

# STATE-OF-THE-ART IN PREDICTING ACTIVATED CARBON PERFORMANCE

Mick Greenbank  
Calgon Carbon Corporation  
P.O. Box 717  
Pittsburgh, PA 15230-07171

Keywords: Ideal Adsorbed Solution, Polanyi Adsorption, Activated Carbon

## Abstract:

Adequate theories of multicomponent gas and liquid phase adsorption have been available for 10 to 15 years. Yet the ideal of using computer simulations to determine treatment costs and to aid in design of real-world environmental systems has never fully materialized. However, current adsorption theories are accurate enough, and quite useful, for making relative comparisons of performance of different carbons and for looking at adsorption versus other technologies for new applications. The use of a gas- and liquid- phase adsorption model is evaluated for predicting performance, optimizing carbon selection, and designing systems for environmental applications.

## I. MODELING ENVIRONMENTAL APPLICATIONS - DEFINITION OF THE PROBLEM

The ideal situation would be to have a computer program that instantly predicts the capital and operating cost of an optimized activated carbon system that solves a specific environmental problem in both the gas and liquid phase. In addition, the program would need to be able to account for variability in conditions and stream composition. This algorithm would allow 'what-if' type analyses to aid in design of an optimal system and account for upsets and shutdowns. Also, in the activated carbon design, the algorithm rhythm would provide instant feed back on performance leading to better activated carbon processing schemes and products. We are not there in 1996, but have made progress.

This is not a statistical error analysis or a review of existing adsorption theories. Instead it is a description of what the most practical theoretical approaches can and cannot do with environmental applications. The discussion is less mathematical and more problematical.

### A. APPLICATION DEFINITION - COMPUTATIONAL PERSPECTIVE

To do a computation of performance of an adsorption system, we need to know each adsorbable component present, including water. Any background components may be important, even if nondetectable using current techniques. For each component we need concentrations and variations in concentration over the life of the system. Also the treatment objective (acceptable effluent composition) should be defined in similar terms. The required system variables are temperature of each carbon particle (Usually approximated as a simple linear or a radial temperature profile through the adsorber) and gas-phase or liquid-phase linear velocity between the particles. The stream must be a single phase, to have effective contact of the contaminants with the carbon particles and to avoid any unpredictable decay in performance. This means that for the gas phase there must be no particulate matter or freely condensed material, for the liquid phase there must be no suspended solids or precipitation within the column.

### B. APPLICATION DEFINITION - REAL WORLD PERSPECTIVE

This ideal of an application description satisfying requirements for computation is rarely, if ever, obtained. Differences between the information required for computation and what is provided by the application definition are listed below.

#### 1. Stream composition

Generally the best case scenario is a stream analysis using a gas chromatograph/mass spectrometer (GCMS) and is usually a first step for both gas and liquid phase applications. This gives a list of compounds and concentrations for a sample taken usually at one moment in time. The GCMS analysis is relatively expensive. Consequently, time averaged values and histories of stream composition are generally not available, and thus variability of composition is not well defined. The major problem with GCMS analysis is that the largest, most adsorbable molecules are also not volatile, and thus are difficult to detect with GCMS. Test methods that are less specific, such as gas or liquid chromatography (GC or LC), measure the major or critical components and give little information on background components. Nonspecific tests such as total organic carbon (TOC), chemical oxygen demand (COD), biological oxygen demand (BOD), color, odor give no useful information and only hint at the composition. However, comparing the results of one of these nonspecific tests to the sum of the concentrations of the known components can be useful to find how much background material is not accounted for in the calculation. Sometimes, this background material can be approximated by substituting model compounds.

## 2. Carbon temperature

The temperature critical to the calculation is the temperature of the carbon where the adsorption is occurring, not the ambient or stream temperature (when gradients are present). Fortunately the carbon temperature profile in the adsorber is usually known or can be approximated.

## 3. Linear velocity or flow rate and its variability

Assuming no flow complication such as plugging or wall effects, the activated carbon is only concerned with the instantaneous linear velocity in the voids between it and its neighbors. This generally can be determined from the mass flow rate, void fraction, and dimensions for a given carbon system design. What generally is not included in the calculations are the fluctuations in the flow rate, or stoppage of flow due to shutdowns.

## 4. Variability of concentration and composition

Variability in stream compositions involves probability of upsets or spills and their magnitude, equipment operating schedules and flow rate changes, and the reliability of the sources of contamination. Few streams are consistent, but many streams that involve a leaching phenomenon, and where the equipment follows a regular routine schedule can become predictable with experience. Unfortunately this experience is generally not available during the design or evaluation stages of a project.

## 5. Other variables affecting performance

Other factors that can affect performance for gas-phase systems are: relative humidity, presence of condensables (including water), dusts or particulate matter (particulate size and amount). Other factors affecting performance of liquid-phase systems are: pH, conductivity, suspended solids (particulate size and amount). For humidity and pH, the effects can be estimated over a range of conditions and the performance detriment determined. Then an economic decision can be made for humidity or pH control or adjustment. The inlet end of a carbon adsorber will act as a particulate filter for dust and suspended matter, with the ability to filter material with diameters greater than one tenth of the smallest carbon particle diameter. However, operation of a carbon adsorber as a particulate filter is awkward and can be more expensive. The decision on whether to use prefilters for particulates is economical and depends on the severity of the problem. Unfortunately the adsorptive performance decay resulting from the lack of a prefilter for particulates can only be approximated crudely.

## 6. Defining treatment objectives

Performance is usually defined by the point at which the treatment objective is exceeded. Although objectives are usually defined, the exact point at which a treatment objective is exceeded sometimes adds uncertainty. For example, predicting the point at which a treatment objective is exceeded can be complicated when the objective is a nonspecific test result such as total hydrocarbon, TOC, BOD, COD, color, or odor, and a wide variety of components are present in the effluent of the carbon system. When the objective is cumulative mass over a time period (for example, kilograms of hydrocarbon per month), determining the calculated point at which the carbon system is exhausted and should be replaced is difficult. Percentage removal objectives for individual components can be difficult due to the potential variability of the influent stream and the time lag of a change in the influent to a change in the effluent. From a computational point of view, the simplest treatment objectives are concentration limits for individual components.

## 7. Regeneration (thermal or extraction)

Incorporation of a regeneration scheme, whether thermal (Steam or hot air), vacuum, or extraction (using a solvent or a pH shift) adds many more variables and uncertainty to the calculations. For example, a correlation of isotherm data as a function of temperature is required for thermal regeneration. Generally the approach is to measure several regeneration cycles and look for the system to reach a steady state. This approach is generally adequate, but does not predict the eventual exhaustion of the carbon with nonregenerable components or other operating inefficiencies that occur later in the life of the carbon bed (such as degradation of the particle to a smaller particle size or slow oxidation of the carbon structure).

## II. THEORETICAL APPROACH TO ADSORPTION

A few computational approaches can be used to approximate adsorptive performance, even within the limitations of the real world descriptions of environmental applications mentioned above. In order to select an adsorption theory for predicting performance in environmental applications, the following criteria must apply. The theory must be applicable: for systems with an unlimited number of components, for use with any of the wide variety of commercial activated carbons, and for the range of system variables present such as temperature, pressure, and pH or humidity. These are not trivial requirements because they imply that a multicomponent isotherm capacity can be determined for any component for any activated carbon over a range of concentrations and temperatures, pressures, pH, or humidity. With all these variables, measuring enough points to define the multicomponent isotherm surfaces is not practical. Therefore, the theoretical approach must predict multicomponent isotherms from single component isotherm data. Also isotherm data on one

activated carbon must generalize to all other commercialized carbons (Libraries of empirical isotherms will not be available for all commercial carbons). At least two approaches can satisfy these computational requirements and the practical limitations on the amount of empirical data required. The Ideal Adsorbed Solution Theory<sup>1</sup> (IAS) incorporating a generalized characteristic curve<sup>2</sup>, and the Polanyi Adsorption Potential Theory<sup>3</sup> incorporating the Hansen-Fackler Modification<sup>4</sup> (Polanyi). The remainder of the discussion on performance prediction will be limited to the use of these two approaches.

#### A. THEORETICAL APPROXIMATIONS AND ASSUMPTIONS

##### 1. Physical adsorption predominates

The adsorbates exhibit no specific interactions with the surface or each other, including chemical reactions on other nonideal behavior. This is a good assumption for most adsorbates on activated carbons. Specific interactions do occur, for example dipole-dipole and dipole-surface oxide interactions, but they are generally less significant than the nonspecific physical attractions. If this is not the case, then a polar adsorbent like Silica gel or alumina should be used instead of a nonpolar activated carbon. If the specific interaction between adsorbates is strong, such as with dimerization, then treat the dimer as the adsorbate.

##### 2. Bulk behavior is observed in the pores

What happens outside the particle happens inside the pores of the activated carbon. In other words, the adsorbates exhibit lateral interactions, bulk solubility limits, and melting points. The carbon structure does not alter the physical properties of the adsorbate. This is a good approximation on nonimpregnated activated carbons.

##### 3. No molecular sieving

All adsorbates have equal access to all portions of the carbon pore structure. Generally this is a good assumption. Molecular sieving or exclusion of large or bulky molecules does occur in activated carbons in specific instances, but it is the exception and not the rule. Also, on commercial activated carbons, the pore structure is purposefully open to provide easy access. Adsorbates excluded are generally so large that they are adsorbed in another part of the structure. When exclusion does occur, accounting for it with mathematical corrections to the single component isotherm is a possibility.

##### 4. Volume-based competition

Application is based on pore filling, and adsorbates compete on a volume basis. An adsorbate with twice the molar volume will compete with two of the smaller molecules. This is a good assumption and is why molar volume is one of the most important properties in determining adsorbability of a molecule.

#### B. STEPS IN THE COMPUTATION

##### 1. Generate single component isotherms

The first step is to generate a set of single component isotherms on a carbon of interest over the range of temperatures and stream conditions. An empirical approach would require a handbook of adsorption isotherms to be determined for each contaminant, on every carbon, over the range of temperatures and pH. The solution is to generate the single component isotherms using a generalized characteristic curve for the carbon and set of specific characteristics for each adsorbate determined on a standard carbon. The IAS theory can also incorporate a generalized characteristic curve<sup>5</sup> to generate the single component isotherms that are very similar to this classic Polanyi approach.<sup>6</sup>

First assume a pair of adsorbate properties, independent of the carbon, which can be used to scale adsorption isotherms to a single characteristic curve. One property is related to relative strength of the adsorptive interaction (Polanyi polarizability), and the other is related to the efficiency of filling the pore structure (molar volume in the pore determined from the maximum adsorption capacity at near saturated conditions). Next assume that the characteristic curve is a function of the carbon pore structure and therefore is a property of the adsorbent and independent of the adsorbate. The characteristic curve is generally presented as a distribution of pore volume over different adsorptive forces, corresponding to different pore sizes. The assumption is that the carbon pore structure is constant and fills on a volume basis and interacts with molecules in the same manner. Differences are in the number of molecules that fit into a pore and the relative strength of the interaction with the carbon structure.

With these assumptions, only one isotherm for a standard adsorbate (for example propane) is required on each carbon to determine the characteristic curve. Several simple techniques are available to generate these data easily.<sup>7</sup> Then one isotherm for each contaminant is required on a standard and well-defined activated carbon to determine the adsorbate molar volume and relative

adsorption strength in the pores. The database of published isotherms on well-defined standard carbons is growing, but is still inadequately small.

## 2. Calculate the multicomponent isotherms

The thermodynamics of adsorption of multicomponent systems on activated carbons, both from the gas-phase and liquid-phase, has been defined by several models,<sup>8</sup> but the most popular have been the Polanyi and IAS theories. Both approaches are thermodynamically consistent<sup>9</sup>, and calculation algorithms are available which can handle a large number of carbons and adsorbates efficiently.<sup>10</sup> The computation determines the partial occupation of the different regions of the pore space (adsorption sites) by the different contaminants. By summing the occupation of all sites by all contaminants, under the stream conditions, a multicomponent loading on the carbon particle is determined.

## 3. Incorporate a kinetic model for mass-transfer resistance

Once the multicomponent thermodynamics has defined the equilibrium state, a kinetic model can be incorporated to account for the diffusion of the adsorbate into the carbon pore structure. The adsorption kinetics has been most often modeled using an approach that incorporates three or four diffusion steps: the interparticle mass transfer (bulk diffusion), intraparticle mass-transfer (pore diffusion), and finally adsorption/reorganization (surface diffusion).<sup>11</sup>

The interparticle step is dependent on flow rates and column packing efficiencies. It is independent of carbon structure except its particle size and shape, and has been adequately modeled using columns of glass beads. Some modelers also add a boundary layer or film diffusion step as a second step in the interparticle (or bulk) diffusion process. The interparticle diffusion process is readily handled mathematically with few empirical parameters.

Intraparticle diffusion is independent of the flow rate or column dimensions but is highly dependent on carbon transport pore structure, often called the macropores and mesopores. Because this transport structure is specific to the carbon pore size distribution and how the pores are connected, the intraparticle diffusion coefficient can only be determined empirically. Unfortunately for nearly all 'well-designed' systems this is the slowest and thus the rate-controlling step in the adsorption process. The surface diffusion or rearrangement steps are independent of the transport pore structure but are dependent on the carbon and processes that are occurring. It also is only modeled empirically.

One goal in commercial adsorption systems design is to ensure the mass transfer zone is less than 20% of the column length to use the capacity of the activated carbon efficiently. For gas-phase adsorption systems it is generally much less than 20%. Therefore, the accuracy of the kinetic model is less critical when dealing with well-designed adsorption systems, especially in the gas-phase. Consequently, crude approximations for the interparticle, intraparticle, and surface diffusion coefficients are often used and are adequate.

## 4. Representation of the adsorbent column

Once the kinetics and thermodynamics are described, then a model is needed to represent the adsorption system. The column dynamics can be represented several different ways,<sup>12</sup> from theoretical plate (or stage-wise equilibrium) approximations, that resemble distillation column models, to calculation of widths of adsorption bands which resemble chromatography approaches. More rigorous approaches using coupled partial differential equations for heat and mass balance can also be used, but are generally not justified unless the system is complex, for example involving a complicated regeneration scheme.

Errors are also introduced when simplifying assumptions are made, like treating nonisothermal column profiles as isothermal or ignoring heat losses and treating the column as adiabatic. The other complications that can be over simplified are competitive displacement resulting in a rollover of displaced component, and concentrations within the column that are higher than the influent. Rollover increases column efficiency, but this increase is often ignored by models.<sup>11</sup> Finally, complications are added by the regeneration process, which is almost always a partial regeneration, and usually runs counter current to the adsorption flow. This results in complicated temperature and loading profiles in the carbon column and broader mass transfer zones. Simplifying approximations for regenerable systems are the same as the ones mentioned above, but are more significant and thus result in larger errors.

## C. RESULTS OF THE COMPUTATION

The results of the computation describe the column performance as order of elution, adsorption band widths, rollover or displacement, mass transfer zone size, and carbon exhaustion rate to a percentage breakthrough or to an effluent concentration limit. The order of elution shows which compounds elute first and will be key in exceeding the treatment objective. The adsorption band widths define

the segregation or chromatographic separation of components on the carbon column that can be important in some purification and separation processes. Rollover or displacement behavior can be important when dealing with separation using desorption processes or adsorbate recovery processes. A mass-transfer zone is predicted for each component present, but only the early eluting components are of interest. The mass transfer zone size of these components dictates the adsorber size and is the key to the system balance between the capital cost of the adsorption system and operating cost for the replacement activated carbon. (Utility costs, for energy and water, are an additional consideration for regenerable systems.)

Finally the predicted exhaustion rates are usually in units of bed volumes treated to an effluent treatment objective, which can be a percentage of the influent concentration or it can be an absolute concentration level. This exhaustion rate determines the absolute operating cost of the system and the change-out or replacement frequency of the activated carbon in the column. The operating cost derived from the exhaustion rate, can be compared directly to costs of alternate technologies.

### III. SOURCES OF ERROR

Accuracy of these methods is highly dependent on complexity and consistency of the stream, the ideality of the components, and the definition of the treatment objectives. The following discussion is not a statistical error analysis, but the relative assessment of the greatest sources of error based on experience running performance prediction calculations for general gas-phase and liquid-phase environmental applications. Table 1 lists a description of the various sources of uncertainty, and the relative importance of the contribution to the overall error of the performance predictions.

#### A. SINGLE COMPONENT ISOTHERM MEASUREMENT AND PREDICTION

The multicomponent adsorption models must also predict the original single component isotherms. Any errors due to oversimplification, when approximating single component behavior are incorporated in the single component prediction and carried over to the multicomponent case. Several examples of the levels of errors for single component predictions are listed in Table 2 for the Polanyi approach.

Major sources of error for the single component predictions are as follows.

1. Inaccuracies in the isotherm test or measurement - equilibrium was not attained, the carbon temperature was not controlled or measured, or the analytical errors were magnified by calculating the adsorption as a small difference between two large measurements.
2. Carbon samples were not representative - samples were contaminated (solvent vapors from the lab), out-of-date and no longer representative of the commercial activated carbon, or highly oxidized which can modify the pore structure.
3. A known isotherm was substituted for an unknown component - using an isotherm for an isomer of the adsorbate, for an adsorbate with similar molecular structures, or for an adsorbate with similar molecular formula and weight.
4. Selection of a single component adsorption theory - Polanyi and IAS can both assume a characteristic curve shape, necessary to be practical, but significantly decreases the accuracy of the predictions.

#### B. MULTICOMPONENT ISOTHERM PREDICTION THEORY

Most of the errors are due to the inherent assumptions of the theories.<sup>13</sup> Typical errors for common components are smaller than the single component values in Table 3, but exceptional errors can magnify theoretical shortcomings and become quite large. Thus, the multicomponent errors primarily reduce the reliability of the performance prediction.

