and the injection of various concentrations of activated carbon. In addition, both toxic equivalents and total dioxins were measured. At low SDA outlet temperatures it was found that the use of small amounts of activated carbon substantially lowered dioxin emissions to as little as 0.08 ng/Nm³ Toxic equivalents and improved system collection efficiency to as much as 99.6%. (Ref. 5)

Table 1. Zurich Pilot Plant Dioxin Emissions and Removal

SDA Outlet Temp. °F	248	248	285	285
°C	120	120	140	140
Additive Rate gr/acf	0	0.75	0	0.25
Dioxin Emissions, ng/Nm³				
2,3,7,8 - TCDD Eadon Equiv.	1.3	0.08	1.5	0.84
Total Dioxin + Furan	60	5.0	66	35.2
Dioxin Removal %				
2,3,7,8 - TCDD Eadon Equiv.	91.3	99.5	92.4	90.3
Total Dioxin + Furan	92.6	99.6	92.3	90.3

On the basis of these experiments, the 400 TPD Zurich incinerator was retrofit with this technology to increase the level of control for mercury and dioxin and was tested for both of these pollutants. The system for injection of dry activated carbon is situated upstream of the spray dryer absorber. The carbon then mixes intimately with the flue gas and lime slurry droplets inside the SDA providing optimum conditions for contact between the activated carbon and the dioxins and mercury present in the flue gas.

After start-up the retrofit was tested to verify pilot plant figures. Though it was determined that the lower the SDA outlet temperature the lower the dioxin and mercury emissions (the system was successfully operated at temperatures as low as 110°C), the removal achieved without using activated carbon was not sufficient to meet the then applicable 0.1 mg/Nm³ mercury outlet limit (note the current limit is 0.05 mg/Nm³). Table 2 shows the summary of results of 25 mercury tests at Zurich with and without using activated carbon. (All mercury measurements were made simultaneously at the SDA inlet and in the stack, and are assumed to be 11% O₂.) These data show that there is a significant effect of using activated carbon. Also, when using activated carbon injection, a low mercury emission was achieved regardless of fluctuations in the inlet mercury level. For example, at 30 mg/Nm³ carbon injection level and at an outlet temperature of 110°C, the inlet mercury level fluctuated from .131 to .650 mg/Nm³ and the outlet concentration varied between .040 and .068 mg/Nm³ (approximately the current regulation level) with an average removal rate of 83%. (Ref. 7)

The dioxin emissions at the Zurich retrofit were measured by the Danish EPA-recognized firm, dk-Teknik, Denmark, sampled according to the Nordic protocol, and analyzed by Umea University. Steady-state conditions, at a constant, low CO level (20-30 ppm dry) were maintained for an extended time before measurements were taken. The results showed that without the activated carbon the quenching of flue gas temperature (from roughly 210°C to 130°C) in the scrubber resulted in a 75% removal efficiency for dioxin. But by adding activated carbon, removal efficiency is increased to 90% at 140°C using 18 mg/Nm³ activated carbon, and to 98.5% removal at 120°C and 59 mg/Nm³ activated carbon. Table 3 summarizes these results. (Ref. 7)

Table 2. Mercury test results at Zurich Josefstrasse

SDA outlet temp. °C	Additive mg/Nm ³	Hg concentration ug/Nm ³ dry			% removal
		SDA Inlet	ESP outlet		
140	0	537	390		27
		343	237		31
		680	417		39
		558	414		26
		406	335		17
		1072	769		28
Average		599	427		28
120	30	539	39		93
		589	31		95
Average		564	35		94
115	0	495	232		53
		643	207		68
		234	117		50
		949	670		29
		736	476		35
		401	250		38
Average		576	325		44
115	30	352	44		88
		353	44		88
		281	29		90
Average		329	39		89
110	0	249	124		50
		224	132		41
		346	212		39
Average		273	156		43
110	30	486	68		86
		650	45		93
		131	44		66
		417	40		90
		269	51		81
Average		391	50		87

Table 3. Dioxin Test Results at Zurich Josefstrasse

SDA outlet temp. °C	Active carbon mg/Nm ³	Total PCDD + PCDF			Eadon Tox. Equivalents		
		SDA inlet	ESP outlet	% rem.	SDA inlet	ESP outlet	% rem
140	0	306	77	74.8	7.7	1.9	75.3
	18	223	33	85.2	7.5	0.79	89.5
120	0	277	69	75.1	6.9	1.8	73.9
	59	455	5.0	98.9	6.0	0.09	98.5

In 1988 NIRO also retrofit its activated carbon injection technology on the 300 TPD Volund rotary system incinerator at Amager in Copenhagen. Downstream of the carbon injection is a SDA and pulse-jet fabric filter. As with the Zurich incinerator, tests showed that with no activated carbon injected, the reduction of SDA outlet temperature had a clear effect on mercury removal. However, the summary of the 19 tests of this full-scale system undertaken in 1989, Table 4, shows that with sufficient additive injection (as much as 70 mg/Nm³) coupled with low outlet temperature (as low as 127°C), mercury emissions were reduced by as much as 97% and were controlled to a level one-tenth of the new 0.05 mg/Nm³ German limit. (Ref. 7)

Table 4. Summary of Mercury Test Results - Amager, Denmark

Mercury concentrations ug/Nm ³ , 10% CO ₂				
SDA outlet temp °C	Activated Carbon mg/Nm ³	SDA inlet	FF outlet	% removal
140	0	171	97	43
	6	255	42	84
	17	224	28	87
	58	633	37	94
120	0	154	37	76
	19	169	20	88
	70	176	5	97

The dioxin sampling and analysis for Amager were the same as for Zurich. The dioxin removal figures (Table 5) show that outlet emissions without activated carbon are reduced about 50% by lowering the outlet temperature from 140°C to 127°C. Injection of activated carbon increased dioxin removal efficiency further to virtually 100%. It is important to note that in one test, where start-up conditions were simulated, the inlet dioxin value increased ten-fold to 50 ng/Nm³, but the outlet value was 0.05 ng/Nm³ Toxic equivalent, half the new German regulation. (Ref. 7)

Table 5. Dioxin Test Results - Amager

SDA outlet temp. °C	Activated Carbon mg/Nm ³	Total PCDD + PCDF ng/Nm ³ , dry			Nordic Toxic Equiv. ng/Nm ³ , dry		
		SDA inlet	FF outlet	% rem.	SDA inlet	FF outlet	% rem.
140	0	132	2.1	98.4	2.8	0.076	99.7
	6	283	1.2	99.6	4.8	0.0075	99.8
	17	276	2.4	99.2	8.3	0.045	99.5
	58	201	1.1	99.5	4.0	0.035	99.1
	58	2170*	3.2	99.9	50.0	0.050	99.9
127	0	254	1.3	99.5	7.7	0.0047	99.9
	19	154	0.4	99.8	5.0	N.D.	100
	70	154	0.7	99.6	4.5	0.002	100

* Simulated Start-up condition

The Kassel, Germany activated carbon retrofit installation, achieved similar results to Zurich and Amager with up to 97% removal and as little as .005 mg/Nm³ outlet value for mercury at 127°C and 70 mg/Nm³ activated carbon added (see Table 6).

Table 6. Summary of Mercury Test Results - Kassel, Germany

SDA outlet temp. °C	Activated Carbon mg/Nm ³	Mercury Concentrations ug/Nm ³ , dry		
		SDA inlet	FF outlet	% removal
137	0	898	582	35
	9	336	175	48
	20	324	57	82
	47	179	19	89
	64	297	52	82

The dioxin results were also similar with up to 99% removal for dioxin/furan and as little as 0.07 ng/Nm³ emission for TCDD Toxic equivalents (see Table 7). (Ref. 7)

It was concluded from these studies of Zurich, Amager, and Kassel that the injection of activated carbon upstream of a spray dryer absorber results in a very low dioxin emission regardless of operating mode (single pass as at Zurich and Amager vs. recirculation as at Kassel), type of dust collector (ESP as at Zurich and fabric filter as at Amager and Kassel), spray dryer outlet temperature, and upset conditions. Insofar as mercury removal is concerned, a combination of low flue gas temperature and the presence of activated carbon in the scrubber reagent corresponded to an increase in removal efficiency and

a decrease in emissions, in many cases below the current European emission standard for mercury of 50 ug/Nm³.

Table 7. Dioxin Test Results - Kassel, Germany

SDA outlet temp. °C	Activated Carbon	Total PCDD + PCDF Toxic Equiv.					
		SDA mg/Nm ³	FF inlet	FF outlet	% rem.	SDA inlet	FF outlet
135	0	380	151	60	9.58	3.46	64
	19	134	12	91	3.21	0.19	94
	19	238	8	97	5.11	0.15	97
	47	298	9	97	5.53	0.13	98
	105	359	7	98	5.94	0.07	99

Research-Cottrell/Teller

Another of the activated carbon injection systems, the Research Cottrell-Teller system, (Ref. 25) has achieved significant reductions of mercury from a medical waste incinerator in Skovde, Sweden. This incinerator processes waste at a rate of roughly 25 tons per day, the combustion temperature is approximately 1000°C achieving a 99.99% reduction in combustibles; and the temperature of the flue gas is reduced by thermal recovery to 140-150°C. The all-dry emission control system has two basic components: (1) a Dry Venturi, into which are blown hydrated lime, activated carbon reagent, and Tesisorb bagcake modifier, and (2) a pulse jet fabric filter, where the cake is permitted to accumulate for 4 to 6 hours between cleaning cycles. The bag filter with a 3-10 mm cake, in essence, serves as the major reactor for acid gas, mercury, and dioxin recovery. The activated carbon was considered more suitable for this application because the anticipated flue gas temperature (135-150°C) exceeded the flyash adsorption temperature.

The performance tests for the Skovde Hospital Incinerator were conducted by Miljokonsulterna of Nykoping, Sweden, a testing group approved by the Swedish environmental authorities. For mercury, inlet values ranged from 294 to 10,170 ug/Nm³, (as much as ten times as much as expected in the design stage) and outlet values ranged from 5 to 25 ug/Nm³ (all values at 10% CO₂). The mercury guarantee was 80 ug/Nm³. Table 8 shows the results of the four tests broken down for inlet, outlet, and percent removal for mercury metal, salts, vapor, and total.

