

**CARBON:
ACTIVATED CARBON**

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ACTIVATED CARBON

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Activated carbon is a predominantly amorphous solid that has an extraordinarily large internal surface area and pore volume. These unique characteristics are responsible for its adsorptive properties, which are exploited in many different liquid- and gas-phase applications. Activated carbon is an exceptionally versatile adsorbent because the size and distribution of the pores within the carbon matrix can be controlled to meet the needs of current and emerging markets (1). Engineering requirements of specific applications are satisfied by producing activated carbons in the form of powders, granules, and shaped products. Through choice of precursor, method of activation, and control of processing conditions, the adsorptive properties of products are tailored for applications as diverse as the purification of potable water and the control of gasoline emissions from motor vehicles.

In 1900, two very significant processes in the development and manufacture of activated carbon products were patented (2). The first commercial products were produced in Europe under these patents: Eponite, from wood in 1909, and Norit, from peat in 1911. Activated carbon was first produced in the United States in 1913 by Westvaco Corp. under the name Filtchar, using a by-product of the papermaking process (3). Further milestones in development were reached as a result of World War I. In response to the need for protective gas masks, a hard, granular activated carbon was produced from coconut shell in 1915. Following

Table 1. Properties of Selected U.S. Activated Carbon Products^a

Property	Gas-phase carbons				Liquid-phase carbons			
	Manufacturer	Calgon	Norit	Westvaco	Calgon	Norit	Westvaco	
particle size, U.S. mesh ^{b,c}		12 × 30	3.8 mm	10 × 25	8 × 30	64% < 325	65-85% < 325	
apparent density, g/cm ³		>0.48	0.43	0.27	0.52	0.46	0.34-0.37	
particle density, g/cm ³		0.80		0.50	0.80			
hardness number		>90	99					
abrasion number					>75			
ash, wt %		<8	6		<10	6	3-5	
BET surface area, N ₂ , m ² /g		1050-1150	1100-1200	1750	900-1000	750	1400-1800	
total pore volume, cm ³ /g		0.8	0.9	1.2	0.85		2.2-2.5	
CCl ₄ activity, wt %		>60						
butane working capacity, g/100 cm ³				>11.0				
iodine number		>1050			>900	800	>1000	
decolorizing index								
Westvaco								>20
molasses number								
Calgon								
Norit								
heat capacity at 100°C, J/(g·K) ^d		1.05				440		
thermal conductivity, W/(m·K)		0.05-0.10						

^aSpecific values shown are those cited in manufacturers' product literature (19). Typical ranges shown are based on values reported in the open literature.

^bUnless otherwise noted.

^cApproximate mm corresponding to cited meshes are mesh: mm ...4: 4.76; 8: 2.38; 10: 2; 12: 1.68; 25: 0.72; 30: 0.59; 325: 0.04.

^dTo convert J to cal, divide by 4.184.

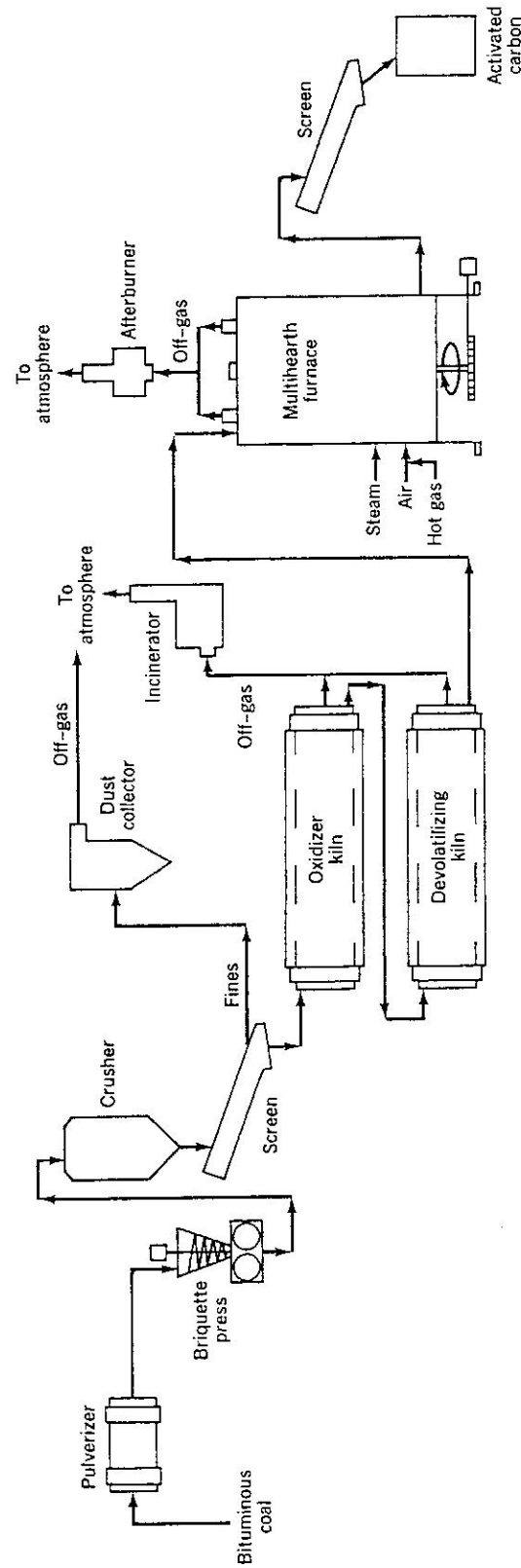


Fig. 1. Thermal activation of bituminous coal.