Major sources of error for the multicomponent predictions are as follows.

1. Choice of the multicomponent theory - in some simple cases the Polanyi and IAS theories are mathematically identical, but for the general case the simple Polanyi approach is less accurate than the IAS, which is less accurate than the Polanyi with the Hansen-Fackler modification.<sup>14</sup>
2. Breakdowns of the basic assumptions (sometimes the effects can be corrected for by adjusting the single component isotherm<sup>15</sup>), for example:
  - Volume-based competition - in rare instances molecular shape can affect the volume competition.
  - Molecular sieving - becomes significant specifically with large molecules and can affect competition in the smaller pores.
  - Chemisorption - nonideal systems involving highly polar or reactive species can have additional specific interactions, such as hydrogen bonding, polar interactions, dimer formation, etc.
  - Bulk behavior in the pores - unique characteristics observed only when the molecule is an adsorbate, usually due to a configuration or interaction due to the carbon structure.

### C. PROBLEM DEFINITION

The two biggest concerns for accurate performance prediction are a precise identification of the background components and definition of the treatment objective. Vaguely defined background components (TOC, BOD, COD) and unknown or nondetectable compounds would add uncertainty to the prediction even if the calculation method was perfect. Empirical means of classifying the competitive effects of background components exist, even when the components are not well defined or detectable.<sup>16</sup> However, these methods can be difficult to carry out and are only approximations.

The definition of the treatment objective also can contribute to uncertainty in the performance prediction when defined vaguely using terms like TOC, BOD, COD, non detectable, color, or odor. To compute adsorptive performance, all treatment objectives must be translated to absolute concentration levels for specific individual components for computation. Occasionally, the computation is run once just to learn the order of elution of the contaminants, which is used to decide which eluting component exceeds the treatment objective. The objective is redefined as an absolute concentration of that critical component and the computation is repeated. Table 2 lists treatment objective definitions and how to convert them to a usable form, and their effect on the accuracy of the results.

### D. MODELING THE ADSORPTION SYSTEM

Other inaccuracies in the predictions are modeling of the adsorption kinetics and choice of models for the column dynamics (adsorbent bands, theoretical plates, etc.). These errors are not as critical for well designed commercial adsorption systems, where the carbon utilization is greater than 80% (the mass transfer zone of the early eluting components is less than 20% of the column). Consequently, the error contribution due to the kinetic model or the column dynamics is generally less than that of the single component isotherm approximations. The exception is for poorly designed systems with shallow beds and high linear velocities, or systems that involve a complex regeneration scheme.

## IV. STATE-OF-THE-ART OF ADSORPTIVE PERFORMANCE PREDICTION

We should neither be satisfied nor be despondent over the previous discussion of current performance prediction methods. The methods are useful evaluation tools, although they fall short of our goals for environmental applications, and the situation can only improve to the future.

### A. WHAT CURRENTLY CAN BE DONE ACCURATELY

The existing techniques have inherent errors due to simplifying assumptions that are necessary to make them easier to use. However, these techniques are adequate for making gross comparisons of technologies or relative performance comparisons for activated carbon product selection.

#### 1. Relative comparison of different carbons

Many major errors in predicting adsorption isotherms cancel when making relative performance comparisons under identical conditions and stream compositions. This is often the case when trying to identify the optimal activated carbon for a specific application. Performance of several different carbon structures can be compared to select the activated carbon product with the optimum performance or price-performance ratio. The absolute performance may not be accurate, but if the same errors were reproduced for each carbon, then selecting the best performing carbon is still possible.

#### 2. Comparison of carbon adsorption to alternative technologies

When comparing activated carbon adsorption to alternative technologies for environmental cleanups, generally differences in performance are large, or gross assumptions had to be made to equate the dissimilar systems. Consequently, the size of these errors is insignificant compared to the differences in performance or the errors introduced by the gross assumptions. When the performance (or price-performance ratio) of carbon adsorption and another technology are similar, the prediction errors can become significant. In this situation, however, the proper conclusion should be that both technologies are equal and no real performance differentiation exists. In these cases, the selection of the best technology will usually be dictated by capital-operating cost ratios, system size, available utilities, or engineering preferences.

#### 3. Describing general behavior of activated carbon columns

The existing models are also useful in "what if" scenarios. Because the Polanyi and IAS approaches have a basis in thermodynamics, many fundamental principals are incorporated in the computations. Consequently, the methods will extrapolate to extreme conditions and predicted behavior of the system under upset conditions.

For example, they can approximate the effects of spikes in the influent concentration during upsets, or spills and dips in concentration during shutdowns (loss of the contaminant source). The bed volumes a carbon system can treat during a spike are always greater than the bed volumes that would

have been treated if the same amount of contaminant had been introduced at the average influent concentration. In terms of mass of contaminant removed per mass of carbon, the spike improved performance. However, the benefit of the spike, a band within the column with more heavily loaded carbon, decreases with additional bed volumes treated after the spike occurs due to dilution and spreading of this band. Thus the benefit of a spike is least for a fresh column and greatest for a column that was nearing exhaustion.

The situation is different for dips in concentration (disappearance of contaminants). The bed volumes a carbon system can treat during a dip are greater than the bed volumes that would have been treated if the dip had not occurred. As for bed volumes treated, the dip improves performance and the life of the carbon. Desorption of the contaminant-loaded carbon does occur, but this is less important than the decrease in influent concentration. With a dip in concentration, contaminants were removed or not added upstream, which reduces the requirements on the carbon system more than the negative effects of extraction or desorption. However, the benefit of the dip is not realized unless the influent returns to its previous concentrations and the carbon system has the opportunity to treat additional bed volumes of contaminated influent. Thus the benefit is greatest for a fresh column and is least for columns nearing exhaustion.

## B. WHAT CURRENTLY CANNOT BE DONE

For most all real-world environmental applications, today's performance prediction techniques are inadequate for making cost guarantees or for determining minor improvements due that would result from evolutionary changes in equipment design.

### 1. Cost guarantees

The average error levels are small enough, and their effect could be incorporated into cost guarantees by conservatively adjusting the specified performance by several standard deviations. Problems arise due to the uncertainty of when the basic assumptions of the theories breakdown. The effects of these breakdowns can be large errors and represent an incalculable risk to business. Rough cost estimates can be made for comparison purposes, which are generally useful for making a decision to investigate carbon adsorption further.

### 2. Engineering design

For engineering design, the computations are useful only for relative sizing or selecting equipment from a catalog list. The computational errors are simply too large to measure improvements in performance due to refinements in designs, for example improved adsorbers flow patterns, optimal height to diameter (H/D) ratios, or inlet/outlet nozzle patterns. In these situations the design changes will only slightly affect performance and the effect is often less than the error in the calculations. Also effects of particulate and suspended matter cannot be considered, which often dictate design.

### 3. Replacing pilot-scale column simulations

Computations with theoretical models are not yet substitutes for on-site, pilot-scale, column simulation tests. This is especially true when the stream and the treatment objectives, or even the background components, are defined vaguely (using color, odor, TOC, BOD, COD, or nondetectable).

## C. WHAT CAN BE DONE TO IMPROVED THE PREDICTION OF ADSORPTIVE PERFORMANCE?

The simplest way to improve the accuracy of any computational method is to incorporate more empiricism or empirically derived variables. However, the approach must also be practical as for data required. Some errors are inherent in the simplifying assumptions required to reduce the amount of empirical data required for performance prediction. For example, the presumption of a characteristic curve greatly reduces the amount of single component isotherm data required, but also is a major contributor to error. The following are several things that could be done now to improve the accuracy of the predictions in a practical manner.

### 1. Standardized activated carbon samples

Isotherms/adsorption data needs to be generated on standard carbons - even commercial carbons of one name change over the years. Carbons should have published carbon characterization curves or an isotherm with a single known component with data ranging more than five orders of magnitude in concentration or in partial pressure.

### 2. A handbook on adsorption characteristics

Accurate single component isotherm data on a wider variety of contaminants over a broader range of temperatures is needed on standard activated carbon samples with known characteristic curves. With this data the empirical adsorbate characteristics can be determined and then assembled in a handbook.

### 3. Additional real-world experience

Comparing more results from real world adsorption systems versus the best theoretical predictions increases the confidence in the reliability of the basic assumptions of the adsorption theories.

Eventually we may learn how to approximate backgrounds empirically and predict the breakdown of theories. We may reassess the relative importance of sources of error of existing models and direct the theoretical and empirical work being done on adsorption on activated carbon to improve the current situation.

#### V. REFERENCES

1. A. L. Meyers and J. M. Prausnitz, *A.I.Ch.E. Journal*, 11, 121(1965) and C. J. Radke and J. W. Prausnitz, *A.I.Ch.E. Journal*, 18, 761 (1972).
2. J. A. O'Brien, A. L. Myers, "Physical adsorption of gases on heterogeneous surfaces. Series expansion of isotherms using central moments of the adsorption energy distribution", *J. Chem. Soc., Faraday Trans. 1* (1984), 80(6), 1467-77
3. A. Wohleber and M. Manes, *J. Phys. Chem.*, 75, 61 (1971). Theory of the Structure of Activated Carbon - Relationship to Adsorption Properties, and Manes and M. Greenbank, In "Treatment of Water by Granular Activated Carbon", M. J. McGuire and I. H. Suffet, Eds., American Chemical Society, Washington, D.C. 1983, p9.
4. R.S. Hansen and W. V. Fackler, *J. Phys. Chem.*, 57, 634 (1953).
5. D.P. Valenzuela, A. L. Myers, O. Talu, I. Zwiebel, "Adsorption of gas mixtures: effect of energetic heterogeneity", *AIChE J.* (1988), 34(3), 397-402
6. R. J. Grant and M. Manes, *Ind. Eng. Chem. Fundamentals* 5, 490 (1966) and M. R. Rosene, M. Ozcan, and M. Manes, *J. Phys. Chem.*, 80, 2586 (1976) and R. J. Grant, M. Manes, and S. B. Smith, *A.I.Ch.E. Journal*, 8(3), 406 (1962).
7. B. P. Semonian and M. Manes, *Anal. Chem.*, 49, 991 (1977) and M. Greenbank, T.M. Matviya, W.G. Tramosch, "Rapid Carbon Adsorption Characterization using Temperature Programmed Adsorption and Desorption", presented at the AIChE Meeting in Los Angeles, CA, November 17, 1991.
8. C. Malara, G. Pierini, A. Viola, "Correlation, analysis and prediction of adsorption equilibria" *Jt. Res. Cent., Comm. Eur. Communities, Ispra, I-21020, Italy, Report to Comm. Eur. Communities, [Rep.] EUR (1992), EUR 13996, 47 pages.*
9. S. Sircar and A. L. Meyers, *A.I.Ch.E. Journal*, 17, 186(1971), and M. Greenbank and M. Manes, *J.Phys.Chem.*, 85, 3050 (1981).
10. J. A. O'Brien, A. L. Myers, "Rapid calculations of multicomponent adsorption equilibria from pure isotherm data", *Ind. Eng. Chem. Process Des. Dev.* (1985), 24(4), 1188-91, and M. Greenbank, Ph. D. Dissertation, Kent State University (1981).
11. J. C. Crittenden, G. Friedman, D.W. Hand, J. Berrigan, T. Speth, "Design of fixed-beds to remove multicomponent mixtures of volatile organic chemicals", *Proc. - AWWA Annu. Conf.* (1985) 1327-46 and J. C. Crittenden, D. W. Hand, "Modeling of adsorption, desorption and displacement in fixed-bed adsorbers", *Fundam. Adsorpt., Proc. Eng. Found. Conf.* (1984), Meeting Date 1983, 185-94. Editor(s): A. L. Myers, G. Belfort, Publisher: Eng. Found., New York, N. Y.
12. M. D. LeVan, D. K. Friday, "Models for thermal regeneration of adsorption beds", *Fundam. Adsorpt., Proc. Eng. Found. Conf.* (1984), Meeting Date 1983, 295-304. Editor(s): A. L. Myers, G. Belfort, Publisher: Eng. Found., New York, N. Y.
13. E. Richter, W. Schuetz, A. L. Myers, "Effect of adsorption equation on prediction of multicomponent adsorption equilibria by the ideal adsorbed solution theory", *Chem. Eng. Sci.* (1989), 44(8), 1609-16
14. M. Greenbank and M. Manes, *J.Phys.Chem.*, 86, 4216 (1982) and M. Greenbank and M. Manes, *J.Phys.Chem.*, 88, 4684 (1984).
15. T. W. Schenz and M. Manes, *J. Phys. Chem.*, 79, 604 (1975) and M. R. Rosene, M. Ozcan, and M. Manes, *J. Phys. Chem.*, 80, 2586 (1976).

16. M. R. Rosene, R. T. Deithorn, J. R. Lutchko, and N. J. Wagner, "High pressure Technique for Rapid Screening of Activated Carbons for use in Potable Water", *Activated Carbon Adsorption of organics from the Aqueous Phase*, Vol. 1, I. H. Suffet and M. J. McGuire editors, Ann Arbor Science, Ann Arbor, Chapter 15 (1980).

**Table 1 Relative Importance of the Different Sources of Errors**

Source of Error in Adsorption Calculations	Typical Error Contribution	Potential for Large Error in Special Cases
<b>Single component isotherm prediction/measurement</b>		
Analytical Errors in measurement	<10%	No
Carbon sample not representative	<20%	Yes
Substitution of an known Isotherm for an unknown component	10 to 100%	Yes
Selection of theory/technique	0 to 100%	Slight
<b>Multicomponent isotherm prediction theory</b>		
Choice of theory IAS vs. Polanyi	0 to 100%	Yes
Volumes-based competition	<10%	Slight
Interactions and accessibility	0 to 100%	Yes
Bulk behavior in the pores	<10%	Slight
<b>Modeling adsorption system</b>		
Selection of the Kinetic approaches	<20%*	No
Choice of Models for Column dynamics	<20%*	No
<b>Problem Definition</b>		
Stream Composition - critical and background components and concentration	10 to 100%	Yes
Background components and nondetectable compounds	50 to 500%	Yes
Treatment Objectives defined vaguely (nondetectable)	<20%	Slight
Nonspecific Test Objective (TOC, BOD, COD, etc.)	10 to 100%	Slight
Temperature - (within each carbon particle - through-out the bed)	<20%	No
Flow rate - Linear velocity/mass flow and its variability	<10%*	No
Variability of concentration and composition,	10 to 100%	No
Complex Schemas-Regeneration processes	20 to 200%	Yes

\* For well-designed adsorption systems with MTZ<20% of column

**Table 2 Errors in Single Component Predictions**

	Average Deviation %	Range of Errors*		Concentration		Loading Range		No. of Points	Probable Cause of Error
		High % Error	Low % Error	High ppm	Low ppm	High cc/100g.carbon	Low		
<b>Gas-phase Adsorption Isotherms (ref.15)</b>									
Methanol @ 22C,60C	275.6%	1082%	-11.1%	3481	387	7.4	0.146	6	Chemisorption at low loadings
Toluene @ 121C	6.7%	34.7%	-6.4%	45	0.066	5.24	0.494	5	Fitting characteristic curve
Trimethyl pentane @ 117C	-61.5%	5.2%	-94.2%	50	0.068	9.36	0.153	16	Molecular sieving
<b>Liquid-phase Adsorption Isotherms (ref.14)</b>									
Pentanol @ 25C	4.9%	21.6%	-19.2%	13800	11	46.8	8.44	14	Fitting characteristic curve
Benzamide @ 25C	1.0%	12.0%	-10.1%	9970	160	34.5	18.1	6	Analytical (random)
o-Phthalic acid @ 25C	-0.5%	8.2%	-14.0%	1990	3.9	19.6	7.22	6	Hydration effects at high loadings

\* negative error means the actual measurement was less than the predicted value

**Table 3 Contributions to Errors in Computing Breakthrough Limits**

Breakthrough Criterion	Example of Criteria	Sources of Additional Computation Error
<b>Specific Objectives - Effluent Level is an Identified Key Component</b>		
1 Absolute concentration	5ppm CHCl3	Analytical accuracy/reproducibility
2 % Breakthrough/removal	99% removal of CHCl3	#1 + Inaccuracy of Influent level Determination
3 Non Detectable	Nondetectable CHCl3	#1+Analytical Sensitivity/background interferences
<b>Grouped Objectives - Effluent Level is a Sum of Several Key Components</b>		
4 Class of Compounds	5ppm Chlorinated Hydrocarbons	#1,2, or 3 + know order of elution and sum breakthrough conc.
5 lb. emissions per month	10 lb. hydrocarbons per month limit	#4+integrate breakthrough curves and sum over several events
<b>Nonspecific Objectives - Effluent Level is a Response of a Detector or Test</b>		
6 TOC	100 ppm TOC	#4 + relative weighting factors for sensitivity to test(TOC)
7 Total Combustibles (by FID)	1 ppm Hydrocarbon as propane	#4 + relative weighting factors for FID sensitivity
8 Nonmethane hydrocarbon	1 ppm nonmethane hydrocarbon	#7 + inaccuracy of methane determination
9 COD	100 ppm COD	#6 + COD interferences (Ex. inorganic reductants)
10 BOD		#6 + BOD interferences (Ex. Low BOD due to toxics present)
11 Color		#6 + Complex formation, color shifts, turbidity corrections
12 Taste or Odor		#6 + T/O panels problems (Ex. Odor interactions, desensitizers)

# SEPARATION AND CONCENTRATION OF VOLATILE ORGANIC CONTAMINANTS BY ACTIVATED CARBON CLOTH FOR CRYOGENIC RECOVERY

Mehrdad Lordgooei, Kelly R. Carmichael, Terrance W. Kelly,  
Mark J. Rood, and Susan M. Larson

Environmental Engineering & Science Program, Department of Civil Engineering  
University of Illinois at Urbana-Champaign, Urbana, IL, USA 61801-2352

**Keywords:** activated carbon cloth, gas purification, electrothermal desorption

## Introduction

New air quality control regulations and economics are causing the development of new devices or the optimization of existing technologies for control of toxic emissions from industrial sources. Toxic chemicals are emitted into the atmosphere from facilities within the United States at a rate of  $1.1 \times 10^6$  kg/year [1]. Volatile organic contaminants (VOCs) account for 47%, and non-halogenated VOCs account for 36% of these toxic emissions [1]. For these emissions, under the 1990 Clean Air Act Amendments (CAAA), the United States Environmental Protection Agency (USEPA) should establish maximum achievable control technology (MACT) standards. MACT standards are based on best control technologies that offer the maximum degree of emission control [2]. MACT will have important effects on specific VOC sources within the next eight years because all MACT standards are required to be promulgated by 15 November 2000, and a source subjected to MACT standards must achieve compliance within three years of promulgation of the standards. Sources that must comply with the new VOC standards are related to food processing, wastewater treatment, electronic manufacturing, petroleum refining, petrochemical manufacturing, asphalt production, pharmaceutical industry, polymer and resin manufacturing, solvent production, and dry cleaning industry.

