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Engineering and Design
ADSORPTION DESIGN GUIDE

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CHAPTER 1
INTRODUCTION

1-1. Purpose. This Design Guide provides practical guidance for the design of liquid and vapor phase devices for the adsorption of organic chemicals. The adsorptive media addressed include granular activated carbon (GAC) and other alternative adsorption carbon media, such as powdered activated carbon (PAC) and non-carbon adsorbents.

1-2. Scope. This document addresses various adsorption media types, applicability, use of various adsorption process technologies, equipment and ancillary component design, availability, advantages, disadvantages, regeneration methods, costs, and safety considerations. The equipment can be installed alone or as part of an overall treatment train, based on site-specific factors.

1-3. Background.

a. Carbon, in various forms, has been used to adsorb contaminants for some time. The first documented use of carbon as an adsorbent was for medical purposes, in the form of wood char in 1550 B.C. The first documented use for water treatment was in 200 B.C. “to remove disagreeable tastes.” In 1785 experimental chemists learned that carbon could accumulate unwanted contaminants from water. Carbon in the activated form was first used as a filter medium in the late 1800s. The understanding of carbon adsorption progressed in the late 19th and early 20th centuries, when vapor phase organic carbon was developed and given its first widespread use as a defense against gas warfare during WWI.

b. The first GAC filters used for water treatment were installed in Europe in 1929. The first GAC filters for water treatment in the United States were installed in Bay City, Michigan, in 1930. In the 1940s, GAC was found to be an efficient purification and separation technology for the synthetic chemical industry. By the late 1960s and early 1970s, GAC was found to be very effective at removing a broad spectrum of synthetic chemicals from water and gases (i.e., from the vapor phase).

1-4. Abbreviations and Acronyms.

ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
AWWA	American Water Works Association
BDST	bed depth service time
BET	the Brunauer, Emmett, and Teller equation
BOD	biological oxygen demand
BTEX	benzene, toluene, ethylbenzene, xylene
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFCs	chlorofluorocarbons

CFR	Code of Federal Regulations
COC	contaminant of concern
COD	chemical oxygen demand
COH	COH Corporation, Inc.
CORECO	College Research Corporation
CRSI	Continental Remediation Systems, Inc.
DB	divinyl benzene
DG	design guide
EBCT	empty bed contact time
EPA	United States Environmental Protection Agency
GAC	granular activated carbon
HPMC	high pressure minicolumn
HTRW	hazardous, toxic, and radiological waste
MCACES	Micro Computer Aided Cost Estimating System
MEK	methyl ethyl ketone
MIBK	methyl isobutyl ketone
MSDS	material safety data sheet
MTZ	mass transfer zone
NFPA	National Fire Protection Association
NRMRL	National Risk Management Research Laboratory
O&M	operations and maintenance
OSHA	Occupational Safety and Health Administration
PAC	powdered activated carbon
PACS	Professional Analytical and Consulting Services, Inc.
PCE	perchloroethene
pH	inverse log of hydrogen ion concentration
ppm	parts per million
PSD	particle size distribution
RA	remedial action
RACER	Remedial Action Cost Engineering and RequirementsSystem
RCRA	Resource Conservation Recovery Act
RH	relative humidity
RREL	Risk Reduction Engineering Lab
SVE	soil vapor extraction
SVOC	semivolatile organic compounds
TCE	trichloroethene
TCLP	toxic characteristics leaching procedure
TSDF	treatment storage or disposal facility
USACE	United States Army Corps of Engineers
USAF	United States Air Force
VOC	volatile organic compounds
WBS	work breakdown structure

CHAPTER 2
PRINCIPLES OF OPERATION AND THEORY

2-1. Types of Adsorption Media.

a. Activated Carbon. Activated carbon can be manufactured from carbonaceous material, including coal (bituminous, subbituminous, and lignite), peat, wood, or nutshells (i.e., coconut). The manufacturing process consists of two phases, carbonization and activation. The carbonization process includes drying and then heating to separate by-products, including tars and other hydrocarbons, from the raw material, as well as to drive off any gases generated. The carbonization process is completed by heating the material at 400–600°C in an oxygen-deficient atmosphere that cannot support combustion.

(1) *General.* The carbonized particles are "activated" by exposing them to an activating agent, such as steam at high temperature. The steam burns off the decomposition products from the carbonization phase to develop a porous, three-dimensional graphite lattice structure. The size of the pores developed during activation is a function of the time that they are exposed to the steam. Longer exposure times result in larger pore sizes. The most popular aqueous phase carbons are bituminous based because of their hardness, abrasion resistance, pore size distribution, and low cost, but their effectiveness needs to be tested in each application to determine the optimal product. The three-dimensional graphite lattice pore structure of a typical activated carbon particle is shown in Figure 2-1.

(2) *Powdered Activated Carbon (PAC).* PAC is made up of crushed or ground carbon particles, 95–100% of which will pass through a designated mesh sieve or sieves. The American Water Works Association Standard (AWWA, 1997) defines GAC as being retained on a 50-mesh sieve (0.297 mm) and PAC material as finer material, while American Society for Testing and Materials (ASTM D5158) classifies particle sizes corresponding to an 80-mesh sieve (0.177 mm) and smaller as PAC. PAC is not commonly used in a dedicated vessel, owing to the high headloss that would occur. PAC is generally added directly to other process units, such as raw water intakes, rapid mix basins, clarifiers, and gravity filters.

(3) *Granular Activated Carbon (GAC).* GAC can be either in the granular form or extruded. GAC is designated by sizes such as 8 × 20, 20 × 40, or 8 × 30 for liquid phase applications and 4 × 6, 4 × 8 or 4 × 10 for vapor phase applications. A 20 × 40 carbon is made of particles that will pass through a U.S. Standard Mesh Size No. 20 sieve (0.84 mm) (generally specified as >85% passing) but be retained on a U.S. Standard Mesh Size No. 40 sieve (0.42 mm) (generally specified as >95% retained). AWWA (1992) B604 uses the 50-mesh sieve (0.297 mm) as the minimum GAC size. The most popular aqueous phase carbons are the 12 × 40 and 8 × 30 sizes because they have a good balance of size, surface area, and headloss characteristics.

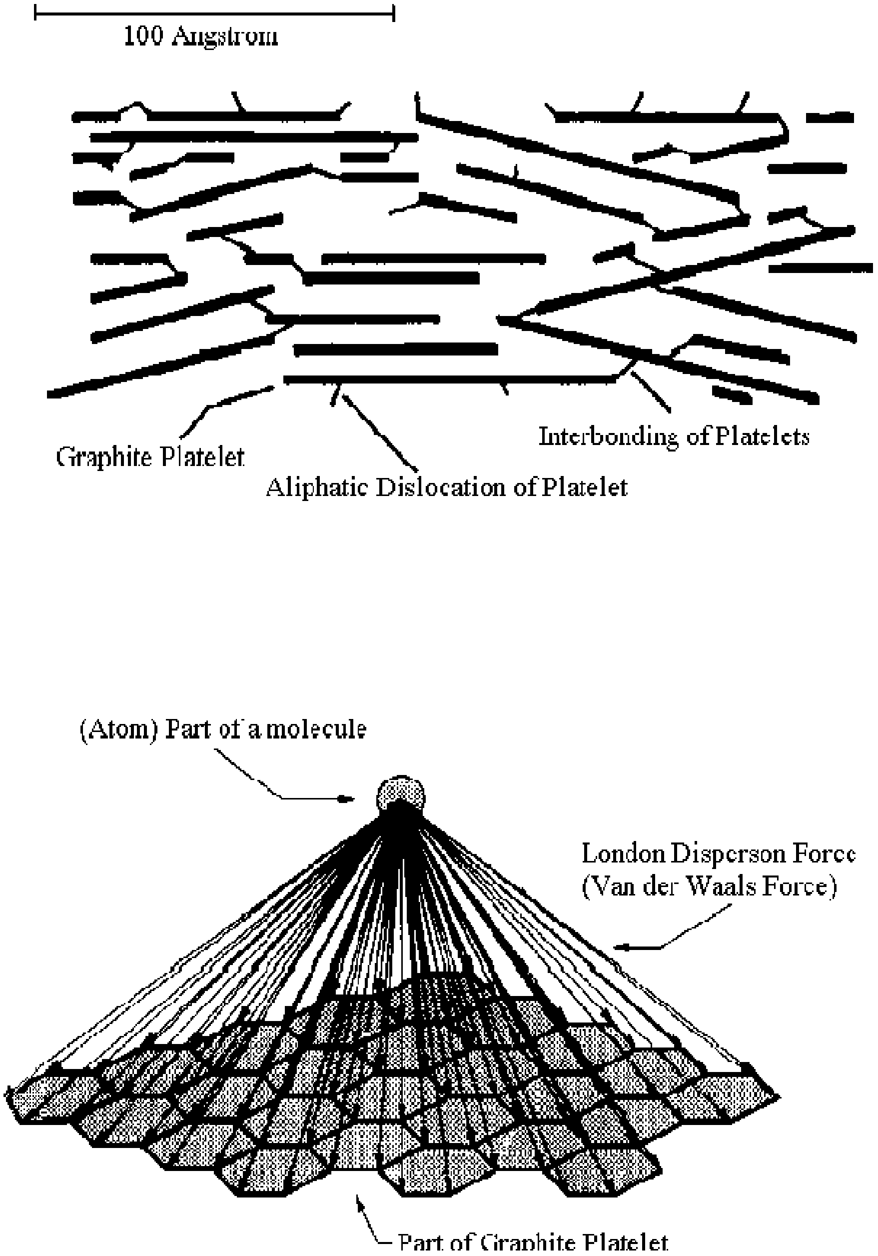


Figure 2-1. Activated carbon structure.

The 12 × 40 carbon is normally recommended for drinking water applications where the water contains a low suspended solid content. The 8 × 30 size is the most commonly used for most applications (Appendix D, Carbonair).

b. Non-carbon. Many alternative adsorption media are in general service today for removing organic constituents from vapor and liquid streams. Organically modified clays, polymeric adsorbents, and zeolite molecular sieves are the primary non-activated-carbon adsorbents currently used in hazardous waste treatment (Black & Veatch, 1998). See paragraph 3-3 for additional information.

2-2. Properties of Granular Activated Carbon. Granular activated carbon properties are defined in ASTM D2652. In addition to these properties, the following paragraphs provide additional information.

a. Particle Size Distribution. A standard test procedure for particle size distribution (PSD) is defined in ASTM D2862. Information derived from this test is used to specify the carbon particle size uniformity. Two particle size criteria are the effective size, which corresponds to the sieve size through which 10% of the material will pass, and the uniformity coefficient, which is the ratio of the sieve size that will just pass 60% of the material to the effective size. Generally, the rate of adsorption will increase as the particle size decreases, as the process step of diffusion to the carbon surface should be enhanced by the smaller particles. Note that another critical aspect of rate of adsorption is the pore size distribution, and development of “transport pores” within the particle that allow effective migration of contaminants to the point of adsorption. However, particle size may not be that important in all cases, as the porous nature of the carbon particles results in large surface areas in all sizes of carbon particles. Headloss through a carbon bed increases as the carbon particle size decreases and as the uniformity coefficient increases.

b. Surface Area. Surface area is the carbon particle area available for adsorption. In general, the larger the surface area is, the greater is the adsorption capacity; however, this surface area needs to be effective. And a high degree of the area needs to be in the “adsorption pore” region, as well as being accessible to the contaminant with an effective “transport pore” structure, for the capacity to be useful. This is measured by determining the amount of nitrogen adsorbed by the carbon and reported as square meters per gram (commonly between 500 and 2000 m^2/g). ASTM D 3037 identifies the procedure for determining the surface area using the nitrogen BET (Brunauer, Emmett, and Teller) method. Nitrogen is used because of its small size, which allows it to access the micropores within the carbon particle.

c. Pore Volume. The pore volume is a measure of the total pore volume within the carbon particles in cubic centimeters per gram (cm^3/g).

d. Iodine Number. The iodine number refers to the milligrams of a 0.02 normal iodine solution adsorbed during a standard test (ASTM D4607). The iodine number is a measure of the volume present in pores from 10 to 28 Å (10^{-10} m) in diameter. Carbons with a high percentage of pore sizes in this range would be suitable for adsorbing lower molecular weight substances from water. Carbons with a high iodine number are the most suitable for use as vapor phase carbons, as water molecules tend to effectively block off and isolate pore sizes less than 28 Å. This restricts mass transfer in the micropores, resulting in poor carbon utilization and excessive cost. Virgin liquid phase carbons generally have an iodine number of 1000. Reactivated liquid phase carbon has an iodine number between 800 and 900.

e. Molasses Number. The molasses number refers to the milligrams of molasses adsorbed during the standard test. The molasses number is a measure of the volume in pores greater than 28 Å in diameter. A carbon with a high percentage of this size pore is suitable for adsorbing high molecular weight substances such as color bodies or other colloids. Carbons with a high molasses number are generally used for decolorizing process liquids. As such, the molasses number specification is generally only used in color removal applications, and is not a valid specification requirement for water treatment. This is a proprietary test, and should not be used in specifying GAC.

f. Abrasion Number. The abrasion number measures the ability of carbon to withstand handling and slurry transfer. Two different tests are used, based on the type of carbon material. A Ro Tap abrasion test is used for bituminous-coal-based GAC, and a stirring abrasion test is used for the softer, lignite-coal-based GAC. The abrasion number is the ratio of the final average (mean) particle diameter to the original mean particle diameter (determined by sieve analyses) times 100. The desired average particle size of the GAC retained should be greater than or equal to 70%. This is of limited value because measuring techniques are not reproducible. Procedures are given in AWWA (1997) B604.

g. Apparent Density. The apparent density is equal to the mass (weight) of a quantity of carbon divided by the volume it occupies (including pore volume and interparticle voids, adjusted for the moisture content). Generally, bituminous-based GAC has a density between 28–40 pounds per cubic foot (pcf), lignite-based GAC has a density of approximately 22–26 pcf, and wood-based GAC has a density of 15–19 pcf (AWWA, 1997).

h. Bulk Density. The bulk density is the unit weight of the carbon within the adsorber. Generally, the bulk density of liquid phase applications is 80–95% of the apparent density and, for vapor phase applications, it is 80–100% of the apparent density. Apparent density is used to determine the volumetric carbon usage rate since the carbon usage rate is typically stated in

$$\frac{\text{mg}}{\text{g}}\left(\frac{\text{mg contaminant removed}}{\text{gram of carbon}}\right) .$$

2-3. Isotherms. An isotherm is the relationship that shows the distribution of adsorbate (material adsorbed) between the adsorbed phase (that adsorbed on the surface of the adsorbent) and the solution phase at equilibrium. Media manufacturers are a source of adsorption isotherms. Many manufacturers are continuing to conduct research on their products and can often supply chemical-specific adsorption isotherms for their products. However, many of these company isotherms are batch isotherms used as proof of concept data (i.e., to show that a particular product can adsorb a particular chemical). Actual working adsorption capacity may be much less than equilibrium batch capacity because other constituents may be present in water, such as total organic carbon, and because of the non-instantaneous adsorption kinetics. So, you should carefully check manufacturer's data and use them with caution when designing an adsorption system. The designer should also ask the manufacturer for contacts at installations using the media, so that scale-up factors and common operational problems can be investigated.

a. GAC Isotherms. There are three generally recognized mathematical relationships that were developed to describe the equilibrium distribution of a solute between the dissolved (liquid) and adsorbed (solid) phases. These relationships help interpret the adsorption data obtained during constant temperature tests, referred to as adsorption isotherms.

- The Langmuir isotherm equation assumes that fixed individual sites exist on the surface of the adsorbent, each of these sites being capable of adsorbing one molecule, resulting in a layer one molecule thick over the entire carbon surface. The Langmuir model also assumes that all sites adsorb the adsorbate equally.

- The Brunauer, Emmett, and Teller (BET) equation also assumes the adsorbent surface is composed of fixed individual sites. However, the BET equation assumes that molecules can be adsorbed more than one layer thick on the surface of the adsorbent. The BET equation assumes that the energy required to adsorb the first particle layer is adequate to hold the monolayer in place.

- The Fruendlich isotherm equation assumes that the adsorbent has a heterogeneous surface composed of adsorption sites with different adsorption potentials. This equation assumes that each class of adsorption site adsorbs molecules, as in the Langmuir Equation. The Fruendlich Isotherm Equation is the most widely used and will be discussed further.

$$\frac{x}{m} = KC^{\frac{1}{n}}$$

where

x = amount of solute adsorbed (μg, mg, or g)

m = mass of adsorbent (mg or g)

C = concentration of solute remaining in solution after adsorption is complete (at equilibrium) (mg/L)

K, n = constants that must be determined for each solute, carbon type, and temperature.

(1) An example of an isotherm for TCE is presented in Figure 2-2. *K* and 1/*n* or *n* values for multiple contaminant mixtures should be determined by laboratory tests.

(2) Single component isotherms may be used for an order-of-magnitude carbon usage estimate or for determining the feasibility of GAC adsorption using suppliers' literature or previously published literature (Dobbs and Cohen, 1980) for individual compounds. Another source of liquid phase isotherm data constants is the EPA Treatability Database maintained by the National Risk Management Research Laboratory (NRMRL), formerly known as the Risk Reduction Engineering Lab (RREL) (http://www.epa.gov/tdbnrmrl). Vapor phase isotherms are not readily available in the literature.

(3) Some general rules of thumb, uses, and caveats that are helpful in isotherm interpretation are as follows:

- A flat isotherm curve indicates a narrow Mass Transfer Zone (MTZ), meaning that the GAC generally adsorbs contaminants at a constant capacity over a relatively wide range of equilibrium concentrations. Given an adequate capacity, carbons exhibiting this type of isotherm will be very cost effective, and adsorption system design will be simplified owing to a shorter mass transfer zone (see Figure 2-2).
- A steep isotherm curve indicates a wide MTZ, with the adsorption capacity increasing as equilibrium concentration increases. Carbons exhibiting this type of isotherm curve tend to be more cost effective.
- A change in isotherm slope generally occurs for wastes that contain several compounds with variable adsorption capacities. An inflection point occurs when one compound is preferentially adsorbed over another and desorption occurs, so that the preferentially adsorbed compound can utilize sites previously used by less adsorbable compounds (see Figure 2-3).

(4) Isotherms can be developed from data obtained in the laboratory and from existing data sources, such as the National Risk Management Research Laboratory (NRMRL) Treatability Database, texts, and suppliers' literature. A typical example of TCE isotherm data, which was obtained from the NRMRL database, is provided in Figure 2-2. A procedure for calculating an isotherm is included in Appendix C.

b. Polymeric, Clay, Zeolite Molecular Sieve Isotherms. Isotherms for these media are developed in the same way as for carbon media. However, most of the isotherm data for non-carbon adsorption media must be obtained from the manufacturer or from laboratory tests.

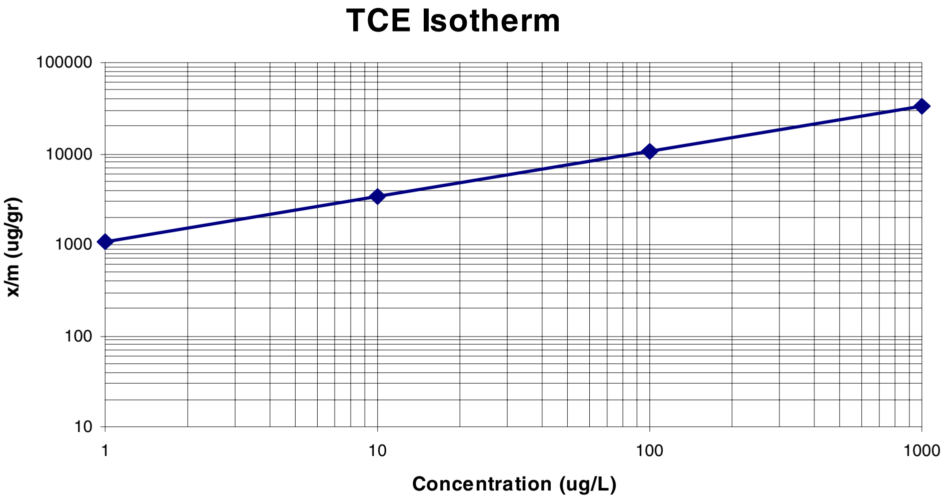
2-4. Isotherm Testing. Isotherms are discussed in Paragraph 2-3, and the process for developing an isotherm is addressed in Appendix C. Although the example in Appendix C is specifically developed for a liquid phase application, the vapor phase method is similar. The following paragraphs highlight the types of information that can be obtained from isotherm testing versus column testing. Isotherms are static, equilibrium tests for a given set of conditions. Ideally, isotherms should not be used for the final design of a liquid phase system. Procedures for laboratory development of an isotherm are presented in a variety of texts (Benefield, 1982) or as specified in ASTM D 3860.

a. Although not advisable for liquid phase applications, published adsorption isotherm data are often used to design vapor phase adsorption systems without bench and pilot testing. For the same contaminant, vapor phase carbon usually has a higher adsorptive capacity than liquid phase carbon, because less adsorptive sites will be taken up by water and humidity. At a 100% relative humidity, the vapor phase carbon's adsorptive capacity will approach the liquid phase carbon adsorptive capacity (Appendix D, Carbonair). However, you should remember that most published isotherm data represent only a single contaminant in a pure medium, and mixed contaminants may behave differently (see Tables 2-1 and 2-2).

b. One source of published isotherms is the *Adsorption Equilibrium Data Handbook* (Valenzuela and Meyers, 1989). This handbook contains many gas/liquid isotherms. While most of the isotherms are for activated carbon, there are some for carbon molecular sieves, silica gel, and zeolites. A source of information on the Fruendlich isotherm equation is the *Carbon Adsorption Isotherms for Toxic Organics* (Dobbs and Cohen, 1980). This particular source used only a 2-hour test period in lieu of the 24-hour period currently used by industry today. Liquid phase and vapor phase applications are different because the mass transfer characteristics of the two phases are different. The mass transfer kinetics of a contaminant from the vapor phase to the solid phase is nearly instantaneous, while the mass transfer kinetics from the bulk liquid phase to the solid phase is influenced by the presence of the solute, and may be the rate limiting step in some instances. There are four phases to the liquid phase adsorption process. The contaminant must first travel from the bulk liquid phase to the liquid film surrounding the carbon particle. Second, the contaminant must travel through the liquid film surrounding the carbon to the interstitial voids. Third, the contaminant must diffuse through the carbon voids in the carbon solid phase, and fourth, finally adsorb onto the carbon. A more comprehensive discussion of the kinetics of adsorption can be obtained from texts (Faust and Aly, 1987).

RREL Treatability Database Ver No. 4.0

TRICHLOROETHYLENE
CAS NO: 79-01-6
COMPOUND TYPE: HYDROCARBON, HALOGENATED
FORMULA: C_2HCl_3
CHEMICAL AND PHYSICAL PROPERTIES:
MOLECULAR WEIGHT: 131.39
MELTING POINT (C): -84.8
BOILING POINT (C): 86.7
VAPOR PRESSURE @ T (C), TORR: 77 @ 25
SOLUBILITY IN WATER @ T (C), MG/L: 1100 @ 25
LOG OCTANOL/WATER PARTITION COEFFICIENT: 2.53
HENRY'S LAW CONSTANT, ATM x M3 MOLE-1: 1.17 E-2 @ 25



ENVIRONMENTAL DATA

REFERENCE DATABASE
FREUNDLICH ISOTHERM DATA

ADSORBENT	MATRIX	K	1/N	Ce UNITS	X/M UNITS
FILTRASORB 400	C	3390	0.146	µg/L	µg/g
WESTVACO WV-G	C	3260	0.407	µg/L	µg/g
WESTVACO WV-W	C	1060	0.500	µg/L	µg/g
HYDRODARCO 3000	C	713	0.470	µg/L	µg/g
FILTRASORB 300	C	28	0.62	mg/L	mg/g
FILTRASORB 400	C	36.3	0.592	mg/L	mg/g
FILTRASORB 400	C	45	0.625	mg/L	mg/g
FILTRASORB 400	C	2	0.482	µg/L	µg/g

Figure 2-2. Trichloroethylene data.

