

Carbon Filters

Effects of Starting Material on Activated Carbon Characteristics and Performance

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The objective of this article is to demonstrate how the choice of starting material determines potential carbon product properties. Activation can only "develop" an activated carbon skeleton, using the building blocks supplied by the original starting material. The resultant activated carbon skeleton defines the adsorption pore structure and thus all the physical adsorption characteristics of the ensuing activated carbon products, and these in turn dictate the performance of the activated carbon product in any application.

This article gives evidence of the effects of starting material selection on the adsorbing pore structure of activated carbon, the resultant performance for removal of trace levels of volatile organic compounds (VOCs) from water, and de-chlorination efficiencies and effectiveness in de-chlorination applications. This evidence will demonstrate the importance of proper starting material selection in determining the optimal carbon for process water treatment applications.

What is Activated Carbon?

Activated carbon can be described as a crude graphite. Graphite is the material used as a lubricant and as the "lead" in pencils. Activated carbon and graphite are among the few pure forms of carbon, with almost not nitrogen, hydrogens, sulfur, or oxygen (as produced). From the perspective of a chemist, activated carbon is an imperfect form of graphite. Its chemical bonding is much like graphite, but it has a fixed rigid structure, no lubricating properties (it's actually abrasive in nature), and several other non-graphitic properties.

Activated carbon also has a more random carbon structure than graphite, and is often referred to as amorphous carbon. This structure results in a high degree of porosity, with more than a million-fold range in pore sizes. The pores range from visible cracks and crevices, to gaps and voids of molecular dimensions between the plates of graphite that form the activated carbon structure. Figure 1 shows the best view we currently have of this carbon structure. It is a typical transmission electron micrograph of an activated carbon structure at about X 2,000,000 magnification. The small lines are the edges of the graphite plates, and the gaps between the dashes are the smallest of the pores.

Intermolecular attractions in the smallest pores result in adsorption forces that cause condensation of adsorbate gases or precipitation of adsorbates from solution. A condensation or precipitation process accurately describes the thermodynamics of the adsorption process. The adsorbed material within these molecular scale pores is not a true condensed or precipitated phase, but its properties can be approximated as such for modeling purposes (1,2).

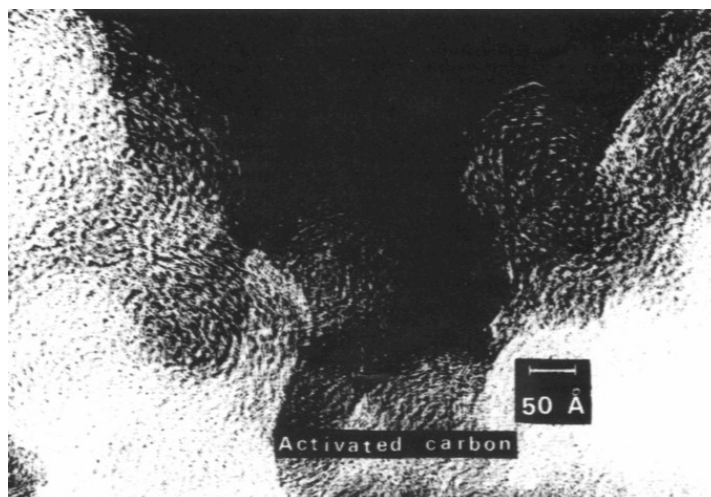


Figure 1. Transmission electron micrograph of activated carbon.

What Causes Physical Adsorption on Activated Carbon?

The elemental force causing adsorption on activated carbon is the London dispersion force or simply the London force. It is named for Fritz London, who derived the dispersion force from the first principles of quantum mechanics in 1931. London forces are the most common of the

six types of van der Waals' forces that are responsible for most non-ideal behavior of gases. The London force is an intermolecular interaction that exists between all molecules (both polar and non-polar), but it is extremely short-ranged. It is responsible for condensation of most gases to liquids, and the reason higher-molecular-weight gases have higher boiling points.

There are four characteristics that distinguish London forces. Because the carbon adsorption force field is derived from London Forces, it also shares these four distinguished characteristics. London forces are:

Nonspecific. London forces exist between all molecules. Therefore, all molecules adsorb on activated carbon to some extent, depending on their vapor pressure and solubility at the carbon temperature.

Temperature-independent. The London forces are unaffected by temperature, and thus the adsorption force field will be constant with temperature. (The carbon adsorption capacities will still be sensitive, however, to the changes with temperature in vapor pressure or solubility of the adsorbing molecules).

Additive. The observed London force is the sum of all the individual interactions of the adsorbate molecule and the neighboring graphite plates composing the carbon structure. The magnitude of the adsorption force will be related to the number of carbon plates, or density of carbon, within the vicinity of the adsorbate molecules.

Short-ranged. The magnitude of the London force is very sensitive to the separation of the adsorbate molecule from the graphite plate. The London force can be considered negligible with a separation greater than about two molecular layers (much like a small magnet on a refrigerator door). Therefore, the adsorption forces will be significant only if the gaps or voids within the carbon structure (pore widths) are less than four or five molecular layers.

The first three characteristics of London forces are shared by another familiar force, gravity. London forces, and consequently the carbon adsorption forces, are analogous to gravitational forces; however, London forces are much shorter-ranged, and operate on a molecular scale instead of an astronomical scale. The gravitational analogy is useful for understanding the effect of adsorption forces on mixtures of gases and liquids (3).

