

PDHonline Course C451 (5 PDH)

Air Pollution Aspects of Thermal Waste Processing Systems

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Air Pollution Aspects of Thermal Waste Processing Systems Applications

Walter R. Niessen, P.E., B.C.E.E.

COURSE CONTENT

Air pollutant emissions have become the focus of public concern and regulatory scrutiny regarding incineration facilities. The fraction of total facility capital cost for system components functionally directed at compliance with air emission limitations is, for many plants, more than 35% of the total investment. In many instances, the award of air pollution permits is the pacing and controlling event in the implementation of incineration facilities. Because of these realities, those wishing to construct and operate incineration systems should explore and understand the relationships between the quantity and characteristics of air pollutant emissions and:

- The specific chemical and physical characteristics of the wastes to be burned;
- The design features of the combustor;
- The operating conditions in the combustor; and
- The control effected by the air pollution control device(s).

With this knowledge, the analyst can institute controls on the types or relative firing rate of the wastes to be burned and/or configure the hardware designs and the operating regimens to assure that no adverse air quality impacts detract from the benefits of incineration as a useful tool in waste management. These topics are discussed in detail in other texts [1].

I. AIR POLLUTANTS FROM COMBUSTION PROCESSES

In the combustion of fuels and wastes, air contaminants are generated that have significance to the design engineer or system analyst in three areas:

- Obtaining permits from regulatory agencies for installation and/or operation of the system;
- Establishing the specifications for air pollution control systems; and
- Establishing the basic design, suggesting modifications to existing designs, or interpreting problems in emission minimization or control.

There are many air pollutants emitted from combustion processes. The most basic is inorganic particulate matter. The total suspended particulate (TSP) is, predominantly, relatively inert "ash": a mixture of benign compounds primarily composed of silicon, aluminum, calcium, iron, aluminum and oxygen. However, this portion of combustor emissions also includes the "heavy metals" of lead, mercury, cadmium, arsenic and other elements that may have significant toxic, carcinogenic and other health effects.

Finally, the inorganic TSP includes an important portion of the small particle size material denoted as " $PM_{2.5}$." $PM_{2.5}$ is the respirable fraction under 2.5 microns in mass mean diameter and has been shown to have an important

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role in both the onset and aggravation of asthma and other respiratory diseases. Data on fine particulate matter shows sulfates and nitrates to be the most abundant species in atmospheric aerosols with sulfates being the predominant contributor to $PM_{2.5}$ [2]. A substantial fraction of the total atmospheric $PM_{2.5}$ is formed outside the stack from SO_x and NO_x precursors (secondary $PM_{2.5}$). However, because of the health concerns regarding $PM_{2.5}$, one might expect more stringent increasing limits to be placed on acid gas and NO_x emissions, even if bag house and wet electrostatic precipitator controls effectively capture the primary $PM_{2.5}$ in the exhaust gases.

A second category of emission includes the combustible solids, liquids, and gases. A portion of these combustibles can be a fraction of the raw waste originally fed to the unit. Beyond this, there are is usually found a complex mixture of products of incomplete combustion (PICs). These include carbonaceous soot and char; carbon monoxide; "hydrocarbons"; and representatives of many classes of carbon-hydrogen-oxygen- nitrogen-halogen compounds such as benzene-soluble organic matter (BSO), polycyclic organic matter (POM) (e.g. benzo-(α)-pyrene) and a variety of polyhalogenated hydrocarbons (PHH), including the isomers and congeners comprising the families of polychlorinated and polybrominated dibenzo furans (PCDF, PBDF), dibenzo p-dioxins (PCDD, PBDD), and polychlorinated and polybrominated biphenyls (PCB, PBB).

Some of the organic and/or inorganic compounds emitted from incinerators exhibit (or are suspected to exhibit) significant adverse health effects. Some of the compounds react in the atmosphere (especially, under the influence of ultraviolet radiation) to generate ozone and a spectrum of oxygenated reaction products that can irritate the eyes and weakened pulmonary systems. With the great strides in sampling and analysis technology in recent years, the emission of these compounds can be quantified, regulated and used a basis for fines and penalties and, of vital importance, continuation of permission to operate.

There are several pollutants where the emission level is directly related to fuel chemistry. These include the sulfur oxides, the halogens and hydrogen halides, trace elements and radioactive elements. Others, such as the nitrogen oxides, show emission levels that are related to both fuel chemistry and the combustion process. Inert particulate emissions are related to the fraction of "ash" in the feed and the fluid flow and other physical processes that can elutriate and convey the material from the combustion zone. Net pollutant emissions of pollutants such as the PICs arise partly from the waste chemistry (contributing "building blocks"), partly from failures in the combustion process (generating the PICs) and partly from successes in the combustion process (destroying a portion of the PICs).

Beyond the engineering utility of emission estimation relationships, the regulatory process in the United States and world-wide now demands detailed consideration of air emissions in the permitting and public participation phases of project development. The preparation of permit applications and the hearings that are increasingly a part of the permit approval process usually predate the availability of hard emission data. When the proposed combustor is of a new design or the waste is unique, the engineer is faced with a need to generate credible emission estimates without a facility/waste-specific data base on which to draw. The emission estimates, however, are often critical to securing a permit to construct and as a basis for environmental impact evaluations, health risk assessments and other analyses where data from the operating facility is not yet available.

The emission estimation methodologies described below attempt to predict the actual concentrations of pollutants in the exhaust of combustion systems and in the discharge after air pollution control. As such, a factor of safety must be applied to provide a reasonable level for "not to exceed" permit limits. This is appropriate (1) in recognition of the uncertainties in the estimation methods, (2) to provide some margin for expected variability in the feed and/or system characteristics and (3), in those situations where the permit limits will be passed on to incinerator system vendors (who will be asked to guarantee permit compliance), to associate the emission requirements with a reasonable and fair level of commercial risk.

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A. Particulate Matter

1. General

"Particulate matter" should be differentiated from the total suspended particulate or TSP which is the sum of inorganic particulate plus the soot, tar and other organic-based substances comprising combustible particulate matter. This is due to the inherent refractory nature of inorganic particulate (emission rates cannot be reduced by better combustion). Also, such a differentiation clearly establishes its primary source: the ash content of the fuel or waste that is burned. In principle, inorganic particulate can also arise from mechanical degradation of refractory, or oxidation and flaking of fireside metal surfaces. However, the great majority of the emission results from the carryover of mineral matter introduced with the fuel or waste. In unusual conditions, where combustion air is drawn from an area with a high dust loading, a portion of the emission could be associated with the air supply.

Important particulate characteristics include size, size distribution, shape, density, stickiness, corrosivity, reactivity and toxicity. Of these, particle size distribution (PSD) has the most important impact on air pollution control. PSD can be expressed as a particle count and as a mass distribution. Most commonly, the greatest mass is associated with the larger particles but the greater number of particles, visual impact (opacity due to light scattering), surface area, health impact and difficulty in capture is found with the smaller particles.

2. Gaseous and Liquid Wastes and Fuels

A desk top assessment of the fraction of the inorganic matter in a fuel that appears in the flue gas is often difficult because of the complexity of the processes involved. Thus, empirical estimation methods are necessary unless the system design is such that essentially all solids which are introduced must leave via the flue gas stream. This is often true for systems burning gaseous or liquid waste. For many conventional gaseous and liquid fuels, combustion systems often do not include air pollution control for particulate matter. When burning liquid or gaseous waste streams, however, sampling or estimation of inorganic content is an appropriate step during the design phase to assure that no control system is needed. Then consideration can be given to either pretreatment of the waste to remove the solid matter or installation of a flue gas particulate air pollution control device.

3. Sludge

"Sludge" refers to biological wastewater treatment plant biosolids. The emissions from burning high organic sludge (such as the tarry material found as distillation bottoms, API separator sludge or petroleum tank bottoms) should be expected to compare favorably to the emission behavior of liquid wastes albeit with adjustment for a higher ash content.

Biosolids are generated through settling of suspended matter (primary treatment) and activated sludge (secondary treatment) or other process step for the conversion of soluble pollutants into organic biomass (biota). Because of the nature of the wastewater collection and treatment process, biological sludge ash is primarily comprised of finely divided inorganic material that can be suspended in fast-moving flue gases with relative ease. The emission rate of inorganic particulate is strongly tied to the type of incineration system and to its operating characteristics.

a. Multiple Hearth Furnace (MHF). The relationships between the uncontrolled pollutant emissions and MHF design and operating conditions are complex. The carry-over of particulate, the formation of carbon monoxide and other combustible pollutants, the emission patterns of the key toxic metals and so forth change in a non-linear manner and in response to different system variables. Therefore, a substantial data base which includes both emission and system variables is needed to characterize system behavior. Also, the data must be collected ahead of and following the air pollution control device (the uncontrolled and the controlled emission rate) such that insightful system-emission relationships may be developed.

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TSP emissions (percent of ash fed to the furnace which is carried over) show a strong correlation to the dry, standard cubic meters per minute of furnace flue gas (DSCM) per kilogram of ash fed to the furnace [3]. For most plants, 2 to 3 percent of the ash in the feed sludge is carried over although, at high excess air rates, the emissions can reach 5 or 6 percent. A suggested linear functional relationship (based on consideration of 19 data points and with a coefficient of determination (r^2) for the least squares fit of the data for differing functional relationships of 0.46 is:

Percent of ash in feed that is emitted = -0.2382 + 0.4955 (DSCM)

The correlation is plausible based on the speculation that the primary mechanism for particulate emission is elutriation of fines in the sludge by the flue gas flow.

b. Fluid Bed. The fluid bed furnace is unique in that except for the solids drained from the bed (a mixture of sludge ash and bed material), all of the sludge ash is blown from the bed. Thus, the dust mass rate (kg/hr) entering the collector is approximately equal to the total feed rate of sludge ash to the furnace plus the time-averaged bed sand make-up rate less the settlement in the ductwork. The latter is negligible (steady state) except in the case where a boiler is installed when there may be some draw-off of solids from a hopper in the boiler.

4. Solid Wastes and Fuels

Unlike liquid or gaseous fuels which may contain little inorganic matter, almost all solid wastes and fuels have substantial ash content. Since these latter fuels are seldom susceptible to pretreatment to reduce emissions, the designer must give careful attention to design features and operating practices to minimize the uncontrolled emission rate. Even with such precautions, it is likely that emission control will be required.

a. Suspension Burning. The maximum inorganic particulate emission rate corresponds to the situation where all noncombustible solids are swept from the combustion chamber. This is largely the case for burners fired with pulverized coal, shredded and air-separated municipal refuse, sawdust, rice hulls, and other *suspension firing* systems. In such systems, a portion of the fly ash may settle in the bottom of the primary furnace or in following chambers or boiler sections. The degree to which settlement reduces emission rate depends on the flue gas properties, on the characteristic dimensions and weight of the fly ash particles (settling rate), and on the velocity of the gas stream relative to the chamber dimensions (transit time).

b. Mass Burning. In mass-burning, the fuel or waste is moved through the combustion chamber on a grate. The introduction of a portion of the combustion air through the grate provides a mechanism whereby some of the ash can be fluidized and carried off with the flue gases. This mechanism is favored by fuels or wastes with a high percentage of fine (i.e., suspendable) ash, by high underfire air velocities, or by other factors that induce a high gas velocity through and over the bed. Secondary inducements to emission include agitation of the bed and the volatilization of metallic salts. Grate systems designed with large air passages (such that a substantial fraction of the fine ash is dropped out) tend to reduce the emission rate.

ASH CONTENT. Ash particles may be entrained when the velocity of the gases through the fuel bed exceeds the terminal velocity of the particles as calculated using Stokes' Law [Eqn. 3] where:

ut	=	terminal settling velocity, m/sec
μ	=	viscosity of gas, kg/m sec ⁻¹
d	=	particle diameter, m
ρ_s	=	density of particle, kg/m ³
ρ_a	=	density of gas, kg/m ³
g	=	gravitational constant, m/sec ²
Č _v	=	drag coefficient, dimensionless

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In the streamline flow region (small particles), the drag coefficient is inversely proportional to the dimensionless Reynold's number N_{Re} .

$$C_x = \frac{24}{N_{Re}} = \frac{24\mu}{du_t \rho_a} \tag{1}$$

where

$$N_{Re} = Reynold's number = \frac{du_t \rho_a}{\mu}$$
 (2)

In the streamline flow region, combining Eqns. 1 and 2 leads to Stokes' Law:

$$u_t = \frac{d(\rho_s - \rho_a)g}{18\mu} \tag{3}$$

For practical purposes, the streamline flow region stops at about $N_{Re} = 0.5$ to 1.0. Thus, for 200 °C gases and particulate densities of 2.5 g/cm³ (2500 kg/m³), Eqn. 2, and thus Stokes' Law is valid only up to diameters of about 90 µm. Above this region, we must use relationships other than Eqn. 1 to characterize the dependence of C_x on N_{Re} . For larger particles, the relation of Schiller and Naumann [4] indicates:

$$C_x = \frac{24}{N_{Re}} [1 + 0.15 N_{Re}^{0.687}]$$
(4)

This relation is valid for $0.5 < N_{Re} < 800$.

Underfire air velocities in municipal incinerators typically vary from a minimum of 0.05 sm³ sec⁻¹ m⁻² of grate area to 0.5 sm³ sec⁻¹ m⁻². Based on the terminal velocity of ash particles it is expected that particles up to 70 μ m will be entrained at the lowest velocities and up to 400 μ m at the highest at a mean temperature of 1100 °C as supported by the observed range of particle sizes of fly ash, the increases in particulate emission with increases in refuse ash content, observed increases in particulate emission with underfire air velocity, and the similarity in the chemical analyses of fly ash and that of the ash of the principal constituents of refuse.

The ash content of refuse is a major factor in determining emission rates. The percentage of the ash carried over ranges mostly between 10 and 20% of the total. The actual percentage carried over for a particular incinerator will, of course, depend on other factors, such as the underfire air rate. Consideration of the particle terminal velocities indicates that he above conclusions apply only to fine particle ash (finer than 400 μ m).

UNDERFIRE AIR RATE. A systematic study of the effects of underfire air, secondary air, excess air, charging rate, stoking interval, and fuel moisture content on the emission rate from an experimental incinerator by the PHS led to the conclusion that the velocity of the underfire air was the variable that most strongly influenced particulate emission rate. The data on 25 and 50% moisture fuel were correlated [5] by:

$$W = 4.35 V^{0.543}$$
(5)

where W is the emission factor expressed in units of kilograms of particulate per metric ton of refuse burned, and V is the underfire air rate (in sm³ sec⁻¹ m⁻² of grate area) which ranged from 0.01 to 0.5 sm³sec⁻¹ m⁻² of grate area.

GRATE TYPE. Stoking has been observed to increase particulate emission rates. In order to assess the effect of grate type on emission factors, data on the different types of units were compiled [6]. The emission rates from reciprocating grate stokers were seen to be significantly higher than those from other grate types. It is probable that higher rates in the reciprocating grate units are due to a combination of greater stoking, higher underfire air rates, and larger furnace sizes than in the other units. Another factor is the difference in grate openings, which can

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result in large differences in the amount of fine ash that can sift through the grate; lower emission rates would be expected from grates that have large amounts of fine ash sifting through the grate.

c. Rotary Kilns. The entrainment of particulate matter from rotary kilns burning hazardous waste and, especially, those used for thermal desorption in soil remediation is a significant operational issue because of its impact on downstream air pollution control and fly ash handling equipment. For that reason, an accurate estimation method for carry over is highly desirable to proper design.

Particulate carry-over is the result of the interplay of a number of factors acting in complex ways [7, 8]:

- The type of kiln (co-current vs. countercurrent)
- The characteristics of the processes waste or soil (esp. the fraction of the silts and clays)
- Mode of oxidation (oxidative vs. pyrolytic which affects gas volume)
- Gas velocity through the kiln
- The use (or absence) of flights or lifters and internal or terminal dams
- The kiln rotational rate
- The percent of the kiln cross-section obscured by the material being processed
- Wall roughness and the presence of crevices, cracks and imperfections
- Feed and exit design features that impact on gas-solid contact opportunities
- Solids feed rate

w

The primary mechanisms responsible for the entrainment of particulate are: edge entrainment, surface entrainment and kiln design entrainment [7].

A functional relationship to estimate particulate entrainment in a rotary kiln was treated by Knodorov and Li [8].

$$w = K_2 \left(DF\omega s^{-1} \theta^{1/2} \right)^{1/2} \frac{u_g^4 \mu_g^{3/2} \rho_g}{\rho_{feed}^{3/2} D^{3/4} d_s^3 n f(C_f)}$$
(6)

where

= Entrainment rate (kg/sec.)

=	Proportionality constant varying with the roughness between
	the kiln wall and the feed solids
=	Inside diameter of the kiln (m)
=	Solid feed rate (kg/sec.)
=	Kiln rotational rate (radians/sec.)
=	Kiln slope (meters/meter)
=	Dynamic angle of repose of the solid (radians)
=	Gas velocity (meters/sec.)
=	Gas viscosity (Newton sec./m ²)
=	Gas density (kg/m^3)
=	Solid density (kg/m^3)
=	Diameter of the feed particles (m)
=	Solid particle size distribution parameter
=	Modification parameter related to the concentration of entrainable fines in the feed

Equation (6) is difficult to apply quantitatively as it includes a number of unspecified constants and parameters but the form of the equation is most useful to illustrate the effect of the critical operational parameters on entrainment rate.

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B. Combustible Solids, Liquids, and Gases

Complete combustion is a basic objective of almost all combustion systems. In most real systems, however, the full attainment of this goal is either impossible or impractical. Thus, some unburned combustible will always be present in the effluent gases. In the 1970's and afterward, one saw the confluence of several forces in the environmental area that focused attention on incompletely burned species:

- The emission characteristics and control technologies for the "basic pollutants" (particulate, NO_x, SO₂ and CO) were relatively well understood. Air quality criteria (denoting the relationship between the long term average concentration of the pollutant and human health effects) had been set. The academic and the regulatory community were seeking new areas of endeavor.
- Analytical equipment and sampling and analysis technique was rapidly evolving such that one could identify the specific chemistry of complex organic species in flue gases. The combustor is an incredibly prolific "chemistry set" when it comes to producing a spectrum of products: a broad range of polynuclear, oxygenated, halogenated and otherwise medically significant species. The concentrations were small but the classes of compounds (POM's, halogenated organic compounds etc.) were provocative.
- Methodologies were emerging, in consort with world-wide interest in hazardous wastes, for the evaluation of the health risk associated with exposure to sub-acute levels of pollutants. Further, the public was looking at "risk" as a new scale against which to evaluate projects. Unfortunately, the conservatism of health risk evaluation methodology, the conservatism inherent in the development of most dose-response data and the (very low) level of risk that the public appeared willing to accept as "accept-able", combined in a screening process that was very severe.

From these factors has come increasing awareness and concern by regulatory authorities throughout the world over the health implications of combustible emissions. This concern emphasizes the importance of careful design and operations to minimize both generation and survival of these pollutants.

1. Pollutant Characterization

The incomplete combustion of carbon-containing fuels or waste materials forms a spectrum of different chemical species. The simplest, carbon itself, can contribute importantly to the opacity of the effluent. This is due both to the refractive index and color of the particles, and to the typically small particle size. Small particles have a greater light scattering power for a given mass loading than coarse particles. Carbonaceous soot can be amorphous in character but is more often graphitic. This is unfortunate since graphitic carbon is more difficult to oxidize than the amorphous material.

A second class of pollutants includes the carbon-hydrogen compounds. The chemical nature of these compounds ranges from methane, ethane, acetylene, and other simple straight and branch-chained aliphatic compounds to complex saturated and unsaturated ring compounds. The health significance of these pollutants varies greatly. The sub-class of complex aromatic compounds (polynuclear organic matter or "POM") includes compounds such as the carcinogenic benz-α-pyrene.

The third class of pollutants includes the carbon-hydrogen-oxygen compounds. These also range from simple compounds such as carbon monoxide and formaldehyde to complex organic acids, esters, alcohols, ethers, aldehydes, ketones, and so forth. These compounds are often associated with "odorous" emissions and show very low minimum detection concentration limits. In particular, aldehydes that are formed as products of incomplete combustion (PICs) are often major contributors to the "burnt" smell.

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The fourth class of pollutants includes the carbon-hydrogen-nitrogen compounds. These include the PICs formed from combustion of amines, N-ring compounds, many proteins and other chemical species. Some also incorporate oxygen in the molecule. These compounds are especially significant due to their participation in the formation of "fuel nitrogen NO_x " and their contribution to odor.

The fifth class of pollutants includes the carbon-hydrogen-oxygen-halogen compounds. These include the chlorinated solvents, fluorinated and chlorinated polymers and many other environmentally significant PIC-derived chemical compounds. Importantly, this class includes the several congeners and isomers of polychlorinated dibenzo p-dioxin, dibenzo furan and biphenyl compounds. The chlorinated solvents and polymers contribute to the formation of the halogen acids (HF, HCl, HBr and HI) that, under U.S. law, often triggers a requirement for "acid gas control". Members of the polychlorinated dioxins, furans and biphenyls are under intense scrutiny by the regulatory community and the general public world-wide. Carcinogenicity and other significant health effects are often associated with these materials.

The incompletely burned or PIC pollutants are associated with almost every criterion of air quality:

- Some are solid particulate or aerosols and contribute to atmospheric haze and solids fallout.
- Some are photochemically reactive and thus participate in the reactions leading to smog.

• Some are recognized as injurious to plants (e.g., ethylene), animal life respiration (e.g., carbon monoxide) or are known to cause cancer in human beings (e.g., benz- α -pyrene) or to promote adverse health effects in animals similar to that of pesticides (e.g., halogenated biphenyls).

Because of the health-related impact of these pollutants, their control assumes an importance out of proportion to the weight emitted.

2. Mechanisms of Formation

By definition, the appearance of combustible material in the effluent of an incineration system reflects a partial failure of the combustion process. As described earlier, this indicates:

- Inadequate residence time to complete combustion reactions and/or
- Inadequate temperature levels to speed combustion reactions to completion and/or
- Inadequate oxygen in intimate admixture with fuel gases to allow oxidation to proceed to completion. This often may be characterized by a lack of adequate mixing of the flow or an insufficient air supply.

These deficiencies affect both the formation and the persistence of combustible pollutants. In burning solids, the formation of hydrocarbon pyrolysis products, carbon monoxide, carbon char, and similar species is an inherent part of the gasification stage of the process. Thus, the appearance of these materials in the flue gas reflects flow bypassing, quenching (by contact with cool surfaces or admixture with cold gases), or thermal cracking (dehydrogenation of carbon-hydrogen compounds at elevated temperatures); all with a subsequent time, temperature, and composition history which prevents burnout.

It should be recognized that even the more complex ring compounds can be formed from the combustion of chemically simple fuels. Thus, polycyclic organic matter is found in the effluent from boilers burning natural gas. It is not known at this time whether such pollutants arise from, for example, the hydrogenation of soot (which has a complex, six-membered ring structure) or from trace hydrocarbons in the fuel.