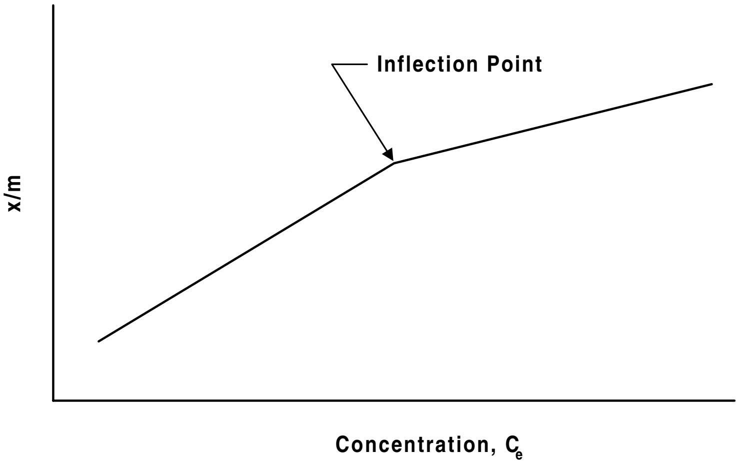


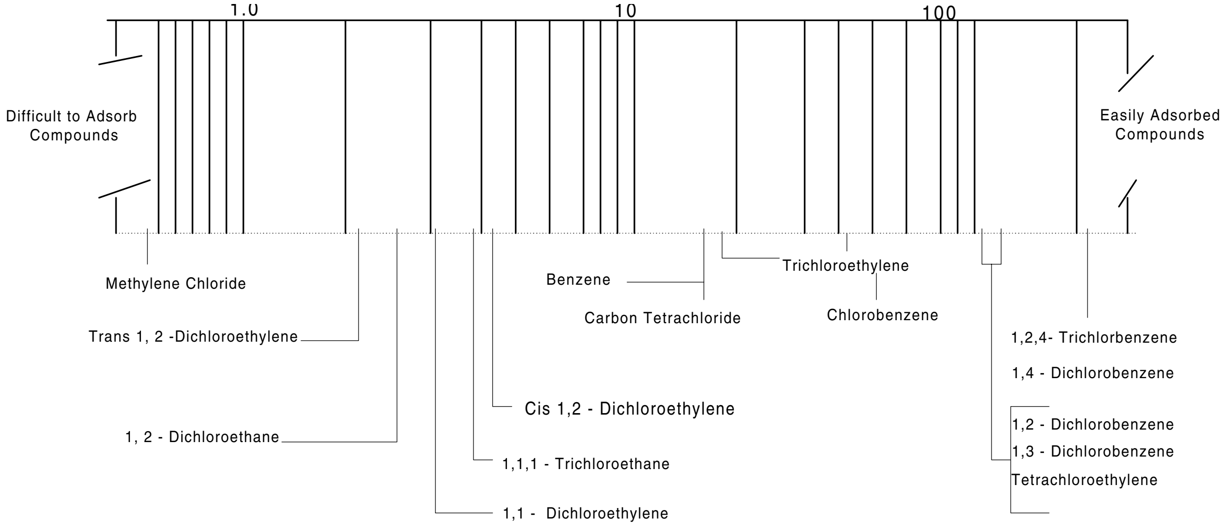
Figure 2-3. Variable capacity adsorption isotherm.

c. Liquid phase isotherms are useful screening tools for determining the following:

- If adsorption is a viable technology.
- The equilibrium capacity, or approximate capacity at breakthrough, so a preliminary estimate of carbon usage can be made.
- The relative difficulty to remove individual contaminants if single-constituent isotherms are used, and the identity of the initial breakthrough compound.
- Changes in equilibrium adsorption capacity relative to the concentration of contaminants in the waste stream, and the effects of changes in waste stream concentration.
- The maximum amount of contaminant that can be adsorbed by GAC at a given concentration.
- The relative efficiencies of different types of carbons to identify which should be used for dynamic testing.

d. Liquid phase column testing will provide such data as contact time, bed depth, pre-treatment requirements, carbon dosage, headloss characteristics, and breakthrough curves. Column testing will also identify how contaminants that are not of regulatory concern, such as iron or color containing compounds, will affect the efficiency of the treatment process.

Table 2-1
Freundlich adsorption isotherm constants for toxic organic chemicals (mean adsorption capacity [mg/g] at equilibrium concentration of 500 µg/L)



		Freundlich Parameters	
		K	l/n
	Benzene	1.0	1.6*
		16.6	0.4**
		49.3	0.6†
		29.5	0.4††
		14.2	0.4§
	Carbon Tetrachloride	11.1	0.8*
		28.5	0.8†
		38.1	0.7**
		25.8	0.7††
		14.2	0.7§
		14.8	0.4§§
	Chlorobenzene	91.0	1.0*
	1,2-dichlorobenzene		129.0
0.4*			
	1,3-dichlorobenzene		118.0
0.4*			
	1,4-dichlorobenzene		121.0
0.5*			
		226.0	0.4**
	1,2-dichloroethene	3.6	0.8*
		5.7	0.5§§
	cis-1,2-dichloroethylene	6.5	0.7†
		8.4	0.5§§

	Freundlich Parameters		
	K	l/n	
trans-1,2-dichloroethylene	3.1	0.5*	
1,1-dichloroethylene	4.9	0.5*	
Methylene chloride	1.3	1.2*	
	1.6	0.7***	
Tetrachloroethylene	50.8	0.6*	
	84.1	0.4§§	
	273.0	0.6***	
1,2,4-trichlorobenzene	157.0	0.3*	
1,1,1-trichloroethane	2.5	0.3*	
	9.4	0.5§§	
Trichloroethylene		28.0	0.6*
	26.2	0.5‡	
	28.2	0.4§§	
Vinyl chloride	Not Reported		

Freundlich equation:
x/m(mg/gm) = K C (mg/1/n)

* Filtrasorb ® 300
** Filtrasorb ® 400
*** Filtrasorb ® 400

§ Hydrodarco ® 1030
§§ Witcarb ® 950

† Norit
†† Nuchar ® WV-G
‡ Filtrasorb ® 300

Table 2-2
Freundlich adsorption Isotherm constants for toxic organic compounds† (Dobbs and Cohen 1980)

Compound	*K*(mg/g)(L/mg)$^{1/n}$	I/*n*
PCB	14,100	1.03
Bis(2-ethylhexyl phthalate	11,300	1.5
Heptachlor	9,320	0.92
Heptachlor epoxide	2,120	0.75
Butylbenzyl phthalate	1,520	1.26
Toxaphene	950	0.74
Endosulfan sulfate	686	0.81
Endrin	666	0.80
Fluoranthene	664	0.61
Aldrin	651	0.92
PCB-1232	630	0.73
∃ - Endosulfan	615	0.83
Dieldrin	606	0.51
Alachlor	479	0.26
Hexachlorobenzene	450	0.60
Pentachlorophenol	436	0.34
Anthracene	376	0.70
4 – Nitrobiphenyl	370	0.27
Fluorene	330	0.28
Styrene	327	0.48
DDT	322	0.50
2 – Acetylaminofluorene	318	0.12
∀ - BHC	303	0.43
Anethole	300	0.42
3,3 – Dichlorobenzidine	300	0.20
(- BHC (lindane)	285	0.43
2 – Chloronaphthalene	280	0.46
Phenylmercuric acetate	270	0.44
Carbofuran	266	0.41
1,2 – Dichlorobenzene	263	0.38
Hexachlorobutadiene	258	0.45
∆ - Nonylphenol	250	0.37
4-Dimethylaminoazobenzene	249	0.24
PCB – 1221	242	0.70
DDE	232	0.37
m-Xylene	230	0.75
Acridine yellow	230	0.12
Dibromochloropropane (DBCP)	224	0.51
Benzidine dihydrochloride	220	0.37
∃ - BHC	220	0.49
n-Butylphthalate	220	0.45
n-Nitrosodiphenylamine	220	0.37
Silvex	215	0.38
Phenanthrene	215	0.44
Dimethylphenylcarbinol	210	0.34
4 – Aminobiphenyl	200	0.26

Table 2 (continued)

Compound	K(mg/g)(L/mg)$^{1/n}$	I/*n*
∃ - Naphthol	200	0.26
Δ - Xylene	200	0.42
∀ - Endosulfan	194	0.50
Chlordane	190	0.33
Acenaphthene	190	0.36
4,4' Methylene-bis (2-chloroaniline)	190	0.64
Benzo[6]fluoranthene	181	0.57
Acridine orange	180	0.29
∀-Naphthol	180	0.32
Ethylbenzene	175	0.53
≅-Xylene	174	0.47
4,6-Dinitro-≅-cresol	169	0.27
∀-Naphthylamine	160	0.34
2,4-Dichlorophenol	157	0.15
1,2,4-Trichlorobenzene	157	0.31
2,4,6-Trichlorophenol	155	0.40
∃-Naphthylamine	150	0.30
2,4-Dinitrotoluene	146	0.31
2,6-Dinitrotoluene	145	0.32
4-Bromophenyl phenyl ether	144	0.68
Δ-Nitroaniline	140	0.27
1,1-Diphenylhydrazine	135	0.16
Naphthalene	132	0.42
Aldicarb	132	0.40
1-Chloro-2-nitrobenzene	130	0.46
p-Chlorometacresol	124	0.16
1,4-Dichlorobenzene	121	0.47
Benzothiazole	120	0.27
Diphenylamine	120	0.31
Guanine	120	0.40
1,3-Dichlorobenzene	118	0.45
Acenaphthylene	115	0.37
Methoxychlor	115	0.36
4-Chlorophenyl phenyl ether	111	0.26
Diethyl phthalate	110	0.27
Chlorobenzene	100	0.35
Toluene	100	0.45
2-Nitrophenol	99	0.34
Dimethyl phthalate	97	0.41
Hexachloroethane	97	0.38
2,4-Dimethylphenol	78	0.44
4-Nitrophenol	76	0.25
Acetophenone	74	0.44
1,2,3,4-Tetrahydronaphthalene	74	0.81
Adenine	71	0.38
Dibenzo[∀*h*]anthracene	69	0.75
Nitrobenzene	68	0.43
2,4-D	67	0.27

Table 2 (continued)

Compound	K(mg/g)(L/mg)$^{1/n}$	I/*n*
3,4-Benzofluoranthene	57	0.37
2-Chlorophenol	51	0.41
Tetrachloroethylene	51	0.56
≅-Anisidine	50	0.34
5-Bromouracil	44	0.47
Benzo[∀]pyrene	34	0.44
2,4-Dinitrophenol	33	0.61
Isophorone	32	0.39
Trichloroethylene	28	0.62
Thymine	27	0.51
5-Chlorouracil	25	0.58
N-Nitrosodi-*n*-propylamine	24	0.26
Bis(2-Chloroisopropyl)ether	24	0.57
1,2-Dibromoethene (EDB)	22	0.46
Phenol	21	0.54
Bromoform	20	0.52
1,2-Dichloropropane	19	0.59
1,2-*trans*-Dichloroethylene	14	0.45
cis-1,2-Dichloroethylene	12	0.59
Carbon tetrachloride	11	0.83
Bis(2-Chloroethyoxy)methane	11	0.65
Uracil	11	0.63
Benzo[*g,h,i*]perylene	11	0.37
1,1,2,2-Tetrachloroethane	11	0.37
1,2-Dichloropropene	8.2	0.46
Dichlorobromomethane	7.9	0.61
Cyclohezanone	6.2	0.75
1,1,2-Trichloroethane	5.8	0.60
Trichlorofluoromethane	5.6	0.24
5-Fluorouracil	5.5	1.0
1,1-Dichloroethylene	4.9	0.54
Dibromochloromethane	4.8	0.34
2-Chloroethyl vinyl ether	3.9	0.80
1,2-Dichloroethane	3.6	0.83
Chloroform	2.6	0.73
1,1,1-Trichloroethane	2.5	0.34
1,1-Dichloroethane	1.8	0.53
Acrylonitrile	1.4	0.51
Methylene chloride	1.3	1.16
Acrolein	1.2	0.65
Cytosine	1.1	1.6
Benzene	1.0	1.6
Ethylenediaminetetraacetic acid	0.86	1.5
Benzoic acid	0.76	1.8
Chloroethane	0.59	0.95
N-Dimethylnitrosamine	6.8×10^{-5}	6.6

The isotherms are for the compounds in distilled water, with different activated carbons. The values of K and $1/n$ should be used only as rough estimates of the values that will be obtained using other types of water and other activated carbon.

2-5. Dynamic Operation Testing. The following parameters must be considered when designing a pilot scale evaluation.

a. Breakthrough Curves. The breakthrough curve can be defined as the "S" shaped curve that typically results when the effluent adsorbate concentration is plotted against time or volume. Breakthrough curves can be constructed for full scale, dynamic, or pilot testing. The breakthrough point is the point on the breakthrough curve where the effluent adsorbate concentration reaches its maximum allowable concentration, which often corresponds to the treatment goal. The treatment goal is usually based on regulatory or risk based numbers (see Figure 2-4).

b. Mass Transfer Zone. The mass transfer zone (MTZ) is the area within the adsorbate bed where adsorbate is actually being adsorbed on the adsorbent. The MTZ typically moves from the influent end toward the effluent end of the adsorbent bed during operation. That is, as the adsorbent near the influent becomes saturated (spent) with adsorbate, the zone of active adsorption moves toward the effluent end of the bed where the adsorbate is not yet saturated. The MTZ is sometimes called the adsorption zone or critical bed depth. The MTZ is generally a band, between the spent carbon and the fresh carbon, where adsorbate is removed and the dissolved adsorbate concentration ranges from C_{O} to C_{e}.

(1) The length of the MTZ can be defined as L_{MTZ}. When L_{MTZ} = bed depth, it becomes $L_{\mathrm{CRIT},}$ or the theoretical minimum bed depth necessary to obtain the desired removal.

(2) As adsorption capacity is used up in the initial MTZ, the MTZ advances down the bed until the adsorbate begins to appear in the effluent. The concentration gradually increases until it equals the influent concentration. In cases where there are some very strongly adsorbed components, in addition to a mixture of less strongly adsorbed components, the effluent concentration very seldom reaches the influent concentration because only the components with the faster rate of movement through the adsorber are in the breakthrough curve. The MTZ is illustrated in Figure 2-5.

(3) Adsorption capacity is influenced by many factors, such as flow rate, temperature, and pH (liquid phase). The adsorption column may be considered exhausted when the effluent adsorbate concentration equals 95–100% of the influent concentration. This is illustrated in Figure 2-5.

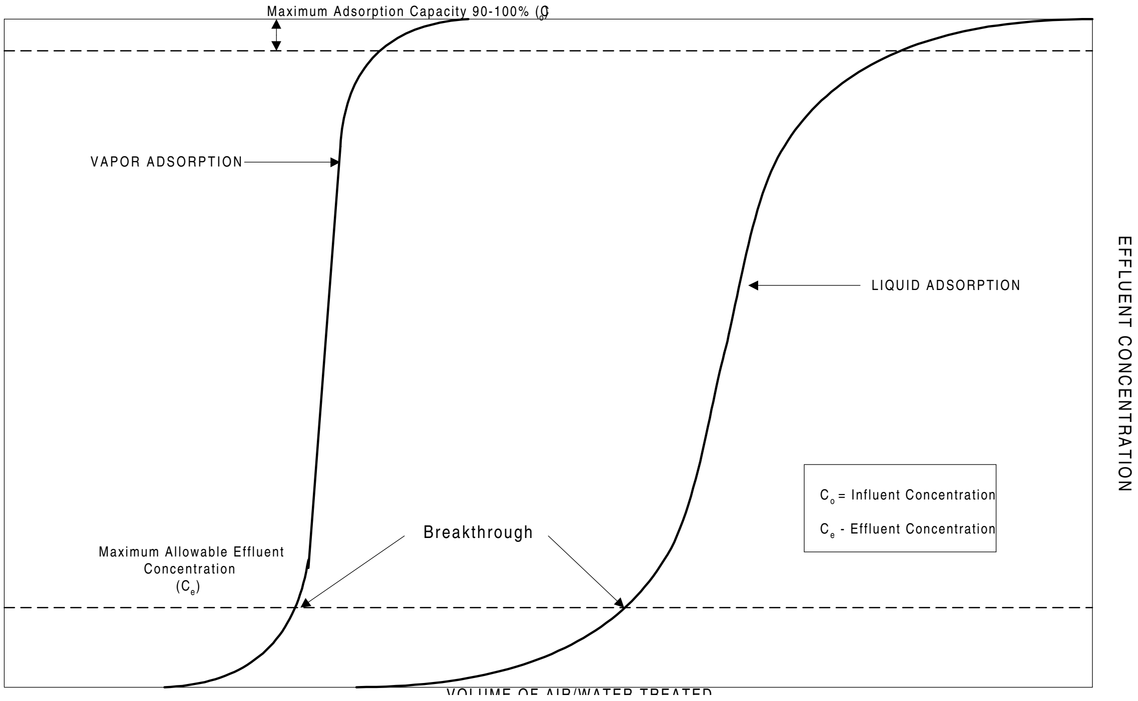


Figure 2-4. Comparison of idealized vapor and liquid breakthrough curves.

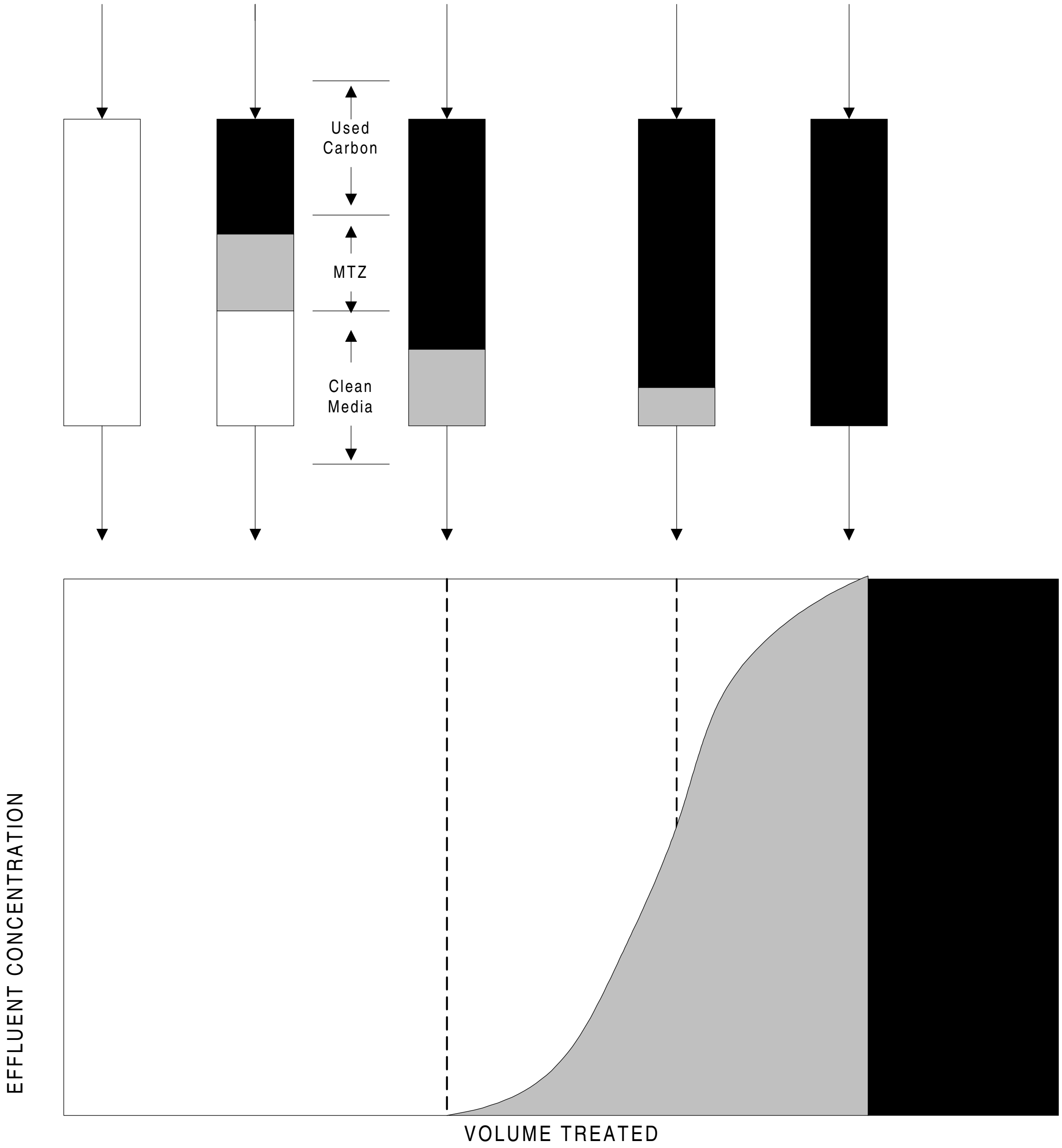


Figure 2-5. Adsorption column mass transfer zone and idealized breakthrough zone.

2-6. Pilot Tests. Pilot studies are almost always recommended for liquid phase applications. After bench scale isotherm tests have provided "proof of concept" data for the media (e.g. GAC), pilot testing should be used to determine if the site-specific conditions will interfere with the media and to test solutions for managing the interferences. Pilot tests will verify the characteristics of the breakthrough curve at selected process parameters, such as surface loading rates and empty bed contact times. For example, there may be competition for adsorption sites among different compounds in the waste stream. Analysis for these competing compounds may not be routinely conducted, so their presence and concentration in the waste stream would not be known. This type of competition can be minimized by selecting a product that selectively adsorbs only the compounds of concern. Also, variations in the water chemistry (pH, buffer capacity, etc.) may affect the performance and capacity of the adsorbent. Pilot tests should also be used to generate scale up factors for the full-scale design.

a. Several manufacturers have mobile pilot systems, and most manufacturers will (for a fee) conduct pilot testing of waste streams for customers. It may be possible to negotiate package deals, where testing costs would be reduced if the pilot scale manufacturer were selected for the full-scale project.

b. There are two basic types of column tests that can be run to determine the parameters mentioned above: the standard pilot column test, and the high pressure minicolumn test. The standard pilot column test consists of four or more carbon columns in series. The columns are 50 to 150 mm (2 to 6 in.) in diameter, generally contain 1.8 to 3.6 m (2 to 4 ft) of GAC, and operate in either the downflow or upflow mode. If suspended solids are a concern for the full scale operation, downflow operation with backwashing capabilities to remove filtered solids is generally the best option. In an upflow mode, the solids would likely plug most distributors. The upflow operation typically generates carbon fines and, thus, gray water. Downflow mode is generally preferred for liquid streams, unless they are susceptible to biological fouling. Four pilot columns are generally selected to ensure that the wave front or mass transfer zone can be tracked through the columns. The column operating characteristics (e.g., surface loading rate, detention time, vertical velocity through the bed) should be similar to those expected in the full scale system. Typically, in full-scale water-treatment applications, except large potable water plants that have adsorbers operating in parallel, the mass transfer zone is contained in the first adsorber in a system having two adsorbers in series. In unique process applications, where the contact time is several hours, three beds in series may be necessary. There are very few systems with four vessels in series. Methods to apply the data to other conditions, such as the bed depth service time (BDST), and Bohart Adams relationships and operating line method are described in various references (Benefield, 1982; Faust and Aly, 1987; AWWA, 1997; Erskine and Schuliger, 1971) A typical pilot column configuration is shown in Figure 2-6.

c. A high pressure water minicolumn (HPMC) test or small scale column test was developed to reduce the length of time required to obtain operational data from a column test (see Figure 2-6). A traditional column test could take a month or more to run, while a HPMC test can be completed in a matter of hours. The HPMC process used is generally manufacturer-specific but depends largely upon mathematical modeling, given the particle size used in the HPMC and test parameters and database of past tests, as well as the experience of the individual interpreting the test data. The apparatus consists of a 0.4- to 2.0-mm-diameter column with a bed depth ranging from 10 to 100 mm. It uses a sample of the subject test GAC, crushed to pass a 60 × 80 mesh or smaller. The minicolumn tests are generally about one order of magnitude less expensive, can be completed quickly, require a smaller volume of water, have minimal chance for biological or other deterioration of the sample, and multiple carbons can easily be tested to obtain the most effective design. Additional information can be obtained from testing labs, carbon manufacturers, and *AWWA Water Quality and Treatment* (1997). A typical apparatus is shown in Figure 2-7. A procedure for estimating GAC performance using a slightly larger diameter column of 25.4 mm ± 0.1 mm is identified in ASTM D3922.

2-7. Spent Carbon Management. Spent carbon has the potential to be regulated for disposal under the *Resource Conservation and Recovery Act* (RCRA). Spent carbon used to treat listed hazardous waste or which exhibits a RCRA hazardous characteristic (ignitable, corrosive, reactive, or exceeding toxicity characteristic leaching procedure threshold levels) must be managed as a hazardous waste after use in an adsorption process and be manifested to a permitted RCRA Treatment, Storage or Disposal Facility (TSDF). This TSDF may be either a disposal or a regeneration facility. If it is managed on-site under CERCLA, a permit is not required, but substantive requirements applicable to TSDFs must be met. On the other hand, if it was not used to treat listed waste, and it does not exhibit a hazardous characteristic, then the spent carbon can be disposed of or regenerated without being subject to RCRA permitting or manifesting requirements. The determination of RCRA status is the legal responsibility of the generator (operator/owner) of the treatment facility. Coordinate with carbon manufacturers, or your local regulatory specialist, for additional information.

2-8. Safety Concerns. The safety concerns unique to carbon adsorption are discussed in EM 1110-1-4007.

