- <u>Pressure- and temperature-swing adsorption</u>. Synthetic polymeric adsorbents are regenerated by applying vacuum and heating, with nitrogen purging of the adsorption bed.
- Membrane separation. The off-gas permeates through membranes that are 10 to 100 times more permeable to organics than to air. Such systems cost more than condensation systems at concentrations greater than10,000 ppmv.
- **Rotor concentration.** Carbon or zeolite adsorbent is regenerated with hot gas that is then treated with a relatively small adsorber or oxidizer.
- Flameless thermal oxidation. The off-gas is passed through a heated ceramic matrix.
- Biotrickling filtration. The off-gas flows co-currently with recirculated water down through a vertical packed tower. The packing has a coating of biofilm. Contaminants are biodegraded to carbon dioxide, water, and acid gases. The pH of recirculated water must be controlled because the acid gases would otherwise deactivate the bacteria in the biofilm. Most halogenated organics have slow biodegradation rates, so this technology applies to dilute air streams, as is often the case with off-gases from strippers.

For systems that use air stripping of halogenated VOCs, data from an economic evaluation by Keller and Dyer (1998) indicate that the lowest net present cost for a 10-year life at a discount rate of 12% is a catalytic oxidizer, without heat recovery, followed by wet scrubber. The oxidizer destroys the organic compounds, and, as described in Section 5.8.3, the scrubber controls acid gases that are generated by the oxidizer.

5.8.1 Carbon Adsorption

Granular activated carbon will effectively adsorb organic vapors at temperatures up to approximately 61° C (130° F). Vapor phase carbon granules are similar to those used for aqueous phase adsorption, but they are coarser and have a higher fraction of smaller micropores. Coarse granules with a high percentage of void space between the granules are preferred in order to minimize pressure drop through the carbon beds. For each organic compound, vapor phase adsorption isotherms are higher than the aqueous phase adsorption isotherms described in Chapter 4.

Most stripper blowers are designed to develop heads on the order of only inches of water column, so the carbon beds must be shallow. In order to obtain enough bed residence time for efficient adsorption of organic compounds, broad shallow beds in horizontal vessels or multiple short vertical canisters in parallel service can be used. Typical bed depths are 1 m, with face velocities in the range of 0.2 to 0.4 m/sec (40 to 80 ft/min) (Stenzel and Merz, 1989).

The adsorption capacity of vapor phase carbon is given for 283 organic compounds by Yaws, Bu, and Nijhawan (1995). Much of these data are derived from a correlation involving temperature, refractive index, and partial pressure.

The colder the temperature, the more efficient is the vapor removal by adsorption. However, at greater than approximately 40% relative humidity, the carbon has a progressively decreased capacity for adsorbing organics. (Synthetic polymeric adsorbents that compete with carbon for adsorption service are generally not affected by humidity.) Because the overhead discharge of a stripper is at 100% relative humidity, it is often economical to increase the carbon bed life by reducing the relative humidity ahead of carbon treatment. If the reduction of relative humidity is achieved by heating the overhead discharge, some potential carbon adsorption efficiency is lost because the temperature of the gas has been raised.

At greater than approximately 50% to 70% relative humidity, water molecules compete effectively with organic vapor molecules for carbon adsorption sites. If a system is installed to reduce the relative humidity of the off-gas, the optimum target is usually 45%. For most unheated stripping operations, raising the overhead air temperature by 25° F will lower the relative humidity from 100% to approximately 45%. At cooler than 90° F, activated carbon will typically remove approximately 90% of many organic compounds. The actual percentage removed will depend on the individual Freundlich isotherms, bed residence time, and bed inlet concentration.

With a heated stripper, the overhead air temperature should first be cooled, with the condensate that forms collected and recycled to the influent. Then the air stream temperature should be heated by approximately 25° F just before entering a carbon adsorber.

The best conditions for carbon adsorption include low temperature and low relative humidity. These conditions can be attained by refrigerating the air exiting from the top of a stripper, removing the liquid condensate that forms, and heating the air approximately 25° F. Such a scheme requires relatively high investment and operating costs for the refrigeration system and is not often used. It should be noted that with immiscible organics, the condensate will have both a water phase and a liquid organic phase that can be separated, or both phases that comprise the condensate can be recycled through the stripper. Note that recycling this relatively small amount of organics does not impair effective stripping, because the bulk of the volatile organics are removed by adsorption on the carbon.