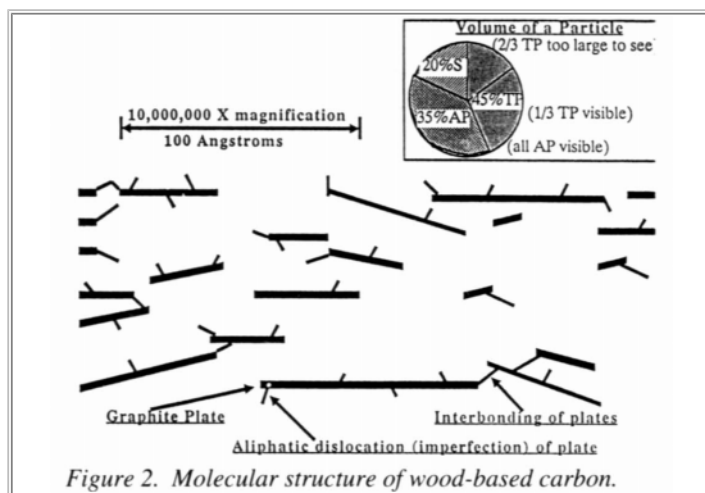


Figure 2. Molecular structure of wood-based carbon.

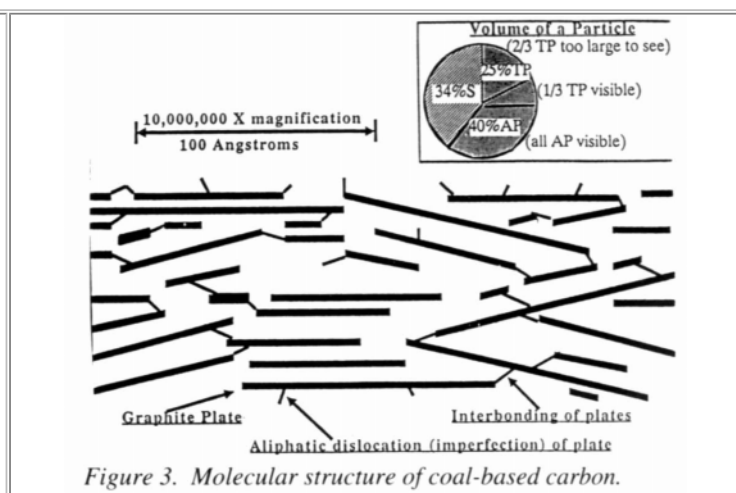


Figure 3. Molecular structure of coal-based carbon.

Regions Within the Carbon Particles

The most important characteristic of activated carbon is also the simplest: the bed density, or apparent density (AD). The AD is the weight of carbon in a standard-size cylinder, filled in a manner to provide the densest possible bed of particles, and is usually stated in units of grams per cubic centimeter (g/cm^3 , also known as g/cc). Since the carbon skeleton is the only mass within the cylinder, the AD relates pore and void volume to the mass of the carbon skeleton.

In simple terms, the inverse of the apparent density is the volume occupied by a specific weight of carbon in its most densely packed configuration. The volume of a bed of carbon particles consists of three regions (Equation 1): the carbon skeleton composing the particle; the pores within the particle; and the voids between particles.

$$\text{Bed volume} = \text{skeletal volume} + \text{pore volume} + \text{void volume} \quad \text{Eq. 1}$$

The carbon skeleton is entirely composed of graphite plates and ash. For almost all activated carbons, these plates have a density similar to graphite, about $2.15 g/cm^3$. The skeleton also includes ash impurities that at low levels can usually be ignored or assumed to be similar to graphite in density. For all carbons in this study, the skeletal density can be assumed to be $2.15 g/cm^3$ (calculated on an ash-free basis).

Voids between the particles. Any regions within a bed of particles outside the carbon pores is void volume between particles. This includes gasp between particles and the volume of visible cracks and crevices of the particle. Visible cracks and crevices are considered part of the particle shape and not pores when the crack or crevice is greater than 0.1 millimeter (mm) wide. (The limit of human sight is 0.1 mm. If the crack is visible to the naked eye, it is generally considered part of the particle shape.) The actual volume of the voids and visible cracks and crevices can be measured precisely by mercury-intrusion porosimetry at 1 pound per square inch absolute (psia) pressure.

The void volume is a function of the particle size distribution: the broader the distribution, the lower the void volume. For all the 12 x 40 and 20 x 50 mesh carbons in this study, however, the volume of the voids and the visible cracks and crevices is nearly the same, about 40% of the volume of the bed.

