FINITE ELEMENT MODELING OF ADSORPTION PROCESSES FOR GAS SEPARATION AND PURIFICATION

Paul H. Humble, Richard M. Williams, and Jim C. Hayes

Pacific Northwest National Laboratory

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ABSTRACT

In the design and fabrication of improvements to automated radioxenon collection systems for nuclear explosion monitoring, there is an ever present need to reduce size, power consumption, and complexity. Most automated systems have used adsorption based techniques for gas collection and/or concentration and purification. These processes include pressure swing adsorption, vacuum swing adsorption, temperature swing adsorption, gas chromatography and hybrid processes that combine elements of these techniques. To better understand these processes, and help with the development of improved hardware, a finite element software package (COMSOL Multiphysics) has been used to develop complex models of these adsorption based operations. The partial differential equations used include a mass balance for each gas species and adsorbed species along with a convection conduction energy balance equation. These equations in conjunction with multicomponent temperature dependent isotherm models are capable of simulating separation processes ranging from complex multibed pressure swing adsorption processes, and multicomponent temperature programmed gas chromatography, to simple two-component temperature swing adsorption. These numerical simulations have been a valuable tool for assessing the capability of proposed processes and optimizing hardware and process parameters.

OBJECTIVES

The objective of this work was the development of mathematical models of adsorption and chromatographic processes used for processing radioxenon from atmospheric air. These models enable a better understanding of adsorption processes and serve as useful tools in the development of improved processes and hardware. The purpose of this work is the development of improved collection and separation techniques for the next international radioxenon systems.

Measuring radioactive xenon in the atmosphere is an important technique in nuclear explosion monitoring, and has been included as one of the techniques used for verification under the Comprehensive Nuclear-Test-Ban Treaty (CTBT). Bowyer et al. (1999) described an automated radioxenon sampler-analyzer (ARSA) system developed for CTBT monitoring that collected and analyzed four xenon radionuclides: ¹³¹mXe, ¹³³mXe, ¹³³Xe, and ¹³⁵Xe. The activity ratios of these radionuclides are unique for a nuclear detonation and the ability to measure these ratios is important in differentiating a nuclear detonation from a nuclear reactor release. Dilution in the atmosphere and radioactive decay require collecting and concentrating xenon from a large volume of air. The ARSA system trapped xenon by passing a stream of compressed, dry, and CO₂ depleted atmospheric air through a cooled charcoal bed. Ringbom et al. (2003) describe the Swedish Automatic Unit for Noble gas Acquisition (SAUNA) that collects xenon using larger charcoal beds at ambient temperatures. Both of these systems use chromatographic techniques for sample purification. There is a need to reduce the cost, size and power requirements of such systems. Since a large portion of the size and energy requirement is dictated by gas processing, better collection and separation techniques are required to develop smaller, cheaper, and lower power systems with greater flexibility.

The separation and purification of trace gasses from atmospheric samples is most often accomplished using processes including cryogenic adsorption, membrane permeation, pressure swing adsorption, temperature swing adsorption, and chromatography. These techniques use differences in adsorption affinity and/or transport properties of gas species in a porous material to accomplish component separation. Chromatographic and adsorption process are especially similar and can be described using the same mass and energy balance equations. Mathematical models of adsorption and chromatographic separations can be used to develop improved processes and hardware for the capture and concentration of xenon from atmospheric air. This paper describes time dependent models of such processes developed and implemented using COMSOL Multiphysics. These models have helped in comparing proposed processes and developing new techniques and hardware to separate and concentrate xenon.

The mathematical equations presented have been used to model both adsorption and chromatographic processes ranging from 1D multi-component chromatography to 3D temperature dependent pressure swing adsorption. These equations are similar to those others have used to model adsorbing systems (Yang 1997, Farooq 1991, Farooq 1993) The models are general enough to simulate separation processes based on kinetic or equilibrium properties. This makes it possible to use the same set of equations to model materials ranging from activated carbon to molecular sieves.

RESEARCH ACCOMPLISHED

Model Description

The following four assumptions and simplifications have been used in developing the mathematical model: 1) The flow of gasses through the porous media is described by Darcy's law. This implies flow through the bed where the gas velocity is proportional to the pressure gradient. 2) The ideal gas law is used to describe the relationship between gas density (concentration), pressure, and temperature. 3) Adsorption equilibrium is described using temperature dependent competitive Langmuir isotherms, and in implementation it is assumed that each species has the same saturation capacity. However, it is possible to use other equations describing multicomponent adsorption. 4) Mass transfer between the gas and adsorbed phase is described using a linear driving force model. This implies that the rate of adsorption or desorption is proportional to the difference between the actual amount adsorbed and the amount that would be adsorbed if the bed where at equilibrium. To model equilibrium driven processes, the rate constant of the linear driving force model is made large enough such that equilibrium is closely approximated. Kinetically driven processes can be modeled by substituting suitable rate constants.

