

“GAC” . . .

To Become “Workhorse” Of Water Purification

Granular Activated Carbon (GAC) will become the workhorse of domestic and industrial water purification during the next decade. The purpose of this series of articles is to put information into the hands of those who will be manufacturing equipment utilizing GAC so as to have a guideline for proper systems design and application.

These articles will be written in three parts. The first will deal with GAC production, application concepts and a glossary of terms and definitions.

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The use of Granular Activated Carbon (GAC) for water purification is pretty much a product of this century. However, the use of carbon ash for medicinal purposes and charred wooden casks for water storage date back a thousand years or more BC.

Water filtration using “charcoal” became popular in the latter half of the 1800’s but since the charcoal was not “activated”, it had limited utility and municipalities sought other methods and sources for potable water.

GAC, as we know it, was first produced in Europe in 1906. Major progress in learning of GAC’s “adsorption” properties was made during and after World War I. GAC was employed to remove odors from meat packing houses and food products. Eventually, the success of these applications established GAC as a most effective method of insuring potable water palatability. However, it was considered too expensive for wide scale municipal use.

In the 1960’s several east coast cities incorporated GAC into their water treatment operations to remove trace organics and improve taste. Other municipalities, such as Honolulu, utilize GAC filtration to remove traces of pesticides from wells supplying the city’s drinking water.

Today, GAC is generally accepted as the best all-around adsorbant available for removal of organic contaminants from water and air streams. By means of the unique selective adsorption properties, GAC can remove objectionable odor, taste, color, turbidity and “dissolved” organics as well as certain ionic species. Properly used, GAC can supplement or replace other water purification operations such as distillation, filtration, precipitation, oxidation, crystallization, and even ion exchange. These articles will attempt to

explain some of the how’s and why’s and provide guidelines for system designs and proper use.

Production

In the USA, GAC is produced primarily from coal, wood, and petroleum. Almost any carbonaceous source can be used and there are varieties of GAC that utilize nut shells, vegetable fibers and animal tissues. Coconut shell, although widely utilized in this country, is generally produced offshore with Philippines and Sri Lanka the major

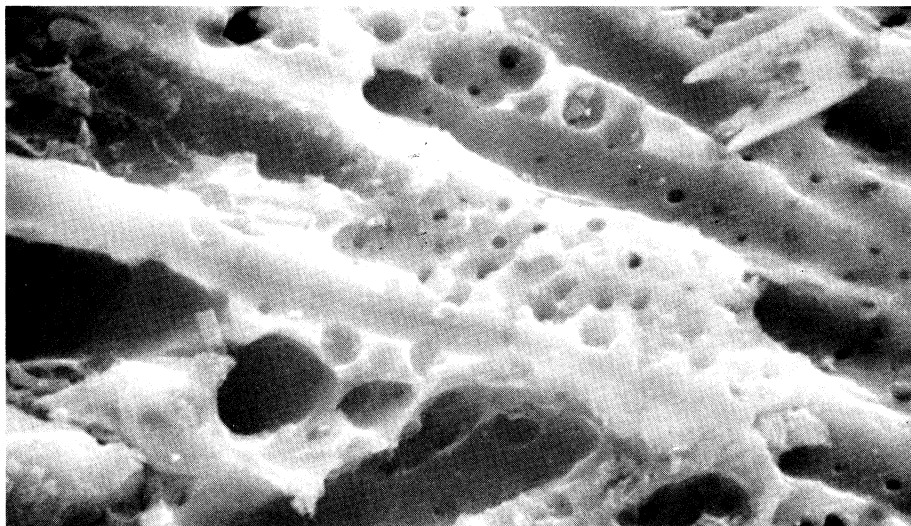


Figure 1

sources. However, coconut shell char is imported into the US and activated locally.