With respect to dioxin, two test results in Table 9 showed the considerable effect on removal efficiency of adding an activated carbon/lime/Tesisorb reagent, with stack temperatures in the range of 136 to 138°C. Overall removal efficiency was 93% to 99%, and the addition of carbon more than doubled removal efficiency achieved by the Tesisorb and lime alone.

Table 8. Specific Mercury Emissions at Skovde Hospital Incinerator

Inlet <u>ug/Nm³(10%CO₂)</u>				Outlet <u>ug/Nm³(10%CO₂)</u>			
<u>Hg Metal</u>	<u>Hg Salts</u>	<u>Hg Vapor</u>	<u>Total</u>	<u>Hg Metal</u>	<u>Hg Salts</u>	<u>Hg Vapor</u>	<u>Total</u>
3.0	286	4.9	254	0.05	7.3	1.6	9.0
19.0	9993	160	10510	0.05	23	1.5	25
2.6	705	191	922	0.01	3.0	3.5	6.5
3.0	389	122	514	0.01	2.8	1.2	4.5

<u>Hg Metal</u>	<u>Hg Salts</u>	<u>Hg Vapor</u>	<u>Total</u>
98.3	97.4	77.3	97.0
99.7	99.8	99.1	99.8
99.6	99.6	98.2	99.3
99.7	99.3	99.1	99.1

Table 9. Dioxin Emissions/Removal at Skovde Hospital Incinerator
ng/Nm³ (10% CO₂) TCDD Equivalent

	Test 2	Test 4	Test 5
Activated carbon kg/hr	0	2	0.2
Ca(OH) ₂ kg/hr	10	39	60
Tesisorb kg/hr	2.2	10.5	10.0
Inlet TE	5.7	9.2	21.3
Outlet TE	2.5	0.6	0.2
Removal	44%	93.9%	99.1%

The dioxin TCDD equivalents guarantee was 2 ng/Nm³. Chlorobenzenes were reduced in two tests 75% and 94%.

Flakt

One of the first tests of the activated carbon/lime injection systems on an old municipal solid waste incinerator in Geiselbullach, in Bavarian southern Germany, began in January 1989. At this plant two lines process 144 TPD. Used in this system was a reagent consisting of 95-97% lime and 3-5% activated carbon. Since this was one of Flakt's first tests, the incinerator outlet temperature of 200 - 220°C was not lowered, involving a slight risk of auto-ignition (Ref. 2). Three tests for dioxin removal efficiency were conducted during the period the activated carbon system was being evaluated. For all tests inlet values were below 5.0 ng/Nm³ Toxic Equivalents and all outlet values met the 0.1 ng/Nm³ limit. (Ref. 13) Additionally, measurements taken by Prof. Hutzinger through the TUV Bayern showed inlet values of 2.2 ng TE/m³ and outlet values clearly below 0.1 ng TE/m³, demonstrating that Sorbalit, even in high temperatures of 180 to 220°C, could be suitable for removal of dioxin and furan from flue gas. (Ref. 17)

With respect to mercury, in spite of the high temperatures, which occasionally reached 240°C, the mercury emission which had normally been in the vicinity of 0.2 to 0.25 mg/m³, clearly sunk to below 0.1 mg/m³. (Ref. 17)

Another plant which has had success in using the activated carbon scrubber additive, Sorbalit, in 2% proportion to 98% lime, is the municipal waste incinerator Berlin-Ruhleben. This plant has seven lines at 12 tons/hour each, totalling over 2,000 TPD. Each line processes about 50,000 to 60,000 m³/hour of flue gas. In 1988 the plant was retrofitted with a Flakt spray dry absorber and fabric filter to replace the Lurgi Electrofilter. The full-scale test of the efficiency of Sorbalit involved over 40 tests for mercury and five isomer-specific tests for dioxin/furan, using two boilers. (Ref. 28) ITU conducted both the sampling and analysis for the German Environmental Agency (UBA) using the VDI 3499 regulation.

The mercury inlet values (all at 11% O₂, dry) ranged from 165.7 ug/Nm³ to 546.1 ug/Nm³, averaging 339 ug/Nm³ for Boiler 2 and 307 ug/Nm³ for Boiler 3. The outlet values ranged from 31.3 ug/Nm³ to 111.7 ug/Nm³, averaging 75.5 ug/Nm³ for Boiler 2 and 63.7 ug/Nm³ for Boiler 3. Thus, the removal efficiency for mercury in these tests were 78% for Boiler 2 and 79% for Boiler 3. (Ref. 28)

The five dioxin tests at Berlin-Ruhleben, summarized in Table 10, demonstrated consistent achievement of the 0.1 ng/Nm³ limit.

Table 10. Dioxin Emissions and Removal Rate for Berlin-Ruhleben

	5/7/90 boiler 3	5/9/90 boiler 3	5/11/90 boiler 3	5/14/90 boiler 3	5/17/90 boiler 2
Inlet					
Sum PCDD+PCDF	212.56	297.88	1042.41	442.74	214.28
Int. Toxic Eq.	4.82	6.93	23.77	10.01	4.67
Outlet					
Sum PCDD+PCDF	2.29	2.73	5.15	4.54	1.58
Int. Toxic Eq.	0.034	0.044	0.082	0.062	0.022
Removal Efficiency					
Sum PCDD+PCDF	98.92%	99.08%	99.51%	99.98%	99.26%
Int. Toxic Eq.	99.29%	99.36%	99.65%	99.38%	99.53%

Another plant at which Sorbalit is used is the 15,000 TPY SVA Schoneiche special waste incinerator with rotary kiln and secondary combustion chamber, and Flakt spray dry absorber system with fabric filter. This was the first full-scale application of Sorbalit to a special waste incinerator. Sorbalit with 2% activated carbon as well as sodium sulfide has been continuously used since 1989, after the plant began operations and initial tests had showed "increased mercury concentrations and ... indefensible dioxin and furan emissions". (Ref. 26) In order to reduce the risk of auto-ignition of the carbon, the maximum bag filter temperature used is 160°C. (Ref. 2)

An extensive program of measurements was undertaken during the months of March, April, August and September 1989 and January and February of 1990. Though acceptable results were obtained in the first two months, the combustion of automobile shredder waste with a mercury content of up to 61.8 mg/kg caused unacceptably high mercury emissions for the August tests. In addition, the four August tests showed dioxin/furan BGA toxic equivalent emission levels of between 3 and 6 ng/Nm³. As a result, the lime was exchanged for Sorbalit and sodium sulfide, and removal efficiency and emissions improved considerably. By December 1989 a removal efficiency for mercury of more than 90% had been achieved with inlet levels ranging from 175 to 1200 ug/Nm³ (averaging closer to 300 ug) and outlets ranging from less than 5 to 50 ug/Nm³, averaging about 25 ug/Nm³. By January 1990 dioxin/furan BGA toxic equivalent emissions had been reduced by two orders of magnitude to below 0.1 ng/Nm³, with one test at that level and three others below 0.03 ng/Nm³. Total dioxin was below the detection limit and total furan was below 0.025 ng/Nm³. (Ref. 26)

Other plants have been tested with activated carbon injection. These include the Palm Beach and SEMASS RDF incinerators, reported by JOY/NIRO in another paper at this conference, as well as installations by LURGI and Research-Cottrell/Teller to be reported at the 1991 AWMA Meeting in Vancouver.

FINAL STAGE ACTIVATED CARBON BED

Hugo Petersen

To take advantage of the different properties and costs of these two types of activated carbon, one firm, Hugo Petersen of Wiesbaden, Germany, has, during the past seven years, developed and tested a two-stage active coke filter for application on natural gas, fuel oil, and coal-fired plants, municipal solid waste incinerators, hazardous waste incinerators, and sewage sludge boilers. (Ref. 3) The first stage consists of the cheaper furnace coke and serves to extract particulate, oxides of sulfur, sulfuric acid, hydrochloric acids, hydrofluoric acids, dioxins and furans, PAH's, PCB's, mercury, and other heavy metals. The second stage, usually consisting of the more expensive, but more highly catalytic formation coke, serves to reduce nitrous oxide via the injection of ammonia/ammonium hydroxides. The water vapor content of the flue gas does not seem to affect the efficiency of adsorption, since the adsorption of water vapor takes place at temperatures below 80°C. (Ref. 22)

The first tests of the Hugo Petersen activated carbon beds on solid waste incinerators were carried out on two plants in Germany: at Hamburg-Stapelfeld using the catalytic formation coke, and at Duesseldorf-Flingern using hearth-type furnace coke. Both tests indicated similar removal efficiencies for all substances sampled. (Ref. 22)

The tests at Flingern were carried out using a hearth-type furnace coke with basic fixed-bed filters; subsequently, a multi-channel filter with furnace coke was used. According to Bernd Johnke, two coke bed depths were tested: 75 cm and 150 cm. With an inlet TCDD Toxic Equivalent value of 3 ng/Nm³ after a semi-dry scrubber, both carbon beds achieved outlet values of

between 0.02 and 0.06 ng/Nm³ Toxic Eq. (a removal efficiency of 98% to 99.3%). Air volume intakes on the pilot bypass facility were 1600 m³/hour. (Ref. 22)

The tests at Stapelfeld were carried out on a fixed-bed reactor with a volume intake of approximately 100m³/hour with the flue gas at roughly 140°C. The test period was over three months with a total of 1,467 operating hours. The following table shows the PCDD/PCDF removals achieved at Stapelfeld in ng/Nm³ (Ref. 22 - Test 1)(Ref. 3 - Test 2)

Table 11. Dioxin emissions/removal at Stapelfeld

POLLUTANT	INLET	OUTLET	REMOVAL EFFICIENCY
<hr/>			
Test 1			
Sum PCDDs	27.10	< 0.134	99.5%
Sum PCDFs	102.47	< 0.010	99.9%
TCDD Toxic Equivalents (International System)	2.633	<0.0061	99.8%
<hr/>			
Test 2			
Sum PCDDs	51.4	0.091	99.8%
Sum PCDFs	216.4	0.007	100%
<hr/>			

Reductions in PCB concentration was equally impressive with a range of 99.1 to 99.5% removal efficiency over five tests.

