ACTIVATED CARBON

MANUFACTURE, STRUCTURE & PROPERTIES

1 HISTORICAL DEVELOPMENT

The first known use of activated carbon dates back to the Ancient Egyptians who utilized its adsorbent properties for purifying oils and medicinal purposes. Centuries later, the early ocean-going vessels stored drinking water in wooden barrels, the inside of which had been charred. (However, by modern definition the carbon used in these applications could not truly be described as "activated"). By the early 19th century both wood and bone charcoal was in large-scale use for the decolorization and purification of cane sugar.

However, it was not until the beginning of the First World War that the potential of activated carbon was really capitalized upon. The advent of gas warfare necessitated the development of suitable respiratory devices for personnel protection. Granular activated carbon was used to this end as, indeed, it still is today.

By the late 1930's there was considerable industrial-scale use of carbon for gaseous and liquid phase application and new manufacturing processes had been developed to satisfy the needs of industry. During the 1939-1945 war, a further significant development took place - the production of more sophisticated chemically impregnated carbon for entrapment of both war and nerve gases.

Modern day uses of carbon are diverse, to say the least. Cameron carbons, for instance, are used in consumer products such as refrigerator deodorizers and at the other end of the spectrum in high technology applications such as nuclear power plant containment systems.

In order to fulfill the requirements of such a variety of industries, Cameron Carbon presently supplies in excess of 30 different types of activated carbon.

The aim of this paper is to inform users and potential users of the manufacture, structure and properties of activated carbon.

2 WHAT IS ACTIVATED CARBON?

Almost all materials containing a high fixed carbon content can potentially be activated. The most commonly used raw materials are coal (anthracite, bituminous and lignite), coconut shells, wood (both soft and hard), peat and petroleum based residues.

Many other raw materials have been evaluated such as walnut shells, peach pits, babassu nutshell and palm kernels but invariably their commercial limitation lies in raw material supply. This is illustrated by considering that 1,000 tons of untreated shell type raw material will only yield about 100 tons of good quality activated carbon.

Most carbonaceous materials do have a certain degree of porosity and an internal surface area in the range of 10-15 m2/g. During activation, the internal surface becomes more highly developed and extended by controlled oxidation of carbon atoms - usually achieved by the use of steam at high temperature.

After activation, the carbon will have acquired an internal surface area between 700 and 1,200 m2/g, depending on the plant operating conditions.

The internal surface area must be accessible to the passage of a fluid or vapor if a potential for adsorption is to exist. Thus, it is necessary that an activated carbon has not only a highly developed internal surface but accessibility to that surface via a network of pores of differing diameters.

As a generalization, pore diameters are usually categorized as follows:

    micropores <40 Angstroms
    mesopores 40 - 5,000 Angstroms
    macropores >5,000 Angstroms (typically 5000-20000 A)

During the manufacturing process, macropores are first formed by the oxidation of weak points (edge groups) on the external surface area of the raw material. Mesopores are then formed and are, essentially, secondary channels formed in the walls of the macropore structure. Finally, the micropores are formed by attack of the planes within the structure of the raw material.

All activated carbons contain micropores, mesopores, and macropores within their structures but the relative proportions vary considerably according to the raw material.

A coconut shell based carbon will have a predominance of pores in the micropore range and these account for 95% of the available internal surface area. Such a structure has been found ideal for the adsorption of small molecular weight species and applications involving low contaminant concentrations.

In contrast wood and peat based carbons are predominantly meso/macropore structures and are, therefore, usually suitable for the adsorption of large molecular species. Such properties are used to advantage in decolorization processes.

Coal based carbons, depending on the type of coal used, contain pore structures somewhere between coconut shell and wood.

In general, it can be said that macropores are of little value in their surface area, except for the adsorption of unusually large molecules and are, therefore, usually considered as an access point to micropores.

Mesopores do not generally play a large role in adsorption, except in particular carbons where the surface area attributable to such pores is appreciable (usually 400 m2/g or more).

Thus, it is the micropore structure of an activated carbon that is the effective means of adsorption.

It is, therefore, important that activated carbon not be classified as a single product but rather a range of products suitable for a variety of specific applications.

3 STRUCTURE

In order to explain the capabilities of activated carbon an appreciation of its structure is most useful.