Each source of raw material produces a different type of GAC. These products vary in chemical and physical properties such as hardness, particle size, density, hardness, pore structure, ash, pH and extractables. Most of these variables are controllable to some extent by the manufacturer. Therefore, there is a tremendous overlapping of properties from one type to another and from one manufacturer to another. All GAC's do all jobs. Some do certain aspects of those jobs better than others. To remain as unbiased as possible, our discussions will attempt to address the "generic" GAC rather than promote a particular type or source. Departures from this will be made purely to pursue the academic interests of the reader.

Technically speaking, GAC is charcoal which has undergone an "activation" process. Activation increases the number and improves the structure of the micropores in the carbon. It is the microporous structure and the carbon surface itself that gives GAC its adsorption properties.

To produce GAC from coal, select grades of bituminous and sub-bituminous (preferably low sulfur) coals are first ground into powder. The powder is then mixed with a suitable binder and recompact into briquettes measuring about 1½ x 4". These briquettes are then crushed, screened and sized. These granules are then "carbonized" to remove volatiles by roasting them in an oxygen free kiln at approximately 900°F. Volatiles can account for 30-35% of the original weight of the coal. The carbonized product is a low grade charcoal. While it is primarily only carbon and mineral, it is low activity and therefore would not have much utility for our purpose in its current form.

Our "charcoal" is then activated by further roasting at 1900-2000°F. This is done in a low oxygen atmosphere with steam. This is done to actually "burn" away part of the carbon and to etch the surface into millions of tiny pores which provides a tremendously large surface area on which organic molecules may adhere (adsorb).

Coconut shell GAC is produced by first charring the fresh shells by roasting. This is typically done in earthen pits. This step first dehydrates the shell and then slowly decomposes the carbohydrate structures of the shell similar to carbonizing in the case of coal. This

shell "char" is then crushed, screened, sized and activated.

Each granule of GAC is highly porous as illustrated by Figure 1. In some types of carbon the pores tend to be relatively uniform in size, shape and distribution. In others, they are very irregular. All in all, it is the overall pore structure that determines the ultimate utility of the GAC. The size and shape of the GAC pores largely determines the type of contaminant molecule that will be adsorbed. The number of pores will determine the quantity (capacity) of that material that can be adsorbed.

Typical GAC's for water purification applications have active micropores with a size distribution of 5 to 10,000 Å (Angstrom). 10,000 Å = 1 micron. 1000 microns = 1 millimeter. Therefore, the period at the end of this sentence may well have a diameter of 1 million Å units. Typical ions, such as sodium, are a few Å in diameter. Organic molecules may be several hundred Å.

If the micropore distribution of the GAC leans towards the smaller size, that particular product may not be suitable for removing large, color body organics. On the other hand, if the pores are very large, the GAC may not be able to "hang on" to smaller molecules since they may be flushed away by fluid

in which they are contained before becoming adsorbed.

The surface area of a typical GAC is approximately 1000 m²/gram. That's a square approximately 105 ft. on each side (about one quarter of an acre!). One cubic foot of GAC (about 25 lbs.) has a surface area of nearly five square miles.

Figure 2 is a graphic illustration of the GAC structure. Three dimensionally, the pores resemble the root structure of a large tree. Organic molecules, or adsorbates, diffuse into the pore openings and collect along the surface (adsorption) of the wall. Smaller molecules may diffuse more deeply. Ionic molecules such as sodium may temporarily collect but are not held.

One may note that in addition to the molecular adsorption, the pore structure of GAC resembles that of any good filter media. Indeed this is true. GAC functions by several mechanisms which we shall list only this time and discuss in more detail in Part II.

