

Chemistry and Physics of Carbon

Edited by LJUBISA R. RADOVIC

Volume **27**



Chemistry and Physics of Carbon

VOLUME 27



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Chemistry and Physics of Carbon

A Series of Advances

Edited by

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VOLUME 27



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Preface

In this presentation of our 27th volume, I want to briefly recapitulate where we stand with this fascinating “old but new material,” as Phil Walker so aptly called carbon in his inaugural preface to this series almost four decades ago. In the intervening period Professors Phil Walker and Peter Thrower, my distinguished predecessors, have assembled authoritative reviews on a remarkable range of materials, including nuclear graphite, activated and molecular-sieving carbons, carbon blacks, cokes, pyrolytic carbons and graphite, doped carbons, carbon fibers and composites, diamonds, filamentous carbon, intercalated graphite, and carbyne. Their applications in a remarkable variety of fields have been analyzed: nuclear reactors, coal gasification, adsorption, separation and pollution control, lubrication and tribology, bioengineering, aerospace engineering, materials reinforcement, metallurgy, electrochemistry, and catalysis, among others. All this using a remarkable variety of chemical and physical characterization methods: optical and electron microscopy, electron spin resonance, infrared spectroscopy, measurements of magnetoresistance and electronic properties, irradiation damage, deformation mechanisms and fracture, chemical kinetics, determination of transport and thermodynamic properties, scattering of light, x-rays, neutrons and electrons. We have also witnessed quite a few shifts in “popularity,” from the dominance of nuclear graphite until the 1960s, to the recent “age” of carbon fibers and composites, and now with fullerenes and carbon nanotubes.

Throughout all these years it was essential to have, in the words of Phil Walker from his inaugural preface, a “monograph series of recent advances in carbon research and development and of comprehensive reviews on past achievements in important areas,” a series that uses a “truly interdisciplinary approach.” In

the 21st century, our goals remain the same, reflecting the amazing vigor and fertility of carbon science and the ability of carbon technology to reinvent itself. But the challenges seem to be greater. With the advances in information technology both facilitating and hampering the transfer of knowledge, it will be even more important for scientists and engineers to be able to rely on authoritative, critical, and comprehensive reviews. As Mary Anne Fox emphasized in her recent analysis of the future of review articles (*Chem. Rev.*, 2000, 100, 11–12), “the critical contribution of a well written review [is in seeing] connections between published works that would be missed by a computer, particularly if they originate in different subdisciplines.” Artificial intelligence and on-line searches are beginning to replace human activities in many areas, but it will be many decades, if ever, before a computer is able to “write” a review of the same caliber as we shall continue to offer our readers in this series.

In Volume 26 we assembled three reviews in which the control of *bulk* properties of carbon was shown to be the key to successful and widely varying applications. The common theme in the present volume is that *surface* properties are crucial in the environmental and electrochemical applications of carbon.

The late Frank Derbyshire and his colleagues set the stage with an eclectic analysis of myriad environmental applications. Frank’s sudden death has been a tremendous loss for the carbon community. This chapter will serve as a lasting testimony to how he enriched our science, and our lives: by communicating a firm grasp of the fundamentals and an infectious zeal to appreciate their connectivity and realize their potential. In vintage Derbyshire words, which we shall cherish forever, “we must strive and reach out in our interactions and collaborations to help to translate the positive aspects of carbon science into new technologies.”

Dr. Turov and Professor Leboda combine their expertise in nuclear magnetic resonance and adsorption phenomena to propose a new tool for a more incisive analysis of adsorbate–adsorbent interactions. Such an analysis is of critical importance in so many applications where it is becoming increasingly clear that adsorbate–carbon interactions are governed by both pore size and surface chemistry effects. These range from the ubiquitous water adsorption to the design of carbon-coated silicas with tailored ratios of hydrophobic to hydrophilic surface sites.

In assembling this volume, it is only natural that we have included another contribution from Poland, with its long tradition of expertise in the surface properties and behavior of carbon materials (see also Vols. 21 and 22). Drs. Biniak, Świątkowski, and Pakuła have prepared a particularly timely review of carbon electrochemistry, a much needed follow-up on a “call-to-action” chapter by León y León and Radovic in Vol. 24. There is great interest today, and many unanswered questions remain, regarding the virtues of specific carbon materials as electrodes and in electroanalysis, electrosynthesis, electrosorption, and electro-

catalysis. It is our hope that the insights offered in this chapter will be particularly helpful in the design of a new generation of batteries and fuel cells, for which a tremendous market has developed over the past few years.

The collaboration of Professors Radovic, Moreno-Castilla, and Rivera-Utrilla has resulted in a comprehensive and unifying in-depth survey of a sorely neglected topic. For an earlier review of liquid-phase adsorption in this series, see the chapter by Zettlemoyer and Narayan in Vol. 2. Here the focus is on activated carbons and aqueous solutions, which are of greatest practical significance, but both organic and inorganic adsorbates are included and contrasted. This has allowed the authors to formulate significant generalizations that translate into recipes for optimizing carbon surfaces and maximizing their uptakes of specific water pollutants. It remains to be seen when and how these advances in our understanding of carbon behavior will result in better carbon products for water treatment, a mature and large-scale technology that Derbyshire and his colleagues have identified as ripe for major (and much needed!) breakthroughs.

As we continue with these efforts to synthesize our knowledge of chemistry and physics of carbon well into the 21st century, I invite your suggestions for reviews to be included in upcoming volumes. Even more important will be your help in identifying potential authors (including yourselves!) who will take the time, and have the expertise, to strike the right balance between comprehensive coverage and critical analysis.

Ljubisa R. Radovic



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1

Carbon Materials in Environmental Applications

Frank Derbyshire,† Marit Jagtoyen, Rodney Andrews,
Apparao Rao, Ignacio Martin-Gullón, and Eric A. Grulke

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I. INTRODUCTION

The tremendous diversity that is available in the structure and properties of carbon materials underscores their utilization in virtually all branches of science and engineering, ranging from high-technology applications to medicine and heavy industry. Moreover, the list of carbons that are currently available or are under development is impressive and is being continually extended. One of the fastest growing areas is in environmental applications, not the least because carbon is compatible with all forms of life. Enormous interest in carbon materials has emerged over the past several years driven by environmental awareness and regulation and the need to find relatively low-cost solutions for protection and remediation. In this respect, the materials of interest are predominantly activated carbons, although there are areas where nonporous carbons also offer advantages.

This chapter is concerned with technologies that allow carbon materials to be used in environmental applications. In attempting to define the scope of this work, the authors have adopted a relatively broad interpretation and have considered where carbon materials can play a role both directly and indirectly in protecting and improving the quality of the environment and human health.

The first section is mainly concerned with some of the emerging technologies for the production of novel activated carbons that may help to fulfill the increasing demands on performance as regulations on environmental pollution become more stringent. The next two sections deal with applications of conventional and new activated carbons in gas and liquid phase applications. The penultimate section considers the uses of carbons supports for zero-valent metal dehalogenation. The

last section briefly describes some of the uses and potential uses of carbons in medical technology and as sensors or detectors for monitoring and control, and to provide means to make more efficient use of energy, thereby lowering the associated emissions.