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Many of the failure mechanisms leading to combustible pollutant generation are common during startup conditions. Most obviously, the furnace is cold such that the furnace walls absorb a must higher proportion of radiant energy than when they have reached operating temperature. This chills the flame and fosters CO and hydrocarbon formation. Also, since startup involves a furnace filled with cold ambient air, the initial minutes of operation involve very high mean excess air levels. Higher excess air and lower gas temperatures produce higher CO levels. Further, during the early stages of startup, burner firing rates are kept low to prevent thermal shock of the refractory. Thus, gas velocities are low and mixing is poor. This also contributes to increased CO emissions

3. Concepts for Control

The most direct and effective approach to the control of combustible pollutants is through enhancement of the combustion process throughout the combustor. In U.S. regulatory language, this control strategy is called "Good Combustion Practice". Much of the material throughout this book relates to various design features and operating techniques to effect complete combustion.

An effective but often costly approach to combustible pollutant control involves the addition of an afterburner zone or a separate afterburner chamber to the basic combustor. Here, the designer concludes that the assured achievement of some minimum temperature (the afterburner set point) will provide an acceptable level of control. The system is then equipped with burners to provide the needed temperature increment. Often the flow patterns and velocity of the flue gas stream and/or the injected burner or secondary air jets are arranged to break up stratified flows and/or foster mixing. Gas temperature sensing and burner control instrumentation is installed to monitor the state of the gases leaving the combustion space and to trigger fuel use when the temperature falls below the set point. Also, the combustion space is designed to afford some increment of residence time that experience or judgment suggests is adequate for the mixing and combustion processes.

A measure of combustible pollutant control is often effected by several types of back-end air pollution control systems. Obviously, there is a reduction in combustible particulate matter by cyclones, fabric filters and other particulate control devices. In addition, wet and dry scrubbers and carbon absorption units reduce combustible pollutants. The reduction of temperature coupled with particle capture is a key element of both wet and dry scrubbers. If the temperature drop results in condensation of aerosols or in increased condensation of high molecular weight compounds on existing particle surfaces, removal occurs. This is an important control mechanism for the dioxin, furan and POM pollutants. These control devices and techniques are discussed later in this Chapter in the Section on air pollution control systems.

C. Gaseous Pollutants Related to Fuel Chemistry

A third group of pollutants is generated by release and/or reaction of elements in the fuel. Common and important among these are sulfur oxides and hydrogen chloride.

1. Sulfur Oxides

Many waste streams and fossil fuels contain sulfur. The sulfur can be present in any or all of its many oxidation states from S^{-2} to S^{+6} . Of particular interest from an air pollution standpoint is the sulfur appearing as organic or inorganic (pyritic) sulfur, free sulfur, or sulfur appearing in organic or inorganic acid forms. In each of these cases, the sulfur can be expected to appear in the fuel gases as sulfur dioxide or trioxide. A portion of the sulfur which exists as inorganic sulfates in fuels or in waste materials such as gypsum-filled wallboard (calcium sulfate) may be released by reduction reactions, especially in the high temperature environment on the grate in mass burning incinerators.

Depending upon the chemical composition (alkalinity) of the mineral ash residues, a portion of the sulfur oxides may be lost from the flue gas by gas-solid reactions. Also, some sulfur may remain with the ash. Typically, however, these losses are relatively small, and in excess of 95% of the sulfur (other than that appearing as inorganic © Walter R. Niessen 2011 Page 10 of 68

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sulfates in the fuel or waste) will be found in the fuel gases from suspension fired combustors [9]. About 70% is released in mass burning systems [10], based on analogy with coal burning plants.

Since waste changes with time, the SO_2 concentration in the exit gases should be expected to change. Table 1 shows the frequency of observation of 30-minute average SO_2 concentrations for several concentration ranges over a 6-month testing program conducted in Germany in 1995.

The proportioning of sulfur between the dioxide and the trioxide forms depends on the chemistry of sulfur in the fuel, the time sequence of temperature and composition of the flue gases, and on the presence (or absence) of catalytic ash material. Although cold-end chemical equilibrium considerations and excess oxygen concentrations favor oxidation to the trioxide, reaction rates are slow, and generally only 2 to 4% of the sulfur appears as the trioxide. Higher proportions of trioxide result from the burning of organic sulfonates, some heavy metal sulfates (which dissociate to SO_3 and an oxide), or to the "burning" of wastes such as discarded automobile batteries, which contain free sulfuric acid.

The equilibrium relationship between the sulfur oxides [12] for partial pressures in atmospheres and temperature in K is given by:

$$SO_2 + 0.5 O_2 \Leftrightarrow SO_3$$

$$K_{p} = \frac{p_{SO_{3}}}{p_{SO_{2}}p_{O_{2}}^{1/2}} atm^{-1/2}$$
(7)
$$log_{10}K_{p} = \frac{5186.5}{T} + 0.611 log_{10}T - 6.7497$$
(8)

Concentration range	Concentration range Number of times		Number of times
$(mg/Nm^3 SO_2)$	30-minute average	(mg/Nm ³ SO ₂)	30-minute average
at 11% O ₂	was in noted range	at 11% O ₂	was in noted range
0-50	100	400-450	25
50-100	380	450-500	20
100-150	425	500-550	20
150-200	275	550-600	20
200-250	175	600-650	15
250-300	75	650-700	10
300-350	60	700-750	5
350-400	60	750-800	0

Table 1 Frequency of Observation of SO₂ in Mass Burn Incinerator APC Inlet [11]

Sulfur oxides have importance as a pollutant due to their health effects (esp. in combination with respirable particulate matter) and their corrosive effects on natural and man-made materials. In the combustion system, sulfur trioxide reacts with water vapor to form sulfuric acid, which has a dew point considerably above that for pure water. To prevent serious corrosion from sulfuric acid (e.g., in the stack), combustion system cold-end temperatures should be limited to a value safely above the sulfuric acid dew point. Pierce [13] presented the data in Table 2 for the percent SO_x as SO_3 .

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	Percent Sulfur in Fuel					
Fuel	<u>0.5</u>	<u>1.0</u>	<u>2.0</u>	<u>3.0</u>	<u>4.0</u>	<u>5.0</u>
Oil - 5% excess air	2%	3%	3%	4%	5%	6%
Oil 11% excess air	6%	7%	8%	10%	12%	14%
Coal 25% excess air	3% - 7%	7% - 14%	14% - 28%	20% - 40%	27% - 54%	33% - 66%

Table 2 Percent Conversion of SO2 to SO3 in Fuel Burning [13]

An an analysis of 35 sets of gas analyses from multiple hearth furnaces burning domestic sewage sludge, Niessen [3] showed a fairly regular partitioning of sulfur oxides between SO_2 and SO_3 (98.46% SO_2 , 1.54% SO_3). The reported uncontrolled SO_2 concentration (corrected to 7% O_2) ranged from 6.98 ppmdv to 1081.47 ppmdv with an average of 577.6 ppmdv and a standard deviation of 353.4 ppmdv.

2. The Halogens and their Acids

The halogens are important constituents of waste. Some of the organic compounds of the halogens are toxic, carcinogenic or otherwise of concern regarding their health effects. Further, the acid gases formed during combustion are strong acids that can attack metals (e.g., in boilers) and can be highly corrosive in their water solutions in scrubbers. Chlorine and hydrochloric acid are generally the most important members of this family although fluorine, bromine, iodine and their acids can be more problematic in system design, operations and pollutant control.

Chlorine appears in waste streams both in inorganic salts (e.g., sodium chloride) and in organic compounds. In the combustion of many industrial wastes and, importantly, in municipal solid wastes, a substantial quantity of organic matter containing chlorine may be charged to the furnace. In the combustion environment (usually containing hydrogen in considerable excess relative to the chlorine) the organic chlorine is converted, almost quantitatively, to hydrogen chloride (hydrochloric acid). In mass burning incinerators, about 35-40% of the stoichiometric HCl generated through combustion is absorbed by alkaline constituents of the ash (Na₂O, CaO etc.).

The importance of hydrogen chloride emissions from combustion sources depends on the quantity in the fuel, but is usually small. Of importance to system designers, however, is the high solubility of hydrogen chloride in scrubber water (or in the condensed "dew" on cold-end surfaces in boilers). Acid attack and chloride corrosion of ferrous metal surfaces is well-demonstrated. A further problem is the stress corrosion cracking phenomenon associated with the austenitic stainless steels (304 stainless and, to a degree, 316 stainless, for example) in the presence of chloride ion under acidic conditions.

As for SO₂, HCl concentration in the exit gases will change with time. The variability is significant since, in many plants, the SO₂ concentration is used as the control variable for all acid gas control (e.g., the lime slurry feed rate to a semi-dry scrubber). Since there is no reason to expect the SO₂ variation to be tracked by other acid gases such as HCl, there may be times when the HCl is over-controlled and other times when HCl is under-controlled.

Stress corrosion cracking is characterized by formation and rapid propagation of cracks in areas under stress (including both mechanical stresses and "locked-in" thermal stresses from welding operations). There is little material removal in such a corrosion process but the resulting mechanical or structural failure can be quite rapid and catastrophic (e.g. the disintegration of high speed fan blades). The presence of HCl or other combinations of chlorides and acidic conditions requires special consideration to the selection of materials of construction. Often, extra low carbon stainless steels (e.g., 316-ELC) or costly high nickel-chromium steels such as the Hastelloy or Inconel alloys are necessary to deal with this problem. Sources of organic chlorine in wastes are shown in Table 3.

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	<u>Chlorine</u>	
Compound	(weight %)	<u>Uses</u>
Polyvinyl chloride	59.0	Bottles, film, furniture
Polyvinylidene chloride	73.2	Film
Methylene chloride	82.6	Solvent
Chloroform	88.2	Anesthetic
DDT	50.0	Insecticide
Chlordane	59.0	Insecticide

Table 3 Percent Chlorine in Common Plastics and Chemicals

In the incineration environment, the halogen acids (HX) and the free elements (X_2) are in dynamic equilibrium with water vapor and oxygen according to the Deacon reaction:

$$2HX + 0.5O_2 \leftrightarrows H_2O + X_2 \tag{9}$$

While the reaction is usually negligible for fluorine and hydrofluoric acid, the conversion can be significant under some conditions for the chlorine, bromine and iodine. For the equilibrium constant given by:

$$K_{p} = \frac{P_{H_{2}O} P_{X_{2}}}{\frac{2}{p_{HX}} P_{O_{2}}} atm^{-1/2}$$
(10)

The temperature dependence of K_p (for partial pressure in atmospheres and temperature (T) in °K) is given by:

Chlorine	$\ln K_{\rm p} = -8.244 + 1.512 \text{x} 10^{-4} \text{ T} + 7,087/\text{T}$	(11)
Bromine	$\ln K_{\rm p} = -18.72 - 1.016 \times 10^{-3} \mathrm{T} + 20,400/\mathrm{T}$	(12)
Iodine	$\ln K_{p} = -25.35 - 1.980 \times 10^{-4} \text{ T} + 35,410/\text{T}$	(13)

D. Nitrogen Oxides

Nitric oxide (NO) is produced from its elements at the high temperatures attained in furnaces and incinerators. At lower temperatures, NO formation is limited by equilibrium (which favors dissociation to the elements) and kinetics. Although only a small portion of the NO further oxidizes to nitrogen dioxide (NO₂) within the furnace, oxidation does take place slowly after leaving the stack at the temperatures and high oxygen concentrations of the ambient atmosphere. The air quality impact of the nitrogen oxides (referred to collectively as NO_x and reported as NO₂) arises from their participation in atmospheric chemical reactions. These reactions, especially those stimulated by solar ultraviolet light (a photochemical reaction), produce ozone and a variety of oxygenated compounds which account for the visibility reduction and eye irritation associated with smog.

In combustion systems, nitrogen oxides arise through fixation of nitrogen from the combustion air with oxygen (thermal generation). Also, NO_x is formed by oxidation of nitrogen entering the system bound in the fuel (fuel nitrogen generation). At very high temperatures, the dominant source of NO_x is thermal generation but, at lower temperatures, fuel nitrogen mechanisms dominate. The keys to the distribution among these mechanisms are the equilibrium and kinetic relationships which control the process.

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1. Thermal Generation

The fixation of nitrogen with oxygen occurs by the following overall chain reaction mechanism after Zel'dovitch [14].

$$O_2 + M \leftrightarrows 2O + M$$
 (14a)
 $O + N_2 \leftrightarrows NO + N$ (14b)

$$0 + 10^{\circ} \rightarrow 10^{\circ} + 10^{\circ} + 10^{\circ}$$

$$N \cdot + O_2 \leftrightarrows NO + O \cdot$$
 (14c)

and, in fuel-rich flames by the additional reaction

$$OH \cdot + N \cdot \leftrightarrows NO \cdot + H \cdot$$
 (14d)

The chain initiating step [Eqn. 14a] involves the collision of oxygen molecules with other molecules in the gas (represented by "M") to form oxygen radicals. Combining the mechanism equations [Eqns. 14a, 14b, and 14c] and correcting for the presence of excess air, results in Eqn. 15 after Bowman [15] for the *net* generation rate of NO_x (noting that, by convention, the molecular weight of the NO_x is taken to be that of NO_2):

$$\frac{d(f_{NO_x})}{dt} = 1.45 \times 10^{17} T^{-1/2} \exp\left(\frac{-69,460}{T}\right) \left[\frac{P}{RT}\right]^{1/2} (f_{N_2}) (f_{O_2})^{1/2} \ sec^{-1}$$
(15)

where (f_{NOx}) , (f_{N2}) , and (f_{O2}) are mol fractions and T is in °K. Equilibrium considerations lead to the following relationship for the overall reaction

$$N_2 + O_2 \leftrightarrows 2 \text{ NO}$$

 $K_p = \frac{(NO)^2}{(N_2)(O_2)} = 21.9 \exp\left(\frac{-43,400}{RT}\right)$ (16)

The rate of formation of NO is significant only at temperatures in excess of 1000 °C due to kinetic limitations, and doubles for every 40 °C increase in flame temperature. Thus, NO_x emissions are encouraged by high flame temperatures (e.g., by air preheat) and high excess air. NO_x can be reduced by:

- Water or steam injection or flue gas recirculation (to lower flame temperature);
- Operation at low excess air (to reduce oxygen concentrations);
- Staged combustion where the fuel is partially burned, heat is withdrawn through boiler surfaces, and then the rest of the required air for combustion is added (the overall effect is to lower the peak temperatures attained after the combustion gases contain a net excess of oxygen); or
- Selection of burner designs ("Low-NO_x burners) which reduce the intensity (volumetric burning rate) of combustion, produce relatively long diffusion flames, or encourages either two-stage combustion or low-temperature gas recirculation.

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2. Fuel Nitrogen Generation

Studies by the U.S. Environmental Protection Agency and other researchers worldwide have suggested an important contribution of fuel nitrogen sources to NO_x emissions from combustion systems. The California Air Resources Board has concluded [16] that fuel nitrogen accounts for 75 to 80 percent of the total NO_x from refuse incineration plants. The mechanism by which the fuel nitrogen is converted into nitrogen oxides was not specified, however, and the data base supporting the conclusion was limited. Laboratory experiments have typically shown that 15 to 100% of the fuel nitrogen can be converted with the higher conversion efficiencies obtained when the fuel nitrogen content is low (<0.5%) or when the combustor is operated lean [17].

Laboratory data clearly show that the NO_x concentrations arising by the fuel nitrogen route can be several times the equilibrium thermal NO_x levels. With time, at furnace temperatures where reactions are fast, the gas phase concentration can be expected to shift toward the equilibrium level to the extent limited by the reaction rate. Thus, if one compares the time variation of observed NO_x concentration in two, isothermal scenarios: Scenario No. 1 with 100% thermal NO_x and Scenario No. 2 with 100% fuel nitrogen NO_x one might expect to see behavior as indicated schematically in Figure 1. Here, the scenario No. 1 thermal NO_x rises slowly toward the equilibrium level and then trending downward with time, approaching the equilibrium value from above. Note that along a real reaction path where the temperature eventually falls (e.g., in a boiler), the reaction will ultimately "freeze" and the final NO_x in the stack gas could be "anywhere".





One might speculate that the nitrogenous compounds in municipal solid waste (grass clippings, protein material in food waste etc.) generate NO_x via the fuel nitrogen mechanism. However, a statistical analysis by Rigo et al. [18] of a comprehensive collection of NO_x data from mass burn MSW incinerators and a phenomenological analysis of the combustion process convincingly suggest that fuel nitrogen is, in fact, of limited importance in MSW incinerator NO_x emissions. In the analysis, mass burn combustion was characterized as a staged process starting with gasification under air-limited conditions on the grate followed by completion of combustion in the over fire space after oxygen addition and mixing from the overfire air system. Along this combustion path, most of the fuel-bound nitrogen in the waste is released in the gasification stage as elemental nitrogen. Subsequent completion of the oxidation process over the bed can produce some NO_x via the thermal NO_x route but to no greater extent than from air-supplied nitrogen.

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3. Emission Estimation

Because of the complexity of NO_x generation and destruction within a combustor, emission estimation without data as a confirmation is uncertain. In many circumstances, however, an estimate is required if, for nothing else, to provide a rough starting point from which to assess the importance of this pollutant. The techniques described below provide such a rough estimate. The uncertainty of the results, however, is significantly greater than for the emission estimates of the other gaseous pollutants.

a. Fuel Nitrogen. A kinetic evaluation by Soete, reported by Bowman [Eqn. 17], can be solved iteratively to estimate the fraction "Y" of fuel nitrogen N_f converted to NO. For $[N_f]_o$ equal to the NO concentration for 100% conversion of N_f to NO and $[O_2]$ the oxygen concentration (g mol/cm³) and temperature T in degrees K, the following obtains:

$$Y = \left[\frac{2}{\frac{1}{Y} - \{\left[2.5x10^3 \left[N_f\right]_o\right] / \left[T \exp(-3150T)[O_2]\right]\}}\right] - 1$$
(17)

The Soete relationship was developed using laboratory burners with several nitrogen-containing fuels. Comparison of Soete predictions evaluated at adiabatic flame temperature conditions with the concentration of NO_x measured in the stack of grate-type solid waste incinerators suggests that the Soete relationship used in this fashion predicts about four-times the measured value at the stack. The demonstrated importance of fuel nitrogen in increasing NO_x emissions can be of particular importance for industrial waste incineration. Organic liquid wastes may contain solvents (e.g., pyridine, amines, or other chemicals) with a substantial "fuel nitrogen" content.

b. Fossil Fuels Because nitric oxide emissions are determined by flame temperature it has been observed [19] for a variety of fuels that the heating value of the fuel provides a better correlating parameter than the mass of fuel. Data are therefore usually converted to units of kilograms of NO_x (expressed as NO₂) per million kcal. The median emission rate for the small scale PHS tests [20] is 1 kg NO_x per 3.27 x 10^6 kcal heat release, or 0.31 kg NO_x per 10^6 kcal. Correlations of NO_x formation that have been proposed by PHS for coal, gas and oil [19] are:

$$kg\frac{NO_x}{hr} = \left(\frac{\frac{kcal}{hr}}{3.24x10^6}\right)^{1.18}$$
 for natural gas (18a)

$$kg\frac{NO_x}{hr} = \left(\frac{\frac{kcal}{hr}}{2.18x10^6}\right)^{1.18} for oil$$
(18b)

$$kg\frac{NO_x}{hr} = \left(\frac{\frac{kcal}{hr}}{1.87x10^6}\right)^{1.18} for \ coal \tag{18c}$$

If the emission rate of 1 kg NO_x per 3.27×10^6 kcal associated with the 2.7 tonne/day PHS municipal refuse test incinerator (0.28 x 10^6 kcal/hr with 2470 kcal/kg refuse) and the corresponding NO_x emission rate (0.0857 kg/hr) are cast into the same functional form as Eqn. 17, the resulting constant term within the brackets is 2.26×10^6 . However, it must be recognized that this correlation provides only rough estimates, since factors such as furnace heat loss and excess air which are known to influence NO_x production are not taken into account. That the data for the three fossil fuels are correlated best with an exponent on firing rate greater than unity is a consequence of the increase in the mean emission factor with increases in furnace size.

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c. Incineration Sources

REFUSE INCINERATORS. The PHS [19] obtained a comparable correlation for refuse combustion in small units with an exponent of 1.14 in place of 1.18. In the absence of sufficient data to obtain a reliable estimate of the exponent for municipal-scale refuse incinerators, the value of 1.18 is recommended to extrapolate data from one size to another. A summary of U.S. municipal waste combustor NO_x emission data is shown in Table 4.

Table 4. Summary of NOx Emission Data from Municipal Incineration Combustors [21]

		NOx Emissions		
	-	(ppm at 7% O ₂)		
Combustor Type	No. Units	<u>Average</u>	<u>Range</u>	
Mass burn, refractory wall	8	155	59-240	
Mass burn, waterwall	24	240	154-370	
Refuse Derived Fuel	5	270	195 - 345	
Modular, Excess Air	8	140	105 - 280	
Modular, Starved Air	5	215	86 - 280	
All Types	51	210	59 - 370	

Emission factors for the combustion of wastes other than municipal refuse can be approximated by analogy with the combustion processes for gas, oil, coal, and (mass burning) refuse. If waste analysis indicates a fuel nitrogen content greater than, say, 0.2%, and/or operation will be at a relatively high excess air level (as is often the case for waste combustion), consideration should be given to increasing the estimate above the emission rate calculated using Eqn. 17. An estimate of the maximum NO_x emission can be made using the equilibrium relationship in Eqn. 15 (evaluated at the adiabatic flame temperature). Experience shows, however, that such a technique produces unrealistically high estimates as do the estimates made with the Soete relationship (Eqn. 17). It may be useful, however, to use the equilibrium and Soete relationships to judge the shape of the emission factor curve as a means to extrapolate or interpolate field data.

LIQUID INJECTION INCINERATORS. For the special case of a liquid injection vortex-type incinerator Kiang [23] developed a dimensional relationship for the formation of NO:

$$log_e[Y] = 2.9 - 1.027S - 0.4665 log_e[percent \ O_2] - \frac{158.2452}{T}$$
(19)

Where:

Y is percent of fuel nitrogen converted to NO (as a percent); S is the mean residence time (seconds); Percent O_2 is the dry percent oxygen (as a percent); and T is the temperature in degrees F.

Kiang found that the formation of NO_x was not related to the specific nature of the nitrogen in the waste chemistry (-NO, -CN, -NH₂ etc.) nor to the partial pressure of water vapor in the incinerator flue gases.

SLUDGE INCINERATORS. In an analysis of over 55 data sets for multiple hearth sludge incinerators, Niessen [3] was unable to develop a statistically significant correlation for the NO_x emission rate as a function of incineration characteristics. As is often the case, no information on sludge nitrogen content (contributing to fuel nitrogen NO_x) was available to match the NO_x data. The average NO_x concentration for the entire data base was 283.6 ppmdv (corrected to 7% O2). The standard deviation of the NO_x data was 165.2 ppmdv.

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A study of NO_x emissions by Goldberg et al. [22] showed that most of the NO_x was derived from the 2% nitrogen found in the sludge solids. Their findings showed:

- High excess air increased NO_x;
- Lowest NO_x was achieved when all of the combustion air was supplied from the center shaft warm air return ducting. Use of ambient air introduced above the burning zone increased NO_x;
- Maintaining low NO_x emissions required a high degree of process stability. This includes stable feed rate, feed characteristics and hearth temperatures.
- Operators need to avoid over-correction when minor process upsets require intervention;
- Increasing afterburner temperatures increased NO_x;
- Increasing cake solids (lower fuel firing) reduced NO_x on a mass per dry ton basis; and
- Increased scrubber water flow (volume per volume of gas) decreased NO_x.