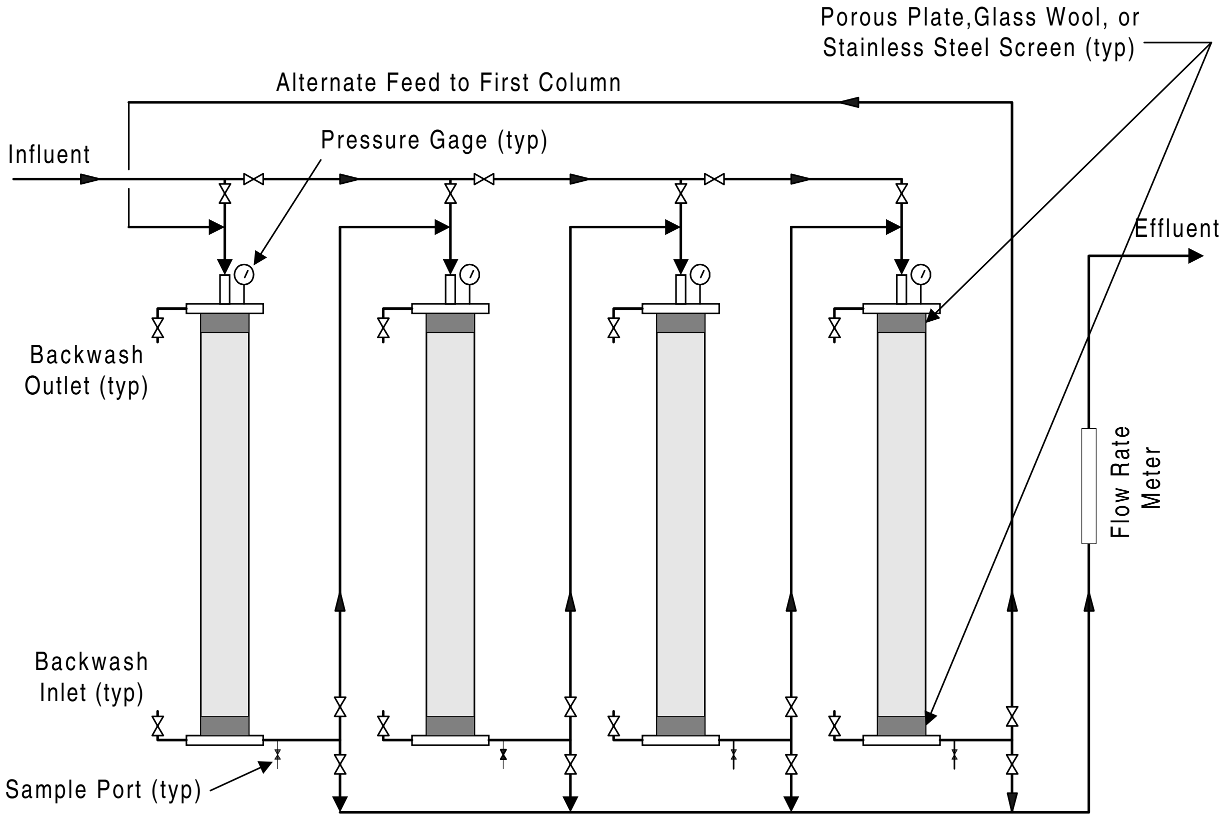


Figure 2-6. Typical pilot column apparatus.

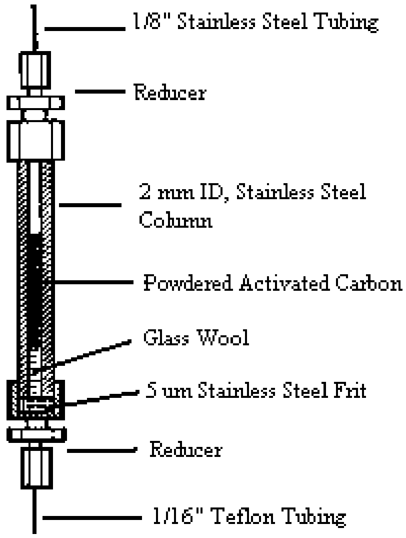


Figure 2-7. Minicolumn apparatus.

CHAPTER 3
APPLICATIONS AND LIMITATIONS

3.1. Carbon Adsorption.

a. Liquid Phase Carbon.

(1) *Applications*. Some typical rules of thumb for types of compounds that are amenable to carbon adsorption are as follows:

- Larger molecules adsorb better than smaller molecules.
- Non-polar molecules adsorb better than polar molecules.
- Non-soluble or slightly soluble molecules adsorb better than highly soluble molecules.
- Based on the polarity or solubility, or both, of the molecule being adsorbed, pH may have an influence on the extent of adsorption.
- Temperature increases the rate of diffusion through the liquid to the adsorption sites, but since the adsorption process is exothermic, increases in temperature may reduce the degree of adsorption. This temperature effect is negligible in water treatment applications and ambient vapor phase applications.

(2) *Chemicals Adsorbed*. The following are examples:

- Alcohols are poorly adsorbed, they are very soluble and highly polar.
- Aldehydes are highly polar, and as molecular weight increases, the polarity decreases, and adsorbability increases.
- Amines are similar in structure to ammonia (NH_3) except the nitrogen is bonded to an organic group. Adsorption is limited by polarity and solubility.
- Chlorinated armoatics, and chlorinated aliphatics are low-polarity and low-solubility compounds, which make them generally quite adsorbable.
- Glycols are water-soluble and not very adsorbable.

- Higher molecular weight organic compounds will generally be more adsorbable owing to adsorptive attraction relative to size.

(3) *Types of Carbon*. Activated carbon is a generic term for a variety of products that consist primarily of elemental carbon. Numerous raw materials can be used to produce carbons, such as coal, wood, and pitch, and agricultural products such as cotton gin waste and coconut shells. Materials most commonly used for liquid phase GAC include both bituminous and lignite coal, and coconut shells.

(a) Bituminous GAC is the one most frequently used for treating low concentrations of low molecular weight organic contaminants in the aqueous phase. Bituminous coal will also have a more fully developed pore distribution, including “transport pores” that improve the rate of adsorption making it effective for water treatment. Bituminous GAC has a relatively large surface area, approximately 900 m^2/g, and an apparent density of approximately 0.50 g/cm^3 (30 lb/ft^3). These carbons are usually harder than other types except coconut, and, therefore, are more abrasion resistant, and can be more vigorously backwashed without damage.

(b) Lignite GAC generally has less total surface area than bituminous GAC. It is a less dense, slightly softer coal, has a higher percentage of meso (transitional) macro pores, and is used more for larger molecules. Therefore, it is used more in decolorizing applications. Lignite GAC has a surface area of approximately 650 m^2/g and an apparent density of approximately 0.50 g/cm^3 (25 lb/ft^3).

(c) Coconut-shell-based GAC generally has a larger surface area than coal-based GAC, and a very large percentage of micropores. Coconut-shell-based GAC has a surface area generally over 1000 m^2/g and an apparent density of approximately 0.50 g/cm^3 (30 lb/ ft^3). Coconut shell based carbons may not have the more fully developed pore structure that coal-based carbons have, because their source is vegetative material. Consideration should be given to rate of adsorption effects in liquid treatment. It is used primarily in vapor-phase applications. Coconut-shell-based carbon is slightly more expensive to produce than coal-based GAC, since only about 2% of the raw material is recoverable as GAC, versus 8–9% for coal-based carbons.

(4) *Isotherms*. Isotherms are discussed in paragraph 2-3.

(5) *Pressure Drop*. Headloss in liquid phase applications varies significantly, depending on the piping configuration, carbon particle size, contact time, and surface loading-rate (generally expressed in liters per minute per square meter [gpm/ft^2]). Typical loading rates are 80–240 Lpm/m^2 (2–6 gpm/ft^2); occasionally, loadings up to 400 Lpm/m^2 (10 gpm/ ft^2) are used. Loadings greater than 240 Lpm/m^2 (6 gpm/ft^2) generally result in excessive headloss through a typical arrangement that has two pre-piped, skid-mounted vessels in series (140 kPa [20 psi] or more primarily from piping losses). In any case, the manufacturer’s literature should be consulted regarding the headloss for a specific application.

(6) *Operating Parameters.*

(a) *Contact Time*. General rules of thumb for moderately adsorbable compounds such as TCE, PCE, and benzene are, first, to go from low ppm levels (approximately 1) to ppb levels requires a minimum empty bed contact time (EBCT) of approximately 15 minutes (some applications have shorter valid contact times given an effective process design), and, second, to go from a medium ppm range (approximately 10) to a low ppb range requires approximately 30 minutes EBCT. Some typical values are identified in Table 3-1. EBCT is related to the contactor dimensions as follows:

$$\text{EBCT} = \frac{V}{Q} \text{ or } \frac{LA}{Q}$$

where

V = bulk volume of GAC in contactor, m^3 (ft^3)
A = cross-sectional bed area, m^2 (ft^2)
L = bed depth, m (ft)
Q = volumetric flow rate, L/s (ft^3/min).

(b) *Adsorber Volume*. Once the optimum contact time (EBCT) and the carbon usage rate are established, the size (volume) of the adsorbers can be determined. Factors that affect the size of the adsorber include the change out rate as well as the carbon usage rate. Generally, for carbon contactor change out, you should consider schedules for other projects at an installation, as well as a reactivation company's fees, to determine the most cost-effective change out schedule. Typically, reactivation companies have compartmentalized trucks with a dry carbon capacity of 9100 kg (20,000 lb), which results in a saturated weight of 18,200 kg (40,000 lb), which is the load limit of most roadways. Off-the-shelf contactors range from 70 kg (150 lb) to as large as 9100 kg (20,000 lb). Optimum carbon usage should be based on column studies. The carbon usage rates at different contact times should be evaluated against the higher initial cost of the larger units and higher operation and maintenance costs of the smaller units. The carbon vessel should have an additional 20–50% bed expansion allowance built in for backwashing the carbon before you place the vessels in service. This expansion allowance is critical in systems where suspended solids are expected, or there is no pre-filtration. The adsorber volume is then calculated from:

$$V = \frac{(CUR \bullet COP)\ S.F.}{\rho}$$

Where:

V = volume of adsorber, ft^3
CUR = carbon usage rate, g/day (lb/day)
COP = carbon change out period, days

ρ = bulk density of carbon, g/cm^3 (lb/ft^3)
S.F. = safety factor to provide extra non-carbon-containing volume for operational uncertainty, 1.2–2.5.

(c) *Bed Depth*. Bed depth is a direct function of the contactor diameter and volume. You can solve for the bed depth (*L*) knowing the adsorber volume (*V*) and adsorber bed area (*A*) using the equation:

$$L = \frac{V}{A}$$

(d) *Carbon Usage*. Carbon usage can be estimated several ways. One method to estimate GAC usage is based on isotherm data using the relationships:

(1) For batch systems:

$$CUR = \frac{\left(C_{\mathrm{o}} - C_{\mathrm{e}}\right) F}{\left(\frac{x}{m}\right)_{C_{\mathrm{o}}}} \tag{3-1}$$

(2) For flow through systems:

$$CUR = \frac{C_{\mathrm{o}}\ V}{\left(\frac{x}{m}\right)_{C_{\mathrm{o}}}} \tag{3-2}$$

Where

C_o = initial concentration (mg/L)

C_e = desired effluent concentration $\left(\frac{\text{mg}}{\text{L}}\right)\left(\frac{\text{mg adsorbed}}{\text{g carbon}}\right)$

$\left(\frac{x}{m}\right)_{C_o} = \frac{x}{m}$ value at concentration C_{o} $\left(\frac{\text{mg contam}}{\text{g carbon}}\right)$

$\left(\frac{x}{m}\right)_{C_e} = \frac{x}{m}$ value at concentration

$$C_e = \frac{\text{mg contamination}}{\text{g carbon}}$$

CUR = carbon usage rate (g/day)

F = volumetric flow rate of contaminated liquid treated/day (L/day).

Relationship 3-1 is generally used to estimate carbon usage for batch systems, and relationship 3-2 is used for continuously operating flow through systems. For multiple constituent wastes, the constituents with the highest GAC usage rates, up to three, can be summed and the overall *CUR* estimated based on that sum. See examples in Appendix A for additional information on the size of adsorbers. Estimates based on isothermal data will only provide a very rough estimate of GAC usage. In most cases a column test must be performed (see paragraph 2-6).

(e) *Backwashing*. Backwashing is the process of reversing the flow through a media bed with enough velocity to dislodge any material caught in void spaces or attached to the media. Backwashing is essential before you bring a typical liquid phase downflow pressure column on-line. Backwashing removes carbon fines generated during the transfer from the shipping container to the contactors. Backwashing also helps naturally stratify the GAC bed, which reduces the likelihood of preferential channeling within the column, and, after future backwashes, helps keep spent carbon at the top of the bed. Redistribution of the adsorbent within a GAC bed that was improperly backwashed when initially installed could result in extending the mass transfer zone (MTZ), potentially reducing the overall adsorption capacity of the adsorber. Backwashing a GAC bed prior to placing a new bed into service also helps de-aerate the bed, further reducing the potential for channeling. Periodic backwashing is usually recommended in the downflow adsorption systems most commonly used at HTRW sites, unless the water treated is low in dissolved and suspended solids. Periodic backwashing serves the same purposes that you would expect in any sand filtration system, to remove solids accumulation, reduce biological growth on the media, and reduce the headloss in the bed. The backwash rate will depend on the carbon density, particle size, and water temperature. Typically, a 30% bed expansion is accounted for in the design. This generally requires approximately 6.3–7.4 Lpm/m^2 (8–14 gpm/ft^2) at a water temperature of 13°C. The GAC manufacturer should be contacted to determine the optimum backwash rate for the carbon supplied. A portion of some poorly adsorbed constituents, such as carbon tetrachloride, may be desorbed during backwashing, but strongly held constituents are not affected.

Table 3-1
Example Case Studies
Treating Groundwater for Non-Potable Use
Influent Concentrations at mg/L Levels, Effluent at the µg/L Levels

Example	Contaminant	Typical Influent Concentration (mg/L)	Typical Effluent Concentration (µg/L)	Surface Loading Rate (gpm/ft^2)	Total Contact Time (minutes)	GAC Usage Rate (lb/1000 gal)	Operating Mode
1	Phenol Orthochlorophenol	63 100	<1 <1	1	201	5.8	Three Fixed Beds in Series
2	Chloroform Carbon Tetrachloride Tetrachloroethylene	3.4 135 70	<1 <1 <1	0.5	262	11.6	Two Fixed Beds in Series
3	Chloroform Carbon Tetrachloride Tetrachloroethylene	0.8 10.0 15.0	<1 <1 <1	2.3	58	2.8	Two Fixed Beds in Series
4	Benzene Tetrachloroethylene	0.4 4.5	<1 <1	1.21	112	1.9	Two Fixed Beds in Series

Table 3-1 (Continued)
Example Case Studies

Treating Groundwater for Non-Potable Use

Influent Concentrations at mg/L Levels, Effluent at the µg/L Levels

Example	Contaminant(s)	Typical Influent Concentration (mg/L)	Typical Effluent Concentration (µg/L)	Surface Loading Rate (gpm/ft^2)	Total Contact Time (minutes)	GAC Usage Rate (lb/1000 gal)	Operating Mode
5	Chloroform Carbon Tetrachloride	1.4 1.0	<1 <1	1.6	41	1.15	Two Fixed Beds in Series
6	Trichloroethylene Xylene Isopropyl Alcohol Acetone	3-8 0.2-0.5 0.2 0.1	<1 <1 <10 <10	2.4	36	1.54	Two Fixed Beds in Series
7	Di-Isopropyl Methyl Phosphonate Dichloropentadiene	1.25 0.45	<50 <10	2.2	30	0.7	Single Fixed Bed

Table 3-1 (Continued)
Example Case Studies
Treating Groundwater for Non-Potable Use
Influent Concentrations at mg/L Levels, Effluent at the µg/L Levels

Example	Contaminant(s)	Typical Influent Concentration (mg/L)	Typical Effluent Concentration (µg/L)	Surface Loading Rate (gpm/ft^2)	Total Contact Time (minutes)	GAC Usage Rate (lb/1000 gal)	Operating Mode
8	1,1,1 Trichloroethane Trichloroethylene Tetrachloroethylene	143	<1	4.5	15	0.4	Single Fixed Bed
9	Methyl T-Butyl Ether Di-Isopropyl Ether	30 35	<5 <1	5.7	12	0.6	Two Single Fixed Beds
10	Chloroform Trichloroethylene	400 10	<100 <1	2.5	26	1.2	Four Single Fixed Beds
11	Trichloroethylene Tetrachloroethylene	35 170	<1 <1	3.3	21	0.2	Three Single Fixed Beds
12	1,1,1 Trichloroethane 1,1 Dichloroethylene	70 10	<1 <1	4.5	30	0.45	Two Fixed Beds in Series
13	1,1,1 Trichloroethane Cis-1,1 Dichloroethylene	25 15	<1 <1	2	35	0.3	Single Fixed Bed

Table 3-1 (Continued)
Example Case Studies
Treating Groundwater for Non-Potable Use
Influent Concentrations at mg/L Levels, Effluent at the µg/L Levels

Example	Contaminant(s)	Typical Influent Concentration (mg/L)	Typical Effluent Concentration (µg/L)	Surface Loading Rate (gpm/ft^2)	Total Contact Time (minutes)	GAC Usage Rate (lbs/1000 gal)	Operating Mode
14	Trichloroethylene	50	<1	1.6	42	0.4	Two Single Fixed Beds
15	Cis-1,1 Dichloroethylene Trichloroethylene Tetrachloroethylene	5 5 10	<1 <1 <1	1.9	70	0.25	Two Fixed Beds in Series

There is an Answer to Groundwater Contamination, O'Brien and Fisher; Water Engineering and Management, May, 1983

(7) *Equipment*. Generally, steel pressure vessels containing granular activated carbon are used. In water treatment, steel vessels must have a protective internal lining to protect them from the corrosive effects of carbon in water. This lining should also possess good abrasion resistance to withstand movement of the hard carbon particles. The treatment systems range in capacity from 70 kg (150 lb) of carbon per unit to 9100 kg (20,000 lb) per unit. Under certain low-pressure applications, fiberglass or other plastic units may be used. In certain applications, ASME rated pressure vessels may be required. Units are generally skid-mounted, pre-assembled by the manufacturer, and delivered to the site. Larger units, i.e., 3 m (10 ft) in diameter, are difficult to ship pre-assembled, so major components, piping, and vessels are assembled in the field. Piping components are typically pressure-rated to match the vessels and included as part of the skid unit. A schematic presenting the major components is provided in Figure 3-1. Criteria for the individual components, such as the distributors, support media, underdrain system, backwash equipment requirements, carbon slurry system, and pumping systems, can be obtained from carbon manufacturers, or from information contained in Corps of Engineers Guide Specification 11225*: Downflow Liquid Granular Activated Carbon Adsorption Units*, http://www.hnd.usace.army.mil/techinfo/cegs/cegstoc/htm.

(a) Most liquid phase granular activated carbon systems are operated in series. This means passing all of the flow through one column bed, a lead column, and then passing flow through another similar sized column bed, the lag vessel. This method offers several advantages over a single column. The series configuration allows the maximum use of the GAC throughout the entire carbon vessel. This assumes, of course, that the mass transfer zone (MTZ) is contained within a single properly sized carbon unit. By placing two or more columns in series, the MTZ is allowed to pass completely through the first (lead) bed as the leading edge of the MTZ migrates into the second (lag) bed. By allowing this to happen, the maximum contaminant concentration is allowed to come into contact with adsorption sites in the lead vessel that require a greater concentration gradient (differential adsorption energy) to hold additional contamination. When the MTZ exits the lead vessel, that vessel is then exhausted, and requires change out with virgin or regenerated GAC. Even though the adsorption capacity of the lead vessel is exhausted, treatment continues in the lag vessel. Then, during change out, the lead vessel is taken off-line and the lag vessel is placed in the lead position. The former lead vessel is then replenished with GAC and then becomes the lag vessel and brought on-line.

(b) A critical component of the adsorber design is the underdrain (collection) system. This underdrain must be designed so that water is collected evenly, such that the mass transfer zone is drawn down in an even, or plug flow, manner to get full value from the installed carbon. In addition, the underdrain may also be used to introduce backwash water, and, therefore, it should be able to introduce water evenly across the entire bed cross section.

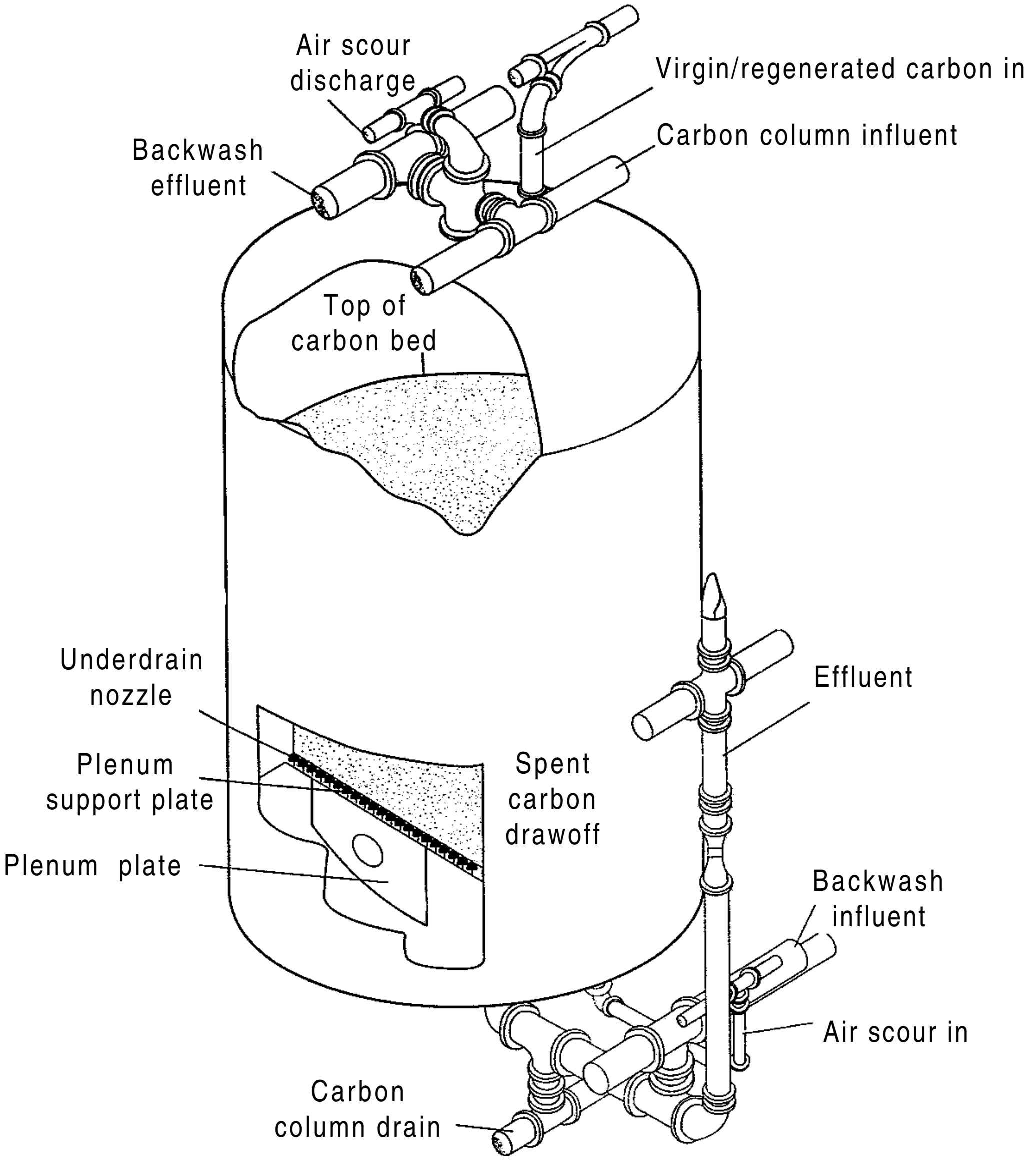


Figure 3-1. Schematic of carbon contactor.

b. Vapor Phase Carbon Adsorption.

(1) *Applications*. Vapor phase activated carbon adsorption is used to treat vapor emissions from processes such as air stripping (illustrated in the Appendix B examples), soil vapor extraction (illustrated in Figure 3-2, and in the U.S. Army Corps of Engineers Design Manual, *Soil Vapor Extraction and Bioventing*, EM 1110-1-4001, http://www.environmental.usace.army.mil EM 1110-1-4001), thermal desorption, landfill off-gas, treatment process vessels, storage tanks, treatment buildings. and treatment processes (odor control).

(2) *Chemicals Adsorbed.* Many volatile organic chemicals can be removed from vapor streams with activated carbon. In general non-polar organic chemicals adsorb better than polar organic chemicals, and higher molecular weight organic chemicals adsorb better than low molecular weight organic chemicals. Examples of hazardous waste chemicals that are easily adsorbed are chlorinated solvents such as trichloroethylene (TCE) and fuel components such as benzene, ethylbenzene, toluene, and xylene (BETX). Examples of chemicals that are not as easily adsorbed are aldehydes, ketones, and alcohols, although these do have better adsorptive characteristics than they do in the liquid phase, as solubility in water is not a factor, and adsorption will improve with increasing molecular weight. Most adsorption of VOCs by activated carbon is exothermic. The heat of adsorption is especially high with ketones, such as methyl ethyl ketone (MEK), and aldehydes. Heat from the vapor phase adsorption of these contaminants has actually built up and ignited bed fires in some installations (Shelly, 1994). The temperature of the bed should be monitored to prevent a “hot spot” from igniting a bed fire. Internal sprinklers are often installed in the carbon vessel as additional fire protection when the probability of bed ignition is high. Another way is to use a CO monitor (Appendix D,TIGG). Low relative humidity (RH) increases the capacity of the carbon bed (because under high RH, the water is adsorbed and blinds the carbon). Manufacturers’ recommendations on the maximum RH vary from as low as 40% to as high as 70%.