Over the last two decades, the discovery of new carbon structures in the form of closed cage molecules has demonstrated that carbon science is alive and well and is a productive font for the synthesis of new materials. Advancements in new and more conventional areas of carbon research and development continue at a very fast pace. Now and in the future, there are perhaps more opportunities than ever before for the development of new materials consisting of carbon or containing one or multiple carbon structures.

II. EMERGING TECHNOLOGIES

A. Activated Carbons

Activated carbons are produced with a wide range of properties and physical forms, which leads to their use in numerous applications (Table 1). For example, their high internal surface area and pore volume are pertinent to their being employed as adsorbents, catalysts, or catalyst supports in gas and liquid phase processes for purification and chemical recovery. General information on the manufacture, properties, and applications of conventional activated carbons can be found in *Porosity in Carbons*, edited by John Patrick [1].

Activated carbons are commonly fabricated in the form of fine powders and larger sized granules, pellets, or extrudates (Fig. 1). However, activated carbons can also be produced as fibers, mesocarbon microbeads, foams and aerogels, and in the form of flexible or rigid solids. The form, as well as other properties, helps to determine the suitability for a specific application. Rates of adsorption or reaction can be orders of magnitude higher for activated carbons with narrow dimensions (e.g., powders and fibers with diameters in the range 10 to 50 μm) than for granular carbons (0.5 to 4.0 mm): in the former case, most of the adsorptive surface is readily accessible, and there is much less dependence on intragranular diffusion (Fig. 2).

Powdered activated carbons are used almost exclusively in liquid phase applications, usually in a batch-processing mode. Operation can be flexible because

TABLE 1

Surface area (BET, nitrogen)	500–2500 m^2/g
Total pore volume	0.5–2.6 cm^3/g
Bulk density	<0.1–0.6 g/cm^3
Widely varying hardness and abrasion resistance	
World consumption	~400,000 tonnes/year

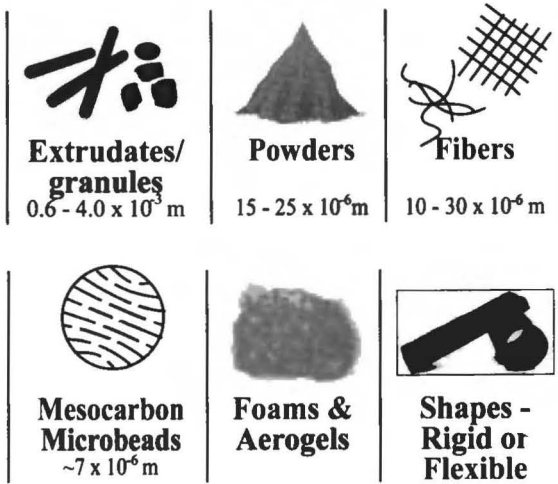


FIG. 1 Forms and properties of activated carbon.

the dosage of activated carbon can be readily adjusted. However, powders present difficulties in handling and are not conducive to use in fixed beds, or to regeneration. In contrast, granular activated carbons are used in both liquid and gas phase applications, lending themselves to continuous or cyclic processing in fixed or moving beds, and are regenerable.

Performance requirements are becoming increasingly more demanding, and there is a growing need for activated carbons with new and improved properties.

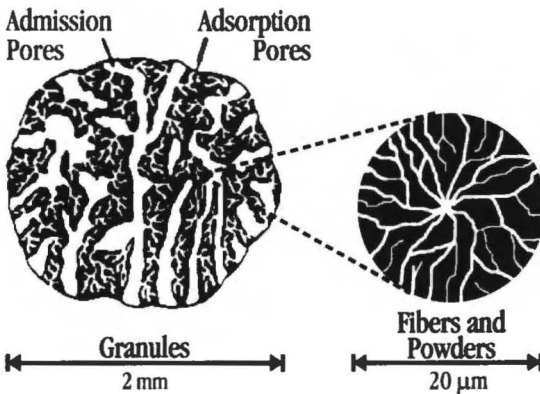


FIG. 2 Schematics showing internal structure of activated carbon forms.

Relatedly, there has been a corresponding increase in research and development, as reflected by the large number of papers that are presented at the various carbon conferences. Advances in activated carbons are expected to emanate from using alternative synthesis routes and precursors, from the development of new forms, and through techniques to modify surface chemistry. Some examples are given in the following sections.

B. Adsorbents and Catalysts by KOH Activation

In the 1970s, researchers at the AMOCO Corporation, USA, developed a process to produce extremely high surface area carbons (over 3000 m²/g) by the KOH activation of aromatic precursors such as petroleum coke and coal [2]. The process was commercialized by the Anderson Development Company, USA, in the 1980s and was subsequently licensed and operated on pilot plant scale by the Kansai Coke and Chemicals Co. Ltd., Japan. At this time, only limited quantities of material have been produced. The activated carbon is predominantly microporous, which is responsible for the high surface area, and the total pore volume is exceptionally high: 2.0–2.6 mL/g.

Examination by high-resolution electron microscopy has revealed that the carbons possess a homogeneous cagelike structure, the walls of which consist of one to three graphitelike layers. It is the delicate nature of this structure that may account for the ability of the carbon to swell and accommodate larger molecules than its microporosity would indicate [3]. Despite its extraordinary properties, the cost, low bulk density, and difficulties in handling have presented obstacles to its successful commercialization.

In a variation of this process, activated carbons have been prepared by the reaction of KOH with coals under carefully selected conditions [4,5] to yield catalysts of high activity suitable for the hydrodehalogenation of organic compounds. Such reactions are very much of interest for environmental protection. In experiments to examine the catalytic activity for the hydrodebromination of 1-bromonaphthalene at 350°C and the hydrodehydroxylation of 2-naphthol at 400°C in the presence of a hydrogen donor, 9,10-dihydronaphthalene, it was found that specific KOH-coal catalysts increased the extent of dehydroxylation by about 40% and of hydrodebromination by a factor of about 3 relative to commercial carbons. The conditions used to obtain the maximum selectivity for the catalysts were different in each case, demonstrating that the catalytic properties of these materials can be tailored to a particular application by adjusting the variables used in their preparation (e.g. concentration of KOH, heat treatment profile and gas atmosphere, coal rank, and method of coal cleaning).

C. Activated Carbon Fibers

There is growing interest in the development and application of activated carbon fibers (ACF), whose unusual properties can be advantageous in certain applica-

tions. ACF can be produced with high surface area, and their narrow fiber diameter (usually 10 to 20 μm) offers much faster adsorption, or catalytic reaction, than is possible for granular carbons. Activated carbon fibers are currently produced from carbon fibers made from polyacrylonitrile and from isotropic pitch precursors that are derived from coal tar and petroleum. Activated carbon is also produced from cross-linked phenolic resins [6], and from viscose [7].