It is easier to achieve higher removal percentages at higher inlet concentrations than at lower concentrations with any adsorption system. However, many air strippers have very dilute overhead concentrations because concentrations are low in the groundwater to start with. Stringent regulations may require that a certain minimum percent removal of organics from the off-gas be achieved. A series of carbon beds may be needed to meet the regulatory limits for organics in the air finally discharged to the atmosphere.

Because of the heat of adsorption, the off-gas temperature is increased by passing through activated carbon. With most air strippers, the organic concentrations are so dilute that this temperature increase is negligible. Heated strippers (or any stripper with a low G/L ratio) may produce an off-gas so rich in organic vapor concentrations that temperature control is needed after carbon adsorption. If the temperature exiting from a first-stage carbon bed is too high, a second-stage bed will not effectively remove the remaining organic vapors, and an interstage gas cooler will be needed.

If the air taken overhead from a stripper goes through vapor phase carbon and the effluent from the bottom of the stripper goes through aqueous phase carbon polishing beds, all of the organic contaminants captured end up adsorbed on carbon. It is logical to ask, "Why bother with the stripper? Why not use all aqueous phase carbon to start with?" The reason is that vapor phase carbon can adsorb more organics per pound of carbon than can aqueous phase carbon. By first stripping almost all of the contaminants in a vapor phase adsorption system, the aqueous phase polishing carbon will last longer before breakthrough occurs. Also, vapor phase carbon adsorbs nonvolatile organics as well as volatile organics.

5.8.2 Regenerating Vapor Phase Activated Carbon

A few states have regional furnaces for activation of virgin carbon and for reactivation. These facilities are used for reactivating both aqueous phase and vapor phase carbon. A typical reactivation unit uses a multi-hearth fired furnace. Steam is injected so that pores open up. Oxygen is limited, and the carbon does not burn. Almost all of the organic compounds, not just highly volatile ones, are vaporized and removed from the carbon at the temperatures used. The organics are combusted in an oxygen-rich afterburner.

The most common method of regenerating vapor phase carbon on-site is to steam it. Aqueous phase carbon might be regenerated with steam but not as thoroughly as with vapor phase carbon. At least two parallel carbon beds are used if continuous adsorption is desired, which is the case with most air stripping operations. While one bed is being steamed to regenerate the carbon, at least one other bed is operating in the adsorption mode.

It should be noted that up to 20% of the working capacity of the carbon can be lost because of retention of organics in the small pores (Stenzel and Merz, 1989).

The steam leaving the carbon bed contains VOCs. This mixed stream is passed through a condenser into an accumulator vessel. Water is separated from immiscible

organic liquids by gravity settling in the accumulator, and the water may be returned to the stripper or to the steam boiler after passing through aqueous phase activated carbon.

Methods other than using steam for applying heat in the absence of oxygen can be applied for regenerating carbon. A carbon system with regeneration can serve as a concentrator for an oxidizer. A portion of the hot exhaust from the oxidizer is recycled through the spent carbon as the regenerating medium. The gases from the carbon regeneration process are much richer than the original air stream being treated. The oxidizer is thereby reduced in size and consumes much less fuel than an oxidizer installed without a carbon system preceding it.

Vacuum can also be applied for removing VOCs from carbon. Some of the best regeneration schemes use vacuum in conjunction with heat. A regeneration system with electric heating under vacuum conditions with nitrogen used to sweep out the organic vapors provides a more thorough job of regeneration than can typical steam heating systems.

Some adsorption/regeneration systems use one hollow wheel filled with activated carbon instead of multiple vessels with fixed beds. The wheel slowly rotates, with one section of the carbon exposed at any given time to the flowing air stream for adsorption of organic vapors in the air. At the same time, another section of the wheel is undergoing regeneration.

When halogenated VOCs are present, regeneration of carbon or of other adsorption media can generate corrosive acids. Equipment must be constructed of appropriate materials accordingly.