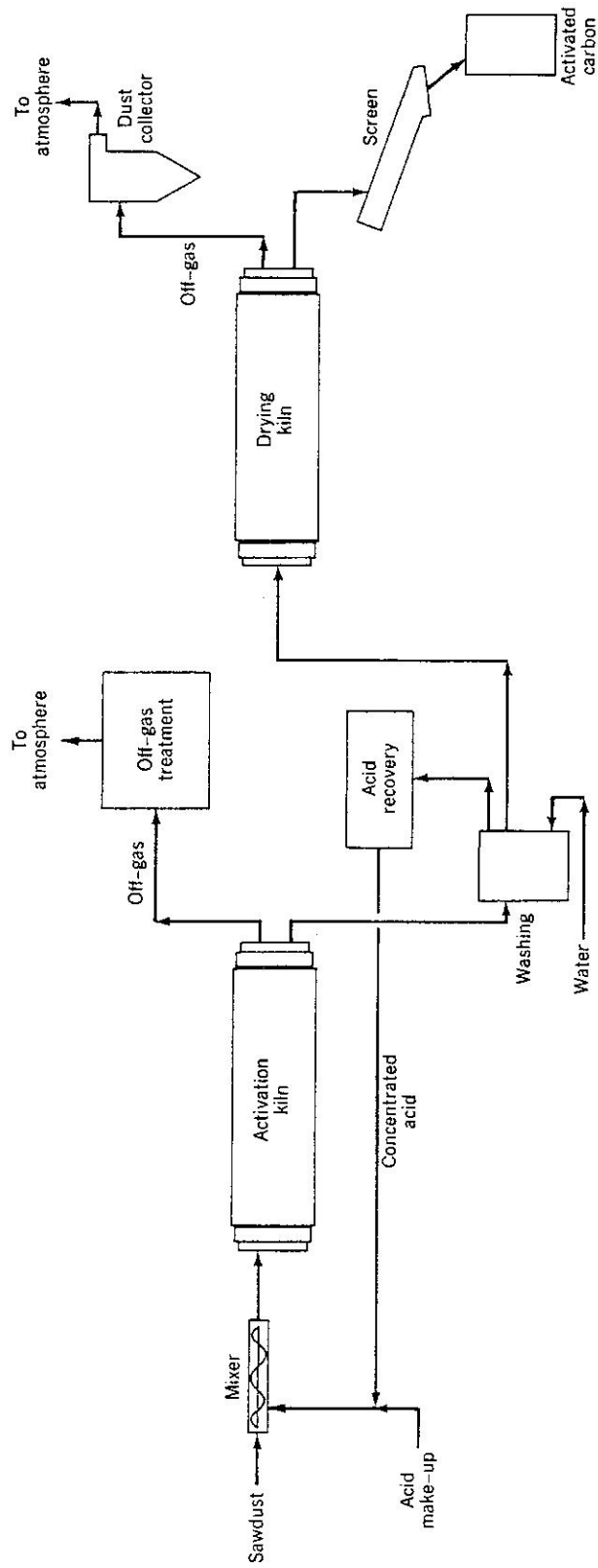


Fig. 2. Chemical activation of wood.

essentially unchanged, but minor fluctuations occurred in response to changes in environmental regulations (38). A similar reaction was noted worldwide (35). The current demand for activated carbon is estimated at 93% of production capacity. The near-term growth in demand is projected to be approximately 5.5%/yr (39).

In 1970 the U.S. Congress enacted the Clean Air Act, the Clean Water Act, and the Safe Drinking Water Act. Because activated carbon can often be used to help meet Environmental Protection Agency (EPA) regulations, the U.S. activated carbon industry reacted by increasing its production capacity. A proposed amendment to the Safe Drinking Water Act in 1979 required the use of granular activated carbon systems, but the amendment was not enacted. In response to the projected increase in demand for activated carbon, production capacity remained high until the late 1980s, but when the anticipated need did not materialize, some production facilities were shut down. Currently, because of stricter EPA regulations implementing all three acts in 1990, the industry will increase production capacity by 25% during the next several years (35,40).

The estimated production capacity of activated carbon in the United States is shown in Table 3 for seven manufacturers (41). The principal producers are Calgon Carbon (37%), American-Norit (26%), Westvaco (19%), and Atochem (10%). Several other companies purchase activated carbon for resale but do not manufacture products.

Table 3. Production Capacity in the United States, Estimated 1990

Company	Location	Capacity, 10 ³ t
Acticarb Division, Royal Oak Enterprises	Romeo, Fla.	6.8
American Norit Co.	Marshall, Tex.	38.6
Barneby and Sutcliffe	Columbus, Ohio	3.0
Calgon Carbon Corp.	Catlettsburg, Ky. and Pittsburgh, Pa.	53.5
Ceca Division, Atochem NA	Pryor, Okla.	15.0
Trans-Pacific Carbon	Blue Lake, Calif.	2.3
Westvaco Corp.	Covington, Va.	27.2
<i>Total</i>		<i>146.4</i>

Western Europe has seven manufacturers of activated carbon. The two largest, Norit and Chemviron (a subsidiary of Calgon), account for 70% of West European production capacity, and Ceca accounts for 13% (42). Japan is the third largest producer of activated carbon, having 18 manufacturers, but four companies share over 50% of the total Japanese capacity (43). Six Pacific Rim countries account for the balance of the world production capacity of activated carbon, 90% of which is in the Philippines and Sri Lanka (42). As is the case with other businesses, regional markets for activated carbon products have become international, leading to consolidation of manufacturers. Calgon, Norit, Ceca, and Sutcliffe-Speakman are examples of multinational companies.