Mechanisms of GAC Function

1. Adsorption
2. Catalytic Reduction
3. Particulate Filtration
4. Ionic Pairing (Plating)
5. Molecular Filtration

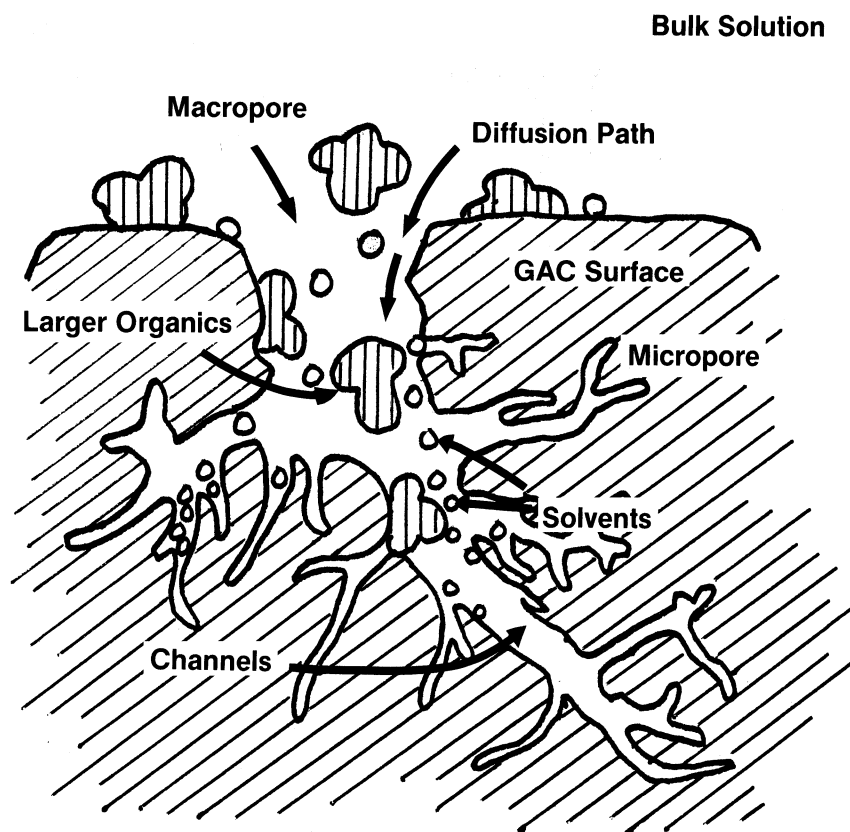
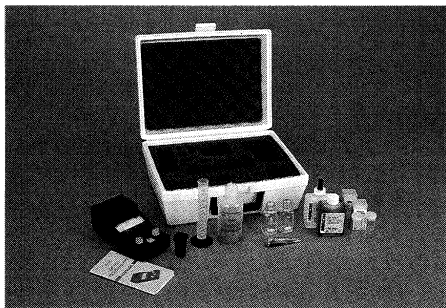


Figure 2

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Concepts

Adsorption and catalytic reduction are the two primary concepts with which we must concern ourselves in using GAC for water purification. Both are "chemical" reaction mechanisms and therefore, both are governed by laws of kinetics (reaction rates) and equilibrium (degree of reaction). The most important element of these concepts is time. Simply stated, "the length of time that a water stream is in contact with GAC determines how much of what is removed." Variables affecting GAC performance will be discussed in more detail in Part II.

The effectiveness of GAC can be determined by measuring how much of a particular contaminant is removed in a specific time or how long it takes to remove a specified amount. Being an equilibrium type of situation, the concentration of the contaminant in the water provides the driving force. As the contaminant is reduced in the water phase, the driving force "pushing" it onto the GAC is also reduced. Therefore, the rate of adsorption is also reduced. Figure 3 illustrates the concept of "half-length".

Simply put, "if it takes x number of seconds to remove 50% of a contaminant, it will take x number of additional seconds to remove 50% of what is left, x more for half of the remainder, and so on." The inset on the graph shows the numerical equivalents of 0 to 10 half length contact times for Curve B. It takes one unit of contact time to remove 50% of contaminant "B". Two units removes 75%, three removes 87.5%, etc. If each unit represents five seconds, we can see that contaminant "B" can be reduced by 99.9% in approximately 50 seconds (5 x 10).

Curve "A" represents a material whose half length is half that of "B". We could therefore run a GAC filter at twice the flow rate of "B" and get equivalent removal in terms of percent per unit time. Curve "C" is half the rate. Curve "D" is one fourth the rate, Curve "E" is one eighth.