Elsewhere, there is considerable interest in exploring alternative routes for the synthesis of ACF and for modifying their properties. Mochida and coworkers at Kyushu University, Japan, have employed ACFs derived from polyacrylonitrile and pitch to study the catalytic oxidation of NO to NO₂ [8] and the oxidation of SO₂ to SO₃ at ambient temperatures: SO₃ is subsequently recovered as sulfuric acid [9,10]. They have found that the catalytic properties of the ACFs can be altered by heat treatment. Economy and coworkers at the University of Illinois, USA, are exploring the production of low-cost alternatives to ACFs by coating cheaper glass fibers with activated phenolic resin [11]. At the University of Kentucky, we have examined the synthesis of fibers and activated fibers from nonconventional isotropic pitches. Whereas most commercial ACFs are microporous, activated carbon fibers produced from shale oil asphaltenes and from some coal liquefaction products are found to possess high mesopore volumes [12,13]. Through the selection of appropriate precursor pitches, it may be possible to produce ACFs with substantially different properties in terms of pore size distribution and surface chemistry, as well as allowing them to be processed more efficiently. In this context, coals present a fertile resource, as heavy coal liquids can be produced relatively cheaply and with a wide range of composition that is determined by the rank and structure of the parent coal and the means by which liquids are produced—pyrolysis, solvent extraction, liquefaction.

D. Monolithic Activated Carbons

Individual fibers and powders present difficulties in handling, containment, and regeneration, and in fixed bed operations they can present an unacceptably high resistance to flow. These problems can be surmounted by their incorporation into forms such as felt, paper, woven and nonwoven fabrics, and rigid monolithic structures. Potential advantages of these forms include facile handling, high permeability, and the possibility of in-situ regeneration. Indeed, regeneration may be accomplished through electrical heating, provided that there is adequate contact between the conducting carbon constituents, thus offering a simple and rapid means of raising the temperature uniformly [11,6,7,14]. In addition, monoliths can be fabricated to a given size and shape, a consequence of which is that completely novel adsorber/reactor designs are possible.

Technology has been developed by the Mega-Carbon Company, USA, to incorporate powders such as high surface area, KOH-activated carbons into robust

monoliths (Fig. 3). Shaped carbons are produced from a slip or pourable suspension of the activated carbon powder and a binder, and the mixture is made rigid by mild heating to set the binding agent. The shape and size of the monoliths is determined by the mold, with the advantage that they can be preformed or formed in situ. In this proprietary process, over 80% of the surface area of the free powder is retained in the monolith. The shapes are strong, with crush strengths up to 18 MPa, and they are stable to temperatures in excess of 300°C. The properties can be adjusted by controlling the composition of the binder mix. Prospective applications under investigation are in gas phase adsorption and gas storage.

A collaboration between the University of Kentucky and the Oak Ridge National Laboratory has led to the development of rigid activated carbon fiber composites [15,16]. The composites can be prepared using any type of carbon fiber, although efforts to date have focused on isotropic pitch fibers. The composites are formed by filtering a water slurry of chopped fibers and powdered resin. The filter cake is then dried and bonded by heating to cure the resin, following which the cake can be carbonized and activated in steam or CO₂. Alternately, the cake can be formed using preactivated carbon fibers, when over 90% of the surface area of the free fibers is retained in the composite after curing. Because of their unique architecture (Fig. 4), the composites are strong, are highly permeable to liquids and gases, and can be machined.

It has been found that the composites can be used in gas phase processes such as the separation of CH₄ and CO₂ [16] or the adsorption of volatile organic compounds from air (see later in this chapter). In the liquid phase, column tests have been used to examine the effectiveness of an activated carbon fiber compos-

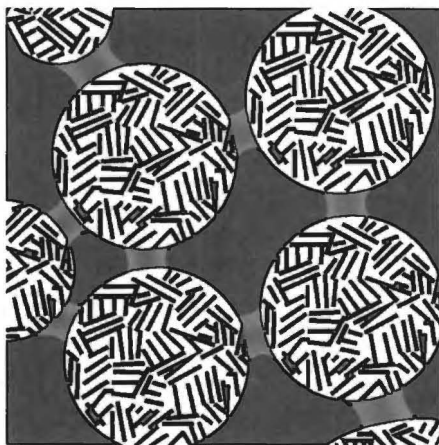


FIG. 3 Activated carbon monoliths (Mega-Carbon Company, USA).

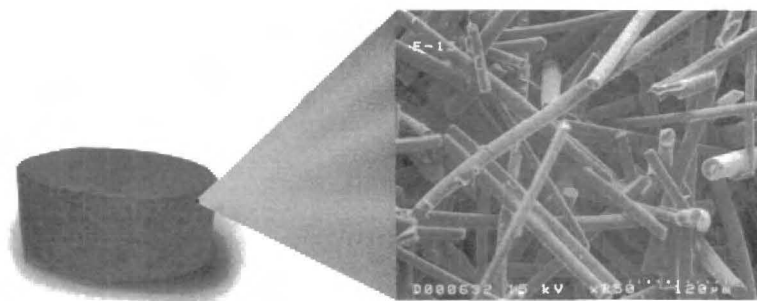


FIG. 4 Structure of rigid activated carbon fiber composite.

ite relative to a commercial granular activated carbon for the adsorption of a common herbicide, sodium pentachlorophenolate or Na-PCP [17]. The breakthrough time was found to be almost ten times longer for the composite than for the equivalent bed of granular carbon. The greater effectiveness of the composite is attributed to its uniform structure, which ensures that the feed is distributed evenly through the column, to the presentation of the adsorbent surface in fiber form, and to the open internal structure, which renders the pore structure readily accessible.

E. Surface Chemistry

The selectivity of activated carbons for adsorption and catalysis is dependent upon their surface chemistry, as well as upon their pore size distribution. Normally, the adsorptive surface of activated carbons is approximately neutral, such that polar and ionic species are less readily adsorbed than organic molecules. For many applications it would be advantageous to be able to tailor the surface chemistry of activated carbons in order to improve their effectiveness. The approaches that have been taken to modify the type and distribution of surface functional groups have mostly involved the posttreatment of activated carbons or modification of the precursor composition, although the synthesis route and conditions can also be employed to control the properties of the end product. Posttreatment methods include heating in a controlled atmosphere and chemical reaction in the liquid or vapor phase. It has been shown that through appropriate chemical reaction, the surface can be rendered more acidic, basic, polar, or completely neutral [11]. However, chemical treatment can add considerably to the product cost. The chemical composition of the precursor also influences the surface chemistry and offers a potentially lower cost method for adjusting the properties of activated

carbons. For example, activated carbon fibers produced from nitrogen-rich isotropic pitches have been found to be very active for the catalytic conversion of SO_2 to sulfuric acid [18].

F. Nonporous Carbons

Outside of the sphere of interest in environmental science and technology that is occupied by activated carbons, the use of other forms of carbon is so broad that there are numerous instances where carbons contribute directly or obliquely to the development, protection, or maintenance of an environmentally friendly society. Examples include diverse applications in the field of medicine, where carbon is attractive, *ceteris paribus*, because of its compatibility with the human body—carbons are chemically and biologically inert; the formation of strong, lightweight, structures that are resistant to chemical attack and can improve the efficiency of energy use; and protection from thermal and acoustic emissions.