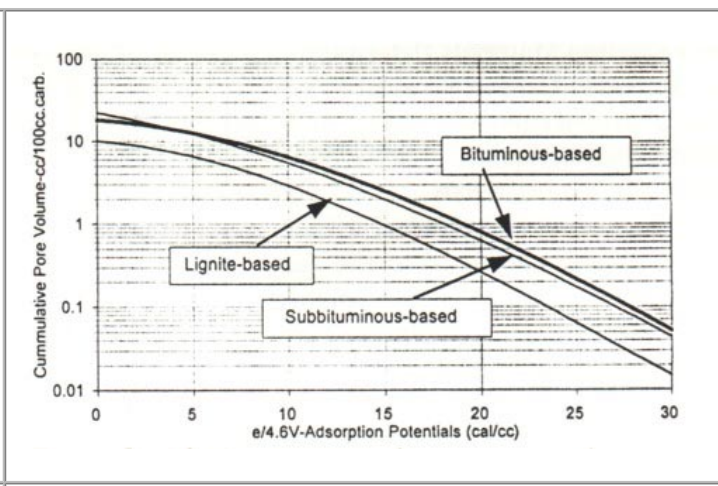
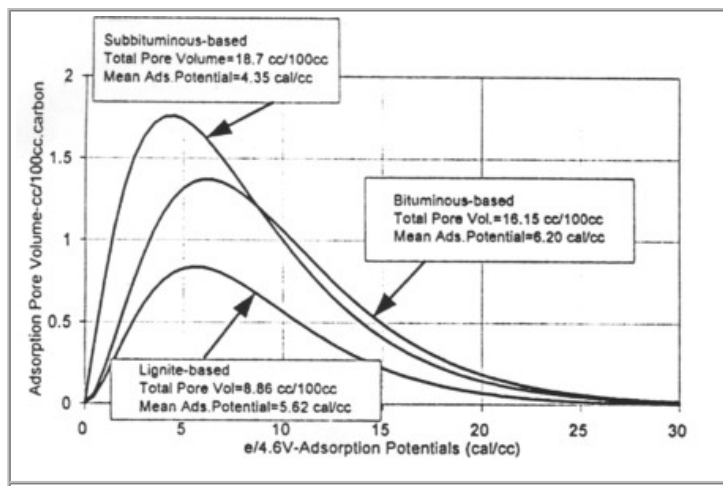


Figure 4. Distributions of adsorption potentials (activated carbons from different coals).

Figure 5. Adsorption potential versus pore volume (activated carbons from different coals)

Types of Pores Within the Carbon Particle

There is a wide variety of pore sizes and types within activated carbon. Pores are normally classified by size as macropores, mesopores, and micropores to distinguish their importance in an application. We classify pores by their function, however, since the pore size cannot be directly measured. Thus there are two types of pores within activated carbon: adsorption pores that adsorb, and transport pores that transport. The analogy we use is that adsorbate molecules are cars, transport pores are carbon highways, and adsorption pores are carbon parking lots. The cars are only stored in the parking lots, and the highways are used to move the cars to the parking lots.

Adsorption pores are the only regions within the carbon particles with significant adsorption forces and any adsorption properties. They are the smallest pores within the particle, consisting of gaps between the graphite plates of only a few molecular diameters in size. (An absolute value for the diameter of a molecule in the confines of the carbon structure is not accurately known.) Because the London forces are distance-sensitive, it is known that there can only be a small range in adsorption pore sizes, about 1 to 5 molecular diameters.

All pores with any adsorption forces present will be filled with a pseudo-condensed or pseudo-precipitated adsorbate at conditions near saturation (pressure or concentration). Therefore, the volume of all the adsorption pores for a given activated carbon can be measured by exposing the carbon to a gas or solution near saturated conditions. A variety of this type of experiments have been adapted by the industry as standard test methods (4). Standard tests, like the iodine number, carbon tetrachloride number, or butane number, basically measure the total volume of the adsorption pores. (The butane number test is the simplest.)

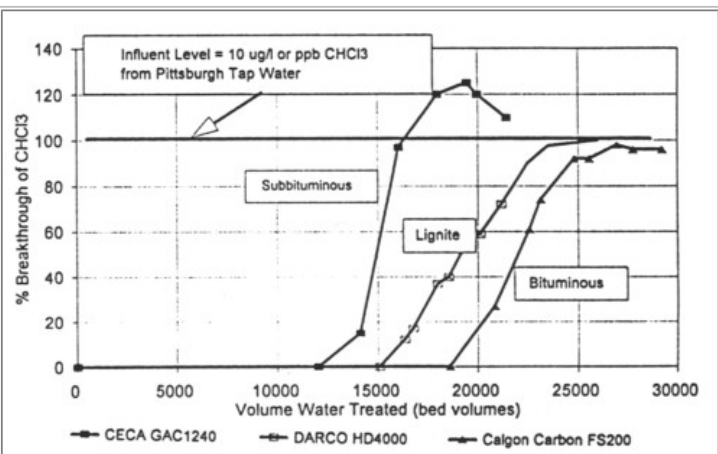
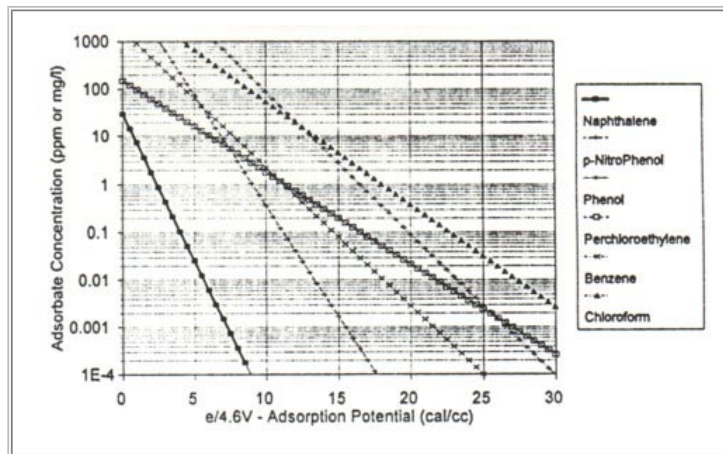


Figure 6. Carbon adsorption force requirements for common liquid-phase adsorbates.