Based on an economic and engineering study about VOC control technologies [3], if the VOCs have a value > \$0.66/kg then carbon adsorption and vapor recovery should be considered. Dyer and Mulholland [3] indicated that carbon adsorption is the most cost effective technology for gas flow rates > 1,000 scfm and VOC concentrations > 500 ppmv. Moreover, variable flow rates and variable VOC concentrations are not disruptive for carbon adsorber performance [4], and they do not produce secondary pollutants. But, conventional carbon adsorbers can achieve recovery efficiencies up to 98% which may not be sufficient for MACT standards.

New carbon adsorption recovery systems can be developed that achieve higher recovery efficiencies while providing better economical and technical advantages over existing ones. For this purpose, we have developed a new activated carbon cloth (ACC) adsorption system that has been integrated with electrothermal desorption and cryogenic condensation to reduce the amounts of VOC emissions to MACT standards and provide for reuse of the VOCs that are recovered.

In this system liquid nitrogen (LN2) is used as the required refrigerant. LN2 can reduce VOC emission concentrations to ppbv levels due to its high cooling capacity and low temperature. One advantage of the LN2 system compared to other refrigeration systems is the multiple use of LN2. First, the cooling capacity of LN2 is used to condense VOCs. Then, the evaporated  $N_2$  can be used for other process needs such as inerting and safety blanketing. Another advantage of LN2 refrigeration over conventional mechanical condensation systems is the absence of moving parts such as compressors. But, LN2 consumption rate is high for typical industrial effluent concentrations. The effluent VOC concentrations are typically <1% by volume due to the limitations caused by their lower explosion limits. Ideal LN2 consumption (minimum mass of LN2 required per unit mass of VOC recovered in an isolated thermodynamical system) is linearly related to the inverse of the VOC concentration (Figure 1). If the VOC concentration can be increased, then LN2 consumption can be decreased. This is due to the fact that some portion of the cooling capacity transfers to the noncondensable carrier gas. Therefore, ACC adsorption technology is used to pre-concentrate the effluent VOCs for an efficient vapor recovery.

In the developed system, ACC adsorption is followed by electrothermal regeneration resulting in formation of a concentrated organic vapor which is cryogenically condensed from the gas phase. Electrothermal desorption allows for optimizing the desorption time and the concentration profile of the desorbed VOC to allow minimal use of cryogen. This system can enable VOC sources to meet air quality control regulations while providing a high quality liquid VOC product for reuse.

## Description of the laboratory scale system

The laboratory scale ACC adsorption-cryogenic vapor recovery system is presented in Figure 2. Sample gas is generated by passing ultra-high purity (UHP)  $N_2$  gas through VOC liquid and saturating the gas stream. The saturated stream is then mixed with the second pure  $N_2$  stream to produce a gas sample with desired VOC concentration and total flow rate. The sample gas generation system is calibrated using a gas chromatograph/mass spectrometer (GC/MS, Hewlett Packard GC 5890 and MS 5971), a gas chromatograph/flame ionization detector (GC/FID, Hewlett Packard GC 5830A), UHP  $N_2$  gas and a Matheson calibrated VOC gas mixture. The calibrated gas stream passes through the fixed bed of ACC, where the organic material is separated from the carrier gas by adsorption. After breakthrough of VOC from the fixed bed, pure  $N_2$  gas is passed through the adsorption bed and electrical power is supplied to the ACC. Electrical energy regenerates the adsorption capacity of the ACC and provides a  $N_2$  gas stream containing desorbed VOC. VOC concentration in the  $N_2$  carrier gas is controlled by the supplied electrical power and the flow rate of the carrier gas. The concentrated vapor stream is then directed to a custom shell-and-tube cryogenic condenser where the VOC is condensed on the condenser's internal cold surfaces. The condensed VOC is transferred from the bottom of the condenser into an Erlenmeyer flask.

## Activated Carbon Cloth Adsorbent

ACC, which is made of woven activated carbon fibers (ACFs), is an efficient adsorbent to separate VOCs from gas streams. Compared with activated carbon pellets (ACPs), granular activated carbons (GACs) or powder activated carbons (PACs), ACCs have a higher contact efficiency, higher specific surface area for a higher specific pore volume, 10 to 100 times faster adsorption and desorption rates [5]. These properties are mainly due to the existence of no macropores, no or little mesopore volume, and more uniform distribution of micropores from the external surface to the core of fiber [6]. ACC's rapid adsorption and desorption rates can reduce the required process cycle time and increase the bed adsorption capacity by reducing the length of mass transfer zone (MTZ). Due to its cloth form, ACC can be installed in different configurational forms inside fixed beds providing different adsorption and desorption performance as well as specific pressure drop (Pa/mg adsorption). Suitability for in-situ electrothermal regeneration and easy handling are other advantages of ACC.

ACC samples were obtained from American Kynol, a subsidiary of Nippon Kynol, located in Pleasantville, NY. Kynol's ACCs are made of novoloid fibers (polymerized cross-linked phenolic-aldehyde fibers). Novoloid fibers have an amorphous network structure containing 76% carbon, 18% oxygen, and 6% hydrogen [9]. These fibers are woven by conventional textile techniques to produce a novoloid cloth. The cloth is then carbonized and activated in an O<sub>2</sub> free atmosphere using steam or CO<sub>2</sub> at 900 °C in a one step process to produce ACC. Carbon content of ACC is typically 95% with oxygen and hydrogen contents of 4% and 0.7%, respectively [10]. Pore volume and pore size of the ACC increase with increasing duration of activation. The resulting micropores are slit shaped and remain uniform from the external surface to the core of the fiber [6].

Kynol™ ACC-5092-20 was identified as a suitable ACC adsorbent for the VOC concentration range of industrial emissions (in the order of 1% by volume). ACC-5092-20 have a higher adsorption capacity than the other Kynol's ACCs for 1% by volume concentration of the VOCs considered for the system evaluation tests (acetone, methyl ethyl ketone and toluene). This is mainly due to the existence of a high specific pore volume and high volume ratio for pore widths in the supermicro, transitional range, and mesopores close to the transitional range. SEM micrographs of the ACC sample are provided in Figure 3. Mesopores and transitional micropores can be seen from the SEM micrograph of the ACC's fiber cross section. The cumulative pore size distribution of the ACC sample in comparison with some other adsorbents is given in Figure 4. Specific surface area and micropore volume of ACC-5092-20 were measured with a Micromeritics ASAP 2400 using nitrogen at liquid nitrogen temperature. The BET specific surface area of the sample was 1592 m<sup>2</sup>/g. The specific micropore volume was 0.69 cm<sup>3</sup>/g.

## Fixed Bed of Activated Carbon Cloth

In the fixed bed ACC layers are installed in parallel to each other in a cross flow fashion. This allows for flexibility in effective adsorption bed length and apparent ACC density. With a 1.14 mm separation distance between each layer, an apparent ACC bed density of 94.5 mg/cm<sup>3</sup> results. The bed packing density can be increased to 800 mg/cm<sup>3</sup> (0.47 total porosity). In the fixed bed, the ACC layers are connected electrically in parallel in three separate modules. The modules are connected electrically in series. The resulting circuit is connected to electrodes of a 120 V a.c. source controlled by a Variac. This arrangement is expected to result in uniform electrical heating and carefully controlled VOC desorption.

## Electrothermal Regeneration of Activated Carbon Cloth

In electrothermal regeneration process an electric current is passed through the fibers. Electrical work due to phonon and defect scattering [11] in ACC is directly transformed to thermal energy in the ACC and the adsorbed VOC. By the continuous flow of electric current, the thermal energy of the adsorbed molecules increase to a level that overcome the surface bonding energy, and the VOC desorbs from the ACC. Since electrical work is transformed to desorption energy directly, the carrier gas temperature can be substantially lower than the ACC temperature. The temperature gradient along the bed is positive, and along the fiber radius is negative (or zero, depending on the value of fiber Biot number). In conventional thermal desorption methods, the temperature gradient along the bed is negative and along the fiber radius is positive. These effects cause positive desorption rate contributions for electrothermal desorption due to the heat transfer, Soret effect and pore effusion. While, mass transfer contributions are negative for conventional thermal desorption methods. Therefore, electrothermal regeneration should have higher energy efficiency compared to conventional thermal regeneration methods. Another advantage of electrothermal desorption is that the energy transfer rate can be very high and controlled easily. This enables careful control of desorption time and effluent VOC concentration profile for a better cryogenic recovery.

## Results and Discussion

The laboratory-scale fixed bed configuration was used to measure breakthrough curves. For each breakthrough test, total gas flow rate through the bed was 5 slpm. VOC concentration of the inlet gas stream was measured before passing through the fixed bed. Gas phase VOC in the bed was sampled from the sampling ports along the bed's length and analyzed intermittently using the GC/MS and continuously using GC/FID (Figure 2). Sample results for MTZ distribution curves describing how acetone concentration changed with time and location within the bed are presented in Figures 5. Breakthrough time was 75 min when using three ACC modules containing 27.05 g ACC and a packing density of 94.5 mg/cm<sup>3</sup>. Breakthrough was followed by a saturation time of 58.5 min. Saturation time is defined as the time required for the effluent concentration (C<sub>out</sub>) to increase from 5% to 95% its inlet concentration (C<sub>in</sub>).

The breakthrough curve for the bed outlet exhibit a standard diffusion mass transfer limited behavior in the form of:  $C_{out} = C_{in} (1 + \exp[K(t - t_s)])^{-1}$  where  $t_s$  is the stoichiometric time (time for C<sub>out</sub>=1/2 C<sub>in</sub> or  $t_s = W_0/C_m F$ , where W<sub>0</sub> is bed VOC adsorption capacity at C<sub>in</sub> and F is the total gas flow rate), and K is a constant that depends on the effective diffusion resistance of the MTZ. From these results, dynamic adsorption capacity of the ACC for 1% by volume acetone is 456 mg/g or 0.581 cm<sup>3</sup>/g. Equilibrium Isotherm for adsorption and

desorption of acetone and ACC-5092-20 can be classified as BDDT type IV isotherm. Due to capillary condensation in mesopores, the isotherm has a hysteresis region at high concentration values. The equilibrium micropore adsorption and capillary condensation capacities of the ACC for 1% by volume acetone were measured to be 401 mg/g and 93.6 mg/g, respectively.

Effect of packing density on adsorption dynamic is presented in Figure 6. A smaller packing density results a shorter breakthrough time and a larger MTZ due to axial dispersion and mixing effects. Increasing packing density from 94.5 mg/cm<sup>3</sup> to 450 mg/cm<sup>3</sup> increases the breakthrough time from 75 min to 91.7 min. Since a higher packing density produces a larger pressure drop, it is possible to find an optimum set of packing density and pressure drop for a minimum cost.

Regeneration tests for a saturated fixed bed of ACC were performed to evaluate the effect of applied electrical power (Figure 7). N<sub>2</sub> gas flow rate through the bed was controlled at 1 slpm for three tests and 0.5 slpm for two tests. Electrical voltage for each test was set at select values to observe the effect of applied electrical power profile on the resulting effluent VOC concentration and bed temperature profiles. Effluent maximum VOC concentrations during desorption range from 18% to 63% by volume. VOC concentration profile and desorption time is readily controlled by carrier gas flow rate and applied electrical power. Increasing VOC concentration was observed with decreasing carrier gas flow rate and increasing applied power. In all five tests, more than 75% of the adsorbed acetone was regenerated at a bulk gas temperature of < 60 °C and an effluent concentration of > 10% by volume. Low resulted bulk gas temperature is indicative of an efficient energy transfer. Effect of generated high effluent concentration values on improvement of LN<sub>2</sub> consumption and amount of vapor recovery can be examined from Figure 1. Moreover, the high effluent concentrations enable the cryogenic condenser to operate at warmer temperatures while achieving high recovery efficiencies.

Cryogenic vapor recovery efforts are discussed in the next paper [12].

### Conclusions

A novel activated carbon cloth (ACC) adsorption/electrothermal regeneration/cryogenic system was developed to separate, concentrate and recover volatile organic contaminants from industrial gas streams. ACC demonstrates good performance characteristics due to its high contact efficiency, high adsorption capacity, and ease in handling. Electrothermal regeneration provided fast desorption rates and efficient energy transfer. Electrothermal regeneration concentrated VOC vapors up to 63% by volume without optimization. Concentrating the gas stream, drastically reduces the amount of cryogen required to condense the VOC from the gas stream end enables the condenser to operate at warmer temperatures while achieving a high recovery efficiency.

### ACKNOWLEDGMENTS

Funding support from the Hazardous Waste Research and Information Center (HWRIC) and Liquid Carbonic are greatly appreciated. We would like to thank Joe and Nancy Hayes of American Kynol Inc. for providing the activated carbon cloth samples. SEM measurements were carried out in the Center for Microanalysis of Materials, University of Illinois, which is supported by the U.S. Department of Energy under grant DEFG02-91-ER45439.

### References

- 1 United States Environmental Protection Agency, *Toxics in the Community, National and Local Perspectives*, USEPA, USA (1991)
- 2 Majumdar, S. *Regulatory Requirements for Hazardous Materials*, McGraw-Hill, Inc., New York, USA (1993)
- 3 Dyer, J. A. and K. Mulholland *Toxic Air Emissions: What is the Full Cost to Your Business, Environmental Engineering, A special supplement to February 1994, Chemical Engineering*, pp. 4-8
- 4 Ruddy, E.N. and L. A. Carrol *Select the Best VOC Control Strategy, Chemical Engineering Progress*, July 1993, pp. 28-35
- 5 Ermolenko, I. N., I. P. Lyubliner, and N. V. Gulko *Chemically Modified Carbon Fibers and Their Applications* p. 62 & 212
- 6 Fujii, R. *Kynol™ Novoloid Fibers*, Nippon Kynol, Inc., Osaka, Japan p. 14
- 7 Cal, M. P. *Characterization of gas phase adsorption capacity of untreated and chemically treated activated carbon cloths*, PhD Thesis, University of Illinois at Urbana-Champaign, Illinois (1995)
- 8 Yang, R. T. *Gas Separation by Adsorption Processes*, Butterworths Publishers, Stoneham, MA (1987)
- 9 Hayes, J. S. JR. *Novoloid Fibers, Kirk-Othmer: Encyclopedia of Chemical Technology*, 3rd Edn, Vol 16, John Wiley & Sons, Inc. (1981)
- 10 Foster, K. L., R. G. Fuerman, J. Economy, S. M. Larson, and M. J. Rood *Adsorption Characteristics of Trace Volatile Organic Compounds in Gas Streams onto Activated Carbon Fibers Chem. Mater.* (1992) Vol 4, No. 5
- 11 Donnet, J. B., and R. C. Bansal *Carbon Fibers*, 2nd Edn, Marcel Dekker, Inc., New York (1990)
- 12 Carmichael, K. R., M. Lordgooei, T. W. Kelly, M. J. Rood, and S. M. Larson, *Desorption and Cryogenic Recovery of Volatile Organic Compounds for Re-Use*, 1996 ACS National Meeting, New Orleans, Louisiana, March 24-28, 1996

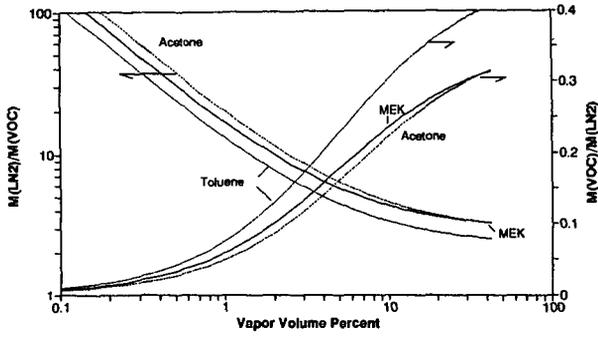


Figure 1. Ideal mass of LN2 required per unit mass of VOC recovered and ideal mass of VOC that can be recovered per unit mass of LN2.