5.8.3 Direct Thermal Oxidizers

Oxidizers combust organic vapors with heating and ignition in the presence of excess oxygen (air), and they do not involve using carbon. Unless the air stream has a relatively high concentration of flammable organic vapors, auxiliary fuel such as natural gas or propane is used to sustain combustion. Because large air volumes are used in air strippers to remove relatively small amounts of organic compounds dissolved in water, the concentration of organics in the air stream is usually so lean that auxiliary fuel must be used. Direct thermal oxidizers are organic vapor incinerators that generally operate at temperatures greater than $1,200^{\circ}$ F (649° C), with intimate contact of the burner flame with the air stream containing organic vapors. Some of the air stream is used as combustion air.

In addition to good mixing throughout the combustion chamber, efficient conversion of organic compounds to carbon dioxide and water vapor depends on having adequate residence time and temperature. A residence time of at least 0.3 sec at greater than

1,200° F (649° C) will usually result in more than 95% destruction efficiency. State or local air pollution control agencies often set the minimum allowable temperature and sometimes the minimum residence time that must be maintained in an oxidizer. In some jurisdictions, 1,400° F (760° C) and 0.5 sec are minimum requirements. With these conditions, hydrocarbon destruction efficiencies greater than 95% are possible. For non-halogenated VOCs, Keller and Dyer (1998) indicate that 98% destruction efficiency is attained with a 0.75-sec residence time at 1,600° F (871° C); for halogenated VOCs, 2 sec at 1,800° to 2,000° F (982° to 1,093° C) is needed for a 98% destruction efficiency.

Straitz (1995) gives the outside diameter and height of thermal oxidizers that are designed for a 0.6-sec residence time at 1,600° F. Examples are as follows: for 100 scfm of off-gas, 14 in. by 16 ft; for 200 scfm, 16 in. by 19 ft; for 400 scfm, 20 in. by 19 ft, and for 1,000 scfm, 30 in. by 16 ft.

When an oxidizer is used for emission abatement, a flame arrestor should be installed in the ducting connecting the stripper overhead with any oxidizer. Such devices prevent backward propagation of flame from the oxidizer to the stripper in the event of a blower failure.

If chlorinated solvents are being stripped, hydrogen chloride gas and chlorine will be emitted from either direct thermal or catalytic oxidizers. Because hydrogen chloride gas forms a hydrochloric acid solution with water, it may be required to water scrub the oxidizer exhaust. The scrubbing solution may have to be neutralized with caustic. Theodore (1996) gives the design basis for packed-column wet scrubbers. Spray towers, trayed columns, and Venturi scrubbers are also used for control of acid gas emissions. Frequently, air quality control agencies require that overall emissions of hydrogen halides and halogens be less than 1 lb/hr (75 g/min) or be abated by at least 99%.

5.8.4 Catalytic Oxidizers

Catalytic units use a fixed or fluidized bed of catalyst for combustion of organic vapors in the air stream from a stripper. The air stream is first heated to a temperature greater than 600° F (316° C). Because catalytic oxidizers use auxiliary fuel to heat the air stream to only approximately half the temperature that direct thermal oxidizers do, potential savings from using catalysts can be significant. This is especially true with air from an air stripper, which typically has very low organic vapor concentrations.

Most units use platinum impregnated on a fixed substrate, the same catalyst system used for most automobile exhaust converters. The preheating does not ignite the organic vapors but prepares them for reaction within the catalyst bed. The conversion of organic compounds to carbon dioxide and water vapor takes place while the air stream passes through the catalyst. Because the reactions are exothermic, the air stream rises in temperature through the catalyst bed.

The temperature rise is distinct, is somewhat proportional to the off-gas organics concentration, and can be used to monitor performance. Too high of an influent gas concentration could cause an excessive temperature rise detrimental to the catalyst, but that is unlikely with dilute concentrations usually encountered with air stripper off-gas. Catalytic oxidizers can readily achieve 95% destruction efficiency with 600° F (316° C) preheat. Either a gas burner with auxiliary fuel or electric heating can be applied for preheating. Higher destruction efficiencies, greater than 99%, are possible with higher preheat temperatures and large catalyst beds.

