33

Control of Hazardous Air Pollutants

I. AIR QUALITY AND HAZARDOUS WASTES

In Chapter 32, we generally address air pollution as a byproduct of another process, such as manufacturing. Air pollution controls are also a necessary component of directly treating other forms of wastes. The goal is to treat the waste to reduce the toxicity, to decrease exposures and, ultimately, to eliminate or at least properly the risks from hazardous substances in the waste. The type of technology applied depends on the intrinsic characteristics of the contaminants and on the substrate in which they reside. The choice must factor in all of the physical, chemical, and biological characteristics of the contaminant with respect to the matrices and substrates (if soil and sediment) or fluids (air, water, or other solvents) where the contaminants are found. Chapter 32 provides the basics of most air pollution control technologies, but when addressing particularly hazardous air pollutants, a number of additional factors must be considered. The selected approach must meet criteria for treatability (i.e. the efficiency and effectiveness of a technique in reducing the mobility and toxicity of a waste). The comprehensive remedy must consider the effects of each action taken will have on past and proceeding steps.

Eliminating or reducing pollutant concentrations in a waste stream begins with assessing the physical and chemical characteristics of each contaminant, and matching these characteristics with the appropriate treatment technology. All of the kinetics and equilibria, such as solubility, fugacity, sorption, and bioaccumulation factors, will determine the effectiveness of destruction, transformation, removal, immobilization of these contaminants. For example, Table 33.1 ranks the effectiveness of selected treatment technologies on organic and inorganic contaminants typically found in contaminated slurries, soils, sludges, and sediments. As shown, there can be synergies (e.g. innovative incineration approaches are available that not only effectively destroy organic contaminants, but in the process also destroys the inorganic cyanic compounds). Unfortunately, there are also antagonisms among certain approaches, such as the very effective incineration processes for organic contaminants that transform heavy metal species into more toxic and more mobile forms. The increased pressures and temperatures are good for breaking apart organic molecules and removing functional groups that lend them toxicity, but these same processes oxidize or in other ways transform the metals into more toxic or more bioavailable forms. So, when mixtures of organic and inorganic contaminants are targeted, more than one technology may be required to accomplish project objectives, and care must be taken not to make trade one problem (e.g. polychlorinated biphenyls, PCBs) for another (e.g. more mobile species of cadmium).

The characteristics of the substrate (e.g. solid waste, soil, sediment, or water) will affect the performance of any contaminant treatment or control. For example, sediment, sludge, slurries, and soil characteristics that will influence the efficacy of treatment technologies include particle size, solids content, and high contaminant concentration (see Table 33.2).

Particle size may be the most important limiting characteristic for application of treatment technologies to sediments. Most treatment technologies work well on sandy soils and sediments. The presence of fine-grained material adversely affects treatment system emission controls because it increases particulate generation during thermal drying, it is more difficult to dewater, and it has greater attraction to the contaminants (particularly clays). Clayey sediments that are cohesive also present materials handling problems in most processing systems. Solids content generally ranges from high (i.e. usually the *in situ* solids content (30–60% solids by weight)) to low (e.g. hydraulically dredged sediments (10–30% solids by weight)). Treatment of slurries is better at lower solids contents; but this can be achieved even for high solids contents by water addition at the time of processing. It is more difficult to change from a lower to a higher solids content, but evaporative and dewater approaches, such as those used for municipal sludges, may be employed. Also, thermal and dehalogenation processes are decreasingly efficient as solids content is reduced. More water means increased chemical costs and increased need for wastewater treatment.

Elevated levels of organic compounds or heavy metals in high concentrations must also be considered. Higher total organic carbon (TOC) content favors incineration and oxidation processes. The TOC can be the contaminant

TABLE 33.1

Effect of the Characteristics of the Contaminant on Decontamination Efficiencies

	Organic contaminants					Inorganic contaminants		
Treatment technology	PCBs	PAHs	Pesticides	Petroleum hydrocarbons	Phenolic compounds	Cyanide	Mercury	Other heavy materials
Conventional incineration	D	D	D	D	D	D	xR	pR
Innovative incineration[a]	D	D	D	D	D	D	xR	I
Pyrolysis[a]	D	D	D	D	D	D	xR	I
Vitrification[a]	D	D	D	D	D	D	xR	I
Supercritical water oxidation	D	D	D	D	D	D	U	U
Wet air oxidation	pD	D	U	D	D	D	U	U
Thermal desorption	R	R	R	R	U	U	xR	N
Immobilization	pI	pI	pI	pI	pI	pI	U	I
Solvent extraction	R	R	R	R	R	pR	N	N
Soil washing[b]	pR	pR	pR	pR	pR	pR	pR	pR
Dechlorination	D	N	pD	N	N	N	N	N
Oxidation[c]	N/D	N/D	N/D	N/D	N/D	N/D	U	xN
Bioremediation[d]	N/pd	N/D	N/D	D	D	N/D	N	N

[a] This process is assumed to produce a vitrified slag.

[b] This effectiveness of soil washing is highly dependent on the particle size of the sediment matrix, contaminant characteristics, and the type of extractive agents used.

[c] The effectiveness of oxidation depends strongly on the types of oxidant(s) involved and the target contaminants.

[d] The effectiveness of bioremediation is controlled by a large number of variables as discussed in the text.

Primary designation
D = effectively destroys contaminant
R = effectively removes contaminant
I = effectively immobilizes contaminant
N = no significant effect
N/D = effectiveness varies from no effect to highly efficient depending on the type of contaminant within each class
U = effect not known

Prefixes
p = partial
x = may cause release of non-target contaminant

Source: US Environmental Protection Agency, *Remediation Guidance Document*, Chapter 7, EPA-905-B94-003, 2003.

TABLE 33.2

Effect of Particle Size, Solids Content, and Extent of Contamination on Decontamination Efficiencies

	Predominant particle size			Solids content		High contaminant concentration	
Treatment technology	Sand	Silt	Clay	High (slurry)	Low (*in situ*)	Organic compounds	Metals
Conventional incineration	N	X	X	F	X	F	X
Innovative incineration	N	X	X	F	X	F	F
Pyrolysis	F	X	X	F	X	F	F
Vitrification	X	F	F	X	F	F	X
Supercritical water oxidation	X	F	F	X	F	F	X
Wet air oxidation	F	X	X	F	X	F	N
Thermal desorption	F	X	X	F	X	F	N
Immobilization	F	X	X	F	X	X	N
Solvent extraction	F	F	X	F	X	X	N
Soil washing	F	F	X	N	F	N	N
Dechlorination	U	U	U	F	X	X	N
Oxidation	F	X	X	N	F	X	X
Bioslurry process	N	F	N	N	F	X	X
Composting	F	N	X	F	X	F	X
Contained treatment facility	F	N	X	F	X	X	X

F: sediment characteristic favorable to the effectiveness of the process; N: sediment characteristic has no significant effect on process performance; U: effect of sediment characteristic on process is unknown; and X: sediment characteristic may impede process performance or increase cost.

Source: US Environmental Protection Agency, *Remediation Guidance Document*, Chapter 7, EPA-905-B94-003, 2003.

of concern or any organic, since they are combustibles with caloric value. Conversely, higher metal concentrations may make a technology less favorable by increasing contaminant mobility of certain metal species following application of the technology.

A number of other factors may affect selection of a treatment technology other than its effectiveness for treatment (some are listed in Table 33.3). For example, vitrification and supercritical water oxidation have only been used for relatively small projects and would require more of a proven track record before implementing them for full-scale sediment projects. Regulatory compliance and community perception are always a part of decisions regarding an incineration system. Land use considerations, including the amount of acreage needs, are commonly confronted in solidification and solid-phase bioremediation projects (as they are in sludge farming and land application). Disposing of ash and other residues following treatment must be part of any process. Treating water effluent and air emissions must be part of the decontamination decision-making process [1].

