



EPA

TECHNICAL BULLETIN

CHOOSING AN ADSORPTION SYSTEM FOR VOC: CARBON, ZEOLITE, OR POLYMERS?

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Choosing an Adsorption System for VOC: Carbon, Zeolite, or Polymers?

This paper will make you more familiar with the issues involved in choosing an adsorber system for your plant, company, or corporation. Carbon, zeolite, and polymer adsorbents have each been used to adsorb Volatile Organic Compounds (VOC) and other pollutants from relatively dilute concentrations in air (from tens to thousands of parts per million by volume) to control emissions. This paper discusses issues involved in deciding which adsorbent to use, what type of adsorption system to use, and whether it is the right emission control technology for you.

WHAT ARE ADSORBERS?

We are referring to adsorbers, not absorbers, because the pollutant is adsorbed on the surface (mostly the internal surface) of a granule, bead, or crystal of adsorbent material. It is not absorbed by a chemical reaction. This is an important difference. The adsorbed material is held physically, rather loosely, and can be released (desorbed) rather easily by either heat or vacuum. By contrast, an absorber reacts chemically with the substance being absorbed, and thus holds the absorbed substance much more strongly, requiring much more energy to release the absorbed substance.

Unfortunately, one of the adsorbents is called “absorbent carbon.” This persisting misnomer came from the time before adsorption became understood in the 1920's. A better term is “activated carbon.” Carbon is activated by the pyrolysis of coal, wood, bark, coconut husks, etc. to remove all the volatile material as a gas or vapor, and leave only the carbon. This carbon might then also be partially oxidized to enlarge its pores.

Another adsorbent is the aluminosilicate crystal structure known as “zeolite,” which has uniformly sized pores (also called windows) throughout its crystal structure. The crystal structure for the 118 established types of zeolite is determined by the ratio of silicon to aluminum in the crystal when the crystal is formed. All naturally occurring zeolite is hydrophilic (having an affinity for polar molecules, such as water) and contains aluminum. Dealuminizing natural zeolite makes it hydrophobic (having affinity for non-polar substances, such as many VOC). Zeolite is dealuminized by chemical replacement of the aluminum with silicon without changing the crystal structure.

Hydrophobic zeolite can also be synthesized in crystals from 1 micron to 1 millimeter in diameter, and these can be bonded into larger granules to lower their resistance to air flow. Since synthesis is expensive, it is usually reserved for making either hydrophobic zeolite or zeolite catalysts with a specific large pore size.

Polymeric adsorbents have pores built in when they are manufactured. These pores can range from macro-porous through molecular sizes, but the smallest pores are usually larger than the

micro-pores of an activated carbon. Polymers are used as granules or beads and, as the name implies, are plastics. They have been observed to desorb faster than carbon. Like carbon, they are not considered highly selective as to which VOC they will adsorb, although any specific polymer will adsorb some VOC better than others.

Choosing the best adsorbent for the situation is not simple. There are several related problems which we will discuss to familiarize you with the different adsorbents and systems.

WHY ARE ADSORBERS IMPORTANT?

Adsorbers have been used principally to control the emission of VOC. The control of VOC emissions typically reduces the concentrations from between 400 and 2,000 parts per million (ppm) to under 50 ppm. Adsorption technology can now extend the range of VOC concentration from 20 ppm to one-fourth of the Lower Explosive Limit (LEL). At the lower end of this range, such small concentrations may be difficult or uneconomical to control by another technology or even by all adsorbents. Incinerators, membrane separators, and condensers may be economically feasible when used in place of adsorbers at the upper end of the range.

In addition to emission control, the adsorber makes recovery of the VOC possible. Recovery of a reusable or marketable VOC can significantly offset the cost of emission control. Adsorbers can also increase the concentration of VOC to allow either destruction by incineration, or recovery by either membrane or condenser to be economically feasible.

HOW DOES ADSORPTION WORK?

The VOC are condensable vapors which appear to condense on the surface of the adsorbent. When the surface has adsorbed nearly as much as it can, the VOC is desorbed as part of regenerating the adsorbent. When desorbed, the VOC vapors are usually at a higher concentration, after which the VOC is either recovered or destroyed. One can think of all adsorbers as capturing VOC from a dilute concentration and releasing it in a higher concentration. Adsorbers can also be thought of as separating the flow of VOC from the air flow of a process.

The actual concentration of the VOC is key to when and how an adsorber would be used. An adsorber becomes nearly useless when the inlet concentration gets so low that the VOC will not be effectively adsorbed, but it allows the recovery of the VOC to be at a high concentration. Safety reasons direct that VOC concentrations are held below one-fourth of the LEL. When the concentration is near one-fourth of the LEL, the VOC can be economically disposed of by an incinerator, captured by a membrane, or recovered with a condenser. However, a VOC concentration below one-fourth of the LEL is too lean to support combustion without adding auxiliary fuel. Therefore, as the VOC concentration exiting the adsorber drops below one-fourth of the LEL, more fuel must be added to give adequate combustion to the VOC in an incinerator.

HOW ARE POLLUTANTS ADSORBED?

Figure 1 shows a molecule above a surface, with the distance from the surface being the normal to the surface. There is a repulsion between the cloud of electrons in atoms that form the surface and those of the molecule, and there is also a Van der Waals nuclear attraction force. The nuclear attraction has a much shorter radius of influence, so there is a short distance (usually nanometers) from the surface where there is a “dip” or a “well” in the potential energy curve as shown in Figure 2. Molecules or atoms that reach this “well” are trapped or “adsorbed” by this potential energy “well” until they can obtain enough kinetic energy to fly out of the well and escape. Kinetic energy converts to potential energy, just as when you jump upward against gravity. Therefore, kinetic energy must be added to allow the molecules to escape, or desorb. Kinetic energy of molecules exhibits itself as the temperature, with hotter being more energetic.

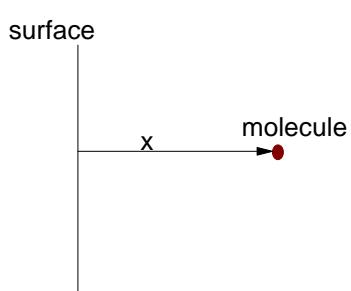


Figure 1. Molecule-Surface Distance

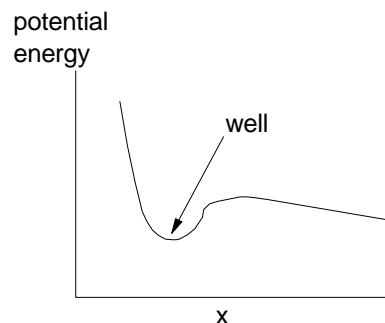


Figure 2. Potential Energy vs. Distance

Historically, carbon was the first material to be observed to have a large amount of area with this property. Zeolite and polymer adsorbents have more recently been found to also have a large amount of internal surface area with this property.