Figure 7. The VOC performances from various starting materials: lignite, sub-bituminous, and bituminous.

Transport pores are the largest pores within the particle. They vary from pores greater than 5 molecular diameters to the cracks and crevices just beyond the limits of sight. (A pore is defined as any void less than 0.1 mm in width). Transport pores consist of a wide variety of different sizes and shapes of pore structures over a 100,000-fold range within a single activated carbon particle.

Transport pores are too large to adsorb and therefore act simply as diffusion paths to transport the adsorbate to the adsorption sites. They are thus related to the adsorption kinetics (rate of adsorption) or mass transfer within the activated carbon particle. Transport pore volume is measured directly by mercury-intrusion porosimetry, but can be approximated by subtracting the void, skeletal, and adsorption volume from

the total bed volume.

How Starting Materials Determine the Activated Carbon Structure

How activated carbon is made. Activated carbon is graphitic in nature; however, its starting materials are not. For example, coal is composed of a wide variety of large organic molecules and would not be referred to as graphitic. Activation can be thought of as a process to convert non-graphitic coal or other starting materials into graphitic activated carbon. Almost any carbonaceous material can be converted into some form of activated carbon, if quality is not a concern. For simplicity, we will limit the discussion to the manufacture of coal-based products.

The activated carbon skeleton is composed of plates of graphitic carbon that must be created from the starting material. This is generally done at high temperatures (greater than 750°C) in an inert or reducing atmosphere (usually steam). At these conditions, the aromatic graphite plate is the most energetically favorable form of carbon. The coal molecules are either stripped out of the structure through volatilization or pyrolyzation, or they combine and condense to form graphite plates. The plates tend to be small and imperfect, and the size and degree of imperfection are related to the chemical building blocks provided by the starting material. The starting material was not graphitic, but the activated carbon graphite plate structure is inherited from the starting material because it provides the building blocks to create the graphitic plates. Further, the effects of thermal processing and chemical rearrangements during activation are determined by the chemistry of the starting materials.

Differences between coals. No two coal seams are alike, and there is a long list of properties to differentiate coals. Consequently, there are thousands of distinguishable coals available in the United States alone. For purposes of this study, the simplest way to differentiate coals is by coal rank (4,5). Coal rank is related to the length of time and temperature at which the vegetable matter was deposited in the ground, and to the temperatures experienced during that period.

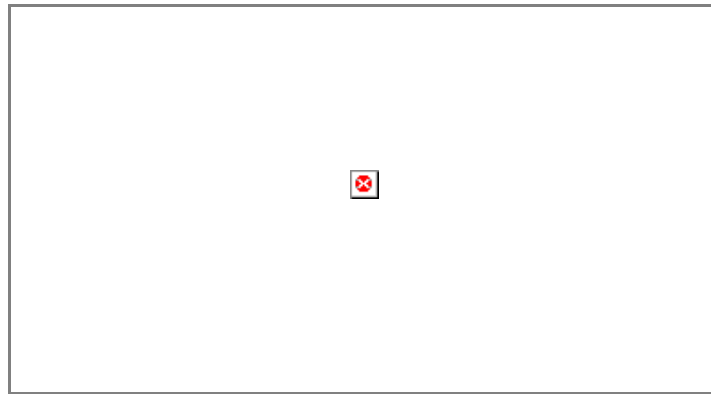


Figure 8. Dechlorination of 5 mg/L Cl₂ with lignite-based versus "bituminous coal-based" granulated activated carbon.

A series of chemical reactions, which collectively are called coalification, condense the hydrocarbons and cellulose molecules in the vegetable matter to a higher carbon content, and a more aromatic and denser form of carbon. The coal rank is basically the extent of coalification of the vegetable matter. Coalification occurs faster at higher temperatures; therefore, deeper coal deposits are warmer and coalify at a faster rate than shallower deposits. The oldest and deepest coal seams have coalified the most and represent the highest rank of coals. At the end of the coalification series is graphite, which occurs in nature only if excessive heat is present (as in deposits next to volcano shafts). A coal rank indicates the extent of the conversion of vegetable matter towards a graphite-like state by the coalification process.

As coalification occurs, the inherent porosity of the vegetable matter is reduced. Without this inherent porous structure, it is difficult, if not impossible, to further develop the pore structure and make an efficient structure for adsorption. Because of this porosity limitation, it is difficult to produce an activated carbon on a commercial scale from coals with a higher rank than bituminous.

Not all bituminous coals are the same. Unfortunately, with this simplified analysis by coal rank, we treat all coals of the same rank as identical in terms of activated carbon manufacture. Several properties of the coal that are not related to rank but that are also critical to carbon manufacture are the preliminary pore structure/porosity, the coking characteristics, and the extent of oxidation. These properties vary from seam to seam and mine to mine even for the coals of the same rank. In any event, most of the coal properties listed above are defined by coal rank, and coal rank will be used in this study to classify starting materials for carbon manufacture.