(3) *Types of Carbon.* Activated carbon used for vapor phase adsorption is different from that designed for liquid phase adsorption. Gas phase carbon has a larger number of small pores than liquid phase carbon.

(4) *Isotherms.* See Paragraph 2-3 for an introduction to carbon isotherms. Isotherms for vapor phase adsorption of organic chemicals tend to be based more on calculated theoretical values, rather than on empirical data, which are limited. They are not as readily available in the literature as those for liquid phase adsorption. Isothermal data may vary greatly from one carbon series to another or among manufacturers. As a result, it is necessary to obtain vapor phase isothermal data from carbon manufacturers. The temperature and relative humidity of the vapor stream has a large effect on the adsorption capacity (the isotherms) of the activated carbon. Carbon adsorption increases as the temperature decreases. For example, lowering the temperature from 77 to 32°F at one site for one activated carbon resulted in increasing the adsorption capacity

by 35%. High relative humidity can have a detrimental effect on the adsorption capacity. The difference in capacity from 0 to 100% relative humidity can be as much as a factor of 10. For example, increasing the relative humidity from 50 to 100% at an HTRW site decreased the adsorption rate from 0.12 g adsorbed per gram of carbon to 0.04 g adsorbed per gram of carbon. As a result, and since relative humidity depends on the temperature, it is often necessary to determine which combination of temperature and relative humidity is the most cost effective. Adjusting the relative humidity to 40 to 50% is often the best compromise. Relative humidity above 50 percent may result in adsorbed and condensed water vapor blocking the pores of the particles and interfering with the diffusion of the contaminants to the adsorption pores.

(5) *Pressure Drop.* Headloss in vapor phase applications varies significantly, depending on piping configuration, carbon particle size, and surface loading rate. Surface loading rate is expressed as ft^3 (m^3) of vapor per ft^2 (m^2) of carbon bed cross-sectional area. For example, if the vapor flow rate is 100 ft^3/min (2.83 m^3/min.) and the cross-sectional area of the carbon bed is 10 ft^2 (0.929 m^2) (i.e., the diameter of the bed is 3.57 ft [1.09 m]), the surface loading rate is (100 ft^3/min)/10 ft^2 = 10 ft/min (3.05 m/min). Typical loading rates are 10–100 ft/min (3.05–30.5 m/min). A typical pressure drop through a vapor phase carbon bed is 1 to 4 in. of water column per foot of carbon bed (8.3 to 33 cm/m). In any case, the manufacturer's literature should be consulted regarding the headloss for a specific application.

(6) *Operating Parameters.* The major operating parameters needed to design a vapor phase carbon adsorption unit are:

- Vapor stream flow rate.
- Contaminants to be adsorbed.
- Concentration of contaminants
- Temperature of the vapor stream.
- Relative humidity of the vapor stream.
- Desired frequency between carbon bed changes.
- Allowable pressure drop.

(7) *Equipment.* The equipment and units needed in the adsorption process depend on the application. A typical process train consists of piping from the source of the volatile emission stream, such as vapor emissions from a soil vapor extraction unit, an induced draft blower, a heat exchanger, to raise or lower the temperature of the vapor stream (to adjust relative humidity), and carbon adsorption vessel or vessels. This is illustrated in the design example in Appendix B.

Additional information can be obtained from the Corps of Engineers Guide Specification 11226, *Vapor Phase Activated Carbon Adsorption Units*, http://www.hnd.army.mil/techinfo/cegs/cegstoc.htm.

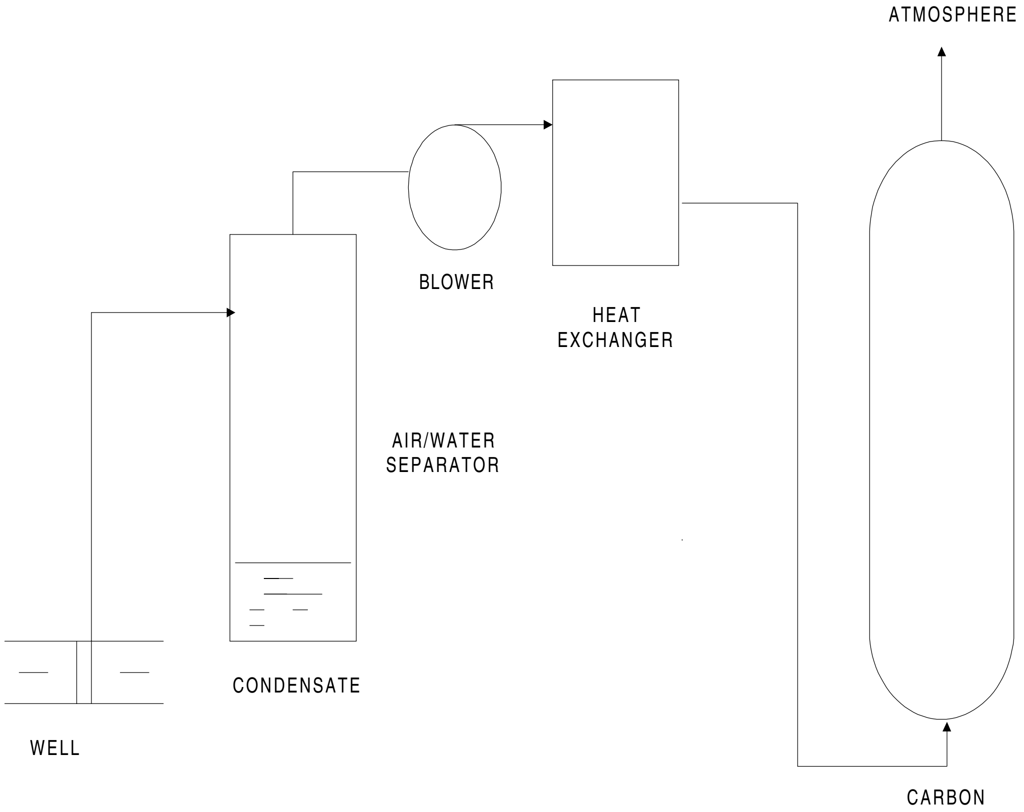


Figure 3-2. Treating off-gas from an in-situ vapor extraction with activated carbon.

3-2. Regeneration, Reactivation, and Disposal of Spent Activated Carbon.

a. Activated Carbon Regeneration and Reactivation. This Paragraph presents information on reactivation and regeneration, options for spent activated carbon that has been used to treat hazardous wastes and industrial process effluents.

(1) As contaminants are adsorbed, the carbon's adsorptive capacity is gradually exhausted. When the carbon's adsorptive capacity is reached, it is considered "spent," and it must be regenerated, reactivated, or disposed of. Although some manufacturers and researchers use the terms "regeneration" and "reactivation" interchangeably, in this document, "regeneration" means removing the contaminants from the carbon without destroying them and "reactivation," which occurs at very high temperatures, means destroying the contaminants and reactivating the carbon. The user must decide which is to be used: on-site regeneration or reactivation, off-site reactivation, or disposal of the spent activated carbon.

(2) Regeneration usually involves removing the adsorbed contaminants from the carbon using temperatures or processes that drive the contaminants from the carbon but that do not destroy the contaminants or the activated carbon. A common regeneration process introduces steam into the spent carbon bed, volatilizing the contaminants and restoring the carbon's capacity to what is called its "working capacity." Steam regeneration does not completely remove adsorbed contaminants. Another common process uses a hot inert gas, such as nitrogen, to remove the contaminants. The stripped volatiles are compressed, and recovered as liquid in a condenser. A third process is pressure swing adsorption. Pressure swing adsorption uses the fact that adsorption capacity is directly proportional to the partial pressure of the contaminants in the surrounding environment. The contaminants are adsorbed at a high pressure (providing higher partial pressure of the contaminant to be adsorbed), and then desorbed at a lower pressure where the capacity is reduced. These regeneration processes are usually run on-site and inside the adsorption vessel. All regeneration processes produce a waste stream that contains the desorbed contaminants. For example, steam regeneration produces a mixture of water and organics from the condensed desorbed vapor.

(3) Other than thermal reactivation at elevated temperatures, regeneration techniques will result in some contaminants remaining adsorbed and unaltered within the carbon particle. These contaminants will be occupying "high energy adsorption pores, or sites," and lower temperature regenerants (<500°F) or capacity corrections will not be able to provide sufficient energy to reverse the adsorptive force. Carbon having these residual contaminants remaining in the high energy adsorption sites will likely have much shorter runs before breakthrough. They might even be unable to attain the desired low-level effluent concentrations when placed back on-line, as compared to virgin grade carbons with all of their high-energy sites available for adsorption. These on-site regeneration techniques are based on capacity recovery processes traditionally

used in solvent recovery operations and may not be suitable for applications driven by an effluent objective.

(4) Spent carbon reactivation off-site involves removing the adsorbed contaminants from the spent activated carbon in a process that is a modification of the one that initially activated the carbon. The contaminants are desorbed and destroyed in the high temperature (typically in excess of 1500°F[800°C]) pyrolizing atmosphere of the reactivation furnace. Several types of furnaces are available, such as rotary kilns and multiple hearths. The furnaces can be heated by a fuel such as natural gas or fuel oil or by electricity. Off-site carbon reactivation manufacturers reactivate spent carbon in large capacity (5 to 60 tons/day) furnaces (Schuliger, 1988). While furnaces of this capacity are not typically cost effective for a single hazardous waste site, smaller furnaces that may prove cost effective are available for on-site use from a number of manufacturers. Reactivation furnaces only produce reactivated carbon, air emissions, and some carbon fines. No organic wastes are produced. Table 3-2 summarizes the information for on-site regeneration, on-site reactivation, and off-site reactivation processes.

b. Selection Criteria for Determining if Spent Carbon Should be Disposed of, Regenerated, or Reactivated.

(1) *Criteria for Determining When to Use On-site Regeneration, Reactivation or Off-site Reactivation, or Disposal.*

(a) On-site reactivation requires space and utility support for the equipment. It also usually requires an air pollution permit for the furnace afterburner. If the site cannot provide the land or utility support, or if obtaining the required permit is not practical, the spent carbon must be regenerated on-site or reactivated off-site.

(b) At some sites, the availability or turn-around times for off-site carbon re-supply may be impractical. In these situations, on-site regeneration or reactivation will be required or the site can provide sufficient storage for both fresh and spent carbon to eliminate the constraint of response time by outside suppliers.

(c) Studies indicate that on-site thermal reactivation is not economical if carbon usage is less than 500 to 2000 lb/day (227 to 909 kg/day). Other studies have found that carbon reactivation unit cost rises rapidly if carbon usage is less than 5000 to 6000 lb/day (2272 to 2727 kg/day) (Pontius, 1990).

(d) Because of liability and economic concerns, some design guides recommend that reactivation should be done off-site whenever possible, regardless of whether land and utilities are available on-site (Faust, 1987).

(e) Two alternates, which are very common today, are:

- Have a service come on-site and remove the spent carbon and replace it with virgin or reactivated. This operation usually takes less than one shift.
- Have an extra adsorber on hand and ship the adsorber with the spent carbon to a reactivator. The vessel will then be returned with virgin or reactivated carbon on it.

(f) When carbon is regenerated on-site, some contaminants may not be desorbed. For example, GAC containing organic contaminants with high boiling points may need to be reactivated instead of regenerated.

(g) In some situations, the loss of adsorption capacity or the rapid breakdown of the target contaminant, causing an unacceptable decrease in on-line time from the build-up of unregenerated contaminants, may be unacceptable. For these applications, reactivation (on- or off-site) will be required.

(h) The desorbed material produced by on-site regeneration processes may or may not be Resource Conservation Recovery Act (RCRA) wastes. In industrial applications, it may be possible to reuse or recycle the desorbed material. In hazardous, toxic, and radiological waste (HTRW) applications, the desorbed material is usually an unrecyclable mixture that requires proper disposal. Hazardous waste streams will have to be properly stored, manifested, transported, and disposed of. If it is not practical to handle a hazardous waste at the site, reactivation (either on-site or off-site) should be considered.

(i) Carbon losses during off-site reactivation in the adsorbers and the carbon transfer and handling systems can be held to 5 to 7% (Zanitsch, 1997). Losses within the reactivation furnace should be between 1 and 5%, while potential total reactivation cycle loss rates can range from 3 to over 10%. Most systems operate with losses of 5 to 7% (Zanitsch, 1997). However, some researchers estimate that approximately 5 to 15% of the spent carbon is destroyed during each reactivation cycle (Faust, 1987). One manufacturer states that, in an on-site reactivation system, the losses range from 3 to 8%. The higher losses are experienced in locations that have a poorly designed carbon handling system, or where the adsorbed organics are difficult to reactivate or are strongly adsorbed on the carbon, or both (Appendix D, TIGG). After the system shakedown is completed and the operators gain experience, carbon losses should decrease to approximately 7% per cycle (Faust, 1987; O'Brien et al., 1987). This loss can be replaced by carbon from the reactivated carbon pool or with virgin carbon. It is possible, although unlikely, that an inorganic contaminant in the replacement reactivated carbon might leach out at unacceptable levels in the effluent. Therefore, if the site must meet inorganic effluent limits, the operator should specify that virgin replacement carbon be used to make up the reactivation losses.

(j) Regeneration or reactivation will be necessary when no disposal site will accept the spent carbon or when the disposal costs would be prohibitive.

(2) *Criteria for Determining When to Dispose of Spent Carbon.* There are several cases where regeneration or reactivation of the spent carbon will not be feasible or will be prohibitively expensive. In these cases, the spent carbon must be disposed of.

(a) If the carbon is contaminated by a substance that damages it irreversibly, it must be disposed of. For example, styrene monomer binds to carbon and then reacts to form (polystyrene) polymers (McLaughlin, 1995). These polymers blind the small micro pores in the carbon and require extreme reactivation energies.

(b) Disposal may be necessary because regeneration/reactivation costs may be prohibitive because of the site's location or because of trace contaminants, such as radioactive particles, that are also adsorbed. Care should be taken to compare total costs for both disposal and reactivation or regeneration. This comparison should include: transportation costs to the disposal or off-site reactivation facility, the cost of the continuing liability for the disposed of spent carbon, the continuing operations and maintenance (O&M) costs for makeup carbon for on- and off-site reactivation, and the capital and O&M costs for regeneration. The reactivators have trucks with three compartments, so on-site storage tanks are not needed. In addition, different RCRA regulations may apply to the spent carbon and to residuals from the on-site regeneration or reactivation process. For example, the spent carbon, the slurry water used to move spent carbon, and the water/contaminant mixture condensed from on-site steam regeneration facilities may all be considered RCRA wastes because of the "derived-from" rule (see 40 CFR 261.3(d)(1) for "derived-from" rule for characteristic waste and 40 CFR 261.3(2)(i) for listed waste). The costs of complying with the appropriate storage, treatment, manifesting, and transportation regulations for these wastes must also be included in the total cost comparison.

(c) The Micro Computer Aided Cost Estimating System (MCACES), the United States Army Corps of Engineers (USACE) cost estimating program, along with the Standard Cost Engineering HTRW Remedial Action-Work Breakdown Structure or the USAF Remedial Action Cost Engineering and Requirements (RACER) system, can be used to estimate the life cycle costs of systems and to compare alternatives.

c. Common Design Concerns for Regeneration of Carbon. Because adsorption vessels and the spent carbon storage vessel will be pressurized or put under vacuum, and in some cases heated (as with on-site steam regeneration), the containers must be designed, fabricated, tested, and marked (or stamped) in accordance with the standards of the applicable *Boiler and Pressure Vessel Code* (ASME, 1992), and must incorporate pressure safeguards, such as rupture disks. Because wet activated carbon is corrosive, the vessel may be built with a corrosion allowance, typically 0.05 in. Most are protected with sprayed on linings, which range from 10 to 45 mils thick. An example of a coating used in carbon adsorption or storage vessels is 30 mils of vinyl ester. Other linings are fiberglass polyethylene, Teflon, and kynar. Once the coating is applied, it should be tested electronically to determine if there are any pinholes in its surface.

(1) Because granular activated carbon is abrasive, carbon loading and transfer piping and pumps should be built with an abrasion allowance. Carbon loading and unloading piping should avoid long runs, areas of low velocity, radical bends, and low spots without cleanouts, line restrictions, or restrictive bends (Faust, 1987). Another concern with piping is corrosion from the waste stream being treated. Chlorinated organics in vapor can corrode normal steels. Corrosion resistant materials such as Hastalloy or Alloy 20 may be considered.

(2) Wet, drained, activated carbon adsorbs oxygen from the air. Therefore, all adsorption and storage vessels should include provisions to ventilate the vessels, and all inspection manways should be designed to support confined space entry procedures. In particular, the area around the manway should be designed to accommodate a rescue tripod. The inspection manways should also support the use of breathing air supplies (Faust, 1987), either as air supply lines or self-contained breathing apparatuses.

d. On-site Regeneration.

(1) *Steam and Hot Inert Gas Regeneration.* Steam and hot inert gas regeneration use the same principle. After the carbon bed reaches the end of its adsorption cycle, it is isolated from the contaminated waste stream. Steam or a hot inert gas (usually nitrogen) is piped into the adsorption vessel to strip the adsorbed contaminants from the carbon bed. The steam or gas can flow either counter-current or co-current to the original waste stream's flow. Currently, most systems use counter-current flow. The combined steam/contaminant or gas/contaminant is condensed and pumped to storage or treatment. Steam and hot inert gas increase the capital costs because more rugged materials are necessary construction and insulation.

(a) Steam/hot gas regeneration systems are used primarily to regenerate vapor treatment beds, because the additional cost to dry out a water treatment carbon bed (raise temperature enough to vaporize all of the water entrained within the carbon pores) before regeneration makes steam/gas regeneration prohibitively costly. However, if the bed can be drained and dried before regeneration, steam/hot gas regeneration may be cost effective.

(b) Steam is the preferred stripping gas, as it is readily available at many industrial sites; however, it may provide lower energy than hot inert gas, depending on the temperature. If it is not available, skid mounted boiler units are available at relatively low cost. Steam works especially well with non-water-miscible organics, such as chlorinated solvents. Non-miscible contaminants have an added advantage in that they can be separated from the condensed water by gravity. Steam is less useful for water-soluble contaminants such as alcohols, aldehydes, or ketones. If steam is used for these types of contaminants, the contaminants can be separated from the condensate by distillation. However, distillation raises the O&M costs of the system. For this reason, hot inert gas is preferred for water soluble contaminants.

(c) The regenerated bed is cooled, either by piping in cool air or water, or by simple radiation. Once the bed is cool, it is placed on standby or put into service as the polish unit. If a vapor adsorber was steam regenerated, the carbon bed must be dried before being put back into service. Conversely, water treatment units that are steam or gas regenerated must be carefully flooded after regeneration to remove any air or gas trapped in the carbon.

(d) The advantages of on-site regeneration include the savings from not having to replace the 5 to 15% of the carbon destroyed during each reactivation cycle, no need for a carbon change out storage vessel, and the potential for recovery of the organic contaminants, with associated economic benefits. At some sites, primarily industrial sites, the recovered material is pure enough to be recycled. Also, the steam required for regeneration is already available at some sites and can often be supplied at minimal cost. Disadvantages include the need for storing the recovered contaminants, capital and O&M costs for a boiler if steam is not available, additional capital and O&M costs if hot inert gas is selected (for the gas, and for the condenser/chiller that will be needed), and the possibility that the system's carbon will have to be reactivated periodically anyway, owing to the buildup of contaminants that cannot be removed with steam or hot inert gas. At hazardous waste sites, there are two other potential disadvantages: the recovered material may be an un-recyclable mixture or steam condensate that must be properly disposed of, and the recovered material may be a RCRA waste, which must be stored, transported, and manifested according to RCRA regulations.

(e) The system configuration for steam regeneration must include a boiler, a feed water supply and treatment system, provisions for disposing of boiler blowdown, a condenser, a gravity separator, and storage for the recovered contaminants, either a tank or drums. If a mixture of petroleum chemicals and chlorinated solvents is being desorbed, the condensate may form three phases. This may complicate the disposal of the condensate. Vapor phase units require a source of drying air, such as process gas exiting an on-line adsorber or compressor. For hot inert gas systems, gas storage must be provided, either in cylinders or tanks, as well as a heater for the gas, a condenser, and contaminant storage. If economically feasible, an on-site gas generator may also be installed. Some systems use air as the stripping gas, avoiding the costs of gas storage. A separator is not usually required for gas systems because the condensate is a single organic phase. In addition, the carbon adsorbers must be plumbed for steam or the stripping gas, and piping to transfer the stripped contaminants to the condenser. A fan or pump for the cooling fluid will be needed if the units must be cooled down faster than radiation will permit. Most of these systems are not designed to be weather-proof and so should be located inside a building and protected from freezing. A typical process flow diagram for steam regeneration is shown on Figure 3-3.

(f) If a manufacturer supplied the carbon regeneration system, they will supply the operation procedures and initial values for regeneration times and temperatures. Bench and pilot testing should also provide initial values for these parameters, especially the bed temperature that must be reached for effective regeneration. However, it must be emphasized that all of these parameters must be confirmed during start up and shakedown of the system. Even if bench or pilot testing was performed, the full scale system's initial values should be varied, because the full scale system's optimal settings will almost certainly vary to some degree from the optimal bench/pilot testing values. If bench and pilot testing were not performed on the actual waste stream, the initial operational system settings from the manufacturer should be conservatively modified (longer regeneration time and higher final regeneration temperature) until optimum parameters for the full-scale system are determined.

(g) The waste streams from most hazardous waste sites are not concentrated enough to generate sufficient heat to ignite the adsorption bed, but if a stream is very concentrated (e.g., soil vapor extraction vapor at the beginning of a remediation), the heat of adsorption should be monitored.

(h) The reported time required to complete a regeneration cycle varied among the manufacturers contacted for this study because of a number of variables, including the contaminant load and the size of the regenerating equipment. One manufacturer advised that a 2000-lb carbon bed could be regenerated in approximately 3 hours using a 20-hp boiler (Appendix D, Continental).

(i) In-vessel steam and hot inert gas regeneration, even using superheated steam, will not reach the temperatures used by reactivation furnaces (at least 1500^{o}F). Therefore, only compounds with boiling points less than the temperature reached in the vessel will be completely desorbed. This is not a serious problem if the contaminant stream is relatively pure, e.g., treating groundwater contaminated by a solvent spill. For a situation like this, the carbon bed can be regenerated by raising its final temperature above the boiling point of the sole contaminant of concern. However, when regenerating with steam, it is not necessary to have the temperature above the boiling point of the contaminants, as steam distillation occurs. To remove all of the contaminant higher temperatures are needed.

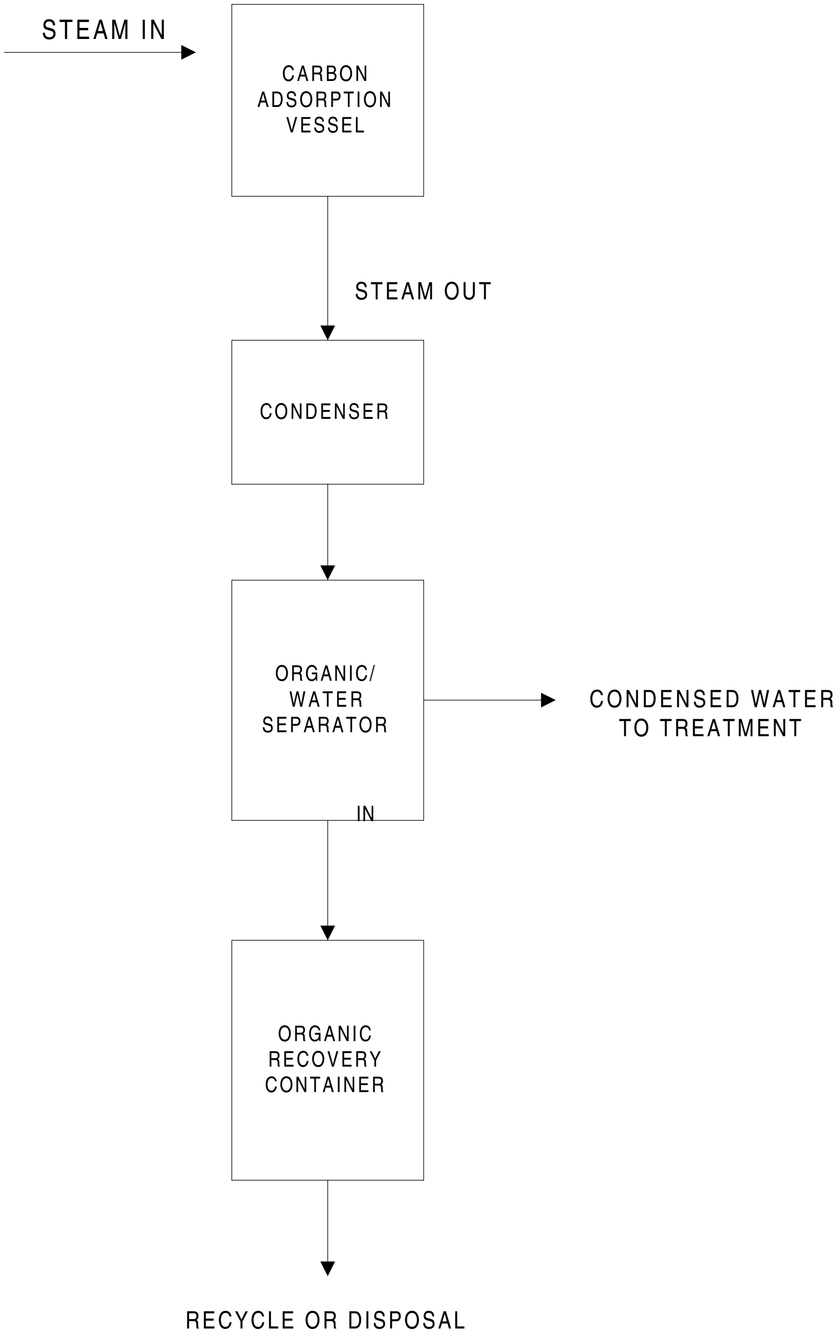


Figure 3-3. Steam regeneration.