Activated carbon is a recyclable material that can be regenerated. Thus the economics, especially the market growth, of activated carbon, particularly

Table 4. Source References for Activated Carbon Test Procedures and Standards

Title of procedure or standard	Source
Standard Definitions of Terms Relating to Activated Carbon	ASTM D2652
Apparent Density of Activated Carbon	ASTM D2854
Particle Size Distribution of Granular Activated Carbon	ASTM D2862
Total Ash Content of Activated Carbon	ASTM D2866
Moisture in Activated Carbon	ASTM D2867
Ignition Temperature of Granular Activated Carbon	ASTM D3466
Carbon Tetrachloride Activity of Activated Carbon	ASTM D3467
Ball-Pan Hardness of Activated Carbon	ASTM D3802
Radiiodine Testing of Nuclear-Grade Gas-Phase Adsorbents	ASTM D3803
pH of Activated Carbon	ASTM D3838
Determination of Adsorptive Capacity of Carbon by Isotherm Technique	ASTM D3860
Determining Operating Performance of Granular Activated Carbon	ASTM D3922
Impregnated Activated Carbon Used to Remove Gaseous Radio-Iodines from Gas Streams	ASTM D4069
Determination of Iodine Number of Activated Carbon	ASTM D4607
Military Specification, Charcoal, Activated, Impregnated	Ref. 54
Military Specification, Charcoal, Activated, Unimpregnated	Ref. 54
AWWA Standard for Granular Activated Carbon	Ref. 33
AWWA Standard for Powdered Activated Carbon	Ref. 34
BET Surface Area by Nitrogen Adsorption	Refs. 6, 8, 9, 55
Pore Volume by Nitrogen Adsorption or Mercury Penetration	Refs. 10, 56-59
Particle Density	Ref. 60

According to the National Board of Fire Underwriters, activated carbons normally used for water treatment pose no dust explosion hazard and are not subject to spontaneous combustion when confined to bags, drums, or storage bins (64). However, activated carbon burns when sufficient heat is applied; the ignition point varies between about 300 and 600°C (65).

Dust-tight electrical systems should be used in areas where activated carbon is present, particularly powdered products (66). When partially wet activated carbon comes into contact with unprotected metal, galvanic currents can be set up; these result in metal corrosion (67).

Manufacturer material safety data sheets (MSDS) indicate that the oxygen concentration in bulk storage bins or other enclosed vessels can be reduced by wet activated carbon to a level that will not support life. Therefore, self-contained air packs should be used by personnel entering enclosed vessels where activated carbon is present (68).

Liquid-Phase Applications

Activated carbons for use in liquid-phase applications differ from gas-phase carbons primarily in pore size distribution. Liquid-phase carbons have significantly more pore volume in the macropore range, which permits liquids to diffuse more rapidly into the mesopores and micropores (69). The larger pores also promote greater adsorption of large molecules, either impurities or products, in many

at any given time. When the first column becomes saturated, it is removed from service, and a column containing fresh carbon is added at the discharge end of the series. An alternative approach is the moving bed column (73). In this design the adsorption zone is contained within a single column by passing liquid upward while continuously or intermittently withdrawing spent carbon at the bottom and adding fresh carbon at the top.

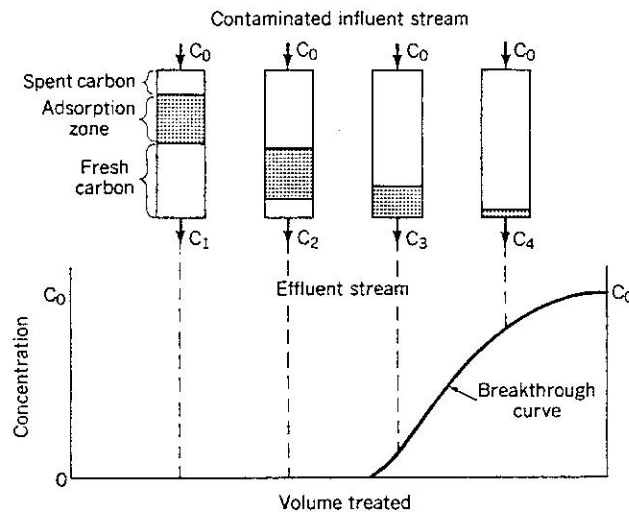


Fig. 4. Adsorption zone and breakthrough curve for fixed bed of granular or shaped activated carbon.

The total activated carbon consumption for liquid-phase applications in the United States in 1987 was estimated to be about 76,700 t, which accounted for nearly 80% of the total activated carbon use. The consumption by application is summarized in Table 5 (74).

Potable Water Treatment. Treatment of drinking water accounts for about 24% of the total activated carbon used in liquid-phase applications (74). Rivers, lakes, and groundwater from wells, the most common drinking water sources, are often contaminated with bacteria, viruses, natural vegetation decay products, halogenated materials, and volatile organic compounds. Normal water disinfection and filtration treatment steps remove or destroy the bulk of these materials (75). However, treatment by activated carbon is an important additional step in many plants to remove toxic and other organic materials (76-78) for safety and palatability.

Groundwater Remediation. Concern over contaminated groundwater sources increased in the 1980s, and in 1984 an Office of Groundwater Protection was created by the EPA (74). This led to an increase in activated carbon consumption in 1987 for groundwater treatment to about 4% of the total liquid-phase usage, and further growth is expected in the 1990s. There are two ways to apply carbon in groundwater cleanup. One is the conventional method of applying powdered, granular, or shaped carbon to adsorb contaminants directly from the water. The other method utilizes air stripping to transfer the volatile compounds

Food, Beverage, and Cooking Oil. Approximately 6% of the liquid-phase activated carbon is used in food, beverage, and cooking oil production (74). Before being incorporated into edible products, vegetable oils and animal fats are refined to remove particulates, inorganics, and organic contaminants. Activated carbon is one of several agents used in food purification processes. In the production of alcoholic beverages, activated carbon removes haze-causing compounds from beer, taste and odor from vodka, and fusel oil from whiskey (82). The feed water for soft drink production is often treated with carbon to capture undesirable taste and odor compounds and to remove free chlorine remaining from disinfection treatment. Caffeine is removed from coffee beans by extraction with organic solvents, water, or supercritical carbon dioxide prior to roasting. Activated carbon is used to remove the caffeine from the recovered solvents (83).

Pharmaceuticals. Pharmaceuticals account for 6% of the liquid-phase activated carbon consumption (74). Many antibiotics, vitamins, and steroids are isolated from fermentation broths by adsorption onto carbon followed by solvent extraction and distillation (82). Other uses in pharmaceutical production include process water purification and removal of impurities from intravenous solutions prior to packaging (83).