We have known for decades that before you can pull a “hard vacuum” (such as 1 micron Hg) even glass systems have to “outgas” adsorbed air. What is unique to these adsorbents is that they have such a large amount of area (mostly internal) with this property per unit of weight, and that this area can be desorbed so readily.

WHAT IS DESORBING?

Desorbing has been accomplished through both temperature and pressure swings. According to the kinetic theory of matter, the molecules gain kinetic energy when heated, and this allows a heated molecule to “fly” out of the well. Heat can be provided as steam, heated nitrogen, or by microwave among other techniques. For vacuum regeneration, the molecule will at some time

have sufficient energy to escape if molecular impacts do not cause it to rebound back into the well. Therefore, desorbing can be accomplished either by heating the adsorbed material or by evacuating the space over it. There is an equilibrium between captured and escaping molecules.

Giving the adsorbed material the kinetic energy to escape or desorb is part of the regeneration of the adsorbent. This regeneration of the adsorbent should be done before all of the absorbent has become unable to hold more, and must be done before the adsorbent can be used again. The remainder of regeneration is drying, cooling, or otherwise preparing the adsorbent to again adsorb the VOC.

WHAT IS THE ADSORPTION ISOTHERM?

Each adsorbent has an adsorption capacity which is referred to as the “adsorption isotherm”. Historically, with carbon, the isotherm was used to measure the pounds of pollutant per pound of adsorbent that could be adsorbed at a given temperature. However, the adsorption isotherm is also a function of pollutant concentration as measured by the partial pressure of the vapor, and it is also a function of the total ambient pressure around the adsorbent. The number of molecules that can be stored in the “well” is pressure dependent, with closer spacing of adsorbed molecules being associated with higher pressure. The adsorption isotherm is still defined as the pounds of material that can be adsorbed per pound of adsorbent.

Thermal regeneration systems use the temperature isotherm; vacuum regeneration systems use the total and partial pressure isotherm; and pressure swing regeneration systems use the total ambient pressure isotherm. The “isotherm” is actually a function of all of these variables. Thus, the “isotherm” is actually a complex function that forms at least a 3-dimensional surface, rather than being either a constant or a two-dimensional plot. The isotherm can either be a linear function or a highly non-linear function depending upon the adsorbent, the pressure, and the material being adsorbed.

The adsorption isotherm is also a function of the amount of adsorption area that molecules of the VOC can reach. Pores on the surface allow entry to the interior area of each of these adsorbents. The interior is where most of the adsorption area exists. Carbon has pores leading to smaller pores, which lead to even smaller pores. This apparently continues *ad infinitum* in carbon, and much of the internal surface area is in these micro-pores. Zeolite has uniform pores that are part of its crystal structure. Polymers have a range of pore sizes, but usually lack the very small micro-pores. Thus, the adsorption isotherm is different for each type of adsorbent and each type of pollutant.

HOW DO I PICK AN ADSORBENT?

There are many kinds of polymer adsorbents, many kinds of carbon adsorbents, and many kinds of zeolite adsorbents. To document all of these variations would make this paper quite a tome, and it would become a handbook rather than a concept paper. We do not intend to adequately

describe all of the variations in such detail. We can only deal with general properties and let specific selections be made by the designers and their customers with the aid of handbooks.

A prime concern is the largest molecular size to be adsorbed versus the pore size of the adsorbent. This is principally a concern with zeolite, where uniform pores can be any size from 3 to 30 angstroms (0.3 to 3 nanometers) for different types of zeolite. Zeolite should not be expected to provide any adsorption area for molecules larger than its pores, nor for molecules for which it does not have affinity. Carbon and polymers also must have pores larger than the largest molecule to be adsorbed. However, the broad range of pore size in carbon and polymers makes this criterion less strict than it is for zeolite. The adsorption area to be reached via the pores should be excluded if the molecule to be adsorbed can neither reach it nor be desorbed from it.

Regardless of the method of regeneration, the adsorption area cannot be regenerated when the adsorbed molecule jumps from a well on one side of the pore to a well on the other side of the pore. This can occur in the micro-pores of carbon and some polymers. Thus, this would prevent desorption from occurring from areas where the micro-pores get too small.

The affinity of the adsorbent for some types of substances can be much greater than the affinity for others. As a result, when there is a stronger affinity for some of the molecules, the molecules having lesser affinity either get held with a smaller adsorption capacity or get released in favor of the molecules for which the affinity is greater. Carbon, which is neither fully hydrophobic or hydrophilic, retains some adsorption area with affinity for both polar and non-polar molecules. Humidity has a noticeable effect on carbon because of this. One research paper has even reported that desorbing of VOC from carbon occurs as steam condenses and the water displaces the VOC.

All naturally occurring zeolite is hydrophilic, having an affinity for polar substances, such as water, but synthetic zeolite can be either hydrophilic or hydrophobic. Polymers are usually hydrophobic unless made specifically with other affinity. For example, amphophilic block copolymers can have both hydrophilic and hydrophobic affinities. Thus, the affinity has to be considered as part of selecting the particular adsorbent.

Some polymers and hydrophobic zeolite are generally much less sensitive to humidity than carbons, and are also much less subject to fire, crumbling, or powdering. Therefore, they require much less frequent replacement. Carbons are cheaper (at least initially). The cost per pound of carbon is about \$2.00, which is up to 20 times less than the cost per pound for either polymers or zeolite. However, the need to replace zeolite is very rare, and the replacement of polymers occurs only slightly more often. Carbon needs to be replaced every six months to five years, or when there is a bed fire. The frequency depends on the type of carbon, the frequency of regeneration, and the temperature at which it operates.

Some polymeric adsorbents were evaluated by General Electric Co. for thermal desorption, and found to desorb faster than carbon, to have larger adsorption capacity in either high or low humidity after conditioning, and to desorb at lower temperatures. The maximum temperature for

desorption must exceed the boiling point for the VOC, but must not exceed the polymer's melting point.

The maximum temperature for desorption is less confining for carbon, which may be taken to a much higher temperature (250 to 350 F) without melting. Carbon frequently catalyzes oxidation reactions when the temperature gets above this range. The same maximum temperature is commonly used for zeolite, but the real limit for zeolite depends on either the pyrolysis temperature, the catalyzation temperature of the adsorbed VOC, or the range of temperatures at which the crystal structure is stable for the zeolite. This metastable temperature range is generally considered to be up to about 1,000 F.

ARE THERE OTHER DESIGN CONSIDERATIONS?

YES! These other factors are described individually below:

MASS TRANSFER ZONE

The Mass Transfer Zone (MTZ), see Figure 3, exists in all adsorbents. In the MTZ, the concentration of VOC in air goes from 100% of the inlet vapor concentration to the lowest available vapor pressure in equilibrium with the desorbed adsorbent.