Prior to experimentation, the furnace NO_x levels were approximately 240 ppmdv. After efforts in the areas noted, the NO_x for four furnaces varied from 67 to 101 ppmdv.

E. Air Toxics

The name "air toxics" has been applied to a spectrum of organic and inorganic compounds found in stack emissions. The U.S. EPA defines air toxics as pollutants known or suspected of causing serious health concerns such as cancer or birth defects. EPA's list of air toxics can be found at the website <u>www.epa.gov/ttnatw01/187polls.html</u>.

The health effects triggering inclusion in the air toxics list are summarized in Table 5. In many (if not most) cases, the concentration of these compounds in the stack gases is small: they are "micropollutants". Thus, after dispersion and dilution of the stack gases by the atmosphere, the resulting average ambient air concentrations and associated

Health effect class	Characteristic impact
Toxic	Kills cells or the organism by poisonous nature. Often, a threshold dose (mg/kg body
	weight) characterizes the onset of impacts.
Carcinogenic	Causes cancer. Often the dose-response function is characterized as a log-log correlation
-	between dosage and the probability of observing cancerous cells.
Mutagenic	Causes mutation of cells.
Teratogenic	Causes changes in cells during pre-natal development. May lead to birth defects or
-	deformity.

Table 5. Health Effect Classifications

inferred health risk consequences are often acceptable. However, since these pollutants are directly related to human health effects, they receive focused attention by both regulatory agencies and the general public.

The incineration of wastes is, not unexpectedly, viewed as an important potential source of air toxics emissions. This results from the fact that, being fired with diverse wastes, contamination by trace metals (some of them toxic) is certainly possible, if not probable. Further, "wastes" may include a variety of toxic organic compounds targeted for disposal or toxics formed as byproducts of industrial preparation reactions. Finally, due to moment-to-moment variation of the feed and other parameters, the incineration environment degrades from time-to-time thus allowing a "puff" of toxic material to escape. The combination of these possibilities leads to intense scrutiny of incineration regarding air toxics.

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1. Metal Emission Rates

The simplest approach to estimating metal emission rates is to assume that the relative proportions of the metal in the emitted particulate matter is the same as that of the metal in the total inorganic fraction of the feed. There are several potential weaknesses in this approach.

- Some metals are trapped in relatively massive bottom ash and are never emitted to any significant degree. The chromium in large pieces of stainless steel is an example of this.
- Some metals are emitted strongly relative to their concentration in the ash. Mercury and its compounds are examples. Because of the high volatility of mercury, almost 100 % of this metal is emitted from the furnace. Other metals such as cadmium, lead and selenium (part of the "semi-volatile metals" group) show lesser but often significant degrees of emission enhancement. Barton et al. [24] ranked several key metals by their "volatility temperature" (Table 6). The volatility temperature is the temperature where the sum of the vapor pressure of all species containing the metal that are present at equilibrium weighted by their relative concentrations is 10⁻⁶ atm.

Metal	Volatility Temp (°C)	Metal	Volatility Temp (°C)
Mercury	16	Antimony	660
Arsenic	32	Barium	849
Thallium	138	Silver	904
Cadmium	216	Beryllium	1216
Lead	627	Chromium	1610

Table 6 Barton Volatility Temperature [24]

In a few instances, the balance between these and other factors influencing emissions has been studied and estimates can be made of the partitioning of feed metals between bottom ash and fly ash emissions. This is the case for sewage sludge incinerators. Estimation methods are presented below for this source category. Care must be shown, however, that overly simplistic approaches to estimation are not applied without consideration of the potential errors.

a. General Factors Affecting Heavy Metal Emission Rates

The controlled (post-APC) emission rate of heavy metals (relative to the metal content of the feed waste) for incinerators reflects the interaction of several waste and system parameters:

- Waste metal content;
- Operating temperature;
- Waste chloride content;
- Flow patterns leading to solids drop-out ahead of APC; and
- APC control efficiency as a function of particle size.

The quantity of each metal in the feed is the basic scalar of emissions. Metals in waste arise from several sources including the waste sources, industrial process conditions, consumer preferences, and so forth. Data on metal content in a variety of wastes can be found in the literature [1]. The metals content in wastes often varies from day-to-day.

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The temperature of the combustion environment has an impact on metal emissions:

- At elevated temperatures, many heavy metal compounds decompose and/or vaporize (Table 7). The higher the temperature, the larger the fraction of the specific metal that is vaporized. This temperature effect is particularly important for mercury, cadmium, arsenic, and (to a lesser degree) lead. Reviewing the boiling points of the oxides of toxic metals in a given waste may be of some value in anticipating volatilization behavior but, especially for hazardous waste incineration or where halogen salts are present, the chlorides and/or bromides may be equally or more important.

Volatility temperature		Volatility temperature	
Deg C at 0% Chlorine	Principal vapor species	(Deg C) at 10% Chlorine	Principal vapor species
1613	CrO ₂ /CrO ₃	1610	CrO ₂ /CrO ₃
1210	Ni(OH) ₂	693	NiCl ₂
1054	Be(OH) ₂	1054	$Be(OH)_2$
904	Ag	627	AgCl
849	Ba(OH) ₂	904	$BaCl_2$
721	Tl_2O_3	138	TIOH
660	Sb_2O_3	660	Sb_2O_2
627	Pb	-15	PbCL ₄
318	SeO_2	318	SeO ₂
214	Cd	214	Cd
32	As_2O_3	32	As_2O_3
14	Hg	14	Hg
	Volatility temperature <u>Deg C at 0%</u> <u>Chlorine</u> 1613 1210 1054 904 849 721 660 627 318 214 32 14	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

Volatility temperature: The temperature at which the vapor pressure is 1×10^{-0} atm.

Table 7 Volatility Temperatures for Various Metals Showing Chlorine Effects [25]

For lead, environmentally important vapor pressure functions (P in atm and T in °K) are given as follows:

• Lead [447]

 $\log_{10} P = -10130/T + 8.28 - 0.985(\log_{10} T)$ (20)

- Lead Oxide [447]
 - $\log_{10} P = -10598/T + 6.012 \tag{21}$

- As temperatures drop, a fraction of the metals condense. Heterogeneous nucleation (condensation on existing particulate) is the dominant mechanism rather than homogeneous nucleation. This favors deposition on the small particles that present a surface area disproportionately greater than their mass fraction. This "fine particle enrichment" phenomenon is particularly important from an emission standpoint since the collection efficiency of most APC systems decreases as the particle size decreases. Thus, the net emission rate of volatile metals usually increases as the combustion temperature increases.

2. Metals Emissions from Municipal Waste Combustors

a. General. Data that indicate the range of uncontrolled emission rates of metals from Municipal Waste Combustors (MWCs) are limited. Other than for the special case of mercury (discussed below), these pollutants are captured in a fabric filter or electrostatic precipitator particulate collection system such that stack emissions are well below regulatory limits. Also, (again, except for mercury), regulations only address the ultimate emission level or

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concentration and do not specify a required collection efficiency. Thus, there is little incentive to collect inlet concentration data.

Studies attempting to close a material balance on heavy metals around MSW furnaces show wide variations. Some of the variation reflects the difficulty in obtaining representative samples; some variation is due to the different process conditions in the incinerators; and, undoubtedly, some is due to differences in the characteristics of the waste itself. Table 8 indicates the reported observed range in the reported fraction of metal in the waste that appears as the "uncontrolled emission rate" (ahead of air pollution control) for three mass burn systems [1].

		Element				
	Cd	Cr	Fe	Hg	Pb	Zn
Low Value	37.3	2.2	0.4	93.5	5.5	13.6
High Value	96.3	7.0	1.0		42.0	58.0

Table 8. Fraction (%) of Metal in Waste Appearing in Furnace Flue Gases

b. Mercury. In MWC furnace gases, the concentration and emission chemistry for mercury and its compounds are variable. Almost all of the mercury in the feed waste appears in the furnace gases because of the high volatility of elemental mercury (boiling point 357 °C) and the fact that all of its compounds decompose at relatively low temperatures,. Mercury pollutant control efficiency data must be taken using simultaneous inlet and outlet determinations since ratios of "controlled emissions measured in the morning" to "uncontrolled emissions measured in the afternoon" are of uncertain validity. Citations of "negative collection efficiencies" in the literature are symptomatic of this effect.

The chemistry of the mercury in the flue gases also has an effect on the accuracy of mercury emission data: elemental mercury (Hg or Hg₂), mercuric or mercurous chloride (HgCl₂ or HgCl) mercuric or mercurous sulfide (HgS or Hg₂S) etc. The chemistry-related effects result from the impact of physical form (gas or solid) and/or reactions in the sampling train on reported mercury quantities. Therefore, data sets under analysis need to be annotated with the specific sampling/analysis methodology used and, if the methodology differs, one must assure that apparent trends or other conclusions are valid.

Also, there are many effects of process variables on mercury control effectiveness. Temperature in the control device is very important. However, other variables such as the inlet mercury concentration and the presence of reactive chemicals such as hypochlorite ions in scrubbing solutions may also influence reported collection efficiency. Another process impact relates to the tendency of some processes (e.g., RDF-fired furnaces) to produce a flue gas with a high concentration of char particles or soot. The strong adsorption characteristic of carbon for mercury and its compounds leads to low apparent mercury concentrations in the flue gas. Since the starting mercury concentration is reduced, the percent mercury control effected by some back-end air pollution control systems discussed below, (activated carbon injection is often used) may appear low.

The consequence of these complexities is that data on mercury emissions and control effectiveness are often inconsistent. Data from several sources may not conveniently "group" nor are process trends (e.g., control effectiveness as a function of temperature) easily visualized by simple data plots. It may not be appropriate to aggregate data for several plants (which may have different mercury chemistries in the waste and in the flue gases) to determine the potential control effectiveness of a particular technology.

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In general, the uncontrolled mercury emission in MWCs has decreased as battery manufacturers (a major source of mercury in MSW) have shifted to new electrochemical concepts. Also, many of the medical uses of mercury including both mercury-containing medicinals (such as calomel creams) and equipment (e.g., blood pressure devices and thermometers) have declined.

3. Metals Emissions from Hazardous Waste Incinerators

The emission of metals from hazardous waste incinerators is highly variable. This reflects the wide range of wastes that are fired in such devices. The general, guidelines for evaluating metal volatilization given above suggests, however, that metal emissions from these units (when the elements are present in the waste) should be relatively high: high temperature operation coupled with the presence of organic chlorine compounds.

4. Metals Emissions from Fluid Bed Sewage Sludge Incinerators

The quantity of each metal in the feed sludge is the basic scalar of emissions. Metals in sludge arise from several sources including industrial discharges (esp. plating wastes), corrosion of plumbing materials, street runoff (esp. deposited lead compounds from lead containing paints and use of gasoline containing tetraethyl lead as an antiknock additive) and other domestic and industrial activities. The metals content varies from day-to-day reflecting a diversity of meteorological and other factors.

As noted, the temperature of the combustion environment has an impact on metal emissions. Fluid bed operating temperatures are selected to minimize fuel use and, also, to mitigate the volatilization process (815-850 °C). Correlations of furnace temperature with emission rate (3,26) show little increase in volatile metal emissions below 870 °C. Sludge chloride content increases the sensitivity of lead and cadmium emissions to bed temperature due to the high volatility of the metal chlorides (PbCl₂ and CdCl₂) at combustion temperatures. Chloride ion concentration in sewage sludge varies widely but is usually below one-half percent (dry basis). However, when the sludge is conditioned with lime and ferric chloride to aid in dewatering, the chloride ion concentration can approach seven to nine percent.

An inherent feature of most fluid bed sludge incinerators is that 100% of the ash content is carried off in the flue gases leaving the bed. In most instances where sludge incinerator emission estimation is necessary, it is desirable to have a technique that calculates the emissions based on the metal content of the raw sludge (which is the type of metals data most available for treatment plants). Where possible (when sludge feed rate and metals analysis are given in association with emission data), sludge heavy metal rates are used as "inlet" values to calculate efficiency. Otherwise, a direct analysis of the "inlet loading" particulate catch can be used.

It should be noted that in passing through the equipment train between the fluid bed and the APC system, a fraction of the particulate may settle out. This material is drawn off from ash hoppers located in the ductwork, beneath boilers etc. Consequently, the inlet loading to the APC system may not close a material balance on total ash or any specific element based on input from the feed sludge. However, the error induced by these (usually unquantified) withdrawals from intermediate system discharge points is such as to make the stack emission estimate conservative.

The most effective method to reduce metal emissions is through installation of highly efficient APC systems. The analysis of fluid bed emission data shown below determined the net metal emissions to be expected with high efficiency trains and explored the possible improvement that is achievable with several APC systems that are cascaded to achieve the target stack emission rate.

c. Emission Data. U.S. data on the emissions [1] of the key metals from incineration of sewage sludge in fluid bed incinerators for fluid beds run at temperatures below about 870°C.

ARSENIC CONTROL. Arsenic concentrations in the ash are generally lower in the Venturi (V) outlet relative to the inlet but increase for the V+ wet electrostatic precipitator (WESP) case. This suggests that volatil-

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ization processes move the arsenic to the very finest particulate fraction. This also shows in that the level of V control of arsenic is considerably below the overall particulate control level.

BERYLLIUM CONTROL. Data indicate that beryllium is usually concentrated in the relatively coarse particulate. This may reflect the characteristics of the source (metal turnings or grinding dust or relatively coarse beryllium containing minerals with soil origins rather than finely divided precipitates of soluble beryllium compounds). There is no observable enrichment process. This is not unexpected in view of the highly refractory character of beryllium oxide, chloride etc. consequently, with the high particulate collection efficiency of V+WESP combination, stack emissions of beryllium are often reported as "zero" or "less than the detection limit". Collection efficiency for beryllium is thus equal to or better than the overall total suspended particulate (TSP) control efficiency.

CADMIUM CONTROL. Data show that the cadmium is concentrated in the finer particulate. A substantial average enrichment factor is shown for the V and a still higher factor for the V+WESP. The enrichment process shifts cadmium from a relatively unimportant constituent in the total sludge ash to a much more significant constituent in the net emitted ash. Overall, cadmium collection efficiencies are significantly lower than the overall particulate control.

CHROMIUM CONTROL. Data for the several sludge sources comprising the data base show the high relative importance of chromium as a constituent in sludge ash. Due to the refractory character of chromium compounds, little enrichment is seen for the V. An enrichment factor of almost two-fold is observed for the V+WESP but this may be due in part to the depletion of lead values by the V thus enriching the apparent chromium content by significantly reducing the total metals. Overall chromium control levels are close to those for total particulate.

LEAD CONTROL. Although lead is often considered as "volatile", the data show a "negative" enrichment factor for a V discharge and still further lead depletion in the V discharge. This strongly suggests that the lead is heavily concentrated in relatively coarse particulate. Overall collection efficiency for lead is very high: generally at or above the total particulate control level.

NICKEL CONTROL. Nickel appears as a significant fraction of total metals. Enrichment phenomena do not appear significant and collection efficiency is only slightly below total particulate control levels.

d. Enrichment Factors. Emission data often show significant enrichment of the metal content of emitted particulate relative to the ash. The degree of enrichment is variable among the test data for any one metal and between metals. Quantification of the enrichment phenomena provides a means to develop estimates of elemental emission rates based on initial sludge chemistry and the (guaranteed) total particulate stack emission rate [1]. For such calculations, the enrichment factor (EF) employed should be conservative.

5. Metals Emissions from Multiple Hearth Sewage Sludge Incinerators)

a. Furnace Emission Characteristics. The heavy metal emission characteristics for multiple hearth furnaces (MHF) are somewhat different than those for fluid beds. As a staged combustion system, the MHF system exhibits the fine particle enrichment process but the key temperature is the combustion hearth temperature rather than the gas exit temperature. The metallic emissions of MHF systems were studied by Niessen [3] based on data from 95 emission tests (including 55 tests ahead of the APC device and 95 at the stack). These data often showed sensitivity to the combustion hearth temperature. Especially for the elements known to exhibit volatilization (arsenic, cadmium, zinc and lead), uncontrolled emissions calculated as a fraction of the element fed to the incinerator increased as the burning hearth temperature increased. The more refractory compounds of beryllium, copper, chromium and nickel showed lesser volatilization behavior. The relative temperature sensitivity was in line with expectations.

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b. Air Pollution Control Metal Capture Niessen [3] analyzed 45 sets of paired inlet-outlet metal concentration data from multiple hearth units burning domestic sewage sludge. The data indicate that the collection efficiency for some metals differs in comparison to the overall TSP collection efficiency. Inlet-outlet data pairs for TSP and for the individual metals showed similar trends to the uncontrolled emissions: sensitivity to the combustion hearth temperature for some elements and a lack of strong sensitivity for others.

F. Emissions of Organic Compounds

1. General

A priori estimation of the emission rates of the spectrum of organic compounds formed by combustion sources on a quantitative, speciated basis is not possible at this time. The time variation in the composition of the feed material and in the combustion process itself and the uncertain efficiency of air pollution control devices for organic compounds produces a scenario too complex to fathom. We know that compounds are both destroyed and created in the system so, unlike the case for elements, "mass balance" approaches to emission estimation for organic compounds are unproductive.

For a hazardous waste incinerator where relatively large concentrations of specific compounds of concern are found in the feed (the Principle Organic Hazardous Constituents or "POHCs"), one is able to track the overall degradation and removal process. One can measure and report a value for the Destruction and Removal Efficiency (DRE). Note, however, that selecting a compound to monitor (the POHC) which is likely to be formed from degradation of other waste components can present a problem to system acceptance testing: you may totally destroy the actual molecules of POHC present in the waste but fail the test because new molecules of POHC are formed.

2. Emissions of Specific Compounds

a. General. For an arbitrary mixed waste and a real incinerator/combustor system, it is not possible quantitatively and with accuracy to estimate the emission rate of incompletely burned POHCs from a first principles analysis. Incinerators are intended and are designed to effect 100 percent destruction. Their inability to do so (to some minor degree) generally is the consequence of a combination of subtle and unanticipated "failures" in mixing, in kinetics and other factors. Quantifying these design or operational problems is simply too complex and uncertain.

A second class of organic pollutant emissions arises from synthesis in the combustor. These pollutants are of several types:

- Fragments of feed organic material (e.g., an ethylene residue arForising from the quenching of dehydrogenation steps in ethane oxidation);
- Partially oxygenated fragments (e.g., the formaldehyde or CO that are formed in the combustion of almost any organic material);
- Compounds synthesized from specific precursor chemicals (e.g., the formation of polychlorinated dibenzo-p-dioxin from dimerization of polychlorinated chlorophenols);
- Compounds synthesized by the "combustor chemistry set" from molecular fragments (such as "de-novo" synthesis of chlorinated methanes when burning mixtures of chlorinated organic compounds); and
- De-novo synthesis that is catalyzed by solids in the combustor flow field (boiler deposits, captured particulate in dry APC devices, particles reacting "on-the-fly")

Clearly, quantitative estimation of emissions generated through these routes is even more outside the range of present day capability than is the estimation of the unburned fraction of feed POHCs. Consequently, in most cases, emission estimates for specific compounds must be based on the results of tests run in similar facilities and with similar wastes. Such data almost invariably show very small quantities of any one species. Further, the vast majority of the mass comprising the emissions are benign or relatively benign compounds.

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b. Polychlorinated Dibenzo-p-Dioxins. The several congeners and isomers comprising the polychlorinated dibenzop-dioxin (PCDD) and polychlorinated dibenzo-furan (PCDF) compounds are a special case in the assessment of organic compound emissions. The adverse health effects following exposure to these two classes of compounds had been considered by many researchers to be particularly significant. Thus, when relatively high concentrations of PCDDs and PCDFs were detected in the fly ash from municipal refuse incinerators in the late 1970's, a world-wide effort was triggered to assess the magnitude of the health effects, to determine how much was being emitted, to find out the chemical mechanisms by which they were being formed, to develop control technologies and so forth. Literally tens of millions of U.S. dollars were spent on tests, studies and developments for this special set of compounds over the following 15 years. An important outcome of the dioxin programs was the "popularization" and politization of health effects as a factor in facility acceptance, siting evaluations, permit approvals etc.

The health response to a chemical can be described in terms of the several acute effects listed in Table 5. Also, there can be a spectrum of non-acute effects ranging from observable but non-lethal disabilities to subtle changes in the biochemical reactions within the organism that have no recognizable adverse health consequence. In all but laboratory situations, human exposure to dioxin has been below the acute toxic level. Although elevated industrial exposures have produced chloracne (a severe skin eruption) and asthenia (numbing of the tactile response), there do not appear to be clear-cut life-threatening toxic responses in human beings for exposures even orders of magnitude above the exposures resulting from refuse combustion.

Carcinogenicity and mutagenicity effects are also questionable in human beings, especially for the low concentration exposures from refuse combustion. Some spontaneous abortions were associated with the massive human exposures in the Seveso incident in Italy (involving the rupture of a process reactor containing a reacting mass of chlorinated phenolic chemicals that also contained dioxin compounds that had formed as side-reactions). In Seveso, however, the role of dioxin per se was clouded by the concurrent release of very large quantities of a spectrum of chlorinated phenolic compounds that have their own adverse health effects.

PCDD toxicity assessments must take cognizance of the fact that there are 75 discrete chemical compounds comprising the PCDD family: from 2 (the dichloro-PCDD compounds) to 8 (the octachloro-PCDD compounds) chlorine atoms (congeners) dispersed in differing spatial relationships (isomers) among the eight sites in the base dioxin molecule. Also, one must consider the several polychlorinated dibenzo furan (PCDF) species that usually occur along with the PCDDs and appear to have the same genesis. The PCDFs include 135 different compounds. In the eyes of most investigators the "Dioxin Problem" is the combined health effect due to both PCDDs and PCDFs.

Each of the 210 dioxin/furan compounds produces a different toxic response in a given receptor organism. There are also significant differences in the toxic response between receptor organisms. For example, the dose at which one half of a population of guinea pigs are killed (the lethal dose for 50% or LD/50) for the most toxic PCDD compound (2,3,7,8 tetrachloro dibenzo p-dioxin or 2,3,7,8 TCDD) is 0.6 μ g/kg. The molecular structure of 2,3,7,8 TCDD is shown in Figure 2. The LD/50 for this compound is ten-thousand times greater (5,051 μ g/kg) for the hamster, a rodent species not greatly unlike the guinea pig. One must decide whether the target species of concern (e.g., human beings) are more like guinea pigs or hamsters. If one simply seizes on the "worst case", one can end up with a too conservative result. If one picks the "best case", one is challenged by project adversaries who see a "white wash."