The system of partial differential equations used to model these processes is derived starting with Darcy's Law (equation 1) and the ideal gas law (equation 2) to define gas velocity and pressure. The variable c_i represents the concentration of species *i* in the gas phase based on the gas phase volume as opposed to the total system volume. A description of the constants and variables appearing in the mathematical model is shown in Table 1.

$$v = \frac{-\kappa}{\varepsilon \cdot \mu} \cdot \nabla P \tag{1}$$

$$P = R \cdot T \cdot \sum_{i} c_{i} \tag{2}$$

Equations 1 and 2 can be combined to provide the convective flux term of an overall time dependent mass balance equation for each gas phase species (equation 3).

$$\varepsilon \frac{\partial c_i}{\partial t} + \nabla \cdot \left(-\varepsilon \cdot D_{i,gas} \nabla c_i - c_i \frac{\kappa}{\mu} \nabla (R \cdot T \sum_{j=1}^n c_j) \right) = F_i$$
(3)

The dispersive term describes gas phase diffusion, but can also be adjusted to account for Taylor dispersion arising from laminar flow mixing in the inter particle flow paths.

There is no convection term for adsorbed species and the overall mass balance equation for adsorbed species simplifies to equation 4. The surface diffusion (dispersion) term can also be neglected in most cases. However, including a dispersive term may improve model stability by decreasing the sharpness of moving fronts in the time dependent model.

$$\frac{\partial c_{iad}}{\partial t} + \nabla \cdot \left(D_{i,sur} \nabla c_{iad} \right) = -F_i \tag{4}$$

The rate of species transfer from the adsorbed phase to the gas phase (F_i) is defined in equation 5. This equation is the linear driving force model with the equilibrium condition modeled using a multi-component Langmuir isotherm where the ideal gas law has been used to convert from partial pressure to gas phase concentrations.

$$F_{i} = K_{i} \cdot \left[c_{iad} - \frac{\rho_{bed} R \cdot T \cdot N_{io} b_{i} c_{i}}{1 + R \cdot T \cdot \sum_{i} (b_{i} c_{i})} \right]$$
(5)

Equation 6 defines the temperature dependent term b_i (related to the Henry constant) in the temperature dependent Langmuir isotherm.

$$b_{i} = \frac{b_{o,i}}{N_{io}} \cdot \exp\left(-\frac{q_{st,i}}{R \cdot T}\right)$$
(6)

Additionally, an energy balance equation that includes convection and conduction is used to model heat transfer in the adsorption bed (equation 7). In the derivation of this equation it is assumed heat transfer between the solid and gas phase is fast enough such that temperature equilibrium is achieved and a single temperature at each point in the bed can be used for both the gas and solid phase.

$$\left((1-\varepsilon)\rho_{s}C_{p,s}+\varepsilon\rho_{g}C_{p,g}\right)\frac{\partial T}{\partial t}+\nabla\cdot\left(-k\nabla T\right)+\rho_{g}C_{p,g}\left(-\frac{k}{\mu}\nabla\left(R\cdot T\cdot\sum_{i}c_{i}\right)\right)=-\sum q_{st,i}F_{i}$$
(7)

v	Gas superficial velocity (m/s)
κ	Permeability (m ²)
3	Bed void fraction
μ	Viscosity (Pa·s)
Р	Pressure (Pa)
R	Gas constant (J/mol·K)
Т	Temperature (K)
c_i	Concentration of species <i>i</i> in the gas phase (mol/m^3)
C_{iad}	Concentration of species <i>i</i> in the adsorbed phase based on bed volume (mol/m ³)
$D_{i,gas}$	Species <i>i</i> diffusion (or dispersion) constant in the gas phase (m^2/s)
$D_{i,sur}$	Species <i>i</i> diffusion (or dispersion) constant in adsorbed phase (m^2/s)
F_i	Rate of species <i>i</i> transfer from adsorbed to gas phase (mol/s·m ³)
ρ_{bed}	Mass of adsorbent per bed volume (g/m ³)
Nio	Maximum number moles of species <i>i</i> on adsorbed phase (mol/g)
K_i	Linear driving force rate constant for species i (1/s)
$b_{,i}$	Henery's law constant for species <i>i</i> divided by N_{io} (1/Pa)
$b_{o,i}$	Temperature independent constant for species $i \pmod{g \cdot Pa}$
ρ_s	Density of solid (g/m ³)
$ ho_g$	Density of gas (g/m ³)
$q_{st,i}$	Infinite dilution isoteric heat of adsorption (J/mol)
k	Thermal conductivity of the bed (W/m·K)
$C_{p,s}$	Solid phase heat capacity (J/g·K)
$C_{p,g}$	Gas phase heat capacity (J/g·K)

Table 1. Description and units for constants and variables appearing in mathematical model

The basic mathematical model consists of mass balance equations (3 and 4) for each gas phase and adsorbed species, and the energy balance equation (7) to describe the transport of heat in the bed and define the temperature. These partial differential equations will describe both adsorption and chromatographic processes. However, the boundary conditions used in implementing the model will be different for these separation processes.