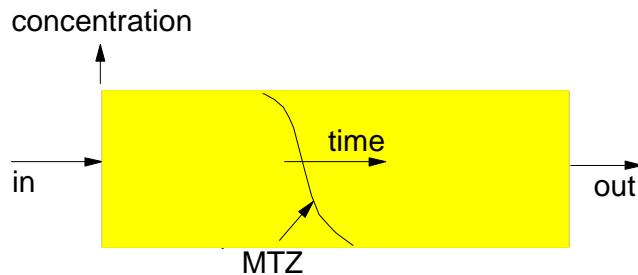


Figure 3. Movement of MTZ with Time

The depth of the bed is the dimension of the adsorbent in the direction of air flow, and the MTZ is usually much shorter than the depth of the bed. The MTZ moves through the bed as the bed reaches its capacity (the absorption isotherm becomes filled). Upstream of the MTZ, the bed has reached its capacity, while downstream the bed remains essentially desorbed. Breakthrough occurs when the MTZ reaches the downstream end of the adsorption bed. Breakthrough is

observed as a rise in the VOC vapor concentration leaving the bed, which may occur at different times for different VOC.

Adsorbents of all types share a characteristic with columns used in gas chromatography, for these too use adsorption. The adsorbed material will desorb spontaneously and migrate downstream with the gas flow in each system. This is caused by the pressure gradient, which is intentionally very low when adsorbers are used as an emission control technology, and rather high in the gas chromatography adsorption column. This migration of pollutants is generally slow enough that it may be neglected when emissions are being controlled. However, this property defines an absolute maximum time for adsorption before regeneration of the bed. Breakthrough is actually a gradual process because the equilibrium between the vapor pressure and the adsorbent is continuously varying. Thus, breakthrough can be defined as any noticeable rise in the effluent concentration.

The MTZ will also migrate to breakthrough independent of the VOC loading. An input spike of VOC, along with the migration of the MTZ, will allow the spread of the VOC and reduce the concentration that will be desorbed at breakthrough. An example of how an adsorber might properly use the migration characteristic of the MTZ is in air flow from a hood in a plant that handles mercaptan. Natural gas is odorless and mercaptan is added to natural gas to provide an olfactory (odor) indication of a leak. If the mercaptan spill gave emissions in concentrations more than one part per billion, people would smell it, and be alarmed because they would think that there was a leak of natural gas. Therefore, hoods where mercaptan is handled are equipped with a suitably sized adsorber. This adsorber captures any vapors from spills and, when the MTZ migrates to breakthrough, the mercaptan is released at a lower concentration in this case. This is because the mercaptan was not a continuous emission, the adsorber did not reach its capacity, and therefore breakthrough occurred at a lower concentration which was below the threshold of smell. For this purpose, desorbing or regeneration is not necessary unless the spills are too frequent.

WORKING CAPACITY

The “conditioning cycles” are the number of cycles (often about five) that are required to achieve a stable amount of adsorption and regeneration. Carbon, after undergoing the conditioning cycles, is capable of adsorbing about 50% of the amount that was adsorbed by the virgin material. Zeolite is capable of adsorbing about 90% of the amount adsorbed by the virgin material. Polymers can vary over the range of 50% to 90%. This “conditioned isotherm” also defines the “working capacity” of the adsorbent. The fact that carbon and some polymers will typically desorb only 50% as much as the virgin material is thought to be caused by the continued recapture of molecules (i.e., depressed vapor pressure) in the micro-pores. VOC can be removed from these micro-pores only by pyrolysis, which would destroy the VOC, and either destroy the polymer or alter the properties of the carbon.

Zeolite has a uniform pore size and therefore does not exhibit this phenomenon. Polymers have an extended range of pore size, and in some respects are similar to carbons, but some polymers are thought to lack the very small micro-pores. Carbon also displays a time-related spreading of VOC from the macro-pores to the micro-pores. Zeolite and polymers show this time dependent spreading to a much less noticeable degree.

The “working capacity” of the adsorbent is determined by the difference between the desorbed conditioned level and the full adsorption isotherm of the adsorbent. Thus, the conditioning effect must be considered when sizing the adsorbent bed. The conditioning effect can require up to twice as much adsorbent in the bed. Since regeneration should occur only about every 8 or 16 operating hours, the capacity of the bed(s) can be determined by the concentration of VOC, the air flow rate, the weight of adsorbent in the bed(s), the type of adsorbent, and the “working capacity” of the adsorbent. In this way, the “working capacity” can have a significant effect on the cost of installing, operating, and maintaining an adsorber.

VAPOR PRESSURE

Carbon and polymers have a linear adsorption isotherm relative to vapor pressure, while zeolite has a very non-linear adsorption isotherm relative to vapor pressure for the molecules it has an affinity to. This linearity makes either carbon or polymers the better adsorbent when the vapor pressure (or concentration) is higher, but the non-linearity makes zeolite the better adsorbent when the vapor pressure (or concentration) is lower. This property allows carbon or polymer adsorbent in a “sacrificial” (or first) bed followed in the air flow by a suitable zeolite in a “polishing” bed to produce the lowest vapor pressure of VOC in the outflow. The lower the partial pressure of the VOC in the outflow, the higher the control efficiency.

MULTIPLE ADSORBENTS

There is also an advantage to using a mixture of adsorbents. A mixture of carbon and zeolite removed mixed vapors of xylene and methanol better than an adsorbent composed of either. Hussey and Gupta of Durr Industries reported this at the Spring 1997 Meeting of American Institute of Chemical Engineers. They noted that the path through the mixture was greater than the path through either of the adsorbents when used alone, and they attributed the increased adsorption to the greater path length. However, both methanol and xylene were adsorbed, and since the authors stated that carbons adsorb xylene well while a six or eight angstrom pore size zeolite adsorbs methanol well, the depth would have had to be the sum of the individual bed depths to yield this result. This paper also observed that at high concentrations, carbon adsorbs better, and can be used as a “sacrificial” bed upstream of a zeolite “polishing” bed.

ADSORPTION MODELS

In order to know just how well the chosen adsorbent will perform, the adsorbent must be tested with the mix of pollutants that are to be adsorbed, and at the concentrations that are expected.

This must be done whether using one adsorbent alone or using a combination of adsorbents. It must also be done for a mixture of VOC vapors. Various multi-space adsorption models can predict how a combination of VOC will adsorb, but these are all based on assumptions that fit the results to the individual experiment. Examples are by V. Gusev and J. O'Brien of Yale University; and C. Jensen and N. Seaton of University of Cambridge; M. Heuchel of the University of Leipzig. The various multi-space adsorption models must be proven to apply to your mix and concentration of VOC, and the chosen adsorbent.