Mining. The mining industry accounts for only 4% of liquid-phase activated carbon use, but this figure may grow as low-grade ores become more common (74). Gold, for example, is recovered on activated carbon as a cyanide complex in the carbon-in-pulp extraction process (82). Activated carbon serves as a catalyst in the detoxification of cyanides contained in wastewater from cyanide stripping operations (73). Problems caused by excess flotation agent concentrations in flotation baths are commonly cured by adding powdered activated carbon (82).

Miscellaneous Uses. Several relatively low volume activated carbon uses comprise the remaining 6% of liquid-phase carbon consumption (74). Small carbon filters are used in households for purification of tap water. Oils, dyes, and other organics are adsorbed on activated carbon in dry cleaning recovery and recycling systems. Electroplating solutions are treated with carbon to remove organics that can produce imperfections when the thin metal layer is deposited on the substrate (82). Medical applications include removal of toxins from the blood of patients with artificial kidneys (83) and oral ingestion into the stomach to recover poisons or toxic materials (82,84). Activated carbon also is used as a support for metal catalysts in low volume production of high value specialty products such as pharmaceuticals, fragrance chemicals, and pesticides (85).

Gas-Phase Applications

Gas-phase applications of activated carbon include separation, gas storage, and catalysis. Although only 20% of activated carbon production is used for gas-phase applications, these products are generally more expensive than liquid-phase carbons and account for about 40% of the total dollar value of shipments. Most of the activated carbon used in gas-phase applications is granular or shaped. Activated carbon use by application is shown in Table 6 (86).

application of a vacuum. The vapor that is pumped off is recovered in an absorber by contact with liquid gasoline. Similar equipment is used in the transfer of fuel from barges (90). The type of carbon pore structure required for these applications is substantially different from that used in solvent recovery. Because the regeneration conditions are very mild, only the weaker adsorption forces can be overcome, and therefore the most effective pores are in the mesopore size range (91). A large adsorption capacity in these pores is possible because vapor concentrations are high, typically 10–60%.

Adsorption of Radionuclides. Other applications that depend on physical adsorption include the control of krypton and xenon radionuclides from nuclear power plants (92). The gases are not captured entirely, but their passage is delayed long enough to allow radioactive decay of the short-lived species. Highly microporous coconut-based activated carbon is used for this service.

Control by Chemical Reaction. Pick-up of gases to prevent emissions can also depend on the chemical properties of activated carbon or of impregnants. Emergency protection against radioiodine emissions from nuclear power reactors is provided by isotope exchange over activated carbon impregnated with potassium iodide (93). Oxidation reactions catalyzed by the carbon surface are the basis for several emission control strategies. Sulfur dioxide can be removed from industrial off-gases and power plant flue gas because it is oxidized to sulfur trioxide, which reacts with water to form nonvolatile sulfuric acid (94,95). Hydrogen sulfide can be removed from such sources as Claus plant tail gas because it is converted to sulfur in the presence of oxygen (96). Nitric oxide can be removed from flue gas because it is oxidized to nitrogen dioxide. Ammonia is added and reacts catalytically on the carbon surface with the nitrogen dioxide to form nitrogen (97).

Protection Against Atmospheric Contaminants. Activated carbon is widely used to filter breathing air to protect against a variety of toxic or noxious vapors, including war gases, industrial chemicals, solvents, and odorous compounds. Activated carbons for this purpose are highly microporous and thus maximize the adsorption forces that hold adsorbate molecules on the surface. Although activated carbon can give protection against most organic gases, it is especially effective against high molecular weight vapors, including chemical warfare agents such as mustard gas or the nerve agents that are toxic at parts per million concentrations. The activated carbon is employed in individual canisters or pads, as in gas masks, or in large filters in forced air ventilation systems. In air-conditioning systems, adsorption on activated carbon can be used to control the buildup of odors or toxic gases like radon in recirculated air (98).

Inorganic vapors are usually not strongly adsorbed on activated carbon by physical forces, but protection against many toxic agents is achieved by using activated carbon impregnated with specific reactants or decomposition catalysts. For example, a combination of chromium and copper impregnants is used against hydrogen cyanide, cyanogen, and cyanogen chloride, whereas silver assists in the removal of arsine. All of these are potential chemical warfare agents; the Whetlerite carbon, which was developed in the early 1940s and is still used in military protective filters, contains these impregnants (99). Recent work has shown that chromium, which loses effectiveness with age and is itself toxic, can be replaced with a combination of molybdenum and triethylenediamine (100).

halogens across a carbon-carbon double bond in the production of a variety of organic halides (85) and is used in the production of phosgene from carbon monoxide and chlorine (115,116).

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Section 2

ACTIVATED CARBONS

Their Use as Adsorbents . . . Their Manufacture . . .
and Structure

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- Historical
- Adsorption as a Separation Process
- Industrial Applications
- Manufacture of Decolorizing Carbons
- Quality Control
- Fundamental Properties
 - (A) Surface Area
 - (B) Pore Volume Distribution
 - (C) Nature of Surface
 - (D) Nature of Adsorbate

HISTORICAL

Activated carbon is no longer new. Modern activated carbon dates back to 1900 when a German patent was issued for the manufacture of a steam activated carbon from carbonaceous raw materials. The first significant application of activated carbons to process work (about 1909) was in sugar refining—still one of the primary uses accounting for millions of pounds of activated carbon a year. Carbon production became significant in Holland in 1911, and in Germany in 1913. United States production began with activated carbons made from peachpits and nut shells for gas-phase adsorption and for use in gas mask filters during World War I.

After the war (1917-1923) American production grew rapidly in the field of liquid-phase adsorption because of the development of new grades of activated carbon manufactured from (1) black ash, a paper pulp waste residue, and (2) lignite. These carbons were used predominantly in sugar refining. Use of activated carbons in the control of taste and odor in water began in America in 1929.

Today, the activated carbon business is world-wide. In addition to the manufacturers in the United States, producers are located in England, France, Holland, Germany, Italy, Russia and Japan. The tradenames are numerous. Common ones are: DARCO, Nuchar, Norit, Pittsburgh and Columbia.