Much of the literature quotes a modified graphite-like structure; the modification resulting from the presence of microcrystallites, formed during the carbonization process, which during activation have their regular bonding disrupted causing free valencies which are very reactive. In addition, the presence of impurities and process conditions influence the formation of interior vacancies, in the microcrystalline structures.

Such theory generally explains pores as the result of faults in crystalline structures.
However, more recent research studies provide a more feasible explanation of the carbon structure.

The generally accepted graphite-like structure theory falls down since the hardness of activated carbon is not in keeping with the layered structure of graphite. Furthermore, the manufacturing conditions are different; in particular the temperature range utilized for activated carbon production is lower than that required for graphitization.

Supporters of the graphite-like structure generally only explain the modified microcrystalline structure and ignore photographic and other methods of examining the residual macro structure.

High magnification electron scanning microscopy, at 20,000x magnification, has revealed the presence of residual cellular structures. These were previously unseen and unsuspected, except in the case of wood based activates which have sufficiently open structures visible to the naked eye.

Cellular units are built from sugars, the most important being glucose. Sugars ultimately will build to cellulose (the most important single unit in cellular construction) and cellulose polymers cross-link to form the wall of individual plant cells. Glucose units are wound into very tight helical spirals and under polarized light these exhibit anisotropy - demonstrating the presence of crystalline structures.

Although not as yet proven, it has been postulated that in the areas of maximum strain in cellulose chains it is conceivable that smaller crystalline units could be produced.

In addition to cellulose, other materials also exist in cell wall structure. Hemi-cellulose, which undergoes degradation more easily than cellulose and Lignin (the structure of which is still unproven) also exists and this is the most resistant to oxidation.

Most theories attribute the structure of activated carbon to be aromatic in origin, thus, allowing the carbon structure itself to be described as aromatic in order to explain active centers, etc.
Structures of the size of cell dimensions obviously do not influence physical adsorption but illustrate that the only material available for oxidation lies within the cell walls themselves.

Final activates consist almost entirely of elemental carbon together with residual ash which, in the case of wood and coconut, originate from minerals within the vessels of living tissues; silica being the only constituent actually incorporated within the cell wall tissue matrix. The ash content of coal is of different composition and due to intrusion of inorganic materials during coalification.

Thus, the overall structure consists of a modified cellular-like configuration with varying ash components depending on the particular raw material.

The cellular-like structure theory offers a logical explanation for the differences in apparent density between activates of wood, coal and coconut.

Wood activates have a very open structure with thin wall cells whereas coconut activates show very thick walls with many pits.

Furthermore, measurements taken from photomicrographs of coconut show good agreement with mercury penetration data. It is known that the carbonization and activation processes destroy, to varying degrees, intercellular walls and sieve plates between cells. The end result on wood is a very open, sponge-like macrostructure seriously reducing the probability of adsorbate contact with cell walls. Activation of coconut produces a composition of rod-like cells in very close contact and large surface cavities are formed by destruction of dividing walls but these are shallow and do not extend through the activate's granule.

The coconut activates thus differ significantly from wood activates in mechanical strength and density. Coconut activates exhibit extensive micropore volume, whereas wood activates have a definite trend to mesopores/macropores and a corresponding change in their basic properties.

In the case of coal based carbons, pre-treatment of the raw coal is necessary in order for it to be processed, since raw coal swells during heating to produce coke-like structures. Control of this is achieved by first grinding the raw coal and mixing it with various additives, such as pitch, before it is introduced to the activation furnace. However, the grinding process destroys the mechanical strength of coal - therefore, ground coal is reconstituted into briquettes prior to processing.

Despite such pre-treatment, mercury penetration data for coal activates support the presence of structures similar to those identified in activates of wood and coconut, but to date no detection of residual plant structures has been found in coal activates. Isotherm determinations reveal extensive micropore structures, although coal activates' pore spectra are different to those of coconut activates with a tendency toward mesopores at lower activation.

The most reliable carbon structure model suggested to date is similar to that of polyamantane ($C_{66}H_{59}$) which allows for a large degree of non-aromaticity, electron transfer and resonance. Progressive activation would tend to increase the number of active sites, and in turn the surface activity, similar to observed reactions with higher activates.

4 ADSORPTION MECHANISM

Activated carbon can be considered as a material of phenomenal surface area made up of millions of pores - rather like a "molecular sponge".