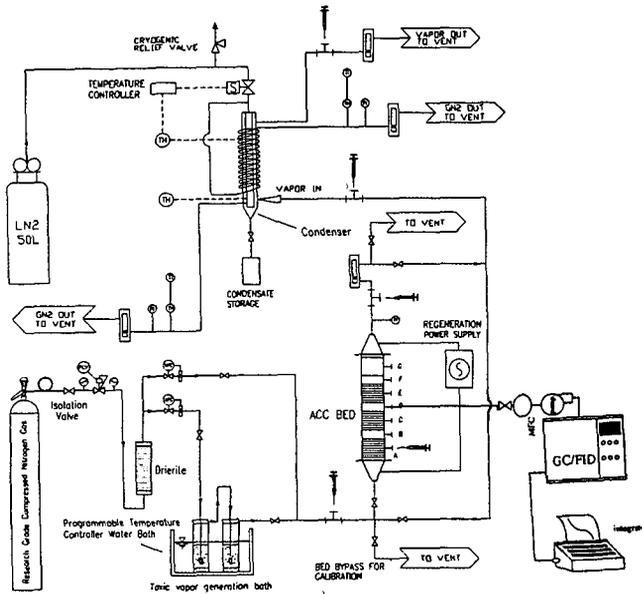


Figure 2. Integrated adsorption/electrothermal regeneration/cryogenic vapor recovery system.

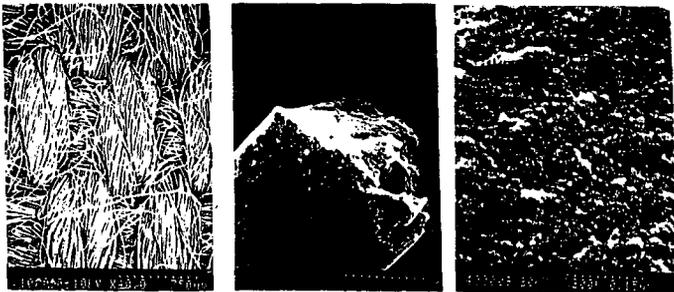


Figure 3. SEM micrograph of ACC-5092-20 and fiber cross section.

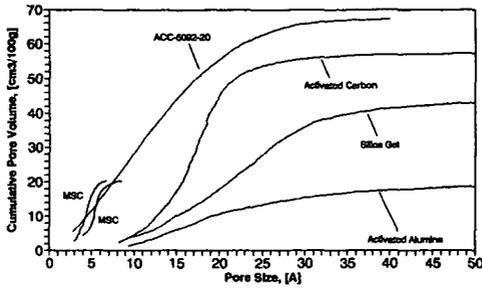


Figure 4. Cumulative pore-size distribution for ACC-5092-20 [7] compared with some other adsorbents [8]

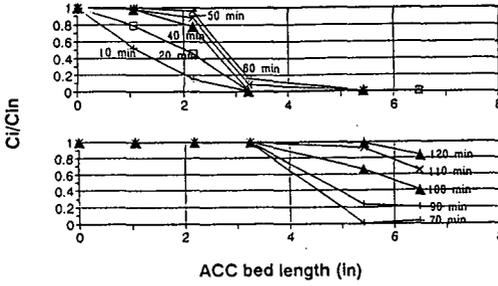


Figure 5. Mass transfer zone movement through the ACC bed. Inlet concentration: 1% acetone in  $N_2$ . Total gas flow rate: 5 slpm.

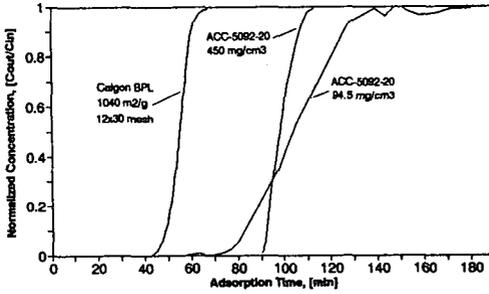


Figure 6. Effect of packing density on the dynamic characteristics of breakthrough.

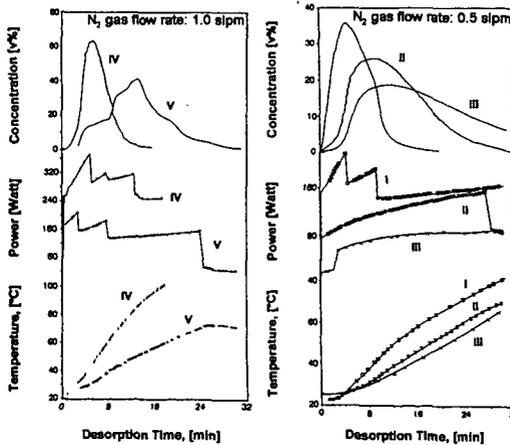


Figure 7. Electrothermal regeneration test results.

## DESORPTION AND CRYOGENIC RECOVERY OF VOLATILE ORGANIC COMPOUNDS FOR RE-USE

K.R. Carmichael, M. Lordgoose, T.W. Kelly, M.J. Rood, S.M. Larson  
Department of Civil Engineering / Environmental Engineering Program  
University of Illinois at Urbana-Champaign  
205 N. Mathews St.  
Urbana, Illinois U.S.A. 62801-2352

**Keywords:** VOC Recovery, Cryogenic Condensation, Gas Cleanup

### Introduction

Both the magnitude and toxicity of emissions of volatile organic compounds (VOCs) have led to public health concern and recent government regulations to reduce VOC emissions. VOCs are a part of the  $1.1 \times 10^9$  kg of toxic chemicals released into the atmosphere from point sources within the United States in 1990 [1]. VOCs appearing on the list of 189 hazardous air pollutants (HAPs) accounted for  $4.5 \times 10^8$  kg/yr of emissions to the atmosphere [1]. Many of these toxic chemicals cause chronic and acute health effects, including cancer [2].

The 1990 Clean Air Act Amendments (CAAA) established technology-based guidelines for the reduction of VOC emissions to the atmosphere from point sources [3]. Under Title I of these amendments, USEPA is required to establish reasonable achievable control technology (RACT) standards for point source VOC emissions in ozone related non-attainment areas. Furthermore, Title III requires USEPA to establish maximum achievable control technology (MACT) standards for point source emissions of 189 HAPs, many of which are considered VOCs. HAP emission standards for point sources based on MACT must be promulgated by November 15, 2000. Sources regulated under Title III must meet permit requirements within three years of promulgation.

Point source VOC emission reduction is generally accomplished by process modification and/or utilization of ancillary control devices [4]. Process modification is generally the most economical method of reducing VOC emissions. Further reduction of VOC emissions require the addition of control devices along the waste stream.

The seven most widely used control devices that remove VOCs from gas streams are: 1) thermal incinerators, 2) catalytic incinerators, 3) flares, 4) boilers/process heaters, 5) carbon adsorbers, 6) absorbers and 7) condensers [5] (Table 1).

**Table 1.** Control devices commercially available for VOC removal from effluent gas streams [4].

Control Device	VOC Content (ppmv)	Flow Rate (scfm)	Capital Cost 1993	Annual Cost 1993	Removal Efficiency	Advantages	Disadvantages
Thermal Incinerator	100-2000*	1000 to 500,000	\$10 to 450/cfm	\$15 to 150/cfm	95-99%+	Up to 95% energy recovery	Halogenated compounds may require additional control
Catalytic Incinerator	100-2000*	1000 to 100,000	\$20 to 250/cfm	\$10 to 90/cfm	90-95%	Up to 70% energy recovery	Catalyst poisoning
Flare [5]		<2,000,000			>98% Steam-assisted	VOC destruction of variable emission conditions	Low heating value VOC requires auxiliary fuel
Boiler [5]		Steady			>98%	Supplement fuel	Variations may affect process
Carbon Adsorber	20-5000*	100 to 60,000	\$15 to 120/cfm	\$10 to 35/cfm	90-98%	Vapor recovery, Pre-Concentrator	High RH may lower capacity, Pore fouling
Absorber	500-5000	2000 to 100,000	\$15 to 70/cfm	\$25 to 120/cfm	95-98%	Vapor recovery	Scale build-up, Liquid waste
Condenser	>5000	100 to 20,000	\$10 to 80/cfm	\$20 to 120/cfm	50-90%	Vapor recovery	Scale build-up, Liquid waste

\* <25% of lower explosion limit; RH is relative humidity

In this paper, discussion will primarily pertain cryogenic condensation of VOCs during regeneration of a carbon adsorber used to concentrate VOCs in effluent gas streams. Condensation of VOCs is especially applicable when recovery and reuse of the VOC in the process stream is economically beneficial. Recovery should be considered when a relatively pure condensate with a monetary value > \$0.66/kg can be recovered [6].

Adsorption has been used often as a pre-concentrator in conjunction with other control devices. This is especially applicable to condensers as will be discussed here. Carbon adsorbers can remove VOCs from relatively low vapor concentration and high flow rate gas streams and desorb at high vapor concentration and low gas flow rates, where condensers operate more efficiently. High inlet VOC concentrations for condensers yield higher removal efficiencies and require lower refrigerant flow rates, thus lowering operating costs. Low gas flow rates require less condensable surface by increasing residence time, again lowering capital costs. Lower gas flow rates also require less refrigerant to cool the carrier gas.

### Design of Contact Condensers

Two general types of condensers are commercially available, direct contact and indirect contact [7]. Direct contact condensers mix the refrigerant with the process gas stream. Heat is more efficiently exchanged due to the intimate contact between the refrigerant and VOC. Direct contact condensation is typically simpler, less expensive to install and requires less auxiliary equipment [7]. However, the refrigerant is

mixed with the process stream. This may prevent refrigerant recycling and/or cause contamination of the refrigerant. Indirect contact condensers utilize a physical barrier across which only heat is exchanged between the refrigerant and the process gas stream. Heat exchange is therefore less efficient in indirect methods. Keeping the refrigerant separate from the process gas stream allows for refrigerant re-use. This is beneficial if the refrigerant undergoes a cyclic mechanical refrigeration process. Indirect contact condensers typically cost more and are more complicated to design and operate [7]. Because of the indirect contactor's advantages, however, it is the most common type of condenser in air pollution control applications [5].

### Refrigerants

The most common refrigerant used in pollutant removal condensers is water [5]. Water is inexpensive and easy to handle. However, because the condenser temperature is limited by the refrigerant temperature, cooling water results in low removal efficiencies for many VOCs (Table 2). Removal efficiencies were determined from the reduction of a 10% acetone stream to the equilibrium saturation vapor concentration. For applications where the process stream needs to be cooled below ambient temperatures, the use of cooling water typically requires auxiliary equipment to chill the water prior to use.

Ethylene glycol and water mixtures are also commonly used refrigerants [8]. Lower operating temperatures can be achieved with this mixture than for pure water, thereby lowering the effluent VOC concentration and recovering more condensate. Ethylene glycol water mixtures are exclusively used with indirect contact condensers to prevent ethylene glycol losses to the effluent gas stream [8]. Auxiliary equipment is needed to cool the mixture to temperatures below the ambient temperature.

Liquid nitrogen (LN2) refrigerant can provide a wide range of condenser temperatures because a controlled LN2 flow rate can be delivered to the condenser. Furthermore, because LN2 undergoes a phase change in the condenser, both the enthalpy of vaporization and specific heat change provide cooling capacity. The use of LN2 as a refrigerant generally requires a vacuum jacketed storage vessel and well insulated or vacuum jacketed delivery lines. However, auxiliary cooling equipment is not necessary, as the refrigerant is available in liquid form from commercial sources. The LN2 can be used in direct or indirect contactors. After it passes through the condenser, the vaporized nitrogen refrigerant can be used as a blanket gas in process streams or as a purge stream during desorption if an adsorber is used as a pre-concentrator. The gaseous nitrogen refrigerant waste stream can be used during desorption as a purge stream to prevent explosive hazards and reduce moisture levels, normally present in air purge streams, that may foul the condenser.

By operating the condenser near the freezing point of the organic, very low effluent VOC vapor pressures can be achieved while still producing a liquid condensate. In high humidity process streams two condensers can be used in series. The first condenser can operate at temperatures above the freezing point of water to remove water vapor from the stream. The second condenser can then be operated at temperatures below the freezing point of water to achieve greater removal efficiencies of the organic and reduce condenser fouling from frozen water vapor.

**Table 2.** Theoretical removal efficiencies for three refrigerants and three VOCs with a 10% by volume inlet gas stream.

Refrigerant	Acetone			Methyl Ethyl Ketone		Toluene	
	Operating Temperature (K)	Saturation <sup>a</sup> Vapor Concentration (ppmv)	Removal Efficiency (%)	Saturation <sup>a</sup> Vapor Concentration (ppmv)	Removal Efficiency (%)	Saturation <sup>a</sup> Vapor Concentration (ppmv)	Removal Efficiency (%)
Water	278	102,000	0	40000	60	5500	94
60% Ethylene Glycol + H2O	240	15000	85	3800	98	420	99+
LN2	200	300	99+	70	99+	2	99+

<sup>a</sup> determined from the Wagner equation [9]

### Experimental Design

Our research efforts have focused on developing, testing and evaluating the integration of cryogenic condensation with carbon adsorption. Regeneration of the carbon adsorber provides a concentrated vapor stream at a low gas flow rate which is then sent to the condenser. Using the adsorber as a pre-concentrator improves the operating efficiency of the condenser by increasing removal efficiency and decreasing refrigerant consumption. LN2 was used as the refrigerant due to its' low achievable temperature range and possible re-use capabilities.

A 1% by volume acetone in nitrogen gas stream was passed through an activated carbon cloth fixed bed at 5 slpm (Figure 1). The adsorbent ACC-5092-20 was manufactured by American Kynol™. Nitrogen BET specific surface area is 1592 m<sup>2</sup>/g, and its' micropore volume is 0.69 cm<sup>3</sup>/g [10]. Apparent ACC bed density is 94.5 mg/cm<sup>3</sup>. Equilibrium adsorption capacity of the ACC was found to be 456 mg/g for 1% acetone in nitrogen [10].

The ACC was electrothermally regenerated by applying an a.c. voltage across the cloth. The temperature of the ACC surface was controlled by the voltage. Acetone concentration in the adsorber's effluent was controlled by the bed's temperature and flow rate of nitrogen carrier gas. During regeneration, acetone concentrations greater than 60% by volume were achieved at nitrogen gas flow rates of 0.5 slpm [11].

A copper shell-and-tube indirect contactor was used to condense the concentrated acetone onto the stream walls. The concentrated vapor stream was passed between the condenser tube and the outside shell. The total condensing surface area was 1241 cm<sup>2</sup>. LN2 was introduced at the condenser tube inlet

counter current to the vapor laden gas stream. LN<sub>2</sub> was also circulated through an 1/8 in. copper tube coil jacket wound around the outside shell of the condenser. LN<sub>2</sub> was delivered with a Cryofab self-pressurizing dewar model CFPB25-115. The temperature of the condenser was controlled by the liquid flow rate of LN<sub>2</sub>. The flow rate of LN<sub>2</sub>, in turn, was controlled by the pressure of the dewar and by an Asco Red-Hat cryogenic solenoid valve. The vapor laden gas stream temperature was monitored using type T thermocouples at the condenser inlet, mid-point and outlet. The nitrogen refrigerant flow rate was also monitored at the outlet of the condenser using a BIOS DC-2 DRY CAL in continuous operation. Inlet and outlet vapor concentrations were monitored by analyzing 150 µl syringe samples with a Hewlett-Packard GC/MS (GC 5890 Series II, 5971 MS).

## Results and Discussion

The ACC fixed bed was integrated with the cryogenic condenser to test acetone removal with condensation. A 1% acetone in nitrogen vapor stream at 5 slpm was passed through the bed at ambient temperatures. At breakthrough, the acetone was desorbed at 1 slpm nitrogen purge stream. The desorbed stream was sent directly to the pre-cooled condenser at ambient temperature and ambient pressure. The condenser log-mean operating temperature was  $220 \pm 9$  K and was at ambient pressure. The acetone vapor concentration at the condenser outlet remained low and fairly constant throughout the desorption cycle (Figure 2). At desorption times between 150 sec. and 1000 sec., the desorbed acetone concentration was greater than the equilibrium vapor saturation concentration. As the vapor cooled in the lines to the condenser, the acetone condensed to the equilibrium vapor concentration of 24% at an ambient temperature of 296 K. The condenser further cooled the vapor to the equilibrium concentration of approximately 0.2% by volume at 220 K. A removal efficiency of 99.0% was found for the integrated test. During the adsorption/desorption cycle, the acetone in the 1% by volume and 5.0 slpm challenge stream was concentrated up to 60%, and the flow rate was decreased by an order of magnitude [10].

Condenser outlet concentrations were also measured for inlet concentrations ranging from 0.25% to 18.3% by volume (Figure 3) to determine VOC removal efficiencies. The acetone in nitrogen challenge gas stream was generated by passing nitrogen gas through liquid acetone in a dual bubbler set-up. The challenge gas flow rate was 0.5 slpm and at ambient temperature. The condenser was pre-cooled to an equilibrium log-mean temperature of  $215 \pm 10$  K for each experiment. Over the entire range, outlet acetone concentrations remained fairly constant near the equilibrium vapor concentration of 0.17% at 215 K as predicted by the Wagner equation. Removal efficiencies are therefore higher for higher inlet concentrations. For instance, the removal efficiency found for an acetone inlet concentration of 18.3% was found to be 98.8%. However, the removal efficiency for an inlet of 0.6% was only 70.5%.

Theoretical and experimental LN<sub>2</sub> refrigerant requirements were also evaluated (Figure 3). The theoretical mass of LN<sub>2</sub> per unit mass of acetone condensed was determined from thermodynamic calculations. At low inlet concentrations, more LN<sub>2</sub> is required to condense a unit mass of acetone. For instance, at an inlet concentration of 2.5% by volume acetone, 10 kg of LN<sub>2</sub> is theoretically required to condense 1 kg of acetone. However, at an inlet concentration of 20% by volume acetone, only 2 kg of LN<sub>2</sub> is required to condense 1 kg of acetone. Experimental results showed the same general trend with deviations from the theoretical curve resulting from heat loss from the condenser. This supports the earlier statement that higher concentration vapor streams result in more efficient recovery of VOC vapor. Therefore at high concentrations the removal efficiency is maximized and the mass of refrigerant per unit mass of acetone condensed is minimized.