With respect to mercury, tests were carried out on Stapelfeld finding inlet values ranging from 61 to 129 ug/Nm³, averaging 83 ug/Nm³, and outlet values ranging from <.4 to 7.1 ug/Nm³, averaging 1.74 ug/Nm³. The removal efficiency ranged from 90 to over 99%, averaging 97.4%. (Ref. 22)

Though the activated carbon bed has been shown to reduce significantly the emissions of dioxin and mercury, it is also capable of reducing nitrous oxide. At the Garath power plant, when ammonia/ammonium hydroxide was added to the activated carbon, NO emissions were reduced by about 50% using hearth-type furnace coke, achieving values of 150-220 mg/Nm³ (171-251 ppm corrected to 7% O₂). Using the more highly catalytic formation coke, emissions were reduced to 100 mg/Nm³ (114 ppm at 7% O₂).

SGP-VA

The Austrian company, Simmering Graz Pauker, has been using back-end activated carbon bed technology for reducing dioxin and furan emissions since 1987, and tests have been conducted on a pilot plant (processing 10,000 to 15,000 Nm³/hr) at the EBS special waste incinerator in Vienna and also at a laboratory scale (200 Nm³/hr). The EBS incinerator was also equipped with an efficient three-stage scrubber.

Test results at the Vienna pilot plant (Ref. 11), operated from January to December 1990, given in original units, are summarized below:

Table 12. Dioxin and Mercury emissions and removal at Vienna

	Inlet	Outlet	Removal
Sum PCDD+PCDF ng/Nm ³	291.645	4.008	98.6%
TCDD International Toxic Eq.	4.2675	0.0530	98.8%
Mercury mg/Nm ³	up to 0.5	0.01 - 0.03	94-98%

Other MSW incineration plants in planning and under construction which employ the SGP-VA activated carbon bed (Ref. 11) include:

o AVR Rotterdam -

6 lines, 155,000 Nm³/hr each, with heat recovery

ESP operating at 170°C

2-stage wet scrubber,

first wet stage for HCl, HF, and heavy metals;

second alkaline stage for SO₂ and HF, operated at 60°C

Activated carbon adsorber - 5 x 15 x 16 meters, for dioxin, and remaining HCl, HF, SO₂, and heavy metals, operated at 110°C

SCR-DeNOx operated at 180°C, followed by

A stack and water treatment plant.

Start-up for first two lines in January, 1992. (Ref. 1)

o Mannheim, Germany - 1 line, 155,000 Nm³/hr, with baghouse, 2-stage wet scrubber, activated carbon adsorber, and SCR-DeNOx. Start-up in 1993.

Other planned installations include activated carbon adsorbers on a new hospital waste incinerator in Dordrecht, Netherlands (start-up August, 1991), a totally reconstructed hospital waste incinerator at the University of Heidelberg (start-up March 1991), and at a special waste incinerator in Rotterdam (start-up December 1991).

CONCLUSIONS

It is clear that use of activated carbon to reduce the emissions of mercury and dioxin/furan as well as other pollutants from MSW and other incinerators is well on its way to becoming a new state-of-the-art. Both the injection and the fixed-bed technologies have provided an additional one to two orders of magnitude of reduction in these emissions above what has already been achieved by using more conventional emission control devices such as wet or dry scrubbers and dust collectors (ESPs and fabric filters). In addition, both technologies have achieved emissions levels considerably lower than the new U.S. standard for dioxin using a variety of existing emission control configurations.

Table 13 summarizes the lowest achieved emissions from the 12 activated carbon-equipped plants/pilots/units for which data was available. The table

Table 13. A PARTIAL LISTING OF MERCURY AND DIOXIN REMOVAL AT INCINERATORS USING ACTIVATED CARBON TECHNOLOGIES WITH REFERENCE NATIONAL STANDARDS

Plant/Country	Year	Mercury emissions ug/Nm ³	Dioxin Emissions ng/Nm ³
EMISSION STANDARDS		Total	Toxic Equiv.
Netherlands		50	0.1
Austria		50	0.1
Denmark			0.1
Germany		50	0.1
Sweden			0.1
U.S.		30	

ACTIVATED CARBON INJECTION INSTALLATIONS (lowest reported values)

Zurich, Switz pilot ¹	1987		5.0	0.08
Zurich, Switz retrofit ^{2,14}	1987	31	5.0	0.09
Amager, Denmark ^{3,15}	1988	5	0.4	<0.002
Kassel, Germany ^{5,6}	1987	19	7.0	0.07
Skovde, Sweden ^{7,8,16}			4.5	0.2
Geiselbullach, Germany ⁹	1989	<100		<0.1
Berlin-Ruhleben Unit 2	1990	41.1	1.58	0.022
Berlin-Ruhleben Unit 3 ¹²	1990	31.3	2.29	0.034
Schoneiche, Germany ¹⁰	1989	5		0.03

FIXED BED ACTIVATED CARBON INSTALLATIONS (lowest reported values)

Flingern, Germany			0.02
Stapelfeld, Germany ¹¹	1987	<0.4	<0.144
Stapelfeld, Germany			0.098
Vienna-EBS	1990	0.01	4.008

Notes:

- | | mercury test | dioxin test |
|---|-----------------|---|
| 1. Outlet temp: 120°C | Injection rate: | 0.75 gr/acf |
| 2. Outlet temp: 120°C | Injection rate: | 30 mg/Nm ³ 59 mg/Nm ³ |
| 3. Outlet temp: 127°C | Injection rate: | 70 mg/Nm ³ 19 mg/Nm ³ |
| 5. Outlet temp: 137°C | Injection rate: | 47 mg/Nm ³ |
| 6. Outlet temp: 135°C | Injection rate: | 105 mg/Nm ³ |
| 7. Outlet temp: 140°C | Injection rate: | n.a. |
| 8. Outlet temp: 136°C | Injection rate: | 0.2 kg/hr |
| 9. Outlet temp: 220°C | | |
| 10. Outlet temp: 160°C | | |
| 11. Outlet temp: 140°C | | |
| 12. All four dioxin tests on this unit were at or below .082 ng/Nm ³ TE and 5.15 ng/Nm ³ PCDD + PCDF; | | |
| 11 mercury tests fell at or below 50 ug/Nm ³ . | | |
| 13. All four mercury tests were at or below 25 ug/Nm ³ with three below 10 ug/Nm ³ | | |
| 14. Three other mercury tests at this condition met the 50 ug/Nm ³ standard. | | |
| 15. The two mercury tests at this condition were 5 and 6 ug/Nm ³ ; all seven dioxin tests using activated carbon were at 0.05 ng/Nm ³ TE or less and at 3.2 ng/Nm ³ or less for PCDD + PCDF. | | |

indicates the outlet flue gas temperature and the amount of activated carbon required to achieve these values. Generally, outlet temperatures were in the 120 to 140°C range. All mercury emission values are below the current European standard of 50 ug/Nm³ and all but one were below the 0.1 ng/Nm³ standard for TCDD Toxic Equivalents. Though these figures are the lowest values reported in a series of tests, many other samples also met the current limits as indicated in the notes for Table 13.

Is activated carbon technology the wave of the future for minimizing MSW incinerator emissions? It certainly appears to be the case for Europe. However, for the United States, since the regulatory authorities are generally not requiring nearly as stringent emission limits for new or existing plants as their counterparts Europe, there is less impetus for vendors to design plants to achieve the lower emission rates that are being demonstrated over the past few years in Europe. Therefore, it may be some time before those who purchase incinerators in this country become aware of and create a widespread demand for these new technologies.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

ACKNOWLEDGEMENTS

I am appreciative of several people who went out of their way to provide me with hard-to-find information: Barbara Zeschmer-Lahl, Bernd Franke, Michael Wilken, Bernd Johnke, Bert Brown, E. Holzerbauer, Kurt Carlsson, Walter Panknin, Aaron Teller, Mike Johnston, David Minott, David Hoecke, and Justus Engelfried.

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EMISSIONS CONTROL OF POLYCHLORINATED DIBENZO-P-DIOXINS AND
POLYCHLORINATED DIBENZOFURANS AT MUNICIPAL WASTE COMBUSTORS

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ABSTRACT

This paper gives the results of an analysis of available emission data of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/PCDF) from municipal waste combustors (MWCs) to evaluate the effectiveness of various air pollution control devices on PCDD/PCDF removal. The effects of flue gas temperature, recycling fabric filter ash, and process additives such as ammonia and Tesisorb™ powder were also analyzed.

The analysis shows that MWCs equipped with a spray dryer followed by fabric filters can achieve PCDD/PCDF removal efficiencies (REs) of 97% and higher. A RE of 94% has been achieved at a combustor equipped with a Thermal DeNO_x system followed by a spray dryer and fabric filters. MWCs equipped with a duct sorbent injection system followed by fabric filters can potentially achieve a RE of 99%. A combustor equipped with a spray dryer followed by electrostatic precipitators (ESPs) has achieved a RE of 64%. Neither a duct sorbent injection system followed by ESPs nor a furnace sorbent injection system followed by ESPs could effectively remove PCDD/PCDF. PCDD/PCDF were not effectively removed from MWCs equipped with ESPs as the only devices to control air pollution.

This paper has been reviewed by the Air and Energy Engineering Research Laboratory, U.S. Environmental Protection Agency, and approved for presentation. The contents of this article should not be construed to represent Agency policy nor does mention of trade names or commercial products constitute endorsement or recommendation for use by the Agency.

For presentation at the Second International Conference on
Municipal Waste Combustion in Tampa, FL, April 15-19, 1991.

INTRODUCTION

Due to the increasing costs and complexities of landfilling operations, disposal of municipal solid waste (MSW) through combustion has gained increasing popularity. However, toxic air pollutants such as polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) have been detected at almost every municipal waste combustor (MWC).⁽¹⁻³⁾ Emissions of these pollutants into the atmosphere have caused serious concerns over possible adverse impacts on the environment and human health. Municipalities across the U.S. have encountered strong resistance in the form of NOT-IN-MY-BACKYARD attitudes from residents living in the neighborhood of the potential sites, despite the fact that more MSW is generated and less landfill space is available for disposal.