The process by which such a surface concentrates fluid molecules by chemical and/or physical forces is known as ADSORPTION (whereas, ABSORPTION is a process whereby fluid molecules are taken up by a liquid or solid and distributed throughout that liquid or solid).

In the physical adsorption process, molecules are held by the carbon's surface by weak forces known as Van Der Waals Forces resulting from intermolecular attraction. The carbon and the adsorbate are thus unchanged chemically. However, in the process known as CHEMISORPTION molecules chemically react with the carbon's surface (or an impregnant on the carbon's surface) and are held by much stronger forces - chemical bonds.

In general terms, to effect adsorption it is necessary to present the molecule to be adsorbed to a pore of comparable size. In this way the attractive forces coupled with opposite wall effect will be at a maximum and should be greater than the energy of the molecule.

For example, a fine pored coconut shell carbon has poor decolorizing properties because color molecules tend to be larger molecular species and are thus denied access to a fine pore structure. In contrast, coconut shell carbons are particularly efficient in adsorbing small molecular species. Krypton and Xenon, for instance, are readily adsorbed by coconut shell carbon but readily desorb from large pored carbons such as wood.

Maximum adsorption capacity is determined by the degree of liquid packing that can occur in the pores. In very high vapor pressures, multilayer adsorption can lead to capillary condensation even in mesopores (25A).

If adsorption capacity is plotted against pressure (for gases) or concentration (for liquids) at constant temperature, the curve so produced is known as an ISOTHERM.

Adsorption increases with increased pressure and also with increasing molecular weight, within a series of a chemical family. Thus, methane (CH_4) is less easily adsorbed than propane (C_3H_8).
This is a useful fact to remember when a particular system has a number of components.

After equilibrium, it is generally found that, all else being equal, the higher molecular weight species of a multi-component system are preferentially adsorbed. Such a phenomenon is known as competitive or preferential adsorption - the initially adsorbed low molecular weight species desorbing from the surface and being replaced by higher molecular weight species.

Physical adsorption in the vapor phase is affected by certain external parameters such as temperature and pressure. The adsorption process is more efficient at lower temperatures and higher pressures since molecular species are less mobile under such conditions. Such an effect is also noticed in a system where moisture and an organic species are present. The moisture is readily accepted by the carbon surface but in time desorbs as the preferred organic molecules are selected by the surface. This usually occurs due to differences in molecular size but can be also attributable to the difference in molecular charge.

Generally speaking, carbon surfaces dislike any form of charge - since water is highly charged (ionic) relative to the majority of organic molecules the carbon would prefer the organic to be adsorbed. Primary amines possess less charge on the nitrogen atom than secondary amines that in turn have less than tertiary amines. Thus, it is found that primary amines are more readily adsorbed than tertiary amines.

High levels of adsorption can be expected if the adsorbate is a reasonably large bulky molecule with no charge, whereas a small molecule with high charge would not be expected to be easily adsorbed.

Molecular shape also influences adsorption but this is usually of minor consideration.

In certain situations, regardless of how the operating conditions can be varied, some species will only be physically adsorbed to a low level. (Examples are ammonia, sulfur dioxide, hydrogen sulfide, mercury vapor and methyl iodide). In such instances, the method frequently employed to enhance a carbon's capability is to impregnate it with a particular compound that is chemically reactive towards the species required to be adsorbed.

Since carbon possesses such a large surface (a carbon granule the size of a "quarter" has a surface area in the order of ½ square mile!) coating of this essentially spreads out the impregnant over a vast area. This, therefore, greatly increases the chance of reaction since the adsorbate has a tremendous choice of reaction sites. When the adsorbate is removed in this way the effect is known as CHEMISORPTION.

Unlike physical adsorption the components of the system are changed chemically and the changed adsorbate chemically held by the carbon's surface and desorption in the original form is nonexistent. This principle is applied in many industries, particularly in the catalysis field, where the ability of a catalyst can be greatly increased by spreading it over a carbon surface.

5 THE MANUFACTURING PROCESS

5.1 Raw Materials

It has already been stated that essentially any carbonaceous material can potentially be activated. In addition to the more common raw materials discussed earlier, others can include waste tires, phenol formaldehyde resin, rice husks, pulp mill residues, corn cobs, coffee beans and bones.

Present total annual world production capacity is estimated at 300,000 tons: available as granular, extruded or powdered product.