The condenser was also evaluated for acetone removal performance at various condenser equilibrium temperatures (Figure 4). A 10% by volume acetone challenge gas stream at 0.5 slpm was sent through the condenser at log-mean temperatures ranging from 209 K to 271 K. The measured outlet concentrations closely approximated the theoretical equilibrium vapor concentration as predicted by the Wagner equation. This indicates that the acetone bulk vapor concentration reached equilibrium with the acetone vapor concentration at the condenser's surface. This would also exist during scale-up if adequate condensing surface is available for the given process stream's vapor concentration, temperature and flow rate.

A model was developed to predict the axial concentration of a vapor along the condenser length. Radial mass transfer was incorporated with the thermodynamic characteristics of the heat exchange between the VOC gas stream and LN<sub>2</sub> refrigerant. For a condenser surface area of 1241 cm<sup>2</sup> and process conditions similar to the experimental conditions, equilibrium concentration is predicted at approximately 30 cm for an inlet concentration of 15% acetone (Figure 5). The laboratory condenser is 62.2 cm long. The model can also be used for designing condensers for a specific process gas stream.

Condenser design can be carried out by first determining the process gas stream characteristics such as VOC vapor concentration, temperature and flow rate. By assuming equilibrium conditions, the desired condenser temperature can be determined from the vapor concentration dependence on temperature at the desired outlet concentration. Once the temperature is known, an appropriate refrigerant can be selected. Then by modeling the axial concentration profile, the appropriate surface area and length can be determined from the condensing surface required to reach the desired outlet vapor concentration.

## Summary and Conclusions

Integration of a carbon adsorber with cryogenic condensation provides a method to recover VOCs from gas streams in a laboratory scale set-up. Experimental results showed that removal efficiencies of >98% can be achieved for acetone in nitrogen gas streams. Modeling and experimental results also show that condensers operate more efficiently at high VOC concentrations and low gas flow rates. Carbon adsorption can remove relatively low concentration VOCs in high flow rate gas streams and desorb at relatively high concentrations and low flow rates. Carbon adsorption/desorption concentrated a 1% gas stream by over an order of magnitude and decreased flow rates from 5.0 slpm to 0.5 slpm. Condenser removal efficiencies increased from 70.5% to 98.8% for inlet acetone concentrations between 0.6% and 18.3% by volume. The mass of LN<sub>2</sub> required to condense a unit mass of acetone was also found to decrease as inlet concentration increased. The Wagner equation proved to be valid for determining the outlet concentration of acetone vapor given the condenser temperature. Cryogenic recovery of VOCs is more efficient when the condenser was integrated with a carbon adsorber.

**References**

- [1] United States Environmental Protection Agency, *National Air Quality and Emissions Trends Report*, EPA 454/R-93-031, USEPA, 1992.
- [2] McIlvaine, R., Haldeman, S. and J. Schwartz *Pollution Engineering*, February 15, 1992, pp. 54-57.
- [3] United States Environmental Protection Agency, 1990 Clean Air Act Amendments, USEPA, 1990.
- [4] Ruddy, E.N. and L.A. Carrol *Chemical Engineering Progress*, July 1993, pp. 28-35.
- [5] United States Environmental Protection Agency, *Control Technologies for Hazardous Air Pollutants*, EPA/625/6-91/014, USEPA, 1991.
- [6] Dyer, J.A. and K. Mulholland *Chemical Engineering*, February 1994, pp. 4-8.
- [7] Buonicore, A.J. and W.T. Davis, Air and Waste Management Association, *Air Pollution Manual*, New York, 1992.
- [8] American Society of Heating, Refrigeration and Air-Conditioning Engineers, *1983 Equipment Volume*, 1983.
- [9] Reid, R.C., Prausnitz, J.M. and T.K. Sherwood *The Properties of Gases and Liquids*, New York, 1977.
- [10] Lordgoel, M., Carmichael, K.R., Kelly T.W., Rood, M.J. and S.M. Larson, *Activated Carbon Cloth Adsorption-Cryogenic System to Recover Toxic Volatile Organic Compounds*, submitted to Gas Separation and Purification, 1995.

**Acknowledgments**

A special thanks for funding support from the Hazardous Waste Research and Information Center (HWRIC) and Liquid Carbonic. We would also like to thank Joe and Nancy Hayes of American Kynol Inc.

**Figures**

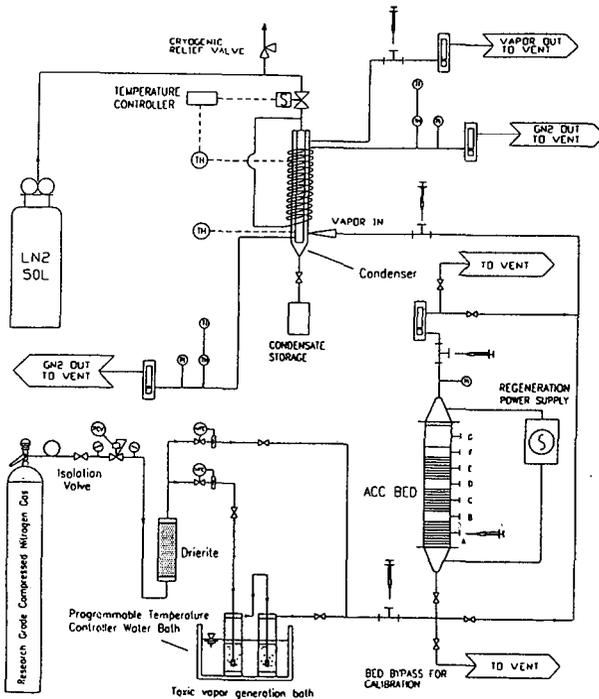


Figure 1. Laboratory condenser set-up integrated with a fixed carbon adsorber.

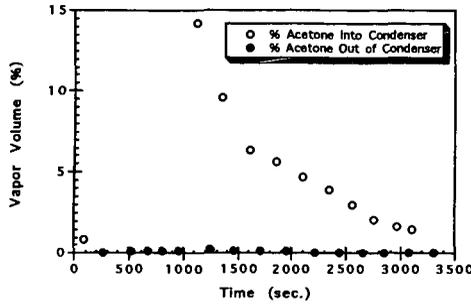


Figure 2. Acetone outlet concentrations from desorption and condensation.

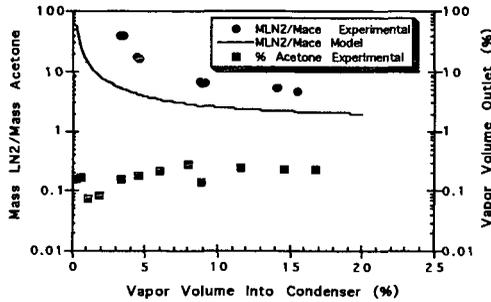


Figure 3. LN2 requirements and condenser acetone outlet concentrations versus inlet concentrations.

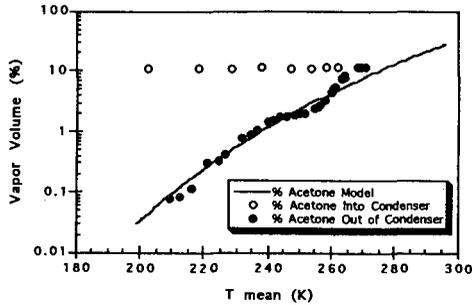


Figure 4. Acetone outlet concentrations versus condenser equilibrium temperature.

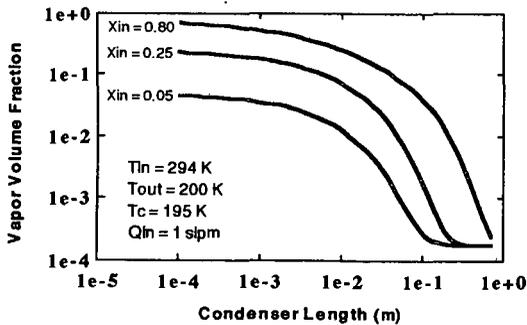


Figure 5. Modeled outlet acetone volume fractions for various condenser lengths.  $X_{in}$  is the inlet vapor volume fraction and  $T_c$  is the condensate film temperature.

## THE ADSORPTION ONTO FIBROUS ACTIVATED CARBON APPLICATIONS TO WATER AND AIR TREATMENTS

Pierre Le Cloirec<sup>(1)</sup>, Catherine Brasquet<sup>(1)</sup> and Etienne Subrenat<sup>(2)</sup>  
(1) UMR Subatech, Ecole des Mines de Nantes, 4 rue Alfred Kastler  
44070 Nantes Cedex 03, France  
(2) Actitex, 16 rue Trézel, 92309 Levallois Cedex, France

**Keywords :** Fibrous activated carbon, adsorption, water, air

### **Abstract :**

The adsorption of polluted fluids is performed by fiber activated carbon (FAC). The adsorption is carried out in a batch or dynamic reactor. Classic models are applied and kinetic constants are calculated. Results showed that the performances of FAC are significantly higher than that of granular activated carbon (GAC) in terms of adsorption velocity and selectivity. The breakthrough curves obtained with FAC adsorbents are particularly steep, suggesting a smaller mass transfer resistance than GAC. The adsorption zone in the FAC bed is about 3.4 mm and is not really dependent on the water flow rate within the studied range. Applications are developed in water and air treatments. Examples are given in the micropollutants removal of an aqueous solution. Air loaded with VOC or/and odorous molecules is treated by fibers. Regeneration of this material is performed by heating by joule effects or electromagnetic induction. These original approaches to water or air treatment processes are successfully put to use.

### **INTRODUCTION**

The removal of organic matter in aqueous or gas phases with granular activated carbon (GAC) is commonly performed for the treatment of waters or VOC (Cheremisinoff and Ellerbusch, 1978; Schulhof, 1979; Bansal et al. 1988). GAC adsorbents have been proved effective in removing a large number of organic molecules (Clark and Lykins, 1989).

Fibrous activated carbon (FAC) has received increasing attention in recent years as an adsorbent for purifying water. The raw materials of FAC are polyacrylonitrile (PAN) fibers, cellulose fibers, phenol resin fibers or pitch fibers and their cloths or felts. They are first pyrolysed and then activated at a temperature of 700-1000°C in an atmosphere of steam or carbon dioxide (Seung-Kon Ryu, 1990).

The main objectives of the present paper is to assess the performance of the FAC adsorbents in water and air treatments. Phenol and its derivatives are the basic structural unit of a wide variety of synthetic organics including many pesticides. Then, phenol was the model compound used throughout the adsorption studies in aqueous solutions. The Volatil Organic Compounds (VOC) are well adsorbed on FAC, an exemple is shown. Two new regeneration method are proposed.

### **MATERIALS AND METHODS**

#### **Activated Carbon Materials**

Activated carbon materials are commercial products proposed by the PICA Company and Actitex Company (France). The main characteristics of the materials used in the present investigations are presented in Table 1. Scanning electronic microscopy pictures of the different adsorbants have been shown elsewhere (Le Cloirec et al., 1990 b)

#### **Water treatments**

Kinetic and equilibrium studies. Activated carbon (about 0.6 g) in the form of GAC or FAC was continuously stirred with 1 liter of an aqueous solution at  $20 \pm 1^\circ\text{C}$  containing initially 100  $\text{mg.l}^{-1}$  as micropollutants. Samples were withdrawn at regular times and then filtered for analysis until a steady state was obtained, up to 300 minutes for GAC. For the equilibrium studied, the activated carbon mass was varied from 0.05 to 0.5 g in 250 ml of solution. The final solution was then filtered and analysed.

Continuous Flow Reactor. A laboratory pilot unit was set up for the continuous flow study (Figure 1). The raw water contained 50  $\text{mg.l}^{-1}$  of micropollutant and was pumped to the adsorption line which was composed of four similar stages. Just one stage is shown on the figure 1. The modules have a diameter of 2.5 cm. The dead volume inside and between the FAC modules was negligible. The water flowed through each FAC module with a given velocity of 0.67 to 2.07  $\text{m h}^{-1}$ . Samples were taken at regular times in the outflow of the FAC modules in order to determine the corresponding breakthrough times.

#### **Air treatments**

Adsorption procedure. A laboratory pilot unit was set up for the continuous flow study. The raw air contained 50  $\text{mg m}^{-3}$  to 50  $\text{g VOC m}^{-3}$  and was sent to the adsorption line. The air velocity through the FAC was in a range between 50 and 1000  $\text{m h}^{-1}$ . Samples were taken at regular times in the outflow of the FAC modules in order to determine the corresponding breakthrough times.

Regeneration. Two kinds of regeneration were tested. The heating of FAC was developed by joule effect (Figure 2) or by electromagnetic induction (Figure 3).

## RESULTS AND DISCUSSION

### Water treatments

The results are presented in terms of adsorption velocity and selectivity compared to activated carbon grains.

**Adsorption velocity.** The kinetic coefficients were calculated for the two activated carbon materials into account the initial slopes of the curves. The Freundlich or Langmuir's models are applied (Table 2) the values of initial velocities are shown in Table 3. Adsorption isotherms were performed for the adsorption of phenol from synthetic solutions. All the isotherms demonstrated a favorable adsorption (Weber and Smith, 1987). The Freundlich equilibrium constants were higher for FAC than for GAC probably because of the higher specific surface area and the microporous structure of the activated carbon fibers. Therefore the FAC materials are more interesting than GAC from the standpoint of adsorption capacities. Therefore FAC was used for the breakthrough experiments. The kinetic coefficient for the FAC was found more than 50 times greater than that for GAC. Suzuki (1991) measured similar intraparticle diffusion coefficients with GAC and FAC. On the other hand, Seung-Kon Ryu (1990) came to the conclusion that the superposition of the adsorption forces generated by the opposite walls of the micropores causes an increase in the adsorption potential inside them. FAC seems to have only micropore which are directly connected to the external surface of the fibers (Le Cloirec et al., 1990; Suzuki, 1991; Abe et al., 1992). The pore size distribution for PAN-based activated carbon fibers concentrate around 2.5 to 2.6 nm (Tse-Hao Ko and co-workers, 1992). Thus adsorbates reach adsorption sites through micropore without additional diffusion resistance of macropore which usually is the rate-controlling step in the case of granular adsorbents (Suzuki, 1991). Moreover, the small diameter of the fibers results in the large external surface area exposed to the flowing fluid. Thus FAC adsorbents provide much faster adsorption kinetics compared with GAC (Baudu and co-workers, 1990, 1991).

**Selectivity.** In order to approach the selectivity of the two adsorbents, adsorptions in batch reactor were performed with a mixture of commercial humic substances and phenol. The results are presented in Figure 4. Similar curves are obtained for the two experiments. The FAC presents a selectivity for the low molecular weight molecules (Phenol) compared to macromolecules (Humic Substances). The adsorption capacities are found to be very closed for different waters as shown in Table 4. The micropore distribution could explain this selectivity.

**Dynamic adsorptions.** Breakthrough experiments were carried out for the adsorption of phenol onto FAC material with different flow rates through the FAC modules. Typical breakthrough curves for a given flow rate of 2.07 m.h<sup>-1</sup> are presented in Figure 5. Very steep breakthrough curves were obtained for all the flow rates used in the present investigation. This characteristic shape has already been mentioned in the review by Seung-Kon Ryu (1990). Again, Suzuki (1991) showed drastic differences between the breakthrough curves obtained in the same experimental conditions with GAC and packed FAC. The sharper breakthrough curves observed for the FAC suggested smaller mass transfer resistance than for the GAC. Similarly, Seung-Kon Ryu (1990) concluded that the adsorption rates of FAC are much higher than those of GAC. Therefore the mass transfer zones are much smaller in the case of adsorption onto FAC. The breakthrough times were measured when the phenol concentration (C) reached 0.05 C<sub>0</sub> (initial concentration). The breakthrough time values obtained for the various thicknesses and flow rates used in the study were introduced into the Bed Depth Service Time (BDST) relation developed by Hutchins (1973) and currently used. Parameters of the BDST relation are shown in Table 6. The N<sub>0</sub> (adsorption capacity) and Z<sub>0</sub> (adsorption zone) values were not really strongly dependent on the flow rate within the range 0.62 - 2.07 m.h<sup>-1</sup>. One might hypothesize that the adsorption reaction was not significantly influenced by the external mass transfer of the solutes through the hydrodynamic boundary layer. The main resistance to the mass transfer might be due to the diffusion through micropores inside the activated carbon fibers. The adsorption capacities (N<sub>0</sub>) were recalculated as a function of the activated carbon weight (Table 5). A good adsorption capacity (about 130 mg/g), close to the maximum surface concentrations determined in the batch reactor, is found with this dynamic system.

### Air treatments

**VOC adsorption.** A large number of works were published on the air treatment with activated carbons. Volatil Organic Compounds (VOC) were found to be well adsorbed onto GAC or FAC. During this study, adsorption onto FAC were performed with different VOC. An exemple is proposed on the figure 6. In this case, the dynamic adsorption capacity is found about 30 %. In order to recover the solvent, an "in situ" regeneration is required.

**Regeneration of FAC.** Two conventionnal methods are currently used to desorb VOC from activated carbon by high pressure steam or preheating fluid (air, nitrogen...). In order to overcome problems found with conventionnal methods, new processes usefull with FAC were considered.

**Regeneration by joule effect.** Recently, a new thermal regeneration process has been used. It consists of submitting the carbon to the passage of an electric current. the carbon can be either granular (Baudu et al., 1992) or fibrous (Le Cloirec et al., 1991). the activated carbon structure is akin to a semi-conductor. Laboratory scale experiments on solvent desorption are very promising. The advantage of such a process is that it can be easily implemented in-situ. Examples of regeneration by joule effect on fibrous carbon is given in the Table 6.