Model Results

One of the first processes modeled using the described equations was gas chromatography in an adsorbing carrier gas. Of interest was how the adsorbing carrier impacts peak shape and separation efficiency. Figure 1 shows the modeling results for a separation of three components in an adsorbing carrier gas. In this simulation two of the components are more strongly adsorbed than the carrier and one component is more weakly adsorbed. Such separations may occur in gas processing after the initial collection. For instance, separating xenon in a gas mixture containing oxygen, nitrogen, and CO_2 using a nitrogen carrier gas. In Figure 1 the first peak on the right corresponds to the gas species with the smallest adsorption affinity, this species has lower affinity compared to the carrier gas. The other two peaks correspond to species with a higher adsorption affinity.

Another basic process that was modeled is the pressure swing enrichment of xenon from a gas consisting of a dilute mixture of xenon in nitrogen. Such an enrichment process is similar to those used in both the ARSA and SAUNA systems. Figure 2 shows how the gas phase concentration changes during depressurization. The finite element model is able to show how the pressure drop through the bed influences the gas phase concentration during the depressurization.

An important feature of these models is the ability to simulate a series of processes such as a pressure swing followed by an increase in temperature or flow of a purge gas. Such processes occur in gas processing when concentrating and isolating a desired product from a multi-component mixture. For instance, a pressure swing step can be used to initially concentrate xenon in air, increasing the temperature can be used to desorb xenon and further increase the gas phase concentration, and then gas chromatography can be used to separate xenon from other species by flowing a carrier gas through the bed.



Figure 1. Simulation of a gas chromatographic separation of 3 components in an adsorbing carrier gas.



Figure 2. Mole fraction of xenon (A) during column depressurization (B). The column was depressurized by setting the outlet pressure to 2 psia. Xe was adsorbed on the column at 80 psia inlet pressure.

The equations presented can also be used to simulate heat and mass transfer in more complex geometries. This makes it possible to model the performance of hardware, and see how factors such as bed diameter and length impact performance. This ability helps in the optimization of hardware and processing. An example of this capability is shown in Figure 3. This figure shows the temperature profile inside an adsorbing cylindrical bed at 10 seconds, where the outside of the bed is held at room temperature (298 K). The bed temperature increases due to the heat of adsorption and heat is dissipated out through the walls of the bed, as well as convection of gas through the bed. Simulations such as these show how the thermal conductivity of the adsorbent, bed geometry, permeability (related to packing size and shape), and pressurization rate influence performance. Many of these parameters are difficult to experimentally measure. For instance, it is possible to measure a few temperatures inside and outside an adsorbing bed, but a simulation can show the temperature at all points inside a bed, and how the temperature profile develops over time. The model allows one to adjust parameters to optimize performance, before a design or process is committed to hardware. Of course, the model results need to be experimentally verified.

In our experience there is a synergy in combining mathematical simulation and experiment. One such example is a pressure swing process for enriching xenon developed using input from a simulation. An experimental device was constructed and tested, but did not perform as expected. It was hypothesized that the discrepancy may be due to higher dispersion in the experimental device compared to the simulation. The simulation was run with increased gas phase dispersion, confirming a negative impact on process performance. The simulation was then used along with permeability and dispersion correlations for packed beds to optimize the bed packing size for the process. Experimental results with the new packed beds were in line with the simulation results. The mathematical model helped identify what design parameters could be involved in the poorer than expected performance, and identify needed improvements. Further experiments verified the simulation results.



Figure 3. This simulation of a pressurizing activated carbon bed shows the temperature profile inside the bed at 10 seconds after pressurization begins.

CONCLUSIONS AND RECOMMENDATIONS

Mathematical models of gas phase adsorption processes have been developed and used to simulate operations used to capture and purify xenon from atmospheric air. The equations derived are general enough to model pressure swing, vacuum swing, temperature swing, and chromatographic processes. Simulation results have been used to verify experimental results, and develop improved hardware and operating procedures. The synergy between simulation and experiment has been an important factor in optimizing processes. Simulation allows better understanding of a process by allowing the visualization of variables not easy accessed experimentally such as the temperature profile, adsorbed phase concentration and gas phase concentration inside the bed. Experimental verification is essential to insure the physics in the model adequately describe reality. This comparison has increased our understanding of adsorption based processes and has been helpful in troubleshooting and improving separation techniques.

The model results are only as good as the parameters going into them. Good isotherm data for adsorbents is especially important. Some of this data can be found in the literature, but data for other adsorbents is desired. Mathematical models are important tools for assessing how a new adsorbent may improve a process. To use these tools adsorption isotherms and other physical adsorbent properties need to be measured. At present, the models have used activated charcoal and molecular sieve properties obtained from the literature. Our future work will include

extending the number of adsorbents that can be modeled. This will require obtaining samples of promising adsorbents and experimentally measuring the adsorption and physical properties of these materials. Numerical simulation with an increased library of materials will be used to identify improved techniques and optimize hardware for processing radioxenon from atmospheric air. The goal of this work is to develop improved collection processes for the next generation international radioxenon systems.

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