

**Finite Element Modeling:
Mercury Capture by Fly Ash Carbon Sorbent in a
Fixed Bed**

An EGEE 520 Final Paper

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Abstract

Mercury can be considered one of the most toxic components in a flue gas. On March 15, 2005 the U.S. EPA passed new mercury emission regulations to permanently cap and reduce these harmful emissions. To comply with this rule, coal-fired power plants will need to implement new mercury control technologies, a promising one being the injection of a carbon sorbent, such as fly ash, into the flue gas stream. Fly ash is a prime candidate due to its inherent porosity, adsorption properties, and on-site availability. Currently 63% of the fly ash produced in this country is disposed as waste, which is another reason to recycle and reuse the fly ash as a carbon sorbent.

As part of this project, vapor-phase elemental mercury adsorption was performed by a fixed-bed fly-ash carbon sorbent system. The system was modeled and analyzed as 2-D finite element. The governing equations used in the model include convection and diffusion equations incorporated with incompressible Navier-Stokes. Many assumptions were made to simplify this project, such as assuming transient, laminar flow through the sample tube and no flow through the insulated boundaries.

The system initially included three local elements: two glass wool sections sandwiching a larger fly ash-packed section. By relating different diffusion coefficients between the fly ash sorbent and glass wool plug, it was shown that the glass wool has a very minimal effect on the adsorbance of the system as a whole. Consequently, the section containing the fly ash was focused on in the model. The progress of the mercury vapor through the element is modeled as it reaches saturation at the outlet of the sample tube.

The results obtained from the COMSOL modeling program showed that velocity development and mercury breakthrough occurs more quickly at the center of the element (sample tube) than at any other point. The slowest velocity development and mercury breakthrough occurs along the sides of the sample tube.

The adsorption through the modeled element behaves as expected based on fully developed laminar flow through a tube or pipe. The adsorption breakthrough curve generated by COMSOL also closely resembles the results obtained via experimentally obtained data. With an increase in reaction rate, or rate of adsorption, breakthrough occurs much more quickly as expected. This behavior also resembles experimental data obtained from fly ash that has a faster adsorption rate.

Overall, COMSOL is an effective modeling tool for this application. It generates results that are consistent with experimentally obtained data and allows for the configuring of all important variables involved in convection and diffusion. Ultimately, more research and investigation would be needed to determine more accurate parameter identification (e.g., force velocity, dynamic viscosity, diffusion coefficient) for the fly ash samples that have been experimented with.

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1. Introduction

Harmful gases emitted from the flues of various combustion processes, including those utilized by coal-fired power plants, have long been a prevalent source of environmental poisoning. Mercury can be considered one of the most toxic components in a flue gas. On March 15, 2005 the U.S. EPA passed new mercury emission regulations to permanently cap and reduce these harmful emissions. Once fully implemented, the Clean Air Mercury Rule will require the reduction of utility mercury emissions by approximately 70% [1]. To comply with this rule, coal-fired power plants will need to implement new mercury control technologies, a promising one being the injection of a carbon sorbent, such as fly ash, into the flue gas stream [2]. Other research performed to remove elemental mercury (Hg^0) from flue gas includes column, fixed-bed reactor systems packed with sorbent, which adsorb the undesired components [3-5].

Fly ash is a prime candidate due to its inherent porosity, adsorption properties, and on-site availability [6]. Currently 63% of the fly ash produced in this country is disposed as waste, which is another reason to recycle and reuse the fly ash as a carbon sorbent [7]. The mercury-laden ash can then be captured by a particulate control device, such as a bag house, to be removed and treated [8]. The porous surface of the sorbent [6], phase transitions or the presence of multiphase systems [9,10], material of which the sorbent is comprised [11], the packing heterogeneity, and the presence of a thermal gradient within the column affect the conditions and results of mercury capture.

As part of this project, vapor-phase elemental mercury adsorption was performed by a fixed-bed fly-ash carbon sorbent system as performed in some previous studies [3,6]. Especially on adsorption systems, as in this project, many different models were maintained in previous studies [12-15]. In most cases, as well as this one, the system is considered and modeled as finite element [16,17].