The regeneration by induction heating (Le Cloirec, 1993; Mocho, 1994). Induction heating can be used to regenerate activated carbon for the purpose of recycling volatile organic carbon. As the technological possibilities offered by induction on an industrial scale have to be taken into account, the FAC was presented as cylinders. Figure 4 shows the activated carbon heating equipment. Experiments developed with ethyl acetate show the best frequency is in a range of 1 to 100 kHz. A regeneration rate of 100% is reached for the activated carbon at the end of an hour. At this time, this kind of regeneration is developed at a laboratory scale for a treatment by FAC of air loaded by solvents.

## CONCLUSIONS

The objective of this study was to determine the efficiency of adsorption of fibrous activated carbon in water and air treatments. Results showed that performance of FAC is significant. FAC have a fast adsorption kinetics and selectivity. Thus, FAC well adsorbed VOC and new regeneration processes were proposed. For air and water treatments new reactors could be developed.

## ACKNOWLEDGMENT

The authors thank G. Dagois, Pica Company, Levallois, France for technical assistance for the activated carbon grains.

## BIBLIOGRAPHY

- Abe, M., Y. Kaneko, W. Agui, and K. Ogino (1992). Removal of humic substances dissolved in water with carbonaceous adsorbents. *Sci. Tot. Environ.*, **117/118**, 551-559.
- Bansal, R.C., J.B. Donnet, N. Stoeckli (1988) Active Carbon, *Marcel Dekker Inc*, N.Y., USA.
- Baudu, M., P. Le Cloirec, and G. Martin (1991). Pollutant adsorption onto activated carbon membranes. *Wat. Sci. Technol.*, **23**, 1659-1666.
- Baudu M., Le Cloirec P., Martin G. (1992) Thermal regeneration by joule effect of activated carbon used for air treatment, *Environ. Technol.*, **13**, 423-435
- Cheremisinoff P.M., F. Ellerbusch (1978), Carbon adsorption Handbook, *Ann Arbor Sci*, Ann Arbor, Mi, USA.
- Clark, M. K., B. W. Lykins (1989). Control of trihalomethane and synthetic organics. In R. M. Clark (Ed.), *Granular activated carbon*, Lewis Publ., Michigan. pp.257-293.
- Hutchins, R. (1973). New method simplifies design of activated carbon systems - Water bed-depth service time analysis. *Chem. Eng.*, **20**, 133-138.
- Le Cloirec P., M. Baudu, G. Martin, G. Dagois (1990 b), Membrane, toiles, fibres ou feutres : des charbons actifs d'utilisations prometteuses, *Rev. Sci. Tech. Défense*, **2**, 111-123.
- Le Cloirec P. Baudu M., Martin G. (1991) Dispositif de traitement de fluide, au moyen d'une structure d'adsorption à couches superposées espacées, et régénération par effet joule. Brevet Européen n° 91460043.2 Dépôt le 20/09/91
- Mocho P., Le Cloirec P. (1994) Regeneration of granular activated carbon by inductive heating. Application in the elimination and recycling of air-born solvent, Vigneron S., Hermia J., Chaouki J. Ed, *Studies in Environmental Science* 61, Elsevier, Amsterdam, 251-262.
- Seung-Kon Ryu (1990). Porosity of activated carbon fibre. *High Temp.- High Pressures*, **22**, 345-354.
- Schulhof P.(1979), An evaluating approach to activated carbon treatment, *J. Am. Water Works Ass.*, **71**, 648-661.
- Suzuki M. (1991), Application of fiber adsorbents in water treatment, *Water Sci. Technol*, **23**, 1649-1658
- Tse-Hao Ko, P. Chiranairadul, Chung-Hua Lin (1992). The study of polyacrylonitrile-based activated carbon fibres for water purification: Part I. *J. Materials Sci. Letters*, **11**, 6-8.

	GAC	FAC
Commercial name	Pica NC 60	Actitex 1501
Size (mm)	3	-
Origin	coconut	viscose
Porosity	microporous	microporous
Specific area (m <sup>2</sup> .g <sup>-1</sup> )	1200	1550

Table 1 : Main Characteristics of Activated Carbons  
(PICA Company, Levallois France for GAC and Actitex, Levallois, France for FAC)

	GAC	FAC
1/n	0.39	0.428
k	0.06	27.7
qm	117	183
b	0.03	0.083

Table 2 : Langmuir and freundlich model parameters of phenol adsorption

	GAC	FAC
$\gamma$ (l. mg <sup>-1</sup> .min <sup>-1</sup> )	5.8 10 <sup>-6</sup>	4.5 10 <sup>-5</sup>

Table 3 : Initial adsorption velocity for phenol removal

Water	Phenol only	HS only	Phenol in the mixture	HS in the mixture
Deionised	40.1	1	34.3	0
Drinking Water	40.3	0.5	32.6	0
River water	44	0	40.2	0

Table 4 : Adsorption capacity (mg g<sup>-1</sup>) of phenol and humic substances (HS) in different waters

U (m/h)	Z <sub>0</sub> (mm)	N <sub>0</sub> (mg.l <sup>-1</sup> )	N <sub>0</sub> (mg.g <sup>-1</sup> )
0.62	3.5	9210	134
1.02	3.3	8925	130
2.07	3.4	8625	126

Table 5 : Adsorption zone and capacity at different flow velocities

Experiment	P (w)	Time to be at 100°C	Regeneration yield (%)
1	240	3 min 45 s	95
2	340	1 min 20 s	100
3	440	55 s	100

Table 6 : Thermal regeneration of fibrous activated carbon by joule effect (Baudu et al., 1992)

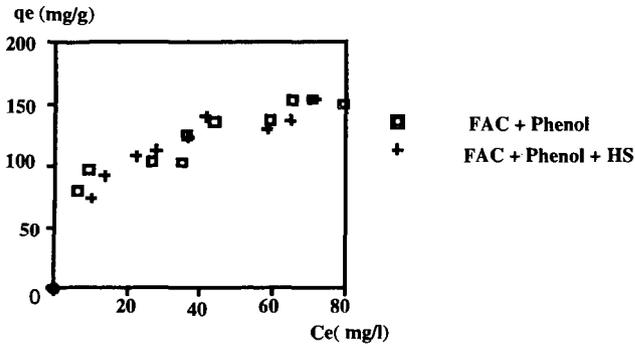


Figure 4 : Adsorption of mixture of humic substances (HS) and Phenol onto FAC

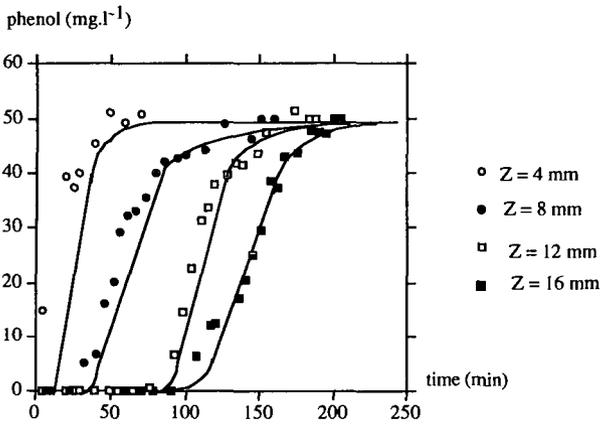


Fig.5 : Breakthrough curves for different thicknesses of FAC (flow rate: 2.07 m.h<sup>-1</sup>; raw water concentration: 50 mg phenol.l<sup>-1</sup>).

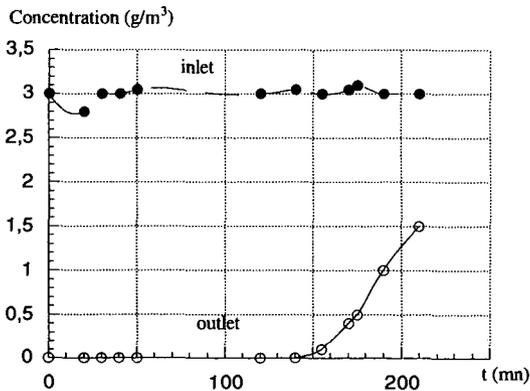


Figure 6 : Breakthrough curve on FAC. Air loaded with perchlorethylene, Velocity : 522 m/h; FAC weight : 7 kg (Baudu et al., 1992)

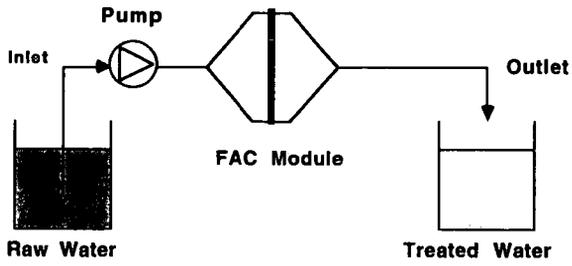


Figure 1 : Continuous flow reactor used in water treatment

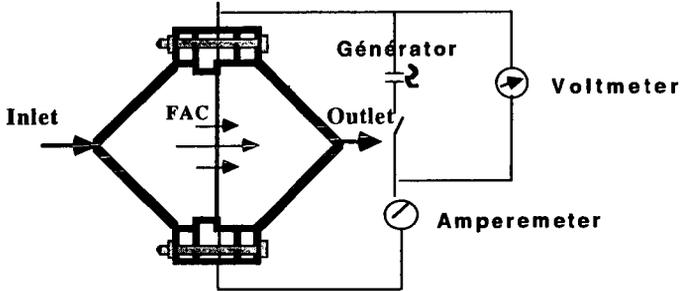


Figure 2 : Heating by joule effect, experimental equipment

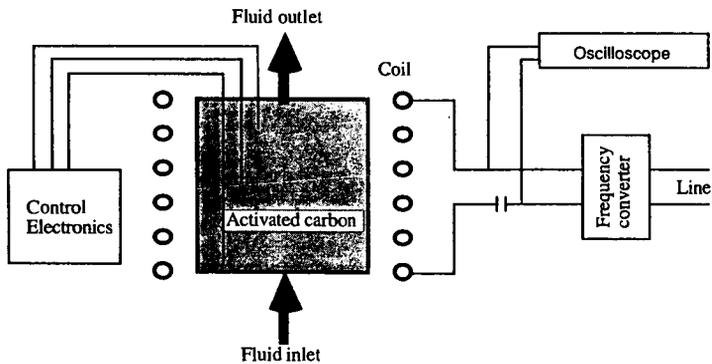


Figure 3 : Heating by electromagnetic induction. Experimental equipment

# THE USE OF CARBON FIBER COMPOSITES AS SUBSTRATE FOR A ZERO VALENT METAL DECHLORINATION SYSTEM.

Rodney Andrews, Billy Spears, and Eric Grulke. Department of Chemical and Materials Engineering, University of Kentucky, Lexington, KY, 40506-0046.

Chris Lafferty. Center for Applied Energy Research, University of Kentucky, Lexington, KY, 40511-8433.

**Keywords:** zero-valent metal, supported catalyst, carbon fiber composite, dehalogenation.

## Abstract

The use of zero valent metals is known to successfully degrade chlorinated hydrocarbons. The use of zinc metal to dechlorinate trichloroethene (TCE) in contaminated groundwater sources has been limited by metal surface area for reaction. A highly porous carbon fiber composite substrate for the zinc metal provides a much higher surface area for reaction in a dechlorination system. The zinc coating applied to the carbonaceous fibers provides higher reaction rates than traditional powdered metal systems. Added advantages of using the zinc coated carbon substrate for ground water clean up are low pressure drop, easy removal and emplacement of composites, and the ability to recharge the zinc coating *in situ*. The novel zinc impregnation method results in a uniform coating of zinc throughout the composite and a greatly increased area for reaction.

## Introduction

The dehalogenation of hydrocarbons by zero-valent metals offers many attractive features for environmental application. The relatively high reaction rates, low cost of the metal catalyst, and non-contaminating nature of the catalyst all make this an attractive system for ground water clean-up. The limiting factor for the dehalogenation reaction is the surface area of the metal available for reaction. Large metal pellets offer slow reaction rates, while fine metal particles lead to faster reaction rates. In this study, a carbon fiber composite is used as a support for zinc plating; producing a supported zinc catalyst with very high surface area for reaction and low resistance to flow. The zinc plated composite system also has the advantage of being regenerable after metal depletion. This regeneration could be performed *in situ*.

The dechlorination of trichloroethene (TCE) by zero-valent zinc is demonstrated with both supported and unsupported zinc systems. Initial rate constants for this reaction are reported. The zinc was placed onto the carbon composite using electrochemical reaction at low current densities and the resistance to flow through the composite was measured and compared to uncoated composite.

## Literature Review

The use of zero-valent metals, mainly iron, tin and zinc, to remediate water containing chlorinated hydrocarbons has been proposed by several researches. The emphasis of most research in this area has been on the use of iron as the metallic catalyst or a modified iron, such as the palladium plated iron granules used by Korte et. al. (1-7) Boronina et. al. (8) have demonstrated the efficacy of using Zn or Sn as the catalytic metal, showing the relatively fast reaction rates obtained using very fine Zn particles in an inert atmosphere.

The destruction of chlorinated species into metal salts and dechlorinated byproducts has been shown to occur at reaction rates ranging from 5 to 15 orders of magnitude faster than that observed for natural abiotic processes. (6) O'Hannesin et. al. have shown that a reactive bed containing Fe filings was able to remove 90% of the trichloroethene (TCE) from groundwater at the Canadian Forces Base, Borden, Ontario site. They concluded that the reaction rate was independent of TCE concentration. In further studies, this group found chlorinated species destruction by granular iron of 13 out of 14 halogenated methanes, ethanes and ethenes. (6)

In building a pilot scale operation for the reduction of TCE using iron filings, MacKenzie et. al. (7) determined several factors controlling the process. The alkalinity of the ground water being treated as well as the amount of dissolved oxygen in the water effect catalytic bed lifetime. The presence of carbonate or oxide forming species in the water leads to a inert layer of metal oxide or metal carbonate forming on the metal surface. This layer greatly reduces the overall reaction rate. (1,5,7,8). MacKenzie et. al. found that a 10 fold increase in aqueous alkalinity reduced the reaction rate by three fold.

Metallic surface area is a controlling factor in the rate of reaction. (1, 8) Boronina et.al. (8) have shown that cryo-particle Zn with a surface area of  $>65 \text{ m}^2/\text{g}$  reduced the concentration of  $\text{CCl}_4$  in water by over 90% in three hours, while granular Zn, having a surface area  $< 1 \text{ m}^2/\text{g}$ , achieved a

reduction of only 25%. A similar correlation between surface area and dechlorinating ability was seen in studies using Sn metal.

### Objectives

This paper describes a novel process for supporting zero-valent zinc on a carbon fiber composite. The study also reports some preliminary rate constants for unsupported and supported zinc dechlorination of TCE.

## Experimental

### Unsupported Zinc Powder

Zinc powder was reacted with an aqueous solution of 1000 ppm TCE under a nitrogen atmosphere. The zinc (from J.T. Baker Chemical) was 60 to 200 mesh in size, and was washed in 0.01 M HCl to eliminate any oxide coating. A vacuum tight reaction vessel was charged with 100 ml of nitrogen saturated water and 10 grams of the washed zinc powder were added. A vacuum was drawn on the system and held for 15 minutes to remove any remaining oxygen. The vacuum was broken by introduction of a nitrogen gas stream. The reactor was kept under a constant positive pressure of nitrogen, and 100  $\mu$ l of TCE was added. High agitation rates were used to insure uniformity of composition. The concentration of chloride ions was measured using a chloride selective electrode.

### Supported Zinc

Carbon fiber composite was manufactured using the process described earlier at this conference at CAER, UK. The composite was carbonized at 600 °C to improve the conductivity of the material. A 10 cm long composite sample with 2.54 cm diameter was placed in the holder of the plating apparatus (Figure 1). This sample was immersed in a chloride zinc bath (Table 1) and a plating fluid at 100 ml/min was passed through the sample. A solid zinc electrode was immersed in the bath and an electrode with 2.5 cm diameter was contacted with the carbon composite. A 10 volt, 0.1 ampere current was applied to the composite. This low current density was allowed to flow until a 2 micron layer of zinc was deposited on the composite which had 17  $\mu$ m diameter fibers.

Scanning electron microscopy and elemental analysis were used to determine the uniformity of zinc coating on the composite support. This composite was then cut and the composite samples used as paddles for agitation in a reactor system as described above in place of the zinc powder.

## Results

### Zinc Plating

SEM showed that the zinc layer was uniform through out the 10 cm length of the composite and had no radial variation. The zinc layer was 2  $\mu$ m in thickness. This ease of control of the plating process would allow the composite plating to be regenerated as needed by flowing a zinc-chloride solution through the composite and applying a current as needed *in situ*.

### Reaction Rates

To determine if TCE dechlorination was occurring, the reaction was monitored for chloride ion concentration in solution using a chloride selective electrode. A typical reaction profile is shown in Figure 2. For this initial study, first order kinetics and total reaction were assumed. Reaction rate constants were determined based on the amount of chloride not released into solution, and are reported on a per gram of zinc basis. The zinc powder was shown to degrade the TCE and the rate of degradation increases with temperature (Table 2).

The reaction rate for the zinc plated composite system is an order of magnitude faster than for the powdered zinc system, indicating that the surface area for reaction of the metal controls the reaction rate. The pressure drop through the zinc plated composite was measured and compared to that of the untreated composite. These values were found to be the same indicating that no increase in pressure drop results from the zinc plating. This pressure drop is low, and the zinc plated composite would be ideal for use in a fixed-bed flow system.