If Curve "D" represented a moderately toxic organic contaminant at 1.0 ppm in water, and we must reduce it to 0.1 ppm for potability we would have to have a retention of 14 units (3.5 for 90% removal times a difficulty factor of 4). If one unit is 10 seconds, we need 2.33 minutes (140 ÷ 60) in our design. Using an empty bed volume of 7.5 gallons/cu. ft., we can figure our flow rate of 3.2 gpm per cu. ft. of GAC. (7.5 gal. ÷ 2.33 min. = 3.22 gpm.).

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For many contaminants, flow rates of 5-10 gpm/cu. ft. will be adequate. For others, 0.25 to 0.50 gpm/cu. ft. will be necessary. Part II of this series will address ratings and design in more detail.

GLOSSARY

To better understand and utilize GAC we should become familiar with the terms most often used to describe various products and how they might affect performance. The following are the basics:

Abrasion Number—usually associated with the RO-tape test. Represents relative degree of particle size reduction after abrasive tumbling with a harder material (usually steel balls). A rating of 100 would indicate no reduction, very, very resistant. A rating of 0 would indicate complete pulverization, very soft. Abrasion number is important in determining how well GAC will stand up to backwashing and handling. A rating of 70 is considered good. Shell GAC's will usually exhibit 90, coal 70, lignite 60.

Absorb—to soak up, as would a sponge. GAC does not absorb.

Activated Carbon—carbon or charcoal that has undergone further heat and steam etching to increase its pore sizes and number.

Activity—sometimes referred to as CT or CCl_4 Number. It is reported as "percent activity" and refers to the percent by weight of carbon tetrachloride that can be adsorbed by a particular GAC. Water phase GAC's are typically 40-60% active. Vapor phase GAC's are 55-70%. Waste treatment GAC's are 30-40%.

Adsorb—to adhere to or on. GAC takes up organics by attractive forces.

Adsorbate—that which is taken up or adsorbed by GAC.

Apparent Density—reported in lbs per cu. ft. as shipped. Not to be confused with backwashed and drained density which is how it measures in the column. Is a higher number than b2/d density. Typical GAC's run 25 to 30 lbs./ft³.

Ash—the non carbon constituent of GAC. Usually does not affect performance. Only water soluble and acid soluble ash would be of concern.

Backwash Flow Rates—depend upon bw/d density. Usually in the 9 to 13 gal. per min. per square foot of column area (gpm/ft²). Higher for warmer water and larger particle size GAC's with higher densities.

Backwashed and Drained Density—a truer measure of the bulk density of GAC in use. GAC is usually sold by the pound. More highly activated GAC's have lower densities. Don't be fooled by an inexpensive (per lb.) GAC that may have very low activity and high density. It will end up costing you more in the long run.

Capacity—the percent by weight, of a contaminant that can be adsorbed by a particular GAC at a given level of leakage. The higher you push your GAC, the higher your leakage will be. Typically, GAC will handle 20-30% loading at saturation (effluent leakage equals influent contaminant level). However, very low leakages dictate very low loading ($\frac{1}{4}$ to $\frac{1}{2}$ %). More volatile, low molecular weight organics will have low adsorption capacities). One must design around the consequences of leakage.