While sugar refining and municipal water treatment are the largest single uses of activated carbon in liquid-phase processes, there are any number of other large uses throughout the chemical industry because adsorption is the most logical method for separating colloidal or dissolved substances at relatively low concentrations where other methods are costly and inefficient. In general, activated carbon is good for adsorption of dissolved organic substances and, with a few exceptions, not good for adsorption of dissolved inorganic substances. Activated carbon can be used in both aqueous and non-aqueous solutions.

Adsorption is the process whereby a surface accumulates and retains molecular or ionic species coming into contact with it. Because adsorption is a surface phenomenon, the extent and properties of the surface will control adsorptive effects. For a particular type of adsorbent, the greater the surface available the greater the amount adsorbed. However, surface properties or conditions can affect the course and type of adsorption. Due to its great porosity, activated carbon is one of the few solids that can provide extremely high surface area per unit weight or unit volume at relatively low cost.

The adsorbed layer forms on the carbon surface only one to several molecules deep. However, since activated carbon can be made to possess from 450 to 1800 square meters per gram, significant quantities of material can be adsorbed by moderate weights of carbon.

ADSORPTION AS A SEPARATION PROCESS

INDUSTRIAL APPLICATIONS

A large number of industrially important separations fall within the scope of adsorption by decolorizing activated carbon. Among these are:

1. Removal of impurities causing color, taste, or odor.
2. Removal of small concentrations of products, which may have no color, taste, or odor, but which cause poor crystal yield or poor crystal habit.
3. Removal of trace quantities of impurities having no original color, but subject to oxidation or other changes which may develop color at a later stage of processing, or after the product has been packaged and sold (color precursors).
4. Removal of constituents causing foam or other undesirable surface-active phenomena, which interfere with other plant processes such as evaporation, agitation, or air-blowing.
5. Removal of impurities causing haze or turbidity, including those which do not precipitate out until after the product is sold (haze precursors, causing poor shelf life resulting in the product being returned by dissatisfied customers).
6. Removal of trace quantities of water from water-immiscible organic solvents, or vice versa.
7. Removal of impurities from a liquid by extracting them with a trace quantity of immiscible solvent, and then adsorbing the resulting solution of solvent and impurities on carbon. This is useful where direct adsorption is unsuccessful.
8. Removal of trace quantities of ionic metals, by complexing with an adsorbable organic reagent and adsorbing the complex.

Two separations not concerned with the removal of impurities are:

1. Concentration of valuable solute from dilute solution by adsorption with recovery by elution.
2. Scavenging of liquids or solutions dispersed in solids (*e.g.*, staining oils in reclaimed rubber, drill mud additives in oil well cements, herbicides or odorous insecticides in soils).

MANUFACTURE OF DECOLORIZING CARBONS

How are these porous, carbonaceous products made? All of them are derived from gaseous, liquid, or solid carbonaceous substances by one of two general methods both of which include thermal decomposition of the starting material. The surface areas and porosities are a combined result of the process and the raw material.

The two general methods of activation are:

1. High-temperature oxidation of a previously charred carbonaceous substance (coke, char, charcoal), and
2. Lower temperature chemical dehydration and/or chemical reaction of a carbonaceous raw material.

The bulk of current production in the United States is made by the high-temperature steam process. Some chemically activated carbon is produced. However, in continental Europe more emphasis is placed on chemical activation.

Precise control of both reaction temperature and reaction time is very important in steam activation processes to impart desired properties. Temperatures usually range upwards from 800°C. Almost any carbonaceous substance can be used as a raw material for steam activation. Our company uses lignite, a low rank coal lying between peat and sub-bituminous coal in the coal series, and wood charcoal. Other commercial raw materials are coal, coke, black ash and peat.

In the Atlas lignite process, crushed lignite (usually below 1 inch in size) is fed to a rotary kiln maintained at temperatures above 800°C. The carbonaceous material is there reacted with steam. Because the reaction is endothermic, heat must be supplied to maintain reaction temperatures. The activated product from the kilns is an intermediate product for the subsequent preparation of various types and grades of commercial activated carbons.

Post activation processing embraces crushing, grading, grinding, acid-washing, water-washing, drying and packaging.

Our common granular grades are screened to 4 x 12, 12 x 20, and 20 x 40, U.S. standard mesh sizes. The powdered grades are ground to 50 to 98 percent minus 325 mesh.

Depending upon the application, activated carbons are supplied in washed or unwashed grades. The purpose of washing (with mineral acids and water) is to remove extractable ash constituents. After washing, activated

carbons are dried by one of four conventional methods: tray, drum, rotary, or flash. Activated carbon manufactured from wood charcoal involves the same steps.

To make activated carbons directly from cellulosic material, primarily wood, chemical activation involving somewhat lower processing temperatures (200° to 650°C) is employed. The activating agents are many, but all are strongly dehydrating substances. The three most commonly used are phosphoric acid, zinc chloride, and sulphuric acid. Each has its limitation. Sulfuric acid-wood mixtures cannot be carried above 200°C, and the product, after leaching, has adsorptive properties only when wet. Activation by phosphoric acid requires temperatures in the range of 375° to 500°C. The reagent is recovered by leaching with water. Problems with the phosphoric acid process are primarily associated with corrosion of the equipment. Zinc chloride activation occurs in the range of 550° to 650°C. The reagent is recovered by leaching with dilute hydrochloric acid and water. Problems may arise from traces of zinc salts remaining in the product. The last two types of carbon can be dried with little or no loss of adsorptive capacity. Other chemicals have been used as activating agents on a research scale: magnesium chloride, ferric chloride, potassium thiocyanate, aluminum chloride, sodium carbonate, and sodium hydroxide.

Large-scale production of carbons by our company dates from 1922, when the first plant for using our original process was erected in the Texas area where huge low-cost lignite deposits and one of the world's greatest natural gas fields were both close by.