(j) If, however, the contaminant stream contains many contaminants, which is the norm for groundwater treatment operations at many hazardous waste sites, those contaminants with boiling points higher than the high temperature reached during steam or inert gas regeneration will not be removed. Because the system operator may not be analyzing for some of the contaminants that are not being removed during regeneration, the operator may not be aware that these compounds are fouling the carbon. Over time, these so-called "heavy boilers" can accumulate on the carbon and reduce its capacity. Because these compounds tend to have higher molecular weights, they clog the intermediate sized pores in the carbon, blocking access to the smaller pores that adsorb the lighter compounds of concern.

(k) Spent carbon can be tested to determine if regeneration is adequately removing the adsorbed contaminants. The overall capacity of the carbon can also be tested.

(l) One method of removing these heavy boiler compounds is to send the carbon off-site periodically to be reactivated. Because steam regeneration will remove most of the contaminants of concern, off-site reactivation need not be done very often, perhaps no more than once per year. The actual off-site reactivation schedule will depend on the volume and composition of the waste stream being treated. Another removal method is to wash the carbon periodically with a solvent that will dissolve the heavier compounds. While this method avoids a carbon change out, it generates another waste stream that must be properly analyzed, stored, and manifested for off-site disposal or recycling.

(m) The potential for this interference from heavy boilers can be investigated during bench or pilot testing if the actual waste stream to be treated is used to test the capacity of the carbon. The amount of the contaminants of concern adsorbed onto the test columns is routinely checked against the amount desorbed after each run. If the amount of contaminants of concern adsorbed decreases over several test runs, then it is possible that some unknown contaminant is accumulating on the carbon and decreasing its adsorptive capacity. If this interference is detected during bench or pilot testing, various solvents can be tested to determine their effectiveness in removing the contaminant. Periodic testing is recommended if the actual waste stream can change. Table 3-2 summarizes information for steam and hot gas regeneration systems and presents brief information on solvent and pressure swing regeneration not discussed further in this Design Guide.

Table 3-2
On-site Regeneration, On-site Reactivation, and Off-site Reactivation Process Summary

Parameter	On-site Regeneration Steam	On-site Regeneration Hot Inert Gas	On-site Regeneration Solvent
Organic Chemicals that can be Desorbed	Most VOCs, Many SVOCs	Most VOCs, Many SVOCs	Any Organic that is Soluble in the Solvent
Carbon from Liquid or Vapor Systems Treated	Most Systems Treat Spent Carbon from Vapor Systems, Due to Extra Drying Costs of Liquid Systems.	Most Systems Treat Spent Carbon from Vapor Systems, Due to Extra Drying Costs of Liquid Systems.	Most Systems Treat Spent Carbon from Liquid Systems, Due to Extra Drying Costs of Vapor Systems.
Size Range or Process Rate	Systems Can Treat Up to 100,000 + cfm	Systems Can Treat Up to 100,000 + cfm	
Advantages	No Carbon Loss, compared to 5 to 15% of the Carbon Mass per Reactivation; Steam is Often Available at No or Low Cost; No Carbon Storage Vessel Needed; Potential for Recovery/Reuse of Contaminants.	No Carbon Loss, compared to 5 to 15% of the Carbon Mass per Reactivation; No Carbon Storage Vessel Needed; Potential for Recovery/Reuse of Contaminants.	No Carbon Loss, compared to 5 to 15% of the Carbon Mass per Reactivation; Ability to Regenerate Problem Contaminants, Such as "Heavy Boilers"; No Carbon Storage Vessel Needed; Potential for Recovery/Reuse of Contaminants.
Disadvantages	Condensate Storage must be provided; O&M and possibly Capital costs for the Boiler System; System Carbon may require Periodic Reactivation; and at Haz. Waste Sites, Condensate may be an Unusable Mixture that must be Disposed. Increased capital cost for materials of construction. Adsorbed organics remain on the carbon-capacity becomes "working capacity" which may cause short runs.	Condensate Storage must be provided; Capital and O&M costs for the Inert Gas System; System Carbon may require Periodic Reactivation; and at Haz. Waste Sites, Condensate may be an Unusable Mixture that must be Disposed. Increased capital cost for materials of construction. Adsorbed organics remain on the carbon-capacity becomes "working capacity" which may cause short runs.	Costs for Solvent Storage and Piping and Makeup Solvent, Problems with Recovering Water Miscible Solvents, Problems with Water Immiscible Solvents Penetrating All the Carbon's Pores, and Flammability Concerns with the Solvents.
Capital Costs (1)	Usually Less Than Reactivation Furnaces.	Usually Less Than Reactivation Furnaces.	Usually Less Than Reactivation Furnaces.
O&M Costs	Estimated at 1/3 of Reactivation. Costs for Steam Condensate Water Must Be Included.	Estimated to Be Approximately Equal To or Slightly More than Steam Regeneration.	Estimated to Be More Than Steam or Hot Inert Gas.

Table 3-2 (Continued)

Parameter	On-site Regeneration Steam	On-site Regeneration By Hot Inert Gas	On-site Regeneration Solvent
Residues to Manage	Water/Waste Mixture if Miscible, Organic Phase & Aqueous Phase if Non-Miscible	Waste Stream Condensate, or Air Emissions if Waste is Oxidized	Solvent/Waste Mixture
Manufacturers	AmCec; Continental Remediation Systems; Dedert; RaySolv; Wesport Environmental Systems; Vara International	RaySolv; Vara International	Waste Min, Design Only, PACS - Bench Scale Process, Only
Health/Safety	ASME Vessels Recommended, Wet Activated Carbon Adsorbs Oxygen, So Design Vessel for Confined Space Entry.	ASME Vessels Recommended, Include Ventilation for Vessel	ASME Vessels Recommended, Store Solvent and Solvent/Waste as per NFPA Standards.
EPA Regulations	Water (Steam Condensate) Treatment, Waste Stream Storage and Disposal or Recycle.	Condensate Stream Storage and Disposal or Recycle.	Water (Steam Condensate) Treatment, Waste Stream Storage and Disposal or Recycle
Pilot Testing Needed	Yes	Yes	Yes
Temperature Concerns	System Temperature Must Exceed COC's Boiling Point.	System Temperature Must Exceed COC's Boiling Point.	In Final Stage, System Temp. Must Exceed Solvent's Boiling Point.
Organic Chemicals that can be Desorbed	VOCs, Some VOCs	All	All

(1) Basis: 1996 Costs

Table 3-2 (Continued)

Parameter	On-site Regeneration By Pressure Swing Regeneration	On-site Reactivation Rotary Kiln	On-site Reactivation Multiple Hearth
Carbon from Liquid or Vapor Systems Treated	Treat Spent Carbon from Vapor Systems, Only. Usually on Storage Tanks or Processes.	Able to Treat Spent Carbon from Liquid or Vapor Waste Treatment Systems	Able to Treat Spent Carbon from Liquid or Vapor Waste Treatment Systems
Size Range or Process Rate	Systems Can Treat Contaminant Concentrations from 1,000 to 500,000 ppm.	Systems Can Reactivate 200 to 1,000 lbs per Hour.	Systems Can Reactivate 500 to 5,000 + lbs per Hour
Advantages	No Carbon Loss, compared to 5 to 15% of the Carbon Mass per Reactivation; No Carbon Storage Vessel Needed; Recovery of a Reusable Condensate Stream.	Complete Destruction of Contaminants; Control over Entire Process; Easier to Maintain than Multiple Hearth.	Complete Destruction of Contaminants; Control over Entire Process; More Fuel Efficient than Rotary Kiln; Better Reactivation Quality Control than Rotary Kiln.
Disadvantages	Higher Capital Costs than Other Regeneration Systems, Operationally Complex Systems, All Systems are Site-specific. Need to either adsorb at high pressures or desorb under vacuum conditions.	Loss of 5 to 15% of Carbon mass per Cycle (Average Loss -7%); Higher Capital Costs; Additional Space, Utility, and Training.	Loss of 5 to 15% of Carbon Mass per Cycle (Average Loss - 7%); Higher Capital Costs; Additional Space, Utility, and Training Requirements;
Capital Costs (1)	$500,000 to Several Million Dollars per System.	$150,000 to $700,000 +	$1,000,000 +/- for a 500 lb per Hour Unit.
O&M Costs	Requested But Not Provided by the Manufacturer	Reported at less than $0.05 per lb.	Costs Not Provided. Fuel Use estimated at 7 scf of Natural Gas per lb of Carbon.
Residues to Manage	Usually, Pure Product. Occasionally, Some Water Condensate.	Air Emissions, Only	Air Emissions, Only
Manufacturers	Radian; Design and Engineering Services, Only	College Research Corp.	Hankin Environmental Systems
Health/Safety	Requested But Not Provided by the Manufacturer	ASME Vessels Recommended, Wet Activated Carbon Adsorbs Oxygen, So Design Vessel for Confined Space Entry.	ASME Vessels Recommended, Wet Activated Carbon Adsorbs Oxygen, So Design Vessel for Confined Space Entry.
EPA Regulations	Condensate Stream Storage and Recycle.	Possible Air Emissions Requirements, Spent Carbon Storage Requirements.	Possible Air Emissions Requirements, Spent Carbon Storage Requirements.

Table 3-2 (Continued)

Parameter	On-site Regeneration By Pressure Swing Regeneration	On-site Reactivation Rotary Kiln	On-site Reactivation Multiple Hearth
Pilot Testing Needed	Yes	Yes	Yes
Temperature Concerns	Heat of Adsorption must be Monitored and Managed by the System.	Reactivation Temperature Must be High Enough to Char and Gassify Contaminants, but Not So High that Excess Activated Carbon is Lost. Also, each Reactivation Stage's (such as Drying) Temperature Must be Controlled.	
Carbon from Liquid or Vapor Systems Treated	Able to Treat Spent Carbon from Liquid or Vapor Waste Treatment Systems	Able to Treat Spent Carbon from Liquid or Vapor Waste Treatment Systems	Able to Treat Spent Carbon from Liquid or Vapor Waste Treatment Systems
Size Range or Process Rate	System Can Reactivate 100 to 200 lbs. Per Hour.	Requested But Not Provided by the Manufacturer.	Limited by Manufacturer Site's Capacity, But up to 20,000 lbs. Of Carbon per Truck Load
Advantages	Complete Destruction of Contaminants; Control over Entire Process; System Footprint is Small; Low Utility Requirements.	Complete Destruction of Contaminants; Control Over Entire Process	Minimal Capital Costs, Especially if No Carbon Storage Vessel is Provided; Convenience, Complete Destruction of Contaminants: Quality Control of Reactivation Process Provided by Manufacturer.

Table 3-2 (Continued)

Parameter	On-site Reactivation Electric Multiple Hearth	On-site Reactivation Electrically Heated Furnace	Off-site Reactivation
Disadvantages	Loss of 5 to 15% of Carbon Mass per Cycle (Average Loss – 7%; Higher Capital Costs; Additional Space, Utility, and Training Requirements. Need to either adsorb at high pressures or desorb under vacuum conditions. Corrosion control required on heater elements.	Loss of 5 to 15% of Carbon Mass per Cycle (Average Loss - 7%); Higher Capital Costs; Additional Space, Utility, and Training Requirements; Corrosion control required on heater elements.	Loss of 5 to 15% of Carbon Mass per Cycle (Average Loss - 7%); High System O&M Costs, Scheduling Concerns with Changeouts, Need to Provide Truck Access for Changeouts. Treatment site does not have permitting concerns. Off-site reactivators will often exchange "pound-for-pound" either virgin or reactivated, and site does not bear makeup requirements.
Advantages	Low volume of off-gas requiring treatment	Low volume of off-gas requiring treatment	
Capital Costs (1)	Manufacturer Prefers to Lease. If Purchased, Cost is $120,000 per Unit plus Royalty per lb of Carbon Reactivated.	Requested But Not Provided by the Manufacturer	Truck Access and possibly, costs for a Spent Carbon Storage Vessel.
O&M Costs	Costs Not Provided. Electricity Use Estimated at 1 to 2 kWh of Electricity per lb Of Carbon.	Costs Not Provided. Electricity Use Estimated at 1 kWh of Electricity per 1.5 to 2 lb Of Carbon.	Included in the Manufacturer’s Reactivation Costs.
Residues to Manage	Air Emissions, Only.	Air Emissions, Only	Manufacturer’s Responsibility
Manufacturers	COH Corp.	Custom Environmental International	Advanced Recovery Tech; Calgon; CETCO; Envirotrol; Nichem; Norit Americas; Service Tech; U.S. Filter/Westates
Health/Safety	ASME Vessels Recommended, Wet Activated Carbon Adsorbs Oxygen, So Design Vessel of Confined Space Entry	ASME Vessels Recommended, Wet Activated Carbon Adsorbs Oxygen, So Design Vessel for Confined Space Entry.	Changeouts Concerns, such as Vessel Pressurization, Change out Valve Sequencing, and Possibly Dust Control.
EPA Regulations	Possible Air Emissions Requirements, Spent Carbon Storage Requirements.	Possible Air Emissions Requirements, Spent Carbon Storage Requirements.	Possible Air Emissions Requirements, and Generator’s Transportation Requirements.
Pilot Testing Needed	Yes	Yes	Yes

Parameter	On-site Reactivation By Electric Multiple Hearth Electrically Heated Furnace	Off-site Reactivation
Temperature Concerns	Reactivation Temperature Must be High Enough to Char and Gassify Contaminants, but Not So High that Excess Activated Carbon is Lost. Also, each Reactivation Stage's (such as Drying) Temperature Must be Controlled.	

(1) Basis: 1996 Costs

(2) *Sampling Requirements.* The spent activated carbon must be tested before a manufacturer will accept it for reactivation. Toxic characteristics leaching procedure (TCLP) analysis, total volatiles scan, PCB testing, and other testing may be required. Also, most off-site reactivators need to predict safe and satisfactory reactivation under their furnace operating parameters in order to accept spent carbons. One manufacturer (Appendix D, NORIT Americas) requires that each spent carbon have a Profile Sheet on file. To fill out this profile the facility operator would need to know if the spent carbon was a RCRA characteristic waste or a RCRA listed waste, the spent carbon's pH, and the Department of Transportation shipping name. In addition, the facility operator would have to be able to answer a number of specific questions, such as does the carbon contain Vinyl Chloride regulated under 29 CFR 1910.1017?

(3) *Manifesting, Transportation, and Placarding Requirements.* When spent carbon meets the definition of a D.O.T. hazardous material (i.e., EPA hazardous waste), specific D.O.T. training requirements (49 CFR 172.700) will apply to persons shipping spent carbon off-site. The classification, management, and off-site disposition of spent carbon must be coordinated closely with the facility operator, and the installation. The facility operator will normally be responsible for the preparation of shipping papers, land disposal restriction notifications, etc. The installation personnel will normally sign the paperwork after it is prepared. Most carbon manufacturers can provide assistance to properly manifest the spent carbon. The carbon shipper is responsible for complying with all transportation and placarding requirements. If the material is a D.O.T. hazardous material, D.O.T. transportation requirements apply. The amount of insurance required per transport should be listed in the contract and reviewed periodically. Finally, the facility operator must be sure to obtain the appropriate Certificate of Destruction or Reactivation from the reactivation facility, listing how the adsorbed organic chemicals were destroyed or disposed of.

(4) *Off-site Carbon Reactivation.* These manufacturers are listed in Appendix D. Some manufacturers offer special services, such as segregating, reactivating, and maintaining a facility's carbon for that facility's own reuse. Makeup carbon for process losses can be obtained from the reactivated carbon pool or can be virgin carbon. Many users require that the makeup carbon be virgin. They do not want to take the chance of using carbon from other sources. However, it is very difficult to ensure complete segregation of small amounts of carbon, i.e., less than10,000 lb, as it moves through a large-scale reactivation process. Users need to verify that good quality control is employed. Off-site regeneration also has the advantage of the site receiving a known amount of constituent-grade product and you need not be concerned over quality of product or amount of makeup carbon required. Table 3-2 summarizes the information on off-site reactivation processes.

3-3 Non-carbon Adsorption.

a. General. Modified clay, polymeric adsorbents, and zeolite molecular sieves are also currently used in hazardous waste treatment. Some of these adsorption media are used primarily as pre-treatment for activated carbon. For example, these media may be used to remove compounds that may, through physical or chemical interactions, degrade the effectiveness of the activated carbon. Modified clay is primarily used as a pre-treatment for liquid phase systems, between an oil/water separator, and as a treatment process sensitive to emulsified oil, such as activated carbon or reverse osmosis. Without the use of the modified clay, the oils would blind the carbon, drastically lower its adsorption capacity, increase the cost of operations, and ultimately complicate the regeneration of the carbon.

(1) The zeolites can also replace activated carbon in several applications. Research indicates that the zeolites are mainly used for high volume vapor stream treatment. Table 3-3 summarizes the key differences among the media. Activated carbon is included for reference.

(2) Some of the polymeric adsorbents appear to be much more selective than activated carbon. For waste streams that have only one contaminant of concern, it may be possible to find an alternative adsorbent that is specific to the contaminant. By only adsorbing the single contaminant of concern, the working capacity of the alternative adsorbent may exceed the capacity of activated carbon, which loses some of its working capacity to competitive adsorption of other compounds in the waste stream. Also, for vapor phase applications, some of these alternative adsorbents are less affected by high relative humidity and high temperatures than activated carbon. For service in these environments, an alternative adsorbent may be able to provide treatment without pre-treatment of the waste stream.

(3) Primary selection criteria for using these alternative adsorbents and systems include the effectiveness of adsorbing the contaminants of concern and the overall lifecycle cost compared to using activated carbon. For most vapor or liquid service, both the proper alternative adsorbent and activated carbon will adequately adsorb the contaminants of concern. The alternative adsorbents usually have higher capital costs and lower operations and maintenance (O&M) costs. So, for short-term (2 years or less) projects, such as a one time spill remediation, the alternative adsorbent will typically not be as cost effective as activated carbon systems. For long term projects, the lower O&M costs of the alternative adsorbent can make activated carbon less cost effective. The Micro Computer Aided Cost Estimating System (MCACES), the U.S. Army Corps of Engineers cost-estimating program, along with the standard Cost Engineering HTRW Remedial Action-Work Breakdown Structure (RA-WBS) or the USAF RACER system, can be used to calculate the lifecycle costs of these systems and to check on a manufacturer's costs for a system.

Table 3-3
Alternative Adsorption Media Summary

Parameter	Primary Treatment	Selective Adsorbent	Affected by High RH	Affected by Temperature	Reacts with Adsorbates	Media Capital Cost *	Media O&M Costs
Activated Carbon (AC)	Yes	No	Yes	Yes	Yes, especially Ketones	Low, $1.00 per lb	High
Modified Clays	No, Pre- treatment	No	NA, Liquid Treatment System	NA	No	Medium, $1.50 per lb (1)	NA, Once Through Material
Polymeric Resins	Yes	Can be Selective	Yes, but not as much as AC	Yes, but not as much as AC	No	High, $8 to $35 per lb	Low
Zeolites	Yes	Can be Selective	Not as much as AC or Resins	No	No	High, $7 to $10 per lb	Low
Parameter	Vapor Service	Liquid Service	Typical Adsorbents	Regeneration Methods	cfm/gpm Range	Health / Safety	Bench / Pilot Testing Needed
Activated Carbon (AC)	Yes	Yes	Nearly All Organics	Multiple; Steam, Pressure, and Solvent	to 200,000 + cfm, to MGD flows	Adsorbs oxygen, corrodes steel	Yes, but not as much as with Resins or Zeolites
Modified Clays	No	Yes	Emulsified Oil & Grease	NA, Once Through Material	2 to 200 gpm	Contains silica, control dust	Yes
Polymeric Resins	Yes	Yes	Chlorinated & Non-Chlorinated VOCs	Multiple; Steam, Solvent, Pressure, Microwave, and Hot Inert Gas	< 500 to 20,000 cfm 1 to 1,000 gpm		Yes
Zeolites	Yes	No	Chlorinated & Non-Chlorinated VOCs	Steam and Hot Air	7,500 to 200,000 cfm		Yes, but not as much as Resins

* - 1998 Costs
RH - Relative Humidity
NA - Not Applicable

NOTES: 1 - Rated medium because media can not be regenerated and reused.

(4) A summary of the technical information needed to evaluate when alternative adsorption media may be selected in lieu of activated carbon is as follows:

- Media description.
- Adsorption system description.
- Availability.
- Estimated purchase and operating cost.
- Advantages and disadvantages for the application.
- Organic chemicals and contaminant ranges that can be adsorbed.
- Adsorption isotherms.
- Regeneration methods.
- Safety data and considerations, including loading, unloading, and handling methods.
- Applications.
- Pressure drop through the media.
- Effects of temperature and relative humidity.
- Any proprietary ownership and use limitations.

(5) For general information on isotherms, breakthrough, pressure drop, pilot tests, bed expansion regulations/disposal, safety concerns, pH (liquid phase), refer to these topics in the activated carbon paragraphs. Non-carbon adsorption media are very different from activated carbon. Design information must be obtained directly from the media manufacturer or the adsorption equipment supplier.

b. Liquid Phase Non-carbon Adsorbents.

(1) *Organically Modified Clays.* This material can be a mixture of anthracite and bentonite clay or bulk clay. The clay in both media has been treated with quaternary amine, which makes the surface of the clay much more active. One manufacturer, Biomin, Inc., reports that

the clay removes emulsified oil and grease, and high molecular weight hydrocarbons, naphthalene, anthracene, COD, BOD, and heavy metals from liquid media. The material can remove up to 60% of its weight in oil and other organic chemicals; however, it cannot be regenerated. Disposal options include its being used as fuel if the oil adsorbed has sufficient heating value. Otherwise, disposal is governed by the type of organic contaminants the clay has adsorbed. Typically, the spent material has been incinerated, blended into cement kiln fuel, or treated biologically (e.g., landfarming), or placed in a landfill.

(a) Modified clay is usually applied as a pre-treatment unit upstream of activated carbon or reverse osmosis units that might be blinded by emulsified oil. While the clay can remove large amounts of free oil, its capacity will be used up rapidly. Therefore, it is usually put on-line downstream of a gravity oil/water separator, so that the clay's capacity is used on emulsified oil only. Another application is as a final polish unit after an oil/water separator and before the treatment stream discharge.

(b) General specifications, design criteria (such as pressure drop through the system), recommended bed depth, hydraulic loading, recommended contact time, bed expansion during backwashing, swelling when wetted, and safety considerations must be obtained from the manufacturer. One manufacturer recommends a minimum bed depth of 3 ft, a hydraulic loading of 2 to 5 gpm/ft^2, a contact time of 15 minutes, and a headloss of 1 to 5 in. of water per foot of bed when contaminated.

(c) No proprietary ownership or use limitations were mentioned in the manufacturers' data. The clay swells by at least 10% and sometimes as much as 20% when wetted, so the adsorption vessel should not be completely filled with the media. Also, the spent clay sticks together in "grapefruit" sized lumps, making it difficult to remove from the adsorber unless there is a side wall manhole. One manufacturer recommends the clay media not be used in fiberglass vessels, as it can be difficult to service these types of tanks once the clay is spent.

(2) *Polymeric Resin Adsorbents*. There are three primary types of polymeric resins for liquid service: carbonized ion exchange resins, divinyl benzene (DB) adsorbents, and post-cross-linked adsorbents. Table 3-4 compares several features of these different media.

(a) Each of these types of resins is manufactured using a different process. Because the manufacturers have greater control over the basic feed stock and processing conditions, these materials can be "fine tuned" to a greater degree than can activated carbon. For example, it is possible to create carbonized resins with pore structures that will adsorb only contaminants of certain molecular weights. As with carbon the EBCTs for liquid phase applications are typically much greater than EBCTs for vapor phase applications.