The advantages that can be obtained through modifying the properties of concrete by the incorporation of carbon fibers provides an illustration of the diverse applications of carbon materials. The world production of concrete is considerably in excess of 5 billion tons per annum [19]. In certain geographic regions where there is a high incidence of powerful natural phenomena, such as earthquakes, concrete structures are unable to withstand unusually high imposed stresses. Concrete per se is brittle, possessing good strength in compression but having poor tensile strength. Traditionally, improvements in these properties have been effected by reinforcement with steel rods. Much lighter structures, combined with high toughness and increased tensile and flexural strengths, can also be obtained by the incorporation of fibers. In the past, natural fibers, such as asbestos, cellulose, and sisal, were used [16]. Recent work has focused mainly on steel, carbon, and polymer fibers, of which steel is the most common. A recent study compared the relative merits of steel fibers, isotropic carbon fibers (from petroleum pitch), and high-grade polyethylene fibers for concrete reinforcement [20]. Of the three fiber types, the carbon fibers possessed the lowest tensile modulus and strength, but were less expensive than the polyethylene fibers on the basis of either unit mass or unit volume. In spite of the inferior characteristics of the carbon fibers, they conferred the highest tensile strength, indicating that their fiber dispersion and/or fiber–matrix bonding is superior.

It is of note that during the 1989 San Francisco earthquake, certain overhead road supports that were retroactively strengthened by cladding with a relatively thin layer of carbon fiber-reinforced concrete allowed them to survive while conventional concrete pillars failed [20]. Similarly, in Japan, which experiences several hundreds of earthquakes each year of widely ranging intensity, carbon fibers have been extensively adopted for concrete reinforcement. More carbon fiber is employed in the Japanese construction industry than anywhere else [21].

Carbon fibers are also of interest as replacements for asbestos fibers in friction materials, such as brake shoes [22]. This move was initially driven in order to avoid the health hazards associated with asbestos. In comparison to asbestos reinforced brake formulations, isotropic carbon fibers have been shown to provide much higher friction performance and superior wear resistance, together with many advantages in operating characteristics. These advantages translate to other friction materials, such as clutch plates, and to a much broader range of applications in which carbon fibers are used as reinforcing or filler materials in various matrices. Carbon fibers in the forms of mats, felts, and paper insulation also present viable replacements for asbestos fibers.

III. GAS PHASE APPLICATIONS

A. Removal of Volatile Organic Compounds (VOCs) from Air

With increasing concerns over air quality, the release of volatile organic compounds (VOCs) into the environment has become a matter of global concern. In the presence of sunlight, VOCs can combine with NO_x , which can be found in significant concentrations in urban areas as a result of emissions from combustion sources, such as internal combustion engines and power plants, to form ozone. While ozone in the upper atmosphere is beneficial in preventing harmful UV radiation from reaching the earth's surface, at ground level it can cause acute respiratory problems for humans, including decreased lung capacity and impairment of the immune defense system. For these reasons, amendments to the Clean Air Act of 1990 were introduced requiring the reduction in emissions of 149 VOCs that are detrimental to air quality [23], and many previously uncontrolled sources are now mandated to reduce VOC emissions [24].

Activated carbons have been used for many years as adsorbents for the removal and recovery of organic solvents from air streams emanating from a range of industrial sources. Typically, the activated carbon is in the form of granules that are contained in appropriately sized absorber beds. The beds are usually used in cyclic operation to effect first removal and then recovery of the solvent for recycle. The same principles have been applied for the entrapment and recovery of volatile organics from other sources, such as in the control of fugitive fuel emissions from vehicles. In many situations, traditional granular activated carbons provide an acceptable level of performance at reasonable cost. However, many of the new and emerging applications present far more demanding conditions and have created a need for higher performance adsorbents.

In the field of VOC control, a distinction can be made between processes that involve high concentrations (1–2%) of pollutants in effluent streams, where recovery and recycle is normally the principal objective, and those with low con-

centrations, typically 10–1000 ppm, where capture and disposal is the preferred route. New regulations limit VOC release to even lower concentrations. In processes where high flow rates are the norm, beds of granular activated carbon (GAC) must be relatively deep in order to provide sufficient contact time for the adequate removal of the adsorbates, thereby incurring a high pressure drop penalty. Over the last ten years several novel forms of activated carbons have been developed that can help to avoid the problems of using deep beds of GAC.

1. Carbon Properties

Although the surface area of activated carbons is an important parameter affecting the performance of these materials, other factors also play significant roles in solvent recovery. A particularly important characteristic is the working capacity, which is the difference between the amount of solvent adsorbed at saturation or equilibrium and the residual amount remaining in the carbon following desorption. Carbons that are highly microporous and have a high equilibrium uptake are not necessarily the best ones for practical use, since narrow micropores can strongly retain the adsorbed phase. There is an optimum pore size distribution for a given application, and that depends primarily on the properties of the adsorbate in question. For example, in automobile canisters containing activated carbon that are used to trap evaporative gasoline emissions, desorption is effected by flowing air at ambient temperature and pressure. To provide a high working capacity under these conditions, the carbon should have significant porosity in the 20–50 Å range [25]. The shape of the adsorption isotherm at different temperatures is also important since this determines the influences of inlet air temperature and adsorptive concentration on the equilibrium adsorption capacity.

The pressure drop over the adsorber bed is controlled by a number of factors including the bed geometry, the size and shape of the activated carbon granules, and fluid density, viscosity, and flow. The energy expenditure associated with overcoming a high pressure drop is undesirable since it can make a considerable contribution to the system operating cost. Hence, a compromise is made between the efficiency of bed use and the process economics. The size of granular carbons can be optimized by using particles that are large enough to give a low pressure drop across the bed, but not so large that there is poor access to the internal surface area: for large pellets the rate of diffusion of organic vapors into the pore structure may be too slow for efficient adsorption at short residence times. In addition to increasing the size of the granules or pellets, the pressure drop can also be reduced by lowering the bed height. However, shallow beds can introduce other problems such as the possibility of channeling and will reduce the time on stream in a cyclic operation.

The mechanical strength of the carbon is another important property. Movement of the granules can occur during cyclic operation causing attrition and creating fines. The generation of fines can contribute to increased pressure drop, ad-

versely affect the flow distribution, and reduce the volume of carbon in the bed. Mechanical strength becomes more important with deep beds, where the carbon at the bottom must support the burden of the bed above.

2. *Organic Solvent Recovery*

One of the largest gas phase applications for activated carbon is in the recovery of solvents from industrial process effluents. Examples of industries that produce solvent-contaminated air streams are dry cleaning, the manufacture of paints, adhesives and polymers, and printing. In many cases, the solvent concentration is high (of the order of 1–2%). The highly volatile nature of many solvents can create unacceptable problems if they are vented to the atmosphere: they can create health, fire, and explosion hazards as well as pollute the environment. The solvents must therefore be removed before the air streams are vented to the atmosphere. There are economic benefits if the recovered solvent can be reused.