TABLE 33.3

Selected Factors on Selecting Decontamination and Treatment Approaches

Treatment technology	Implementability at full scale	Regulatory compliance	Community acceptance	Land requirements	Residuals disposal	Wastewater treatment	Air emissions control
Conventional incineration		✓	✓	✓			✓
Innovative incineration		✓	✓	✓			✓
Pyrolysis		✓					✓
Vitrification	✓	✓					✓
Supercritical water oxidation	✓						
Wet air oxidation							
Thermal desorption					✓	✓	✓
Immobilization				✓			✓
Solvent extraction					✓	✓	
Soil washing					✓	✓	
Dechlorination							✓
Oxidation	✓						
Bioslurry process	✓						✓
Composing				✓			✓
Contained treatment facility				✓		✓	✓

✓: the factor is critical in the evaluation of the technology.
Source: US Environmental Protection Agency, *Remediation Guidance Document*, Chapter 7, EPA-905-B94-003, 2003.

II. PRE-CONTROL CONSIDERATIONS

A. Estimating Contaminant Migration

Estimating potential contaminant releases (i.e. "losses" as defined by environmental regulators) from various combinations of treatment technologies is difficult due to the variability of chemical and physical characteristics of contaminated media (especially soils and sediments), the strong affinity of most contaminants for fine-grained sediment particles, and the limited track record or "scale-up" studies for many treatment technologies. Off-the-shelf models can be used for simple process operations, such as extraction or thermal vaporization applied to single contaminants in relatively pure systems. However, such models have not been appropriately evaluated for a number of other technologies because of the limited database on treatment technologies, such as for contaminated sediments or soils [1].

B. Treatability Tests

Standard engineering practice for evaluating the effectiveness of treatment technologies for any type of contaminated media (solids, liquids, or gases) requires first performing a treatability study for a sample that is representative of the contaminated material [1]. The performance data from treatability studies can aid in reliably estimating contaminant concentrations for the residues following treatment, as well as possible waste streams generated by a technology. Treatability studies may be performed at the bench-scale (in the laboratory) or at pilot-scale level (e.g. a real-world study, but limited in number of contaminants, in spatial extent, or to a specific, highly controlled form of a contaminant, e.g. one pure congener of PCBs, rather than the common mixtures). Most treatment technologies include post-treatment or controls for waste streams produced by the processing. The contaminant losses can be defined as the residual contaminant concentrations in the liquid or gaseous streams released to the environment. For technologies that extract or separate the contaminants from the bulk of the sediment, a concentrated waste stream may be produced that requires treatment offsite at a hazardous waste treatment facility, where permit requirements may require destruction and removal efficiencies greater than 99.9999% (i.e. the so-called rule of "six nines"). The other source of loss for treatment technologies is the residual contamination in the sediment after treatment. After disposal, treated wastes are subject to leaching, volatilization, and losses by other pathways. The significance of these pathways depends on the type and level of contamination that is not removed or treated by the treatment process. Various waste streams for each type of technology that should be considered in treatability evaluations are listed in Table 33.4.

TABLE 33.4

Selected Waste Streams Commonly Requiring Treatability Studies

Contaminant loss stream	Treatment technology type						
	Biological	Chemical	Extraction	Thermal desorption	Thermal destruction	Immobilization	Particle separation
Residual solids	X	X	X	X	X	X	X
Wastewater	X	X	X	X			X
Oil/organic compounds			X	X			X
Leachate						X[a]	
Stack gas				X	X		
Adsorption media			X	X			
Scrubber water					X		
Particulates (filter/cyclone)				X	X		

[a] Longe-term contaminant losses must be estimated using leaching tests and contaminant transport modeling similar to that used for sediment placed in a confined disposal facility. Leaching could be important for residual solids for other processes as well.

Source: US Environmental Protection Agency, *Remediation Guidance Document*, Chapter 7, EPA-905-B94-003, 2003.

III. CONTAMINANT TREATMENT AND CONTROL APPROACHES[1]

The life cycle viewpoint is instructive in controlling hazardous air pollutants. Five steps in sequence define an event that results in environmental contamination of the air, water, or soil pollution. These steps individually and collectively offer opportunities to intervene and to control the risks associated with hazards and thus protect public health and the environment. The steps address the presence of waste at five points in the life cycle:

SOURCE →
RELEASE →
TRANSPORT →
EXPOSURE →
RESPONSE

As a first step, the contaminant source must be identifiable. A hazardous substance must be released from the source, be transported through the air, water, or soil environment, reach a human, animal, or plant receptor in a measurable dose, and the receptor must have a quantifiable detrimental response in the form of death or illness. Intervention can occur at any one of these steps to control the risks to public health and to the environment. Of course, any intervention scheme and subsequent control by the engineer must be justified by the environmental engineer as well as the public or private client in terms of scientific evidence, sound engineering design, technological practicality, economic realities, ethical considerations, and the laws of local, state, and national governments.

A. Intervention at the Source of Contamination

A contaminant must be identifiable, either in the form of an industrial facility that generates waste byproducts, a hazardous waste processing facility, a surface or subsurface land storage/disposal facility, or an accidental spill into a water, air, or soil receiving location. The intervention must minimize or eliminate the risks to public health and the environment by utilizing technologies at this source that are economically acceptable and based on applicable scientific principles and sound engineering designs.

In the case of an industrial facility producing hazardous waste as a necessary byproduct of a profitable item, as considered here for example, the engineer can take advantage of the growing body of knowledge that has become known as life cycle analysis [4]. In the case of a hazardous waste storage facility or a spill, the engineer must take the source as a given and search for possibilities for intervention at a later step in the sequence of steps as discussed below.

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[1] The principal sources for this section are collaborations with two prominent environmental engineers, Ross E. McKinney and J. Jeffrey Peirce.

Under the life cycle analysis method of intervention, the environmental manager considers the environmental impacts that could incur during the entire life cycle of (1) all of the resources that go into the product; (2) all the materials that are in the product during its use; and (3) all the materials that are available to exit from the product once it or its storage containers are no longer economically useful to society. Few simple examples exist that describe how *life cycle analysis* is conducted but consider for now any one of a number of household cleaning products. Consider that a particular cleaning product, a solvent of some sort, must be fabricated from one of several basic natural resources. Assume for now that this cleaning product currently is petroleum based. The engineer could intervene at this initial step in the life cycle of this product, as the natural resource is being selected, and consequently the engineer could preclude the formation of a source of hazardous waste by suggesting instead the production of a water-based solvent.

Similarly, intervention at the production phase of this product's life cycle and suggested fabrication techniques can preclude the formation of a source of certain contaminants from the outset. In this case the recycling of spent petroleum materials could provide for more household cleaning products with less or zero hazardous waste generation, thus controlling the risks to public health and the environment. Another example is that of "co-generation," which may allow for two manufacturing facilities to co-locate so that the "waste" of one is a "resource" for the other. An example is the location of a chemical plant near a power generation facility, so that the excess steam generated by the power plant can be piped to the nearby chemical plant, obviating the need to burn its own fuel to generate the steam needed for chemical synthesis. Another example is the use of an alcohol waste from one plant as a source for chemical processes at another.

As discussed in Chapter 30, the product under consideration must be considered long before any switches are flipped and valves turned. For example, a particular household cleaning product may result in unintended human exposure to buckets of solvent mixtures that fumigate the air in a home's kitchen or pollute the town's sewers as the bucket's liquid is flushed down a drain. In this way, life cycle analysis is type of systems engineering where a critical path is drawn, and each decision point considered.