(b) Pressure drops through the various media are usually included in the manufacturer information. One manufacturer reports that pressure drops for liquid phase systems ranged from

1 psi/ft (23 kPa/m) of bed depth for a flow rate of 10 gpm/ft^2 to 10 psi/ft (226 kPa/m) for a flow rate for 100 gpm/ft^2. Pressure drop from one manufacturer is a function of the velocity of the liquid through the adsorption bed raised to a power (i.e., pressure drop = K_1 (velocity)^{K_2}). Manufacturers' literature often represents this as a straight line on a log-log graph. Resins are patented by their manufacturers. A license or other agreement is required to use them. Some resins can be regenerated with steam, but specific information on regeneration must be obtained from the manufacturer.

(c) Water temperature is not usually a problem for groundwater and wastewater treatment. If the contaminated water's temperature is near a specific contaminant's boiling point, however, the resin's desorption kinetics may be so fast that desorption occurs almost as rapidly as adsorption. In this case, the resin's working adsorption capacity will be too low to adequately adsorb the contaminant. For example, vinyl chloride is a gas at room temperature. Vinyl chloride-contaminated waters may have to be cooled, or extra capacity may need to be built into the adsorption bed, in order to get adequate adsorption.

(d) Polymeric resins do not tolerate significant biological fouling. Polymeric resins can support biological growth, but the temperature of the steam regeneration (298°F) is usually sufficient to kill any biological film. All three primary types of polymeric resins, carbonized ion exchange resins, vinyl benzene (DB) adsorbents, and post-cross-linked adsorbents are also used for vapor adsorption. Table 3-4 compares several features of these different media. Table 3-5 lists the organic contaminants that can be adsorbed by three manufacturer's products.

(3) *Zeolite Molecular Sieves.* Zeolite molecular sieves are not used in liquid applications.

c. Vapor Phase Non-carbon Adsorbents.

(1) *Polymeric Adsorbents.* Each type of phenolic resin is manufactured using a different process. Because the manufacturers have greater control over the feed stock and processing conditions, it is possible to create carbonized resins with pore structures that will adsorb only contaminants of certain molecular weights. Divinyl benzene adsorbents are hydrophobic, allowing them to be used in high relative humidity environments. These resins usually have very fast adsorption kinetics, which allows the empty bed contact time (EBCT) of the adsorber to be reduced. For example, a typical activated carbon EBCT for a vapor phase unit is 2 to 4 seconds. For a resin vapor phase adsorber, EBCTs can be as little as 0.02 seconds, allowing the designer to use much smaller adsorbent beds. The advantage of polymeric resins is that they do not react with the contaminants during adsorption to the degree that activated carbon does. For example, activated carbon adsorption is generally an exothermic reaction and there have been instances of activated carbon bed fires while treating highly contaminated streams. Polymeric adsorbents are much less reactive, allowing for fewer engineered safety controls on the system (Calgon, 1994).

(a) Pressure drops for gas through the various media must be obtained from the manufacturer. Typical pressure drops for a 40-cfm/ft^2 vapor velocity ranged from approximately 4.5 in. of water per foot of bed depth to 45 in. of water per foot of bed depth.

(b) All the resins lose adsorption capacity as temperature increases. They also lose capacity as relative humidity increases, but at a lower rate than activated carbons do. As expected, the hydrophobic resins do better than the hydrophilic resins in high relative humidity service.

(2) *Zeolite Molecular Sieves.* Zeolite molecular sieves are natural or man-made minerals composed of silicon and aluminum. These media have many of the same advantages as the polymeric resins. Zeolites are mainly used for high volume vapor stream treatment. The zeolites can be made hydrophobic, so they can be used in high RH environments. The engineered zeolites can be manufactured with uniform pore diameters, creating materials that selectively adsorb contaminants based on the contaminant's molecular size or weight. Because they are made entirely from inorganic oxides of silicon and aluminum, zeolites can withstand temperatures up to 800°C in dry air and up to 500°C in humid or steam environments. This temperature resistance allows zeolites to be regenerated at high temperature with air, eliminating the formation of contaminated condensate. Like the resins, zeolites are much less reactive than activated carbon when adsorbing ketones and other reactive organic chemicals. Also, zeolite's resistance to high temperatures allows the operator to burn off high boiling compounds or polymerized materials, like styrene, from the zeolite without damaging the media.

(a) Manufacturers can produce zeolites especially for control of volatile organic chemicals that can adsorb the following organic compounds: benzene, toluene, xylene, phenol, cumene (isopropyl benzene), methylene chloride, trichloroethylene vinyl chloride monomer, alcohols, aldehydes, nitriles, aliphatics, CFCs, ketones, organic acids, and low molecular weight pesticides. Large molecules, such as multi-aromatic ring compounds, will not be adsorbed by zeolites because the molecules are too large to fit through the molecular sieve pore openings. These small pore sizes and the uniformity of pore sizes in the zeolites may prevent fouling by heavy boilers. The adsorption capacity of the zeolites is approximately 0.1 to 0.15 g of contaminants per gram of zeolite. Table 3-6 summarizes this information from UOP, a manufacturer of zeolites.

Table 3-4
Comparison of Polymeric Adsorbents

Parameter	Carbonized Ion Exchange Resin	Divinyl Benzene Resin	Post-Crosslinked Resin
Physical Shape	Spherical Beads	Spherical Beads	Spherical Beads
Surface Area	550 to 1100 (m^2/g)	400 to 700 m^2/g	900 to 1100 m^2/g
Sales Price *	$35/lb	$8 to $16/lb	$16 to $25/lb
Hydrophobic or Hydrophilic	Hydrophilic	Hydrophobic	Variable Hydrophobicity
Pore Size Distribution	Unique Pore Size Distributions	Larger Average Pore Sizes	Unique Pore Size Distributions
Crush Resistance	High, compared to AC	High, compared to AC	High, compared to AC
Reactivity of Resin Surface	Reactivity lower than AC	Reactivity lower than AC	Non-catalytic Adsorption Surface
*1998 Rates AC – Activated Carbon			

(b) The zeolites are used in three different applications: pressure swing systems, temperature swing fixed bed systems, and temperature swing wheels.

(c) Temperatures affect the adsorption capacity of the zeolites. Adsorption capacity fell from approximately 0.15 g/g 22°C to approximately 0.12 g/g at 60°C. However, as the media were designed to operate in very high temperature waste steams, temperature effects above 60°C are not expected to be significant. In most of the cases, the different RH adsorption curves are relatively similar, indicating no significant loss of capacity at high RH levels. Again, as the media have been engineered to be hydrophobic and organophilic, this was expected.

(3) *Organically Modified Clays.* Organically modified clays are not used in vapor applications.

d. Regeneration. Polymeric media can be regenerated at low temperatures, allowing nearly all systems to use on-site regeneration. Some activated carbon systems must ship the carbon offsite for reactivation. The polymeric media use a variety of regeneration methods, including hot nitrogen gas or air, microwave or infrared heating, and temperature-vacuum. These media are usually produced in the form of beads. The beads have high crush resistance, so attrition during loading and regeneration is usually much less than with activated carbon. While an activated carbon system can lose up to 12% of the carbon during each reactivation cycle, resin systems can operate at practically zero loss. For example, when American Society of Testing Materials (ASTM) Method D 5159, *Standard Test Method for Dusting of Granular Activated Carbon*, is used to test resins, the amounts of dust generated are so low as to be statistically insignificant.

Table 3-5
Organic Contaminants Adsorbed by Polymeric Media

Trade Name	OPTIPORE V493	OPTIPORE V502	OPTIPORE XUS 43565.01	OPTIPORE V323
Manufacturer	Dow	Dow	Dow	Dow
Media Type	Post-Cross Linked	Post-Cross Linked	Post-Cross Linked	Post-Cross Linked
Contaminant	Formaldehyde, MEK, Methanol, Terpene, Styrene, Toluene, Xylene, Acetone, Methanol, Isopropyl Alcohol, Butyl Acetate, Methylene Chloride, 1,1,1-TCE, TCA, and PCA	Toluene, Xylene, MEK, Acetone, Methanol, Isopropyl Alcohol, Butyl Acetate, Methylene Chloride, 1,1,1-TCE, TCA, and PCA	Xylene, MEK, MIBK, Acetone, Methanol, Isopropyl Alcohol, Butyl Acetate, Methylene Chloride, TCA, and PCA	Styrene

Trade Name	AMBERSORB 563	AMBERSORB 563*, 564, 572, & 575	AMBERSORB 600	Hypersol-Macronet Sorbent Resins **
Manufacturer	Rohm & Hass	Rohm & Hass	Rohm & Hass	Purolite
Media Type	Carbonaceous	Carbonaceous	Carbonaceous	Crosslinked Polystyrene
Contaminant	1,1,2-Trichloroethene and Chloroform	TCE, VC, MEK, Methanol, Cyclohexanoee, and Dichloromethane	TCE	Pesticides, Herbicides, Phenol, and Chlorinated Phenols

* - Ambersorb 563 was listed separately and grouped with Ambersorb 564, 572, and 575.
** - Purolite did not provide data matching specific resins to specific contaminants.

Table 3-6
HiSiv Zeolite Information Summary

	Zeolite			
	HiSiv 1000	HiSiv 3000	HiSiv 4000	HiSiv 5000
Contaminants Adsorbed	Larger molecules, such as toluene and MIBK	Small molecules, such as acetone, ethanol, and methylene chloride	Larger molecules, such as isopropyl acetate and trichloroethylene	VOC mixtures, such as printing or paint-spray solvents
Application	Moderate concentrations with average humidity	High humidity applications	Low contaminant concentrations, high humidity	Low contaminant concentrations, high humidity
Regeneration	High temp. or reduced pressure, purge with air, steam, or other gasses	High temp. or reduced pressure, purge with air, steam, or other gasses	High temp. or reduced pressure, purge with air, steam, or other gasses	High temp. or reduced pressure, purge with air, steam, or other gasses
Physical Forms	Powder, Extrudate, 1/8 in. Tri-Lobe, ¼ in. Tri-Lobe	Powder, Extrudate, 1/8 in. Tri-Lobe, ¼ in. Tri-Lobe	Powder	1/8 in. Tri-Lobe

HiSiv zeolites are manufacturered by Universal Oil Products.

CHAPTER 4
CAPITAL AND OPERATING COSTS

4-1. RACER. The Remedial Action Cost Engineering and Requirements (RACER) estimating software (Talisman Partners, Ltd., 1998) is an adequate tool for developing cost estimates for liquid and vapor phase adsorption technologies. RACER is a parametric cost modeling system that uses a patented methodology for estimating costs. RACER cost estimating technologies are based on generic engineering solutions for environmental projects, technologies, and processes. The generic engineering solutions were derived from historical project information, industry data, government laboratories, construction management agencies, vendors, contractors, and engineering analysis.

4-2. Estimating. To develop an estimate for the liquid or vapor phase technologies within RACER, you must at least provide values for required parameters that affect the cost for the technology. These parameters include system redundancy, total organic concentration and safety level. RACER will also estimate O & M costs for these technologies and spread these costs into the out years for the duration of the O & M.

APPENDIX-A
LIQUID PHASE ADSORBER DESIGN EXAMPLE

A-1. Problem. Given the following pilot study information, design a liquid phase granular activated carbon (GAC) adsorption system for treating RDX-contaminated groundwater.

a. Background data.

(1) *Given.*

- Flow rate: 15.8 L/s (250 gpm)
- Contaminant concentration influent: 69 ug/L
- Contaminant concentration effluent: 4 ug/L

(2) *Determine.*

- Surface loading rate.
- Empty bed contact time and number of columns.
- Column nominal diameter and mass of GAC/column.
- Bed depth.
- Volume of water treated per change out period.

b. Isotherm evaluation. A number of carbons were evaluated on the basis of isotherm results, and the most promising carbon was selected for the pilot test and the results of the test are graphically presented in Figure A-1. A second option to this process is to hire an independent laboratory to conduct accelerated carbon column pilot testing, evaluate several carbons, and recommend one.

c. Pilot test. Based on Figure A-1, the number of bed volumes versus the concentration at which the effluent reaches our maximum allowable concentration of 4 μg/L is 22,000. Comparing the number of bed volumes treated using two columns in series, we see the number of bed volumes treated before breakthrough equals 54,000, or approximately 145% more bed volumes than using a single column. Using two columns in series, each with a detention time of 2 minutes, means that the first column will be nearly exhausted with the effluent concentration corresponding to 67/69 × 100 = 97% of the influent concentration. To most effectively use the carbon in a system with two columns in series, the detention time in each column should be 6 minutes. This will ensure that the lead column GAC is fully exhausted before the adsorption zone passes completely through it and before to the effluent in the lag column reaches the maximum allowable concentration. The pilot plant information is provided in Table A-1.

Table A-1
Pilot plant data

Carbon Sample	XYZ Carbon Company
Column Inside Diameter	108 mm (4.25 in. [0.354 ft])
Column Area	9150 mm^2 (0.0985 ft^2)
Bed Volume	5.56 L (0.197 ft^3 [1.47 gal])
Flow Rate	2.84 L/m (0.75 gpm)
Hydraulic Loading	310 Lpm/m^2(7.6gpm/ ft^2)
Bed Depth	0.61 m (2 ft)
EBCT (each column)	2 min
RDX Influent Conc	69 µg/L
Weight of GAC per Column	2.32 kg (5.1 lb)
Weight of RDX per Column	14.2 g (0.0310 lb)
Run Time	150 days

A-2. Solution.

a. Surface Loading Rate. The surface loading rate is given by the pilot test, but as a rule of thumb, the rate should be between 80–400 Lpm/m^2 (2–10 gpm/ft^2). The range of the pilot is near the high side of the range, so the system will be sized to limit the hydraulic loading rate to 310 Lpm/m^2 (7.6 gpm/ ft^2), but will be sized to accommodate standard sized vendor equipment. The diameter and resultant surface loading rate are calculated below.

b. Empty Bed Contact Time (EBCT) (Pilot Test). The contact times used vary by type of contaminant, but generally are in the 2–20 minute range, depending of course on the contaminant. The 2-minute contact time per column provided by the GAC pilot system limited the potential adsorbance by the GAC. The pilot data (Figure A-1) indicate a significant increase in the mass of RDX adsorbed per unit weight of carbon based on a minimum contact time of 4 minutes (2 minutes per column times two columns), and an even greater increase for a contact time of 6 minutes. A contact time based on GAC equipment size with a minimum contact time of 6 minutes per bed (assuming two beds in series) will be used.

c. Nominal Column Diameter. Diameter is equal to the flow rate 15.8 L/s (946 L/m) (250 gpm) divided by the loading rate, 310 Lpm/m^2 (7.6 gpm/ft^2) or 3.05 m^2 (32.9 ft^2), which equates to $(4 \times A/B)^{0.5}$ = 1.97 m (6.5 ft) in diameter. Referring to manufacturers literature, we find that the nearest diameter unit is either a 1.54-m (5-ft) or a 2.4-m (8-ft) diameter unit. A 2.4-m (8-ft) diameter unit has an area equal to 4.67 m^2 (50.3 ft^2), which makes our loading rate = [(946 L/m)/4.67 m^2] = 203 Lpm/m^2 (250 gpm/50.3 ft^2 or a 5.0 gpm/ ft^2 loading rate). This is in the normal 80–400 Lpm/m^2 (2–10 gpm/ ft^2) range. A 1.54-m (5-ft) diameter unit has an area equal to 1.86 m^2 (19.6 ft^2), which makes our loading rate = [(946 L/m)/1.86 m^2] = 509 Lpm/m^2 (250 gpm/19.6 ft^{2}or a 12.75 gpm/ ft^{2}loading rate). This is above the normal 80–400 Lpm/m^2 (2–10 gpm/ ft^2) range. So, two 8-ft diameter units will be selected.

d. Bed Depth. A minimum of 6 minutes/column should be used: 6-minute EBCT × 0.946 m^3 = a minimum carbon contact volume of 5.68 m^3 (1500 gal/7.48 gal/ft^3 = 200 ft^3). Bed depth is equal to the bed volume divided by the column area or 5.68 m^3/4.67 m^2 = 1.22 m (200 ft^3/50.3 ft^2 or 4 ft). By referring to Figure A-1, we see that the adsorption zone slightly exceeds the 1.22-m (4-ft) bed depth (two columns × 0.61 m of GAC/column), and the effluent concentration in the first column is slightly less than the influent concentration. The RDX concentration in the effluent of the third column does not exceed the 4 μg/L until well into the test (approximately 110,000 bed volumes). Again, manufacturer literature gives the amount of carbon per bed to be generally about 4535 kg (10,000 lb), which corresponds to a bed depth of 2.3 m (7.5 ft) for the 2.44-m (8-ft) diameter columns. The resulting EBCT is, therefore:

$$\frac{2 \text{ beds} \times 4535 \text{ kg of GAC per bed}}{420 \text{ kg/m}^3 \text{ of GAC}} = 22 \text{ m}^3 \text{ of GAC } (770 \text{ ft}^3)$$

$$\frac{22 \text{ m}^3 \text{ of GAC}}{(0.946 \text{ m}^3\text{/minute})} = 23 \text{ minutes}$$

e. Anticipated Volume of Water Treated per Change out Period. Contact time for the pilot was 6 minutes. Actual contact time is 23/6 × 100 or 383% longer. The change out period for the full-scale system can be approximated by multiplying the ratio of the difference in the contact time by the pilot test run time to breakthrough.

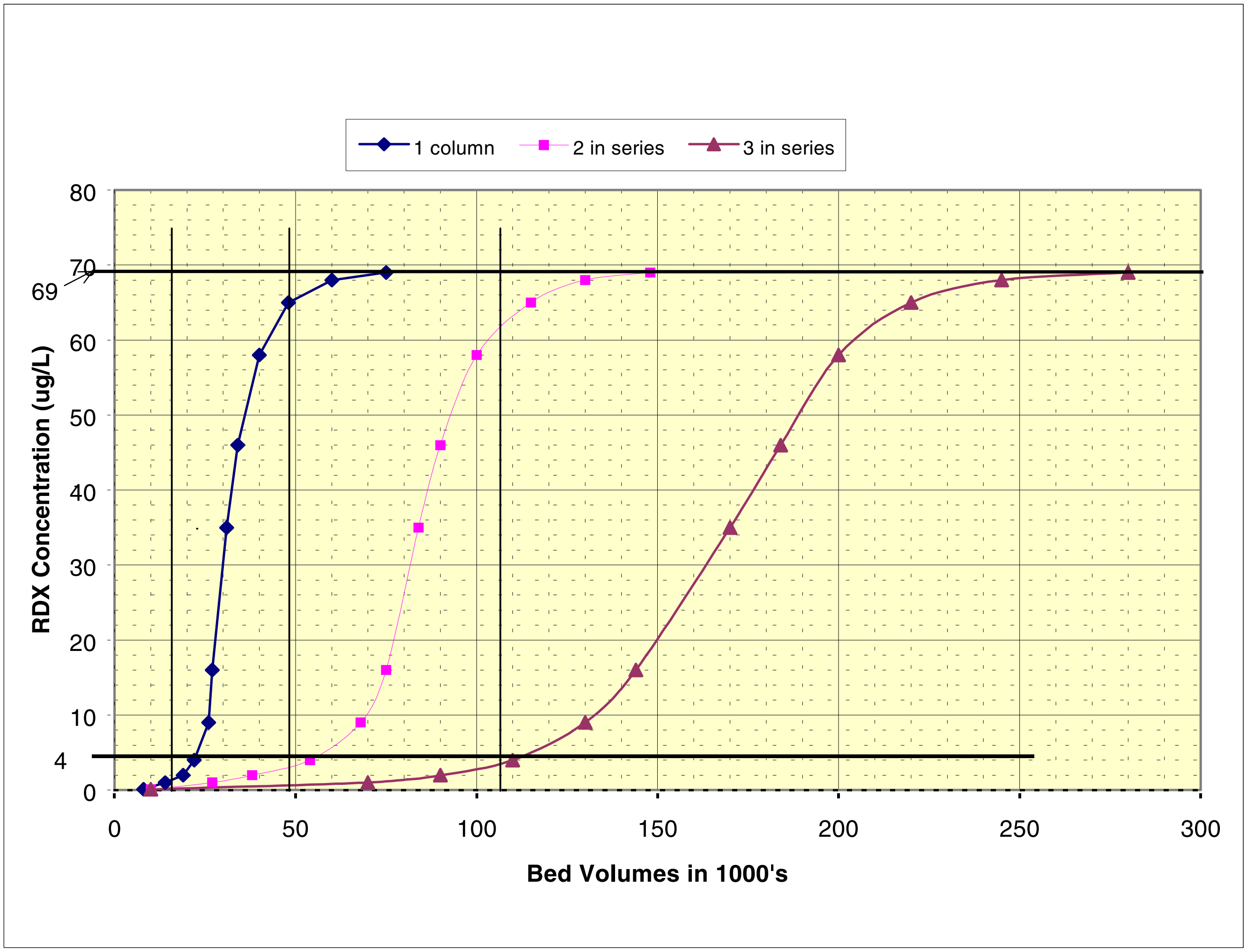


Figure A-1. Example.

f. Optional Method One.

- Breakthrough period: 3.83 × 150 days = ~574 days (~**19 months**)
- Volume treated:

574 days × (0.946 m^3/min) × (1440 min/day) = **781,925 m^3** (2.07 × 10^8 gal)

g. Optional Method Two.

- Estimated carbon usage for a single bed:

  22,000 bed volumes × 5.56 L/bed volume = 122,320 L (39,660 gal)

  2.32 kg GAC × 1000 g/kg = 2320 g (5.1 lb)

  2320 g/122,320 L = 0.0190 g/L or 19.0 g/1000 L (0.16 lb/1000 gal)

- Estimated carbon usage for two beds in series:

  54,000 bed volumes × 5.56 L/bed volume = 300,240 L (79,320 gal)

  4.64 kg GAC × 1000 g/kg = 4640 g (10.2 lb)

  4640 g/300,240 L = 0.0155 g/L or 15.5 g/1000 L (0.13 lb/1000 gal)

- Estimated carbon usage for three beds in series:

  110,000 bed volumes × 5.56 L/bed volume = 611,600 L (161,600 gal)

  6.96 kg GAC ×1000 g/kg = 6960 g (15.3 lb)

  6960 g/611,600 L = 0.0113 g/L or 11.3 g/1000 L (0.06 lb/1000 gal)

- Anticipated volume of water treated per changeout period using 11.3 g/1000 L treated:

  Carbon volume: 9,070 kg or 9,070,000 g

  Utilization rate: [9,070,000 g/(11.3 g/1000 L)] = 8.03×10^8 L (2.1×10^8 gallons)

  8.03×10^8 L/(946 L/min) = 849,000 minutes

  849,000 min × (1 day/1440 min) × (1 month/30 days) = **~19 months**

APPENDIX B
VAPOR PHASE CARBON DESIGN EXAMPLES

B-1. Example 1—SI Units. This example will illustrate the design calculations for sizing a vapor phase activated carbon treatment unit. The treatment train for this example consists of a blower, an air stripper, a heat exchanger, and carbon vessels to treat air from the air stripper containing the following volatile organic chemicals (VOC): perchloroethylene (PCE), trichloroethylene (TCE), benzene, and toluene (see Figure B-1). The water containing the VOCs enters the top of the air stripper column and flows generally downward through the packing material. At the same time, air flows upward through the column (countercurrent flow). As water and air contact, the VOCs are transferred from the water phase to the air phase. The water leaves the bottom of the column depleted in VOCs. The VOCs that have been transferred to the air exit the top of the column in the air phase. This air phase then flows through a heat exchanger where it is heated from 289 to 300 K to lower the relative humidity from 100 to 50%. From here, the air phase flows through vessels filled with activated carbon. The activated carbon adsorbs the VOCs. The air phase, depleted of VOCs, is discharged to the atmosphere.

a. Parameters.

- Flow rate of the air phase entering the air blower: 1 m^3/s.
- Temperature of the vapor stream into the blower: 305 K.
- Run time between carbon changes: 3 months/vessel.
- Number of carbon vessels: two (in series).
- Atmospheric pressure 87.6 kPa (elevation of site approximately 1600 m above sea level).
- Temperature of air phase leaving the air stripper: 289 K.
- Contaminants and their concentrations leaving the air stripper in the air phase:
    - Perchloroethylene (PCE): 15 ppmv.
    - Trichloroethylene (TCE): 14 ppmv
    - Benzene: 9 ppmv.
    - Toluene: 5 ppmv.

b. Design Steps.

(1) Determine the amount of carbon needed for 3 months.

(2) Determine the size of the carbon adsorption vessels.

(3) Determine the total pressure drop through the treatment train:

(a) Air stripper and associated piping, valves, and instrumentation.

(b) Air stripper to heat exchanger piping, valves, and instrumentation.

(c) Heat exchanger.

(d) Heat exchanger to carbon vessels piping, valves, and instruments.

(e) Carbon vessels.

(f) Piping between carbon vessels.

(g) Carbon vessel to ambient air discharge point.

(4) Determine the type and size of the blower.

(5) Determine the type and size of the heat exchanger.

c. Detailed calculations.