BED FIRES

All adsorption is exothermic, that means that adsorption gives off heat and causes a temperature rise. This property has been used for heat storage, but is not desirable for adsorption of VOC. Carbon or metals on the carbon have been known to catalyze the oxidation of some pollutants when the adsorbent is hot, resulting in bed fires which also consume part or all of the carbon. This is a hazard when adsorbing certain hydrocarbons (such as ketones or turpentines) at ambient temperatures that are close to those that cause the VOC to oxidize. Such a carbon bed fire can either alter the pore size of the remainder of the bed, or oxidize the bed to ash. These fires have been suppressed by humidification of the air, leaving some water in the bed after steam regeneration, and by intentional cooling of the carbon. Polymers usually are used at temperatures which do not lead to bed fires, but this must be assured. Zeolite is not flammable, but can catalyze oxidation if the temperature gets high enough. The pore size of the zeolite is not affected by temperatures that stay within the metastable range. Normally, in case of a bed fire with zeolite, only the VOC would be lost if the air flow is controlled to limit the temperature. If the temperature rises above the metastable range, the pore size of the zeolite will be reduced and the density of the zeolite will be increased.

OFF-SITE ADSORBENT REGENERATION

Some customers use the regeneration of the carbon off-site. For example, some “perc” dry cleaners use this technique. They replace their carbon canisters instead of regenerating them on the premises. This requires determining whether you want the bother of a boiler, fuel, and the labor charges that this entails (or else the vacuum pump and refrigerated condenser) or are willing to pay someone else to regenerate your adsorber for you. Speaking in economic terms, while remote regeneration spares you the direct expense of a boiler and its operation (or a vacuum pump and its operation) the regeneration facility will charge you a fee that will cover all costs, plus labor, collection, replacement, regeneration, disposal, and profit. This fee should be less per customer when it is spread across a customer base than when one firm must handle it alone. A shared capability would distribute the cost. However, if your adsorber loading is large enough, it should cost less to have your own regeneration capability.

AFFINITY

The affinity between the VOC to be adsorbed and the adsorbent must be considered. If the

affinity for one molecule in the flow is sufficiently greater than the affinity for another, then the adsorbent will preferentially adsorb the molecule for which it has the greater affinity, and allow transport of the other to occur at up to air flow velocity. Thus, the bed upstream of the MTZ would become saturated with the molecule for which the adsorbent had greater affinity (assuming that the pore size allowed it), while passing other molecules of lower affinity to adsorbent further through the bed and ultimately to the exhaust. As the MTZ moves through the bed, it would cause the release of the molecule with lower affinity, while adsorbing the molecules for which it has higher affinity.

HOW CAN ADSORBERS BE REGENERATED?

There are three methods of regeneration: Thermal Swing Regeneration, Vacuum Regeneration, and Pressure Swing Adsorption. We shall discuss these separately.

THERMAL SWING REGENERATION

The traditional carbon adsorber system uses steam to raise the temperature of the adsorbed VOC and boil it from a carbon adsorbent after the carbon has adsorbed the VOC. This has become known as a thermal swing regeneration adsorber system. It is so named because the temperature is usually swung between ambient and 250 to 350 F in regeneration.

A thermal swing adsorber system is shown schematically in the diagram of Figure 4. Vapor in the air is transported into one adsorber (two are shown, but any larger number can be used), while the other is being regenerated. Steam flows into the adsorber being regenerated to heat the adsorbent, and thus desorb the VOC. After the VOC are desorbed, cooling air from a blower is admitted in place of the steam. When the adsorbent has cooled and dried to the extent intended, the “conditioned” adsorption capacity has been restored, and the bed is now regenerated.

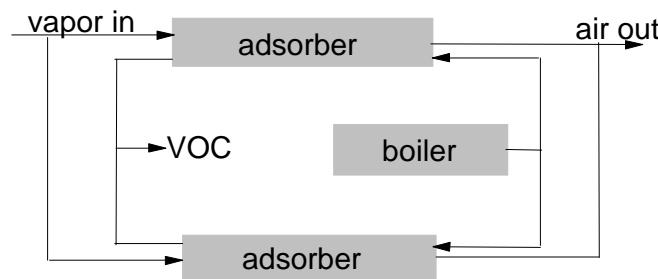


Figure 4. Thermal Swing Adsorber
(steam regeneration)

Regeneration occurs in a preset time if the average VOC concentration is according to the design parameters. However, if either the air flow or the concentration vary unpredictably, a sensor should be used. A predictable air flow and concentration would allow the regeneration to occur at a given time before the breakthrough occurs. If the timer were properly set, it would avoid any breakthrough emissions. A sensor should be used to control regeneration if either the air flow or the concentration of VOC is unpredictable, or if the timer were improperly set.

Prior to breakthrough, the emission concentration is actually very low, and a sensor would have to sense a concentration reading above this level to start regeneration of the adsorber bed. While some greater concentration of VOC will pass through before any regeneration occurs with a sensor, this may allow either more (by having a higher threshold) or less emissions (if the timer allowed breakthrough to happen) than using a timer. However, any increase in emissions may actually be a trivial amount when compared with the amount of the controlled emissions. Either a timer or a sensor can be suitable, if properly set and properly used. Either one can be unsuitable, if improperly set or improperly used.

Thermal regeneration has historically used steam, but other heat sources have been tried successfully. These include: microwaves, embedded heaters, and heated nitrogen. These have been used with all adsorbents. Thermal regeneration becomes more practical when VOC have lower vapor pressures.

VACUUM REGENERATION

To enhance solvent recovery, and eliminate contamination of the VOC by steam, a vacuum regeneration system may be used. Figure 5 shows a schematic of a vacuum regeneration adsorption system. This uses a vacuum pump to lower the pressure in the adsorber to below the vapor pressure of the adsorbed VOC, which causes the VOC to boil off at the temperature that is ambient within the adsorbent, instead of at a higher temperature. In the process of boiling, the temperature of the adsorbent will actually go below the normal outside ambient temperature. This method can be used with carbon, polymer, and zeolite adsorbents.

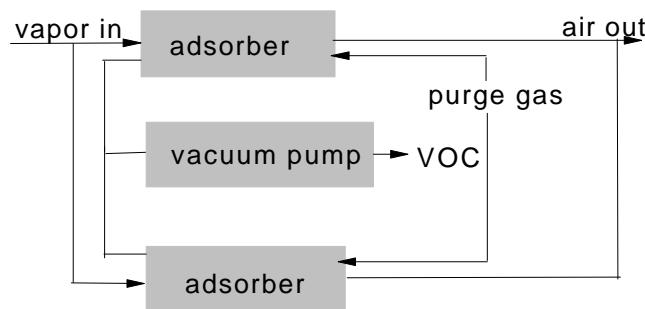


Figure 5. Vacuum Regeneration Adsorber

Sometimes a small flow of purge gas is used to enhance transport of the VOC vapor. The VOC vapor is then recovered by separation (condensation, membrane separation, compression, or some similar process) of the flow from the vacuum pump.

The purity of the recovered VOC is not affected by the vacuum, but may be affected by the mixture of the VOC vapors or the purity of the purge gas. If there are mixed VOC vapors that are being controlled, the recovered VOC will also be mixed unless the pore size or affinity of the adsorbent or the temperature of condensers separate the vapors. The purity of the purge gas is especially important when a water-soluble VOC, such as an alcohol or a ketone, is to be recovered and the purge gas contains moisture. The water vapor will be adsorbed and desorbed along with the VOC vapor, and the VOC may require subsequent purification if it is to be reused. Contamination by moisture has been avoided by using dry nitrogen as a purge gas. The recovered VOC is otherwise as pure as the VOC vapor.