Most of the developed nations have facilities to activate coconut shell, wood and coal. Third world countries have recently entered the industry and concentrate on readily available local raw materials such as wood and coconut shell.

Coconut shell contains about 75% volatile matter that is removed, largely at source by partial carbonization, to minimize shipping costs. The cellulosic structure of the shell determines the end product characteristics, which (at 30-40% yield on the carbonized basis) is a material of very high internal surface area consisting of pores and capillaries of fine molecular dimensions. The ash content is normally low and composed mainly of alkalis and silica.

Coal is also a readily available and reasonably cheap raw material. The activate obtained depends on the type of coal used and its initial processing prior to carbonization and activation.

It is normal procedure to grind the coal and reconstitute it into a form suitable for processing, by use of a binder such as pitch, before activation. (This is typical for extruded or pelletized carbon). An alternative method is to grind the coal and utilize its volatile content to fuse the powder together in the form of a briquette. This method allows for blending of selected materials to control the swelling power of the coals and prevents coking. If the coal is allowed to "coke" it leads to the production of an activate with an unacceptably high proportion of large pores. Blending of coals also allows a greater degree of control over the structure and properties of the final product.

Wood may be activated by one of two methods, i.e. steam or chemical activation, depending on the desired product. A common chemical activator is phosphoric acid, which produces a char with a large surface area suitable for decolorization applications. The carbon is usually supplied as a finely divided powder which since produced from waste materials such as sawdust, is relatively cheap and can be used on a "throw-away" basis.

Since activated carbon is manufactured from naturally occurring raw materials, its properties will obviously be variable. In order to minimize variability it is necessary to be very selective in raw material source and quality and practice a high level of manufacturing quality control.

5.2 Methods of Manufacture

Activated carbon can be produced by either steam or chemical activation, both of which require the use of elevated temperature.

Chemical activation is achieved by degradation or dehydration of the, usually cellulosic, raw material structure. Steam activation, however, initially involves the removal of volatiles, followed by oxidation of the structure's carbon atoms.

5.2.1 Chemical Activation

The raw material used in chemical activation is usually sawdust and the most popular activating agent is phosphoric acid, although zinc chloride and sulfuric acid are well documented. Others used in the past include calcium hydroxide, calcium chloride, manganese chloride and sodium hydroxide, all of which are dehydrating agents.

The raw material and reagent are mixed into a paste, dried and carbonized in a rotary furnace at 600 degrees C. When phosphoric acid is the activating agent the carbonized product is further heated at 800-1000 degrees C during which stage the carbon is oxidized by the acid. The acid is largely recovered after the activation stage and converted back to the correct strength for reuse.

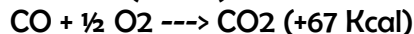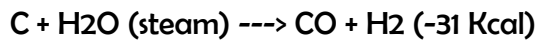The activated product is washed with water and dried.

Activity can be controlled by altering the proportion of raw material to activating agent, between the limits of 1:05 to 1:4. By increasing the concentration of the activating agent, the activity increases although control of furnace temperature and residence time can achieve the same objective.

5.2.2 Steam Activation

The use of steam for activation can be applied to virtually all raw materials.

A variety of methods have been developed but all of these share the same basic principle of initial carbonization at 500-600 degrees C followed by activation with steam at 800-1,100 degrees C.

Since the overall reaction (converting carbon to carbon dioxide) is exothermic it is possible to utilize this energy and have a self-sustaining process.

$$C + H_2O \text{ (steam)} ---> CO + H_2 \text{ (-31 Kcal)}$$
$$CO + \tfrac{1}{2} O_2 ---> CO_2 \text{ (+67 Kcal)}$$
$$H_2 + \tfrac{1}{2} O_2 ---> H_2O \text{ (steam) (+58 Kcal)}$$

$$C + O_2 ---> CO_2 \text{ (+94 Kcal)}$$

A number of different types of kilns and furnaces can be used for carbonization/activation and include rotary (fired directly or indirectly), vertical multi-hearth furnaces, fluidized bed reactors and vertical single throat retorts. Each manufacturer has their own preference.

As an example, production of activated carbon using a vertical retort is described below.

Raw material is introduced through a hopper on top of the retort and falls under gravity through a central duct towards the activation zone. As the raw material moves slowly down the retort the temperature increases to 800-1000 degrees C and full carbonization takes place.