Under the plan, the disposal of this solvent's containers must be considered from a long-term risk perspective. The challenge is that every potential and actual environmental impact of a product's fabrication, use, and ultimate disposal must be considered. This is seldom, if ever, a "straight line projection."

B. Intervention at the Point of Release

Once a contaminant source has been identified, the next step is to intervene at the point at which the waste is released into the environment. This point of release could be at the top of a stack or vent from the source of pollution to a receiving air shed, or it could be a more indirect releases, such as from the bottom most layer of a clay liner in a hazardous waste landfill connected to surrounding soil material. Similarly this point of release could be a series of points as a contaminant is released along a shoreline from a plot of land into the air, from an evaporation pond, from a landfill, near a river or through a plane of soil underlying a storage facility (i.e. a so-called "non-point source").

C. Intervention as the Contaminant Is Transported in the Environment

Wise site selection of facilities that generate, process, and store contaminants is the first step in preventing or reducing the likelihood that they will move. For example, the distance from a source to a receptor is a crucial factor in controlling the quantity and characteristics of waste as it is transported.

Meteorology is a primary determinant of the opportunities to control the atmospheric transport of contaminants. For example, manufacturing, transportation, and hazardous waste generating, processing, and storage facilities must be sited to avoid areas where specific local weather patterns are frequent and persistent. These avoidance areas include ground-based inversions, elevated inversions, valley winds, shore breezes, and city heat islands. In each of these venues, the pollutants become locked into air masses with little of no chance of moving out of the respective areas. Thus the concentrations of the pollutants can quickly and greatly pose risks to public health and the environment. In the soil environment the engineer has the opportunity to site facilities in areas of great depth-to-groundwater, as well as in soils (e.g. clays) with very slow rates of transport. In this way, engineers and scientists must work closely with city and regional planners in early in the site selection phases.[2]

D. Intervention to Control the Exposure

As mentioned in Chapter 1, the receptor of contamination can be a human, other fauna in the general scheme of living organisms, flora, or materials or constructed facilities. In the case of humans, as we discussed previously, the contaminant can be ingested, inhaled, or dermally contacted. Such exposure can be direct with human contact to, for example, particles of lead that are present in inhaled indoor air. An exposure also can be indirect as in the case of human ingestion of the cadmium and other heavy metals found in the livers of beef cattle that were raised on grasses receiving nutrition from cadmium-laced municipal wastewater treatment biosolids (commonly known as "sludge").

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[2] This goes beyond zoning. Obviously, the engineer should be certain that the planned facility adheres to the zoning ordinances, land use plans, and maps of the state and local agencies. However, it behooves all of the professionals to collaborate, hopefully before any land is purchased and contractors are retained. Councils of Government (COGs) and other "A-95" organizations can be rich resources when considering options on siting. They can help avoid the need for problems long before implementation, to say nothing of contentious zoning appeal and planning commission meetings and perception problems at public hearings.

Heavy metals or chlorinated hydrocarbons similarly can be delivered to domestic animals and animals in the wild. Construction materials are also sensitive to exposure to air pollutants, from the "greening" of statutes through the de-zinc process associated with low pH rain events to the crumbling of stone bridges found in nature. Isolating potential receptors from exposure to hazardous air pollutants the engineer has an opportunity to control the risks to those receptors.

The opportunities to control exposures to contaminants are directly associated with the ability to control the amount of hazardous pollutants delivered to the receptor through source control and siting of control systems and hazardous waste management facilities. One solution to environmental contamination could be to increase their dilution in the air, water, or soil environments. We will discuss specific examples of this type of intervention later in this chapter.

E. Intervention at the Point of Response

Opportunities for intervention are grounded in basic scientific principles, engineering designs and processes, and applications of proven and developing technologies to control the risks associated with contaminants. Let us consider thermal processing as a class of hazardous control technology that is widely used in treating wastes, but which has a crucial air pollution component.

IV. THERMAL TREATMENT PROCESSES

A. Thermodynamics and Stoichiometry

Contaminants, if completely organic in structure, are, in theory, completely destructible using principles based in thermodynamics with the engineering inputs and outputs summarized as:

$$\text{Hydrocarbons} + O_2\,(+\text{ energy?}) \rightarrow CO_2 + H_2O\,(+\text{ energy?}) \quad (33.1)$$

Contaminants are mixed with oxygen, sometimes in the presence of an external energy source, and in fractions of seconds or several seconds the byproducts of gaseous carbon dioxide and water are produced to exit the top of the reaction vessel while a solid ash is produced to exit the bottom of the reaction vessel.[3] 3K Energy may also be produced during the reaction and the heat may be recovered. A derivative problem in this simple reaction could be global warming associated with the carbon dioxide.

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[3] Numerous textbooks address the topic of incineration in general and hazardous waste incineration in particular. For example see Haas, C. N., and Ramos, R. J. *Hazardous and Industrial Waste Treatment*. Prentice-Hall, Inc., Englewood Cliffs, NJ, 1995; Wentz, C. A. *Hazardous Waste Management*. McGraw-Hill, Inc., New York, NY, 1989; and Peirce, J. J., Weiner, R. F., and Vesilind, P. A. *Environmental Pollution and Control*. Butterworth-Heinemann, Boston, MA, 1998.

Conversely, if the contaminant of concern to the engineer contains other chemical constituents, in particular chlorine and/or heavy metals, the original simple input and output relationship is modified to a very complex situation:

$$\begin{gathered}\text{Hydrocarbons} + O_2\,(+\ \text{energy?}) + \text{Cl or heavy metal(s)} + H_2O \\ + \text{ inorganic salts} + \text{nitrogen compounds} + \text{sulfur compounds} \\ + \text{ phosphorus compounds} \rightarrow CO_2 + H_2O(+\ \text{energy?}) \\ + \text{ chlorinated hydrocarbons or heavy metal(s) inorganic salts} \\ + \text{ nitrogen compounds} + \text{sulfur compounds} \\ + \text{ phosphorus compounds} \end{gathered} \tag{33.2}$$

With these contaminants the potential exists for destruction of the initial contaminant, but actually exacerbating the problem by generating more hazardous off-gases containing chlorinated hydrocarbons and/or ashes containing heavy metals are produced (e.g. the improper incineration of certain chlorinated hydrocarbons can lead to the formation of the highly toxic chlorinated dioxins, furans, and hexachlorobenzene). All of the thermal systems discussed below have common attributes. All require the balancing of the three "*T*'s" of the science, engineering, and technology of incineration of any substance:

1. *T*ime of incineration
2. *T*emperature of incineration
3. *T*urbulence in the combustion chamber

The advantages of thermal systems include: (1) the potential for energy recovery; (2) volume reduction of the contaminant; (3) detoxification as selected molecules are reformulated; (4) the basic scientific principles, engineering designs, and technologies are well understood from a wide range of other applications including electric generation and municipal solid waste incineration; (5) application to most organic contaminants which compose a large percentage of the total contaminants generated worldwide; (6) the possibility to scale the technologies to handle a single gallon per pound (liter per kilogram) of waste or millions of gallon per pound (liter per kilogram) of waste: and (7) land areas that are small compared to many other facilities (e.g. landfills).

Each system design must be customized to address the specific contaminants under consideration, including the quantity of waste to be processed over the planning period as well as the physical, chemical, and microbiological characteristics of the waste also over the planning period of the project. The space required for the incinerator itself ranges from several square yards to possibly on the back of a flat bed truck to several acres to sustain a regional incinerator system. Laboratory testing and pilot studies matching a given waste to a given incinerator must be conducted prior to the design, citing, and construction of each incinerator. Generally, the same reaction applies to most thermal processes, i.e. gasification, pyrolysis, hydrolysis, and combustion [3]:

$$C_{20}H_{32}O_{10} + x_1O_2 + x_2H_2O \xrightarrow[\Delta]{} y_1C + y_2CO_2 + y_3CO + y_4H_2 + y_5CH_4 + y_6H_2O + y_7C_nH_m \qquad (33.3)$$

The coefficients x and y balance the compounds on either side of the equation. The delta under the arrow indicates heating. In many thermal reactions, C_nH_m includes the alkanes, C_2H_2, C_2H_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, and benzene, C_6H_6. The actual reactions from test burns for commonly incinerated compounds are provided in Table 10.1.