Plate characteristics are predetermined by starting material. The coal starting material will provide the building blocks to create the graphite plate structure; therefore, the starting material defines the activated carbon product in terms of the following:

1. The size and shape of the graphite plates.
2. The number of non-graphitic imperfections or extent of graphitization during activation.
3. The number of plate interconnections and thus the rigidity of structure.
4. The sizes of the gaps, spacing, and angles between the plates; and the plate orientations.

5. The extent of crystalline order or randomness within the structure.

Figures 2 and 3 are representations of the graphite plate structures one would expect with carbon made from, respectively, wood and bituminous coal. These representations are at a higher magnification than that in Figure 1, but they show the same type of information. The wood-based product has smaller-diameter plates with a greater number of imperfections per weight of carbon. Also, the wood-based production has larger gaps, wider spacing, and wider angles between the plates. (In both Figures 2 and 3, all plates would be bound together. In many cases, however, the interplate bond is not in the level shown in the picture, but would be behind the surface shown on the page).

Plate characteristics determine the carbon pore structure. The adsorption pore structure is determined by the gaps and voids between the graphite plates. These gaps and voids in turn define the distribution of adsorption forces (potentials) present in the structure. This distribution of potentials defines the adsorption capacities at equilibrium and the shape of the adsorption isotherm (the relationship between adsorbate concentration and adsorption capacity on the carbon). The nature of the transport pores and their accessibility to the adsorption pores define the adsorption kinetics and the rates of adsorption.

Other carbon characteristics are inherited from the starting material. The starting material defines the relative magnitude of several physical characteristics, based on the graphite plate structure formed when the coal is calcined at temperatures above 1,500°F. The maximum possible density is a characteristic limitation of the starting material. During activation, product density is reduced as carbon atoms are removed from the carbon skeleton. As activation time increases, more carbon atoms are removed from the carbon skeleton, making the product more porous and thus structurally weaker than the starting material.

A starting material with a low density will thus produce a final product with lower density. As a result, the hardness, abrasion resistance, and dustiness characteristics of the final product are inherited from the starting material. Finally, a portion of the activated carbon transport pore structure, representing the middle range of transport pore sizes, is not affected greatly by activation, and has transfer properties similar to the starting material. As a result, a nonporous starting material such as a high-rank anthracite coal, will, in the final activated carbon products, result in few transport pores and slow adsorption rates.

Inorganic impurities within the activated carbon are inherited from the starting material and remain almost unchanged. They are basically rocks or plant minerals that are present in the coal seam. High-ash coals make for high-ash activated products. Other impurities that are related to the starting material are hetero-atoms (hydrogen, oxygen, nitrogen, sulfur, and others). These hetero-atoms are mostly removed during the activation processing, but some carbon-nitrogen-carbon and carbon-sulfur-carbon bonds can survive activation, and will affect the purity and chemical reactivity of the final product. Ash levels are related to the activated carbon chemisorption (chemical adsorption) or catalytic properties. Ash constituents can cause problems in terms of toxicity, contact pH, or soluble salts in the leachate. Finally, leaching characteristics are a function of both ash level and ash constituents.

Chemical reactions and reaction rates. Carbon is a relatively inert reducing agent. The chemical reactivity with respect to strong oxidizing agents (such as hypochlorous acid or ozone) is directly related to the chemical nature and stability of the starting material. The chemical nature and reactivity of the starting material also defines the steam gasification rates within the activation furnace. This property is important because it relates to rate of activation and also longevity in the reactivation process.

How to Distinguish Between Activated Carbons

Description of activated carbons used in this study. Activated carbons from the entire coalification series are not commercially available to the water treatment industry at this time; therefore, we restrict our study to three major activated carbon products, chosen to represent the range of coal-based starting materials from lignite to sub-bituminous to bituminous. The products were selected to have similar particle size.

Standard test methods: physical property tests. The carbon manufacturers and the American Society for Testing and Materials (ASTM) have a series of standard test methods to measure the physical properties of the particles of granular activated carbon (6). Table A lists the apparent density, particle size, particle size distribution, hardness, abrasion number, and other characteristics of each type of carbon used in the testing.

Impurities in the carbon are primarily the inorganic ash minerals. For water purification, only the water-leachable ash is of concern; therefore, the critical properties of the ash are percentage of ash leachable at an acidic pH (worst-case scenario) and at a neutral pH (typical case). The pH of a water extract of fresh carbon is also indicative of whether the leachable constituents are acidic, basic, or neutral. This data is also included in Table A.

Adsorption number tests. The carbon manufacturers and the ASTM also have a series of standard test methods to measure the adsorption capacities of granular activated carbon under a fixed set of conditions (6). Table A lists the test results for iodine number, carbon tetra-chloride number, and butane number (and its associated butane retentivity and butane working capacity). The activity numbers are all related to the total volume of the adsorption pores.

Total characterization of the adsorption pore structure. The adsorption number tests give only a single-point comparison of the carbons that represents the total volume of the adsorption pores; nothing about the type of pores present can be inferred. To understand the distribution of the different types of adsorption pores, we determine the adsorption potential distribution of the carbon using non-isothermal adsorption-desorption measurements (7, 8). This is then converted to a measure of the distribution of adsorption pore volumes available over the range of different adsorption forces present (adsorption potentials). The data are then presented as a statistical distribution of pore volumes in the carbon at the different adsorption forces. The results are presented as a differential distribution in Figure 4 and as a cumulative distribution in Figure 5.