The catalyst must maintain adequate activity. If chlorinated solvents are being stripped, the usual platinum catalysts will become deactivated. At low chloride concentrations, this deactivation may not be significant, even after a long period of time. US-manufactured catalysts are now available that do not deactivate in the presence of even high chloride concentrations (Buck and Hauck, 1992). A Danish firm is marketing a catalyst that is effective with chlorinated and brominated hydrocarbons (Ondrey, 1995). HCl, Cl₂, HBr, and Br₂ that form can be removed with a caustic scrubber. Keller and Dyer (1998) indicate that halogen-tolerant catalysts can treat gas streams with up to 5,000 ppmv of equivalent chlorine or bromine content; temperatures must be higher or space velocity must be lower than with non-halogenated VOC destruction. Space velocity is defined as actual cubic feet per hour or actual cubic meters per hour divided by catalyst volume in cubic feet or cubic meters, and it is typically 7,500 to 15,000/hr with halogenated VOCs.

Certain heavy metals will poison catalysts. Lead, especially in the form of tetramethyl lead, which is volatile and was used in some gasoline blends, will quickly poison a platinum catalyst if not converted first to lead oxide in a preheating flame. Platinum catalysts can be deactivated by phosphorus, arsenic, cadmium, alkali metals and iron. According to Bar Ilan et al. (1994), catalyst manufacturers can restore some activity by removing these substances with wet chemical cleaning and with baking off of soot and other organics.

5.8.5 Auxiliary Fuel Consumption and Heat Exchange

A rapid method of estimating auxiliary fuel consumption with an oxidizer for an air stripping system is illustrated below. Fuel costs usually greatly outweigh other operating costs if the stripping system is automated so that operator attendance is only occasional. Oxidizers are well insulated, with relatively minor radiation losses to the atmosphere. Because of this, fuel consumption can be approximated from the amount of heat needed to raise the temperature of the stripper overhead air. The approximate amount of heat needed to be supplemented by the auxiliary fuel is given by Equation 5-30.

Air heating duty = (air flow rate) (Δ T) Cp – (fuel value of the organic vapors) (5-30)

in which ΔT is the heat rise provided to the influent stripper off-gas; the air flow rate is in pounds per unit of time, and Cp is the average specific heat of air over the temperature range involved. Moisture content has been neglected; for heated strippers, the heating rate for water vapor should be accounted for. For the temperature range of most oxidizer systems, Cp is 0.24 Btu/lb of air/°F of temperature rise (for water vapor, Cp is approximately 0.5 Btu/lb of air/°F). As noted for Equation 5-16, the density of air is 0.076 lb/standard ft³ for 60° F standard temperature. If the air flow rate is known in standard cubic feet, the density is multiplied by air flow rate to obtain units in pounds. Using the example given in Figure 5-4 for 200 scfm (21,888 lb/day) of air at 60° F, the air heating duty for a catalytic oxidizer with preheating to 650° F is calculated as follows:

Given: The air mass flow rate is 21,888 lb/day; the temperature rise is from 60° to 650° F; and the gasoline TPH vapor rate is 7.59 lb/day, from Figure 4-6.

Assumptions: The heating value of the gasoline hydrocarbons involved is approximately 20,000 Btu/lb; no heat recovery is used.

Find: Heat duty required from auxiliary fuel

Step 1: Determine heat duty to increase the air temperature, without considering the fuel value of the organic vapors, as given by Equation 5-31.

 $(21,888 \text{ lb/day}) (650^{\circ} \text{ F} - 60^{\circ} \text{ F}) (0.24 \text{ Btu/lb/}^{\circ}\text{F}) = 3,099,300 \text{ Btu/day}$ (5-31)

Step 2: Determine net duty, using the assumed heating value for the organic vapors, as given by Equation 5-32.