2,3,7,8 Tetrachloro dibenzo-p-dioxin (TCDD)

Figure 2 Structure of 2,3,7,8 tetrachloro dibenzo-p-dioxin (TCDD)

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The U.S. EPA and many other health groups worldwide apply a "Relative Toxicity Factor" to the mass emission of each compound or group of compounds in the PCDD/PCDF family to provide a weighted estimate of the health significance where the distribution of compounds among the 210 PCDD/PCDF compounds differs. The factor normalizes the health effect of a given dose of a compound to that of 2,3,7,8 tetrachloro dibenzo p-dioxin (2,3,7,8 TCDD), the most toxic of all the 210 PCDD/PCDF compounds. Laboratory animal dose-response data were used to determine the factors. There are two sets of factors used in the United States for "dioxin risk assessments." These include the U.S. EPA factors (developed by the EPA Cancer Advisory Group or "CAG") and the Eadon factors used by the New York State Department of Health (NYDOH). European countries vary: some have their own numbers and some have adopted the U.S. EPA values. µg/kg. The toxicity equivalence factors used by EPA may be reviewed at: http://www.epa.gov/raf/files/tefs-for-dioxin-epa-00-r-10-005-final.pdf.

Numerous theories have been proposed to account for PCDD/PCDF emissions but no consensus has been reached. The four principal classes of the theories [27, 28, 29, 30, 31, and 32] are:

- CDD/CDF compounds are present in the waste and survive passage through the combustion environment undestroyed;
- CDD/CDF compounds are formed in the course of gas-phase reactions involving chlorinated precursors such as chlorobenzenes, chlorophenols or polychlorinated biphenyls;
- CDD/CDF compounds are formed in the course of heterogeneous gas/solid reactions involving surface reactions of gas phase precursors and fly ash; and
- CDD/CDF compounds are formed at relatively low temperatures (250-600 °C) in solid phase reactions on the surface of fly ash involving metal chlorides or chlorine in the flue gas and fly ash carbon (de novo synthesis).

The "survival" theory has been weakened by several detailed analyses of waste that suggest that not all wastes contain CDD/CDF compounds even though they are found in almost all effluents. Also, survival of these species at relatively modest temperatures (say, over 600 $^{\circ}$ C) makes them unlikely to escape destruction [329, 330, 528].

In-furnace reactions could generate the precursor compounds and the reactions forming the CDD/CDF compounds are known and not unreasonable: especially those involving well-configured precursors (e.g., chlorophenols, chlorobenzenes, PCBs) where the number of steps and the complexity of steps between precursor and CAD/CDFs is limited. However, although this route is plausible, the low concentrations of the precursors make it difficult to conclude that this is the dominant source of the CDD/CDF compounds.

Bench-scale experiments by several investigators have provided convincing evidence that CDD/CDF compounds can be created downstream of the furnace via a catalytically assisted reaction on the surface of fly ash with maximum tetra- to octa-PCDD and PCDF formation near 300 °C. As the temperature falls below 250 °C, the reaction rate falls quickly to near zero. The precursor materials involved are simple: carbon char and inorganic chlorides. Interestingly, most researchers do not show a correlation of CDD/CDF generation with the HCl concentration in the flue gases and there has been no conclusive scientific evidence that specific solid waste components (such as polyvinyl chloride plastics) are responsible for any significant fraction of the total CDD/CDF. Much of the data show that at temperatures between 200 and 300 °C, generally more than 80% of the mass of the compounds are in the gaseous emissions rather than adsorbed on the emitted particulate.

Tests on 12 MWC's in Belgium [33] showed a strong correlation between the formation of PCDD/PCDF compounds and the operating temperature of the ESP used for particulate control. The authors conducted a regression analysis of the natural log of the emitted PCDD/F concentration (ng TEQ/Nm³) against the ESP temperature (°C). Their correlation showed:

$$Log_e[PCDD/F] = 0.016T - 3.001 (R^2 = 0.85)$$

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Their analysis showed a weaker (more scatter) but significant dependency between the PCDD/F concentration in the collected fly ash and the ESP temperature. No dependency was seen in their data between PCDD/F concentration and the concentration in the flue gases of HCl, HF, PAH, SO₂ or the total dust loading. A modest correlation ($R^2 = 0.63$) was observed showing increasing PCDD/F with increases in CO for CO ranging from 15-30 to 125 mg/Nm³ (wet basis).

Based on this generation hypothesis, it is clear that CDD/CDF can be minimized through operation of the MWC such as to (1) minimize formation, carryover and persistence of carbonaceous particulate and (2) minimize the residence time of any carbonaceous particulate in the critical 300 - 450 °C reaction zone. The specific design and operational strategies to accomplish these objectives include:

- Mix solid waste prior to firing to minimize irregularities in heat release, moisture content and oxygen demand. This will avoid cold areas on the grates where char formation occurs and poor combustion conditions to burn out what char does form;
- Effect good mixing in the over fire space using both overfire air jets and furnace configuration to assure achievement of high and uniform temperatures (>950 °C), extended residence time at temperature (one to two seconds) and uniform and adequate oxygen concentrations (>3% O₂) to facilitate combustion of soot and char particles before the flue gases enter the boiler passes and begin to cool;
- Minimize the residence time of particulate in the boiler passes in the temperature range where CDD/CDF compounds form. Generally, this parameter is not practical as a control concept due to the high cost and limited flexibility available for the boiler design;
- Minimize the residence time of particulate in the post-boiler gas conditioning and air pollution control equipment in the temperature range where CDD/CDF compounds form. In tests on an electrostatic precipitator (ESP) operating in the range of 150 to 300 °C, the CDD/CDF concentration in the gases leaving the ESP was found to be as much as 200 times the inlet concentrations. Further, the ratio of increase across the ESP increased as the working temperature increased. In other plants (presumably, where the carbonaceous char was well burned out, temperatures were low and the ESP efficiency was high) small decreases have been measured. In general, when using an ESP, operation at the lowest practical temperature is critical; and
- Consider use of semi-dry scrubber to both accomplish acid gas reduction but, importantly, to reduce the gas temperature to below the CDD/CDF formation reaction zone. The semi-dry scrubber effluent temperature (the inlet temperature to the particulate control device) is of the order of 145 °C such that CDD/CDF reactions are greatly slowed. Also, as discussed below, injection of activated carbon (for mercury capture) is also effective to adsorb CDD/CDF compounds.

II. Air Pollution Control for Thermal Processing Systems

Section I give the analyst several tools to evaluate the uncontrolled emission rate of pollutants: the mass loading of particulate matter or the concentration of gaseous pollutants at the inlet of air pollution control (APC) devices. When available, data from physically comparable facilities that are burning comparable wastes under comparable operating conditions can also be used (subject only to the thoughtful determination that, indeed, the situation is truly comparable for all key aspects: waste, design and operations).

In most cases, the target outlet loading is well defined by local, state or federal regulations. Thus, the selection of an air pollution control device appears relatively straightforward: review the available art to determine the optimum technology to reduce the pollutant loading from the known or conservatively estimated inlet level to (or below) the outlet loading specified by regulation. This approach to selecting a technology selection often leads to different selections at different times or in different places.

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For example, a simple wetted baffle gave acceptable performance and was well-priced for APC on U.S. municipal incinerators in the early 1950's. Then, the only regulated pollutant was particulate matter and the regulations were not very stringent. In the 1970's, a few plants installed high energy scrubbers or cyclones but the dominant move was to the dry electrostatic precipitator (ESP) that controlled particulate to the more stringent New Source Performance Standards arising from the Clean Air Act of 1970. The economics of the ESP were helped greatly by the emergence of the gas-tight waterwall boiler designs that limited excess air (flue gas volume). In fact, the initial movement of incinerator construction to waterwall designs in the 1970-1973 time period was primarily driven by the need to reduce flue gas volume, not to recover energy. In the 1980's, regulations in many states added requirements for the control of acid gas emissions (primarily targeted on SO₂ and hydrochloric acid). Coupled with still more stringent particulate standards, the semi-dry absorber or "dry scrubber" (described below under "absorbers") followed by a fabric filter moved to the leadership position. Thus the "right technology" is ever-changing and is set by the combination of local and federal regulations that control emission rate.

The process of selecting an optimal APC technology is complex. Defining the meaning of "optimum" requires consideration of several technical, economic and other criterions. The criteria include:

Pollutant removal efficiency (relative to all regulated pollutants and giving attention to the potential generation of new pollutants in the course of abating others)

Capital Investment to include:

Basic APC device, its installation, foundations, ash handling equipment etc.
Fans, pumps and piping
Foundations and structural support
Ductwork to incinerator and to fan and stack
Insulation
Instrumentation and control systems
Electrical supply, motor control centers etc.
Water supply, sewer and portion of treatment system
Working capital in spare parts
Allowance for device replacement (useful life)

Operating Cost to include:

Operating labor
Special costs for training in operations and maintenance
Operating parts and supplies
Absorbents, reagents and similar consumables
Fuel
Electricity

Fan power
Pump power
Device power (esp. for electrostatic precipitator but also for shakers, air compressors etc.)

Water
Maintenance labor
Maintenance parts and supplies
Wastewater treatment and disposal
Ash treatment and disposal
Contract maintenance expenses (e.g., for instrumentation maintenance)

Impact on incinerator availability (reliability) and capacity

Operability and maintainability (including consideration of compatibility with general plant operating and maintenance labor skills, maintenance facilities and tools)

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Compatibility with Layout limitations

Compatibility with Other Regulations (noise, odor, illumination, visible plume, icing of adjacent roadways or electrical wires)

The detailed design and selection of APC systems is a major technical area in itself. However, several topics unique to incineration applications of air pollution control merit attention. The topics divide the problem of selecting an APC technology three ways: by *control* device, by *pollutant* and by *source* (incinerator) type.

A. Equipment Options for MWC Air Pollution Control

1. Settling Chambers

A settling chamber is a distinct chamber or zone where the gas velocity is reduced such as to permit gravity settling of particulate to occur. The controlling physical relationship (Stoke's Law) is described in Equation 3. The capture of particulate by settling is sensitive to re-entrainment so settling chambers are often designed with a wet bottom wherein a sluice of water is used to both trap and convey solids. Clearly, settling chambers are not highly efficient and their applicability in modern plants is nil as a means to meet emission regulations. They were, however, the standard in the U.S. municipal incinerator industry in the 1950's and 1960's.

The settling process is, however, always operative in an incinerator system and merits consideration by the designer. Any duct or chamber in an incinerator will act as a settling chamber to some degree. Unless provision is made to draw off the settled particulate, the material that settles in the duct or at the bottom of a chamber will accumulate and partially block the flow passage. In some cases, the settled material will sinter or fuse thus limiting the ease with which it may be removed. The increased velocity due to the blockage will eventually limit further deposition but will increase the pressure drop in the flow system, will reduce the mean residence time in the system and may introduce undesirable flow irregularities. For that reason, many flow passages, boiler passes etc. are equipped with cone bottoms and double dump valves (described below under "cyclones") or the like to facilitate regular removal of settled solids.

The settling chamber concept is also applied as a means to remove larger bits of gas-borne solids. For example, incinerators that burn solid wastes can expect periodic release of relatively large pieces of material than is still burning or smoldering: a "sparkler". If such a glowing or burning particle is introduced to a fabric filter APC device, one of the bags may be perforated or a fire may be started. Therefore, a knock-out chamber (a simple, flow-reversing down/up leg in the ductwork) is often incorporated in the flow system.

2. Cyclones and Inertial Collectors

"Cyclone" denotes the most common member of a family of particulate control devices that depend on inertial forces to remove relatively large, massive particulate materials from a gas stream. The removal efficiency of a cyclone is related to the angular velocity achieved in the vortical flow zone within the cyclone separator. As the rotational velocity within the device increases, progressively smaller particles reach the collection area at the outer wall and are captured. The inlet ducting is often tailored (a tangential, helical or involute entry) and/or internal vanes are used to facilitate the vortical acceleration and deceleration in order to minimize pressure losses.

Cyclone collection efficiency increases directly as a strong function of the aerodynamic particle size and density. The efficiency is often characterized by the " d_{p50} cut size" which denotes the particle diameter where 50% is collected and 50% escapes. Lapple [34] used empirical data to correlate the cut size to the number of turns of the vortex within the cyclone (N_e) and a combination of particle, gas and hardware characteristics. Although somewhat more accurate and elegant predictive equations are available [1], Lapple's correlations are:

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$$N_e \cong \frac{1}{H} \left(L_b + \frac{L_c}{2} \right) \tag{23}$$

$$d_{p50} = \left(\frac{9\mu_g W}{2\pi N_e \rho_p V_g}\right)^{1/2}$$
(24)

Where:

Н	= Height of the inlet duct to the cyclone
L _b	= Length of the cylindrical portion of the cyclone
L _c	= Length of the conical portion of the cyclone
μ_{g}	= Gas viscosity
W	= Width of the inlet duct
π	= Constant (3.14159)
ρ_p	= Density of the particle
Vg	= Gas velocity in the inlet duct

The pressure drop across the collector is related to the efficiency with which static pressure energy is used to accelerate the gas to the peak rotational velocity and then is recovered as the gas decelerates and then exits the device. Studies by Shepherd and Lapple [35] showed empirically that the pressure drop (expressed as the number of inlet gas velocity heads) depends inversely on the square of the exit diameter with a proportionality that depended on the inlet configuration. The inlet gas velocity head is calculated as: $0.5\rho_g V_g^2$ and their relations showed:

$$\Delta P = \frac{1}{2} \rho_g V_g^2 K \left(\frac{HW}{D_e^2}\right) \tag{25}$$

where ΔP is given in Pascals (Newtons per square meter), the gas density in kilograms per cubic meter, and the inlet gas velocity in meters per second. The dimensionless constant K is 16 for a tangential inlet and 7.5 for a cyclone equipped with an inlet vane. Inlet velocities for cyclones range from 6 to 25 m/s although common velocities range from 15 to 18 m/s. At velocities greater than 25 m/sec, scouring of the cyclone by the particles will increase.

Cyclones are fabricated of carbon steel for softer particulate (e.g. wood sawdust or sander dust). Most fly ash materials are very abrasive and the collection cone of a ordinary carbon steel cyclone would rapidly erode and perforate. Therefore, hardened, abrasion-resistant cast iron or similar materials are used for the cones in fly ash applications. For high temperature applications where low efficiency is acceptable, (e.g., removal of the bulk of the coarse particulate from the flue gas leaving a fluid bed sludge incinerator), a refractory lining is cast in a large diameter steel casing.

For higher gas flow rates combined with high efficiency (requiring a number of small cyclones in parallel), a rectangular array of several cyclones are mounted in a tube sheet fed from a common plenum and discharging to a common ash hopper. This array is known as a multiple cyclone or "multiclone collector". The performance is comparable to that of any of the individual cyclones in the array.

If not done properly, the discharge of dust from a cyclone can significantly reduce collection efficiency. Specifically, the dust must be withdrawn without allowing outside air to leak into the low pressure regime in the cone. Even a small in-leakage flow will re-suspend the dust. This sensitivity to leakage can be exploited in reverse: drawing off about 15% of the total gas flow through the hopper increases collection efficiency as much as 40 to 50 percent.

A double dump valve is normally used to discharge the ash and control in-leakage. With such a device, two dust valves are positioned one above the other. The uppermost valve opens first and dust falls from the hopper into the space between the valves. Then the top valve closes. Now, the lower valve opens and the dust is discharged. In

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low-cost dust valve designs, the valves are actuated by the weight of the dust. Unless the counterweights are carefully balanced and the pivot bearings regularly and properly lubricated, these valves can and do leak air. Better designs used compressed air cylinders to give positive opening and closing action for the double dump valve mechanisms.

3. Wet Scrubbers

Wet scrubbers include a broad class of APC devices with, often, a dual functionality: removal of particulate matter and absorption of one or more gaseous pollutants. The gas cooling and humidification taking place in a wet scrubber may be important (and, sometimes, undesirable) side-effects. The focus of design depends on the regulatory and flue gas contamination scenario. Although wet scrubbers can be effective for particulate and gas removal, their operation introduces a process waste (an aqueous discharge) needing either a sewer or a receiving stream. This new effluent may require monitoring and/or treatment and almost certainly will require a permit. These disadvantages often encourage the use of dry collectors as the preferred alternative.

For particulate removal, all wet scrubbers use the same basic principle: they create a wet surface (most often, a dispersion of droplets) to act as a "target" for particles and they accelerate the gas to develop a velocity differential between the target and the particle-laden gas. The particulate is then captured by three mechanisms:

- Impaction wherein the particle directly impacts on the wet surface or droplet
- Interception wherein the particle comes close enough to the wet surface or droplet to be captured
- Diffusion wherein the particle is driven by Brownian motion and impacts the wet surface or droplet and is captured.

The collection efficiency of all three collection mechanisms are enhanced by increases in the concentration of target droplets, the velocity differential between particle and droplet and the inertial characteristics (mass) of the particles. The pressure drop across the device is related to the efficiency with which static pressure is converted into velocity head and then recovered after particle collection is effected. The specific contour of the Venturi scrubber is aimed at optimizing this energy conversion process. It is not surprising, therefore, that Venturi designs are able to show the highest collection performance at a given pressure drop.

Wet scrubbers targeted on particulate collection fall into five groups:

- Venturi Scrubbers
- Mechanically Aided Scrubbers
- Pump Aided Scrubbers
- Wetted-Filter Scrubbers
- Tray or Sieve Scrubbers

In modern incineration applications with stringent particulate limits, the Venturi and tray/sieve scrubbers are, by far, the most common and will be the foci of this brief presentation. In most applications, a "quencher" is installed upstream of the wet scrubber to cool and humidify the combustion gases before entering the scrubber proper. This is particularly important when the scrubbing liquid incorporates dissolved or suspended solids. Without a pre-quench with relatively clean water, the contact of hot (esp. > 250 °C), dry gas with the liquid leads to flashing of the water and formation of an aerosol of fine particulate that is hard to collect in the downstream zones of the scrubber.

a. Venturi Scrubbers The Venturi is the most common scrubber concept used in incineration applications. This dominant position reflects the high particulate control efficiency that is achievable over the range of particles between 0.5 and 5 microns in diameter, the acceptable gas-liquid contact to achieve acid gas absorption (see below) and the mechanical "openness" of the Venturi and its flow system. Also, since the Venturi can be designed with an adjustable throat dimension, collection efficiency can be maintained over a range of gas flow rates. The benefit of

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"openness" of the liquid and gaseous flow passages relates to the lack of high pressure nozzles, high liquid rates, small diameter perforations and the like and can be important with flows that include accumulated solids.

The Venturi scrubber has three zones: the *convergent zone* where the gas is accelerated in a smoothly converging duct to its maximum velocity; the *throat zone* where the liquid is introduced using a spray or, more simply, by overflowing a weir; and the *divergent zone* where the gas is decelerated in a smoothly diverging duct to or near its original velocity. In the throat region, the large differential between the gas and liquid velocity acts, if necessary, to shatter the liquid flow into myriad small target droplets. The throat is the location where the velocity differential is greatest and, thus, where the majority of the particle-droplet collisions occur. The discharge from the Venturi (carrying a substantial flow of abrasive, particle-laden liquid water moving at high speed) is often directed through a right-angle turn. At the turn, the water is allowed to pool in this "flooded elbow" to slow and provide a sump for the excess fluid.

The key parameters influencing collection efficiency in a Venturi scrubber are the pressure drop (a scale of the throat velocity and, thus, the gas-to-droplet velocity differential) and the liquid-to-gas ratio (a scale of the concentration of droplets). The liquid-to-gas ratio is commonly between 0.7 and 2.7 liters/cubic meter and the throat velocity between 0.5 and 1.2 meters per second. The estimated pressure drop across the Venturi scrubber has been correlated by Hesketh [268] as:

$$\Delta P \cong 2.584 \ x \ 10^{-3} \ V_a^2 \ \rho_a \ A_{throat}^{0.133} \ (L/G)^{0.78} \tag{26}$$

where: ΔP

 A_{throat} = Venturi throat area (square cm)

L/G = Liquid-to-Gas ratio (liters/cubic meter)

Calvert [36] suggested an estimation methodology for application to individual particles of diameter d_p microns. By application of the methodology to a mass-averaged particle diameter representing each of several particle size ranges that are known mass fractions of the total dust loading, the methodology can be extended to estimate the overall particulate abatement efficiency where the size distribution is known.

The Calvert methodology begins with the characterization of several APC design and operational parameters starting with application of his correlation for pressure drop (ΔP) in cm H₂O as it relates to the throat velocity (Vt₂ in meters per second and the liquid-to-gas ratio (L/G) in liters per minute per cubic meter per minute. The Calvert pressure drop is calculated as:

 $\Delta P = 0.01022 V_t^2 \left(\frac{L}{G}\right) \tag{27}$

The physical properties of the gas and liquid are dependent on the actual physical situation involved but the following estimation algorithms may be useful for air and (pure) water:

Mean free path (λ m) for air at a throat temperature T_{throat} ($^{\circ}$ K)

$$\lambda = 6.7 x \, 10^{-8} \left(\frac{1033.24}{1033.24 - \Delta P} \right) \sqrt{\frac{273.1}{T_{throat}}}$$
(28)

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Viscosity (kg/meter-second) for air

$$\mu_g = 2.23 \, x \, 10^{-5} \, \sqrt{\frac{T_{throat}}{294.1}} \tag{29}$$

Water viscosity (poise) for a liquid temperature of T_w (°C)

$$\mu_w = \left[2.1482 \left(T_w - 8.435 + \sqrt{8078.4 + (T_w - 8.435)^2}\right) - 120\right] x \ 10^{-4}$$
(30)

Calvert adjusts the estimated collection efficiency with an empirical correction factor to account for the effect of particle wetability and other effects. His dimensionless coefficient (γ) varies from 0.1 to a suggested and conservative value of 0.25 for hydrophobic (hard to wet - such as an oil aerosol) particles to 0.4 to 0.5 for hydrophilic (easy to wet - such as for soluble compounds, acids or fly ash with SO₂ and SO₃) particles. The factor increases at L/G ratios below about 0.2 liter per cubic meter and approaches 0.5 for large scrubbers.

The first step is the calculation of the term A as given by:

$$A = 1.257 + 0.4 \exp\left(\frac{-1.1 \, d_p}{2.0 \, \lambda x \, 10^6}\right) \tag{31}$$

Then, the term C is calculated as given by:

$$C = 1 + \frac{2A\lambda x 10^6}{d_p} \tag{32}$$

The mean droplet size (m) of the scrubbing fluid is then calculated from:

$$d_{d} = \left[\frac{18.5}{V_{throat}} \sqrt{\frac{\sigma_{w}}{\rho_{w}}} + 2.82 \left(\frac{\mu_{w}^{2}}{\sigma_{w}\rho_{w}}\right)^{0.255} \left(\frac{L}{G}\right)^{1.5}\right] x \ 10^{-3}$$
(33)

Then, the inertia parameter Ψ is calculated from:

$$\Psi = \frac{C\rho_p V_{throat} d_p^2}{9d_d \mu_g \, x \, 10^{12}} \tag{34}$$

and the parameter F from:

$$F = \left(\frac{1}{\Psi}\right) \left[-0.7 - \Psi \lambda + 1.4 \log_e \left(\frac{\Psi \lambda + 0.7}{0.7}\right) + \frac{0.49}{(\Psi \lambda + 0.7)}\right] \quad (35)$$

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Finally, the fractional collection efficiency η is calculated from:

$$\eta = 1 - exp\left[0.036364 \left(\frac{L}{G}\right) V_{throat} \rho_w d_d \left(\frac{1}{\mu_g}\right) F\right]$$
(36)

b. Spray Tower Scrubbers Spray tower scrubbers with sodium hydroxide alkali rather than lime-based alkali to avoid buildup of gypsum (CaSO₄) deposits are used extensively on MSW combustion units in Japan and Western Europe. In principal, rubber-linings over mild steel could be used to control corrosion in the initial, hot-gas region. However, the risks of high temperature exposure with lining destruction and/or catastrophic attack of the steel if there is a 'holiday' (a perforation in the lining) leads most facilities to use Hastelloy or other corrosion-resistant (but expensive) high nickel-chromium steel in the hot zone. Cooler zones can and often do use FRP. Often, the scrubber is followed by a dehumidification chamber for plume suppression.