We also manufacture other activated carbons from wood charcoal by the high-temperature steam process (since 1933) and from wood by the chemical activation process using phosphoric acid (since 1939). The carbons from these two processes, while more costly, are of economic value because of their unusual properties.

Precise control of the activation process is required. Conditions must be varied to meet the inevitable changes in composition that are found in natural raw materials. To insure the highest possible product uniformity, carbons are carefully analyzed on a shift basis for those properties of paramount interest to the customer.

Because our major concern is with the decolorizing type of carbon, our remarks will primarily apply to this material.

**QUALITY
CONTROL**

All major manufacturers of this type of activated carbon measure activity by some form of molasses decolorization test. This test, while arbitrary in every respect, does rate carbons for such major applications as cane, corn, and beet sugar refining. Long experience has shown it to be a good index of efficiency for other uses as well. However, for water and waste treatment carbons, special activity control tests are used. Other properties subjected to quality control are water extractables, pH, filterability and moisture.

(A) Surface Area

Activated carbon is truly a rigid sponge as a result of the manufacturing procedure. During the charring of any carbonaceous substance, considerable volatile matter is given off. In the course of the evolution of this volatile matter, a large number of internal spaces are formed, referred to as pores. Pores can mean cracks and crevices as well as the conventional connotation of cylinders or cones.

One of the reasons activated carbon is such an excellent adsorbent is because of its tremendous surface area on which molecules from gaseous or liquid phases are concentrated. It is one of the few substances extant which can be developed to present such fantastic areas per unit weight, *viz.*, 450-1800 sq m/g.

Surface areas are measured by nitrogen sorption and established techniques.

A major factor controlling the amount of adsorption is surface area available to the material being adsorbed. In manufacture it is desirable to develop maximum surface commensurate with economics and use. However, if we have an activated carbon with a large surface area it is still necessary to get the molecules to this area. For example, if we have an activated carbon with a surface area of 1300 sq m/g but with pore openings at the particle surface of only 20 Å diameter and material of 30 Å diameter to be adsorbed, any adsorption will be restricted to the external surface of the particle and will be negligible. Thus, a good adsorbent is a combination of large surface area and sufficient pathways to that area. To give us an insight, even if imperfect, to such access routes, we measure pore volume and pore volume distribution across the range of pore radii, *viz.*, 2.5 Å to 50,000 Å radius.

FUNDAMENTAL PROPERTIES

(B) Pore Volume Distribution

The specific pore volume of an activated carbon is determined from the differences of the specific volume of the carbon particles including pores and the specific volume of the carbon particles excluding pores. The first specific volume is determined in mercury, because it is the only common liquid which will not penetrate the pores of carbon at atmospheric pressure. The second specific volume is determined in helium, which, because of its small molecule, will penetrate the pores of the carbon particle completely and is not adsorbed at room temperatures.

To determine the volume in the pores of various radii, we use three techniques:

1. Mercury intrusion for coarse pores greater than 125 Å radius.
2. Nitrogen desorption for fine pores less than 125 Å radius to 20 Å radius.
3. Water desorption for fine pores less than 125 Å radius to 2.5 Å radius (not always applicable).

Ritter and Drake in 1945 reported an adaptation of a procedure by Washburn (1925) for the measurement of incremental pore volume by mercury intrusion. The equation applicable to this technique is:

$$r = \frac{-2 \sigma \cos \Theta}{P}$$

r = pore radius in Å

σ = surface tension of mercury = 470 dynes/cm

Θ = contact angle between mercury and carbon, assumed to be 140°

P = pressure, absolute, in dynes/sq cm

In units better suited to our purpose the equation becomes:

$$r = \frac{106.5 \times 10^4 \text{ Å}}{\text{psi abs}}$$

By noting the volume change of mercury for an out-gassed carbon sample in the capillary of a dilatometer as pressure is applied, the volume increments for various pore radii are obtained up to the limit of the apparatus. In our porosimeter the maximum pressure is 10,000 psig. This value is equivalent to 106 Å radius. To increase the range we must be able to increase pressure.

$$20,000 \text{ psig} = 53 \text{ Å radius}$$

$$30,000 \text{ psig} = 35 \text{ Å radius}$$

$$50,000 \text{ psig} = 21 \text{ Å radius}$$

However, too high pressures can crush the carbon particles.

We measure the finer pores by means of nitrogen desorption. If only pore volume is desired, we measure the volume of gas adsorbed at the saturation pressure of the gas. But this pore volume seldom agrees with that measured by helium and mercury densities because of the difficulty of obtaining a true reading at saturation pressure.

The equation applicable to this method is:

$$V_p = \frac{V_s M}{V_m \rho_a}$$

V_p = volume of adsorbed phase in the pore volume

V_s = volume of gas (STP) adsorbed per gram of adsorbent at saturation pressure

M = molecular weight of adsorbate

V_m = molecular volume of adsorbate

ρ_a = density of adsorbed phase (0.808 g/ml for nitrogen at its boiling point)

In nitrogen desorption, the pressure is decreased stepwise from saturation. Nitrogen molecules condensed in the pores of the adsorbent do not evaporate as readily as they would from the bulk of liquid owing to the

lowering of vapor pressure over the concave meniscus of the condensed liquid in the pores. This lowering is given by the Kelvin equation :

$$\ln P/P_s = \frac{-2 V\sigma \cos \theta}{rRT}$$

P = measured pressure

P_s = saturation pressure

V = molal volume of the liquid adsorbate

σ = surface tension of adsorbate

θ = angle of contact of liquid adsorbate with adsorbent

r = radius of curvature of meniscus

R = gas constant

T = absolute temperature

If cylindrical pores and a zero contact angle are assumed, r may be considered equal to pore radius. If we assume that at any point on the desorption isotherm, all pores of smaller radius than r are filled with condensed vapor, it is possible to plot a curve of the volume of pores with radii smaller than r , against r . This procedure gives pore sizes which are too small. Corrections must be made for nitrogen still adsorbed on the walls or surface of the pores.