The main technologies available for the removal of solvents and other VOCs are adsorption on activated carbon, thermal or catalytic incineration, biofiltration, or combinations of these methods. Adsorption over activated carbons offers high efficiency for VOC removal at both low and high concentrations, and it is more cost effective at low concentrations than incineration techniques. Incineration offers a method of destroying VOCs with the formation of relatively innocuous products, principally water and CO₂, but it is only viable for effluent streams containing high concentrations of VOCs. At low concentrations the high-energy requirements for treating dilute air streams at high flow rates make this approach prohibitively expensive. Biofiltration is used mainly for air flows with low VOC concentrations, where the low operating cost gives an advantage: at high concentrations (>10,000 ppm) the removal efficiency is too low.

In conventional solvent recovery, solvent-laden air is first passed through an adsorber bed of GAC. The solvent is adsorbed on the carbon and clean air is exhausted to the atmosphere. When breakthrough of the solvent occurs (that is, when the solvent concentration in the cleaned gas stream exceeds the limit of acceptability, normally ~10% of the inlet concentration), the inlet stream is directed to a second adsorber bed, while the first bed is regenerated. An example of a solvent recovery process is shown in [Fig. 5](#). To recover the solvent, it is desorbed by passing a hot low-pressure gas through the bed in a direction counter-current to the air flow. The most commonly used stripping agent is steam, but hot air or nitrogen are also used. As the flow of steam heats the carbon, the solvent is released and carried away. A typical steam demand is 0.3 kg steam per kg activated carbon [26]. The mixture of solvent and steam is condensed, when the solvent can often be separated and recovered by decanting. If the solvent is soluble in water, distillation is required for separation. The process can be made semicontinuous by the use of multiple carbon beds so that, at any time, one or more beds are being desorbed while others are in the adsorption mode.

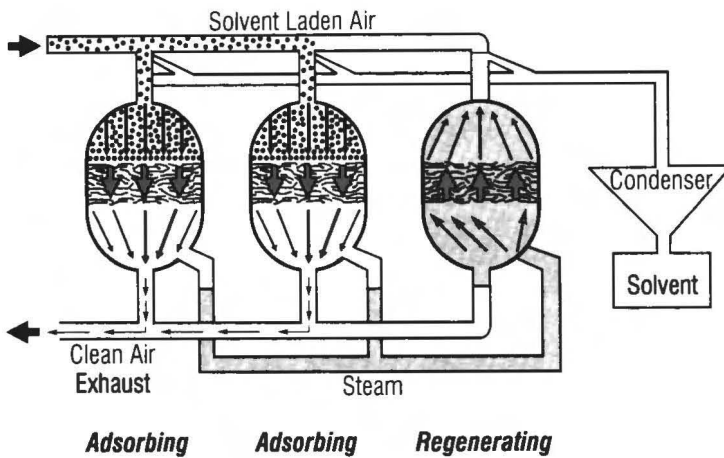


FIG. 5 Solvent recovery process using activated carbon beds.

Commercial activated carbon adsorbers have the capacity to treat air volumes from about 50 m³/min to over 15,000 m³/min. A list of solvents that are commonly recovered by activated carbon is given in [Table 2](#) [27,28].

Interactions with the carbon surface can make the recovery of certain solvents, such as ketones and chlorinated hydrocarbons, difficult. Ketones and aldehydes can polymerize, releasing large amounts of heat. When this happens in a part of the bed with poor heat transfer, the temperature can reach the ignition point of the solvent. "Fires always start with hot-spots in parts of the bed where the airflow is reduced due to poor design. The susceptibility of the carbon bed to autoignition can be reduced by removing soluble alkali sodium and potassium salts, that may be present as impurities in the activated carbon and which can function as combustion and gasification catalysts" [29].

Chlorinated hydrocarbons can be hydrolyzed to form highly corrosive hydrogen chloride, which can lead to rapid degradation of the materials of construction

TABLE 2 Solvents Recovered by Activated Carbon Adsorption

toluene	acetone	tetrahydrofuran
heptane	ethyl acetate	white spirit
hexane	methyl ethyl ketone(MEK)	benzene
pentane	naphthalene	xylene
carbon tetrachloride	methylene chloride	petroleum ether

used in the adsorber. These reactions are assisted by the higher temperatures and steam concentrations that are experienced during the desorption cycle. The catalytic effect of the carbon surface is such that even apparently stable solvents such as carbon tetrachloride can be readily hydrolyzed.

3. *Evaporative Loss Control Devices (ELCDs)*

Automotive emissions make a large contribution to urban and global air pollution. In gasoline fueled vehicles, emissions arise from the by-products of combustion and from evaporation of the fuel itself, **Fig. 6**. The exhaust from modern internal combustion engines is now cleaned up very effectively by the inclusion of a catalytic converter in the exhaust system, and further improvements have been made via advanced engine design. As older, less efficient vehicles with poor emission control measures are replaced by those conforming to modern standards, interest has inevitably focused upon uncontrolled emissions due to the evaporation of gasoline. To conform with increasingly stringent government air pollution control standards, it has become necessary to fit an activated carbon canister on motor vehicles to prevent the emission of volatile petroleum constituents.

The first Clean Air Act of 1970 required hydrocarbon emissions to be lower than 0.25 grams/km. By 1971 charcoal canisters were installed in US automobiles to trap gasoline vapors. Later amendments to the Clean Air Act state that all US automobiles must have a canister that will cope with both running and refueling losses from 1998. Similar legislation is following in Europe and other parts of the world. The carbon canister, also called an evaporative loss control device (ELCD), is located between the fuel tank and the engine, **Fig. 7**. Evaporation occurs due to fluctuations in ambient air temperature from night to day. As the temperature rises, it causes the fuel tank to heat and release gasoline vapors.

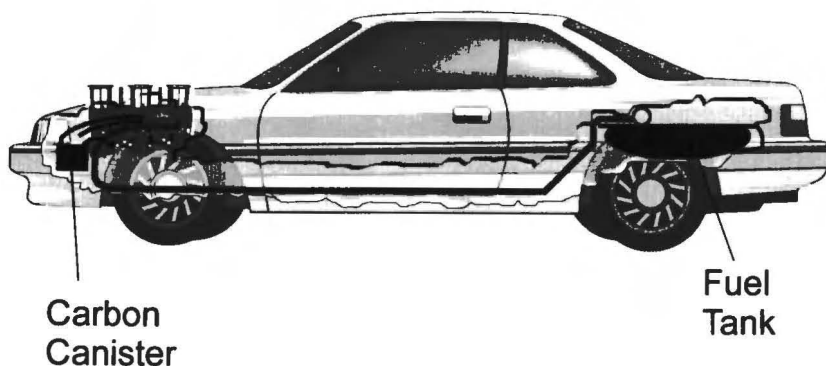


FIG. 6 Evaporative losses from gasoline-powered vehicles.