Such systems, with careful design, can achieve 95% HCl removal, 99% HF removal, 90% SO₂ removal and a high degree of trace metals and organic compounds.

c. Tray/Sieve Scrubbers Tray scrubbers are, typically, cylindrical structures within which are mounted one or more horizontal platforms (trays). The trays are perforated and include a weir to establish a working water depth and a drain pipe leading to the next lower tray (a "downcomer"). Scrubbing fluid is pumped to the top tray and pools to a depth set by the weir. Gas passes up through the perforations providing good contact between the countercurrent liquid and gaseous flows. This is the "sieve tray" tower form of this type of contactor and is in common use for mass transfer (e.g. absorber) operations. When particulate removal is of importance, an impingement baffle is incorporated as a "target" over the perforations.

The tray tower (usually with two to four trays) is often used in conjunction with Venturi scrubbers on sewage sludge incinerators and in other applications where one or more of the following functions are sought:

- Collection of carry-over droplets from a Venturi
- Incremental particulate control (these units are usually inadequate to meet particulate standards)
- Acid gas control (by addition of caustic soda alkali to the scrubbing fluid)
- Cooling of the flue gases (sub-cooling) as described in the next section.

The collection efficiency (η) for hydrophilic particles of aerodynamic diameter d_p microns by water on sieve plates have been correlated [37] by the expression:

$$\eta = 1 - \exp(-40 \,\rho_{foam} \Psi_{hole}) \tag{37}$$

where ρ_{foam} is the density of the foam on the tray (gram/cubic cm) and Ψ is the inertial parameter evaluated for conditions in the sieve holes. Specifically, V_{hole} is the velocity through the sieve hole (cm/sec), μ_g the gas viscosity (poises) and d_h is the hole diameter (cm).

$$\Psi_{hole} = \frac{V_{hole} d_p^2}{9\mu_a d_h} \tag{38}$$

The effect of the impingement target on particulate control is not reliably provided by theory or supported with welldocumented empirical relationships.

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d. Scrubber Accessories The equipments described below are often associated with scrubber installations.

1) Subcooling and Plume Reduction

In some instances, subcooling of the exhaust gases after a wet scrubber is desired. The reasons for this additional process step include (1) humidity reduction to avoid dense plumes that might obscure an adjacent highway, foster ice build-up on utility wiring or buildings in the winter or simply call attention to the incinerator operation (visible, dense plumes) or (2) pollutant reduction where lower gas temperatures increases condensation and deposition of pollutants such as mercury and its compounds, dioxin/furan compounds etc. In most instances, subcooling is limited to installations near to wastewater treatment plants where large quantities of low cost effluent can be made available. The practice is quite common for wastewater treatment sludge incinerators in the United States. In those instances, the impingement tray scrubber is generally used as the subcooler.

In instances where plume reduction is needed but the water resources are lacking to use subcooling methods, reheat of the plume may be employed. Clearly, there may be significant energy costs for plume reheat. However, constraints on the quantity or cost of water and/or permit limitations on the maximum temperature of discharge water may require this approach.

Analysis of a plume suppression process is straightforward. In this discussion, reference will be made to Figure 3: a psychometric (humidity - temperature) chart. One begins in the furnace after the last boiler (heat withdrawal) pass when the temperature and humidity of the gases are at point "A". On entering the scrubber, the gases are humidified. Assuming that the scrubber water is recirculated, the scrubber water and the leaving gas temperature will approach the wet bulb condition of the flue gases at point "B", moving along the adiabatic saturation curve A-B. One notes that in passing through the scrubber, the temperature drops and the humidity increases.



Figure 3 Psychometric Chart for Plume Subcooling

If the meteorological conditions in the surroundings are those at point "C", the plume gases, as they discharge from the stack and mix with the ambient air, will (approximately) start to move along through the sequence of temperature-humidity states defined by the straight line B-C. As long as the hypothetical mixed gas state is to the left of the saturation curve, moisture will condense and a visible plume will form. The gas state remains on the saturation curve and the liquid moisture appears as a fog of small, light-scattering droplets . . . a visible plume.

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In order to resolve this circumstance, two alternatives present themselves. The first approach is to reheat the gases (at approximately constant humidity) from point "B" to point "D" such that the mixing line after plume discharge is just tangent to the saturation curve at point "E". The second approach is to use additional gas-water contact with fresh cool water such as to subcool the flue gases: moving the flue gas state down along the saturation curve to point "E". The analysis of either scenario involves relatively simple heat and material balances but can be laborious. A utility computer program may be appropriate if the calculations must be made frequently. Analytical expressions for the dew point temperature, the saturation curve and the saturation humidity [1] are useful in the design of such programs.

2) Mist Elimination

In the course of passing through a scrubber, the flue gases carry off a significant amount of liquid water in the form of small droplets. These droplets incorporate both dissolved and insoluble particulate matter. The capture and return of these droplets to the scrubber liquid system is often critical to the achievement of the "R(emoval)" element of efficiency needed to meet the DRE for hazardous waste incinerators and, also, in meeting the particulate removal goal. This function is accomplished in the mist elimination equipment that follows the scrubber prior to the stack.

The factors contributing to selection of a proper mist elimination system include:

- The droplet particle size distribution;
- The acceptable pressure drop;
- The susceptibility of the separator to plugging by solids (if present);
- The liquid handling capability of the separator;
- Whether the separator can be integrated into existing equipment or must be in a standalone vessel;
- The available materials of construction as constrained by process features; and
- Cost for the mist eliminator and appurtenances.

Droplets formed through mechanical action (bubbling, boiling, shear of liquids from the surface of trays or heat exchanger) are usually coarse, ranging from 6 to 800 μ m in diameter. Pressure atomization spray nozzles almost always generate droplets larger than 50 - 200 μ m while two-phase (air or steam) atomization can generate mists with particles of 10 μ m or less. Chemical reactions (e.g., the formation of sulfuric acid mist from the reaction of SO₃ with moisture) can generate droplets most of which are less than 1 μ m.

Most mist eliminators use one or another type of impingement concept to collect the droplets. These include baffles, chevrons, wire meshes or fiber beds. These devices capture droplets by several mechanisms: inertial impaction, direct interception and diffusion. A dimensionless group, the Separation Number (N_s) can be calculated for each mechanism. Comparing N_s for the three collection mechanisms gives a relative measure of the importance of each mechanism in effecting mist elimination for a given application. A higher N_s corresponds to a higher collection efficiency.

a) Inertial Impaction. Inertial impaction collects those particles where the momentum is sufficiently high to break through the streamlines and impact on the target surface.

b) Direct Interception. Direct interception involves passage of a particle close enough to the baffle target that the distance from the particle centerline to the target is less than one-half of the particle diameter. Thus, the particle touches the target and can be collected.

c) Diffusion. Diffusion acts to collect still smaller particles (typically below $1.0 \mu m$) which exhibit random, Brownian motion. These particles can be driven to impact the target even if the gas velocity is zero.

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d) Demister Alternatives.

BAFFLE TYPES. The baffle type demister (e.g. the vane or chevron-shaped devices 2) are common in relatively low-duty applications. The chevron demister systems are formed from sheet metal and they impose a surface in the path of the droplet leaving the scrubber that requires a "zig-zag" motion of the gas. The droplet impacts the surface and drains off.

This class of demister is acceptable where removal goals are limited to droplets larger than 40 μ m (special designs can get as low as 15 μ m) and where low pressure drop (typically 10-15 mm H₂O) is important. The spacing between the baffles ranges from 5 to 75 mm with a total depth in the flow direction of 150 to 300 mm. Higher gas velocities can be tolerated if the unit is run with the gas flow horizontal (facilitating drain-off of liquid).

WIRE MESH TYPES. The knitted-wire-mesh mist eliminator is by far the most common system used in the chemical process industries. The material is fabricated from wires of from 0.1 to 0.28 mm diameter and the overall pad has a void fraction from 95 to 99%. The pad thickness varies from 10 to 30 cm. Collection efficiency approaches 100% for particles larger than 3 μ m. Turndown of wire-mesh pads is about 30 percent.

Pressure drop in wire mesh mist eliminators is usually less than 25 mm H_2O . When particularly high efficiency is desired, two pads are run in series with the first pad (of fine wires) run above its flooding velocity (where some liquid holdup occurs) and the second (of coarser wires) operates below flooding and acts to collect the large coalesced droplets blown off the first unit. When build-up of dissolved or suspended solids in the liquid is a problem, the pads can be irrigated with spray wash systems. Spraying should be directed toward the leading edge of the pad. Spraying the trailing edge causes more liquid holdup on the pad and decreases vapor load capacity. A typical washing rate is 120 liters/minute per square meter of mesh.

FIBER-BED TYPES. Fiber-bed mist eliminators use very small diameter fibers (<2.0 μ m) to capture very small droplets. The surface area of a fiber-bed unit can be 3 to 150 times that of a wire mesh unit for equal gas volumes. Units designed around the impaction mode of collection use face velocities of from 60 - 180 meters/minute. If diffusion capture is the design approach, only 3 - 12 meters/minute can be used. The capital cost of these devices is high relative to the baffle or wire mesh demisters. Also, the pressure drop (100 - 300 mm H₂O) is high.

OTHER TYPES. Some demisters use vanes, tangential inlets and/or rotating elements to impart a cyclonic spin to the flow. The inertial forces carry the droplets to the periphery of the chamber where they coalesce and drain into the liquid sump. In other applications (esp. when the solids content of the droplets is high), a Venturi scrubber or wet electrostatic precipitator is used for demisting.

4. Electrostatic Precipitators

a. Dry Electrostatic Precipitator Systems The electrostatic precipitator (ESP) uses electrical forces to move particulate matter in a flowing gas stream to a collecting surface. A typical unit is shown in Figure 4. The particles are electrically charged by passage through a corona: a region characterized by a luminous blue glow within the ESP containing a high concentration of gaseous ions. Either positive or negative ions or electrons can be generated in a corona but, for industrial gas cleaning operations, the negative corona is most commonly used. The charging process is most effective with large particles since they sweep a proportionally larger cross-sectional area and accumulate more electrons as they pass through the corona region. The converse can reduce ESP efficiency: inadequate particle charging with high concentrations of sub-micron particles leading to "space-charge quenching" (high voltages with low currents).

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Figure 4. Typical Rigitrode Electrostatic Precipitator (showing inlet perforated plate to minimize eddies

Since the particles form a continuous layer on the collection plates, all of the ion current must flow through the dust layer. This current creates an electrical field in the dust layer that can become large enough to cause local electrical breakdown, injecting new ions (of the wrong polarity) into the space between the discharge electrodes and the collection plates. This reduces the charge on the particles and may cause sparking. This breakdown condition is called "back corona" and leads to a reduction in collection efficiency.

The electrical field that drives the charged particles is created by applying a high DC voltage (40 to 75 kilovolts DC) with a negative polarity between the corona generating electrode and either flat or concentric cylindrical collecting plates. Normally, ESPs operate at the maximum voltage as sensed by the rate of spark over between the high tension electrodes. The corona current densities range from 0.1 to 1 milliamp/m² depending on the gas and dust conditions.

An optimum sparking rate of 90 to 100 sparks per minute per section of ESP is common. Conventional automatic control devices for ESPs continuously ramp-up the voltage until sparking ensues; then back off and start increasing again. If a unit is adjusted to avoid sparking generally means that the maximum efficiency potential of the ESP is not being achieved. One must also be careful that misalignment of electrodes, condensation (esp. with SO₃-containing © Walter R. Niessen 2011 Page **38** of **68**

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gases) and/or dust accumulation in and about the high voltage penetrations of the ESP shell do not impact adversely on the spark over rate.

Many older ESPs are fabricated using the "Plate-Wire" design where the high voltage corona-generating electrodes are long wires (plain or barbed), supported at the top from insulators and kept straight and in tension with a weight at the bottom. The wires hang between banks of flat, parallel, collecting plates. More recent designs use discharge electrodes that are mast-like structures (rigid frames), where electrode strips, often fitted with barbs or other "points", are supported between sections of frame tubing attached to a structural carrier both front and rear and supported by insulators. A third electrode design, the rigid electrode type shown in Figure 4, has a top-supported electrode hanging the full height of the ESP from a frame attached to insulators. A lesser number of ESPs are fabricated using the "Flat Plate" design (patented by United McGill Corporation) where the high voltage discharge electrodes are plates. In this design, the corona-generating electrodes (needles or hanging wires) are mounted at the leading and, occasionally, also at the trailing edge of the "discharge plate".

The collection surface is the total plate area used for particulate collection: a series of steel plates formed into a curtain and supported from the top. The plates are spaced in rows across the width, typically on 300 to 400 centimeter centers. Note that in calculating the surface area for collection, the curtain assembly is treated as a plane and includes both sides of the plates. Since breakdown of the electric field by spark-over significantly degrades collection, the alignment of the collection surface and the discharge electrodes must be maintained within tight tolerances. For that reason, some manufacturers add stiffener bars to the collection plates to maintain straightness.

In either design, the particles build up as a cake on the collection plates and for dry ESPs, are removed periodically by rapping the plates with pneumatic, electrical or mechanical hammers. In normal operation, dust buildup of 6 to 25 mm is allowed before rapping is initiated. The rapping mechanisms apply a minimum acceleration of 100 "g's" to the collection surface as measured at the farthest point from the rapper impact. Rappers are also applied to the inlet flow smoothing distribution plates and to the discharge electrodes. The rapping frequency and duration is usually adjustable and varies from a few minutes to several hours depending on the type and quantity of dust and the rapping technique. Sticky and high resistivity fly ash is more difficult to clean than dry, low resistivity ash.

Some re-entrainment occurs upon rapping. This is especially so for dusts that strongly holds a charge (high resistivity) where the individual particles tend to repel one another thus forming a soft, easily broken up cake. Stack gas opacity monitors in a power plant often show discrete spikes (say, from a baseline of 5% to 10% or 15% depending on the intensity of the rapping) that coincide with the onset of rapping. The percent of collected particulate that is re-entrained has been measured at approximately 12 percent in plate-wire ESPs and up to 15 percent in flat plate ESPs operating with high transit velocities (>1,5 meter/second). The re-entrainment ratio is zero for tubular ESPs. Re-entrainment falls to zero in a wet ESP and is significantly reduced if the fly ash is sticky. Very fine particle size material tends to form a dust cake that does not break up as easily on rapping; this reduces the re-entrainment ratio. The loss in efficiency due to the re-entrainment process encourages a reduced frequency of rapping. A strategy of infrequent rapping is not achievable when high particulate inlet loading accelerates the build-up of cake or when high resistivity ash characteristics impair collection (see below).

Ash falls from the collection plates into pyramidal hoppers supported from the lower grid. Hopper side angles should be at least 60 degrees from the horizontal to facilitate flow of ash through a dump valve that assures a continuous gas seal. Hopper heaters and vibrators are used to initiate ash flow since hopper dumping is intermittent.

The sequence of particle charging and collection is usually repeated several times within a single precipitator. These collection zones or "fields" are separately energized (often at different voltages). In general, the overall ESP efficiency increases as the number of fields is increased. In municipal incinerators, one finds from two to five field ESPs with, in general, newer units having the larger number of fields.

1.) Theory and Design Principles. In theory, a particle moving in an electric field is accelerated in proportion to the magnitude of the charge and the field intensity and slowed by the Stokes' Law drag forces. For © Walter R. Niessen 2011 Page **39** of **68**

λ

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very small particles (less than about 0.5 micron in diameter), a correction is to the drag force relationship is needed (the Cunningham slip correction factor). This is because the basic formulation of Stokes' Law presupposes a continuum of gas-particle interaction. However, as the particle becomes small relative to the mean free path of the gas (λ), this is no longer the case. The dimensionless Cunningham factor C', which is the ratio of the actual settling velocity for fine particles to that predicted by Stokes' Law, adjusts for this change in the character of the gas-particle collisions.

$$C' = 1.0 + \frac{2\theta\lambda}{D_p} \tag{39}$$

where:

= Mean free path of the gas molecules (m)

$$\frac{1}{\sqrt{2\pi nd_m^2}}$$

(30)

 $\begin{array}{ll} n & = Gas \mbox{ molecular density (molecules per m^3)} \\ d_m & = Gas \mbox{ molecule diameter (meters)} \\ D_p & = Particle \mbox{ diameter (meters)} \\ \theta & = 1.257 + 0.4 \mbox{ exp(-1.1D_p/2\lambda) (dimensionless)} \end{array}$

The limiting or terminal velocity of the particle in this scenario (usually denoted "w") is called the migration or drift velocity and is given by:

(40)

$$w = \frac{E_c E_o D_p C N}{4\pi\mu_g} \tag{41}$$

where:

$$\begin{array}{ll} E_c & = Charging field strength (electrostatic volts/cm) \\ E_o & = Collecting field strength (electrostatic volts/cm) \\ D_p & = Particle diameter (cm) \\ C' & = Cunningham Correction Factor \\ \pi & = Constant 3.14159... \\ \mu_g & = Gas viscosity (g/cm-sec) \end{array}$$

Collection efficiency is usually correlated using the "Deutsch-Anderson Equation:

$$\eta = 1 - \exp\left[-\frac{A_o}{Q}w\right] \tag{42}$$

where:

$$\eta$$
 = Collection efficiency

 $A_o = Collection area (m²)$

Q = Gas volume flow rate (m^3/sec)

w = Migration velocity (m/sec)

It should be noted that equation 42 does not include corrections for the various types of re-entrainment nor does it consider particle size or particle charging effects. However, the Deutsch-Anderson is a useful and effective predic-

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tive tool if an "effective migration velocity w_e ," an empirical proportionality constant (the "precipitation rate parameter"), is used rather than the theoretically defined migration velocity. The effective migration velocity is back-calculated from efficiency measurements,

The most important design variable to size an ESP is the specific collection area (SCA). The units of SCA are square meters (of collection surface) per actual cubic meters of gas flow. In English units, SCA is commonly reported in $ft^2/1,000$ acfm. Note that the SCA is equal to the parameter group A/Q in the Deutsch-Anderson equation.

The collection efficiency of an ESP is related to the several factors discussed above. These factors result in a significant variation in the collection efficiency with particle size for a given ESP device. In particular, the ESP is less efficient for smaller particles (less than 2 microns) than for larger ones. This contrasts with the fabric filter systems that show high and relatively uniform collection efficiency for small particles.

The flow field entering an ESP must be slowed and smoothed in order to evenly distribute the gas over the face of the bank of collecting plates. The force tending to divert the charged particles to the collection plates is relatively weak and eddies or other flow disturbances will both inhibit initial collection and can act to re-entrain material that is already collected. Most commonly, turning vanes are used (if appropriate) to minimize the effect of upstream duct turns and one or more perforated diffuser plates are mounted at the entrance to the ESP. The diffuser plates use round holes 5 to 7 cm in diameter with an open area of between 50 and 65 percent of the total.

Flow uniformity can be assessed quantitatively by measuring the velocity profile of the flow field across the face of the ESP. Indications of poor distribution can sometimes be obtained by observations of patterns of build-up in ducts and on the collecting and/or flow distribution plates. Good gas flow variation should approximate a Gaussian (normal) distribution with a standard deviation of approximately 1.25. The "flatter" the flow profile, the better. The Industrial Gas Cleaning Institute recommends that 85% of the local velocities be within \pm 25% of the mean and that no single velocity vary more than \pm 40%. The consequences of poor distribution can be profound. Excessive reentrainment can often be detected by an abnormal size distribution in the exit dust (a favoring of the larger particles that are preferentially re-entrained).

2.) Operational Features. The pressure drop through the ESP is usually not high and indeed is often lower than the associated collection system and ductwork. Typical ranges of pressure drop across the several ESP components are presented in Table 9. The largest pressure drop is associated with the enlargement loss at the inlet transition. Gas velocity through the ESP varies between designs but the maximum acceptable is about 1.5 meter/second for plate-wire ESPs and 1 meter/second for flat-plate ESPs and when resistivity is low and re-entrainment minimization is critical.

	Typical pressure drop (Pascals)			
Component	Low range	High range		
Diffuser	2.5	22.4		
Inlet transition	17.4	34.8		
Outlet transition	1.7	3.7		
Baffles	0.15	30.6		
Collection plates	0.07	2		
Total	22.4	94.6		

Table 9	Typical	ESP	Pressure	Drop	(Pascals	;)
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Efficiency reduction also results from the bypassing of the collection zone. This includes gas flow through the hoppers and over the top of the collection plates. This "sneakage" (the fraction of the gas flow that bypasses the collection zone) is minimized through the use of baffles. Measured sneakage in plate-wire ESPs approximates about seven percent and ten percent in flat plate ESPs.

The electrical resistance characteristics of the collected dust layer (the resistivity, usually expressed in units of ohm centimeters) is an important system property. Dust resistivity values can be classified into three groups:

10^4 to 10^7 ohm-cm
10^7 to 10^{10} ohm-cm
above 10 ¹⁰ ohm-cm

Ideally, the resistivity is in the range 10^6 to 10^{10} ohm-cm. The resistivity of the cake varies widely between different dusts. A set of data for municipal incinerator plants, for example, showed peak resistivity values from $2x10^8$ to $1.2x10^{11}$ ohm-cm at 12% H₂O. The peaks occurred at from 123 to 154 °C.

Carbon, alkali metal salts and adsorbed sulfur trioxide or moisture reduce resistivity. Inorganic clays and minerals such as alumina increase it. Resistivity is also a (concave downward) function of temperature and decreases as the moisture content of the flue gases increases. Resistivity prediction models based on dust chemistry have been developed. It should be noted that the material used (total dust or collected dust), the location of measurement (laboratory or in-situ) and the testing method affect the values determined for resistivity.

A dust resistivity that is too high or too low can produce undesirable results:

Low resistivity cake ($<10^{+8}$ ohm centimeters) will bleed off the charge on the particles such that the attractive forces weaken and re-entrainment can begin to occur.

High resistivity cake (> $2x10^{+11}$ ohm centimeters) will firmly hold its charge such that, as the cake builds, the voltage drop across the dust layer increases thus impairing collection efficiency. In severe cases, the electric field in the layer is large enough to cause local electrical breakdown (back corona), thus reducing efficiency.

Several factors affect the collection efficiency of an ESP system. These include:

- Collection plate area per unit gas flow rate (specific collection area SCA)
- Gas velocity through the collector
- Size distribution and electrical properties (resistivity) of the particles
- Number, width and length of gas passages
- Electrical field strength and degree of high-tension sectionalization
- Particle in-field residence time
- Gas temperatures and humidity (effects on resistivity)
- Re-entrainment or disturbance of the flow field in the ESP due to flow eddys arising from air inflow past the dust valves on the hoppers, sinking flow along cold surfaces where the enclosure insulation has been removed, or air in-leakage around poorly sealed man ways and other access doors.