3,099,300 Btu/day - [20,000 Btu/lb (7.59 lb/day)] = 3,099,300 Btu/day - 151,800 Btu/day = 2,947,500 Btu/day net (5-32)

The temperature rise in this example is 650° F - 60° F, or 590° F. For a direct thermal oxidizer operating at, for example, $1,300^{\circ}$ F, the temperature rise would be 1240° F. The air heating rate could be calculated from Equation 5-30 and would be approximately (1,240/590) (3,099,300 Btu/day), or 6,513,800 Btu/day, minus 151,800 Btu/day fuel value of TPH vapor. The net heating duty is more than double the amount calculated in Equation 5-32 for the catalytic unit.

With either a direct thermal oxidizer or a catalytic oxidizer, a heat exchanger can be added to the system to save auxiliary fuel. The most common heat exchanger uses metal surfaces or tubes to separate air from the stripper overhead and the oxidizer exhaust. Recuperative heat recovery is accomplished by heat transfer between the two gas streams. The amount of heat saved is approximately proportional to the amount of heat exchange surface. Exchangers are rated by the percent of gross air heating saved, without taking into account the fuel value of the organic vapors. Typical standard designs provide 50%, 65%, or 70% in savings.

Keller and Dyer (1998) recommend that the exhaust gases be maintained at least 100° F above (38° C above) the acid dew point temperature to avoid exchanger corrosion.

Straitz (1995) gives the percentage of heating saved as equal to $(t_2 - t_1)/(T-t_1)$ times 100%, in which t_2 is the stripper off-gas temperature after warming in the heat exchanger, t_1 is the temperature leaving the stripper, and T is the oxidation temperature.

Another type of heat recovery is attained using regenerative oxidizers that provide more than 90% in fuel savings. These devices have at least two extra chambers surrounding a firebox that contains an auxiliary fuel burner. The extra chambers are filled with gravel or ceramic packing that provides a mass with high heat capacity and allows air flow through the mass. The hot exhaust flowing from the firebox through the solids heats the mass for a relatively short period of time. Valves are then automatically repositioned so that stripper overhead air passes through the chamber containing the heated mass before the air enters the firebox. More than 90% of the air heating duty is thereby accomplished before the air contacts the auxiliary fuel burner flame. The burner duty is minimal using these systems. Smith Environmental (Ontario, California) recommends in an interview by Chemical Engineering (September 1996) that regenerative oxidizers be avoided if vapor concentrations exceed 20% of the LEL. Overheating at 10% to 20% of the LEL should be avoided by either admitting dilution air or reducing the depth of the ceramic packing material. With typical air stripping, concentrations do not exceed 10% of the LEL. With high organic vapor concentrations, either no heat recovery or a recuperative heat exchanger should be used instead of a regenerative unit.

Renco (1994) compares regenerative heat recovery with conventional recuperative heat exchange, and recommends regenerative systems for flows greater than 10,000 scfm with flammable vapor concentrations below 10% of the LEL. Virtually all stripping towers operate below this air rate, but they usually have such low vapor concentrations. For large stripping systems, it would pay to compare the costs and savings of regenerative units with recuperative units. Klobucar (1995) compares the two types of heat recovery and gives a method of accounting for operating costs, taking into account fan electrical energy consumption, as well as fuel consumption. An example is shown with pressure drop through a regenerative unit at a 25-in. w.c. versus a 12-in. w.c. through a recuperative unit. Klobucar also compares such systems with a hybrid emission abatement system using vapor phase activated carbon or zeolite adsorption with hot-air absorbent regeneration. The hot air exhaust

contains the organic vapors at perhaps 10 times the concentration of the main air stream and is fed to a direct thermal oxidizer with recuperative heat recovery.

If there is a chance that organic vapor concentrations can approach the LEL in a heat exchanger, controls should be added that automatically open a dilution air damper or a heat exchange bypass damper at 10% to 20% of the LEL.

5.9 Main System Design Parameters

This section summarizes, by way of an example, important parameters that impact air stripper system design and evaluation. A packed air stripper with carbon polishing of the liquid effluent is used in the example for removing gasoline hydrocarbons from groundwater. As shown in the Chapter 4 on carbon adsorption, a stripper effluent gasoline TPH concentration of 0.35 mg/L corresponds to a reasonably long carbon life. Aqueous phase carbon will reduce the effluent concentration from this level to near nondetectable levels. With this polishing action by the carbon, and considering that the air emission abatement equipment and operations will cost less if air volume is minimized, the low end of the A/W range for gasoline strippers will be chosen — namely, A/W is 30.