## Conclusions

Zero-valent zinc metal has been shown to successfully dechlorinate TCE in aqueous solution. The rate of this reaction is determined by the surface area of metal available for reaction. A novel process for depositing zinc metal onto a carbon fiber composite produces a reaction system with high surface area of metal. This zinc plated composite has a reaction rate an order of magnitude higher than that of powdered zinc.

## References

- <sup>1</sup>Sivavec, Horney and Baghel. "Reductive Rechlorination of Chlorinated Ethenes by Iron Metal and Iron Sulfide Minerals.", Emerging Technologies in Hazardous Waste Management VII, Special Symposium, Atlanta, Georgia, Industrial and Engineering Chemistry Division, American Chemical Society, Sept. 17 -20, 1995.
- <sup>2</sup>Liang and Goodlaxson. "Kinetics and Byproducts of Reductive Dechlorination of Ground Water TCE with Zero-Valence Iron", Emerging Technologies in Hazardous Waste Management VII, Special Symposium, Atlanta, Georgia, Industrial and Engineering Chemistry Division, American Chemical Society, Sept. 17 -20, 1995.
- <sup>3</sup>Orth and McKenzie. "Reductive Dechlorination of Chlorinated Alkanes and Alkenes by Iron Metal and Metal Mixtures.", Emerging Technologies in Hazardous Waste Management VII, Special Symposium, Atlanta, Georgia, Industrial and Engineering Chemistry Division, American Chemical Society, Sept. 17 -20, 1995.
- <sup>4</sup>Korte et. al. "The Use of Paladized Iron as a Means of Treating Chlorinated Contaminants.", Emerging Technologies in Hazardous Waste Management VII, Special Symposium, Atlanta, Georgia, Industrial and Engineering Chemistry Division, American Chemical Society, Sept. 17 -20, 1995.
- <sup>5</sup>Agrawal, Liang and Tratnyek. "Phenomena Affecting Remediation of Organic Groundwater Contaminants with Iron Metal at Solid-Water Interface.", Emerging Technologies in Hazardous Waste Management VII, Special Symposium, Atlanta, Georgia, Industrial and Engineering Chemistry Division, American Chemical Society, Sept. 17 -20, 1995.
- <sup>6</sup>O'Hannesin, Gillham and Vogan. "TCE Degradation in Groundwater Using Zero-Valent Iron.", Emerging Technologies in Hazardous Waste Management VII, Special Symposium, Atlanta, Georgia, Industrial and Engineering Chemistry Division, American Chemical Society, Sept. 17 -20, 1995.
- <sup>7</sup>MacKenzie et. al. "Pilot-Scale Demonstration of Chlorinated Ethene Reduction by Iron Metal: Factors Affecting Iron Lifetime.", Emerging Technologies in Hazardous Waste Management VII, Special Symposium, Atlanta, Georgia, Industrial and Engineering Chemistry Division, American Chemical Society, Sept. 17 -20, 1995.
- <sup>8</sup>Boronina, Klabunde and Segeev. "Destruction of Organohalides in Water Using Metal Particles: Carbon Tetrachloride/Water Reactions with Magnesium, Tin, and Zinc.", *Environmental Science & Technology*, vol. 29, no. 6, pg. 1511, June, 1995.

Table 1: Chloride Zinc Bath

ZnSO <sub>4</sub> *7H <sub>2</sub> O, g/L	240
zinc, g/L	55
NH <sub>4</sub> CL, g/L	15
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> *18H <sub>2</sub> O, g/L	30

Table 2: First order reaction rate constants for dechlorination of TCE by zero-valent zinc.

Type of Zinc	Temperature (°C)	k (min <sup>-1</sup> g <sup>-1</sup> )
Unsupported Zinc Powder	25	0.000007
Unsupported Zinc Powder	30	0.00001
Unsupported Zinc Powder	40	0.00002
Supported Zinc on Composite	25	0.00025

Figure 1: Diagram of composite plating apparatus.

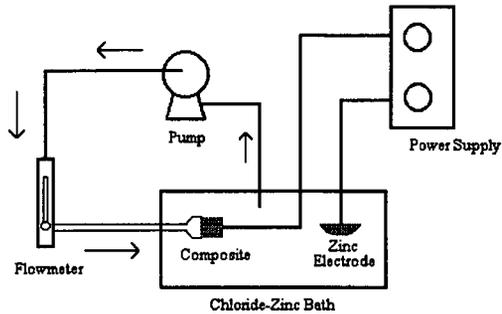
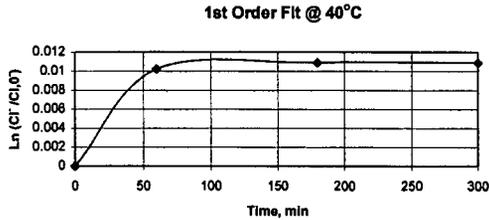


Figure 2: Typical reaction profile for powdered zinc degradation of aqueous TCE. Temperature = 40 °C, Initial rate constant, k, = 0.00002 min<sup>-1</sup> g<sup>-1</sup>.



## IMPREGNATED CARBONS FOR THE ADSORPTION OF H<sub>2</sub>S AND MERCAPTANS

Stephen Boppart  
Norit Americas Inc.  
1050 Crown Pointe Pkwy, Suite 1500  
Atlanta, GA 30338

**Keywords:** H<sub>2</sub>S, Oxidation, Activated Carbon, Potassium Iodide

### Introduction:

Activated carbon has been used for many years for the adsorption of H<sub>2</sub>S and Mercaptans from natural gas streams, carbon dioxide, and sewage vents. It is widely thought that the carbon pore surface catalyses the oxidation of H<sub>2</sub>S to elemental sulfur and higher oxidized forms of sulfur<sup>1,2</sup>. However, due to the poor loading capacities achieved at ambient conditions, most commercial activated carbon employed for H<sub>2</sub>S adsorption contain some sort of impregnant, such as NaOH, KOH, or KMnO<sub>4</sub>, to enhance the loading capacity on the carbon.

By far the most widely used impregnated carbons used for H<sub>2</sub>S adsorption has been NaOH and KOH impregnated carbons. These carbons show greatly increased Sulfur loading capacities, however due to high heats of reactions involved, are prone to bed fires. Non-impregnated carbons, which have undergone pore surface modification are also commercially available. These carbons fail to meet the same high loading capacities as caustic impregnated carbons, however it's manufacturer claims that that simple water wash is all that is required to achieve partial regeneration of the carbon.

A relatively new carbon type, NORIT ROZ 3, has been developed, which not only increases the Sulphur loading capacity significantly over caustic impregnated carbons, but it is not as susceptible to bed fires. This carbon differs from caustic impregnated carbons commercially available in two distinct ways. First the base carbon used has a higher pore volume, especially in the meso and macro pore range. Secondly, Potassium Iodide, is used as an impregnant.

This paper will present laboratory and field data of both caustic impregnated carbons and NORIT ROZ 3, as well as laboratory data of a surface modified carbon, Calgon Centaur™ HSV.

### Laboratory studies:

#### Carbon types:

Three commercially available carbons were tested for their ability to adsorb H<sub>2</sub>S. These were Calgon IVP, Centaur HSV and NORIT ROZ 3. In table 1, the carbon characteristics are listed. All three carbons vary significantly.

NORIT ROZ 3 is a highly activated peat based carbon which has a high degree of macro and mesopores. It is impregnated with minimum 2 % potassium iodide.

Calgon IVP is a bituminous based activated carbon typical for vapor phase applications. It has been impregnated with Sodium Hydroxide.

Calgon HSV is a non-impregnated bituminous coal product which has been treated to enhance its catalytic activity.

---

™ TM of the Calgon Corporation, Pittsburgh, PA

### Reaction Mechanism:

For the oxidation of H<sub>2</sub>S, a certain amount of water vapor must be present. Hedden et al<sup>3</sup> have proposed the following mechanism. Water is adsorbed, forming a film of water on the pore surface. H<sub>2</sub>S and O<sub>2</sub> diffuse down into the carbon pores and are dissolved in the water. The O<sub>2</sub> is adsorbed on the carbon surface and breaks down into radicals. These oxygen radicals then react with the dissolved hydrosulfide ions, forming elemental sulfur and water (figure 1).

Since the radical formation occurs on the pore surface of the carbon, it might be concluded that surface area would be a predominant factor in this reaction.

T.K Ghosh et al<sup>1</sup> found however, that the amount of surface area of a carbon has no effect on the oxidation of H<sub>2</sub>S. Ghosh concluded that carbons which had high pore volumes, not high surface areas, achieved higher rates of conversion of H<sub>2</sub>S.

Further oxidation to sulphur dioxide and sulfuric acid can occur. In the presence of NaOH, Na<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>3</sub> can also be formed. Klein et al<sup>2</sup> suggest that the addition of KI as a catalyst not only increases the reaction velocity, but also limits the formation of sulfuric acid.

### Test description:

The standard test used to measure the performance of carbon for H<sub>2</sub>S adsorption is a dynamic test. Humidified air (RH 75 %, 20°C) containing 1 % vol. (10,000 ppm) of H<sub>2</sub>S is passed through a column of carbon (diameter 3.9 cm, bed height 22.9 cm) at a linear velocity of 8.8 cm / second (6350 ml/min.). This results in a contact time of 2.7 seconds. The test is stopped at breakthrough concentrations of 50 ppm.

The adsorptive capacity of a carbon is given in g/ml, which is calculated as follows:

$$\text{Adsorption capacity} = (\text{H}_2\text{S}) * F * T_{\text{BT}} / V_{\text{C}}$$

Where: (H<sub>2</sub>S) = Concentration, in g/ml  
F = Flow, in ml / min.  
T<sub>BT</sub> = Break through time, in minutes  
V<sub>C</sub> = Volume of carbon, in ml

### Lab results:

The results of the tests are given in table 2. Of all three carbons tested, only NORIT ROZ 3 achieved the 0.14 g/ml which has become the standard in the odor control market. After breakthrough, the carbon in the top, middle and bottom of the column were analyzed for total sulfur content and the results were corrected back to % sulfur adsorbed per ml of virgin product. The results are presented in table 3.

With Calgon Centaur HSV, the mass transfer zone is very long, as it can be observed that the middle of the bed had much lower loading capacities than the bed inlet (0.06 vs 0.11 g/ml). This was also the case with NORIT ROZ 3, although not as dramatic as with the Calgon Centaur HSV. Curiously, with the caustic impregnated carbon, the bed inlet has a lower Sulfur loading capacity than the middle of the bed. This could possibly be due to high heats of reaction drying the bed, limiting the amount of H<sub>2</sub>S which could react.

Previous tests carried out NORIT ROZ 3 resulted in an equilibrium loading capacity of approximately 120 wt. % (0.54 g/ml). These tests were done with an humidified air stream (20°C, RH 80%), with a H<sub>2</sub>S concentration of 0.5 vol. % (5,000 ppm) for 450 hours.

This clearly shows that this accelerated test, lasting only a few hours, does not allow sufficient time for the H<sub>2</sub>S to oxidize to maximum loadings. It can be argued that the accelerated H<sub>2</sub>S oxidation test has limited relevance to actual field performance due to the high H<sub>2</sub>S loadings, short run time and that no other organic compounds are co-adsorbed. Questions have also been raised about the reproducibility of this test. In addition, Koe et al.<sup>4</sup> found that, for caustic impregnated carbons, the actual field trials show Sulphur loadings which are only 30 % that of laboratory loadings. A detailed discussion of this is

beyond the scope of this paper, however it is evident that actual field data will give a much better understanding of the relative performance of carbons.

#### Field Data:

Two case studies were conducted with NORIT ROZ 3.

##### Case 1:

A single adsorber containing 7,000 lbs of NORIT ROZ 3 was installed at a sewage odor filter in the Netherlands. The size and conditions of the installation are listed in Table 4. After odor breakthrough, carbon from various depths within the bed was analyzed, the results appearing in Table 5.

It can be clearly seen from the carbon analysis, that the odor was due to organic compounds breaking through the bed. The upper 1/2 of the carbon bed did in fact not even have any sulphur loading on the bed. The inlet portion of the bed did achieve very high Sulphur loadings in addition to high organic loadings. It can be assumed that if the bed had been run until H<sub>2</sub>S breakthrough, that the average sulphur loadings would have been much higher.

##### Case 2:

At a sewage discharge station, a small adsorber was filled with 1764 lbs of NORIT ROZ 3. Previously this adsorber was filled with KOH impregnated bituminous based carbon. After odor breakthrough, both carbons were sampled from the top, middle and bottom portions of the bed and analyzed with the following results:

A marked difference in bed life and loading capacity was noticed between the KOH impregnated carbon and the NORIT ROZ 3. In fact the NORIT ROZ 3 lasted 275 % longer than the KOH impregnated carbon. This was in spite of the fact that the bed containing the caustic carbon had 13.4 % more carbon on a % wt basis.

It is interesting to note that even after 11 months of adsorption, the middle of the bed containing NORIT ROZ 3 did not reach equilibrium loadings, with S loadings of 47.1 wt % for the bottom vs, 25.5 wt % for the middle. The KOH impregnated carbon on the other hand seemed to have reached its maximum loading at 12 % loading in both the top and middle sections of the bed. This would suggest that the reaction rate of a caustic impregnated carbon is more rapid than that of the KI impregnated carbons.

#### Bed Fires:

NORIT ROZ 3 has been installed in over 70 installations world wide in addition to over 100 sewage gas breathing filters. In all of these installations, no bed fire has ever occurred. Caustic impregnated carbons do have somewhat higher heats of reaction, however this alone fails to explain why so many bed fires have occurred in the field with caustic impregnated carbons.

#### Conclusion:

The accelerated oxidation test does not give a representative view of activated carbons field performance. This is primarily due to the short test period which would not allow sufficient time for the oxidation reaction to go to completion. It appears that the KI impregnated carbons and the surface modified carbons have a slower rate of reaction than caustic impregnated carbons and thus would be negatively biased in such a test.

In both long term laboratory tests and actual field cases, NORIT ROZ 3 achieved very high loading capacities for both organic and sulphur bearing compounds. This can be attributed to the high pore volume and KI impregnant.

#### Acknowledgments:

The author would like to thank Dr. Margriet Reimerink and Karla Thierig for their valuable input and laboratory support in writing this paper.

<sup>1</sup>"Catalytic oxidation of low concentrations of Hydrogen Sulfide", T.K Ghosh and E. Tollefson Presented at the meeting of the Canadian Gas Processors Associations, March 14, 1985.

<sup>2</sup>"Catalytic oxidation of hydrogen sulfide on activated carbons", J. Klein & K-D Henning, Bergbau-Forschung GmbH, Essen, FRG. Carbon and Catalysis conference, London, December 19, 20, 1983

<sup>3</sup>"Adsorptive Reinigung von Schwefelwasserstoffhaltigen Abgasen", K. Hedding and B.R. Rao. VDI-Bericht Nr.253 S.37/42, Duesseldorf, VDI-Verlag, 1976.

<sup>4</sup>"Comparisons of field and laboratory loading capacity of activated carbon." L.C.C. Koe & N.C. Tan. Department of Civil Engineering. National University of Singapore. Water, Air, and Soil Pollution 50:193:203, 1990

Table 1: Carbon Characteristics.

Carbon Type	NORIT ROZ 3	Centaur HSV	Calgon IVP
Bulk Density, g/L	0.450	.600	.530
Micropore volume, ml/g	0.32	0.25	.031
Mesopore volume, ml/g	0.11	-	0.06
Macopore volume, ml/g	0.41	0.14	0.21
Total pore volume, ml/g	0.84	-	0.58

Mesopore volume not available for Centaur HSV

Table 2: Results of accelerated H<sub>2</sub>S Oxidation test

Carbon type	Adsorptive capacity (g/ml)
NORIT ROZ 3	0.15
Calgon Centaur HSV	0.06
Calgon IVP	0.11

Table 3: Sulfur analysis of spent carbon from table 2

Carbon Type (g/ml)	Bottom (g/ml)	Middle (g/ml)	Top (g/ml)
NORIT ROZ 3	0.16	0.14	0.02
Calgon Centaur HSV	0.11	0.06	0.02
Calgon IVP	0.07	0.12	0.01

Table 4: Process conditions (Case 1)

Carbon Bed Height	2 m
Carbon Bed Diameter	2.1 m
Flow Rate	2400 m <sup>3</sup> /hr
H <sub>2</sub> S Concentrations	15-40 ppm
Breakthrough	Odor
Contact Time	10.4 seconds
Relative Humidity	70-80 %

Table 5: Sulfur loading as a function of bed depth (case 1)

Bed Height	55 cm	115 cm	170 cm	190 cm
H <sub>2</sub> O loading (wt %)	39.3	9.6	12.7	2.7
Organic loading (wt %)	42.1	22	2.4	4.1
Sulphur loading (wt %)	25.5	5.9	<1	<1

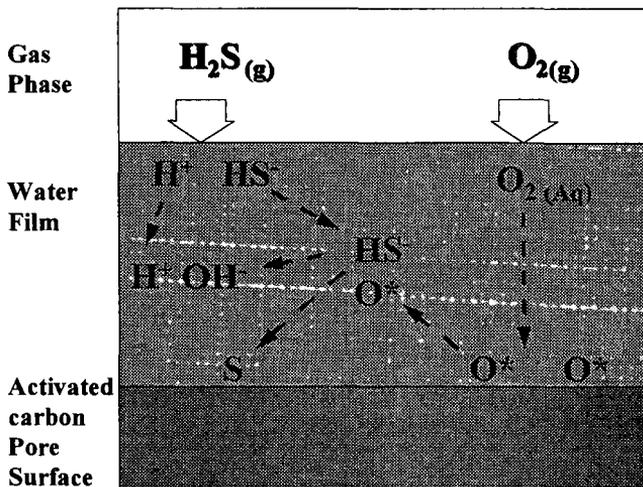
Table 6: Process Conditions (Case 2):

	NORIT ROZ 3	KOH carbon
Carbon Bed Height	3.4 ft	2.83 ft
Carbon Bed Diameter	5 ft	5 ft
Flow direction	up	down
Flow Rate	1200 cfm	1200 cfm
H <sub>2</sub> S Concentrations	10-25 ppm	10 - 25 ppm
Carbon Quantity	1764 lbs	2000 lbs
Contact Time	3.3 s	2.8 s

Table 7 Sulfur loading capacities, (Case 2):

	NORIT ROZ 3	KOH carbon
Top of Carbon bed, S loading, wt %	26.2 %	12.9%
Middle of bed, S loading, wt %	25.5%	11.8%
Bottom of bed, S loading, wt %	47.1%	5.4%
Average Sulfur loading, wt % dry basis	32.9%	10.0%
Bed life	11 months	3-4 months

Figure 1: Proposed reaction mechanism for the oxidation of H<sub>2</sub>S



M. B. Rao and S. Sircar  
Air Products and Chemicals, Inc.  
7201 Hamilton Boulevard  
Allentown, PA 18195-1501

Keywords: Carbon membrane, Surface flow, Gas separation

## 1. Introduction

Petroleum refineries are among the largest users of hydrogen in the chemical industry. Hydrogen is used in hydrogenation, desulfurization and denitrogenation processes and a large source of hydrogen in refining operations is the production of aromatic compounds which are used as octane enhancers in gasoline. Environmental regulations are requiring refiners to reduce the amount of aromatic compounds in transportation fuel and, thus, the total amount of hydrogen produced in dehydrogenation processes is being reduced. In addition, refineries are being forced to use crudes which are higher in sulfur which further increases the total  $H_2$  needs. This requires refiners to make or buy hydrogen by conventional methods such as Steam-Methane Reforming or to recover hydrogen from their processes. The purpose of this paper is to describe the preparation and performance of a new carbon-based gas separation membrane and its application in two new processes for hydrogen recovery from refinery waste streams.