The desorbed VOC are sometimes purified by distillation, skimming, or membrane separation. The recovered VOC is then either recycled in the process that released it, used elsewhere in the plant, or sold. If the purity of the VOC is too low for economical recovery, or the value of the recovered solvent too low, the VOC would be destroyed in the vapor state. Choices of an appropriate process for destruction include flameless oxidation, thermal incineration, or catalytic incineration.

When a zeolite adsorber is divided into several fixed beds in cascade flow as in Figure 6, and when granules of appropriate zeolite are used, the several types of VOC vapors can be adsorbed in separate beds. European firms have already adopted zeolite fixed beds. The acceptance may be based upon the fact that Europe and Asia are prime sources of natural zeolite.

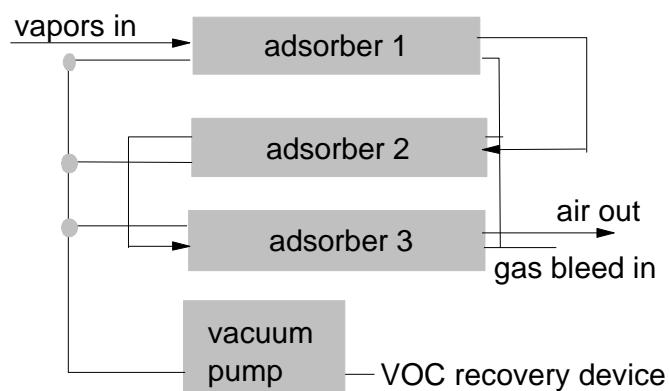


Figure 6. Cascade Vacuum Separation

The VOC can then be recovered individually from these beds, and the resulting VOC can be purer than the mixed vapors. The key is in the selection of the zeolite. While nobody currently advertises the commercial availability of this vacuum regenerated zeolite adsorption system, research supporting it has been done. It is the next logical step, and its development is anticipated.

VAPOR CONCENTRATOR

Although adsorbers have historically been used independently as a pollution control device, the vapor concentrator has also appeared. The vapor concentrator is intended to raise the concentration of VOC vapor to provide more economical treatment in either combustion or condensation devices.

The typical concentration ratio (output VOC concentration divided by input VOC concentration) that can be obtained from a vapor concentrator can range to well over a thousand. However, when the actual concentration of a combustible VOC is near one-fortieth of the LEL, you can economically justify using a rotary vapor concentrator, which may also include an incinerator. Figure 7 shows a rotary vapor concentrator. This is used where the VOC vapor is in a large air flow, and must be concentrated before it can be incinerated economically. (The concentrator air bleed is usually about 10% of the input air flow with an incinerator, and thus the concentration ratio is about ten.) Therefore, if the initial concentration is one-fortieth of the LEL, the resulting concentration is about one-fourth of the LEL. This means that, for incineration, a minimum of fuel would have to be added to assure enough heating value for adequate incineration.

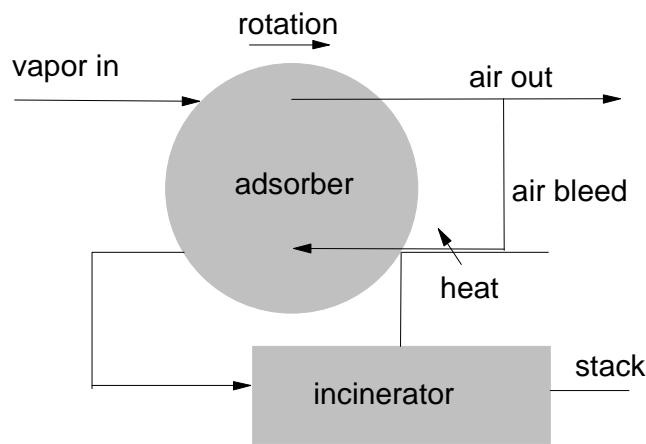


Figure 7. V O C Concentrator

The adsorbent is mounted in a wheel that is rotating either vertically or horizontally. If the wheel is rotating about a horizontal axis, the air flows axially through sectors in the wheel. If the wheel rotates about a vertical axis, the air flows radially through segments on the rim of the wheel. The adsorbent is located in relatively shallow beds in the sectors or the segments. The adsorbent can be zeolite alone, a mixture of zeolite with carbon, a mixture of zeolite with polymer adsorbents, or either carbon or polymer adsorbent beds with zeolite beds downstream.

As shown in the rotary vapor concentrator diagram, the air bleed is heated by the incinerator, and the heat is then fed to a sector or segment of the rotating wheel to regenerate the adsorbent. This sector or segment is isolated by seals which allow the VOC to be recaptured and sent to the incinerator at a higher concentration than was present in the input air flow. This allows the VOC to have a greater heating value per cubic foot and, therefore, less additional fuel is required to raise the temperature to a level where the destruction or recovery efficiency (DRE) of the incinerator is above 98 %. The VOC is incinerated to provide heat to the air bleed for regeneration of the adsorbent bed.

An alternative would be to regenerate at a lower temperature and condense the VOC. The temperature would have to be above the minimum temperature for regenerating the VOC with that adsorbent and the cost of refrigerated condensation would have to be included. This would use a “heat pump” to send the heat of condensation to the air bleed for desorbing the VOC. The fact that this uses only a tenth as much air flow reduces the cost of refrigeration. Both options are available.

It is important for safety that the maximum concentration remain below one-fourth of the LEL, so the concentration ratio should be controlled to assure this. The closer the higher concentration gets to one-fourth of the LEL, the less fuel must be added to supplement the heating value of the VOC. The limit of one-fourth of the LEL is imposed by Occupational Safety and Health Administration (OSHA) and the National Fire Prevention Association (NFPA) for fire and explosion safety.

As a result of using the rotary vapor concentrator, the incinerator can be much smaller, requiring only about 10% of the volume otherwise required to provide an equal residence time. The cost of an incinerator in the *OAQPS Control Cost Manual* is proportional to the air flow rate times the residence time raised to either the 0.25 or 0.55 power, depending upon the type of incinerator. Therefore, using the concentrator also produces savings in the cost of the incinerator.

Fluidized bed concentrators have also been developed which are analogous to the rotary vapor concentrator. It is claimed that these are capable of raising the VOC concentration in the air flow by as much as 10,000:1. However, since carbon is not an efficient adsorbent at such low concentrations of VOC, zeolite or polymers may have been used as adsorbents or mixed with the carbon to allow such low concentrations to be adsorbed. The use of such an adsorber might be related to odor reduction, in which such low concentrations would be normal. The operating cycle is otherwise very similar to the rotating wheel concentrator. However, the cycle is based

upon fluidized transfer of the adsorbent from the adsorption bed to the desorption region. It uses the rate of adsorbent transport versus the rate of air flow to obtain the concentration ratio.