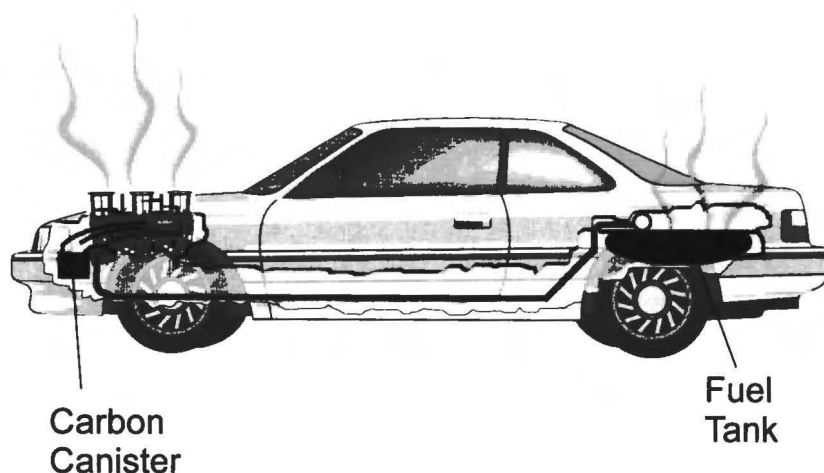


FIG. 7 Evaporative loss control device (ELCD).

Gasoline vapors are also vented from the fuel tank during refueling as they are displaced by liquid gasoline. These vapors are also captured by the ELCD canister. The canister is regenerated by a bypass flow of combustion air when the engine is running. The vapor-laden air is then directed to the inlet manifold. The desorbed gasoline thus forms part of the fuel mixture to the engine, with the secondary benefit of a small but significant increase in fuel efficiency.

4. Removal of VOCs at Low Concentrations

Examples of sources of effluent air containing low concentrations of VOCs are in the vent stacks from flexiographic printing (mixtures of acetates and alcohols), paint booths in automotive assembly plants, and bakeries where the major VOC released is ethanol (~ 3 kg ethanol/1000 kg dough processed) [30]. Volume flows are typically in the range of 10,000–14,000/hr. Another significant VOC is styrene, a common monomer that is used in the production of a variety of industrial products including the manufacture of fiberglass-reinforced products such as recreational and sports vehicles and car and truck body parts. The consumption of styrene was about 4.0 billion kg in 1989, and reported styrene emissions were around 15 million kg/year in 1990 [30].

New environmental regulations are concerned with controlling low-level VOC emissions that require advanced adsorption technologies. When the concentration of VOCs is in the low ppm range, and the air flow is large, the beds of GAC must be relatively deep in order to provide sufficient contact time for adequate removal of the adsorbates. In turn, this requires large fans that are very energy-

demanding to overcome the high pressure drop. In addition, the mass transfer zone (MTZ) in GAC beds is extended under these conditions. The MTZ is the region of the bed between the activated carbon that is already saturated and the point where the gas phase concentration of the adsorbate is at the maximum acceptable limit in the effluent stream, Fig. 8. Breakthrough is reached when the leading edge of the zone advances to the end of the bed. The length of the zone is a measure of the adsorption efficiency of the bed. The longer the zone, the shorter the on-stream time and the smaller is the fraction of the full adsorbate capacity that has been utilized at breakthrough. The rate of adsorption is slow on GAC, particularly at low adsorbate concentrations. Beyond the initial adsorption at the outer layers of the granules, the rate of adsorption is controlled by the slower process of intraparticle diffusion.

New technologies are being developed and commercialized to meet the more stringent demands for VOC removal, and to surmount the problems associated with conventional technology. In one example, a honeycomb structure, made of activated carbon, or a substrate impregnated with activated carbon or zeolite powder, is used in a rotary concentrator to adsorb organic vapors and recover them

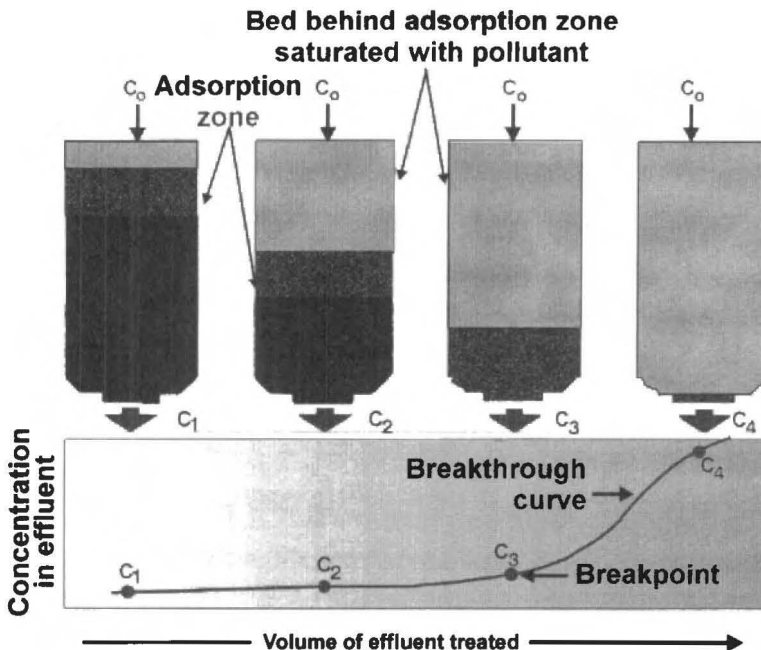


FIG. 8 Progression of adsorption front through adsorber bed.

in concentrated form, when they can be destroyed by thermal or catalytic oxidation.

A schematic of a rotary concentrator is shown in Fig. 9. The wheel rotates slowly (1–3 rotations per hour) with about 90% of its face exposed to the incoming air stream. The remainder of the face is in a regeneration sector where a counterflow of hot air desorbs the VOCs for subsequent incineration. The rotary adsorber increases the VOC concentration by a factor of 100, so there is little need for supplemental fuel in the small oxidizer that can be used to destroy the VOCs. This technology has been used for the removal of styrene emissions in the plastics molding industry. The process is also used with automotive paint booths where modular rotary concentrators and a regenerative thermal oxidizer are used to capture and destroy VOCs.

Activated carbon fibers (ACFs) offer a choice of other carbon forms for VOC removal. As discussed earlier, the narrow diameter of the fibers provides ready access of adsorptive species to the adsorbent surface. The incorporation of ACF into permeable forms such as felt, paper, and rigid monoliths helps to surmount the disadvantages of using loose fibers. Rigid ACF composites have been prepared at the University of Kentucky and examined for their potential for the removal of low concentrations of VOCs [31].

The open internal structure of the composites presents little resistance to the flow of fluids and allows them direct access to the activated fiber surfaces. Consequently, the composites offer a potential solution to the problems of removing low concentrations of VOCs from large volumes of air. In comparative trials, equivalent weights of GAC and an ACF composite were tested for their ability to remove butane at 20 ppm in a flow of nitrogen carrier gas, Fig. 10. The weight uptake of butane at breakthrough was twice as high on the composite as on the GAC. In addition, the structure of the ACF composites means that they are not susceptible to the attrition problems associated with packed granular beds during adsorption/desorption cycling.

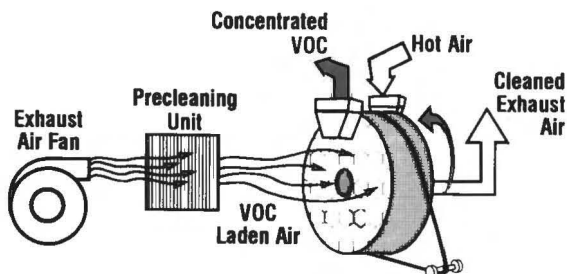


FIG. 9 Schematic of rotary concentrator for VOC recovery.