Currently, no system has been developed solely for the purpose of controlling the emissions of PCDD/PCDF from MWCs. The present practice to control their emissions is in conjunction with the control of particulate matter (PM) and acid gases. To control PM emissions, electrostatic precipitators (ESPs) and fabric filters (FFs) are commonly used. At three facilities, Tesisorb* powder was injected into the flue gas to condition the filter cake and to reduce the pressure drop across the FF. To control the emissions of acid gases (HCl and SO₂), lime-based sorbents are utilized in three different technologies: furnace sorbent injection (FSI), duct sorbent injection (DSI), and spray dryer (SD) absorption. To control the emissions of nitrogen oxides (NO_x), Exxon's Thermal DeNO_x process is installed in three MWCs in California. Ammonia (NH₃) was injected into the upper section of the combustor and reacted with NO_x to form nitrogen (N₂) and water.

This paper gives the results of an analysis of available PCDD/PCDF emissions field test data from three types of MWCs including mass burn (MB), modular (excess-air and starved-air), and refuse-derived fuel (RDF). The main purpose is to see how various air pollution control devices (APCDs) and their operating conditions affect the control of PCDD/PCDF emitted from MWCs. The effect of temperature and the impact of adding Tesisorb powder or NH₃ on controlling PCDD/PCDF emissions will be examined. The influence of recycling FF ash into the flue gas on PCDD/PCDF emissions control will also be analyzed.

* Tesisorb is a trade mark of R-C Environmental Services and Technologies.

EMISSION DATA SOURCES

The PCDD/PCDF emissions data collected for this work were taken from reports published by the U.S. Environmental Protection Agency⁽¹⁻³⁾ and Environment Canada.⁽⁴⁾ Two phrases, "uncontrolled emission" and "controlled emission" are constantly used throughout the text. The uncontrolled emission is the amount of PCDD/PCDF measured before the APCDs. The controlled emission is the amount of PCDD/PCDF measured after the APCDs. Unless otherwise specified, the emissions are presented in nanograms per dry, standard cubic meter (ng/dscm) of flue gas and normalized to 7% O₂.

UNCONTROLLED PCDD/PCDF EMISSIONS

The typical levels of uncontrolled PCDD/PCDF emissions from MWCs of different types and capacities are summarized in Table 1.⁽⁵⁾ The overall capacities for the large, mid-size, and small MWC plants are greater than 600 tons per day (tpd), between 200 and 600 tpd, and less than 200 tpd, respectively.⁽⁶⁾ For mass burn refractory combustors, typical uncontrolled PCDD/PCDF emissions are 4,000 ng/dscm. At large mass burn waterwall combustors, typical emissions are 500 ng/dscm. Mid-size mass burn waterwall and modular excess air combustors have typical uncontrolled emissions of 200 ng/dscm. The typical emissions from three types of combustors, small mass burn waterwall, RDF, and mass burn rotary waterwall, are 2,000 ng/dscm. Typical emissions at modular starved air combustors are 400 ng/dscm.

RESULTS AND DISCUSSION

EFFECTIVENESS OF SD/FF

The effectiveness of the APCD consisting of a spray dryer followed by fabric filters (SD/FF) on PCDD/PCDF removal can be seen from the data in Table 2. Tests were conducted at the following facilities, Biddeford (in Biddeford, ME), Mid-Connecticut (in Hartford, CT), Quebec City (in Quebec, Canada), and Marion County (in Marion, OR). Combustors at the first two facilities were fired with RDF. The Quebec City data were generated from the pilot plant tests conducted at its Unit No. 3 combustor which was a mass burn unit with waterwall. The Marion County combustors are mass burn units with waterwall. The results in Table 2 show that the calculated REs are higher than 95%, regardless of the differences in mechanical designs of these combustors. Also included in this table are the data from the Penobscot facility (in Orrington, ME) where the combustors burned RDF and were equipped with waterwall, although the uncontrolled emissions were not available and the RE could not be calculated.

EFFECTIVENESS OF THERMAL DENO_x SYSTEM

Exxon's NH, based Thermal DeNO_x process has been installed at three California facilities: Commerce (in Commerce), Stanislaus

County (in Crows Landing), and Long Beach (in Long Beach). These MWCs are equipped with SD/FF to control acid gases and PM emissions. The PCDD/PCDF emissions from these facilities are shown in Table 3. At the Commerce MWC, the RE is 87.7% for the tests conducted in 1987 when the combustor burned residential refuse. The RE is 94.5% for the tests conducted in 1988 when the combustor burned commercial and residential wastes. The RE is 99.6% for the tests conducted in 1988 when the combustor burned commercial refuse. The uncontrolled emissions were not reported from MWCs at the last two locations and the REs cannot be calculated. Comparison of the overall data in Table 3 with those in Table 2 indicates that the installation of the Thermal DeNO_x system followed by the SD/FF does not appear to affect the control of PCDD/PCDF emissions.

EFFECTIVENESS OF DSİ/FF

Several MWCs employed a duct sorbent injection system followed by fabric filters (DSI/FF) to control air pollution. The PCDD/PCDF emissions data from such MWCs are shown in Table 4. The effectiveness can only be seen by the pilot plant tests conducted at Quebec City No. 3 combustor, because no uncontrolled emissions were reported from other MWCs. During the pilot plant tests, the temperature of the flue gas entering the FF was changed from about 204 to 111°C. The results shown in Table 4 indicate that almost all of the PCDD/PCDF were removed.

EFFECTIVENESS OF SD/ESP

The effectiveness of APCD consisting of a spray dryer followed by electrostatic precipitators (SD/ESPs) can be seen from the data obtained from the tests conducted at Unit No. 2 combustor at Millbury, MA. The emission data are shown in Table 5. The RE is 64.3%. The performance of the SD/ESP at the Portland facility (in Portland, ME) cannot be calculated because uncontrolled emissions were not reported. Comparison of the data in Table 5 with those in Table 2 indicates that the SD/ESP system is much less effective at controlling PCDD/PCDF emissions than the SD/FF system.

EFFECTIVENESS OF DSİ/ESP

The effectiveness of APCD consisting of a duct sorbent injection system followed by electrostatic precipitators (DSI/ESPs) can be seen from the test data obtained at Dayton Unit No. 3 combustor in Dayton, OH. The results listed in Table 6 show that the controlled emissions are higher than the uncontrolled emissions, indicating that such a system cannot remove PCDD/PCDF. However, it has to be noted that the uncontrolled emissions are very low as compared to all the data presented earlier. Furthermore, comparison of the data in Table 6 with those in Table 3 indicates that DSİ/ESP is much less effective than DSİ/FF to control PCDD/PCDF emissions.

EFFECTIVENESS OF FSI/ESP

The effectiveness of the APCD consisting of a furnace sorbent injection system followed by electrostatic precipitators (FSI/ESPs) can also be seen from the results of tests conducted at the Dayton Unit No. 3 combustor. The data are shown in Table 7. Three tests were conducted at a flue gas temperature of about 201°C (measured at the inlet of the ESPs) and another three tests were at 148°C. The lower flue gas temperature was achieved by spraying water into the duct. The test results show that at both temperatures more PCDD/PCDF are generated after the flue gas passed through ESPs, an indication that such an APCD cannot remove PCDD/PCDF. Also listed in Table 7 are the data reported by the combustor located in Alexandria, VA, where no uncontrolled emissions were reported and the effectiveness of the APCD cannot be calculated.

EFFECTIVENESS OF ESP

The effectiveness of ESPs alone to control PCDD/PCDF emissions can be seen from the data listed in Table 8. These data were reported by the following facilities: Dayton Unit No. 3, Peekskill (in Peekskill, NY), North Andover (in North Andover, MA), Oswego County (in Fulton, NY), and Pinellas County (in St. Petersburg, FL). With the exception of the tests conducted at the Peekskill facility, all other test data show that more PCDD/PCDF have been generated as the flue gas passed the ESPs, indicating that the ESPs installed at these MWCs cannot remove PCDD/PCDF. The Peekskill data indicate that the average RE is about 46.9%.

Although ESP is the most popular APCD installed in the MWCs, most of the units reported only the controlled emissions. This is especially true for the older units. The following facilities did not report the uncontrolled emissions: Pigeon Point (in Pigeon Point, DE), Lawrence (in Lawrence, MA), Oneida County (in Rome, NY), Pope/Douglas (in Alexandria, MN), Quebec City Unit No. 3 (pilot plant tests), Red Wing (in Red Wing, MN), Tulsa (in Tulsa, OK), Akron (in Akron, OH), Albany (in Albany, NY), Hampton (in Hampton, VA), Chicago-NW (in Chicago, IL), Hamilton-Wentworth (in Hamilton, Toronto, Canada), Niagara Falls (in Niagara Falls, NY), Philadelphia-NW (in Philadelphia, PA), and Saugus (in Saugus, MA). The effectiveness of ESPs cannot be evaluated from these MWCs.

EFFECT OF RECYCLING FF ASH

FF ash was recycled into the SD during the pilot plant tests conducted at Quebec City No. 3 combustor. The effect on PCDD/PCDF emissions can be seen from the emission test data shown in Table 9. The flue gas temperatures are almost the same, at around 140°C. With ash recycling, the two-run averaged uncontrolled emission is 2,157 ng/dscm and the RE is 99.9%. Without ash recycling, the two-run averaged uncontrolled emission is 1,764 ng/dscm and the controlled emissions are below the detection limit, giving a RE of 100%. These results indicate that practically no apparent effect is observed when FF ash was recycled.

EFFECT OF TESISORB POWDER

Tesisorb powder was injected in the flue gas stream at the Marion County, Commerce, and Dutchess County (in Poughkeepsie, NY) facilities. The original intention of using this material was to condition the filter cakes and to reduce the pressure drops across the filter bags so that the bags did not require as frequent cleaning. All the MWCs are mass burn units. The corresponding APCDs installed in the combustors are SD/FF, Thermal DeNO_x/SD/FF, and DSI/FF.