5.9.1 Concept and Process Design

The influent TPH is given as 13,000 μ g/L, or 13.0 mg/L. The stripping efficiency for TPH would be (influent - effluent)/influent, or (13.0 - 0.35)/13.0 = 0.973. The next steps illustrated are as follows:

- Mass balance
- Calculation of volumetric air flow rate
- Calculation of vapor concentrations
- Initial development of P&ID, plot plan, and site plan
- Use of an air stripping computer program

Mass balance example. Figure 5-4 shows the system illustrated in Figure 5-1, with the contaminant removal efficiencies and corresponding effluent concentrations shown. In addition to the TPH concentrations, the diagram shows concentrations of contaminants of most concern to pollution control authorities, the aromatic compounds. Note that the sum of the aromatics concentrations is not equal to the TPH concentration because TPH includes nonaromatics that are not shown.

In this example for gasoline hydrocarbons, the stripping factor R could be approximated by using H for octane. Use of an air stripping computer program would give the corresponding depth of packing for the chosen A/W ratio and the effluent concentrations for the individual aromatic compounds.

The mass flow rates, g/day or lb/day, are equal to the volumetric water flow rate times the concentration. The water rate is 50 gal/min (272,160 L/day). Because1 g equals 1,000 mg, the influent TPH mass rate at 13 mg/L is 3,580 g/day (7.80 lb/day); the effluent at 0.35 mg/L is 95.3 g/day (0.21 lb/day). The tower overhead vapors contain 7.59 lb/day of TPH, determined by subtracting the effluent mass flow rate from the influent mass flow rate. Figure 5-4 shows these values for TPH and values for the same parameters determined in identical fashion for each of the aromatic compounds of interest.

Volumetric air flow rate. Figure 5-4 also shows the air flow rate, on a dry weight basis — that is, air humidity is not taken into account, and it is assumed that the incoming air is saturated. At air temperatures up to 25° C, the moisture vapor content of air cannot exceed 2% by weight. The calculated values are still accurate enough for designing the air blower and ductwork. (As discussed earlier, for vapor phase carbon adsorption, the relative humidity of the air being treated is important for designing carbon systems.) For an influent flow rate of 50 gal/min (6.68 ft³/min) and an A/W of 30, the air flow rate is 6.68 ft³/min (30), or 200 ft³/min. If the incoming air is the same temperature as the groundwater, as in this simplified example, there would be some cooling effect because of evaporation if the incoming air were not saturated.

For these calculations, it is convenient to express air volumes in standard cubic foot, and air flow rates in standard cubic foot per minute as scfm or SCFM. A standard cubic foot is a cubic foot of air measured at 1 atm (29.92 in. of mercury column, in. Hg or 760 mm Hg) and at standard temperature. (An actual cubic foot of air, acf, is the volume at its actual pressure and temperature). The chemical engineering standard temperature of 60° F, equivalent to 520° R, is used in examples throughout this book.

Figure 5-4 could be enhanced to include values of acfm as well as scfm for air flow rates. Assuming that the incoming air is at sea level and at 1 atm, there would be 29.9 in. Hg of pressure entering the tower just below the bottom of the packing. The incoming air temperature is given as 60° F, so the incoming acfm equals the scfm rate of 200 at a standard temperature of 60° F. The total pressure drop through the tower is assumed to have been computed in this example to be 5 in. w.c., equivalent to 0.38 in. Hg. The diagram shows a negative-pressure stripping system, i.e., the air blower induces atmospheric air into the tower. The gauge pressure in the tower overhead duct leading to the blower suction would be -0.38 in. Hg. The absolute pressure would be 29.9 in. Hg - 0.38 in. Hg, or 29.5 in. Hg. For the temperature and pressure temperature-volume relationship holds quite accurately. The ideal gas law is used to relate actual and standard conditions as follows:

acfm = scfm (29.9 in. Hg)/[(absolute actual pressure) (actual temperature)]/520 (5-33)