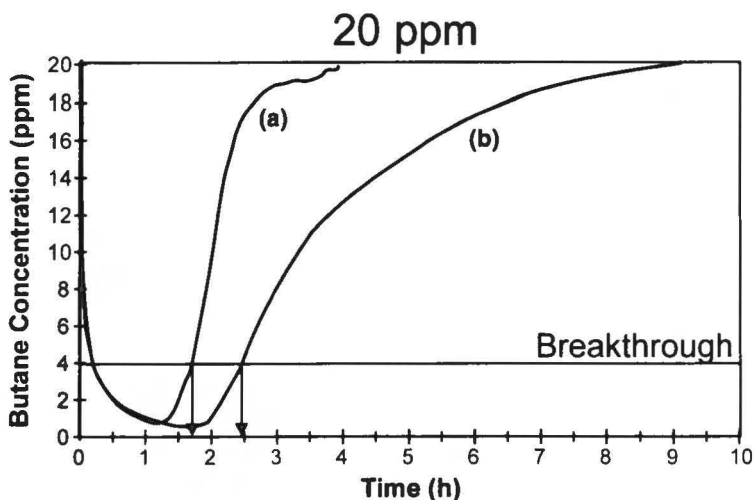


FIG. 10 Butane breakthrough curves for activated carbon beds: (a) fiber composite; (b) granular (20 ppm butane in nitrogen).

B. Purification of Landfill Gas

Landfill sites present sources of air pollution due to the presence of VOCs and to the generation of gases by aerobic or anaerobic microbial digestion of organic wastes. The gases emitted are typically composed of 55% methane and 45% CO_2 with trace amounts of VOCs and other less desirable contaminants. Trace organic compounds have not only been identified in landfill gas but also in the atmosphere downwind from them [32]. The trace contaminants are mainly aromatic hydrocarbons and halogenated aromatic hydrocarbons and include harmful compounds such as toluene, trichloroethylene, and benzene. Many of these compounds are so toxic that strategies to control them have been implemented. Of particular concern are carcinogenic agents such as vinyl chloride [33], for which Canada has a recommended maximum exposure limit of 3 mg/m^3 . The maximum level recorded by one study performed downwind from a landfill was measured at 2.9 mg/m^3 . Activated carbon has been found to be an efficient adsorbent for the removal of several of these halogenated hydrocarbons from landfill gas [34].

The significant volumes of gas evolved from large landfill sites and the high proportion of methane that is present makes it a potentially valuable energy resource. This has been recognized by Air Products and Chemicals, Inc., USA, who have developed technology to recover methane at yields of over 90% [35]. In this process (Fig. 11), pressurized landfill gas is passed through a bed of activated carbon to remove the trace impurities. The emergent flow of pure carbon

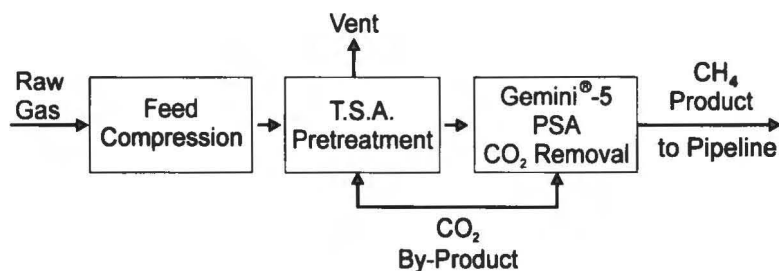


FIG. 11 Landfill gas treatment system.

dioxide and methane is then passed through a second bed of activated carbon maintained at high pressure to selectively adsorb the carbon dioxide and yield the required high-purity methane. The second bed is regenerated off-line by reducing the pressure. The carbon dioxide produced may then be channeled back as a hot gas to regenerate the first bed by stripping impurities, which then are incinerated.

C. Air Conditioning

Increasing public awareness and general concerns over air quality, and a growing incidence of allergic reactions to air pollutants, have generated a demand for improved treatment of the air that is supplied to public spaces. Such environments include airports, hospitals, submarines, office blocks and theaters. Granular activated carbon filters are commonly used in conjunction with air conditioning equipment for the removal of noxious trace contaminants from air that is recycled to populated areas. The recirculation and purification of air has the added economic advantages of reducing heating or refrigeration costs. Other applications include the use of activated carbons in domestic kitchen cooker hoods to adsorb cooking odors and vapors and activated carbon filters incorporated in air purifiers for private homes. High efficiency particulate air (HEPA) filters have been available for some time for the removal of allergens and dust. In more sophisticated air treatment systems, HEPA filters are combined with activated carbon adsorbents for the removal of human and cooking odors.

Smaller occupied spaces are also beginning to receive attention. For example, activated carbon filters have been introduced in automobile passenger cabins to remove odorous contaminants from inlet air and increase passenger comfort. These filters are installed only by a few manufacturers at present: Mercedes, BMW and Porsche in Germany and in the Mercury Mystique and Ford Contour models in the USA [36]. Particulate filters are normally integrated into automobile climate control systems to remove dust and pollens, and these can now be

augmented to remove odors that originate in exhaust fumes, rural emissions, and those generated within the car, particularly cigarette smoke and food odors. Cigarette smoke has been found to contain ethene, ethane, acetaldehyde, formaldehyde, NO_x , and isoprene at concentrations from 1000 to 1800 ppm. These contaminants can be reduced to concentrations of 1–2 ppm by the use of an efficient activated carbon filter.

D. Mercury Vapor Adsorption

Mercury is one of a number of toxic heavy metals that occur in trace amounts in fossil fuels, particularly coal, and are also present in waste materials. During the combustion of fuels or wastes in power plants and utility boilers, these metals can be released to the atmosphere unless remedial action is taken. Emissions from municipal waste incinerators can substantially add to the environmental audit of heavy metals, since domestic and industrial waste often contains many sources of heavy metals. Mercury vapor is particularly difficult to capture from combustion gas streams due to its volatility. Some processes under study for the removal of mercury from flue gas streams are based upon the injection of finely ground activated carbon. The efficiency of mercury sorption depends upon the mercury speciation and the gas temperature. The capture of elemental mercury can be enhanced by impregnating the activated carbon with sulfur, with the formation of less volatile mercuric sulfide [37]: this technique has been applied to the removal of mercury from natural gas streams. One of the principal difficulties in removing Hg from flue gas streams is that the extent of adsorption is very low at the temperatures typically encountered, and it is often impractical to consider cooling these large volumes of gas.

E. Protective Filters

The consequences of chemical warfare were first realized in the trenches of World War I when the Germans released chlorine gas on the Allied forces. The Allies quickly developed a means of protection from inhaling the choking gas by the use of gas masks containing granular activated carbon. The continued threat of chemical warfare and the development of highly advanced and toxic chemical and biological weapons has led to a much greater degree of sophistication in the design of adsorbents used in gas masks. Because of the wide range of offensive gases that are potentially available, the activated carbon is required to remove gases by both physical adsorption (e.g., nerve gases) and by chemical adsorption (e.g., hydrogen cyanide, cyanogen chloride, phosphine, and arsine). To accomplish this, the activated carbon is impregnated with a complex mixture of metal compounds that include copper, chromium, silver, and sometimes organic species. These sophisticated carbons are also utilized in filters for underground shel-

ters, and in inlet filters for armored vehicles and other forms of military transport. Threats from percutaneous nerve gases require complete body protection by the use of suits that contain activated carbon in a form that allows rapid and effective adsorption (fine granules or fibers).