Listed in Table 10 are the test results from the above facilities. These data indicate that, on the average, REs of 97.5 and 94% are achieved at the Marion County and the Commerce facilities, respectively. No uncontrolled emissions were reported from the Dutchess County facility, and the RE cannot be calculated. Comparison of the data in Table 10 with those in Tables 2 and 3 indicates that the addition of Tesisorb powder into the flue gas transport duct does not affect the removal of PCDD/PCDF.

EFFECT OF FLUE GAS TEMPERATURE

The effect of flue gas temperature on PCDD/PCDF removal can be seen from the test data summarized in Table 11 which includes the data from two MWCs, one from the pilot plant tests conducted at Quebec City Unit No. 3 and the other from Dayton Unit No. 3. At the former facility, the pilot plant was equipped with DSI/FF to control acid gases and PM emissions. The pilot plant test results indicate that the uncontrolled PCDD/PCDF emissions were lowered to 887 ng/dscm when the flue gas temperature at the inlet of the FF was 111°C, the lowest temperature tested. The uncontrolled emissions are 2 or 3 times higher at other test temperatures, 204, 141, and 121°C. The flue gas temperature was reduced by spraying water into the mixing chamber between the combustor and the pilot plant APCD.

The Dayton No. 3 combustor was equipped with FSI/ESP to control acid gases and PM emissions. The uncontrolled PCDD/PCDF emissions are 38.1 and 14.2 ng/dscm when the flue gas temperatures at the inlet of the ESPs were at 201 and 148°C, respectively. The flue gas temperature was reduced by spraying water into the flue gas. The results indicate that, as the flue gas cools in the transport duct, the uncontrolled PCDD/PCDF emissions decrease.

At this Dayton combustor, the PCDD/PCDF emissions were also measured without injecting sorbent into the flue gas duct. In this case, only ESPs were used to control air pollution. The data were taken while the flue gas temperatures at the inlet of the ESPs were 299, 278, and 202°C. The corresponding uncontrolled emissions decreased from 252, to 214, and to 32.8 ng/dscm.

The above results indicate that the uncontrolled PCDD/PCDF emissions can be reduced if the flue gas temperature is lowered.

CONCLUSIONS

Available emission data of PCDD/PCDF from MWCs were analyzed to see how APCDs and their operating conditions affect the removal of PCDD/PCDF.

The analysis shows that the PCDD/PCDF REs are 97% or higher for the tests conducted at the Biddeford, Mid-Connecticut, and Marion County facilities. These combustors are equipped with a SD/FF. A RE of 94% has been achieved at the Commerce combustor equipped with a Thermal DeNO_x/SD/FF system. MWCs equipped with a DSI/FF system can potentially achieve a RE of 99%, as suggested from the pilot plant test data obtained at Quebec City No. 3 combustor. A RE of 64% has been reported at the Millbury No. 2 combustor equipped with a SD/ESP system. Data obtained from tests conducted at Dayton No. 3 combustor, utilizing either a DSI/ESP or a FSI/ESP system, indicate that neither of these two control techniques can remove PCDD/PCDF. PCDD/PCDF were not removed, in general, from MWCs equipped with ESPs alone to control air pollution.

Recycling of FF ash to the SD, or addition of NH₃ or Tesisorb powder to the flue gas did not have an apparent effect on PCDD/PCDF removal. An important parameter to control PCDD/PCDF emissions is the flue gas temperature through the APCDs. Field test data indicate that the uncontrolled emissions could be reduced if the flue gas temperature entering the PM control devices (FF and ESP) was lowered.

Many MWCs did not report or were not required to report the uncontrolled emissions, and the RE could not be calculated. The analysis is based on a rather limited amount of data, and the conclusions stated above should not be deemed final. More data and tests are needed to see whether the above conclusions can be generalized to any MWCs in the U.S.

GLOSSARIES

APCD	air pollution control device
DSI	duct sorbent injection
DSI/ESP	duct sorbent injection followed by electrostatic precipitator
DSI/FF	duct sorbent injection followed by fabric filter
ESP	electrostatic precipitator
FF	fabric filter
FSI	furnace sorbent injection

FSI/ESP furnace sorbent injection followed by electrostatic precipitator
MB mass burn
MB/R mass burn refractory
MB/RWW mass burn rotary waterwall
MB/WW mass burn waterwall
MEA modular excess-air
MSA modular starved-air
MSW municipal solid waste
MWC municipal waste combustor
PCDD polychlorinated dibenzo-p-dioxin
PCDF polychlorinated dibenzofuran
PM particulate matter
RDF refuse-derived fuel
RE removal efficiency
SD spray dryer
SD/ESP spray dryer followed by electrostatic precipitator
SD/FF spray dryer follower by fabric filter

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Table 1. Typical Uncontrolled PCDD/PCDF Emissions⁽⁵⁾

Combustor Type	Emission ^(a) (ng/dscm at 7% O ₂)
Mass burn refractory (MB/R)	4,000
Large mass burn waterwall (MB/WW)	500
Mid-size mass burn waterwall Modular excess air (MEA)	200
Small mass burn waterwall Refused-derived fuel (RDF) Mass burn rotary waterwall (MB/RWW)	2,000
Modular starved air (MSA)	400

Note: ^(a) All concentrations reflect the sum of the tetra-through octa-chlorinated PCDD/PCDF homologues only.

Table 2. PCDD/PCDF Emissions From MWCs Equipped With SD/FF.^(3,4)

Location of MWCs (type/design)	FF Temperature (°C)	Inlet Temperature (°C)	Uncontrolled Emission (ng/dscm)	Controlled Emission (ng/dscm)	PCDD/PCDF RE (%)
Biddeford (RDF)		137	903	4.38	99.5
Mid-Connecticut (RDF)		133	1,019	0.66	99.9
Quebec City Unit No. 3 (MB/WW) pilot plant tests with FF ash recycled		140	2,157	1.26	99.9
pilot plant tests without FF ash recycled		139	1,764	ND ^(a)	100.0
Marion County (MB/WW)		133	43.0	1.26	95.7
Penobscot (RDF/WW)		146 ^(b)		2.39	

Note: (a) ND = not detected (below the detection limit).

(b) Value estimated from other tests.

Table 3. PCDD/PCDF Emissions From MWCs With Thermal DeNO_x/SD/FF.⁽³⁾

Location of MWCs (type/design)	FF Inlet Temperature (°C)	Uncontrolled Emission (ng/dscm)	Controlled Emission (ng/dscm)	PCDD/PCDF RE (%)
Commerce (MB/WW) 1987 tests, combustor burning residential refuse	135	28.1	3.47	87.7
1988 tests, combustor burning commercial and residential refuse	NR ^(a)	446	9.59	94.5
1988 tests, combustor burning commercial refuse	NR ^(a)	783	2.78	99.6
Stanislaus County (MB/WW) Unit No. 1.	145		6.25	
Unit No. 2.	146		6.53	
Long Beach (MB/WW)	152 ^(b)		4.14	

Note: ^(a) NR = not reported.

^(b) Value estimated from other tests.

Table 4. PCDD/PCDF Emissions From MWCs Equipped With DSI/FF.^(3,4)

Location of MWCs (type/design)	FF Inlet Temperature (°C)	Uncontrolled Emission (ng/dscm)	Controlled RE (%)	PCDD/PCDF
Quebec City No. 3 (MB/WW) (pilot plant tests)	204 141 121 111	1,597 2,277 2,361 887	7.35 0.49 ND ^(a) 2.43	99.55 99.98 100.00 99.75
Claremont (MB/WW) Unit No. 1 Unit No. 2	225 ^(b) 245 ^(b)		37.60 32.30	
Dutchess County (MB/RWW) Unit No. 1 Unit No. 2	192 ^(b) 197 ^(b)		4.83 17.90	
St. Croix (MEA)	105 ^(b)		7.73	
Wurzburg (MB/WW)	190		40.40	

Note: (a) ND = not detected (below the detection limit).

(b) Value estimated from other tests.

Table 5. PCDD/PCDF Emissions From MWCs Equipped With SD/ESP.⁽³⁾

Location of MWCs (type/design)	FF Inlet Temperature (°C)	Uncontrolled Emission (ng/dscm)	Controlled Emission (ng/dscm)	PCDD/PCDF RE (%)
Millbury Unit No. 2 (MB/WW)	123	170	59.2	64.3
Portland (MB/WW)	141		173	

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Table 6. PCDD/PCDF Emissions From MWCs Equipped With DSI/ESP.⁽³⁾

Location of MWCs (type/design)	FF Inlet Temperature (°C)	Uncontrolled Emission (ng/dscm)	Controlled Emission (ng/dscm)	PCDD/PCDF RE (%)
Dayton Unit No. 3 (MB/R)	152	5.31	57.2	-6,360

Table 7. PCDD/PCDF Emissions From MWCs Equipped With FSI/ESP.⁽³⁾

Location of MWCs (type/design)	FF Inlet Temperature (°C)	Uncontrolled Emission (ng/dscm)	Controlled Emission (ng/dscm)	PCDD/PCDF RE (%)
Dayton Unit No. 3 (MB/R)	201	38.1	1,481	-4,182
	148	14.2	659	-6,490
Alexandria (MB/WW)	183 ^(a)		54.86	

Note: ^(a) Value estimated from other tests.

Table 8. PCDD/PCDF Emissions From MWCs Equipped Only With ESP.⁽³⁾

Location of MWCs (type/design)	FF Temperature (°C)	Inlet Temperature (°C)	Uncontrolled Emission (ng/dscm)	Controlled Emission (ng/dscm)	PCDD/PCDF RE (%)
Dayton Unit No. 3 (MB/R)	299 278 202	252 214 32.8	17,100 14,500 866	-	-9,140 -6,990 -2,640
Peekskill (MB/WW)					
Apr/1985 tests, combustor=normal	237 ^(a)	NR ^(b)	107.3		
Nov/1985 tests, combustor=start-up	215	11,432	9,570		15.4
Nov/1985 tests, start of campaign, combustor=normal load	229	478	263		44.5
Nov/1985 tests, end of campaign, combustor=normal load	244	617	179		69.0
Nov/1985 tests, combustor=high load	234	438	126		71.7
Nov/1985 tests, combustor=low load	225	228	148		34.1
North Andover (MB/WW)	313	245	362		-43.1
Oswego County (MSA)					
combustor=normal, start of campaign	257	175	353		-118.0
combustor at mid-range temp., 954°C	251	195	301		-53.4
combustor = normal, end of campaign low combustor temp., 899°C	255 242	359 732	412 819		-30.9 -12.0
Pinellas County (MB/WW)	281	54	100		-95.0

Note: (a) Value estimated from other tests.