Of all of the thermal processes, incineration is the most common process for destroying organic contaminants in industrial wastes. Incineration simply is heating wastes in the presence of oxygen to oxidize organic compounds (both toxic and non-toxic). The principal incineration steps are shown in Fig. 33.1.

B. Applying Thermal Processes for Treatment

A word of warning when choosing incineration as the recommended technology: The mere mention of "incineration" evokes controversy in communities. There have been real and perceived failures. It is also important to note that incineration alone does not "destroy" heavy metals; it simply changes the valence of the metal. In fact, incineration can increase the leachability of metals via oxidation, although processes like slagging (operating at sufficiently high temperatures to melt and remove incombustible materials) or

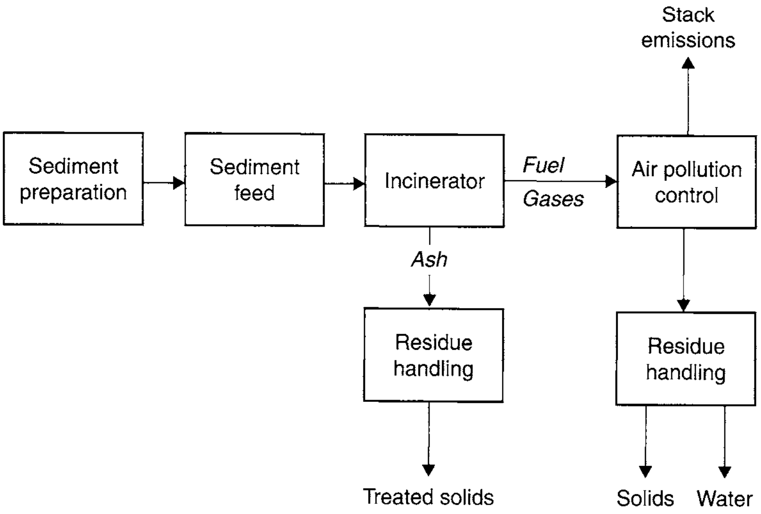

Fig. 33.1. Steps in the incineration of contaminants. *Source*: US Environmental Protection Agency, *Remediation Guidance Document*, Chapter 7, EPA-905-B94-003, 2003.

vitrification (producing non-leachable, basalt-like residue) actually reduce the mobility of many metals.

Leachability is a measure of the ease with which compounds in the waste can move into the accessible environment. The increased leachability of metals would be problematic if the ash and other residues are to be buried in landfills or stored in piles. The leachability of metals is generally measured using the toxicity characteristic leaching procedure (TCLP) test, discussed earlier. Incinerator ash that fails the TCLP must be disposed of in a waste facility approved for hazardous wastes. Enhanced leachability would be advantageous only if the residues are engineered to undergo an additional treatment step of metals. Again, the engineer must see incineration of but one component within a systematic approach for any contaminant treatment process.

There are a number of places in the incineration flow of the contaminant through the incineration process where new compounds may need to be addressed. As mentioned, ash and other residues may contain high levels of metals, at least higher than the original feed. The flue gases are likely to include both organic and inorganic compounds that have been released as a result of temperature induced volatilization and/or newly transformed products of incomplete combustion (PICs) with higher vapor pressures than the original contaminants.

The disadvantages of hazardous waste incinerators include: (1) the equipment is capital intensive, particularly the refractory material lining the inside walls of each combustion chamber that must be replaced as cracks form whenever a combustion system is cooled and/or heated; (2) the operation of the equipment requires very skilled operators and is more costly when fuel must be added to the system; (3) ultimate disposal of the ash is necessary and particularly troublesome and costly if heavy metals and/or chlorinated compounds are found during the expensive monitoring activities; and (4) air emissions may be hazardous and thus must be monitored for chemical constituents and controlled.

Given these underlying principles of incineration, seven general guidelines emerge:

1. Only liquid purely organic contaminants are true candidates for combustion.
2. Chlorine-containing organic materials deserve special consideration if in fact they are to be incinerated at all; special materials used in the construction of the incinerator, long (many seconds) of combustion time, high temperatures (>1600°C), with continuous mixing if the contaminant is in the solid or sludge form.
3. Feedstock containing heavy metals generally should not be incinerated.
4. Sulfur-containing organic material will emit sulfur oxides which must be controlled.
5. The formation of nitrogen oxides can be minimized if the combustion chamber is maintained above 1100°C.

6. Destruction depends on the interaction of a combustion chamber's temperature, dwell time, and turbulence.
7. Off-gases and ash must be monitored for chemical constituents, each residual must be treated as appropriate so the entire combustion system operates within the requirements of the local, state, and federal environmental regulators, and hazardous components of the off-gases, off-gas treatment processes, and the ash must reach ultimate disposal in a permitted facility.

V. THERMAL DESTRUCTION SYSTEMS

The types of thermal systems vary considerably. Five general categories are available to destroy contaminants: (1) rotary kiln; (2) multiple hearth; (3) liquid injection; (4) fluidized bed; and (5) multiple chamber.

A. Rotary Kiln

The combustion chamber in a rotary kiln incinerator as illustrated in Fig. 33.2 is a heated rotating cylinder that is mounted at an angle with possible baffles added to the inner face to provide the turbulence necessary for the target three "*T*'s" for the contaminant destruction process to take place. Engineering design decisions, based on the results of laboratory testing of a specific contaminant, include: (1) angle of the drum; (2) diameter and length of the drum; (3) presence and location of the baffles; (4) rotational speed of the drum; and (5) use of added fuel to increase the temperature of the combustion chamber

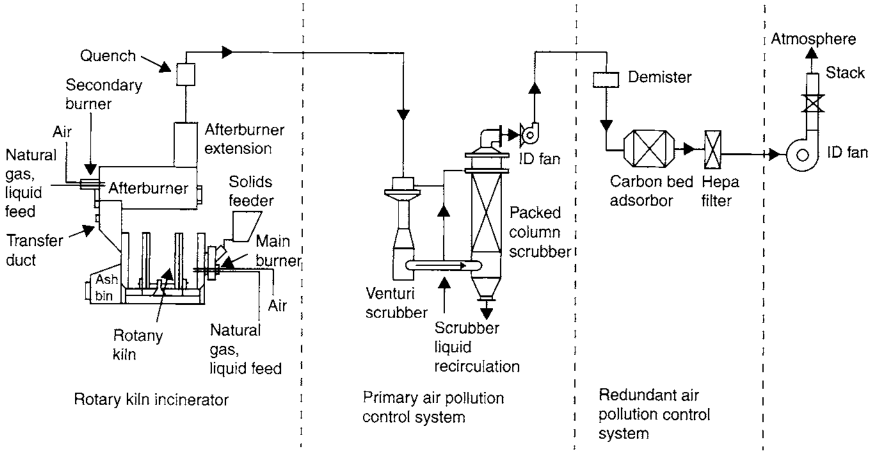

Fig. 33.2. Rotary kiln system. *Source*: US Environmental Protection Agency, 1997, Lee, J., Fournier Jr., D., King, C., Venkatesh, S., and Goldman, C. *Project Summary: Evaluation of Rotary Kiln Incinerator Operation at Low-to-Moderate Temperature Conditions.*

as the specific contaminant requires. The liquid, sludge, or solid hazardous waste is input into the upper end of the rotating cylinder, rotates with the cylinder-baffle system, and falls with gravity to the lower end of the cylinder. The heated upward moving off-gases are collected, monitored for chemical constituents, and subsequently treated as appropriate prior to release, while the ash falls with gravity to be collected, monitored for chemical constituents, and also treated as needed before ultimate disposal. The newer rotary kiln systems [4] consist of a primary combustion chamber, a transition volume, and a fired afterburner chamber. After exiting the afterburner, the flue gas is passed through a quench section followed by a primary air pollution control system (APCS). The primary APCS can be a venture scrubber followed by a packed-column scrubber. Downstream of the primary APCS, a backup secondary APCS, with a demister, an activated carbon adsorber, and a high-efficiency particulate air (HEPA) filter can collect contaminants not destroyed by the incineration.