It is possible to attain the desired control efficiency by altering the design specifications for each of the above parameters. Further, several positive characteristics of an ESP are important when considering their use in controlling incinerator emissions. These include:

- High overall collection efficiency and reliability
- Relatively low power requirements
- Ability to accommodate flue gas temperatures in the range of 120 to 320 °C with the lower limit dictated by the gas dew point.

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- Minimal change in collection efficiency over a wide range of particle size
- Minimal fire hazard potential

In applications with municipal solid waste, the potential design and operating problems include:

- Variations in flue gas temperature and fly ash resistivity
- Condensation of corrosive flue gas constituents
- Variation in incinerator processing and emission rate
- Deviations between design and actual gas flow rates
- Low collection area or excessive velocity (low specific collection area SCA)

The major adverse effect of these problems is to lower the collection efficiency. Corrosion problems can be alleviated through construction to avoid air leakage into the ESP and insulation and external heating of the unit to avoid cold spots where condensation can occur. Corrosion is normally not a problem as long as the flue gas temperature remains above 130°C. Also, at high flue gas temperatures, fly ash resistivity is more predictable and particulate collection efficiency is enhanced.

b. Wet Electrostatic Precipitator Systems Wet electrostatic precipitators (WESP) remove collected dust particles by continuous or periodic irrigation of the collection plates with water sprays or a water film. Both flat plate and tubular designs are found in practice. Since the dust is wetted, re-entrainment is not a problem. Often, water sprays are used upstream of the WESP to bring the gases to the saturation point. Unevaporated water from preconditioning can either be treated separately from the primary WESP wastewater treatment system or can be passed forward for use as the plate irrigation water in the WESP itself.

WESP applications may or may not have a requirement for significant wastewater treatment handling depending on the quantity of water used to irrigate the collection plates and transport the collected dust. Some systems use very little water and produce a sludge-like residue. Others use a clarifier and solids concentrator (often a vacuum filter), sometimes with pH adjustment and with flocculation aids.

WESPs used in sewage sludge service operate at much lower discharge electrode voltages (1,000 to 6,000 volts dc) and are usually located after a conventional Venturi-impingement tray scrubbers system. The primary target for the WESP is the sub-micron particulate matter with particular focus on heavy metals and soot.

5. Fabric Filter (Bag house)

Filtration is a very effective means to remove fine particulate from a gas stream. Removal efficiency remains high in comparison to most other control technologies for sub-micron particulate. This is the particulate fraction that is of special significance in the emissions of respirable particulate ($PM_{2.5}$ and PM_{10}) and of many carcinogenic and toxic organic aerosols and heavy metals. It is not surprising, therefore, that the use of filtration-based devices in incineration applications has grown significantly as regulations have become more and more stringent.

Filtration devices are of two types: cloth or fabric filters and in-depth or bed filters. Fabric filters are generally found as an array of long, cylindrical bags mounted in a structure (a "bag house") as shown in Figure 5. Bed filters can be of several types but, in incineration applications are most often a deep, packed bed (a "gravel bed" filter).

The key characteristics of fabrics for use in gas filtration include:

- Temperature A maximum continuous service temperature higher than the normal working temperature. Peaks in temperature and ther duration must be considered if the temperatures do not reliably hold at or below the norm.
- Corrosiveness Some gas constituents are aggressive and will attack the fabric. The inherent resistance to such attack is specific: gas to fiber.

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- Hydrolysis Flue gas humidity can affect the strength and dimensional stability of the fabrics.
- Cost Obvious in importance but evaluated in the light of air-to-cloth ratio (affecting the number of bags), unit cost per bag, loss during installation (important with some bags that are sensitive to mishandling) and expected service life (replacement cost).

The three most important criteria of performance for filtration devices are collection efficiency, pressure drop and useful life. The collection efficiency is inherently high and includes contributions from the fabric itself but, more importantly, from filtration by the cake of collected dust. Thus, pressure drop and efficiency vary throughout the cleaning cycle. The low point in both pressure drop and efficiency occurs immediately after cleaning of the bag. The high points are just prior to cleaning when the thickness of the accumulated dust cake is at a maximum. The cost for fan power (directly related to pressure drop) is the principal operating cost element for a fabric filter. The useful life is important as it affects bag replacement cost. There are tradeoffs possible between the first cost of the bags and bag life which, unfortunately, are difficult to assess a priori and which are often specific to a particular application and its unique dust and gas characteristics.



Figure 5. Pulse Jet Design Bag House

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Several basic fiber properties are summarized in Table 10.

	_	Resistance to:						
<u>Fabric</u>	Max. working temperature <u>(deg. C)</u>	<u>Abrasion</u>	Flex	Mineral <u>Acid</u>	Organic <u>Acid</u>	<u>Alkali</u>	<u>Fluoride</u>	<u>Solvent</u>
Acrylic	80	G		G	G	F		G
Cotton	85	G	Р	Р	G	G	Р	Е
Fiberglass	260	P,G	Р	VG	E	P,F	Р	Е
Modacrylic (Dynel)	80	F		VG	VG	G		G
Nylon (Nomex)	205	Е	G	F	F	VG	G	Е
Polyamide	105	Е		Р	F	VG		Е
Polyester	135	E		G	G	G		Е
Polypropylene	95	E	Р	Е	Е	Е	Р	G
Teflon	260	F,G	P,F	Е	E	Е	P.F	Е
Wool	100	F,G		F	F	P,F		G

Table 10 Fabric Filter Characteristics

The pressure drop and collection efficiency of a fabric filter are difficult to estimate from first principles. Since the collection medium is predominately the cake itself, theoretical relationships involving the collision and capture of particles on a matrix of bag fibers are interesting but substantially impotent. Theory can, however, indicate the expected dependency of the several variables as a guide to data analysis and correlation. Extensive discussions of filtration theory can be found in several references.

The face velocity V_f is often called the "Air-to-Cloth Ratio" and abbreviated in text as A/C. A/C is defined as the volumetric gas flow rate divided by the total filtration area. Therefore, this important parameter has the net dimensions of a velocity (length/time) and, thus, varies between English and metric units by the factor:

 A/C_{metric} (meters/minute) = $A/C_{English}$ (feet/minute) x 0.3048 (43)

The installed cloth area depends on the A/C ratio based on the collection area in active use at any point in time. Because of maintenance, cleaning or other outages, the area installed must, necessarily, be larger than the minimum area calculated from the gas flow rate and the target A/C ratio.

Particle collection by a fabric filter arises as a combination of five classical mechanisms involving interactions between a particle moving in a gas stream and a filter fiber :

- Gravity wherein the larger particles settle out of the gas stream (negligible for most finely divided particulate);
- Direct Interception where the particle, following a streamline and in stream line flow directly collides with the fiber;
- Inertial Impaction where the particle track diverges from the streamlines due to inertial forces and impacts on the fiber (primarily for particles > 5µm);

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- Diffusion where the smaller particles, say, within a factor of 10 to 100 times the diameter of gas molecules, are driven by random molecular collisions (Brownian motion) to collide with the fiber (dominant for sub-micron particles); and
- Electrostatic Attraction where the particle and/or the fiber are electrically charged such that electrostatic forces increase the tendency for the particle to migrate to and impact the fiber.

Each of these mechanisms can be formulated in a capture efficiency relationship and combined to yield an overall efficiency. The inability of theory to predict pressure drop or efficiency performance indicates the difficulty inherent in analyzing the behavior of filtration systems from first principles alone. Nonetheless, theoretical analysis can be seen to be useful in suggesting approaches to correlate data and, when necessary, to extrapolate or interpolate to new operating points when limited data are available. Clearly, the latter use involves risk. However, such risks may be reasonable when the alternative is baseless linear extrapolation or the like.

a. Baghouse Classifications As the dust cake builds and the pressure drop across the fabric filter increases and, at some point, the bags must be cleaned. In most equipment, a timer is used to control the cleaning cycle although a pressure drop monitor can also be used. Normally, the pressure drop limits are set at between 1.2 and 5 kPa. The methodology used to clean the bags differentiates the three basic classes of fabric filter: (1) mechanical shaking which flexes the fabric to break up and dislodge the dust cake; and (2) reversal of the air flow and (3) pulse-jet cleaning which both flex the fabric and reverse the flow to remove the dust. Selection of the cleaning method is based on the type of fabric used, the pollutant collected, and industry experience. The cleaning methods are compared in Table 6.

_	Cleaning Method			
Parameter_	Shaker	Reverse Flow	Pulse Jet (individual bags)	Pulse Jet (compartmented bags)
Cleaning	Off-line	Off-line	On-line	Off-line
Cleaning time	High	High	Low	Low
Cleaning uniformity	Average	Good	Average	Good
Bag attrition	Average	Low	Average	Low
Ruggedness	Average	Good	Good	Good
Fabric type ^a	Woven	Woven	Felt/Woven ^a	Felt/Woven ^a
Filter velocity	Average	Average	High	High
Power cost	Low	Low to medium	High to medium	Medium
Dust loading	Average	Average	Very High	High
Max. temperature ^b	High	High	Medium	Medium
Collection efficiency	Good	Good	Good ^c	Good ^c

^a With suitable lacking, woven fabrics can perform similar to felted.

^b Fabric limited.

^c For a properly operated system with moderate to low pressure, the collection efficiency may rival other methods

Table 6 Comparison of Bag Cleaning Methods [1]

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1) Mechanical Shaking. Shaker-type bag houses are the oldest form of fabric filter. In this class, the bags are cleaned by the simple expedient of shaking the bag (generally, in the horizontal plane and from the top) via linkage to a mechanical (a motor driving an eccentric), electrical or pneumatically actuated shaking mechanism. The flow of dirty gas enters the bags from an air plenum at the bottom of the bag house and the cake builds on the inside of the bag. Shaker bag houses are generally less efficient for dust removal than the pulse jet systems as they plug more quickly because the shaking action does not release the dust cake completely or easily.

In operation, the bag house is normally divided into compartments such that at least one compartment can be dampered out of service while the bags are cleaned. After a short delay following isolation of the compartment, shaking is initiated. Typically, these devices are designed for A/C ratios of 0.6 to 1.8 m³/min/m² [548]. Mechanical shaking is reliable and often has the lowest capital cost of the three alternatives although there is a penalty associated with the overcapacity to allow for the retirement of one compartment during cleaning. Also, the violent action of shaking, in general, produces more fabric wear and shorter bag life than the other cleaning strategies.

2) Reverse Air. In reverse air cleaned systems, the flow of dirty gas enters the bags from an air plenum at the bottom of the bag house and the cake builds on the inside of the bag. When the pressure drop reaches the set point, flow through the compartment to be cleaned is stopped. Then, a gentle, reverse flow of filtered, warm gas is initiated for about 10 to 30 seconds, back-flushing and collapsing the bags (concave inward) within one compartment at a time. Reverse air bag houses are generally less efficient for dust removal than the pulse jet systems as they plug more quickly because the gentle reverse air flow action does not create sufficiently high gas velocities throughout the filter element to dislodge the dust cake. The total cleaning cycle, including valve opening and closing and dust settling extends over 1 to 2 minutes. The gas used is usually taken from the outlet of the fan, downstream of the baghouse. Cold outside air generally cannot be used because of potential problems with condensation. Typically, these devices are designed for A/C rations of 0.3 to 0.9 m³/min/m². Note that the reverse flow adds to the net total volumetric flow rate through the baghouse; thus increasing capital cost (more bags at a given A/C ratio). Usually, a "cage" that is fabricated of metal wire is mounted inside the bag with rings about one meter apart to provide internal support to avoid collapse and/or to support the bag during cleaning and operation. Woven filter media are generally used at a low face velocity (from 0.6 to 1.2 meters/minute). The gentle cleaning process extends bag life.

3) Pulse-jet. In pulse-jet cleaning, a solenoid valve is electronically opened and a short, high pressure burst of compressed air is discharged into the open end of a row of the cylindrical bags. Newer designs allow use of air at from 70 to 350 kPa. The burst of air, with a duration of about 0.05 to 0.1 seconds is repeated every 30 seconds to 2 minutes depending on the pressure build-up rate. Most often, a Venturi nozzle is used to inspire additional air from the exhaust plenum. The large total volume of air rushes down the bag as a shock wave that is reflected from the closed bottom. The pulsing flexion in the bag combined with momentary local reverse flow dislodges the dust cake from the outside of the bags in a very short period of time: generally less than one-half second. Thus, no significant filtration capacity must be provided to provide reserve capacity for the cleaning cycle. There is no need to shut down a compartment. As with the reverse air, an internal metal cage is often used to support the bag which is normally closed at the bottom and open at the top. Typically, these devices are designed for A/C rations of 1.5 to 4.6 $m^3/min/m^2$. Both felted and bulk-knitted filtration fabric can be used.

4) Other Design Features

Hoppers. In general, the filtration vessel has a conical or pyramidal hopper bottom sloped at least 60 degrees from the horizontal. A slide gate or rotary valve discharges the collected dust to a screw conveyor or receiving vessel. The hopper may need to be insulated to avoid condensation with consequent corrosion and clumping or bridging of the collected dust. Often, rappers are added to assist in clearing the hopper.

Cages. A wire cage is used in reverse air and pulse jet bag houses to support the bags. The cage is fabricated of wires (often 11 gauge) of mild steel, galvanized steel or stainless depending on the potential for corrosion attack. The wires (10 to 20 in number with more wires evening out the support to extend bag

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life) are held in position by rings. For reverse air, the rings are about one meter apart and about 20 cm apart for pulse jet cages.

Bag Size. The diameter of the bags vary from as little as 5 cm to 20 cm. Smaller diameter bags clean easier but more bags are required to achieve the needed filtration area. Thus, for most applications, the preferred size is 12 to 15 cm with a length of 1.8 to 2.5 meters.

Bag Removal. Pulse-jet collectors could remove the bags from the bottom of the tube sheet or from the top through the clean-gas plenum. The top removal option is generally preferred although it is slightly more expensive. Removal of a top hatch provides access to the clean-air plenum. This removal strategy does not require entry by workers into the dirty-air side of the unit which is required for the reverse air or shaker alternatives. Typically, removal of the bags in a pulse jet system involves unfastening of the cage top and lifting out the bag and cage together. Note that this requires overhead clearance slightly greater than the bag length.

Superficial Gas Velocity. Beyond the surface area, one must achieve a bag placement so the dust particles released during pulse jet bag cleaning will drop and not remain suspended in the gas flow between the bags. This criterion (the free space velocity or superficial upward gas velocity) is a maximum of about 25 m/min for very fine dusts (talc, carbon black); 45 m/min for fine (less than 200 mesh) particles; 75 m/min for granular materials; and 90 m/min for pelleted materials [645].

3. Bag Life

Bag life is not easy to predict from theory or laboratory measurements. The common laboratory tests for fabrics (e.g., the MIT flex test, elongation to break, tear strength and the Mullen burst test) fail to correlate with field data. An increase in the percent of bag failures per year with the A/C ratio [276] is qualitatively correct in that the shortest bag life corresponds to the highest A/C ratio. However, the data range from 0.1% to about 10% per year (a 100-fold variation) at an A/C of 4.

Overall bag life in service is highly variable; depending on the type of bag, cleaning method and frequency, pollutant characteristics and other factors. A two-year life is a typical average.

Note that reverse-air baghouses that suffer bag failure direct a high velocity, abrasive air jet out of the torn bag toward its neighbors, often causing three or four others to fail. Thus, early detection and correction of bag failure is especially important [276].

c. Operational Characteristics A fabric filter yields almost constant collection efficiency over a range of inlet loadings. Therefore, the performance of a bag house differs from an ESP or wet scrubber where the collection efficiency is a design feature that varies as the design or operating conditions vary. Collection efficiencies above 99 percent should be expected after the cake character has developed (after several loading and cleaning cycles). There will be some improvement in efficiency for new bags (where pinholes have not developed), at low A/C ratio, and where cleaning frequency is minimized (since the cake itself is the primary dust collection medium).

The pressure drop across the bag house is an important guide to the operating condition and an indicator of problems. High pressures arise from excessive gas volumes, mudding or other blinding of the filtering fabric, hopper overload that blocks the bags or an inoperative cleaning mechanism. Low pressures indicate fan or motor problems, broken or unclamped bags, plugged inlet ducting or a closed damper and/or leakage between sections of the baghouse. Note that the relatively high pressure drop across the bags does exert a self-equalizing effect that helps to even out the flows to individual bags and rows of bags within a compartment.

A broken or unclamped bag leads to an immediate jump in the opacity of the cleaned gas. Therefore, an opacity meter or triboelectric monitors are valuable devices to signal the onset of this catastrophic failure mode. Less © Walter R. Niessen 2011 Page 48 of 68

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severe, however, is the progressive breakdown of the bags as a consequence of repeated flexing and other mechanical or chemical abuse. This leads to the gradual development of pinholes that slowly increase the outlet loading of particulate as the operating life of the bag is extended.

Power costs for mechanical shaking approximate 6.5×10^{-5} kW per hour of operation per square meter of cloth area. For a pulse-jet system, compressed air use is about 120 sm³ per hour of operation per 1,000 sm³/minute of gas cleaned [541].

Safety considerations for fabric filters are important if the collected dust is combustible and, therefore, there is a probability of a dust explosion. Friction of synthetic filter media against the metal cages can generate a static change on the cage which can lead to sparks and ignition. Therefore, the cages should be grounded to keep the resistance to ground less than 5 ohms and the bags should include preferably two grounding wires sown into them linked to the cage and the grounded tube sheet [645].

5. Bag house Applications for Incineration Systems

Increasing regulatory concern regarding emissions of heavy metals (often, as a fume or condensed onto very fine particulate), respirable particulate (PM_{10} and $PM_{2.5}$), and, generally, a ratcheting down of permitted total particulate loading has greatly increased the use of fabric filters for incineration systems. This is particularly true for the municipal incineration in combination with spray dryer absorbers. Another potentially important feature expanding the use of fabric filters involves the catalytic filtration concept where catalysts are added to the filter media for destruction of gas-phase dioxin/furans.

The pulse-jet concept is preferred in incinerator applications and is the dominant type of industrial fabric filters. Generally, the bag houses are outside collection type (dirty gas flows from outside the bag) with short, small diameter bags (12-15 cm) that are less than 7 meters long and that are fabricated of felted fabrics. In general industrial service, these units are usually operated at 1.2 to 1.8 meters/min A/C ratio but municipal incinerator units are designed at A/C ratios as low as 0.6 meters/min.

Because of the potential for plugging, the temperature of the dirty gas must be a minimum of 25 to 50 $^{\circ}$ C above the stream dew point. If the dew point is crossed, moisture can condense and cause corrosion, "mudding up" (high pressure drop as wet, pasty cake closes off air flow through the filtration media), bag rupture and the need to shut down the baghouse and have the bags removed and cleaned.

6. Absorbers

Absorption is a process for the removal of one or more components from a gas mixture. Absorption is often thought of as involving contact of a gas with a liquid (as in a wet scrubber). However, the principles are applicable in completely dry systems (e.g., the absorption of acid gases by injected lime dust) or "semi-dry" systems. For the latter type, the absorption of acid gases occurs on lime slurry droplets where the slurry is injected in quantities and with particle sizes and lime concentrations such that complete evaporation of the slurry water occurs.

The particulate abatement technologies described previously use a variety of physical principles to effect capture of individual particles. In absorbers, the mechanism by which pollutants are captured involves a mass transfer flux driven by molecular and eddy diffusion from a region of high concentration to one of low concentration. Capture can involve a reversible (equilibrium) association of pollutant (usually present with a large quantity of diluting carrier gas that does not absorb) with an absorbing material. Contact between the liquid and gas in wet scrubber absorbers can be of three basic types:

• Countercurrent - where the strongest absorbing liquid is in contact with the weakest pollutant concentrations in the gas and vice versa; a common configuration with weak absorbents embodied by a

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vertical column with liquid feed at the top and gas introduced at the bottom. Note that if trays are inserted into the column, the behavior across any tray is crossflow but, tray-to-tray, is countercurrent.

• Concurrent - where the strongest absorbing liquid is in contact with the strongest pollutant concentrations in the gas and vice versa as in the Venturi scrubber and the dry and semi-dry scrubbers used for acid gas control in municipal incinerators. The concurrent approach is acceptable when the absorption reaction is substantially complete (i.e., acid gases absorbed in strong alkaline reagents).

• Crossflow - where one stream flows perpendicular to the other stream. This principle is used in spray chambers where the gas travels horizontally while spray drops fall vertically, the tray scrubbers noted above and in some packed tower systems.

a. Wet Packed Towers for Removal of Pollutant Gases One of the more common absorber devices for the removal of acidic gases is the packed tower. Here, a vertical, cylindrical column is erected. A given depth of the column is filled with a packing material that is chemically inert and designed to give a minimum of pressure drop and a maximum of gas-liquid contact area. In accord with good practice, the size of the packing is not more than 1/20th of the column diameter. The column is operated at between 50 and 75 percent of the flooding rate. Flooding rate is defined as the gas volumetric flow rate that, for the tower diameter and packing would inhibit the flow of liquid down through the tower to the degree that flow would, substantially, be blocked.

b. Dry Absorbent Contactors for Acid Gas Pollutant Control The highest removal efficiency for gaseous pollutants is often achieved using a wet scrubber with appropriate chemical addition such that the equilibrium partial pressure of the target pollutant is very low. An example would be HCl scrubbed with a caustic soda solution. Although the wet contactors are efficient, they produce a wastewater requiring treatment and disposal, they present not insolvable but problematic corrosion problems, they generate a visible plume (unless special and costly countermeasures are taken) and they often present numerous operation and maintenance problems with plugging, solids buildup and the like. The dry absorbent systems avoid many of these problems and, although they present their own deficiencies, they find use in some incineration applications for acid gas abatement.

Dry sorbent injection involves the injection of solid, alkaline material into the flue gases of an incinerator to effect gas-solid reactions in the (short) time available prior to discharge to the stack. Technology based on this approach dates to the 1960s when significant efforts were made in the U.S. and Europe to use dry limestone injection for SO_2 control. To facilitate uniform dispersion of the sorbent, a Venturi section is generally incorporated into the ducting such that the gas velocity is about doubled at the throat

The effectiveness of dry sorbent injection is limited. Reaction times are relatively short. Plugging of the pore structure of the alkali by reaction products reduces reagent utilization such that large quantities of reagent relative to the theoretical minimum requirement for acid gas neutralization (the stoichiometric ratio Φ) are required; usually more than five times the SO₂ plus HCl rate. The most effective control for HCl is achieved in the cooler regions of the furnace. These facts led several municipal refuse incinerator plants (esp. in Europe) to add a separate contact chamber with reagent (usually hydrated lime) injection after the boiler to increase the residence time for HCl absorption reactions in the zone of the lowest temperature in the system. Sodium bicarbonate can achieve 90% HCl control with an Φ of 2.0 but at a substantially higher reagent unit cost and with potential regulatory problems associated with disposal of the residue with its content of soluble sodium salts. The combination of dry injection with a fabric filter has a special advantage: the alkaline absorbent is deposited with the particulate in the cake on the filtering medium. Thereafter, the filter cake acts as an alkaline absorbent and continues to remove acid gases. This increases the utilization of reagent.

c. Dry Absorbent Contactors for Volatile Pollutant Control There is a class of pollutant that is partly or largely in the gas phase at "normal" dry particulate control temperatures (say, 150 - 300°C). Lowering the temperature ahead of the particulate control device may assist by condensing a larger fraction of the pollutant onto the surface of the extant particulate matter. This is, in fact, effective and adds to the attractiveness of wet and semi-dry collectors. © Walter R. Niessen 2011 Page **50** of **68**

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However, some enhanced removal in an all-dry system is possible if a material is added to the flue gases that selectively adsorbs or captures the volatile pollutant. This is the case for the addition of activated carbon and sodium sulfide (Na_2S) to the flue gases of municipal incinerators.