The technology used by the military has been adopted by industry to provide protection to workers against hazardous vapors and gases that may be encountered in certain industrial processes. As with the military, this involves individual protective respiratory devices, air treatment filters, and protective clothing. Depending upon the nature of the hazard, the carbons may be impregnated to enhance their ability to remove the toxic species.

F. Flue Gas Cleanup

Appreciable interest has been generated in the use of activated carbons for flue gas cleanup, especially for the removal of SO_x and NO_x : the adsorption of mercury from flue gases was discussed earlier. From the environmental point of view, emissions from the combustion of fossil fuels in power plants and similar industrial processes are major contributors to a lowering of air quality. The flue gases carry traces of SO_2 and NO_x , which can be oxidized and converted to their acid forms in the presence of atmospheric water vapor, and they may also combine with other volatile organics to form ozone and smog. Similarly, low level SO_3 and NO_x emissions from automobiles, while insignificant for individual vehicles, become a large source of pollution when multiplied by the millions of vehicles that are on the roads.

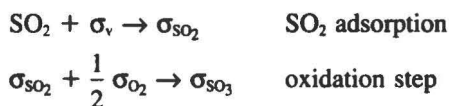
As early as the 1950s [38], after an acid/smog cloud enveloped London, leading to the deaths of thousands from respiratory ailments, measures were introduced to reduce the overall emissions of sulfur compounds and particulates from domestic and industrial combustion. With increasing awareness of the impact on human health and the environment, many other industrialized nations also began to put restrictions on allowable emissions from combustion and other sources. These restrictions have become increasingly more stringent and have encouraged the expansion of research programs in the area of flue gas cleanup, looking towards new materials and processes.

These factors have led to a broad need for technologies capable of reducing both point and distributed sources of SO_x and NO_x . For the control of emissions from power generation fossil fuels, the removal of SO_x has been achieved using wet or dry scrubbing/adsorption processes. These technologies have high energy costs associated with the operation of the scrubbing towers, as well as significant costs associated with raw materials, and materials handling and disposal. The removal of NO_x has been addressed through the introduction of low- NO_x burners (which has created a secondary problem of carryover of carbon into the ash, making the latter unacceptable in many cases for use in cement manufacture)

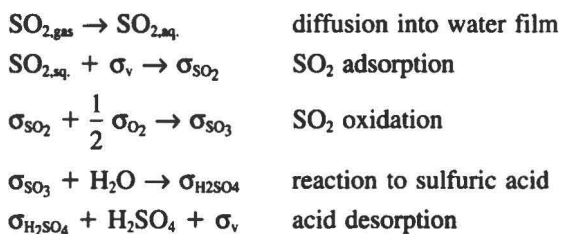
and by selective reduction processes, thermal (SR) and catalytic (SCR), in which reaction with NH_3 reduces the NO_x to nitrogen. The driving force for future technological development has been towards lower cost, more effective technologies. Activated carbons present a possible basis for new approaches to emissions control for both point combustion sources and distributed sources, including automotive emissions.

1. SO_x Removal

The SO_2 in flue gas streams is typically present at concentrations between 500 and 2000 ppm. It can be removed by adsorption on activated carbons, where it can be oxidized to SO_3 and converted to sulfuric acid if oxygen and water are present. The pathway for SO_2 removal depends upon conditions [39], dry or humid. Under dry conditions (with/without O_2),



Under humid conditions,



where σ_i = surface site containing component i and σ_v = vacant site.

(a) *Dry Adsorption and Oxidation.* Under dry conditions, SO_2 can be adsorbed onto activated carbon and then oxidized to SO_3 in the presence of oxygen. In this process, when the adsorptive capacity is reached, the carbon must be regenerated to recover gaseous SO_2 or SO_3 . Many factors influence the capacity of activated carbons for SO_x adsorption. Davini [40] found that activated carbons with basic surface groups have a higher capacity to adsorb SO_2 than carbons with predominately acidic functional groups. Heat treatment of activated carbons in an inert atmosphere provides a means to produce more basic functionality by the removal of CO_2 from carboxylic acid groups, leaving more basic $\text{C}=\text{O}$ groups [41]. This phenomenon was first discovered during investigations of the ‘‘active coke’’ process for desulfurization by Juntgen [39]. Moreno-Castilla et al. [42] support this conclusion and further show that the active sites of interest for this process are in narrow micropores (i.e., those pores accessible to benzene and n -hexane).

(b) *Catalytic Conversion to H₂SO₄*. The presence of both oxygen and humidity enhances SO₂ uptake on activated carbon [43]. The adsorbent capacity is increased by a factor of 2 or 3 in the presence of oxygen and by a factor of 20 to 30 if water is also present [44], Table 3.

When water is present in the gas stream, it reacts with the SO₂ and O₂ to produce sulfuric acid on the carbon surface, and can subsequently desorb. The overall SO₂ adsorption capacity is enhanced due to its solubility in the water film that forms on the carbon surface. Conversely, active sites for SO₂ capture are simultaneously reduced by water coverage. In general, the SO₂ adsorption characteristics of an activated carbon are dependent upon its physical form, the pore structure, the surface area, and the surface chemistry. Similarly, both temperature and contact time also affect the efficiency of the process. The temperature for practical application is usually between ambient and 200°C, with ambient to 50°C being favored due to the decreasing solubility of SO₂ in water at higher temperatures.

The sulfuric acid tends to desorb slowly from the carbon surface, and if the acid occupies all the active sites for SO₂ oxidation and hydration, the carbon becomes inactive for further adsorption of SO₂, as illustrated in Fig. 12. When a gas stream containing SO₂ is passed through a bed of activated carbon, there is complete removal of SO₂ for a period, during which the SO₂ is removed by both physical and chemical adsorption (Zone I). At the breakthrough point, the SO₂ concentration downstream of the adsorber unit begins to rise, as all the physical adsorption sites are occupied and only chemical adsorption and reaction to produce H₂SO₄ are available for SO₂ removal (Zone II). The SO₂ removal may further decrease due to the production of acid, which occupies some of the active sites and can lead to catalyst deactivation (Zone III) as the carbon surface becomes saturated. If there is almost no acid desorption, Zone III hardly exists, and the breakthrough plots go directly from 0 to 100%.

For this process to be viable, the activated carbon must be regenerable, or, preferably, the acid is removed at a rate fast enough to allow a steady state of

TABLE 3

Sample	Adsorbed amount (mmol/g)		
	Only SO ₂	5% O ₂	5% O ₂ , 10% H ₂ O
A	0.10	0.34	2.3
FE-100-600			
B	0.18	0.56	3.8
FE-200-800			
C	0.13	0.26	2.7
FE-300-800			