The rotary kiln is applicable to the incineration of most organic contaminants, it is well suited for solids and sludges, and in special cases liquids and gases can be injected through auxiliary nozzles in the side of the combustion chamber. Operating temperatures generally vary from 800°C to 1650°C. Engineers use laboratory experiments to design residence times of seconds for gases and minutes or possibly hours for the incineration of solid material.

B. Multiple Hearth

In the multiple hearth illustrated in Fig. 33.3 generally contaminants in solid or sludge form are fed slowly through the top vertically stacked hearth; in special configurations hazardous gases and liquids can be injected through side nozzles. Multiple hearth incinerators, historically developed to burn municipal wastewater treatment biosolids, rely on gravity and scrapers working in the upper edges of each hearth to transport the waste through holes from upper hotter hearths to lower cooler hearths. Heated upward moving off-gases are collected, monitored for chemical constituents, and treated as appropriate prior to release; the falling ash is collected, monitored for chemical constituents, and subsequently treated prior to ultimate disposal.

Most organic wastes generally can be incinerated using a multiple hearth configuration. Operating temperatures generally vary from 300°C to 980°C. These systems are designed with residence times of seconds if gases are fed into the chambers to several hours if solid materials are placed on the top hearth and allowed to eventually drop to the bottom hearth exiting as ash.

C. Liquid Injection

Vertical or horizontal nozzles spray liquid hazardous wastes into liquid injection incinerators specially designed for the task or as a retrofit to one of the other incinerators discussed here. The wastes are atomized through the

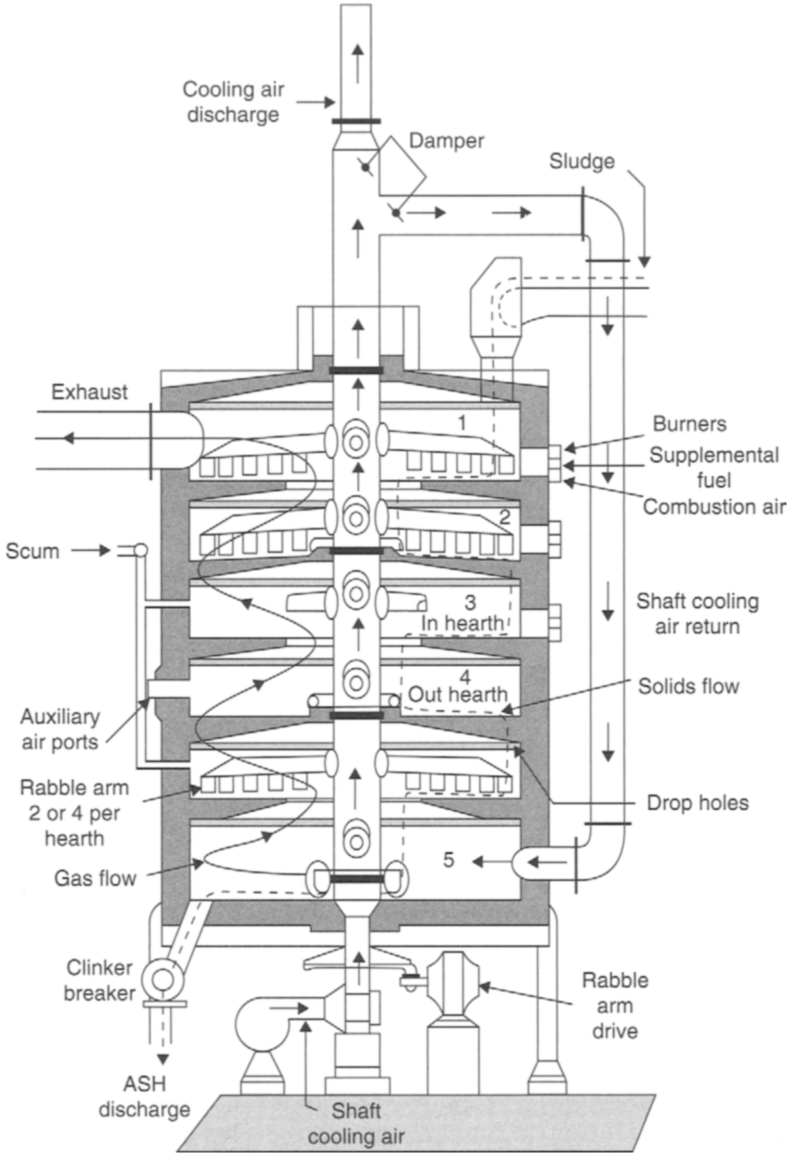

Fig. 33.3. Multiple hearth incineration system. *Source*: US Environmental Protection Agency, *Locating and Estimating Air Emissions from Sources of Benzene*, EPA-454/R-98-011, Research Triangle Park, NC, 1998.

nozzles that match the waste being handled with the combustion chamber as determined in laboratory testing. The application obviously is limited to liquids that do not clog these nozzles, though some success has been experienced with hazardous waste slurries. Operating temperatures generally vary from

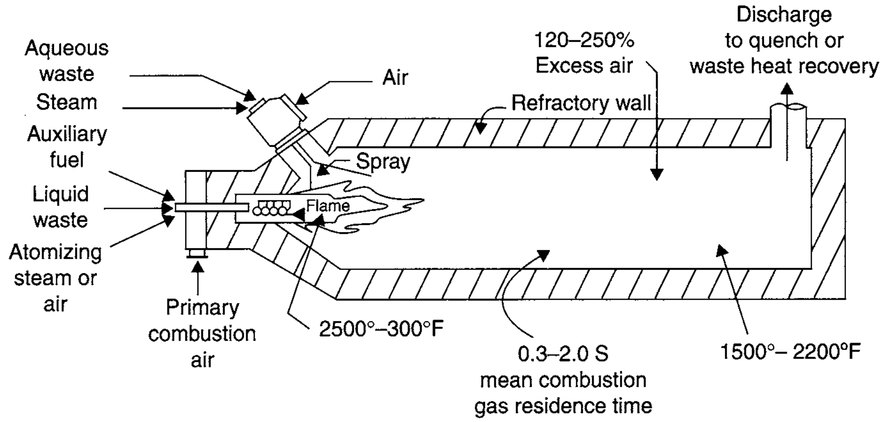

Fig. 33.4. Prototype of liquid injection system. *Source*: US Environmental Protection Agency, *Locating and Estimating Air Emissions from Sources of Benzene*, EPA-454/R-98-011, Research Triangle Park, NC, 1998.

650°C to 1650°C (1200°F to 3000°F). Liquid injection systems (Fig. 33.4) are designed with residence times of fractions of seconds as off-gases, the upward moving off-gases are collected, monitored for chemical constituents, and treated as appropriate prior to release to the lower troposphere.