(1) *Determine the amount of carbon needed for 3 months*. For this example, initially assume that two carbon vessels in series will be used. The air phase from the air stripper will flow through the first vessel (the lead vessel) that adsorbs most of the organic vapors. The air phase will then flow through the second vessel (lag vessel) and be discharged to the atmosphere. After the effluent concentration equals the influent concentration, the flow will be redirected first through the lag vessel. This assumes that the second vessel contains the same amount of carbon as the first vessel. The lag vessel now becomes the lead vessel. The other vessel will have the exhausted carbon regenerated or replaced and put back on-line as the lag vessel. The length of time that a carbon vessel should remain on-line is very site-specific. In this example, design the system for 3 months between carbon changes of the lead vessel. It is difficult to determine the exact amount of carbon needed. Below is a method of estimating the amount of activated carbon that is needed.

(a) *Calculate the Partial Pressure of Each Contaminant in the Vapor Stream.* Assume that the pressure in the carbon vessel is the same as the discharge pressure (87.6 kPa). If this pressure is too different from the actual pressure, the partial pressure will need to be recalculated for the correct pressure in the carbon vessels. The weight of contaminant that can be adsorbed per weight of activated carbon can be estimated from isothermal data supplied by the carbon manufacturer or from the literature (see Paragraph 3-3a). From these data, the weight of contaminant adsorbed per weight of carbon was estimated from the Fruendlich isotherm relationship:

$$\frac{x}{m} = KC^{\left(\frac{1}{n}\right)} \quad .$$

The values of *K* and (1/*n*) were obtained for one carbon type at 298 K. These values must be obtained for each type of carbon being evaluated and for each temperature (see Table B-1).

Table B-1
Fruendlich isothremal data

Contaminant	Temp.	*K*	*C* (kPa)	1/*n*	*x/m*
PCE	298 K	1.0	1.3×10^{-3}	0.144	0.384
TCE	298 K	0.95	1.2×10^{-3}	0.263	0.162
Benzene	298 K	0.388	0.79×10^{-3}	0.131	0.152
Toluene	298 K	0.565	0.44×10^{-4}	0.111	0.240

See appendix C for generation of isotherms. See Paragraph 2-3 for a discussion of *K* and 1/*n*.

(b) *Determine the Weight of Each Contaminant to be Adsorbed Per Unit Time.*

$$\frac{\text{g mole air}}{\text{min}} = n = \frac{PV}{RT} = \frac{\left(87.6\ \text{kPa} \times \dfrac{1\ \text{m}^3 \times 60\,\dfrac{\text{s}}{\text{m}}}{\text{s}}\right)}{\left(8.31 \times 10^{-3}\ \dfrac{\text{m}^3\text{kPa}}{\text{g mole K}} \times 289\ \text{K}\right)}$$

$$= \frac{2.19\ \times 10^3 \text{g mole air}}{\text{min}} = \frac{2.19\ \text{kg mole air}}{\text{min}}$$

$$\frac{\text{kg mole PCE}}{\text{min}} = \frac{2.19\ \text{kg mole}}{\text{min}} \left(\frac{15\ \text{ppmv PCE}}{10^6\ \text{ppmv air}}\right)$$

$$= \frac{3.28 \times 10^{-5} \times \text{kg mole}}{\text{min}}\ \text{PCE}$$

$$\frac{\text{kg PCE}}{\text{min}} = \left(\frac{\text{kg mole PCE}}{\text{min}}\right)(\text{molecular weight of PCE})$$

$$= \frac{3.28 \times 10^{-5}\ \text{kg mole}}{\text{min}}\ \text{x}\ \frac{166\ \text{kg}}{\text{g mole}} = \frac{5.44 \times 10^{-3}\ \text{kg PCE}}{\text{min}}$$

$$\frac{\text{kg PCE}}{\text{3 months}} = \left(\frac{\text{kg PCE}}{\text{min}}\right)\left(\frac{1440\ \text{min}}{\text{day}}\right)\left(\frac{30\ \text{day}}{\text{mo}}\right) 3\ \text{months}$$

$$= 5.44 \times \frac{10^{-3}\ \text{kg}}{\text{min}} \times 1440 \times 30 \times 3 = \frac{706\ \text{kg PCE}}{\text{3 months}}$$

$$\frac{\text{kg carbon}}{\text{3 months}} = \left(\frac{706\ \text{kg PCE}}{\text{3 months}}\right)\left(\frac{\text{g carbon}}{0.384\ \text{g PCE}}\right)$$

$$= \frac{1839\ \text{kg carbon}}{\text{3 months}}$$

$$\text{kg carbon for } \frac{\text{TCE}}{3\ \text{months}} = 3213 \text{ kg}$$

$$\text{kg carbon for } \frac{\text{benzene}}{3\ \text{months}} = 1311 \text{ kg}$$

$$\text{kg carbon for } \frac{\text{toluene}}{3 \text{ months}} = 507 \text{ kg}$$

$$\text{Total lb carbon for 3 months } (1839 + 3213 + 1311 + 507) = 6870 \text{ kg}$$

This calculation is only an estimate of the quantity of carbon required. Manufacturers recommend calculating the carbon needed for the three or four most prevalent constituents and then adding a safety factor. Safety factors may be as little as 20% more carbon than calculated for non-regenerable systems to as much as 100% for a very conservative design. Applying this to this example, we can see that the estimated carbon total *M* becomes:

$$(6870 \text{ kg})\,(2) = (13740) \text{ kg for 3 months}$$

(2) *Determine the Size of the Carbon Adsorption Vessels.*

(a) *Estimate the Diameter of the Carbon Vessel.* The designer often has the option, within limits, of using a large diameter vessel that is short or a smaller diameter vessel that is tall. Both will hold the same amount of carbon. As a starting point, calculate the diameter for a reasonable superficial velocity. Superficial velocity (V) is the velocity that the vapor would attain through the carbon bed that if this vessel were empty ($V = Q/A,$ where Q is the vapor flow rate and A is the cross-sectional area of the vessel). Many carbons can be used over a large range of superficial velocities. Manufacturers' literature lists superficial velocities from 2.5 cm/s to several hundred. Typical superficial velocities are 5 to 50 cm/s. As superficial velocities increase, the pressure drop through the vessel increases. This results in increased energy costs. For this example, initially assume a superficial air velocity through the carbon vessels of 25 cm/s. Calculate the resulting diameter *D* of the vessel as follows:

$$A = \frac{Q}{V}$$

$$A = \left[\frac{3.14}{4}\right]\left[D^{2}\right]$$

Combining yields:

$$D = \left[\frac{4Q}{3.14V}\right]^{0.5} = \left[\frac{4\left(\frac{1\ \text{m}^3}{s}\right)}{(3.14)\left(\frac{25.4\,\text{cm}}{\text{s}} \times \frac{1\ \text{m}}{100\ \text{cm}}\right)}\right]^{0.5} = 2.24\ \text{m}$$

(b) *Estimate the depth of the carbon in the vessels.*

$$M = [Vol][\text{carbon density}]$$

$$Vol = \left[\left(\frac{3.14}{4}\right)\right]\left[\left(D^2\right)(H)\right]$$

where

Vol = volume of the carbon in the vessel
M = weight of the carbon
H = depth of the carbon in the vessel.

Combining, rearranging and estimating the carbon density to be 489 kg/m^3 yields

$$H = \frac{(4)(M)}{(3.14)\left(D^2\right)(\text{carbon density})}$$

$$= \frac{(4)(13740\,\text{kg})}{(3.14)\left((2.24\ \text{m})^2\left(489\,\frac{\text{kg}}{\text{m}^3}\right)\right)}$$

$$= 7.2\ \text{m}$$

The carbon vessel is too deep. By decreasing the superficial velocity through the carbon bed from 25 to 12.5 cm/s and repeating the calculations done in Paragraphs B-1*c*(2)(a) and B-1*c*(2)(b) above, the diameter of the vessel becomes 3.2 m and the carbon depth becomes 3.6 m. These are acceptable (an alternative is to use four vessels 2 × 2). Vessels available from manufacturers will dictate their exact height and diameter.

(3) *Calculate the Total Pressure Drops Through the Units in the Process Train.* The actual pressure drops must be calculated for each application. They will most likely differ much from those chosen here to illustrate the calculation procedure.

(a) *Blower Through Air Stripper, Valves, and Instruments.* 13 cm H_2O (estimate).

(b) *Air Stripper to Heat Exchanger Piping, Valves, and Instruments.* 2.5 cm of H_2O (estimate).

(c) *Heat Exchanger.* 2.5 cm of H_2O (estimate).

(d) *Heat Exchanger to Carbon Vessels Piping, Valves, and Instruments.* 2.5 cm of H_2O (estimate).

(e) *Carbon Vessels.* The pressure drop through the carbon bed is a function of the type and size of carbon, the velocity of the vapor through the carbon bed, and the depth of the bed. For one specific carbon in manufacturers' literature, the pressure drop through the carbon is 6 cm H_2Oper meter of carbon. For the 3.6-m bed of carbon in this example, the pressure drop is 21 cm of H_2O for the lead vessels and 21 cm of H_2O for the lag vessel, for a total of 42 cm of H_2O (see Figure B-1).

(f) *Between Carbon Vessels.* 2.5 cm of H_2O (estimate).

(g) *Carbon Vessels to Ambient Air Discharge Point.* 2.5 cm of H_2O (estimate).

(4) *Determine the Size and Type of Blower.*

(a) *Size of Blower.* Design the blower to handle 1 m^3/s for the above total system pressure drop. The exit pressure from the blower is the pressure leaving the carbon units (87.6 kPa) plus the pressure drop through the treatment train. The blower exit pressure is as follows:

$$= 87.6 \text{ kPa} + \left(\left(13 + 2.5 + 2.5 + 2.5 + 42 + 2.5 + 2.5\right) \text{cm H}_2\text{O}\right) \frac{\left(9.8 \times 10^{-2} \text{kPa}\right)}{\left(\text{cm}\right)}$$

$$= 94.2 \text{ kPa}$$

Blower performance curves should be obtained from the manufacturer. In the absence of this information, the design engineer can estimate the power from thermodynamic relationships as follows. (See an engineering thermodynamics book for an additional discussion and development of these relationships.)

$$P = \left[\left(P_1\right)\left(V_1\right)\right]\left[\frac{k}{\left(k-1\right)}\right]\left[\left(\frac{P_2}{P_1}\right)^{\frac{(k-1)}{k}}-1\right]$$

P = Power, kW

P_1 = Inlet pressure in kPa = 87.6 kPa

P_2 = Outlet pressure in kPa = 94.2 kPa

$V_1 = \text{Inlet Volume} = 1\,\frac{\text{m}^3}{\text{s}}$

C_p = Heat capacity at constant pressure

C_v = Heat capacity at constant pressure

$k = \text{ratio of specific heats } \frac{C_\text{p}}{C_\text{v}}$ (k = 1.4 air; 1.31 methane; 1.3 CO_2)

Substituting yields:

$$\text{Power} = 87.6\text{ kPa} \times \frac{1\ \text{m}^3}{\text{s}} \quad \left[\frac{(1.4)}{(1.4-1)}\right]\left[\left(\frac{94.2}{87.6}\right)^{\left[\frac{(1.4-1)}{1.4}\right]}-1\right]$$

$$= 6.4\text{ kW (at 100\% efficiency)}$$

In the absence of manufacturers' data, estimate the efficiency of the blower and motor combination to be 40%. The actual size of the motor is then:

$$\text{Power} = \frac{6.4\text{ kW}}{40\%} = 16\text{ kW}$$

(b) *Type of Blower.* High-pressure centrifugal blowers are often used in this type of application.

(5) *Determine the Size and Type of Heat Exchanger.* The relative humidity (RH) of the vapor stream entering the carbon vessels should not exceed 40 to 70% (see Paragraph 3-1*b*). A heat exchanger is used to raise the temperature (lower the RH) or lower the temperature (raise the RH) as needed. High RH reduces the adsorption capacity of the carbon. High temperature reduces the capacity of the carbon. A good compromise between temperature and humidity is to raise or lower the RH to about 50%. The type of heat exchanger depends on the amount of

heating or cooling needed. Assume that in the air stripper the vapor stream is cooled to 289 K (the temperature of the water in the air stripper). Assume the vapor leaving the air stripper is saturated with moisture (100% RH). A psychrometric chart tells us that the temperature must be raised in a heat exchanger from 289 to 299.8 K to lower the RH to 50%.

- The Fruendlich isothermal data listed in earlier are for 298 K. In this example, this is close to the 300 K vapor temperature of the vapor entering the carbon units. If the temperature difference is large, the weight of contaminant adsorbed per weight of carbon (*x/m*) must be determined for the new temperature and all subsequent calculations repeated.

- In addition to increasing the pressure, the blower also raises the temperature of a vapor stream. If the vapor goes directly from the blower to the carbon units, the temperature may need to be reduced, not heated, in a heat exchanger. It is difficult to estimate the temperature rise. The temperature rise must be obtained from manufacturer's blower literature.

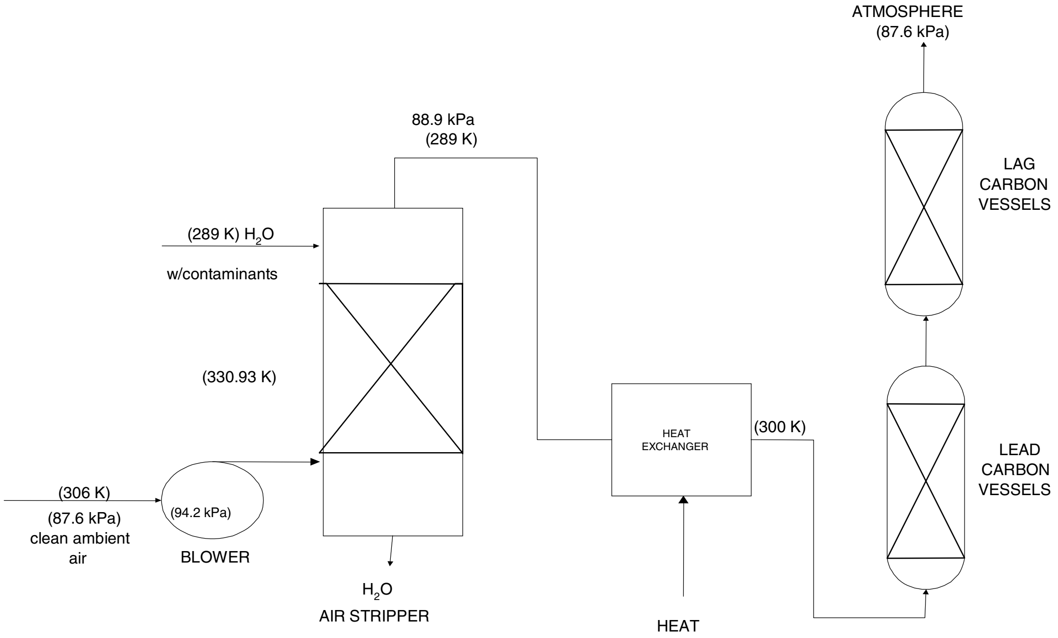


Figure B-1. Vapor phase activated carbon treatment train (SI units).

B-2. Example 2—English units. This example will illustrate the design calculations for sizing a vapor phase activated carbon treatment unit. The treatment train for this example consists of a blower, an air stripper, a heat exchanger, and carbon vessels to treat air from the air stripper containing the following volatile organic chemicals (VOC): perchloroethylene (PCE), trichloroethylene (TCE), Benzene, and toluene (see Figure B-2). The water containing the VOCs enters the top of the air stripper column and flows generally downward through the packing material. At the same time, air flows upward through the column (countercurrent flow). As water and air contact, the VOCs are transferred from the water phase to the air phase. The water leaves the bottom of the column depleted in VOCs. The VOCs that have been transferred to the air exit the top of the column in the air phase. This air phase then flows through a heat exchanger where it is heated from 60°F to 80°F to lower the relative humidity from 100 to 50%. From here, the air phase flows through vessels filled with activated carbon. The activated carbon adsorb the VOCs. The air phase, depleted of VOCs, is discharged to the atmosphere.

a. Parameters.

- Flow rate of the air phase leaving the air stripper: 2000 ft^3/min.
- Temperature of the air phase into the blower: 90°F.
- Run time between carbon changes: 3 months/vessel.
- Number of carbon vessels: two (in series).
- Atmospheric pressure: 12.7 psia (elevation of site approximately 1 mile above sea level).
- Temperature of air phase leaving the air stripper: 60°F.
- Contaminants and their concentrations leaving the air stripper in the air phase:
  - Perchloroethylene (PCE): 15 ppmv.
  - Trichloroethylene (TCE): 14 ppmv.
  - Benzene: 9 ppmv.
  - Toluene: 5 ppmv.

b. Design Steps.

(1) Determine the amount of carbon needed.

(2) Determine the size of the carbon adsorption vessels.

(3) Determine the total pressure drop through the process train.

(a) Air stripper and associated piping, valves, and instrumentation.

(b) Air stripper to heat exchanger piping, valves, and instrumentation.

(c) Heat exchanger.

(d) Heat exchanger to carbon vessels piping, valves, and instruments.

(e) Carbon vessels.

(f) Piping between carbon vessels.

(g) Carbon vessel to ambient air discharge point.

(4) Determine the type and size of the blower.

(5) Determine the type and size of the heat exchanger.

c. *Detailed Calculations*.

(1) *Determine the Amount of Carbon Needed*. For this example, initially assume that two carbon vessels in series will be used. The air phase from the air stripper will flow through the first vessel (the lead vessel) that adsorbs most of the organic vapors. The air phase will then flow through the second vessel (lag vessel) and be discharged to the atmosphere. After the effluent concentration equals the influent concentration, the flow will be redirected to flow first through the lag vessel. This assumes that the second lag vessel now becomes the lead vessel. The other vessel will have the exhausted carbon regenerated or replaced and put back on-line as the lag vessel. The length of time that a carbon vessel should remain on-line is very site-specific. In this example, design the system for 3 months between carbon changes of the lead vessel. It is difficult to determine the exact amount of carbon needed. Below is a method of estimating the amount of carbon that is needed.

(a) *Calculate the Partial Pressure of Each Contaminant in the Air Phase*. Assume that the pressure in the carbon vessel is the same as the discharge pressure (12.7 psia). If this pressure is too different from the actual pressure, the partial pressure will need to be recalculated for the correct pressure in the carbon vessels.

$$\text{Partial pressure of PCE} = (\text{total system pressure}) \frac{\text{ppmv contaminant}}{10^6 \text{ ppmv air}}$$

$$\text{Partial pressure of PCE} = (15 \text{ ppmv})\ (12.7 \text{ psia}) \bullet (10^{-6}) = 1.9 \times 10^{-4} \text{ psia}$$

$$\text{TCE} = (14 \text{ ppmv})\ (12.7 \text{ psia}) \bullet (10^{-6}) = 1.8 \times 10^{-4} \text{ psia}$$

$$\text{Benzene} = (9 \text{ ppmv})\ (12.7 \text{ psia}) \bullet (10^{-6}) = 1.1 \times 10^{-4} \text{ psia}$$

$$\text{Toluene} = (5 \text{ ppmv})\ (12.7 \text{ psia}) \bullet (10^{-6}) = 0.63 \times 10^{-4} \text{ psia}$$

The weight of contaminant that can be adsorbed per weight of activated carbon can be estimated from isothermal data supplied by the carbon manufacturer or from the literature (see Paragraph 3-3*a*). From these data, the weight of contaminant adsorbed per weight of carbon was estimated from the Fruendlich isotherm relationship:

$$\frac{x}{m} = KC^{\frac{1}{n}} \quad .$$

The values of *K* and 1/*n* were obtained for one carbon type at 77°F. These values must be obtained for each type of carbon being evaluated and for each temperature (see Table B-2).

Table B-2
Fruendlich Isothermal Data

Contaminant	Temp	K	C (psia)	$\frac{1}{n}$	$\frac{X}{m}$
PCE	77°F	1.4	1.9×10^{-4}	0.156	0.368
TCE	77°F	1.4	1.8×10^{-4}	0.23	0.193
Benzene	77°F	1.1	1.1×10^{-4}	0.131	0.151
Toluene	77°F	0.7	6.3×10^{-5}	0.111	0.239

See Appendix C on generation of isotherms. See Section 2-3 for a discussion on *K* and 1/*n*.

(b) *Determine the weight of each contaminant to be adsorbed per unit time.*

$$\frac{\text{1b mole PCE}}{\text{min}} = n = \frac{PV}{RT}$$

$$\frac{\text{1b mole PCE}}{\text{min}} = \frac{\left(1.9\times10^{-4}\ \text{psia}\right)\left(2000\,\frac{\text{ft}^3}{\text{min}}\right)}{\left(\frac{10.73\,\text{ft}^3\ \text{psia}}{\text{lb mole}\,^\circ\text{R}}\right)\left(460+60^\circ\text{R}\right)}$$

$$= 6.8\times10^{-5}\ \frac{\text{lb mole}}{\text{min}}$$

$$\frac{\text{lb PCE}}{\text{min}} = \left(\frac{\text{1b mole PCE}}{\text{min}}\right)(\text{molecular weight of PCE})$$

$$= \left(\frac{6.8\times10^{-5}\ \text{lb mole}}{\text{min}}\right)(166)\ \frac{\text{lb}}{\text{lb mole}}$$

$$= 1.1\times10^{-2}\ \frac{\text{lb PCE}}{\text{min}}$$

$$\frac{\text{lb PCE}}{\text{3 months}} = \left(\frac{\text{lb PCE}}{\text{min}}\right)\left(\frac{\text{1440 min}}{\text{day}}\right)\left(\frac{\text{30 day}}{\text{mo}}\right)\left(\text{3 months}\right)$$

$$= \left(1.1\times10^{-2}\right)(1440)\ (30)\ (3)$$

$$= 1465\ \text{lb}\ \frac{\text{PCE}}{\text{3 months}}$$

$$\frac{\text{lb carbon}}{\text{3 months}} = \left(\frac{\text{1465 of PCE}}{\text{3 months}}\right)\left(\frac{\text{lb carbon}}{\text{0.368 lb PCE}}\right)$$

$$= 3981\,\frac{\text{lb carbon}}{\text{3 months}}$$

$$\text{lb carbon for } \frac{\text{TCE}}{\text{3 months}} = 5720 \text{ lb}$$

$$\text{lb carbon for } \frac{\text{Benzene}}{\text{3 months}} = 2662 \text{ lb}$$

$$\text{lb carbon for } \frac{\text{Toluene}}{\text{3 months}} = 1138 \text{ lb}$$

$$\text{Total lb carbon for 3 months} = (3981 + 5720 + 2662 + 1138) = 13501 \text{ lb}$$

This calculation is only an estimate of the quantity of carbon required. Manufacturers recommend calculating the carbon needed for the three or four most prevalent constituents and then adding a safety factor. Safety factors may be as little as 20% more carbon than calculated for non-regenerable systems to as high as 100% for a very conservative design. Applying a conservative safety factor of 100%. we see that the estimated carbon total (M) becomes:

$$M = 13,501 \times 2 = (27,002) \text{ lb for 3 months}$$

(2) *Determine the Size of the Carbon Adsorption Vessels.*

(a) *Estimate the Diameter of the Carbon Vessel*. The designer often has the option, within limits, of using a large diameter vessel that is short, or a smaller diameter vessel that is tall. Both will hold the same amount of carbon. A third option is to use two vessels in parallel. As a starting point, calculate the diameter for a reasonable superficial velocity. Superficial velocity (V) is the velocity that the vapor would attain through the carbon bed if this vessel were empty ($V = Q/A$, where Q is the vapor flow rate and A is the cross-sectional area of the vessel). Many carbons can be used over a large range of superficial velocities. Manufacturers' literature lists superficial velocities from 5 ft/min to several hundred. Typical superficial velocities are 10 to 100 ft/min. As superficial velocities increase, the pressure drop through the vessel increases. This results in increased energy costs. For this example, initially assume a superficial air velocity through the carbon vessels of 50 ft/min. Calculate the resulting diameter of the vessel as follows:

$$A = \frac{Q}{V}$$

$$A = \left[\frac{3.14}{4}\right]\left[D^2\right]$$

Combining yields:

$$D = \left[\frac{4\,Q}{3.14\,V}\right]^{0.5} = \left\{\left[\frac{4\ (2000\ cfm)}{(3.14)\ \left(50\ \frac{ft}{\text{min}}\right)}\right]\right\}^{0.5} = 7.1 \text{ ft}$$

(b) *Estimate the Depth of the Carbon in the Vessels.*

$$M = [Vol\,][\text{carbon density}]$$

$$Vol = \left[\left(\frac{3.14}{4}\right)\right]\left[\left(D^{\,2}\right)(H)\right]$$

where

Vol = volume of the carbon in the vessel
M = weight of the carbon
H = depth of the carbon in the vessel.