PRESSURE SWING ADSORBER

Figure 8 shows a schematic diagram of a pressure swing adsorption system. This is used for separation of gases or vapors from air based upon their adsorption isotherms being a function of total pressure, as well as vapor pressure, and temperature. It is also used to separate pollutants from flue gases.

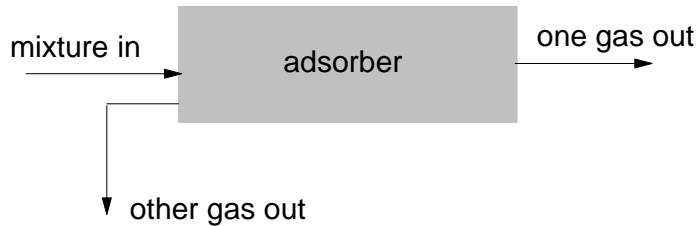


Figure 8. Pressure Swing Adsorption

The mixture of gases or vapors is admitted to pressurize the adsorber, which contains the adsorbent. Some gases are adsorbed more quickly than others, and the cycling frequency is used to separate these. In other cases, one gas or vapor is adsorbed preferentially and the cycling frequency is less important. After admitting the gas mixture, the gas that is not adsorbed as strongly is vented, which brings the pressure to a lower level. When this venting is stopped, the pressure is further reduced to desorb the other gas or vapor. This has been used to separate oxygen from air, carbon dioxide from air, carbon dioxide from flue gas, sulfur dioxide from flue gas, and gasoline vapors from tanks venting to the atmosphere. It is effective when the preferentially adsorbed gas or vapor has a relatively large concentration.

This is not usually considered as a control technology. The vapors have to be at concentrations of tens of thousands of parts per million, rather than the hundreds or thousands of parts per million which are usually controlled as emissions. However, they are used in control of vapors from vents on VOC storage tanks (such as gasoline).

ARE ADSORPTION SYSTEM DESIGN TOOLS AVAILABLE?

EPA has design equations for the thermal swing carbon adsorber in the *OAQPS Control Cost Manual*. These equations are used in the *Air Compliance Advisor* (ACA) and the *CO\$T-AIR* spreadsheet software (See References). The design equations for polymer and zeolite adsorbers and other adsorption systems have not yet been determined by EPA, but should be analogous when the differences have been accounted for. These differences have to do with weight of adsorbent, superficial air flow rate, cost of a vessel which must withstand evacuation, etc.

The designers of an adsorption system really earn their fee. They must choose the type of system to be compatible with the VOC and the purpose. They must choose (or help choose) the adsorbent, the size and number of beds, the construction of the container for each bed, the regeneration method, the time that the adsorber should be used before regeneration (determined by air flow and the concentration of VOC), how many beds should be used in parallel, the choice of boiler or vacuum pump, the instrumentation and controls that will operate these in the proper sequence at the proper time, and the location and sequencing of pipes and valving for the operation. Then they must execute a design in which all of these things work together. They must assure that the adsorber does not experience breakthrough in too short a time. They must have the unit meet the customer's specifications, and they must keep an eye on the costs, and assure the costs are not excessive.

As a result, they must be familiar with the system they are designing. That is the rub, for each designer will choose the system that they are most familiar with, unless it is absolutely ruled out by the customer. The system that all designers are familiar with is the thermal swing carbon adsorber system, for it has been used for several decades. They are often not familiar with the newer systems, regeneration techniques, or adsorbents. The newer systems, regeneration techniques, and adsorbents have distinct advantages over the older ones.

WHAT CONTROL EFFICIENCY SHOULD YOU EXPECT TO GET?

You should expect a well designed adsorber system to achieve 95% - 98% control efficiency at input concentrations between 500 and 2000 ppm in air. This is independent of follow-up systems such as an incinerator or a condenser. Therefore, the control efficiency of a combined adsorber and incinerator might be:

$$\text{adsorber efficiency} \times \text{incinerator efficiency} = 95\% \times 98\% = 93.1\%$$

while the efficiency of a combined adsorber and condenser might be:

$$\text{adsorber efficiency} \times \text{condenser efficiency} = 95\% \times 99\% = 94.05\%$$

The actual control efficiency of both the adsorber and the follow-on device will be involved. Neither the efficiency of the adsorber nor the efficiency of the follow-on device is more dominant,

but whichever one that has the lower efficiency will cause more loss in the total efficiency.

WHAT TYPE OF SOURCES CAN USE ADSORPTION TECHNOLOGY?

VOC and organic hazardous air pollutant emissions can be controlled, recovered, recycled, or concentrated for additional treatment by adsorption technology. This includes emissions from: dry cleaning, degreasing, paint spraying, solvent extracting, metal foil coating, paper coating, plastic film coating, printing, pharmaceuticals, rubber, linoleum, and transparent wrapping. Any process that generates VOC emissions at low concentrations (as low as 20 ppm) at relative high air flows (greater than 5,000 acfm) should consider adsorption technology to concentrate VOC in the emission stream prior to final treatment and either recycling or destruction.

HOW MUCH DO ADSORBERS COST?

Procedures, data, and equations for sizing and estimating the capital and annual costs of thermal swing (“regenerative”) carbon adsorption systems are given in the *OAQPS Control Cost Manual* (5th edition, February 1996). For the users’ convenience, these *OAQPS Control Cost Manual* equations have been incorporated into the *CO\$T-AIR* control cost spreadsheets and the *Air Compliance Advisor* program, all of which can be downloaded from the CATC Web page. We must emphasize, however, that these equations provide “study” (+/- 30% accuracy) cost estimates for only those adsorbers that use activated carbon. Cost-estimating procedures for polymer or zeolite-based adsorption systems have yet to be developed by EPA. Those interested in the latter should contact one or more vendors of those systems. (See extensive vendor list at the end of this bulletin.)

Carbon adsorber costs depend on a variety of facility, regulatory, sizing, and cost parameters. For that reason, no meaningful cost rules-of-thumb can be developed. Facility parameters include, first of all, the exhaust gas and pollutant characteristics--volumetric flow rate, temperature, pressure, VOC composition, VOC loading, and moisture and particulate contents. Another important facility parameter is its status, *i.e.*, new or existing. At an existing facility, the cost of installing the adsorber equipment typically will be higher. The difference between this higher installation cost and the cost of installing the same control system at a new facility is termed the “retrofit penalty”.

Depending on how the regulation is written, the most pertinent regulatory parameter is either the mandated VOC outlet concentration or the corresponding adsorber control efficiency required to meet it. Sizing parameters include the material of construction (304 stainless steel is typical for carbon adsorbers), amount of insulation, pressure drop, adsorbent working capacity, and whether the system is factory-assembled (“packaged”) or built on site (“custom”).