D. Fluidized Bed

Contaminated feedstock is injected under pressure into a heated bed of agitated inert granular particles, usually sand, as the heat is transferred from the particles to the waste, and the combustion process proceeds as summarized in Fig. 33.5. External heat is applied to the particle bed prior to the injection of the waste and continually is applied throughout the combustion operation as the situation dictates. Heated air is forced into the bottom of the particle bed and the particles become suspended among themselves during this continuous fluidizing process. The openings created within the bed permit the introduction and transport of the waste into and through the bed. The process enables the contaminant to come into contact with particles that maintain their heat better than, for example, the gases inside a rotary kiln. The heat maintained in the particles increases the time the contaminant is in contact with a heated element and thus the combustion process could become more complete with fewer harmful byproducts. Off-gases are collected, monitored for chemical constituents, and treated as appropriate prior to release, and the falling ash is collected, monitored for chemical constituents, and subsequently treated prior to ultimate disposal.

Most organic wastes can be incinerated in a fluidized bed, while the system is best suited for liquids. Operating temperatures generally vary from 750°C to 900°C. Liquid injection systems are designed with residence times

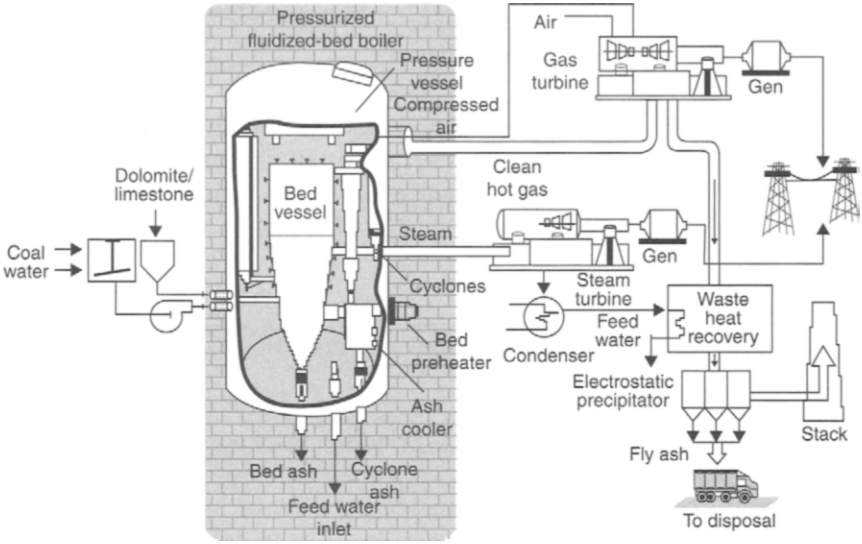

Fig. 33.5. Pressurized fluidized bed system. *Source*: US Department of Energy, 1999, TIDD PFBC Demonstration Project.

of fractions of seconds as off-gases, the upward moving off-gases are collected, monitored for chemical constituents, and treated as appropriate prior to release to the lower troposphere.

E. Multiple Chamber

Contaminants are turned to a gaseous form on a grate in the ignition chamber of a multiple chamber system. The gases created in this ignition chamber travel through baffles to a secondary chamber where the actual combustion process takes place. Often the secondary chamber is located above the ignition chamber to promote natural advection of the hot gases through the system. Heat may be added to the system in either the ignition chamber or the secondary chamber as required for specific burns.

The application of multiple chamber incinerators generally is limited to solid wastes with the waste entering the ignition chamber through an opened charging door in batch, not continuous, loading. Combustion temperatures typically hover near 540°C for most applications. These systems are designed with residence times of minutes to hours for solid hazardous wastes as off-gases are collected, monitored for chemical constituents, and treated as appropriate prior to release to the lower troposphere. At the end of each burn period the system must be cooled so that the ash can be removed prior to monitoring for chemical constituents and subsequent treatment prior to ultimate disposal.

VI. DESTRUCTION REMOVAL

A. Calculating Destruction Removal

Federal hazardous waste incineration standards require that hazardous organic compounds meet certain destruction efficiencies. These standards require that any hazardous waste undergo 99.99% destruction of all hazardous wastes and 99.9999% destruction of extremely hazardous wastes like dioxins. Recall that destruction removal efficiency (DRE) is calculated as:

$$\mathrm{DRE} = \frac{W_{\mathrm{in}} - W_{\mathrm{out}}}{W_{\mathrm{in}}} \times 100 \tag{33.4}$$

where W_{in} is the rate of mass of waste flowing into the incinerator and W_{out} is the rate of mass of waste flowing out of the incinerator.

For example, let us calculate the DRE if during a stack test, the mass of pentachlorodioxin is loaded into incinerator at the rate of $10\,\mathrm{mg\,min^{-1}}$ and the mass flow rate of the compound measured downstream in the stack is 200 picograms (pg) $\mathrm{min^{-1}}$. Is the incinerator up to code for the thermal destruction of this dioxin?

$$\mathrm{DRE} = \frac{W_{\mathrm{in}} - W_{\mathrm{out}}}{W_{\mathrm{in}}} \times 100 = \frac{10\,\mathrm{mg\,min^{-1}} - 200\,\mathrm{pg\,min^{-1}}}{10\,\mathrm{mg\,min^{-1}}} \times 100$$

Since $1\,\mathrm{pg} = 10^{-12}\,\mathrm{g}$ and $1\,\mathrm{mg} = 10^{-3}$, then $1\,\mathrm{pg} = 10^{-9}\,\mathrm{mg}$. So

$$\frac{10\,\mathrm{mg\,min^{-1}} - 200 \times 10^{-9}\,\mathrm{mg\,min^{-1}}}{10\,\mathrm{mg\,min^{-1}}} \times 100 = 999999.98\%\ \text{removal}$$

Even if pentachlorodioxin is considered to be "extremely hazardous," this is better than the "rule of six nines" so the incinerator is operating up to code.

If we were to calculate the DRE during the same stack test for the mass of tetrachloromethane (CCl_4) loaded into incinerator at the rate of $100\,\mathrm{L\,min^{-1}}$ and the mass flow rate of the compound measured downstream is $1\,\mathrm{mL\,min^{-1}}$. Is the incinerator up to code for CCl_4? This is a lower removal rate since 100 L are in and 0.001 are leaving, so the DRE = 99.999. This is acceptable, i.e. better removal efficiency than 99.99% by an order of magnitude, so long as CCl_4 is not considered an extremely hazardous compound. If it were, then it would have to meet the rule of six nines (it only has five).

By the way, both of these compounds are chlorinated. As mentioned, special precautions must be taken when dealing with such halogenated compounds, since even more toxic compounds that those being treated can end up being generated. Incomplete reactions are very important sources of environmental contaminants. For example, these reactions generate PICs, such as dioxins, furans, carbon monoxide (CO), polycyclic aromatic hydrocarbons (PAHs), and hexachlorobenzene. Thus, the formation of unintended byproducts is always a possibility with thermal systems. An extensive discussion can be found in Chapter 7, for example, on the various processes that can lead to the formation of dioxins and furans. In particular, see the thermal relationships in Table 7.5 and Fig. 7.6.

VII. OTHER THERMAL PROCESSES

A. Processes Other than Incineration

Incineration is frequently used to decontaminate soils with elevated concentrations of organic hazardous constituents. High-temperature incineration, however, may not be needed to treat soils contaminated with most volatile organic compounds (VOCs). Also, in waste feeds with heavy metals, high temperature incineration will likely increase the volatilization of some of these metals into the combustion flue gas (see Tables 33.5 and 33.6). High concentrations of volatile trace metal compounds in the flue gas pose increased challenges to air pollution control. Thus, other thermal processes, i.e. thermal desorption and pyrolysis, can provide an effective alternative to incineration.