The retained phase is a composite of multilayer adsorption and capillary condensation. The reduction in the pressure results not only in emptying the largest pore of its capillary condensate but also a reduction in thickness of the physically adsorbed layer. As the pressure is reduced further this process of desorption continues into smaller and smaller pores.

From such desorption data and using the method of Barrett, Joyner and Halenda and the multilayer adsorption data for non-porous solids reported by Pierce, we calculate the pore volumes for specific pore radii ranges. The method depends upon two fundamental assumptions :

1. The pores are cylindrical, and
2. the amount of adsorbate in equilibrium with the gas phase is retained by the adsorbent by two mechanisms.
 - (a) physical adsorption on the pore walls, and
 - (b) capillary condensation in the remaining pore volume.

The smallest pore that can be measured satisfactorily by nitrogen desorption is about 20 Å radius. This limitation is due to the possibility of changes in the liquid density and surface tension in very small capillaries

and to the appreciable amount of physical adsorption of the nitrogen. A comparison of the true pore radius and that calculated by the Kelvin equation for the same relative pressure is shown in Table I.

Table I
COMPARISON OF TRUE PORE RADIUS AND
KELVIN PORE RADIUS AT THE SAME
RELATIVE PRESSURES OF NITROGEN

Relative Pressure P/P_s	Statistical Number of Adsorbed Layers n	Thickness of Adsorbed Layers (3.6 \AA) [*] n	True Pore Radius (r_p) \AA	Kelvin Pore Radius (R_k) \AA	Estimated maximum number of molecules in plane at \perp to capillary wall**
0.149	1.08	4.2	9.3	5.0	3
0.220	1.28	4.6	10.9	6.3	7
0.385	1.52	5.5	15.5	10.0	14
0.469	1.65	5.9	18.5	12.6	23
0.620	1.95	7.0	27.0	20.0	50
0.684	2.12	7.6	32.7	25.1	60

*Thickness of one molecule of nitrogen in adsorbed form

$$= \frac{\text{Molal volume of liquid } N_2 \text{ at } t^\circ\text{C in } \text{\AA}^3}{(\text{Area of one molecule of liquid } N_2 \text{ in } \text{\AA}^2) (\text{Avogadro's No.})}$$

$$= \frac{34.67 \times 10^{24} \text{ \AA}^3}{16.2 \times 6.025 \times 10^{23}}$$

$$= 3.6 \text{ \AA}$$

**Diameter of nitrogen molecule in liquid state

$$= \left(\frac{\text{Molal volume of liquid } N_2 \text{ at } t^\circ\text{C}}{(\text{Avogadro's number}) (0.71)} \right)^{1/3}$$

$$= \left(\frac{34.67 \times 10^{24} \text{ \AA}^3}{6.025 \times 10^{23} \times 0.71} \right)^{1/3} = 4.32 \text{ \AA}$$

This calculation is based on the assumption of closest packing in a liquid, and spherical shape of the nitrogen molecule. The volume of a unit cell for closest packing of spheres is $0.71d^3$.

As the pore radius becomes small, the adsorbed layer becomes an appreciable part of the pore volume. The number of nitrogen molecules at the meniscus is quite small.

The concept of a meniscus in equilibrium with a vapor ceases to have a precise meaning as the pore radius approaches the diameter of the adsorbate molecule. Consequently, extension of the Kelvin equation to the measurement of pores of very small radius cannot be rigorously justified.

The measurement of pore sizes larger than 1000 Å radius is limited by the rapid change of meniscus radius with relative pressure near saturation pressure, as shown in Table II.

Table II
MENISCUS RADIUS VS. PRESSURE

P/P_s	$P (P_s = 760.00)$	Radius, Å
0.9811	745.64	524
0.9905	752.78	1029
0.9925	754.22	1291
0.9981	758.56	5064
0.9985	758.86	6367
0.99905	759.28	10067
0.99952	759.63	20038
0.99981	759.86	50240

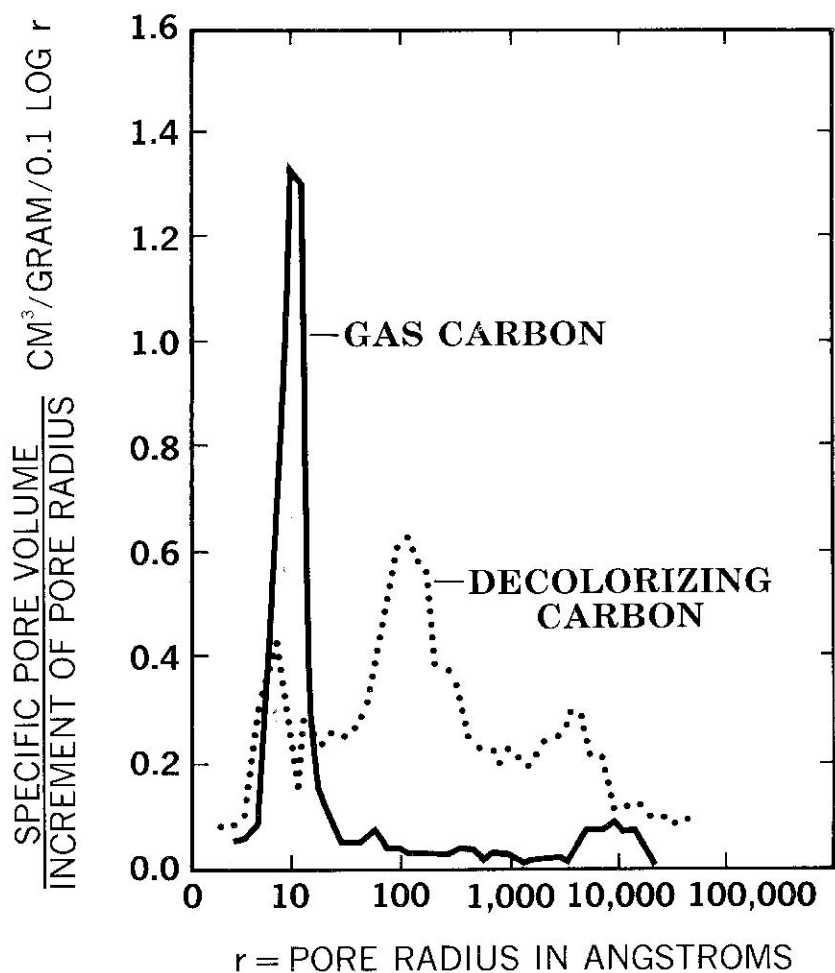
Exact values of pore radius have no real meaning at this size because of lack of precision due to experimental difficulties.