One of the most important design parameters is the adsorption time. This time is often selected to be compatible with production schedules. For example, an adsorber controlling a printing operation that runs in eight-hour shift increments might have an eight-hour adsorption time. At

the end of each shift, the adsorber bed(s) would be regenerated in time to be put back on line before the next shift begins. Clearly, as the adsorption time increases, so does the amount of adsorbent required and, hence, the size, number, and cost of the adsorber vessels. But while shorter adsorption times result in smaller adsorber systems and lower capital costs, higher annual costs are required because the adsorbent must be regenerated more frequently. These primarily consist of increases in the steam requirement (for bed regeneration) and electricity demand (for the bed drying/cooling fan). With steam regeneration the user has the option of either generating steam on-site via an existing boiler or purchasing a new boiler dedicated to that purpose.

Alternatively, the user may choose to purchase the steam from an outside source.

The above decisions and selections are within the user's purview. However, the user will not have to be concerned with such details as sizing the steam lines, selecting the bed drying/cooling fan, designing the adsorber vessels, etc. Those kinds of specifications are determined by the adsorber vendor whose application experience and knowledge of the adsorption process is much more extensive.

The cost and cost-related parameters, such as the annual operating hours, also heavily influence the "bottom line". These include prices for carbon, electricity, steam, operating and maintenance labor, and replacement adsorbent (including the replacement labor cost), as well as the interest rate and the useful lives of the adsorbent and the rest of the control system. One of the most critical cost parameters is the value assigned to the recovered VOC. As the example below illustrates, if the quantity of recovered VOC is large enough, its value can offset the annual costs, resulting in a net annual credit. Obviously, this value must be chosen carefully, keeping in mind both the current market price of the VOC and the purity of the recovered organics. The greater the purity, the higher the value. (For more information on these and other parameters, refer to Chapter 4 ("Carbon Adsorbers") of the *OAQPS Control Cost Manual*.)

Consider the following hypothetical illustration. Four existing printing operations emit toluene (an ink solvent) in quantities large enough to attract the attention of a state air pollution control agency. The agency's regulations for these printing operations require that 98% of the toluene be removed before the exhaust may be vented to the atmosphere. The smallest of these operations emits 50 lb/hour of toluene at a flow rate of 5,000 actual cubic feet/minute (acf m), while the largest emits 1,250 lb/hour at a 50,000 acfm flow rate. The other two emit 250 lb/hour each at 5,000 and 50,000 acfm, respectively. What would be the capital and total annual costs (TAC) of steam regeneration carbon adsorber systems installed to control the toluene from these operations?

The Table 1 lists these costs for each of the four adsorber systems. Computed via the *CO\$T-AIR* carbon adsorbers spreadsheet, these costs reflect **second quarter 1998** prices for equipment, carbon, utilities, labor, and toluene. Price sources consulted included the Department of Energy's *Monthly Energy Review* (electricity and distillate oil for steam production), the Bureau of Labor Statistics (printing and publishing labor), and the *Chemical Marketing Reporter* (toluene). (**Note:** All costs have been rounded to two significant figures.)

As we might expect, the capital costs increase with both increasing gas flow rate and toluene emission rate. Larger flow rates require larger and more costly adsorber vessels, decanters, condensers, and other equipment. By the same token, as the emission rate increases, more carbon must be provided for adsorption. Note that the unit capital cost ranges from \$22/acfm to \$87/acfm--a factor of four ratio. Such a wide range discourages the use of such rules of thumb for capital cost estimating.

Gas Flow Rate (acfm)	Toluene Emitted (lb/hr)	Capital Cost		Total Annual Cost (Credit)	
		1,000 \$	\$/acf m	1,000 \$/yr	\$/million acf
5,000	50	240	48	43	18
	250	430	87	(19)	(8.0)
50,000	250	1,100	22	110	4.6
	1,250	1,700	33	(280)	(12)

Table 1. Cost of Thermal Swing (“regenerative”) Carbon Adsorption Systems

Other important inputs to these costs include:

- * Operating hours/year: 8,000
- * Adsorption and desorption times: 8 and 4 hours, respectively.
- * Inlet gas temperature: 77 F.
- * Annual interest rate: 7%
- * Equipment lives (years): 10 (adsorber system); 5 (carbon)

The total annual cost (TAC) does not vary smoothly, however. Note that, for the 5,000 acfm systems, increasing the emission rate from 50 to 250 lb/hour decreases the TAC from \$43,000/year to a net credit of \$19,000/year. The annual costs for the 50,000 acfm systems behave similarly. Clearly, the toluene recovery credit heavily influences the TAC. This credit, in turn, depends on three parameters: the inlet emission rate, the control efficiency, and the value assigned to the recovered organic. The first two parameters will be essentially constant for a given emission source and control system. But, as discussed above, the expected recovery value can vary significantly according to market conditions and, for that reason, it must be selected carefully. Finally, the unit TAC ranges widely, from a credit of \$12/million acfm treated to a cost of \$18/million acfm.

As we have shown, both the capital and total annual costs for these hypothetical systems cover a broad range. And remember that these costs vary so widely for adsorbers removing the same VOC (toluene) emitted from the same type of source (printing operation) based upon identical

input parameters (air flow rate and toluene emission rate excepted). Consider that the adsorption of other VOC's (and VOC mixtures) could require much more or less carbon, that other sources could require much shorter or longer adsorption/desorption times, and that the input parameters could be vastly different under other control scenarios. Thus, the only conclusion we can safely draw about carbon adsorber costs--or, for that matter, the costs of *any* type of control system--is *no* conclusion. You must get quotes from vendors, consultants, or designers.

For rotary vapor concentrators, zeolite is frequently used (either with or without other adsorbents) as the adsorbent in vapor concentrators because it is more effective in adsorbing lower concentrations of VOC. The cost of such a system depends upon air flow and VOC concentration, and runs from about \$1000 to \$1500 per ton of VOC destroyed at 100 ppm, to \$3,250 per ton of VOC destroyed at 20 ppm, according to Munters ZEOL.

DECISIONS, DECISIONS...

Does your process have VOC emissions? Can you smell that your process is operating? If so, your process probably emits a VOC, and the emissions of the VOC probably should be controlled. Do emissions exceed 10 tons per year (55 pounds per day)? Do the emissions exceed your operating permit? Any "yes" answer means that you probably are emitting a VOC that is in need of control. Check with your state or local agency that issues operating permits if you are in doubt. VOCs often (but not always) have between 2 and 16 carbon atoms. VOCs also react in ultraviolet light (sunlight) with NO to multiply the NO₂ which creates ozone.

If you are not sure whether an emission from your plant is a VOC, call EPA's Clean Air Technology Center (CATC) at 919-541-0800, or contact the CATC by FAX at 919-541-0242, or by e-mail at catcmail@epamail.epa.gov and you will be referred to someone who can help you determine this. We also have a CATC Web page at www.epa.gov/ttn/catc if you prefer to contact us by that route.

If your process emits a VOC in any amount larger than 20 pounds per day, then you should look into the topic of controlling emissions. We have seen several advertisements on the Internet at URL's (Internet addresses) for adsorber system designers and manufacturers. You can also use a search algorithm, and commercial advertisements usually come first in their output.