(b) NR = not reported.

Table 9. Effect Of Recycling FF Ash.⁽⁴⁾

Location of MWCs (type/design)	FF Inlet Temperature (°C)	Uncontrolled Emission (ng/dscm)	Controlled Emission (ng/dscm)	PCDD/PCDF RE (%)
Quebec City Unit No. 3(MB/WW)				
with FF ash recycled	140	2,157	1.26	99.9
without FF ash recycled	139	1,764	ND ^(a)	100.0

Note: ^(a) ND = not detected (below the detection limit).

Table 10. PCDD/PCDF Emissions From MWCs With Tesisorb Powder Injection.⁽³⁾

Location of MWCs (type/design)	FF Inlet Temperature (°C)	Uncontrolled Emission (ng/dscm)	Controlled Emission (ng/dscm)	PCDD/PCDF RE (%)
Marion County (MB/WW) equipped with SD/FF				
combustor = normal	133	43.0	1.26	95.7
combustor = shut down	145	61.6	1.91	97.4
combustor = start up	149	435	3.36	99.5
Commerce (MB/WW) equipped with Thermal DeNO _x /SD/FF				
1987 tests, combustor burning residential refuse	135	28.1	3.47	87.7
1988 tests, combustor burning commercial and residential refuse	NR ^(a)	446	9.59	94.5
1988 tests, combustor burning commercial refuse	NR ^(a)	783	2.78	99.6
Dutchess County (MB/RWW) equipped with DSI/FF				
Unit No. 1	192 ^(b)		4.83	
Unit No. 2	197 ^(b)		17.90	

Note: (a) NR = not reported.

(b) Value estimated from other tests.

Table 11. Effect Of Flue Gas Temperature.^(3,4)

Location of MWCs (type/design)	FF Temperature (°C)	Inlet Uncontrolled Emission (ng/dscm)	Controlled Emission (ng/dscm)	PCDD/PCDF RE (%)
Quebec City Unit No. 3 (MB/WW)				
pilot plant equipped with DSI/FF	204	1,597	7.35	99.55
	141	2,277	0.49	99.98
	121	2,361	ND ^(a)	100
	111	887	2.43	99.75
Dayton Unit No. 3 (MB/R)				
with FSI/ESP	201	38.1	1,481	-4,182
	148	14.2	659	-6,490
with ESP	299	252	17,100	-9,140
	278	214	14,500	-6,990
	202	32.8	866	-2,640

Note: (a) ND = not detected (below the detection limit).

DESIGN AND OPERATION OF PULSE-JET FABRIC FILTERS
FOR INCINERATION AIR POLLUTION CONTROL

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MIKROPUL ENVIRONMENTAL SYSTEMS

ABSTRACT

Pulse-jet fabric filters have gained acceptance as a viable control method for air emissions from incineration. A pulse jet can capture fine particulate emissions with far less energy expenditure than a wet scrubber. Their initial cost is also less than electrostatic precipitators. With the addition of sorbent chemicals injected upstream of the pulse-jet, these fabric filters can also achieve compliance with regulations governing gaseous emissions. Pulse-jets have been used on a wide variety of incineration applications, including infectious hospital waste, low level radioactive waste, various hazardous materials, and simple volume reduction of bulk waste.

However, incineration is a vigorous application for pulse-jets or any fabric filter. The aggressive and corrosive gas stream created by incineration can easily attack the pulse-jet components. Operation of incinerators and their pollution control devices, including pulse-jets, is often less than what is considered acceptable practice. Also, selection of pulse-jets and their components for incinerator off-gas filtration is frequently done on the basis of lowest initial cost. These combined factors have resulted in reduced pulse-jet and pulse-jet component service life and repeated incidents of non-compliance with air emission rules.

To insure adequate service life and to maintain emissions at a compliance level, it is important that a pulse-jet fabric filter be designed, equipped and operated with the unique conditions imposed by incineration kept in mind. Selection of materials of construction for this fabric filter and its components must be based on worst case scenarios. Still, the cost of such materials should be reasonable. Design and sizing of a pulse-jet must recognize the wide variety of conditions a single incinerator both "sees" and, in turn, creates. Changes in feed stock quantity and type are two main reasons for these wide variety of conditions, frequent down-time on the incinerator is another reason. Shut-down and start-up of the incinerator lead to more problems with a pulse-jet filter than on-line operation.

The paper will review the various options one has in pulse-jet design, filter media selection, and choice of materials of construction. Recommendations will be made on which of these are most appropriate for various incinerator applications. New

technology, which has only recently been utilized in incinerator pulse-jet filters, will be highlighted. Guidelines for correct operation of both the pulse-jet and the incinerator will also be offered.

INTRODUCTION

Pulse-jet fabric filters (or baghouses) are being successfully utilized as the control technology for incinerator emissions for a broad range of applications. Municipal, industrial, hospital, hazardous, and even radioactive waste incineration emission can be effectively and efficiently collected using pulse-jet (and other) fabric filters. Their inherent design flexibility, their excellent particulate capture and their relatively low capital and energy costs have recently resulted in the selection of pulse-jets over the more traditional incinerator emission controls, i.e. electrostatic precipitators and wet scrubbers. With the addition of absorbents, such as lime or sodium bicarbonate, injected upstream of the fabric filter, acid gases produced by incineration can also be controlled. Various studies, conducted in both Europe and North America, have shown that even organic and heavy metal toxics, either formed or liberated by incineration, can be effectively captured with pulse-jet filters.

There is no question that when compared with the pulse-jet fabric filter, other technologies do have some advantages. Control systems with electrostatic precipitators certainly consume less electrical power than fabric filters and are more tolerant of gas temperature excursions. Though not exempt from maintenance, (including extensive replacement of internal parts), the precipitator is also generally considered to require less cost for this category than fabric filters. Regular replacement of filters is required by pulse-jets and other fabric filters.

Wet scrubbers are more effective in controlling acid gases than absorbent addition systems employing pulse-jet or other baghouses. Scrubbers can have a substantial initial cost advantage, too. They also enjoy an artificial advantage in the way the liquid waste stream is viewed. Often this scrubber waste blowdown can be discharged directly to a municipal sewer. Dry waste, whether from a fabric filter or a precipitator, containing the same type and amount of contaminants as the liquid stream, must usually be handled as a special or even hazardous waste. This might change, of course.

Yet fabric filters, and particularly pulse-jet baghouses, are being chosen as the control technology for many incinerator installations. The primary reason for their acceptance is their ability to capture particulate, even low and sub-micron particles, efficiently and at a relatively low cost, both in capital and operating expenses. Whether a particulate liberated during incineration, a acid gas molecule or a heavy metal condensate, pulse-jets (and other fabric filters) can capture these emissions.

However, to achieve this potential for high capture efficiency and to maintain it, the selection, design, fabrication, installation and operation of a pulse-jet fabric filter must all be done carefully. Failure to do so can lead to excess emissions, high operating expense and significantly hinder operation of the whole incineration system. The purpose of this paper is to prevent these from occurring. By offering the design and operational guidelines listed below, it is the author's hope that future pulse jet filter incinerator emission control systems will be a success.

DISCUSSION

The focus of this paper will be pulse-jet dust collectors. In general, the guidelines given will also apply to other fabric filters, i.e. shakers or reverse-gas dust collectors. Pulse-jets are used more often than the other fabric filters for control of incinerator emissions since they are more economical, particularly for lower gas volumes.

Figure 1 is an artist's cross-sectional view of a pulse-jet dust collector (MikroPul's design). Some license has been taken to show all components. Different manufacturer's use differing designs but the basic principles are common. "Dirty" gas is passed through the collector's filter elements and the particulate entrained in the gas is captured by the fibrous filter media. The "cleaned" gas then passes through the collector. The filter elements require support, e.g. a wire cage, to prevent collapse from the pressure differential across these filters.

As the captured particulate matter increases on the surface of these filter elements, the pressure differential increases. To prevent it from becoming excessive, some of the particulate must be removed from the filters. This is accomplished by compressed air pulse cleaning. A certain percentage of the filter's have compressed air rapidly injected into their hollow center. This produces a pressurized volume inside of the filter element, at a pressure greater than the pressure differential occurring

previously. This reverse differential produces rapid flexing of the filter fabric and a reverse flow of air through the fabric. The combination of flexing and reverse flow dislodges the majority of the accumulated particulate and this particulate or dust falls into a collection hopper positioned beneath the filter elements. Gravity is relied upon to remove the dust from this hopper, through a rotary valve or other device that provides a gas seal, thus minimizing gas leakage in the dust removal process.

The pulse cleaning is repeated at regular intervals or on a demand basis, determined by the level or the rate of rise of the pressure drop across the filters. In either case, all filters will be cleaned repeatedly.

Pulse-jets are utilized in various configurations for incinerator emission control. The simplest is a stand alone system where the pulse-jet is essentially the only control device. This configuration is typically used for simple volume reduction of waste, usually by industrial users who are discarding packaging materials. Plastics are not supposed to be incinerated in such a system, though inevitably some are. The gas temperature must be reduced prior to entering the pulse-jet filter. With these simple systems this is usually accomplished by passing the incinerator exhaust gas through a waste heat recovery boiler or similar heat exchanger or by simply diluting the gas with ambient air.

A more refined approach and one capable of collecting acid gases is injection of absorbent chemical, e.g. hydrated lime, into the incinerator exhaust stream prior to the pulse jet. The use of temperature controlling equipment, such as a heat recovery system, and the addition of moisture to the gas stream, which reduces temperature further, will allow the pulse-jet collector control system to achieve removal efficiencies of over 90% for HCl gas. This has been demonstrated. SO₂ removal with such a system is less efficient, normally in the 60-70% range, though better results have been reported. See Figure 2.