Combining, rearranging and estimating the carbon density to be 30 lb/ft^3 yields :

$$H = \left[\frac{(4)\ \ (M)}{(3.14)\ \ (D^2)\ \ (\text{carbon density})}\right]$$

$$= \left[\frac{(4)\ \ (27{,}002)}{(3.14)\ \ (7.1)^{\,2}\ \ (30)}\right]$$

$$= 23 \text{ ft}$$

The carbon vessel is too deep. By decreasing the superficial velocity through the carbon bed from 50 to 25 ft/min and repeating the calculations done in Paragraphs B-2*c*(2)(a) and B-2*c*(2)(b) above, the diameter of the vessel becomes 10 ft and the carbon depth (*H*) becomes 11 ft. These are acceptable (an alternative is to use four vessels, 2 × 2). Vessels available from manufacturers will dictate their exact height and diameter.

(3) *Determine the Total Pressure Drops through the Units in the Process Train.* The actual pressure drops must be calculated for each application. They will most likely differ much from those chosen here to illustrate the calculation procedure.

(a) *Blower through Air Stripper, Valves, and Instruments.* 5 in. of H_2O (estimate).

(b) *Air Stripper to Heat Exchanger Piping, Valves, and Instruments*. 1 in. of H_2O (estimate).

(c) *Heat Exchanger*. 1 in. of H_2O (estimate).

(d) *Heat Exchanger to Carbon Vessels Piping, Valves, and Instruments*. 1 in. of H_2O (estimate).

(e) *Carbon Vessels*. The pressure drop through the carbon bed is a function of the type of carbon, the velocity of the vapor through the carbon bed, and the depth of the carbon bed. For one specific carbon in manufacturers' literature, the pressure drop through the carbon is 0.8 in. of H_2O per foot of carbon bed. For the 11-ft bed of carbon in this example, the pressure drop is 9 in. of H_2O for the lead vessels and 9 in. of H_2O for the lag vessel, for a total of 18 in. of H_2O (see Figure B-1).

(f) *Between Carbon Vessels*: 1 in. of H_2O (estimate).

(g) *Carbon Vessels to Ambient Air Discharge Point:* 1 in. of H_2O (estimate).

(4) *Determine the Size and Type of Blower*.

(a) *Size of Blower*. Design the blower to handle 2000 cfm for the above total system pressure drop. The exit pressure from the blower is the pressure leaving the carbon units (12.7 psia) plus the pressure drop through the treatment train. The blower exit pressure is as follows:

$$= 12.7 \text{ psia} + (5 + 1 + 1 + 1 + 18 + 1 + 1) \text{ in. } H_2O) \frac{(0.036 \text{ psia})}{(\text{in. } H_2O)}$$

$$= 12.7 + (28)\,(0.036)$$

$$= 13.8 \text{ psia}$$

Blower performance curves must be obtained from the manufacturer. In the absence of this information, the design engineer can estimate the adiabatic (theoretical) horse power from thermodynamic relationships as follows. (See an engineering thermodynamics book for an additional discussion and development of these relationships.)

$$HP = \left(\frac{(P_1)(V_1)}{[33000]}\right) \times \left[\frac{k}{(k-1)}\right]\left[\left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}} - 1\right]$$

HP = horsepower (hp)

$P_1 =$ inlet pressure in $\dfrac{\text{lb}}{\text{ft}^2} = \left(\dfrac{12.7\ \text{lb}}{\text{in.}^2}\right)\left(\dfrac{144\ \text{in.}}{\text{ft}^2}\right) = \left(\dfrac{1829\ \text{lb}}{\text{ft}^2}\right)$

$P_2 =$ outlet pressure in $\text{lb}/\text{ft}^2 = \dfrac{13.8\ \ \text{lb}}{\text{in.}^2} = \dfrac{1987\ \ \text{lb}}{\text{ft}^2}$

33000 = conversion factor

$V_1 =$ inlet volume $= \dfrac{2000\ \text{ft}^3}{\text{min}}$

$C_p =$ heat capacity at constant pressure

$C_v =$ heat capacity at constant volume

$k =$ ratio of specific heats $\dfrac{C_P}{C_v}$ $(k = 1.4$ air; 1.31 methane; 1.3 $CO_2)$

Substituting yields:

$$HP = (1829)\ \frac{(2000\ \frac{\text{ft}^3}{\text{min}})}{33,000}\left[(\frac{1.4}{1.4-1})\right]\left\{\left(\frac{1987}{1829}\right)^{\left[\frac{(1.4-1)}{1.4}\right]} - 1\right\}$$

$= 9.3\ HP$ (at 100% efficiency)

Prior to obtaining manufacturers data, a very rough estimate of the electrical motor size can be obtained by multiplying the adiabatic blower horse power (*HP*) by 40%. Using this number, we calculate the estimated size of the electric motor horse power is as follows:

$$\text{Electric motor } HP = \frac{9.3}{40\%} = 23\ HP$$

This value should not be used for final design; it should only be used if an initial estimate is needed. Manufacturer's data must be used for final design calculations.

(b) *Type of Blower*. High pressure centrifugal blowers are often used in this type of application.

(5) *Determine the Size and Type of Heat Exchanger*. The relative humidity (RH) of the

vapor stream entering the carbon vessels should not exceed 40 to 70% (see Paragraph 3-1b). A heat exchanger is used to raise the temperature (lower the RH) or lower the temperature (raise the RH) as needed. High RH reduces the adsorption capacity of the carbon. High temperature reduces the capacity of the carbon. A good compromise between temperature and humidity is to raise or lower the RH to about 50%. The type of heat exchanger depends on the amount of heating or cooling needed. Assume that in the air stripper the vapor stream is cooled to 60°F (the temperature of the water in the air stripper). Assume the vapor leaving the air stripper is saturated with moisture (100% relative humidity). A psychrometric chart tells us that the temperature must be raised in a heat exchanger from 60 to 80°F to lower the relative humidity to 50%.

- The Fruendlich isothermal data listed in section 1a is for 77°F. In this example, this is close to the 80°F vapor temperature of the vapor entering the carbon units. If the temperature difference is large, the weight of contaminant adsorbed per weight of carbon (*x/m*) must be determined for the new temperature and all subsequent calculations repeated.

- In addition to increasing the pressure, the blower also raises the temperature of a vapor stream. If the vapor goes directly from the blower to the carbon units, the temperature may need to be reduced, not raised, in a heat exchanger. It is difficult to estimate the temperature rise. The temperature rise must be obtained from manufacturers' blower literature.

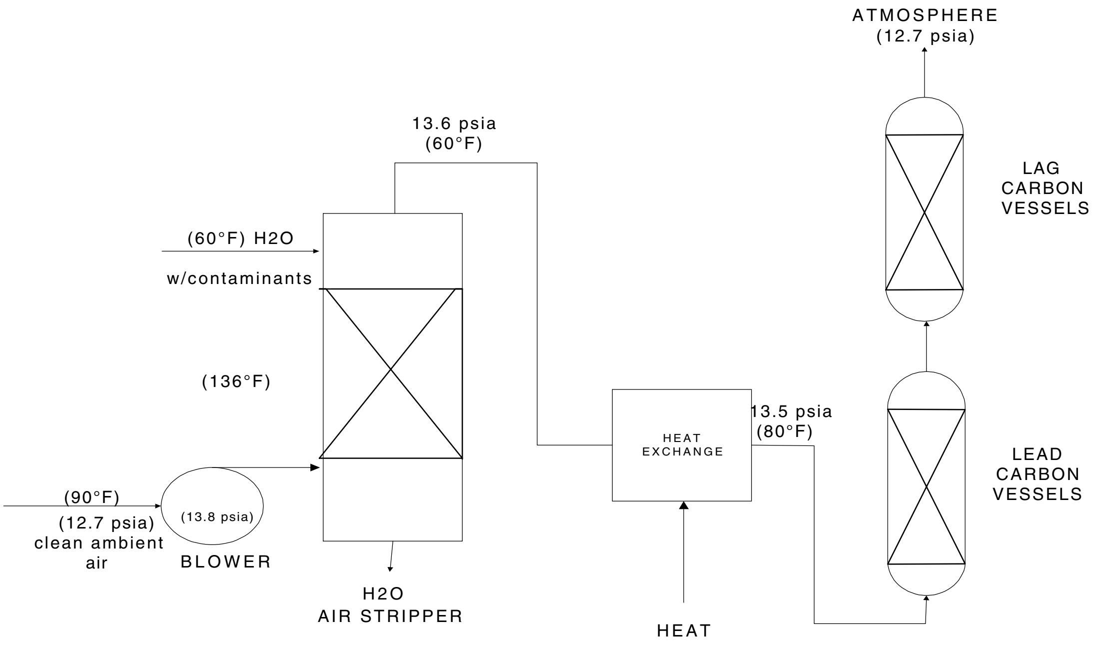


Figure B-2. Vapor phase activated carbon treatment train (English units).

APPENDIX-C
GENERATION OF ISOTHERMS

C-1. General. Generation of an isotherm from laboratory data is straightforward. The isotherm is plotted in log-log form to ensure that it approaches a straight line, making it easier to read and interpret, and to apply the Freundlich equation. After the data are plotted on a log-log scale, we can define the equation of the line by taking the log of each side of the Freundlich equation. This allows you to determine the values of K and $1/n$. The logarithmic version of the Freundlich equation is a straight line in the form of $y = mx + b$, where b is the y-intercept for $x = 0$. In our case K equals the x/m intercept when the log of the concentration C (adsorbate remaining) equals one unit, the log of which is zero. The value of m, the slope of the line, is equal to $1/n$, which can be solved by rearranging the equation to:

$$\frac{1}{n} = (\log \frac{x}{m} - \log K) \;/\; (\log C)$$

There are two ways you can generate the isotherms:

- From laboratory data.
- From existing data (see Figure 2-2).

a. Isotherm Generation from Existing Data. Given TCE as the contaminant,

$$K = 1060\ \mu g/g,\ \frac{1}{n} = 0.500.$$

To generate an isotherm from

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log C$$

we can rewrite to

$$\log \frac{x}{m} = \log 1060 + 0.500 \log C$$

$$\log \frac{x}{m} = 3.025 + 0.500 \log C$$

$$\log \frac{x}{m} = 3.025 + 0.500 \log C$$

and for various values of *C,* plot an isotherm. Try

$$C = 1, 10, 100, 1000\ \mu g/L$$

$$\log \frac{x}{m} = 3.025, 3.525, 4.025, 4.525$$

$$\frac{x}{m} = 1060, 3350, 10600, 33500$$

Which results in the curve shown in Figure C-1.

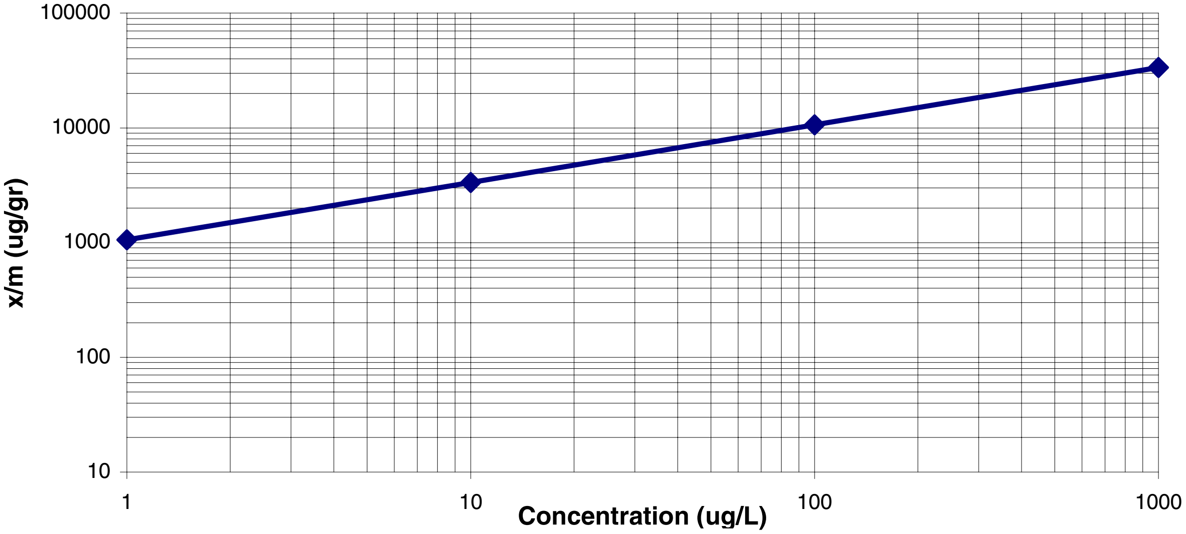


Figure C-1. TCE isotherm.

b. Example Isotherm Problem. The following laboratory data were collected in a batch adsorption study. Plot the data according to the Freundlich isotherm and determine the values for the constants 1/*n* and *K*. A volume of 500 mL is placed in each flask, and the waste has an initial concentration of 100 µg/L.

Flask Number	Carbon Weight (mg) ***(m)***	Flask Volume (ml)	Final TOC (mg/L) **(C)**	Adsorbate Adsorbed (mg) ***(x)***	x/m ***(mg/g)***
1	965	500	3.5	48.25	50.00
2	740	500	5.2	47.40	64.05
3	548	500	8.0	46.00	83.94
4	398	500	12.5	43.75	109.92
5	265	500	20.5	39.75	150.00
6	168	500	33.0	33.50	199.40
7	0	500	100.0	0	0

Example Calcs:

x= (100 mg/L - 3.5 mg/L)*(500 mL volume/1000 mL/L) = 48.25 mg

x/m= (48.25 mg/0.965 g) = 0.05mg adsorbate/mg of Carbon

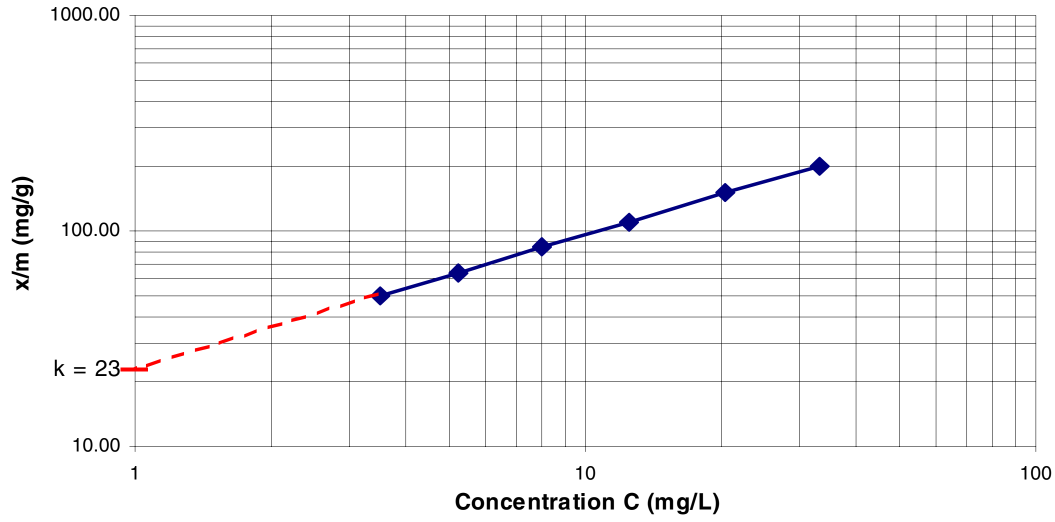


Figure C-2. TOC isotherm and lab data.

c. Solution.

(1) Calculate the values of *x* and *x/m* from the data. Refer to Figure C-1.

(2) Plot values of *x/m* vs. *C* on log-log paper in a manner similar to that shown in Figure C-1 (see Figure C-2).

(3) Determine the values of the constants *K* and 1/*n*.

(a) To determine the intercept of a line on a log-log plot, the value of the intercept must read at the point where the value of the abscissa is equal to 1.0. To determine *K* from Figure C-2, locate a value of *C* = 1.0 and read *K* = 23.0.

(b) The slope of the line will yield a value of 1/*n*. The slope of a log-log plot can be determined by scaling or by the following calculations.

$$\log \frac{x}{m} = \log K - \frac{1}{n} \log C$$

$$\frac{1}{n} = \frac{\log \frac{x}{m} - \log K}{\log C}$$

For a point on the line at *x/m* = 0.70, *C* = 6

$$\frac{1}{n} = \frac{\log\ 0.07 - \log\ 0.023}{\log\ 6} = \frac{-1.154 - (-1.638)}{0.778}$$

$$\frac{1}{n} = 0.622$$

$$n = 1.607$$

(c) The Freundlich equation then becomes

$$\log \frac{x}{m} = \log\ 0.023 - \frac{1}{1.607} \log C$$

$$\log \frac{x}{m} = 1.638 - 0.622\ \log C$$

APPENDIX D
MANUFACTURERS

Advanced Recovery Technologies Corp.
4784 Evanston Ave.
Muskegon, MI 49442
(616) 788-2911

Biomin, Inc.
Ferndale, MI 48220

Calgon Carbon Corporation
P.O. Box 717
Pittsburgh, PA 15230-0717
(412) 787-6700 (800) 422-7266
http://www.calgoncarbon.com

Carbonair Environmental Systems
2731 Nevada Ave. N.
New Hope, MN 55427

Colloid Environmental Technologies Co. (CETCO)
1350 West Shure Drive
Arlington Heights, IL 60004-1440
(847) 392-5800
http://www.cetco.com

Continental Remediation Systems, Inc.
Wellesley, MA.

Envirotrol, Inc.
(412) 827-8181

Nichem Co.
373 Route 46 West
Building D
Fairfield, NJ 07004
(973)882-0988

Norit Americas, Inc.
Route 3, Box 69-6
Pryor, OK 74361-9803
(918) 825-5570

Talisman Partners, Ltd.,
Englewood, CO 80111

TIGG Corporation
Pittsburgh, PA 15228
(412) 257-8520
www.tigg.com

U.S. Filter/Westates
2523 Mutahar Street
P.O. Box E
Parker, AZ 85344
(520) 669-5758

APPENDIX E
UNITS AND CONVERSION FACTORS

Quantity	Conversion
Length	1 m = 100 cm = 3.28084 ft = 39.3701 in.
Mass	1 kg =10^3 g = 2.20462 1b$_m$
Force	1 N = 1 kg (m/s ^{2}) = 0.224809 1b$_f$
Pressure	1 bar = 10^5 kg/(m s^2) = 10^5 N/m^2 =10^5 Pa = 10^2 kPa =0.986923 atm = 14.5038 psia =7 50.061 torr
Volume	1 m^3 = 10^6 cm^3 =35.31417 ft^3
Density	1 g/cm^3 = 10^{-3} kg/m^3 = 62.4278 lb$_m$/ ft^3
Energy	1 J= 1 kg (m^2/s^2) = 1 N m = 1 m^3 Pa = 10^{-5} m^3 bar = 10 cm^3 bar = 9.86923 cm ^{3} (atm) = 0.239006 cal = 5.12197×10^{-3} ft^3 psia = 0.737562 ft lb$_f$ = 9.47831×10^{-4} (Btu)
Power	1 kW = 10^3 W = 10^3 kg (m^2/s^3) = 10^3 J/s = 239.006 cal/s = 737.562 ft lb$_f$/s = 0.947831 Btu/s = 1.34102 hp

Values of the universal gas constant *R*

$= 8.314\ \mathrm{J\ mol^{-1}\ K^{-1}} = 8.314\ \mathrm{m^3\ Pa\ mol^{-1}\ K^{-1}}$

$= 8.314 \times 10^{-3}\ \mathrm{m^3\ kPa\ mol^{-1}\ K^{-1}} = 8314\ \mathrm{cm^3\ kPa\ mol^{-1}\ K^{-1}}$

$= 82.06$ cm 3 (atm) $\mathrm{mol^{-1}\ K^{-1}} = 62.356\ \mathrm{cm^3}$ (torr) $\mathrm{mol^{-1}\ K^{-1}}$

$= 1.987$(cal) $\mathrm{mol^{-1}\ K^{-1}} = 1.986$(Btu)(lb mole)$^{-1}$ (°R)$^{-1}$

= 0. 71302 (ft)^3 (atm)(lb mo1)$^{-1}$(°R)$^{-1}$ = 10.73(ft)^3 (psia) (1b mol)$^{-1}$(°R)$^{-1}$

= 1,545(ft)(lb$_f$)(lb mol)$^{-1}$(°R)$^{-1}$

APPENDIX F
REFERENCES

ASME 1992

ASME Boiler and Pressure Vessel Committee, Subcommittee on Pressure Vessels, 1992. *ASME Boiler and Pressure Vessel Code*, Section VIII, *Rules for Construction of Pressure Vessels*. American Society of Mechanical Engineers, 345 E. 47th St., New York, NY 10017

ASTM D 5158-98

Standard Test Method for Determination of the Particle Size of Powdered Activated Carbon by Air Jet Sieving. American Society for Testing and Materials, West Conshohocken, PA.

ASTM D 2652-94

Standard Terminology Relating to Activated Carbon. American Society for Testing and Materials, West Conshohocken, PA.

ASTM D 2862-97

Standard Test Method for Particle Size Distribution of Granular Activated Carbon. American Society for Testing and Materials, West Conshohocken, PA.

ASTM D 3037-93

Test Methods for Carbon Black-Surface Area by Nitrogen Adsorption. American Society for Testing and Materials, West Conshohocken, PA.

ASTM D 4607-94

Standard Test Method for Determination of Iodine Number of Activated Carbon. American Society for Testing and Materials, West Conshohocken, PA.

ASTM D 3860-98

Standard Practice for Determination of Adsorptive Capacity of Activated Carbon by Aqueous Phase Isotherm Technique. American Society for Testing and Materials, West Conshohocken, PA.

ASTM D 3922-89

Standard Practice for Estimating the Operating Performance of Granular Activated Carbon for Removal of Soluble Pollutants from Water. American Society for Testing and Materials, West Conshohocken, PA.

ASTM D 5159
Standard Test Method for Dusting of Granulated Activated Carbon. American Society for Testing and Materials, West Conshohocken, PA.

AWWA 1997
American Water Works Association 1997. *AWWA Standard for Granulated Activated Carbon*, ANSI/AWWA B604-96. AWWA, 6666 W. Quincy Ave., Denver, CO 80235.

Benefield et al. 1982
Benefield, L.D., J.F. Judkins, B.L. Weand, 1982. *Process Chemistry for Water and Wastewater Treatment*. Prentice-Hall, Inc., Publishers, Englewood Cliffs, NJ 07632.

Black & Veatch 1998
Black & Veatch Waste Science, Inc., *Alternative (Non Activated Carbon) Processes for Adsorption of Organics*, Report prepared for U.S. Army Corps of Engineers.

Calgon 1994
Calgon Carbon Corporation, 1994. *Equipment Bulletin-Ventsorb-PE.* Pittsburgh, PA.

Dobbs and Cohen 1980
Dobbs, R.A., and J.M. Cohen, 1980. *Carbon Adsorption Isotherms for Toxic Organics*, U.S. Environmental Protection Agency, EPA-600/8-80-023.

EM 1110-1-4001
Soil Vapor Extraction and Bioventing.

EM 1110-1-4007
Safety and Health Aspects of Hazardous, Toxic, and Radioactive Waste Remediation Technologies.

Erskine and Schuliger 1971
Erskine, D.B. and W.G. Schuliger, 1971. “Activated Carbon Processes for Liquids,” *Chemical Engineering Process*, Vol. 67, Noll, November.

Faust and Aly 1987
Faust, S.D., and O.M. Aly 1987. *Adsorption Processes for Water Treatment*, Butterworth Publishers, Boston, Massachusetts.

Guide Specification 11225
Downflow Liquid Activated Carbon Adsorption Units.

Guide Specification 11226
Vapor Phase Activated Carbon Adsorption Units.

McLaughlin 1995
McLaughlin, H.S., 1995. “Regenerate Activated Carbon Using Organic Solvents,” *Chemical Engineering Progress*, July, pp. 45–53.

O'Brien and Fisher 1983
1983. “There is an Answer to Groundwater Contamination,” *Water Engineering and Management*, May.

O'Brien et al. 1987
O'Brien, R.P., J.L. Rizzo, and W.G. Schuliger, 1987. “Removal of Organic Compounds from Industrial Wastewaters Using Granular Carbon Column Processes,” *Control of Organic Substances in Water and Wastewater* (B.B. Berger, ed.) Noyes Data Corp., Park Ridge, NJ.

Pontius 1990
Pontius, F.W., ed., 1990. *Water Quality and Treatment, A Handbook of Community Water Supplies*, Fourth Edition, McGraw-Hill, Inc. Publishing Company, New York, NY.

Schuliger et al. 1988
Schuliger, W.G., G.N. Riley, and, N.J. Wagner, 1988. “Thermal Reactivation of GAC: A Proven Technology, ” *Waterworld News*, Vol. 4, No. 1, January/February.

Shelley 1994
Shelley, S., ed, 1994. “Reduce the Risk of Adsorbent Bed Fires During Recovery, ” *Chemical Engineering*, December, Plant Notebook Feature.

Valenzuela and Myers 1989
Valenzuela, D.P., and A.L. Myers. 1989. *Adsorption Equilibrium Data Handbook*. Prentice Hall, Englewood Cliffs, New Jersey, 07632,. ISBN 0-13-008815-3.

Zanitsch and Lynch 1997
Zanitsch, R.H., and R.T. Lynch, 1997. “Selecting a Thermal Regeneration System for Activated Carbon,” *Carbon Adsorption Handbook*, Calgon Carbon Corporation.