TABLE 33.5

Conservative Estimates of Heavy Metals and Metalloids Partitioning to Flue Gas As a Function of Solids Temperature and Chlorine Content[a]

	871°C		1093°C	
Metal or metalloid	Cl = 0%	Cl = 1%	Cl = 0%	Cl = 1%
Antimony	100%	100%	100%	100%
Arsenic	100%	100%	100%	100%
Barium	50%	30%	100%	100%
Beryllium	5%	5%	5%	5%
Cadmium	100%	100%	100%	100%
Chromium	5%	5%	5%	5%
Lead	100%	100%	100%	100%
Mercury	100%	100%	100%	100%
Silver	8%	100%	100%	100%
Thallium	100%	100%	100%	100%

[a] The remaining percentage of metal is contained in the bottom ash. Partitioning for liquids is estimated at 100% for all metals. The combustion gas temperature is expected to be 100–1000°F higher than the solids temperature.

Source: US Environmental Protection Agency, *Guidance on Setting Permit Conditions and Reporting Trial Burn Results: Volume II, Hazardous Waste Incineration Guidance Series*, EPA/625/6-89/019. EPA, Washington, DC, 1989.

TABLE 33.6

Metal and Metalloid Volatilization Temperatures

	Without chlorine		With 10% chlorine	
Metal or metalloid	Volatility temperature (°C)	Principal species	Volatility temperature (°C)	Principal species
Chromium	1613	CrO_2/CrO_3	1611	CrO_2/CrO_3
Nickel	1210	$Ni(OH)_2$	693	$NiCl_2$
Beryllium	1054	$Be(OH)_2$	1054	$Be(OH)_2$
Silver	904	Ag	627	AgCl
Barium	841	$Ba(OH)_2$	904	$BaCl_2$
Thallium	721	Tl_2O_3	138	TiOH
Antimony	660	Sb_2O_3	660	Sb_2O_3
Lead	627	Pb	−15	$PbCl_4$
Selenium	318	SeO_2	318	SeO_2
Cadmium	214	Cd	214	Cd
Arsenic	32	As_2O_3	32	As_2O_3
Mercury	14	Hg	14	Hg

Source: Willis, B., Howie, M., and Williams, R., *Public Health Reviews of Hazardous Waste Thermal Treatment Technologies: A Guidance Manual for Public Health Assessors*, Agency for Toxic Substances and Disease Registry, 2002.

When successful in decontaminating soils to the necessary treatment levels, thermally desorbing contaminants from soils have the additional benefits of lower fuel consumption, no formation of slag, less volatilization of metal compounds, and less complicated air pollution control demands. So, beyond monetary costs and ease of operation, a less energy (heat) intensive system can be more advantageous in terms of actual pollutant removal efficiency.

B. Pyrolysis

Pyrolysis is the process of chemical decomposition induced in organic materials by heat in the absence of oxygen. It is practicably impossible to achieve a completely oxygen-free atmosphere, so pyrolytic systems run with less stoichiometric quantities of oxygen. Because some oxygen will be present in any pyrolytic system, there will always be a small amount of oxidation. Also, desorption will occur when volatile or semivolatile compounds are present in the feed.

During pyrolysis [5] organic compounds are converted to gaseous components, along with some liquids, as coke, i.e. the solid residue of fixed carbon and ash. CO, H_2, CH_4, and other hydrocarbons are produced. It these gases cool and condense, liquids will form and leave oily tar residues and water with high concentrations of TOC. Pyrolysis generally takes place well above atmospheric pressure at temperatures exceeding 430°C. The secondary gases need their own treatment, such as by a secondary combustion chamber, by flaring, and partial condensation. Particulates must be removed by additional air pollution controls, e.g. fabric filters or wet scrubbers.

Conventional thermal treatment methods, such as rotary kiln, rotary hearth furnace, or fluidized bed furnace, are used for waste pyrolysis. Kilns or furnaces used for pyrolysis may be of the same design as those used for combustion (i.e. incineration) discussed earlier, but operate at lower temperatures and with less air than in combustion.

The target contaminant groups for pyrolysis include semivolatile organic compounds (SVOCs), including pesticides, PCBs, dioxins, and PAHs. It allows for separating organic contaminants from various wastes, including those from refineries, coal tar, wood preservatives, creosote-contaminated and hydrocarbon-contaminated soils, mixed radioactive and hazardous wastes, synthetic rubber processing, and paint and coating processes. Pyrolysis systems may be used to treat a variety of organic contaminants that chemically decompose when heated (i.e. "cracking"). Pyrolysis is not effective in either destroying or physically separating inorganic compounds that coexist with the organics in the contaminated medium. Volatile metals may be removed and transformed but their mass balance, of course, will not be changed.

C. Emerging Thermal Technologies

Other promising thermal processes include high-pressure oxidation and vitrification [6]. High-pressure oxidation combines two related technologies, i.e. wet air oxidation and supercritical water oxidation, which combine high temperature and pressure to destroy organics. Wet air oxidation can operate at pressures of about 10% of those used during supercritical water oxidation, an emerging technology that has shown some promise in the treatment of PCBs and other stable compounds that resist chemical reaction. Wet air oxidation has generally been limited to conditioning of municipal wastewater sludges, but can degrade hydrocarbons (including PAHs), certain pesticides, phenolic compounds, cyanides, and other organic compounds. Oxidation may benefit from catalysts.

Vitrification uses electricity to heat and destroy organic compounds and immobilize inert contaminants. A vitrification unit has a reaction chamber divided into two sections: the upper section to introduce the feed material containing gases and pyrolysis products, and the lower section consisting of a two-layer molten zone for the metal and siliceous components of the waste. Electrodes are inserted into the waste solids, and graphite is applied to the surface to enhance its electrical conductivity. A large current is applied, resulting in rapid heating of the solids and causing the siliceous components of the material to melt as temperatures reach about 1600°C. The end product is a solid, glass-like material that is very resistant to leaching.

VIII. INDIRECT AIR IMPACTS

In addition to direct treatment, air pollution is also a concern for other means of treating hazardous wastes, especially when these wastes are stored or treated more passively, such as in a landfill or aeration pond. Leachate collection systems (see Fig. 33.6) provide a way to collect wastes that can then be treated. However, such "pump and treat" systems can produce air pollutants. Actually, this is often intentional. For example, groundwater is treated by drilling recovery wells to pump contaminated groundwater to the surface. Commonly used groundwater treatment approaches include air stripping, filtering with granulated activated carbon (GAC), and air sparging. Air stripping transfers volatile compounds from water to air (see Fig. 33.7). Groundwater is allowed to drip downward in a tower filled with a permeable material through which a stream of air flows upward. Another method bubbles pressurized air through contaminated water in a tank. The air leaving the tank (i.e. the off-gas) is treated with methods described in Chapter 32 for removing gaseous pollutants. Filtering groundwater with GAC entails pumping the water through the GAC to trap the contaminants. In air sparging, air is pumped into the groundwater to aerate the water. Most often, a soil venting system is combined with an air sparging system for vapor extraction, with the gaseous pollutants treated, as in air stripping.