The activation zone, at the bottom of the retort, covers only a small part of the total area available and it is here that steam activation takes place. Air is bled into the furnace to convert the product gases, CO and H2 into CO2 and steam which, because of the exothermic nature of this reaction, reheats the firebricks on the downside of the retort, enabling the process to be self-supporting.

Every 15 minutes or so, the steam injection point is alternated to utilize the "in situ" heating provided by the product gas combustion. The degree of activation (or quality) of the product is determined by the residence time in the activation zone.

The resulting product is in the form of 1" to 3" pieces and requires further processing before being suitable for its various end uses. This entails a series of crushing and screening operations to produce specific mesh ranges.

Certain products may undergo further processing such as drying, acid washing or chemical impregnation to satisfy particular requirements.

6 PROPERTIES AND QUALITY CONTROL TESTING

Because of the diverse end uses to which a carbon may be applied, it is difficult for manufacturers to conduct specific tests related to any one application. A manufacturer can undertake some specialty tests after agreement with the user but this is the exception rather than the rule. The size and number of pores essentially determine a carbon's capacity in adsorbing a specific compound. Since pore size and total pore volume determinations are quite lengthy, they are impractical as a means of quality control during manufacture. It is, therefore, necessary to relate the carbon's surface capabilities to a standard reference molecule.

6.1 Carbon Tetrachloride Activity

The most widely used method is to measure the carbon's capacity to adsorb carbon tetrachloride (referred to as CTC) and express this as a w/w %. This is determined by flowing CTC laden air through a sample of carbon of known weight, under standard conditions, until constant weight is achieved. The apparatus essentially consists of a means to control the supply of air pressure, produce a specified concentration of CTC and control the flow rate of the air/CTC mixture through the sample. The weight of CTC adsorbed is referred to as the carbon's % CTC activity. However, this test does not necessarily provide an absolute or relative measure of the effectiveness of the carbon for other adsorbates or under different conditions. CTC activity is now universally accepted as a means of specifying the degree of activation or quality of activated carbon. Commercially available carbons range from 20% to 90% CTC activity.

6.2 Surface Area

The internal surface area of a carbon is usually determined by the BET method (Brunauer, Emmett and Teller). This method utilizes the low-pressure range of the adsorption isotherm of a molecule of known dimensions (usually nitrogen). This region of the isotherm is generally attributed to monolayer adsorption. Thus, by assuming the species is adsorbed only one molecule deep on the carbon's surface, the surface area may be calculated using the equation:

$$S = \frac{X_m N A}{M}$$

S = specific surface in m2/g
Xm = sorption value (weight of adsorbed N2 divided by weight of carbon sample)
N = Avagadro's Number, 6.025 E+23
A = cross-sectional area of nitrogen molecule in angstroms
M = molecular weight of nitrogen

Most manufacturers will specify the surface area of their products but as with CTC activity, it does not necessarily provide a measure of their effectiveness, merely demonstrating their degree of activation. It is also impractical to utilize surface area measurement as a means of quality control since this is a very lengthy procedure.

6.3 Hardness

The hardness and resistance to attrition of activated carbons is becoming more and more important.

The loosely applied term of "hardness" is somewhat difficult to measure on activated carbon.

Three forces can mechanically degrade an activated carbon - impact, crushing and attrition. Of these three, the force of attrition, or abrasion, is the most common cause of degradation in actual end use. At the present time, there are two commonly used methods available to evaluate a carbon's hardness.

The first of these is the Ball-pan Hardness Test.

A screened, weighed sample of carbon is placed in a special hardness pan with a number of stainless steel balls and subjected to combined rotating and tapping action for ½ hour. The particle size degradation is measured by determining the weight of carbon retained on a sieve (with an opening closest to one half the opening of the sieve defining the minimum nominal particle size of the original sample). The ball-pan hardness method has been used widely in the past and has a broad history in the activated carbon industry for measuring the property loosely described as "hardness". In this context, the test is useful in establishing a measurable characteristic, conceding that it does not actually measure in-service resistance to degradation, it can be used to establish comparability of differing batches of the same material. This test actually applies all of the three forces mentioned earlier, in a variable manner determined by the size, shape and density of the particles.

The second method used is the Stirring Bar Abrasion Test.