## 2. Selective Surface Flow™ Mechanism

Surface diffusion on nanoporous membranes is an attractive choice for practical separation of gas mixtures because the separation selectivity is determined by preferential adsorption of certain components of the gas mixture on the surface of the membrane pores, as well as by selective diffusion of the adsorbed molecules [1]. The Selective Surface Flow (SSF™) mechanism is shown schematically in Figure 1 for a mixture of hydrogen and hydrocarbons. The hydrocarbons are more strongly adsorbed on the pores than hydrogen on the high-pressure side of the membrane. These adsorbed components diffuse along the pore surface to the low-pressure side of the membrane where they desorb into the permeate stream. If the pores of the membrane are made small, the adsorbed layer of hydrocarbons serves to block the gas phase flow of hydrogen across the pore. Thus, the feed gas is depleted in the hydrocarbons and an enriched hydrogen stream is withdrawn at feed pressure. This is in contrast to typical polymeric membranes which selectively permeate hydrogen. Permeation selectivities of these membranes can be very high because the adsorption selectivity is high even at low feed pressure. The hydrocarbon permeability across the membrane will be high because the diffusivity for surface diffusion is orders of magnitude higher than typical diffusivities for these components through a polymeric matrix. This allows the membrane thickness to be 1-3 microns rather than the submicron membrane thicknesses typically needed for polymeric membranes. We have developed a novel nanoporous carbon-based membrane which exhibits these properties and shows very attractive gas separation properties for hydrogen/hydrocarbon and carbon dioxide/methane/hydrogen mixtures.

## 3. Membrane Preparation

We have prepared very thin, defect-free, nanoporous carbon membranes by converting a thin-film of polyvinylidene chloride polymer to carbon by pyrolysis. A polyvinylidene chloride (PVDC) latex (55 wt% solids) was cast on a porous graphite support; the film thickness was estimated to be between 5 and 10 microns. The coated support was then carbonized to temperatures between 600 and 1000C under nitrogen to convert the PVDC to carbon. This coating and carbonizing procedure was repeated up to five and the resultant carbon layer had a thickness of 1-3 microns.

Permeation properties of the carbon membrane were measured using a plate and frame membrane module. A schematic representation of the module is shown in Figure 2. It can hold 6 flat sheet carbon membranes to provide a total membrane area of ~0.5 ft<sup>2</sup>. The purge gas passed through the module countercurrent to the feed direction. The module was instrumented to allow measurement of feed and effluent gas flows and compositions.

The pore size of the membrane was estimated by comparing the pure methane diffusivity through the membrane to the methane diffusivity through zeolites of known pore structure [1]. It was found that methane diffusivity through the carbon membrane is in the activated diffusion regime

and the mean pore size is ~ 5.5A. This suggests that these membranes will exhibit the Selective Surface Flow properties.

#### 4. Practical Applications of SSF™ Membranes

##### 4.1 Recovery of Hydrogen From Refinery Fuel Gas

Refinery waste streams are typically used as fuel within the plant. They contain 20-50% H<sub>2</sub> and C<sub>1</sub>-C<sub>4</sub> hydrocarbons are available at pressures of 50 to 150 psig. Conventional separation methods are not amenable to hydrogen recovery from these streams because of low hydrogen recovery efficiency or high energy of separation. Pressure swing adsorption (PSA) process are commonly used in hydrogen separation and purification, however, the overall hydrogen recovery is low when the feed gas contains hydrogen concentrations less than ~50-60% [2]. Additionally, hydrogen PSA systems cannot handle C<sub>4</sub>+ hydrocarbons because these constituents are not easily desorbed from the adsorbent. Polymeric membranes are used in refineries for hydrogen recovery however they typically require high feed gas pressure (>300 psig) and they produce hydrogen at the low pressure side which requires recompression before being fed to a PSA system [3]. The use of two compression steps (feed and permeate) make this process very energy intensive.

A process to recover a good portion of the H<sub>2</sub> from such mixtures without further compression of the feed gas while rejecting a substantial portion of the hydrocarbons and has been patented by Air Products and Chemicals, Inc. [4]. The refinery waste gas is fed to an SSF™ carbon membrane module at the available pressure. The H<sub>2</sub>-enriched stream on the high pressure side of the membrane can then be compressed and separated in a conventional pressure swing adsorption (PSA) process to produce ultra-pure H<sub>2</sub>. The waste gas from the PSA system containing some H<sub>2</sub> and lower hydrocarbons can be used to provide the low-pressure purge stream for the membrane. Figure 3 shows a schematic flow sheet for such a membrane-PSA hybrid scheme.

The performance of the carbon membranes for separation of a multicomponent H<sub>2</sub>-hydrocarbon mixture was tested in plate-and-frame membrane module. A gas mixture containing 40.9% H<sub>2</sub>, 20.2% CH<sub>4</sub>, 19.8% C<sub>2</sub>H<sub>6</sub>, 9.2% C<sub>3</sub>H<sub>8</sub> and 9.9% C<sub>4</sub>H<sub>10</sub> (mole %) at 50 psig was used as the feed gas and a purge gas consisting of H<sub>2</sub>, CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> mixtures (typical PSA waste of Figure 3) was passed through the module in a countercurrent direction to the feed gas flow. The module was operated at -11.0°C and 25°C. It was found that the membrane could be used to produce a H<sub>2</sub>-enriched gas containing 56.0% H<sub>2</sub> while rejecting (to the lower pressure side) 100.0% C<sub>4</sub>H<sub>10</sub>, 92.0% C<sub>3</sub>H<sub>8</sub>, 67.5% C<sub>2</sub>H<sub>6</sub> and 36.0% CH<sub>4</sub>. The H<sub>2</sub> recovery in the membrane was 63.0%. The H<sub>2</sub>-rich gas was produced at 48 psig from the membrane unit (see Figure 3). These membrane clearly show Selective Surface Flow properties --- high rejection of heavier hydrocarbons and high hydrogen recovery at feed pressure.

The hydrocarbon-rich membrane reject gas could be used as fuel. The recovered H<sub>2</sub>-rich gas from the membrane could be further compressed to a pressure of 200 psig and fed to a conventional PSA system in order to produce a 99.99+% H<sub>2</sub> product with an overall H<sub>2</sub> recovery of ~43.0% from the waste feed gas. Thus, the nanoporous membrane can be used to recover a valuable chemical (H<sub>2</sub>) from a waste gas using only one compressor between the high pressure effluent and the PSA system.

A comparison of the relative energy requirement for recovering H<sub>2</sub> by this process and to make hydrogen using conventional Steam-methane reforming shows that the membrane/PSA hybrid process requires 15% energy less than reforming [6].

##### 4.2 Enhanced Hydrogen Recovery in Hydrogen Manufacture

Steam Methane Reforming (SMR) followed by separation of the reformer product (typically 75% H<sub>2</sub>, 20% CO<sub>2</sub>, 4% CO, and 1% CH<sub>4</sub>) in a pressure swing adsorption (PSA) system is the method of choice for H<sub>2</sub> manufacture today. The reject stream from the PSA (5 psig) contains a significant amount of hydrogen (approximately 20% of the PSA feed) which is used as fuel for the reformer (See Figure 4). The H<sub>2</sub> in PSA reject stream cannot be economically recovered by conventional technology because the hydrogen concentration and pressure are low.

SSF™ membranes have the advantage of operating very efficiently even at low pressures. These membranes can be used to increase the overall hydrogen recovery of the SMR/PSA process by recovering and recycling part of the hydrogen from PSA reject gas. A schematic diagram of the process patented by Air Products and Chemicals, Inc. [5] is shown in Figure 5. The reject of the PSA is compressed from 5 to 30 psig. An SSF™ membrane module is then used to selectively remove CO<sub>2</sub>, CO and CH<sub>4</sub> and enrich the hydrogen. The enriched hydrogen product from the membrane can be compressed and recycled to the PSA unit. A countercurrent CH<sub>4</sub> sweep gas is used on the low-pressure side of the membrane at 3 psig.

The performance of the SSF™ membranes for separation of CO<sub>2</sub> and CH<sub>4</sub> from H<sub>2</sub> was measured at 294K using a feed gas containing 35% H<sub>2</sub>, 55% CO<sub>2</sub>, and 10% CH<sub>4</sub>. It was assumed that CO behaves similar to CH<sub>4</sub>. The feed pressure was maintained at 30 psig and a low-pressure CH<sub>4</sub> sweep gas used at a flowrate of 15% of the feed flowrate and pressure of 3 psig. Under these conditions, the membrane was able to reject 87.5% of the CO<sub>2</sub>, 64.3% of the CH<sub>4</sub> while recovering 55% of the H<sub>2</sub>.

The overall hydrogen recovery from a SMR/PSA system shown in Figure 5 was calculated using the above membrane performance. The membrane selectively rejects the CO<sub>2</sub>, CO and CH<sub>4</sub> thereby reducing the flow of the recycle stream to the PSA feed and enriching the H<sub>2</sub> concentration. The addition of the recycle does not significantly change the PSA feed composition so that the PSA H<sub>2</sub> recovery remains constant. The overall hydrogen recovery for this process was 89.9% compared to a hydrogen recovery of 80% for the base case without the SSF membrane. This significant improvement in H<sub>2</sub> recovery is only possible because the SSF™ membrane can be operated efficiently at such low feed-gas pressure.

## 5. Summary

A novel microporous carbon membrane has been developed that uses adsorption and surface flow as the means of gas separation. These membranes have significant advantages in terms of energy efficiency and overall process performance for the separation of H<sub>2</sub> from refinery waste gas streams compared to conventional methods.

## 6. References:

1. M. B. Rao and S. Sircar, "Nanoporous Carbon Membranes for Separation of Gas Mixtures by Selective Surface Flow," *J. Membrane Sci.*, **85**, 253 (1993).
2. L. Lancelin, E. Rudelstrofer, M. A. Scholler, "Hydrogen Purification by Pressure Swing Adsorption," *Hydrogen Symposium of the French Association of Petrochemicals Engineers*, Feb. 26, 1976.
3. K. J. Doshi, U.S. Patent 4,460,695 (1987).
4. M. B. Rao, S. Sircar, J. M. Abrardo, and W. F. Baade, U. S. Patent 5,447,559 (1995).
5. M. Anand, M. B. Rao, and S. Sircar, U. S. Patent 5,435,836 (1995).
6. DOE Report, "Novel Selective Surface Flow Membranes for Recovery Of Hydrogen From Was Gas Streams," Work performed under Co-operative Agreement No. DE-FC04-93AL94461, August 1995.

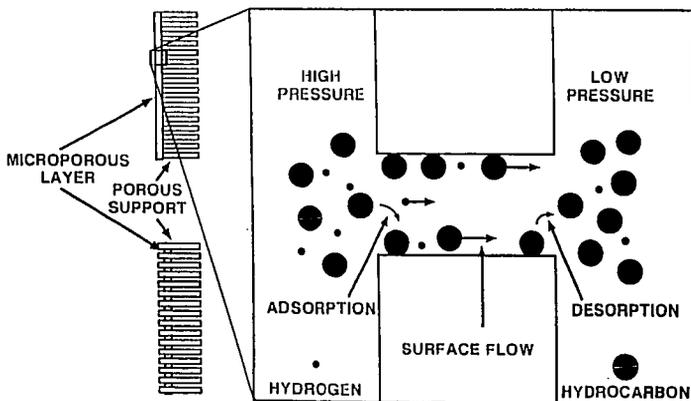


Figure 1: Mechanism of Gas Separation by Selective Surface Flow

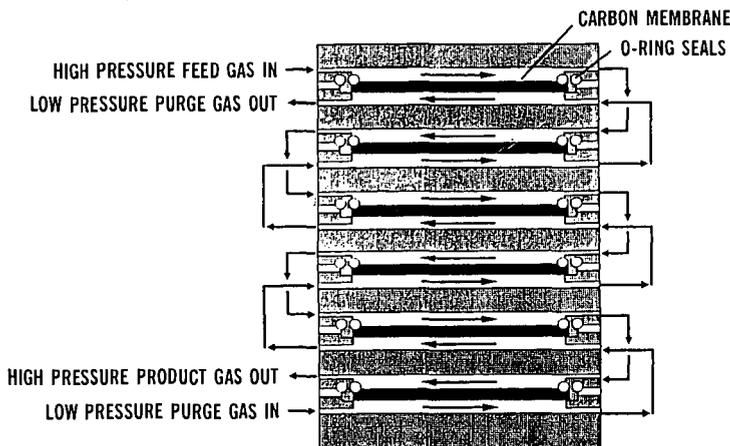


Figure 2: Plate-and-Frame Membrane Module

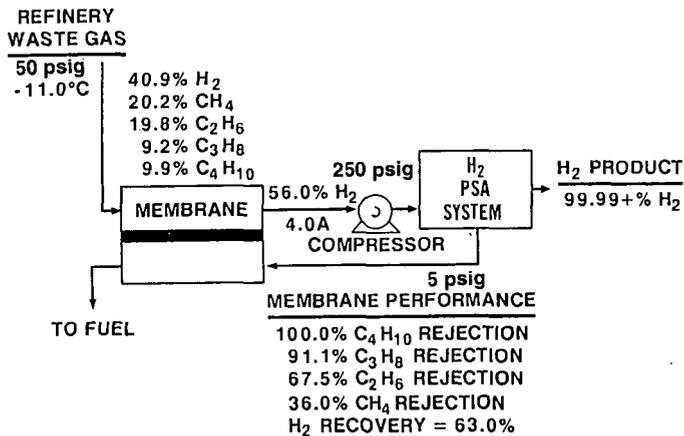


Figure 3: Process for Recovery of H<sub>2</sub> from Refinery Waste Streams

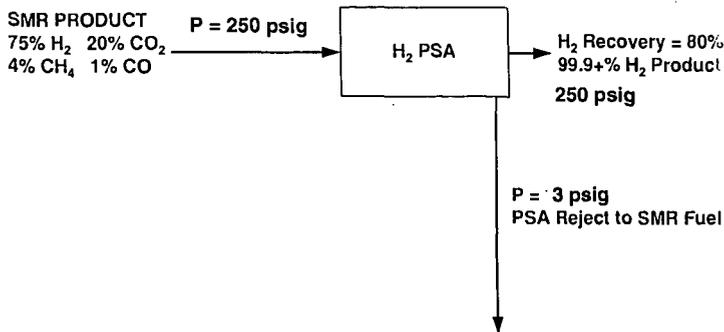


Figure 4: Conventional Process for H<sub>2</sub> Production

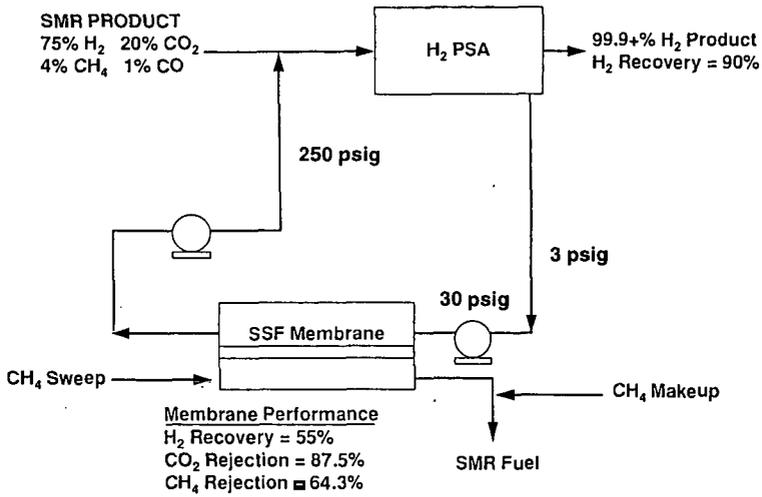


Figure 5: Enhanced H<sub>2</sub> Production using SSF Membranes