The use of a spray dryer absorber prior to the pulse-jet filter is a more rigorous approach than dry absorbent injection. Such systems require slurry preparation systems in addition to the spray dryer. They are significantly more expensive than dry injection systems, but may be more effective in acid gas removal. In large incinerator control systems, where absorbent chemical costs can be significant, the better utilization of the absorbent by such systems can justify the added expense. See Figure 3.

A hybrid system that is gaining popularity is the combined dry filter/wet scrubber concept. Utilizing the fine particulate

control provided by a pulse-jet filter and the excellent acid gas removal efficiency of the wet scrubber, these systems provide excellent capture efficiencies for dry particulate, heavy metals and most organics. Since particulate loading to the scrubber is minimal, low pressure drop packed or spray towers can be used, keeping energy costs low. See Figure 4.

The key to all these systems is the pulse-jet filter. In order for the control system to work effectively and, hence, for the total incinerator system to work well, the dust collector must be operating correctly with a minimum of downtime. To achieve this, the pulse-jet must be designed and operated with the unique demands of incineration in mind.

Incineration is a rigorous application for pulse-jet filters. Wide swings in gas volume, temperature and moisture content, frequent downtime, variation in particulate character, changes in acid gas concentration and the potential of combustion of collected dust all contribute to causes of pulse-jet downtime and excess emissions.

What are the causes of such downtime and increased emissions with pulse-jets on incinerator applications? The following is a partial list of items that can lead to difficulties:

1. Fire
2. Filter failure
3. Filter blinding/High △P
4. Corrosion
5. Dust discharge problems.

Fire was a persistent cause of problems with incinerator fabric filters and precipitators. Typically, such fires occurred in simple systems where waste was burned to reduce volume. In a pulse-jet fabric filter, fires will damage the filters, the wire cages, and warp the tubesheet and other components. A severe fire or repeated fires will require nearly complete replacement of the dust collector.

When an operator of a pulse-jet or other fabric filter experience a fire, his/her first response is to order "fireproof" filters. Frankly, most fabrics that are used for filtering incinerator exhaust do not support combustion. It is the collected dust that catches fire not, at least initially, the filter bags. To prevent fires, one must eliminate at least one of the three items that contribute to combustion; fuel, ignition source and oxygen. To stop fires, the same procedure must be followed. Since

incinerators tend to operate with significant excess air, controlling oxygen is difficult. Eliminating in-leakage of air has some effect. Preventing fuel and an ignition source occurring in the dust collector is the other approach. The best way to accomplish this is to insure complete combustion of the waste in the incinerator. Utilizing waste heat recovery boilers also helps since large hot cinders can be stopped by impaction on the heat exchanger elements, and the cooler gas will cool cinders. Long duct runs, with multiple elbows, also promote cooling and, in some cases, help complete combustion. Various industries, such as primary metals and wood products have fire prevention experience. They use mechanical collectors, place the induced draft fan upstream of the dust collector and use spark and/or fire detection and extinguishing systems. These extinguishing systems use CO₂, dry chemicals or other agents. Fast acting isolation dampers are often required with these systems. They do add substantially to the cost of a fabric filter.

The simplest extinguishing system, the water deluge system with temperature activated sprinkler, is not recommended for incinerator pulse-jets. While acceptable for systems where the collected dust is just char, an absorbent chemical injection system should not use sprinkler systems. Water would turn a fabric filter collecting hydrated lime into a large lime slaker.

Fortunately, fires in incinerator pulse-jet collectors are less prevalent than they once were. Retention chambers for organics destruction, waste heat recovery, more emphasis on obtaining complete combustion, absorbent injection (perhaps the absorbent acts as an inerting material, helping to remove fuel from the fire equation) and the auxiliary equipment associated with absorbent injection systems probably all have contributed to reducing the fire potential.

One operating practice that will help reduce fire potential in pulse-jet filters is to keep the dust collection hoppers free of material. This helps remove the fuel factor from the fire equation.

FILTER FAILURE

Filter failure is generally considered to be a breach in the integrity of the filter, causing excessive emissions. Improper design, fabrication, and installation of the filters and/or the dust collector will also cause excessive emissions. However, this discussion will focus on failures during service, rather than at start-up.

Filter failure is caused by a loss of strength of the filter fabric, eventually leading to a hole or tear in the fabric. This hole or tear allows excess emissions to pass through the filter. The holes will enlarge over time from the flexing caused by pulse cleaning and from abrasion by the passing dust.

Dust abrasion can wear holes through filters as will repeated contact with other objects in the dust collector. These include another filter, walls of the collector or the wires of the support cage. These failures are not unique to incineration, though corrosion of the wire cage will accelerate wear, particularly if a wire weld breaks.

Loss of strength of the filter is caused by chemical and/or over temperature degradation of the fibers. The aggressive chemicals present in incinerator exhaust will attack filter fabrics. Operation of a dust collector at temperatures greater than its filters' can withstand degrade the fiber's that make up that fabric. In either case, the weakening of the fibers combined with the flexing caused by filter cleaning will induce the eventual failure.

To avoid failure, the filter fabric must be compatible with the gas conditions and constituents. One has to select the right filter or control the gas conditions and constituents or do both. With incineration systems, usually both must be done.

There are only a few fibers or fabrics that are suitable for incineration exhaust streams and each has some drawbacks. Chart 1 lists these fabrics and a general description of their capabilities. In addition, some other constraints must be recognized. Ryton will be attacked by nitric acid, bromine, and even oxygen in quantities greater than 10-15% of the gas. Fiberglass will be readily attacked by HF and in the woven form must be operated at lower gas/filter area (air/cloth) ratios than felted fabrics. It is prone to flexing failure. Other acidic gas constituents will attack glass as well as the remaining fabrics, with the exception of Teflon. However, such attack can be avoided by absorbent addition and maintaining the gas temperature above the acid gas dewpoint temperature. More on this later.

Homopolymer acrylic is typically used with lower temperatures, and absorbent injection and humidification, since it will tolerate higher moisture gas streams. Nomex is particularly susceptible to chemical attack but has been used successfully with simple (no plastics) waste volume reduction systems. P-84 is a newer fiber and there is limited experience with this fabric with incinerator applications. It is not as tolerant of the various aggressive

chemicals in incinerator gas when compared to Ryton or Teflon. Its higher temperature limitation offers advantages when considering temperature excursions of the gas stream. P-84 felt also is a superior filter media compared to woven fiberglass, Ryton or Teflon, and can achieve very restrictive outlet emission levels.

Goretex is an expanded PTFE membrane that is laminated to various felt or woven fabrics, such as those listed here or even to fabrics made from expanded PTFE. It is a proprietary product of W.L. Gore and Associates. Since the patents on this product are near expiration, similar products are being introduced by other suppliers. The PTFE membrane usually provides excellent filtration (low emission levels), low pressure differential and extended filter life. However, the fabric substrate must be compatible with the gas conditions and constituents if this type of filter is used.

Cost of the filters made from these fabrics vary considerably and this cost factor has tended to favor some of these fabrics. Woven fiberglass has been a prominent choice because of its lower initial cost and also because of its high upper temperature limit. In some cases, it has been misapplied, and been replaced with some of the other fabrics listed. However, rather than simply exclude woven fiberglass, it is important to remember that all the fabrics listed have failed prematurely or had excessive emission with some incinerator or similar gas stream. One must be careful to accurately characterize the constituents and conditions of the incinerator exhaust and be sure that the filter selected is compatible with that exhaust. One must also be wary of the tendency to select a fabric with a heavy emphasis on its cost.

FILTER BLINDING/HIGH △P

Filter "blinding" is a problem that occurs with all fabric filters. The nature of both the incinerator emissions and the efforts to treat those emissions make incinerator dust collectors more susceptible to this condition. "Blinding", for the purposes of this discussion, will refer to any condition that overly restricts gas flow through the filters. Due to the high pressure drop caused by blinding and subsequent loss of gas flow (when this excess ΔP affects fan performance), blinding is the leading cause of filter replacement.

The main cause of blinding is the interaction of the particulate in the gas with the filter fabric. Water, either as a vapor or in droplet form, often affects this interaction. In some cases, dust particles will agglomerate on the filter's surface to

form a highly impermeable dust cake. Often this cake is difficult to remove by filter cleaning. In other cases, particulate penetrates deep within the filter's media before being captured. This restricts the gas passages within the media.

A "mechanical" problem that will cause filter blinding is insufficient or improper cleaning. In a pulse-jet filter, filter cleaning may be improved by altering the pulse pressure, the pulse duration and/or pulse frequency. Misalignment of the pulse distributing pipes or improper operation of the pulse valves will contribute to blinding and must be corrected.

If filter cleaning is not the problem (or the solution) than other techniques must be used. Most of these are preventative measures and have little effect on blinding that has already occurred with operating filters. Sometimes shutting down the fabric filter (stop gas flow) and pulse-cleaning the filters for an extended period will result in partial recovery from the blinded condition.

The use of dry chemical filter aids, applied to the filters prior to exposure to incinerator exhaust, does help prevent blinding. Continuous seeding with such filter aids can also improve filter performance though this increases the equipment and operating effort needed. Limestone is a common precoat material but various silicates have superior performance. Neutralite, from BHA Group, is one such filter aid. The chemicals used for sorbent injection, such as hydrated lime, have some precoat effectiveness but they are far from ideal.

Ammonia or sulfur trioxide gas injection upstream of fabric filters collecting coal fly-ash have demonstrated an improvement in filter dust cake, lowering ΔP . This technique, if proven effective with incineration ash, would be economically justified for large incinerator systems.

The design of the dust collector's inlet configuration has been shown to affect collector performance. Standard pulse-jet designs use a solid or perforated baffle placed in the path of the collector's inlet to "diffuse" the gas and particulate streams. These designs produce poor gas distribution in the collector, creating high turbulence, dust re-entrainment, high filter ΔP and, even abrasive wear of the filters. Inlet configurations such as that shown in Figure 1 (MikroPul's patented Cascadair™ inlet diffuser), or similar concepts distribute the inlet gas stream evenly throughout the collector. Gas turbulence and dust re-entrainment are greatly reduced, resulting in lower filter ΔP .