Combination of the sorption and porosimeter techniques has given us a picture of the pore volume distribution over the measureable range of pore radii. With these techniques we are able to follow the physical structural changes that occur during the activation process. Some typical distribution curves are shown in figures 1 through 3. A so-called gas adsorbing carbon (Columbia G) and a typical decolorizing carbon (granular DARCO) are shown in Figure 1.

The main distinction between gas-adsorbing and decolorizing carbons lies in pore volume distribution, areas being similar. Gas adsorbing activated carbons usually show only bi-modal pore volume distribution, *i.e.*, peak volumes in the micropore (3-50 Å radius) and in the macropore (1000-50,000 Å radius) ranges, with little pore volume in the transitional pore (50-1000 Å radius) range. Decolorizing activated carbons show three dis-

tinct peaks, *i.e.*, one in each of the three pore radii ranges. The presence of significant pore volume in the transitional pore range gives an open structure which permits ready access of solutions or liquids to the micro-pore structure resulting in rapid attainment of adsorption equilibrium for smaller adsorbates. In addition it improves accessibility and subsequent adsorption for larger molecular and colloidal substances.

Figure 1
PORE VOLUME DISTRIBUTION
OF TYPICAL
ACTIVATED CARBONS



In Figure 2 the pore volume distribution curves are given for three decolorizing activated carbons produced by the steam activation process from the same raw material. The tri-modal pore volume distribution is evident in the three levels of activity. The pore volumes increase in the transitional and macropore ranges and decrease in the micropore range with increasing activity based on molasses decolorization.

The differences in pore volume distributions between various activated carbons made by different processes from different raw materials but all used for liquid-phase separations are not so much in the distributions of the pore volumes over the pore radius spectrum (since they all show tri-modal distributions with peaks in the same pore radii ranges) as in the magnitude of pore volume and surface area associated with such distribution, as seen in Figure 3. The significant characteristic of the chemically activated grade is a surface area of 1600 to 1800 sq m/g which is considerably higher than that of steam activated carbons.

BET nitrogen surface area by itself is not a measure of adsorption capacity nor is pore volume. In Table III BET nitrogen surface areas and total pore volumes are compared with surface areas and pore volumes on pores with radii greater than 20 Å for several activated carbons.

Table III
AREA & PORE VOLUMES
OF TYPICAL ACTIVATED CARBONS

	TOTAL		> 20 Å RADIUS	
	AREA m ² /g	PORE VOLUME ml/g	AREA m ² /g	PORE VOLUME ml/g
DECOLORIZING				
	665	0.952	150	0.628
	900	3.238	169	2.558
	1337	2.328	247	1.076
	1011	0.854	45	0.516
	1339	0.996	56	0.593
	1234	1.611	535	1.331
	1776	2.133	320	1.508
GAS ADSORBING				
	1053	0.585	22	0.138
	1101	0.663	59	0.237
	1246	0.676	30	0.171

In general, decolorizing activated carbons have about the same surface areas as gas adsorbing activated carbons but larger total pore volumes. The ratio of area to pore volume for decolorizing activated carbons is usually less than 1200 m²/ml of pore volume.

Figure 2

**PORE VOLUME DISTRIBUTIONS OF TYPICAL
DECOLORIZING ACTIVATED CARBONS**

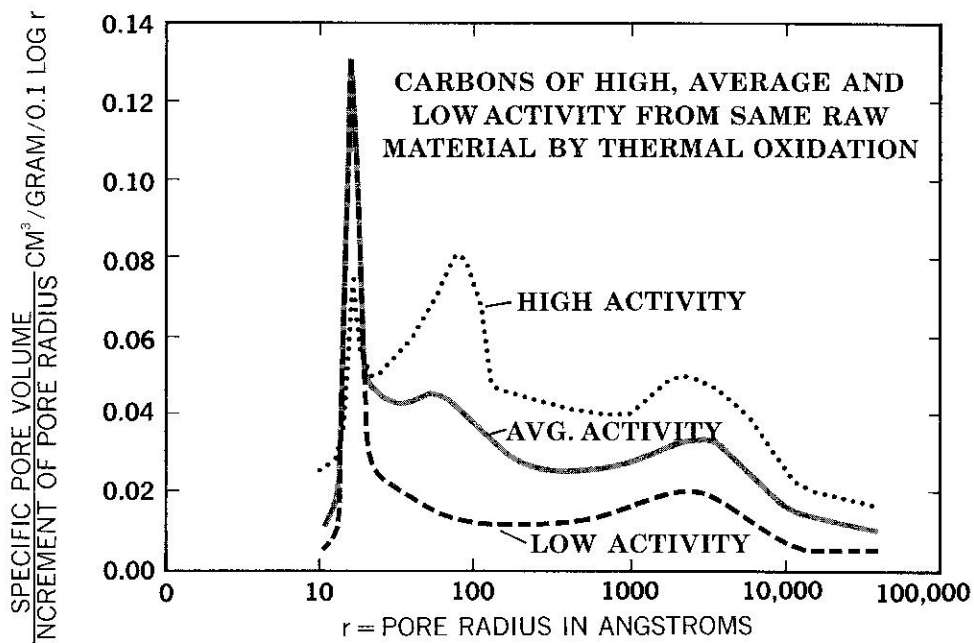


Figure 3

**PORE VOLUME DISTRIBUTIONS OF TYPICAL
DECOLORIZING ACTIVATED CARBONS**