These statistical distributions can further be simplified for comparative purposes to three values: the total adsorption pore volume

(normalization constant or area under the distribution); the average adsorption force present in the carbon (the mean of the distribution); and the relative adsorption force (an abscissa scale factor that is a relative measure of the width of the distribution). The values for these three parameters are given in Table A.

The adsorption potential distributions can be used to predict equilibrium adsorption isotherm capacities for gas-phase and liquid-phase adsorbates, using the Polanyi Adsorption Potential theory (1-3). Figure 6 shows the conversion of solute concentrations to adsorption potentials (adsorption force requirements) for a selected series of adsorbates. With Figure 6, it is possible to translate the adsorption potential distribution into adsorption isotherms.

Table A

Differences in Physical Properties Between Activated Carbons				
<i>Starting Materials</i> Carbon type	°	<i>Lignite</i> Liquid-phase	<i>Subbituminous</i> Liquid-phase	<i>Bituminous</i> Liquid-phase
Physical Description of the Carbon Granules				
Apparent density (g/cm ³)		0.407	0.485	0.560
Particle type		Granular	Granular	Granular
Screen size	Mesh	12 x 40	12 x 40	12 x 40
Screen, % on	12	8.6	0.4	0.3
% on	16	37.6	34.8	38.0
% on	20	31.2	33.0	37.8
% on	30	21.0	21.5	17.4
% on	40	1.5	9.1	5.9
% pass	40	0.1	1.2	0.6
Mean particle diameter (MPD)	(mm)	1.19	1.05	1.08
Hardness (% change in MPD)		58.4	85.8	81.2
Abrasion	°	52.9	81.0	72.2
Moisture level, dried @ 100°C (weight %)		5.40	0.80	0.56
Adsorption-Pore-Volume Distribution				
Total adsorption pore vol.	(cm ³ /100g)	21.76	38.53	28.83
Total adsorption pore vol.	(cm ³ /100 cm ³)	8.86	18.69	16.15
Relative adsorption force	relative	2.90	3.61	3.25
Mean adsorption potential	(cal/cm ³)	5.62	4.36	6.20
Accuracy of fit to data	(%)	1.45	1.57	1.59
Transport pore vol. (by diff.)	(cm ³ /100g)	79.15	38.67	31.80

Comparing Carbon Column Performance

The relative performance of columns of the three 12 x 40 mesh carbons were compared using small-scale 100x325 mesh carbon columns. The particle size reduction maintained the sample integrity (activity levels) and relative particle size distribution. Each column contained 1.1465 grams of carbon, and treated water on a down-flow manner, at a flow rate of 3.2 cubic centimeters per minute. For this study a typical VOC, chloroform, was removed from a sample of a Pittsburgh, PA., tap water spiked to 10parts per billion (ppb). The breakthrough or exhaustion curves were determined for 10 ppb (micrograms per liter) chloroform from the spiked sample of tap water. The curves are shown in Figure 7 where, to simplify the comparison, the abscissa is in bed volumes treated.

Measuring equilibrium adsorption isotherm capacities. The equilibrium adsorption isotherm capacity is nearly independent of particle size; therefore, time and materials can be saved by using a small 100 x 325 mesh carbon (9). The equilibrium adsorption isotherm capacity of the carbon column is determined as the total mass contaminant removed until the effluent concentration equals influent levels (i.e., the column is saturated and at equilibrium). The isotherm capacities were determined for 10 ppb (micrograms per liter) chloroform from a sample of Pittsburgh tap water, and are reported in Table B.

Measurement of the adsorption kinetics. The relative adsorptive efficiencies of the 100 x 325 mesh carbons were determined as the percentage of carbon used in the 100x325 mesh carbon columns at 10%, or 1-ppb chloroform breakthrough. The mass transfer zone (MTZ) was the fraction of the column not utilized in units of length. The fraction carbon utilized was the ratio of the mass contaminant removed at 1-ppb breakthrough, divided by the equilibrium adsorption capacity determined above. The percentages of carbon utilizations are listed in Table B.

This column efficiency is not strictly scalable to the 12 x 40 mesh case, but is indicative of a fast or slow transport pore structure (only the largest pores and longest transport paths are not included in the comparison). If the scale factors for all three carbons are assumed to be similar to the bituminous-based case, then predictions can be made for volumes of water treated and time-on-line for a commercial-scale vessel (10 inches diameter and 44 inches deep with a 10% bed expansion) (9). These calculations are listed at the bottom of Table B.