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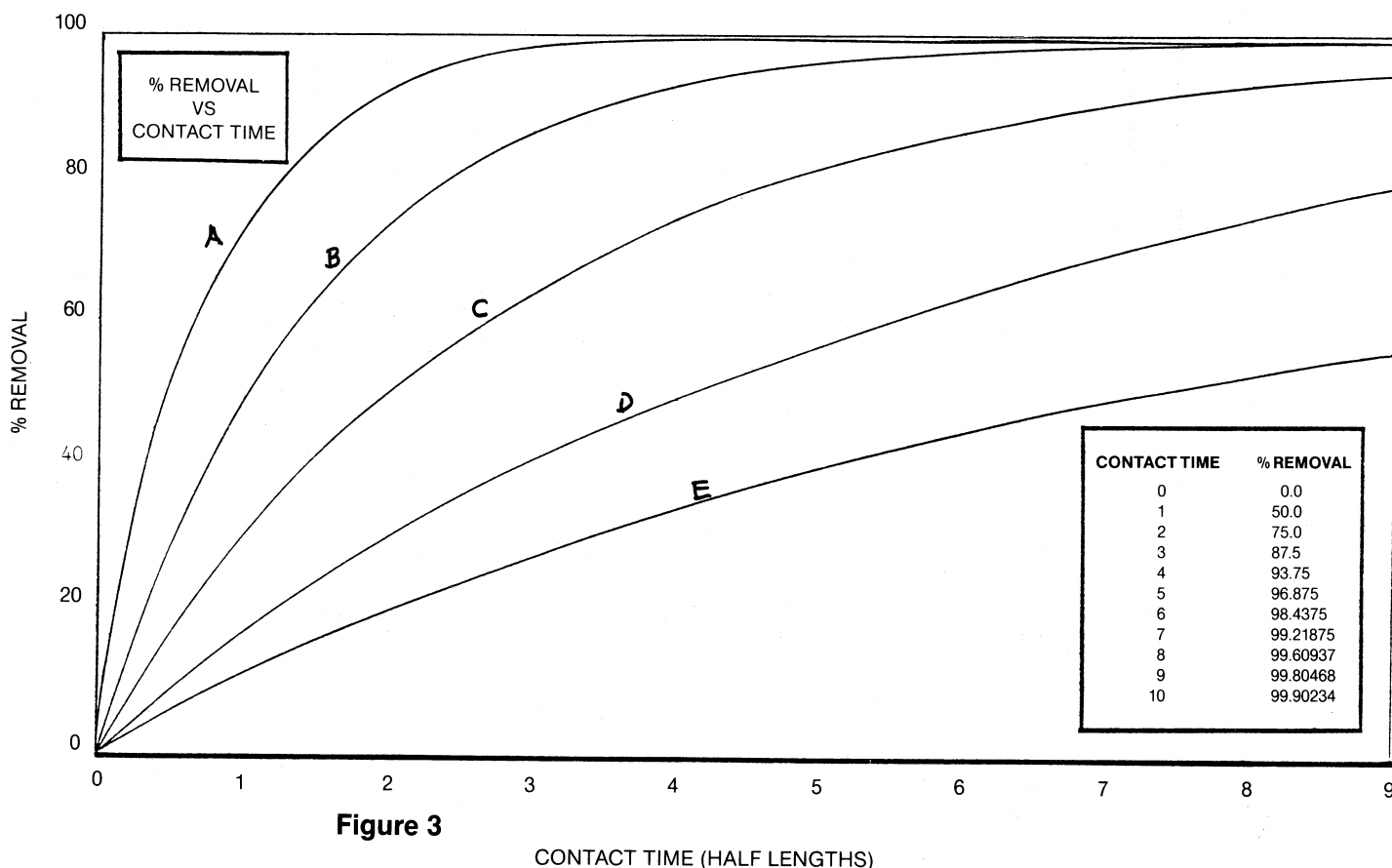


Figure 3

CONTACT TIME (HALF LENGTHS)

GAC:

From page 23

Carbon—an element represented by the chemical symbol "C". Found in all plants, sugars, proteins, organics and hydrocarbons. Combines readily with oxygen to form carbon dioxide (CO) and dioxide (CO₂). Often used erroneously as a synonym for GAC.

Carcinogen—Known to cause cancer in laboratory animals and humans. Some are toxic even at non detectable limits. For insurance, very long contact times are used for removal of these compounds with GAC.

Charcoal—an adsorbant product made of carbon and exhibiting about one-third the surface area and activity of GAC.

Chloramine—a stabilized form of chlorine, produced by combining chlorine with ammonia. Does not react with organics as readily as free chlorine (to form THM's). Also, is much more difficult to remove from water with GAC.