Regulatory agencies often require two or three pairs of these systems as design redundancies to protect the integrity of a hazardous waste storage or treatment facility. A primary leachate collection and treatment system must be designed like the bottom of the landfill bathtub. This leachate collection system must be graded to promote the flow of liquid within the landfill from all points in the landfill to a central collection point(s) where the liquid can

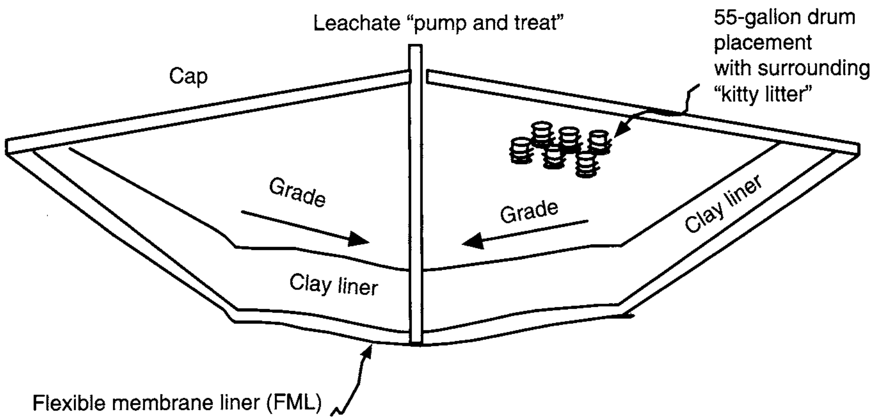

Fig. 33.6. Leachate collection system for a hazardous waste landfill. *Source*: Vallero, D., *Engineering the Risks of Hazardous Wastes*. Butterworth-Heinemann, Boston, MA, 2003.

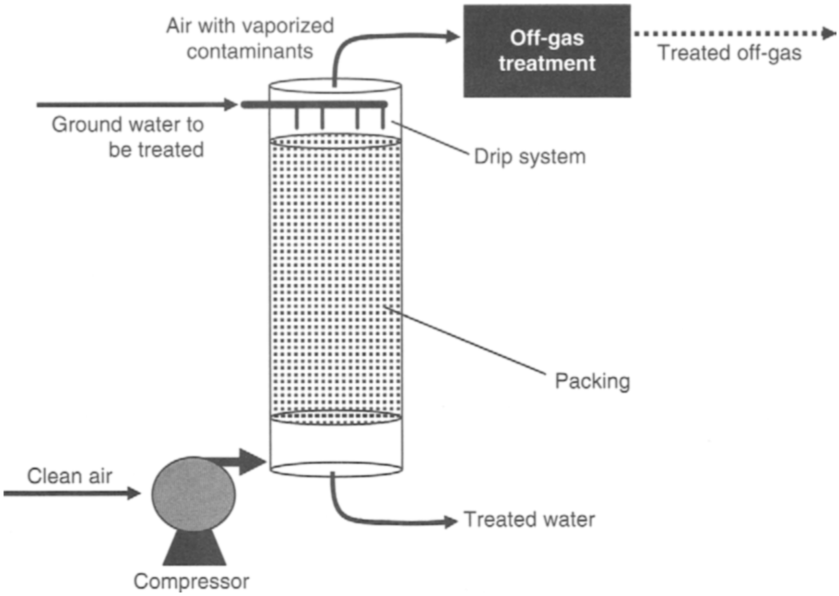

Fig. 33.7. Schematic diagram of air stripping system to treat volatile compounds in water.

be pumped to the surface for subsequent monitoring and treatment. Crushed stone and perforated pipes are used to channel the liquid along the top layer of this compacted clay liner to the pumping locations.

Thus, directly treating hazardous wastes physically and chemically, as with thermal systems and indirectly controlling air pollutants as when gases are released from pump and treat systems require a comprehensive approach. Otherwise, we are merely moving the pollutants to different locations or even making matters worse by either rendering some contaminants more toxic or exposing receptors to dangerous substances.

REFERENCES

1. US Environmental Protection Agency, *Remediation Guidance Document*, Chapter 7, EPA-905-B94-003, 2003.
2. Smith, J. K., and Peirce, J. J., Life cycle assessment standards: industrial sectors and environmental performance. *Int. J. Life Cycle Assess.* **1** (2), 115–118 (1996).
3. Biffward Programme on Sustainable Resource Use, 2003, *Thermal Methods of Municipal Waste Treatment*, http://www.biffa.co.uk/pdfs/massbalance/Thermowaste.pdf.
4. US Environmental Protection Agency, Lee, J., Fournier Jr., D., King, C., Venkatesh, S., and Goldman, C. *Project Summary: Evaluation of Rotary Kiln Incinerator Operation at Low-to-Moderate Temperature Conditions*, EPA/600/SR-96/105, Cincinnati, OH, 1997.

5. Federal Remediation Technologies Roundtable, *Remediation Technologies Screening Matrix and Reference Guide*, 4th ed, 2002.
6. US Environmental Protection Agency, *Remediation Guidance Document*, Chapter 7, EPA-905-B94-003, 2003.

SUGGESTED READING

Haas, C. N., and Ramos, R. J., *Hazardous and Industrial Waste Treatment*. Prentice-Hall, Inc., Englewood Cliffs, NJ, 1995.

Koester, C., and Hites, R., Wet and dry deposition of chlorinated dioxins and furans. *Environ. Sci. Technol.* **26**, 1375–1382 (1992); and Hites, R., Atmospheric Transport and Deposition of Polychlorinated Dibenzo-*p*-Dioxins and Dibenzofurans.

Peirce, J. J., Weiner, R. F., and Vesilind, P. A., *Environmental Pollution and Control*. Butterworth-Heinemann, Boston, MA, 1998.

Stieglitz, L., Zwick, G., Beck, J., Bautz, H., and Roth, W., *Chemosphere* **19**, 283 (1989).

US Environmental Protection Agency, *Guidance on Setting Permit Conditions and Reporting Trial Burn Results: Volume II, Hazardous Waste Incineration Guidance Series*, EPA/625/6-89/019, Washington, DC, 1989.

US Environmental Protection Agency, Lee, J., Fournier Jr., D., King, C., Venkatesh, S., and Goldman, C., *Project Summary: Evaluation of Rotary Kiln Incinerator Operation at Low-to-Moderate Temperature Conditions*, EPA/600/SR-96/105, Cincinnati, OH, 1997.

US Environmental Protection Agency, *Locating and Estimating Air Emissions from Sources of Benzene*, EPA-454/R-98-011, Research Triangle Park, NC, 1998.

Vallero, D., *Engineering the Risks of Hazardous Wastes*. Butterworth-Heinemann, Boston, MA, 2003.

Wentz, C. A., *Hazardous Waste Management*. McGraw-Hill, Inc., New York, 1989.

Willis, B., Howie, M., and Williams, R., *Public Health Reviews of Hazardous Waste Thermal Treatment Technologies: A Guidance Manual for Public Health Assessors*, Agency for Toxic Substances and Disease Registry, 2002.

QUESTIONS

1. Your company's waste stream contains a large percentage of clay-sized particles with a high content of organic compounds and chromium. Which treatment technologies are good candidates for this waste? What other assumptions do you need to make and how may these assumptions be eliminated from your decision; i.e. how can you close the "data gap"?
2. What if 20% of the organic fraction in the above waste stream is chlorinated? How would that affect your selection of treatment approaches?
3. Your city has decided to use supercritical oxidation to treat a low solid content PCB-contaminated waste. What problems, if any, do you see with this approach?
4. What characteristics of a waste increase the likelihood that it should be treated thermally? When is incineration preferable to pyrolysis and vice versa?
5. What precautions should be taken in selecting a treatment process for a halogenated waste? For a heavy metal-laden waste?
6. What are the "three T's" of thermal destruction? Give an example of problems that may ensue if each is neglected?

7. What is the best thermal destruction system for wastes containing 2,3,7,8-tetrachlorodibenzo-p-dioxin? For liquid solvents? Support your answers.
8. Is the multiple hearth system good for treating a liquid waste that breaks down at temperatures >1000°C? If the waste also contains Hg and Ni, what is the preferable treatment approach?
9. What is the difference between air stripping and sparging? Give a situation where stripping would be preferred and one where sparging is better. Explain.