Table B

Differences in Column Performance Between Activated Carbons				
<i>Starting Materials</i> Carbon type		<i>Lignite</i> Liquid-phase	<i>Sub-bituminous</i> Liquid-phase	<i>Bituminous</i> Liquid-phase
Apparent density (g/cm ³)		0.407 Granular	0.485 Granular	0.560 Granular
Lab-Scale Column Performance-ACT Technique (1.1465 g carbon, 3.2 cm³/min flow rate, 100X325 mesh) (ACT laboratory procedure described by Rosene et al. in Reference 8.)				
Empty-bed contact time	(minutes)	0.88	0.74	0.64
Volume to 10% breakthrough	(bed vol.)	16100	13000	19300
Chloroform breakthrough capacity	(mg/cm ³)	0.185	0.149	0.221
Chloroform capacity at saturation		0.218	0.169	0.256

% Carbon utilization in column	(mg/cm)	84.9	88.2	86.3
Mass transfer zone as % of column		15.1	11.8	13.7
Commercial-Scale Column Performance (44 inches deep x 10 inches dia. [2 ft² of carbon], assuming same laboratory scaling factors for all carbons)				
Weight of carbon in column	(pounds)	50.7	60.5	69.8
Empty-bed contact time	(minutes)	7.0	7.0	7.0
Mass transfer zone as % of column		15.7	14.6	19.5
Maxx transfer zone length	(inches)	6.9	6.4	8.6
Volume treated at saturation	(gallons)	296,436	230,390	349,321
Time on line at saturation	(days)	92.2	71.7	108.7
Volume at 10% breakthrough	(gallons)	249,845	196,656	281,094
Time on line to breakthrough	(days)	77.7	61.2	87.5

Dechlorination efficiencies. This is the measurement of carbon chemical reactivity for strong oxidizing agents. Standard test methods are available for measuring the efficiency of activated carbons for de-chlorination (10). The test used by the industry determines the de-chlorination "half-length" as the length of carbon column required to decrease a 5-milligrams-per-lieter (mg/L) chlorine concentration in distilled water by half at a rate of 36 meters per hour (m/h) superficial linear velocity, at 25°C and at a pH of 7.5. The chlorine concentration profiles in the carbon bed generated from the half-length values are shown in Figure 8 for bituminous- and lignite-based carbons at two different particle sizes. The performance of the sub-bituminous product would be between the lignite and bituminous curves.

How Carbon Test Results Compare Physical Properties. Bed density of activated carbon is related to the size and number of graphite plates in the structure and is proportional to the coal rank (lignite bed density is less than that of sub-bituminous, which is less than that of bituminous).

Hardness and abrasion resistance are also related to the size and chemical nature of the graphite plates. The relative results again followed coal rank (lignite < sub-bituminous < bituminous).

Skeletal density was the same for all carbons tested and was equal to 2.15 g/cm³ (lignite = sub-bituminous = bituminous = graphite). The void volume between particles was also similar for all products tested.

Ash-leaching characteristics tend to be specific to the type of ash constituents present; therefore, leaching characteristics are dependent on the coal seam and its geographical location. In general, the higher levels of leachables for the western lignite and sub-bituminous coals are due to soluble ash constituents in the carbon that were inherited from the coal. The ash composition and ash content in coal is determined by the environment experienced by the coal seam during its formation (5), and therefore would be related to the climate history of that specific region of the country.

Adsorption pore structure. Total adsorption pore volume was sensitive to the degree of activation of the particular carbon product used in the study. The carbon products selected for this study were readily available commercial liquid-phase carbons, in a 12 x 40 mesh size, and manufactured from the different ranks of coals. Unfortunately the activity level, or degree of activation, was different for the products selected. As a result, the iodine number, carbon tetrachloride number, and butane number were all in relative agreement with the measurement of total adsorption pore volume, and indicated the degree of activation for the specific carbon products selected (lignite product < bituminous product < sub-bituminous product). The total pore volume parameter would be most important for strongly adsorbed components such as naphthalene at any concentration, or p-nitrophenol or perchloroethylene concentrations greater than 100 parts per million (ppm), in streams such as heavy industrial wastewaters (see Figure 6).

More important than how many adsorption pores are present is what type of adsorption pores are present. The slope of the cumulative distributions in Figure 5 gives an indication of how quickly the isotherm capacity will decrease with decreasing concentration, and has to do with the strength of the adsorption forces. This is also indicative of the mean adsorption force over the distribution. In both cases, bituminous appeared to have the strongest forces, on average, followed by sub-bituminous and lignite. Strong adsorption forces are more important at lower concentrations and for weakly adsorbed components such as chloroform or for soluble components such as phenol (see Figure 6). Stronger adsorption forces also help to prevent desorption during swings in the influent concentration.

Column performance. A clear advantage for trace removal of chloroform is shown by the breakthrough curve for the bituminous-based product in Figure 7. This is the predicted effect of an adsorption potential distribution with a stronger average adsorption force. However, the lesser performance for the sub-bituminous product versus the lignite product is not readily explained. The removal advantage of the bituminous product translates to the full-scale adsorber as well; 87.5 days on-line for bituminous versus 77.7 for lignite and 61.2 for sub-bituminous, as calculated in Table B.

Equilibrium adsorption capacities. As with the breakthrough curve, the adsorption capacity for chloroform at 10 ppb is also great for the bituminous-based product.

Kinetics and adsorption rates. The volume of the transport pores is predictably greater for the lower-density products (lignite > sub-bituminous > bituminous). As a result, the mass transfer zone comparison in Table B for the commercial-scale column show faster adsorption for the low-rank, low-density products (lignite = sub-bituminous > bituminous).