Contact Time—or Empty Bed Contact Time. The time (in minutes) fluid is in contact with GAC. Assumes 7.5 gal. per cu. ft. of GAC. Divide gpm flow into 7.5 times total cu. ft. to get contact time in minutes. (ie 1 gpm/ft³ = 7.5 ÷ 1 = 7.5 minutes).

Dechlorination—removal of free chlorine from water by catalytic reduction. GAC has ability to "remove" nearly five lbs. of chlorine per lb. of GAC.

Effective Size—taken from the particle size distribution profile. It is

that size screen (mm) which allows 10% of the sample to pass through.

Hardness Number—similar to Abrasion number except it measures weight reduction. Again, 100 means no loss, 0 means the sample was completely crushed. Hardness values of 90 are common.

Iodine Number—reported in mg of elemental iodine adsorbed per grain of GAC. 1000 means the sample adsorbed 1000 mg/gm or 100% of its own weight. Iodine No. is a relative measure of a GAC's ability to adsorb low molecular weight organics. It also correlates well to surface area for most water phase GAC's. Very high I. No.'s do not necessarily mean good performance in aqueous systems since it may indicate a very high number of very small pores, not suitable for water and also suggests a weaker body structure. I No.'s of 900 min. are generally used for water treatment. Those above 1100 are usually associated with vapor phase systems. I No.'s of 300-500 may be perfectly suitable for adsorption of heavy oils in waste applications.

Leakage—the level of contaminant not adsorbed by GAC on a single pass design. Usually goes up as age and loading of GAC increases. Cut off leakage determines the point of replacement.

Mean Particle Diameter—refers to size profile of a given GAC. Reported in mm. Typical 8 x 30 mesh = 1.6mm, 12 x 40 = 1.0mm and 20 x 50 = 0.6mm. Does not affect adsorptive performance but does affect hydraulic performance.

Moisture Content—reported as percent. Usually 2% max. Beware of high moisture GAC. The water has no activity.

Molasses Number—a measure of the degree of decolorization of a stock solution for a GAC. Indicates relative degree of high molecular weight organic adsorption. Obviously important to consider for tannin removal. Water phase GAC's usually have a 200 min. softer GAC's such as lignites are higher (better) ie 300. GAC's with higher numbers of smaller pores are usually lower.

Oxidizing Agent—see reducing agent.

Particle Size—reported as US standard mesh. (range) ie 12 x 40, 8 x 30, 20 x 50. Generally, finer particle size GAC's exhibit better kinetics and ultimate capacities. Also are more expensive and present greater pressure drops.

Pressure Drop—pressure loss measured between the inlet and outlet of a column. Typically reported as psi per foot of bed depth for a given temperature and flow rate.

Reducing Agent—material which has the ability to reduce the oxidation state of a material. Also, the ability to remove oxygen. GAC can reduce oxygen content of water as well as the oxidation state of chlorine (it converts free chlorine to chloride). GAC can also reduce peroxide and other oxidizing agents.

Service Flow Rate—depends upon application and type of GAC. Usually 1 to 2 gpm per cu. ft. of GAC.

Surface Loading—refers to hydraulic flow rate (loading) of column in gpm per square ft. (gpm/ft²) of surface area. Typically 4-8 gpm/ft².

THM's—tri-halomethanes, such as HC Cl₃ (chloroform). Known to be carcinogenic. Readily removed by GAC.

Uniformity Coefficient—a ratio of screen sizes from the particle size distribution profile. It is the size of the screen (mm) which permits 60% of the sample to pass divide by the screen (mm) which allows 10% to pass. A U.C. of 1.0 indicates perfect uniformity. Typical values are 1.5 to 2.0.

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THE AUTHOR

Charles "Chubb" Michaud was born and raised in northern Maine. He received his BS in Chemical Engineering from the University of Maine in 1963 and his MS the following year. Michaud joined Rohm and Haas Co. in 1964 and since 1982 has headed up Systematix Co. in Brea, CA. Systematix is involved in systems design and distribution of filter media, including GAC and Purolite ion exchange resins. Michaud and his wife, Valeda have three college-age children.