In this procedure, a sample of carbon is placed in a cylindrical vessel where an inverted T-shaped stirrer is turning rapidly at a controlled rate. The percentage reduction in average particle size, resulting from the T-bar action, is recorded after 1 hour. This method measures attrition of the carbon, as long as the particle size is smaller than a 12 mesh. There is evidence showing that the results of this method are influenced by particle geometry.

Whichever of these tests is performed on carbon it is generally accepted that granular coconut based carbons show the least rate of physical degradation.

This is possible due to two factors. First, granular coconut carbon is produced from pieces of raw coconut shell whereas, most other carbons are produced from reconstituted powders. In consequence, carbons other than coconut based types, can only breakdown to a powder or dust.

Coconut carbon essentially chips and breaks into smaller pieces and thus degradation to powder, is a relatively lengthy process. Second, as outlined earlier, the coconut carbon structure is different to other types, producing a material of relatively high density and physical strength.

6.4 Mesh Size

The physical size, or mesh size, of a carbon must be considered in relation to the flow rate in the system it is to be used.

Naturally, the smaller the carbon's mesh size, the greater its resistance to flow. Thus, it is usual to select the smallest mesh size carbon that will satisfy the pressure drop limitations of the system.

6.5 Ash Content

Ash content is less important except where the carbon is used as a catalyst support since certain constituents of the ash may interfere or destroy the action of precious metal catalysts. Ash content also influences the ignition point of the carbon—this may be a major consideration where adsorption of certain solvents is concerned.

6.6 Density

The density of carbon is, of course, of great importance to many users in estimating the weight required to fill a vessel.

6.7 Interrelation of Properties

There is a relationship between BET surface area and CTC adsorption and this is taken into account when specifications are formulated. CTC activity, density and ash content are interrelated and provide a simple means of manufacturing control.

As quality, or degree of activation increases, CTC activity and ash content increase and density decreases.

Furthermore, CTC activity being equal, coconut carbons show higher density and lower ash content than coal based carbons. Wood based carbons show much lower density than either coal or coconut carbons but ash contents midway between coal and coconut carbons.

Thus, these properties are not only a means of controlling quality during manufacture but may also assist in determining the raw material and quality of an unknown carbon.

CTC activity, density, hardness, mesh size and raw material information will enable selection of a suitable carbon for most common applications (excepting those utilizing chemisorption as the prime mechanism).

6.8 Other Tests

Many other tests such as methylene blue, iodine number, molasses number, phenol value, ABS (alkyl benzene sulfonate) value etc., can be carried out but these are usually only relevant to specific end-uses.

7 IN-SERVICE CONTAMINATION OF CARBON IN VAPOR PHASE APPLICATIONS

7.1 Surface Exhaustion

In almost every application of activated carbon the surface will eventually become saturated (or exhausted). This may occur within a few weeks, several months or many years depending on the conditions of service.

Saturation is inevitable since the carbon surface has a finite number of reaction sites and when these are all occupied an adsorption potential no longer exists.

Carbon is a very non-selective sorbent and has a great affinity for a wide spectrum of organic compounds. Although, a carbon may be designed and employed to remove a very specific compound from a process stream in doing so it will undoubtedly adsorb most other components in the stream thus creating a cumulative affect on the rate and degree of saturation. In fact if so called "clean air" were to be passed through a carbon filter it would eventually become saturated, even though the concentration of contaminants may be in the ppb range.

7.2 Surface Regeneration

In many applications (utilizing base, non-impregnated carbon) the surface can be regenerated or reactivated in-situ, using steam or other heat treatment processes, thus allowing reuse of the carbon many times over. This principle is used to great advantage in the recovery of volatile organic solvents ..... the desorbed contaminants (i.e. solvents) being recovered from the steam used to strip the carbon surface.

In situations where the adsorbed contaminants are not readily desorbed by steam, thermal reactivation in a kiln (similar to that used in the activation process) is necessary.

In the case of chemically impregnated carbons, reactivation is seldom possible since the chemisorbed contaminants are chemically fixed on the carbon's surface and the impregnant cannot be returned to its original state.

Although the predominant mechanism of an impregnated carbon is one of chemisorption, some physical adsorption, to varying degrees, will also take place. In theory the physically adsorbed species could be removed from a saturated impregnated carbon by reactivation. However, the reactivated carbon would remain inactive towards those species requiring a chemisorption removal mechanism since the impregnant would either still be exhausted or be chemically changed by the reactivation conditions.