Activated carbon has been shown to be effective in removing a fraction of elemental mercury and its compounds from the gas phase and to scavenge high molecular weight compounds including PNHs and polychlorinated dibenzo p-dioxin and polychlorinated dibenzo furan compounds. The mechanism is assumed to be adsorption onto the carbon surface. Other than a relatively simple bin and injection device, the cost of adding this control is minimal. For the semi-dry contactors described below, carbon can be added with the lime in the slurry that is subsequently atomized and dried in the flue gas stream.

Sodium sulfide (Na_2S), can be injected as a solution at a point where the local gas temperature is high enough for rapid and complete evaporation to facilitate capture of mercury vapor after reaction to form the solid sulfide. The mercuric sulfide is subsequently removed by the particulate control device.

d. Semi-Dry Absorbent Contactors for Gaseous Pollutant Control As noted above, alkaline reagents show their highest utilization (low Φ) for a given level of control if the temperatures are low and if reaction time is long. These two process features led to the development, testing and implementation of the spray dryer absorber, fabric filter control concept for application to resource recovery systems. In this technology, a large chamber is added following the boiler when the temperature has been reduced to, say, 230 °C. At the top of the chamber, a water slurry of hydrated lime is injected through a spray dryer atomizer. The gas temperature and water quantities are kept in balance such that evaporation is rapid and complete in, say, two seconds or less. A conservative margin is added to the mean residence time to assure a dry particulate as input to the bag house or ESP.

The lime is slaked to $Ca(OH)_2$ using a minimum of two slakers, each designed for 100 percent capacity. Mechanical rotary atomizers have been used to produce a mist of finely divided droplets. The rotary atomizers typically consist of a 3,600 rpm motor coupled to a step-up gearbox to give a atomizer wheel speed of between 10,000 and 20,000 rpm. Slurry is introduced into the center of the wheel and extends over the rotating surface as a thin film. Two-fluid nozzles are also used to form the fine droplets. In these systems, 4.75 to 6.1 atmosphere compressed air provides the energy for disintegration of the slurry.

In comparing the two atomization methods one sees:

- The rotary atomizers produce a smaller droplet size and a narrower size distribution than do the twofluid nozzles. This improves collection efficiency.
- The high speed and sophistication of the mechanical devices requires a well-trained maintenance staff with special tools and equipment. The two-fluid nozzle can be maintained with common tools.
- The rotary atomizer has higher maintenance and capital costs but reduces reagent cost through its higher collection efficiency.
- For large systems (> 2,800 m³/min) the capital, maintenance and power costs for the two techniques are about equal.
- Gas flow turndown is much lower on a rotary atomizer (2.5:1) versus a two-fluid nozzle (20:1) but reagent flow turndown is much higher on a rotary atomizer (20:1) versus a two-fluid nozzle.

The water evaporation has two effects: cooling of the flue gases from about 300 $^{\circ}$ C to about 150 $^{\circ}$ C and the generation of a distributed field of acid absorbent particles (a mixture of CaO and Ca(OH)₂. Following the spray dryer chamber, the gas can be passed to an ESP or, more conventionally, a fabric filter. The ESP effects removal of

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the solid reactants (and other flue gas particulate). The fabric filter option accomplishes particulate removal but, also, provides another opportunity for acid gas contact as the acid gases pass through the dust cake. About 15 to 20 percent of the removal occurs on the filter cake [38]. The spray dryer absorber - fabric filter combination has achieved above 95% HCl removal and above 80% SO₂ removal while accomplishing general particulate control to levels well below regulatory requirements.

An example of a spray dry absorption system is shown in Figure 6. The tall, large diameter cylindrical vessel is the spray dryer (top fed). The rectangular boxes are the fabric filters. The smaller cylinder on the right is the lime storage tank.



Figure 6. Spray Dry Absorber System for Acid Gas Control

7. Specialized Abatement Technology

a. NO_x Control

1) Waste (Fuel Nitrogen) Control $-NO_x$ formation from fuel nitrogen sources can be important. Indeed, the NO_x concentrations via this mechanism can even exceed equilibrium levels. Consequently, one should consider the possibility of reducing the concentration of fuel nitrogen in the wastes being burned.

2) Low NO_x Burners – The NO_x appearing in combustor flue gases arises from fuel nitrogen and/or thermal sources. This generation matrix suggests a strategy for control:

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- Operate the initial stage of combustion under air-starved (reducing) conditions during which nitrogenous fuel chemistry is destroyed without generation of NO_x.
- Use diluent gas or heat removal to reduce the temperature of the off-gas from the first stage.
- Add the air required to complete combustion (now purely a thermal NO_x scenario) but, due to stage 2 processes, achieving a flame temperature low enough to produce low or acceptable NO_x flue gas concentrations.

Integration of the first and third process steps into a single device (staged combustion) constitutes the basic characteristic of a low- NO_x burner or LNB. The LNB generally produces a long flame length (occasioned by the air-starved zone's behavior) and has a large diameter. Such physical dimensions and operational characteristics can present significant problems with installation and flame impingement in retrofit situations. The LNB can usually achieve about 60% NO_x reduction, yielding a flue gas concentration of about 48 ppmdv (at 3% O₂) compared with about 120 ppmdv with standard burners [39].

Recent developments of ultra-low NO_x burners (ULNB) incorporate internal flue-gas recirculation to dilute and cool the flame. Tight oxygen control, minimal air leaks and advanced control systems (often including feedback from continuous emission monitoring instruments and automatic controls on stack dampers and air inlet registers) are needed to achieve good performance. Although more costly than the simpler LNB, the ULNB can achieve about 80% control (24 ppmdv at 3% O_2).

3) Combustion Zone Control and Flue Gas Recirculation – The staged combustion strategy involving control of the overall combustion environment to maintain a starved air combustion (reducing) condition or a low oxygen condition such that the fuel nitrogen is released as molecular nitrogen before entering a zone with a significant oxygen concentration is inherent in the operating strategy of the starved air type of "modular combustion unit" used for municipal, medical and industrial refuse. Further, in conventional mass burn incinerators, the grate combustion zone where most of the waste gasification occurs is distinctly reducing in nature. It is speculated that much of the fuel nitrogen contained in biomass waste material (e.g., grass clippings) is released in this zone of the furnace thus reducing the direct relationship between feed nitrogen content and flue gas NO_x emissions.

COMBUSTION ZONE CONTROL. Control of the combustion environment (temperature, oxygen concentration, degree of mixing, residence time) can be a powerful tool with which to reduce NO_x generation. MWCs typically employ a moving grate with two major sources of combustion air. Primary air is supplied through plenums located under the grate, and is forced through the grate to dry and gasify the waste. Secondary air is injected through nozzles located in the furnace walls immediately above the grate to provide turbulent mixing to complete the combustion process. On an overall stoichiometric basis, the secondary air provides the majority of the excess air to the combustion process.

With the VLNTM process, a proprietary technical design and process trademarked and patent pending by Covanta Energy Group, Inc., the secondary air stream is reduced, and a "VLNTM" gas stream is introduced through a new series of nozzles, installed at a higher elevation in the furnace. The VLNTM gas is taken from the roof of the lower furnace, above the last grate section [40] beyond the fireline in normal operating conditions, is relatively cool and has a high oxygen content. In conventional designs, a large fraction of this ash cooling zone flow remains coherent and does not substantially participate in combustion reactions with the fuel-rich gases rising from the gasification zone closer to the waste feed point. Consequently, the gas stoichiometry just ahead of the plane of secondary air injection ranges from reducing (oxygen deficient) at the front face and cooler and highly oxygen-rich at the back wall. By withdrawing gas from the ash cooling zone, the gas at the overfire air injection plane is generally hotter and more uniform. The secondary air jets, therefore, can provide combustion air efficiently, induce mixing and increment the mean temperature and while staying near or slightly below the stoichiometric point. Thus, fuel-NO_x in the gases is reduced. The final air addition (the VLN[™] gas stream) is made after some of the gas heat has been drained off through radiant transfer leading, overall, to a two-stage combustion-type NO_x reduction. © Walter R. Niessen 2011

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The relative amounts of primary and secondary air and the VLNTM gas stream are controlled to yield the optimal gas composition and temperature to minimize NO_x while simultaneously maintaining high burnout and low CO. The combination of these combustion changes in the VLNTM process yields an increase in furnace efficiency (more steam per ton of MSW fired), as well as lower NO_x emissions.

	Conventional WTE	VLN Process
Unabated NO _x (ppmdv @ 7% O2)	270 - 350	130 - 180
NO_x emissions when operated in conjunction with conventional SNCR system (ppmdy @ 7% O_2)	150 - 205	< 60

Comparison of Conventional and VLNTM NO_x Emissions on WTE boilers

FLUE GAS RECIRCULATION. Flue gas recirculation involves recirculation of cooled furnace gases to the combustion zone. Recirculation reduces temperature (minimizing thermal NO_x) and reduces the mean oxygen concentration (affecting both fuel nitrogen and thermal NO_x) generation. This technique yields about 50% of the NO_x as is generated by conventional mass burn technology but involves increased capital cost, a loss of flexibility in the combustor design and operation, and some increases in fan power usage.

Refuse and sludge incineration in both bubbling and circulating fluid bed incinerators with flue gas recirculation show NO_x emissions that are about 20 to 50% of that from a mass burn system. This may reflect the combination of low excess air operation (typically, the fluid bed systems operate at about 40 to 60 percent excess air in comparison to 80 to 120 percent in mass burn systems) and the withdrawal of heat in the waterwall and in-bed boiler tubes which reduces thermal NO_x formation.

4) Reduction Technologies

SELECTIVE, NON-CATALYTIC REDUCTION (SNCR). Thermal DeNO_x is the proprietary process concept initially developed and commercialized by the Exxon Corporation. Ammonia at a mol ratio to NO_x of between 2:1 and 3:1 is injected into the furnace gases in the temperature zone from 760 to 1100 °C although temperatures above 925 °C are preferred. Although the original applications used an injection grid within the flue gas stream, more recent installations inject the ammonia from wall injectors. Important requirements for good conversion include: good mixing, adequate residence time, and no impingement of the injected reagents on the boiler tubes. A more critical variable is the gas temperature. SNCR is most effective in the narrow temperature range from 925 °C to 1065 °C although it can be used in zones as low as 870°C to as high as 1200°C. However, outside the optimal range, reaction kinetics or less favorable equilibria reduce effectiveness. The principal reactions are:

$4NO + 4NH_3 + O_2 \longrightarrow 4N_2 + 6H_2O$	$(NH_3:NO = 1:1)$
$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$	(NH ₃ :NO = 2:1)

For temperatures between 870 °C and 1200 °C, the first equation dominates while at higher temperatures the second equation becomes increasingly important. At lower temperatures, the reactions are too slow and unreacted ammonia (known as "ammonia slip") is emitted. This failure mode is costly regarding reagent cost and causes a new pollution problem in its own right. Some jurisdictions severely regulate emitted ammonia concentrations.

The major ammonium products formed through side-reactions are ammonium sulfate $[(NH_4)_2SO_4]$ and ammonium bisulfate $[NH_4HSO_4]$. Ammonium sulfate is a dry, fine particulate (1 to 3 microns in diameter) that may contribute to

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plume formation and $PM_{2.5}$. The bisulfate is a highly acidic and sticky compound which, when deposited on downstream equipment such as air heaters, contributes to fouling and corrosion.

In the initial development of the process, anhydrous ammonia was the principal reductant used. Concern regarding the safety of compressed gases on-site led to development of embodiments of the process using aqueous ammonia. Although the tankage required is much larger and the shipping costs for the reagent are high (ammonia ships as a 28 weight percent solution), the safety issue has made the aqua ammonia approach preferred. A second SNCR technology (NO_x-OUT) of similar effectiveness which avoids the risk or costs of ammonia is based on the use of urea as the reductant; injected as a 5 weight percent concentration aqueous solution. Urea degrades to ammonia in a two-step process:

$$O=C-(NH_2)_2 \rightarrow NH_3 + HN=C=O$$
 (isocyanic acid)

$$HN=C=O+H_2O \rightarrow NH_3+CO_2$$

The urea-based process development was originally sponsored by the Electric Power Research Institute (EPRI) in the United States and subsequently commercialized and patented by Fuel Tech. The overall chemical reaction is:

$$2O=C-(NH_2)_2 + 4NO + O_2 \rightarrow 4N_2 + 2CO_2 + 4H_2O$$

The urea-based system nominally operates in the same temperature range and via the same chemical reactions as the ammonia-based technology. With use of proprietary additives, the temperature "window" for the process can be widened to span from 650 to 1100°C.

SELECTIVE, CATALYTIC REDUCTION (SCR). Selective catalytic reduction (SCR) involves ammonia reduction over a catalyst bed [375]. In most cases, titanium oxide and vanadium oxide catalysts are used. Control efficiencies from 90% to 97% have been recorded.

The three major reactions occurring on the SCR catalyst are:

$$4NH_3 + 2NO + 2O_2 \rightarrow 3N_2 + 6H_2O$$
$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O$$
$$8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O$$

These reactions are basically the same as with SNCR but SCR achieves the same or better control levels as SNCR (commercial systems achieve 80 percent removal of NO in power plants with essentially no NH₃ slip) but at a 1:1 ammonia to NO ratio (about one-half the ammonia consumption) at lower temperatures. Control levels as high as 97 percent NO removals have been reported but at 40 ppm NH₃ slip. Disadvantages may include an energy penalty for reheat and the first cost and replacement cost of the catalyst. Catalyst poisoning and/or deactivation during temperature excursions exacerbate the catalyst cost issue. Also, since SCR uses ammonia as the reductant, the safety issues and costs for storage and handling of the reagent reappear. Pressure drop across the catalyst bed is significant in some designs (increasing fan power costs)

The use of SCR has an additional advantage to the SNCR in that incinerator plant data indicate that dioxins and furans are oxidized to a significant degree on the titanium, titanium-tungsten-vanadium and platinum SCR catalysts [551].

• Low temperature SCR

Installation and operation of SCR at low temperatures (from 150 to 360°C) is possible for relatively clean gas streams and, if applicable, offers several advantages in installation cost and a modest pressure drop. Control efficiencies above 90% have been recorded. The pelletized catalyst systems used (such as in the Shell DeNOx © Walter R. Niessen 2011 Page 55 of 68

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system) have a high activity and are often used in a multiplicity of reacting beds arranged in thin layers in a lateralflow reactor system. Low temperature SCR is very sensitive to ammonium bisulfate precipitation (thus presenting difficulties for sulfur-containing wastes with SO₂ in the flue gases) and to fouling by particulate matter.

• Medium temperature SCR

Medium-temperature SCR operates between 260 and 385°C using honeycomb, metal plate or corrugated catalyst designs. These catalyst systems can withstand high sulfur and particulate loadings and can be equipped with soot blowers to purge particulate buildup. Downflow configurations are favored for high particulate matter situations. If temperature excursions above, say, 440°C occur, sintering of the catalyst can occur with consequent reduction in activity.

• High temperature SCR

Most reactor beds use ceramic honeycomb monoliths with square cell geometry, ranging in cell density of between 1.4 and 60 cells per square centimeter. This type of reactor, with its high surface area per unit volume yet low pressure drop, offers distinct technical advantages over other catalyst supporting materials such as random packing (rings or pellets). Increasing the cell density increases catalytic activity and improves mass transfer to the catalyst surface but at the price of an increasing tendency to plug and increased pressure drop per unit volume of gas treated. To avoid plugging and catalyst poisoning, the bed is usually sited after the particulate control device. In incinerator operations where particulate control involves a bag house to clean the gas ahead of the SCR system, the flue gas is generally limited to a maximum temperature of, say, 260°C so reheat (with attendant fuel cost) is needed to use this technology.

REBURNING. The post waste-burning zones can be brought back into a reducing condition by addition of an auxiliary fuel (usually natural gas) in conjunction with flue gas recirculation. Sufficient fuel should be supplied at a low location in the furnace to produce a hot, oxygen deficient zone with a stoichiometric ratio (Φ) less than 1.0, say 0.9. Under these conditions, NO_x formed in the bed and in the hot zone just over the bed is reduced to nitrogen. Overfire air is then added over the reburning zone to complete the combustion process [41].

5) Wet Scrubber Control

Nitrogen dioxide (NO₂) as the acid anhydride of nitrous acid can be easily scrubbed with caustic solutions. However, nitric oxide (NO) cannot. Since most combustion systems contain mixtures of the two oxides but favor the formation of NO, achieving high levels of NO_x removal requires a combination of an oxidation step to convert the NO to NO₂ followed by adsorption in an alkaline medium. Although NO oxidizes to NO₂ in the presence of excess oxygen, the oxidation rate at low temperatures and low NO concentrations makes gas phase oxidation strategies impractical. Oxidants such as ClO₂ react rapidly with NO in the gas phase. Oxidation in the liquid phase is slower, however, because the rate of absorption of NO is slow. The reactions with ClO₂ are:

 $2NO + ClO_2 + H_2O \rightarrow NO_2 + HCl + HNO_3$

Stoichiometric chlorine dioxide has been shown to eliminate about 95 percent of the NO in less than 2 seconds. There are problems, however, due to the reactive and hazardous nature of the chlorine dioxide. Other combinations result in some NO removal if NO_2 concentrations are high or if oxidants such as SO_2 are present. However, in most cases, direct scrubbing is an ineffective or problematic approach to remove NO.

An exception is the NO_x scrubber [42] that uses surface active, alkali media in a packed tower design with exceptionally large mass transfer surface. For total NOx concentrations in excess of 2000 ppmdv, a NO₂:NO mol ratio of 2:1 or greater and an O₂:NOx mol ratio greater than 5:1, between 90 and 99 percent NOx removal can be achieved. Several liquid-phase oxidants such as H_2O_2 , KMnO₄ or NaOCl can be used. The latter, scrubbing at a pH of about 9, is the most cost-effective. The optimum pH increases with contact time. © Walter R. Niessen 2011 Page **56** of **68**

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b. Mercury Control

Mercury, as an elemental pollutant, appears in MWC and other incinerator flue gases in trace quantities because of the presence of mercury and/or its compounds in the waste fed to the unit. It is not, as with dioxins and the like, "formed" within the system. Owing to its variable source characteristics, the mercury concentration in waste as well as the mercury emission chemistry is quite variable. Therefore, control efficiency determinations must be made based on simultaneous inlet-outlet sampling and using sampling and analytical methods that capture all mercury forms. The ratio of the controlled emissions measured at one time to the uncontrolled emission measured at another time is of uncertain meaning and utility. Citations of "negative collection efficiencies" in the literature are symptomatic of this problem.

Mercury data are strongly influenced by the nature of the mercury chemistry in the emission: elemental mercury (Hg or Hg₂), mercuric (+2) or mercurous (+1) chloride (HgCl₂ or HgCl), mercuric or mercurous sulfide (HgS or Hg₂S) etc. These chemistry-related effects result from the interactions between the physical form (gas or solid) and/or chemical reactions in the sampling train on the reported mercury concentration and, thus, the reported capture efficiency. Such problems are being resolved as the sampling and analysis protocols continue to receive attention. The consequence of this continuing development, however, is that data sets may not be comparable if the sampling/analysis methodology differs.

Finally, many <u>process</u> variables affect both mercury emission character and mercury control effectiveness. Temperature is very important. Thermochemical calculations indicate that mercury compounds convert to elemental mercury in the high temperature regions of the combustor. As the gas cools, some of the mercury is converted to ionic forms with mercuric being the preferred valence state. In the presence of HCl, this often leads to the presence of mercuric chloride (HgCl₂).

Other process variables include the inlet mercury chemistry and concentration and the presence of adsorptive surface on particulate. One finds, for example, that RDF type MWC systems with fly ash having high carbon content effect some intrinsic mercury control. Also, reactive chemicals (e.g., OCl⁻ ion) in wet scrubber solutions may influence collection efficiency. Thus, the analyst must carefully research all of the potentially important variables in assessing data from different source types and control system characteristics on the apparent control effectiveness or lack thereof.

The control technologies applicable to mercury involve four strategies:

- Cooling of the flue gases such that condensation and absorption onto fly ash occurs. Removal is effected in the particulate control device;
- Wet scrubbing, a combination of substantial gas cooling coupled with particulate control;
- Addition of chemicals to the flue gases that react with mercury vapor to produce a solid reaction product. Removal is effected in the particulate control device; and

• Addition of materials to the flue gases that absorb mercury vapor and the vapor of mercury compounds thus trapping them. Removal is effected in the particulate control device.

1) Cooling – The first approach (cooling) is effected to a degree by the "dry scrubber" technology (dropping the temperature to about 130 °C). Further, the heavy particle concentration following the dry scrubber provides a large surface area for condensation and adsorption of mercury and its compounds. Data indicate that between 15 and 46 percent mercury removal can be associated with the cooling and particulate removal of the dry

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scrubber system itself (no carbon injection). Although the mercury is ultimately captured in the particulate control device that follows, one could ascribe to the dry scrubber the enhancement in collection achieved by the temperature reduction. However, removal efficiency is considerably enhanced at the much lower temperatures (say, 60°C) achieved in wet scrubber systems.

2) Wet Scrubber – The mechanism through which a wet scrubber contributes to the achievement of acceptable mercury control is hard to confidently identify. Somewhat less than 40% control is generally achieved by either a bag house or ESP collector simply through the collection of particulate (solid phase mercury compounds and some surface adsorption of vapor). The wet scrubber does not achieve the levels of particulate collection of either of these devices. The impact of the wet scrubber is on the gas phase mercury chemistry: elemental mercury and mercury compounds in the vapor state. The mercury compounds are removed by enhanced condensation at the much lower working temperatures of wet scrubbers (typically less than 65 °C) or solvation of water-soluble salts vis-à-vis dry and relatively hot ESP or bag house systems. The elemental mercury, however, with water or alkaline scrubbing, would still not be expected to be removed to a significant degree since only about 20% of the total mercury appears as elemental mercury vapor. If active chlorine is added to the scrubbing water (e.g., as sodium hypochlorite), one might expect that the mercury would be converted to the chloride and, then, is scrubbable. This may be an exploitable characteristic of wet scrubbing control.

The data base for assessment of this technology is cloudy. The majority of the available data are on European and Japanese plants where wet scrubbers have been added following ESP or bag house particulate control systems. Interpretation of European data is difficult due to differences in their sampling and analysis protocols and, due to mercury adsorption on carbonaceous fly ash, the unclear incremental contribution from the scrubber in the overall mercury reduction.

Wet scrubbers are an expensive approach (in capital) and, through the need for wastewater treatment, increased fan power, and, perhaps, the needs for reheat, the operating cost is very high. Some plants have used additives such as trimercapto-s-triazine (TMT) to stabilize condensed mercury compounds to minimize revolatilization. The reagent cost is relatively low for both mercury and acid gases, but the other operating expenses are not. As to the expected control level, assuming that the concept involves both a wet scrubber and either a bag house or ESP but without carbon addition, one would expect total control levels no more than the 60& to 70% range.