Various fabric treatments can reduce the tendency towards blinding. Singeing of felt fabrics is a simple, cheap technique that can reduce filter surface blinding. Silicone and Teflon emulsions have been shown to improve resistance to blinding. HCE and Tuflex II, from Mendardi-Criswell, are, respectively, such fabric treatments. Constructing fabrics with finer fibers and with lower permeability (porosity) improves the fabric's filtration performance. The finer fibers increase the surface area fine particles can adhere to and the lower porosity resists particle penetration into the filter media.

The presence of high moisture will increase the tendency towards blinding. Water droplets, from condensation or a poorly operating spray dryer or spray cooler, will quickly cause blinding of the filters. Maintaining liquid injection systems upstream of the dust collector is important.

All these measures should be considered and most followed. Yet, the best way to combat filter blinding is to recognize it can occur. To minimize the effect of such blinding, one must size (design) the dust collector properly. With pulse-jet collectors, Air/Cloth ratios of 3-4:1 (ACFM/ft² filter area) are preferred, with the more demanding incinerator applications tending to the lower figure.

CORROSION

Since incinerator exhaust contains corrosive chemical constituents, the potential for corrosion of a fabric filter's components is high. Though material selection is a standard technique used to combat corrosion, the wide variety of gas constituents and the possibility of high temperatures precludes the use of many corrosion resistance approaches. For example, the use of 300 series stainless steel is contraindicated due to its susceptibility to chloride attack. While various high nickel alloys have shown that they are capable of withstanding incinerator exhaust, they are prohibitively expensive.

In general, pulse-jet fabric filters for incinerator applications are fabricated from carbon steel. To resist corrosive effects, it is important to establish operating criteria that prevent the dust collector's operating temperature from being at or below the acid dewpoint of the gas. The dust collector must be fully insulated and in-leakage of cool ambient air must be prevented. This means gasketed joints (flanges), doors and hatchways, dust discharge devices, etc. should be as leak-free as

possible. In addition, at start-up, the dust collector must be preheated to correct temperature (above acid dewpoint). At shut-down the collector's temperature must be maintained above dewpoint while purging the system with hot, dry, acid-free gas until the acid constituents are removed from the collector. The use of hopper heaters (or heat-tracing) on the dust collector, preheating and purge heating using the auxiliary fuel firing needed by the incinerator, and, if necessary, adding a supplementary heating system, will allow an incinerator operator to conform with these guidelines. These practices have worked well with fabric filters on coal-fired boilers. Unfortunately, many existing incinerator dust collectors are not operated in this fashion. While the collectors will be insulated and normally operated above acid dewpoint, start-up and shut-down practices are not strictly adhered to, and corrosive attack occurs. With absorbent injection systems, the "dirty side" of the collector, the region upstream of the filter surface, tend to survive. The absorbent acts to neutralize the acid droplets formed. Also, this area tends to be the hottest area of the collector.

The so-called clean air plenum is the area that suffers most from corrosion, since absorbent is not present in this region and it tends to be cooler. Eventually, all components will suffer, including filters, resulting in excessive emissions and the need to repair or replace components.

In some instances, various coatings have been applied to the gas contact steel surfaces to add some additional corrosion protection. To work, these coatings, primarily coal tar derivatives, must be applied under proper ambient conditions to oxide-free steel. This means dedicated abrasive cleaning. Also, these coating systems have definite upper temperature limitations and the gas must be kept below these limits. If temperature excursions are expected, emergency cooling systems should be included in the dust collector system. This is also a good idea for protecting the filters. Coating the wire filter support cages helps extend the life of the cages and the filters. Two cautions: 1) The localized heat concentration from dust collector heat tracing may not be compatible with the coating. This must be checked. 2) Such coatings are not substitutes for proper start-up, operating and shut-down practices. Coatings will extend component life when the dust collector is operated correctly.

DUST DISCHARGE

A problem that will occur with incinerator fabric filters is

blockage or bridging of the collected particulates in the collection hopper. Since the absorbent chemicals, e.g. hydrated lime, will cake up in the presence of moisture, the dry absorbent systems are most susceptible. Once a blockage occurs, it must be cleared quickly, since the collector's operation is adversely affected. Such blockage will lead to abrasion of the filters. To prevent such blockages or at least reduce the frequency of them occurring, the following guidelines are offered. First, the dust discharge device or devices should be insulated, have a minimum of air in-leakage and very important, run continuously. The size and speed of these devices must be able to remove the collected dust quicker than it enters the dust collector.

Since condensation will promote hopper blockages, it is important to avoid condensation. This is not easy to do in practice. Some of the dust will adhere to the collector's inside surfaces. It tends to form an insulating layer and this results in a thermal gradient being formed. Even with insulation and operation of the collector above gas dewpoint, this thermal gradient can permit localized condensation to occur. When this occurs, this dust layer can grow, eventually causing a blockage. Steep hopper walls, heat tracing and hopper vibrators will all help prevent significant dust layers from accumulating. The coating systems mentioned above may also help since their "slicker" surface tends to reduce dust build up. Again, the compatibility of coating systems, heat tracing and vibrators must be checked.

A technique that has worked in other dry material handling systems is the addition of "flow aids". Silica gel is a common flow aid that prevents hopper blockages. Blended with a dry absorbent, it will probably improve the dry injection system operation as well as the fabric filter's.

ADDITIONAL RECOMMENDATIONS

Following are some other practices and equipment suggestions that will improve the operation of a pulse-jet fabric filter venting an incinerator.

Since maintaining the filters in good operating condition is critical, it is important to monitor that condition. Filter pressure drop is the traditional monitoring method. Less used, but recommended, are particulate emission detection devices. Continuous emission monitors (CEM) are quite expensive but another class of device, called broken bag detectors, are reasonable. They will detect even small increases in particulate emissions, thus giving an early warning of trouble. Investigating the cause of such emissions can result in preventing a more difficult problem.

Several firms make these detectors, including Auburn International, Babbitt International and Anderson.

Investigating the cause of filter failure, rather than just replacing filters, will result in increased filter life. The suppliers of the dust collectors and the filters generally have some capability to test filters but a third party opinion may also be warranted. Several firms can perform filter evaluations. These firms include ECC, ETS and Grubb Filtration Testing Services.

The various configurations of incinerator emission control systems using pulse-jet filters have some operation difficulties which occur more with a particular configuration. The spray dryer absorber and dry injection with humidification systems are more prone to filter wetting (and thus, blinding) and dust discharge problems. Failure of the liquid sprays will lead to temperature excursions so an adequate warning system, back-up cooling or gas bypass systems are recommended.

The configuration with just the filter collector is, as noted before, more prone to fire and also temperature swings. This system, in some cases, may also be prone to higher particulate emission levels so precoating and high efficiency bags are warranted.

When a wet scrubber is used downstream of the pulse-jet filter, it is usual to use a packed bed wet absorber. These are prone to plugging if exposed to particulate. Thus it is extra important to prevent emissions and detect them if they occur. Broken bag detectors are certainly warranted with these systems.

CONCLUSION

Pulse-jet fabric filters have demonstrated that they have the capability to successfully treat incinerator emissions. To insure success of such a system, it must not only be well designed but also operated and maintained properly. Monitoring the important parameters of inlet and outlet gas temperature, filter ΔP and, emissions will help prevent minor problems from becoming major ones, as long as they are investigated quickly. Following the guidelines discussed above will reduce the need for maintenance and insure a system that will achieve compliance with emission regulations.

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TECHNICAL REPORT DATA <i>(Please read Instructions on the reverse before completing)</i>			
1. REPORT NO. EPA-600/R-92-209c	2.	3.	EB 93-124196
4. TITLE AND SUBTITLE Proceedings: 1991 International Conference on Municipal Waste Combustion, Volume 3. Sessions 1C, 2C, 3C, 4C, 6C, 7C, 8C, 9A, and 10A/C		5. REPORT DATE November 1992	6. PERFORMING ORGANIZATION CODE EPA/ORD
7. AUTHOR(S) Miscellaneous		8. PERFORMING ORGANIZATION REPORT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS See Block 12		10. PROGRAM ELEMENT NO.	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Air and Energy Engineering Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Proceedings; 2/91-9/92	14. SPONSORING AGENCY CODE EPA/600/13
15. SUPPLEMENTARY NOTES AEERL project officer is Theodore G. Brna, Mail Drop 62B, 919/541-2683. Vol. 1 contains Sessions P, 0, 1A, 2A, 3A, 4A, 6A/B, 9C, and 10B. Vol. 2 contains Sessions 1B, 2B, 3B, 4B, 7A/B, 8A/B, and 9B.			
16. ABSTRACT The three-volumes document 82 presentations by authors from 15 countries at the Second International Conference on Municipal Waste Combustion (MWC) in Tampa, Florida, April 16-19, 1991. The Conference fostered the exchange of current information on research concerning MWC, ash disposal and treatment, and flue gas cleaning as well as unit operating experience, regulatory developments, and plant siting considerations. Topics discussed included overviews on MWC from Canada, Europe, and the U.S.; MWC processes; dry/wet flue gas cleaning developments and operating experience; ash characterization, treatment, utilization, and disposal; chlorinated dioxin/furan control; environmental compliance; health risk; quality control/assurance; municipal waste management; mercury emission control; sampling and analysis; economic and social issues; and regulatory effects.			
17. KEY WORDS AND DOCUMENT ANALYSIS			
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Furans	Pollution Control	13B
Waste Disposal	Health	Stationary Sources	15E 06N
Combustion	Quality Assurance	Municipal Waste	21B 13H, 14D
Ashes	Mercury (Metal)	Dioxin	07B
Flue Gases	Sampling	Health Risk	14B
Halohydrocarbons	Analyzing		07C
Economics			05C
18. DISTRIBUTION STATEMENT Release to Public		19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 503
		20. SECURITY CLASS (This page) Unclassified	22. PRICE