Chemical reactivity. Figure 8 shows that all the bituminous and lignite carbons had a fast de-chlorination rate (subbituminous was not tested). The effect of particle size, 20 x 50 mesh versus 12 x 40 mesh, was more important than coal starting material; therefore, all sizes and types of carbons would have de-chlorinated the water from 5 ppm to less than 0.1 ppm in the top 10% of a column with 5 minutes of contact time. All carbons were fast, but at the same particle size the lignite was faster than the bituminous product. This is because of the smaller plate size and higher percentage of carbon atoms that can react at the edge of the plates. Steam gasification rates for activation and

reactivation of carbon will also follow this same trend with coal rank. If adequate contact time is not available, then reducing the carbon mesh size is a better action than changing carbon starting materials.

How Differences in Starting Materials Relate to Carbon Performance Observed differences in carbons and ultimate consequences: Higher apparent density carbons. These carbons can be backwashed at higher water velocities without loss of carbon through the overflow. The required backwash rate is dictated by the size and density of the material to be removed. A fine low-density floc requires only a low flow rate, but a higher-density large precipitate or a macroscopic worm may require a very high backwash rate. A higher-density carbon provides better opportunity to use the backwash for density separation, with the contaminant on top of the bed.

During de-chlorination, each hypochlorous acid molecule removes one carbon atom from the carbon structure, a process that weakens the carbon granules. By definition, denser carbons have more carbon atoms per particle and thus maintain structural integrity after de-chlorination. The bituminous product has the greatest density and therefore the most durable particles.

Greater hardness/abrasion resistance carbons. The harder and more abrasion-resistant product produce less fines during backwashing or reactivation. Fewer fines also mean fewer losses as well as less nuisance (e.g., less carbon dust in the product water).

Greater total adsorption-pore-volume carbons. Higher total adsorption-pore-volume means better adsorption capacity in high-concentration streams.

Stronger average adsorption-force carbons. Stronger adsorption forces translate to a better trace removal capacity or less sensitivity to concentration changes.

Faster-adsorbing carbons usually have a better transport pore structure, which allows mass transfer of the adsorbate from outside the particle to the adsorption pore in less time. This physically means that the water does not have to be in contact with the carbon as long, and thus the carbon column contact time can be reduced. Faster carbons can be used in smaller beds and at higher flow rates with only a small reduction in carbon utilization. In well-designed long-contact-time adsorbers, this usually is not a concern.

More chemically reactive carbons. These carbons will de-chlorinate in a smaller bed or at a higher flow rate. For hypochlorous acid, however, the reaction rates with carbon are fast enough that most commercial carbons have more than adequate kinetics and minimum bed depth requirements.

Criterion for optimal carbon selection: VOC removal from potable water/groundwater. The carbon should have a maximum adsorption isotherm capacity in the trace region to give the maximum volume of water treated per bed volume of carbon.

De-chlorination. The carbon should have a small-enough graphite plate size or number of reactive sites to give full de-chlorination in a reasonable amount of time (or bed depth).

Reactivation. In situations where it is desirable to recycle activated carbon, reactivation may be the answer. To be reactivated, the carbon should have the largest possible graphite plate size, a high density, and high hardness/abrasion number for lowest chemical reactivity and greatest survivability in the reactivation furnace.

Backwashing. To withstand the rigors of backwashing, carbon particles should have good hardness/abrasion resistance and the highest density possible.

Selecting the best activated carbon.

Table C summarizes some guidelines for choosing the appropriate kind of activated carbon.

Optimal starting materials for different applications: Removal of VOC from potable water or groundwater. Carbon based on bituminous coal is preferred because of the stronger average adsorption force and trace removal isotherm capacities, presumably due to the larger graphite plate size. Kinetics should not be a factor in a well-designed carbon column with adequate contact time to ensure good carbon utilization. (The mass transfer zone is not a significant percentage of the column.) If adsorption kinetics are a concern, increasing the contact time by decreasing the flow or increasing the size of the carbon column is generally the best solution.

De-chlorination. All carbons work well. The slowest activated carbons are fast enough for de-chlorination-type reaction in typical water filters. If contact time is a problem, then a reduction in particle size should suffice. Changing carbon starting materials is usually not necessary.

Reactivation of the spent carbon. Carbon based on bituminous coal would be preferred because of its higher density, better abrasion/hardness number, and the slower gasification rate. This rate is slower because the bituminous structure is less chemically reactive, resulting in gasification of adsorbate char rather than of carbon skeleton. The denser, harder product produces higher yields and fewer fines.

Table C

Selecting the Best-Performing Activated Carbon		
Benefits/liabilities of certain starting materials		
Lignite	Sub-bituminous	Bituminous
Low-ranked coals		High-ranked coals

Most chemically reactive	Highest density
Best transport structure	Strongest average adsorption force
Smallest MTZ	Harder/more abrasion resistant
Cheaper coal price	Higher trace adsorption capacity

Backwashing. Again, the higher density and better abrasion/hardness number favor carbon based on bituminous coal. The higher density allows for higher backwash rates without losing carbon to the overflow. The abrasion resistance produces fewer fines.

In general, the low-ranked coals (like lignite and sub-bituminous) offer a lower cost per ton of coal, faster gasification rates, and less expensive manufacture. The question in process water applications, however, is what concessions are made in terms of the performance of the resulting activated carbon.

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