3) Formation of Solid Reaction Products – Reacting mercury vapors to generate a solid reaction product has been effected in Sweden, Germany and in trials in British Columbia [43]. The plants inject a solution of sodium sulfide (often, about 10 to 15 weight percent by weight Na_2S) upstream of a spray dryer absorber in gases at temperatures between 130 and 250°C. The reactions are not totally clear but appear to be:

and

$$Hg_{gas} + Na_2S \cdot H_2O \rightarrow HgS_{solid} + NaOH$$

$$HgCl_{2gas} + Na_2S \cdot H_2O \rightarrow HgS_{solid} + NaCl \cdot H_2O$$

The sulfide is then removed in the particulate control device. Capital costs and reagent costs are low. However, the explosive, odorous and toxic nature of the hydrogen sulfide gas that is released in small but significant amounts when the sodium sulfide is dissolved in water presents an operational hazard. There may be some proprietary features to the sodium sulfide addition. The performance of the sodium sulfide system appears to be somewhat less than that of activated carbon at comparable cost. It is reported that Na_2S feed rates vary from 0.05 to 0.5 kg/ton of MSW depending on the amount of mercury in the flue gas, the level of control required and the level of carbon present in the fly ash.

4) Carbon Adsorption – This process technology involves injection of activated carbon into the flue gases followed by physical and chemical adsorption of vapor-phase mercury and its compounds onto the carbon. "Doping" of the carbon with chemicals (such as sulfides) that create strong chemical bonds to elemental mercury may enhance

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capture. In combination with the removal of solid-phase mercury compounds in the particulate control device, high overall control efficiencies are realized.

Of the several technologies for mercury control, there is more experience with injection of dry activated carbon than with alternatives where the carbon is added to the lime slurry tank and injected into the flue gas stream through the spray dryer absorber (SDA) system. The captured mercury compounds are ultimately found in association with the fly ash. Capital costs are relatively low and, due to the low dosage rates (about 60 milligrams per cubic meter of flue gas) the chemical costs are medium to low (in absolute dollar terms). In concept, activated carbon addition can be made either ahead of or after a spray dryer and before either a fabric filter or an electrostatic precipitator. Most facilities inject the carbon ahead of the spray dryer, just after the economizer section of the boiler and in association with a fabric filter dust collector.

Mercury collection efficiency with carbon injection is related to the injection rate (kilograms of carbon per ton of refuse burned), to the initial mercury concentration and to temperature. Higher carbon addition rates and lower temperatures favor high removal efficiency. With spray dryer systems (where temperatures are below 150 °C), collection is better than the electrostatic precipitator (ESP) systems which typically operate above 230 °C.

Carbon is injected in the dry state using a pneumatic injection system. The carbon is stored in bulk in a simple silo, and reclaimed by gravity through a weigh-feeder, swept up in an eductor and is blown to injection orifices between the economizer outlet and the SDA. With injection at the rate of about 0.4 kilograms per ton of refuse being burned, control efficiencies of between 85 and 95 percent appear to be reliably achievable in most plants.

As the carbon unit rate decreases, one sees a drop in collection efficiency as illustrated in tests run at the Stanislaus County CA facility. The data from the Stanislaus tests [44] were correlated with an r^2 of 0.777 by:

$$\ln(Hg_{out}) = 5.66 - 0.2652 \,(\Lambda)^{0.5} + 0.000724 (Hg_{in}) \tag{44}$$

Where Hg_{out} and Hg_{in} are the outlet and inlet mercury concentrations, respectively in units of μ gm/dscm and " Λ " is the carbon concentration in the flue gas in mg/dscm. The tests showed no statistically significant effect of carbon injection location (economizer outlet or spray dryer inlet); no effect of carbon type (wood-based, coal-based and lignite-based carbon were tried); and no significant effect of ammonia concentration (present as "ammonia slip" from the NO_x control system).

The dosage rate of carbon is established by a series of tests to determine the optimal injection rate that comfortably meets permit requirements. Plotting the injection rate against the target requirements (a given percent removal or a stack concentration), provides the set point in kilograms of carbon per hour for use in normal plant operation. The adequacy of the set point is normally confirmed through periodic retesting.

c. Control of Dioxins and Other Hydrocarbon Pollutants

1) Good Combustion Practice – Although back-end APC approaches to limiting organic compound emissions including CDD/CDF are possible, the fact that a number of simple, low temperature chemical reactions are, most likely, the dominant source of the compounds emphasizes the importance of destroying organic precursors before the compounds leave the furnace: a "control" concept called "Good Combustion Practice" or GCP. Analysis of refuse incinerators shows six major areas of design that impact on the achievement of substantially complete oxidation of hydrocarbon species [45]:

• Temperature at the fully mixed location (usually defined as the plane just above the highest overfire air jet inlet) a minimum of 1000 °C;

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- Amount and distribution of combustion air (to assure availability of oxygen);
- Mixing;
- Particulate matter (PM) carryover (to minimize the amount of graphitic carbon reaching the temperature zones in the boiler and APC systems where dioxin formation occurs);
- Downstream temperature; and
- Stability of waste feed rate (to keep temperatures stable and high).

Reaction time is indirectly addressed by the temperature, combustion air, mixing and PM carryover components. With good mixing, the destruction of the CDD/CDF precursors in the gas phase is rapid at relatively modest temperatures (say, 600°C); far less time is required than the one or two second residence time often set as a minimum. Reactions of organic compounds and char associated with PM, however, are much slower and may be controlled by diffusion of oxygen into the particle rather than oxidation kinetics. For these more refractory precursors, the higher target temperature and longer times are appropriate.

The achievement of these target conditions in the combustion environment requires a well-designed and operated overfire air system in combination with prudent use of underfire air controls to avoid excessive particulate carryover. Blending of the incoming waste to minimize areas on the grate with wet waste is also important. Achievement of good mixing must extend over the practical operating range of the unit. Problems can arise at low load when an overfire air flow rate that is tied in the process control computer to the overall refuse burning rate is turned down. Then, penetration of the fuel-rich gases from the grate by the cross-flow air jet may become inadequate.

Although GCP must be regarded as the primary and most effective strategy for dioxin reduction, data indicate that various elements of the back-end APC systems also impact on dioxin emissions. Most importantly, the use of an ESP for particulate control without a spray dryer absorber system to further cool the gases after they leave the economizer holds the captured fly ash for extended periods of time at a temperature where CDD/CDFs form by oxychlorination of residual carbon in the fly ash. Thus, unless the carbon residual is very small (probably, less than 2 percent loss on ignition for the fly ash), the mass emission rate of CDD/CDF compounds may actually increase across the ESP despite the removal of the CDD/CDF material associated with the particulate matter.

When the ESP is run "cold" or a bag house collector is installed after a spray dryer absorber, significant CDD/CDF reductions are normally achieved. The reduction is usually better with the bag houses due to the passage of the flue gas through the filter cake such that the condensed submicron CDD/CDF is captured and additional material is adsorbed on fly ash and sorbent particles. Both the ESP and bag house alternatives following a spray dryer are made still more effective in CDD/CDF reduction when carbon injection is practiced using the dry method, the wet method or the wet method using carbon-enhanced lime-based sorbent in place of lime. Some improvement should be expected from carbon injection for the emissions of other high molecular weight organic compounds (e.g. PAHs).

2) Catalytic Destruction

CATALYTIC FILTER. Catalytic filtration involves the addition of a dioxin-active catalyst to the felt filtration media used in fabric filter baghouses. The catalyst acts on gaseous PCDD species. If the filtration media is enhanced using a Teflon® membrane to improve fine particle capture, the filtration combination also effectively removes PCDD/F species adsorbed on solid phase pollutants. Catalytic filtration was conducted on the flue gases of a medical waste incinerator. The inlet PCDD/F concentration was 2.57 ng TEQ/Nm³ at 11% O₂ and the clean gas concentration was 0.075 ng TEQ/Nm³ at 11% O₂. Full-scale tests in three MWC's showed reductions in effluent concentrations of dioxins/furans to significantly less than 0.1 ng TEQ/Nm³ at 11% O₂. At the UIOM plant in

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Thonôn-les-Bains, France (a 100 ton/day Volund grate unit with an ESP following the boiler and sodium bicarbonate injection ahead of a fabric filter using the catalytic filter system), uncontrolled emissions were 1.9 ng I-TEQ/Nm³ at 11% O_2 . The post filter, clean gas concentrations were 0.0114, 0.0047, 0.0060 and 0.0260 ng I-TEQ/Nm³ at 11% O_2 .

CATALYSIS WITH SCR. As discussed above regarding NO_x control using SCR, the catalysts used for SCR often show some significant removal of dioxins in addition to their catalytic function in NO_x reduction.

3) Dry Scrubber Absorption

The condensation or attachment of dioxin/furan species onto particles can be seen as a potentially attractive control technology. While the degree of control may not be sufficient to meet increasingly stringent effluent regulations, the control that is achieved may be an important part of the overall control strategy. Data indicate that lime spray absorption followed by fabric filtration is highly effective for organic vapor control and superior to the spray absorber-ESP combination. Lower flue gas temperatures by spray absorption and flue gas humidification before dry sorbent injection favor improved organics removal.

4. Dry Sorbent Injection Technology

Dry sorbent injection (DSI or "dry-dry scrubbing)" has been seen by many in the field as a means for existing facilities to effect significant reductions in the emission of acid gases and minor reductions in condensable organic emissions with a modest capital and operating cost investment and minor layout impact. The process concept involved in dry injection is simple: injection of dry, powdered limestone, hydrated lime or sodium-base alkali (carbonate or bicarbonate) into the flue gas with subsequent collection using the particulate control device. The alkaline additive absorbs HCl, HF, SO₂ and other acid gases. The particulate matter increases the surface area available for condensation of high molecular weight organic matter such as the dioxin and furan compounds and polynuclear hydrocarbons.

However, the actual processes involved in dry injection are complex. Parameters that affect the degree of removal include the temperature at the point of injection, the chemical form of the additive, the temperature at the back end of the flue gas train and the concentrations of acid gases and hydrocarbons to be removed. The temperature effect produces the three sub-groups in dry injection technology: high temperature furnace injection, moderate temperature duct injection and low-temperature duct injection (HTFI, MTDI and LTDI, respectively). Calcium-based alkali injection is the baseline of the technology. Sodium alkalis remove acid gases quite adequately. However, the calcium alkalis are preferred due to the lack of field data for sodium-based systems, the high solubility of the sodium chloride/sulfite/sulfate reaction products (causing some problems in disposal) and the high relative cost of the sodium chemicals.

HTFI has been used with both conventional and fluid bed combustors. When the operating temperatures exceed 760 to 1,100 °C and with sufficient residence time, limestone will calcine to lime and is a preferred and lower cost alkali. In conventional refuse incinerators, lime or limestone can be injected into the furnace using the existing overfire air system (or with dedicated injectors). In general, HTFI is focused on SO₂ control since the equilibrium for the HCl removal reaction is not favorable at high temperatures. The overall effectiveness for SO₂ reduction is between 40% and 60% with efficiency increasing as the back-end flue gas temperature decreases.

MTDI and LTDI injection usually involve hydrated lime (Ca(OH)₂). MTDI involves injection in the temperature range from 200 to 315 °C and LTDI at about 150 °C. Reaction is rapid and, with one to two seconds of residence time ahead of the particulate control device, removal is adequate. Injection means can involve a simple lance but, in most plants, injection is made at a Venturi constriction located after the economizer and ahead of the particulate control system. Removal of both SO₂ and HCl is effected. The best removal corresponds to the lower temperature operations and to those where a fabric filter is used for particulate control (thus, giving an opportunity for gas-solid

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reaction both in suspension and as the solids accumulate in the filter cake). Overall collection effectiveness for the fabric filter embodiment ranges from 40 to 50% for SO_2 while from 80 to 90% control is achieved for HCl.

Some control effectiveness has been claimed for the medium and low temperature dry sorbent injection technology with respect to dioxin/furan compounds. The claims are based on a process concept involving the availability of additional surface area for condensation of these and other low vapor pressure compounds in combination with a presumed benefit of removing HCl from the gas phase. The data are too limited to conclusively show the advantages, however.

III. CONTROL STRATEGIES FOR INCINERATOR AIR POLLUTANT CONTROL

A. Air Pollution Control through Process Optimization

The air pollutants generated in incineration systems include mineral and combustible particulate, sulfur oxides, nitrogen oxides, hydrogen halides, incompletely burned "total hydrocarbons" (actually, a diverse mixture of compounds of carbon, hydrogen, oxygen, nitrogen, halogens etc.) and carbon monoxide. Some pollutants are fragments of original waste components. Others are entirely new species, created in the chemistry laboratory that is the combustion environment. The relationships between the design and operating parameters of the incinerator/waste system and the emission rates of pollutants are complex but, at least, broadly understandable. This understanding should provide the basis for the first level of "air pollution control". The general relationships available include:

Waste Control

Exclusion of certain wastes (e.g., auto batteries as a source of lead, mercury batteries as a source of mercury compounds, gypsum wallboard as a source of sulfur oxides)

Feed Rate (affecting the mean residence time in the system and the average flow velocities that induce turbulent mixing)

Air Supply

Underfire air flow affects particulate loading through elutriation and, perhaps, heavy metal emissions through excessive bed temperatures)

Overfire air flow affects combustible pollutants through stimulation of vigorous mixing to assure that the oxygen concentration is maintained everywhere greater than zero but nowhere in so much oversupply as to cool and quench combustion)

Excess air affects the generation of nitrogen oxides and the oxidation rate of combustibles)

Temperature Control

- *Gas temperature* impacts strongly on combustion rate (kinetics). Of particular importance is the temperature in failure zones (near walls or other cooled surfaces or where tramp air from leakage points enters the flow so that the local temperature is very low compared to the mean temperature measured in the center of outlet ducts) such that combustion is "quenched"
- *High temperatures* can lead to volatilization of several metal compounds and, ultimately, increased heavy metal emissions
- *Low temperatures* in the back end of units equipped with boilers and scrubbers can lead to condensation of volatilized metal and heavy organic compounds

It is easy to focus entirely on "back end" treatment for APC. And yet, there is great power in using these causality relationships and others [1] to find design and/or operating levers to significantly reduce the demands on the back end.

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B. Control Selections for Incinerator Types

The designation of a particular item of hardware as the "optimal" APC system is not a simple task nor is the "answer" static and universally valid. Rather, the characteristics of one's' particular waste (present and forecast) establish a preferred incinerator concept. Then, the combination of waste characteristics and the selected incinerator hardware fixes (within limits) the uncontrolled emission rate of the several possible air pollutants. One then looks at the uncontrolled emissions and the extant (and forecast) emission regulations at the federal, state and local level. Beyond these relatively firm factors, one must also consider the policies and practices, the financial resources, the personnel skills and the performance flexibility needs of the ultimate owning organization. At that point, the "best" APC technology and most of the key design and operating features should fairly spring from the list of candidates.

1. Municipal Refuse Incinerators

In the early days of municipal waste incineration in the United States, the regulatory focus was entirely on particulate. The emission standards of that time could be met with simple wetted baffle "scrubbers." Passage of the Clean Air Act in 1970 tightened the particulate code substantially. In combination with the shift to waterwall construction (minimum air in-leakage and tolerance of high gas temperatures), these regulations introduced the dry ESP as the accepted control device. Interestingly, the requirement for ESPs to meet particulate codes was the driving force for the initial introduction of heat recovery features to U.S. municipal incinerator practice: one could not afford to install an ESP at the high excess air levels commonly used with (leaky) incinerators of all-refractory construction. By 1970, the ESP had already become dominant for European facilities.

In the mid/late 1970's, the regulatory spotlight in the U. S. shifted to the polychlorinated dioxin/furan compounds. The proper control technology for these materials focuses on upgrading the combustion environment. Burn out the precursors and there will be little or no dioxin. The data on emission factors suggests that combustion control, by itself, is an effective solution and that the dioxin problem is now well in hand.

In parallel with the dioxin/furan controls, the requirements for back-end treatment underwent a major change: extending the control requirement to include "acid gases": most importantly, HCl and SO₂. The solution to the requirement for acid gas control was the combination of the semi-dry absorber with lime slurry addition followed by a fabric filter. This system also cooled the gases, and, thus, further reduced dioxin/furan and mercury emissions. The excellent fine-particle control effected by the fabric filter also significantly reduces emissions of heavy metals.

In the early 1990's, attention moved to mercury and to the nitrogen oxides. Mercury can be controlled to an acceptable degree through injection of activated carbon ahead of the fabric filter. As discussed above, operational hazards with the sulfide makes the carbon option preferable. Activated carbon injection has also shown effectiveness in reducing dioxin/furan and other high molecular weight hydrocarbons (PNH, PCBs) to levels below those achieved by combustion control. Modern plants also address nitrogen oxides control to the 50-65% level using ammonia or urea solution injection into the flue gases in the superheater region (selective, non-catalytic reduction or SNCR technology).

Therefore, at the present, "optimum" control for municipal waste combustors involves high quality combustion controls and mixing systems, urea/ammonia and carbon injection, semi-dry spray dryer absorbers and a fabric filter (plus, a tall stack that effects dispersion and avoids building downwash). The direction of U.S. regulatory agencies is difficult to predict. However, one might speculate that greater control will be required for metals and, perhaps, for nitrogen oxides. This could lead to the use of a dry followed by a wet electrostatic precipitator (replacing the fabric filter) with reheat ahead of catalytic, ammonia-based NO_x reduction. Plants with this APC flow sheet are operating in Europe.

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2. Biological Wastewater Treatment Sludge Incinerators

Until 1992, air pollution emission limits for sludge incinerators in the United States focused on the control of particulate matter. The relatively lenient particulate emission standards called out in U.S. law were substantially endorsed without change by all of the states. The federal emission limitation of 1.3 pounds of particulate per dry (English) ton of sludge burned can be readily met using a Venturi and/or tray type wet scrubber with an overall pressure drop of the order of 10 kilopascals. Often, the combination of Venturi and tray tower was used to effect particulate control and, with substantial once-through water flow to the tray section, to subcool the flue gases to condense excess water and effect plume suppression.

In the late 1980's and early 1990's, one began to see a shift in the APC concepts selected for U.S. sludge incinerator upgrades and for new facilities. Specifically, one notes an increase in the use of a wet electrostatic precipitator downstream of a Venturi and impingement tray scrubber. This increment in control substantially reduces total particulate emissions but the particular objective sought in this control increment was a reduction in the emission of heavy metals and high molecular weight hydrocarbon aerosols. Recent EPA pressure for mercury reduction has suggested the addition of carbon injection and a bag house after the Venturi but the cost for this option is problematic.

For multiple hearth furnaces, stringent total hydrocarbon regulations promulgated in late 1992 led to installation of separate afterburners (typically operated at 700 to 850 °C). An alternative design involved re-work of the system to move the sludge feed point to the second hearth and to add burners and simple refractory baffles to the top hearth. The latter concept is known as a "Zeroth Hearth Afterburner". In general, none of the fluid bed incinerators required modification or augmentation to achieve the total hydrocarbon requirements.

3. Hazardous Waste Incinerators

The regulation of air emissions from hazardous waste incinerators initially focused on means to assure destruction of the toxic organic matter in the feed and on control of acid gases (particularly, HCl). This led to concern over the severity of the combustion environment (monitored through temperature, oxygen concentration, and total flow rate) and, usually, to the addition of Venturi scrubbers with alkali for particulate and acid gas capture. In the mid and late 1980's, it became clear that the effluent gases could and often did include heavy metals. This led to increased regulatory attention being paid to metals emissions and, often, to requirements for health risk assessments on the implications of metals emissions. However, in most instances, the Venturi scrubber systems can satisfactorily achieve acceptable emission levels. In large plants in the U.S. and in Europe, the spray dryer with fabric filter combination or the Venturi-wet ESP combinations have become accepted.

Only in the rare case where an entirely gaseous organic waste or an organic liquid without dissolved or suspended solids is being burned will no follow-up control be required to meet emission regulations. The presence of chlorine or other halogens general requires a scrubbing or absorption step. Suspended ash will require particulate control. In some specialized cases, such as the combustion of nitrates or nitric acid wastes, NO_x control is necessary. However, in most cases, NO_x control is not a requirement thus allowing both the combustion conditions and the APC device to focus on the environmentally more significant particulate matter, dioxins, heavy metals and other hazardous emissions.

The most commonly used APC a system on hazardous waste incinerators involves a water quench followed by highenergy Venturi scrubber. Although this approach is effective for most particulate matter, the high pressure drop (3 to 40 kPa) contributes significantly to the operating cost of the incineration facility. A spray dryer absorber or packed tower absorber may be added for acid-gas removal and a demister to capture any carry-over droplets. If metal aerosols are important, an ionizing wet scrubber or wet ESP may be preferred. If high molecular weight organic matter and, especially, dioxin/furan compounds are involved, activated carbon injection may be appropriate.

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C. Continuous Emission Monitoring

1. General

Increasingly, regulatory agencies demand continuous emission monitoring (CEM) of pollutant emissions. In the 1980's, the primary pollutants monitored included particulate (opacity), SO_2 , NO_x and CO_2 but by the early 1990's, CEM use was extended to include HCl, CO, ammonia and total hydrocarbons (THC). The output from CEM systems are used both to confirm continuing compliance with air emission regulations and as input to process control.

2. Non-Dispersive Infrared (NDIR) Monitoring

In systems with a large stack (long path length), non-dispersive infrared (NDIR) gas analysis is relatively low in cost, accurate, rugged, low in maintenance, offers automatic calibration and exhibits a fast response. Units are available that meet EPA, RCRA and most state requirements for CO, CO₂, HCl, HF, HC, SO₂, NO_x (or NO, NO₂, N₂O separately), and NH₃.

For small incinerators IR technologies may not be applicable due to the short absorption path length across the small diameter stacks. This may require use of CEM's with gas sampling. Note, however, that for units with fabric filter or ESP particulate control, the clean gas plenum of the bag house or ESP can be used as the gas volume sampled using IR. Using this strategy, the effective path length can be several meters and measurement accuracy and range are correspondingly high.

3. Triboelectric Fabric Filter Leak Monitoring

Opacity is important both as a regulated plume characteristic and as an indication of fabric filter bag breakage. For many years, opacity was measured as a gross measure of changes in particulate concentration by transmittance monitoring using a light beam. However, the reading can be affected by misalignment or clouding of the lenses, atmospheric conditions, the color of the particulate, fumes in the gas stream and other factors. Opacity is also to inaccurate and unreliable to provide early detection of bag leaks in a fabric filter system.

The USEPA study as part of their Fabric Filter Bag Leak Detection Guidance compared three methods for detection of stack particulate. They showed the resolution to be:

Opacity monitors	2 mg/m^3
EPA Method 5 stack test	6 mg/m^3
Triboelectric	0.005 mg/m^3

Triboelectric technology is based on the principle that when particles conveyed in a pipe collide with or come close to an electrically isolated and earth-grounded probe a charge transfer results. The charge transfer (the triboelectric current) takes place on a continuous basis because the particle flux is continuous. The magnitude of the current can be used to indicate bag breakage and can also be used, with proper calibration, for continuous particulate concentration monitoring.

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