When you have to control emissions of VOC, you have to make several decisions:

1. Will the VOC be destroyed or recovered? What re-use value will it have? This will affect the design of the system, and the economics of operating it. Perhaps you will want all options investigated.
2. If the VOC are to be recovered, how pure does it have to be? How much cost can be avoided by not buying VOC with the purity that you require? If it must be very pure, you must decide whether you are going to distill the VOC after recovery, or how that can be achieved.

3. If purity is either not needed or not possible, and the VOC is not water soluble, you might use a condenser with a skimmer to separate the condensed moisture or steam from the VOC.
4. You must decide whether you will use carbon, zeolite, or polymeric adsorbents. Each has its advantages, each has its disadvantages. You must make this preliminary decision with expert consultation before hiring a designer, because designers will design the kind of system that they are most familiar with. There are many designers for systems having carbon regenerated by steam because this system has been around for decades, but you will have fewer designers and consultants available for newer systems and adsorbents.

5. There are several firms that offer rotary or fluidized bed concentrators. Some of these are:
 (Note: Naming of these sources does not imply an endorsement, and this list is known to be abbreviated and incomplete.)

ABB Paint Finishing	1400 Stephenson Hwy.	Troy, MI 48099
Durr Environmental, Inc.	40600 Plymouth Rd.	Plymouth, MI 48170
Engelhard	101 Wood Ave.	Iselin, NJ 08830-0770
JWP AMCEC	2625 Butterfield Rd.	Oak Brook, IL 60521
Met-Pro Corp.	160 Cassel Road	Harleyville, PA 19438
Munters ZEOL	79 Monroe St	P.O.Box 600 Amesbury, MA 01913-0600

6. Some other sources for adsorber design and/or construction are: (see Note above)

AMCEC Corp.	2525 Cabot Dr.	Suite 205	Lisle, IL 60532
ACR Activated Carbon Resources Inc.			Westport, CT
American Air Filter	P.O.Box 35690		Louisville, KY 40232-5690
American Environmental Int'l	5 Revere Dr	Suite 200	Northbrook, IL 60062-9998
Aquest Corp.			Somers, NJ
Atochem Inc. / CECA Division	266 Harristown Rd.		Glen Rock, NJ 07452
Barneby & Sutcliffe	P.O. Box 2526		Columbus, OH 43216
Baron-Blakeslee Inc.	2001 N. Janice Ave.		Melrose Park, IL 60160
COH Corp.	2000 Eastern Pkwy		Brooklyn, NY 11233
Calgon Carbon Corp.	P.O.Box 717		Pittsburgh, PA 15230-0717
Carbtrol Corp.	39 Riverside Dr.		Westport, CT 06880
DR Technology	Hidden Pines Drive		Clarksburg, NJ 08510
Dedert Corp.	2000 Governors Dr.		Olympia Fields, IL 60461-1074
Ducon Environmental Syystems Co.	110 BiCounty Rd.		Farmingdale, NY 11735-3923
Envirotrol Inc.	432 Green St	P.O.Box 61	Sewickley, PA 15143
Filcorp Industries			Milton, VT
FMG	P.O.Box 3043		Union Gap, WA 98903
Green and Green Associates			Lexington, MA
Hydrogroup Inc.	1011 Hwy 22		Bridgewater, NJ 08807
HCT Corp.	325 Lennon Lane	Suite 200	Walnut Creek, CA 94598

HydroQuip, Inc.	63 N Washington St.	N. Attleboro, MA 02761
Independent Equipment Corp.	Rte. 202N	Three Bridges, NJ 08887
KX Industries		Orange, CT
Kensington Corp.		Madison, CT
Nuclear Consulting Services Inc. (NUCON)	P.O.Box 29151, Columbus, OH 43229-1022	
Penney Engineering Inc.		Mansfield, MA
Peroxidation Systems Inc.	4400 E. Broadway, Suite 602	Tucson, AZ 85711-3558
Prime Carbon		Bow, NH
R H Reimer Associates		Needham, MA
Remedial Systems Inc.	56 Leonard St.	Foxboro, MA 02035
Service Tech Inc.		Swansea, MA
Tetrasolv		Plymouth, MA
Tigg Corp.	800 Old Pond Rd.	Bridgeville, PA 15017-3415
Unisorb Corp.	1310 Genoa St.	S. Houston, TX 77587
VARA International	1201 19th Place	Vero Beach, FL 32960
Waste Min Inc.		Groton, MA
Westgates Carbon Inc.	2130 Leo Ave.	Los Angeles, CA 90040-1634
Westport Environmental Systems	251 Forge Rd.	Westport, MA 02790-0217
Wintek Corp.	RR3 Box 337 Lime Rock Lane	Califon, NJ 07830
Zimpro-Passavant Inc.	301 Military Rd.	Rothschild, WI 5474

SOME REFERENCES: (some with Internet URL for the web page)

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www.activated-carbon.com/enviro.html

Envirosense
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es.epa.gov/program/regional/state/wi/actcarbo.html

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www.activated-carbon.com/probsol1.html

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PADREO Vapor Treatment Process
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Gas-Surface Dynamics
www.ssci.liv.ac.uk/~darling/dynamica/index.html
www.ssci.liv.ac.uk/~darling/dynamica/history/ancient.html

The Desorption Process
alpha.qmw.ac.uk/~ugca000/surfaces/scc/scat2_5.htm

PE Curves & Energetics of Adsorption
alpha.qmw.ac.uk/~ugca000/srfaces/scc/scat2_4.htm

Adsorption Kinetics - The Rate of Adsorption
alpha.qmw.ac.uk/~ugca000/srfaces/scc/scat2_3.htm

How do Molecules Bond to Surfaces?
alpha.qmw.ac.uk/~ugca000/srfaces/scc/scat2_2.htm

CO\$T-AIR Spreadsheets
www.epa.gov/ttn/catc

Air Compliance Advisor
www.epa.gov/ttn/catc

Institute of Clean Air Companies
www.icac.com

TECHNICAL REPORT DATA <i>(Please read Instructions on the reverse before completing)</i>		
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15. SUPPLEMENTARY NOTES For more information call the CATC Information Line at (919) 541-0800 or access the CATC Web Page at www.epa.gov/ttn/catc		
16. ABSTRACT <p>The purpose of this document is to educate people as to what an adsorption system is, how it operates, and how to choose between the different systems. Adsorption systems are used widely to control Volatile Organic Compounds (VOC) emissions. The familiarity with these systems is needed to make an informed selection of both the adsorbent and the system that uses it.</p>		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
carbon, zeolite, polymeric, thermal swing, vacuum regeneration, pressure swing, vapor concentrator, internal area, adsorption area, adsorption isotherm, mass transfer zone, steam, vacuum, incineration	air pollution control, volatile organic compounds carbon adsorbers zeolite adsorbers polymeric adsorbers vapor concentrators incinerators	
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