The system was modeled and analyzed as 2-D finite element [18]. In the system, concentration distribution and flux change are of significant importance. First of all, the boundary conditions, such as concentration of mercury vapor, diffusion coefficients, and flow speed, were determined for the 2-D finite element. The transport through the porous fly-ash carbon sorbent, involving convection and adsorption, was modeled following Darcy's Law [19,20], which is a laminar flow model for flows through porous media, and the Galerkin model for flow [21,22]. Conservation and mass transport equations were determined along with initial and boundary conditions for the model.

The global system includes three elements. The sample tube is packed with glass wool at both ends to hold the sorbent in place with minimal effects on mercury sorption. Each glass wool section is considered a separate element sandwiching the fly ash section in-between. The global nodes were identified in the system, and a conversation between local and global nodes was determined.

The second part of the project is a computational section that evaluates the data that has been obtained. All initial and boundary conditions were transferred into COMSOL

Multiphysics. The formulas which were developed from initial and boundary conditions were also transferred onto COMSOL by using a 2-D finite element program in order to model the solution. As final step, validations and a complete parametric study were performed between theoretical and computational solutions for correlation of results. The correlation was analyzed and conclusions were made according to the efficiency of the method that was followed.

2.1. Governing Equations

These equations are used for the revised solution model which indicates the ultimate study. They include convection and diffusion equations incorporated with incompressible Navier-Stokes. The convection and diffusion equations are as follows:

$$\delta_{ts} \frac{\partial c}{\partial t} + \nabla \cdot (-D \nabla c) = R - \underline{u} \cdot \nabla c$$

$$\nabla = \underline{i} \left(\frac{\partial}{\partial x} \right) + \underline{j} \left(\frac{\partial}{\partial y} \right) + \underline{k} \left(\frac{\partial}{\partial z} \right)$$

The incompressible Navier-Stokes equations are as follows:

$$\rho \frac{\partial \underline{u}}{\partial t} + \rho (\underline{u} \cdot \nabla) \underline{u} = \nabla \cdot [-\rho \underline{I} + \eta (\nabla \underline{u} + (\nabla \underline{u})^T)] + \underline{F}$$

$$\nabla \cdot \underline{u} = 0$$

The variables in these equations can be defined as follows: Δ = del operator, δ_{ts} = time-scaling coefficient, D (anisotropic) = diffusion coefficient (m^2/s), c = concentration (mol/m^3), R = reaction rate ($mol/(m^3 \cdot s)$), u = x-velocity, v = y-velocity (from velocity vector), ρ = density (kg/m^3), η = dynamic viscosity ($Pa \cdot s$), F_x = volume force, x-direction (N/m^3), F_y = volume force, y-direction (N/m^3)

2.1.1. Assumptions

Many assumptions were made to simplify this project. A transient, laminar flow of gas through the sample tube is assumed. Also, the fixed bed is said to be packed uniformly with carbon sorbent. The mineral wool plug used to hold the sample in place has only a very slight effect on the diffusion of the gas through the sample tube. Since the tube is a uniformly packed cylinder, the flow in the z-direction can be modeled as the flow in the y-direction; therefore a 2-D analysis is sufficient for this project. c_1 is the concentration at the entrance of the sample tube. c_2 , the concentration at the outlet of the sample tube, is initially 0 mol/m^3 until the breakthrough point, which is the instant when mercury vapor finally reaches and exits the sample tube outlet. Another assumption made is that all of the mercury present in the gas is adsorbed by the carbon sorbent until it becomes saturated moving along the sample tube from the inlet to the outlet.

2.1.2. Boundary and Initial Conditions

The boundary conditions prescribed for this model are that there is no flow out of the glass tube boundary – the top and bottom boundary layers are insulated (refer to figure 2.1). Also, the mass flow rate of gas through the sample tube is set at 40 mL/min. The initial condition is that at $t = 0$, $c_1 = 10 \text{ mol/m}^3$ and $c_2 = 0 \text{ mol/m}^3$.

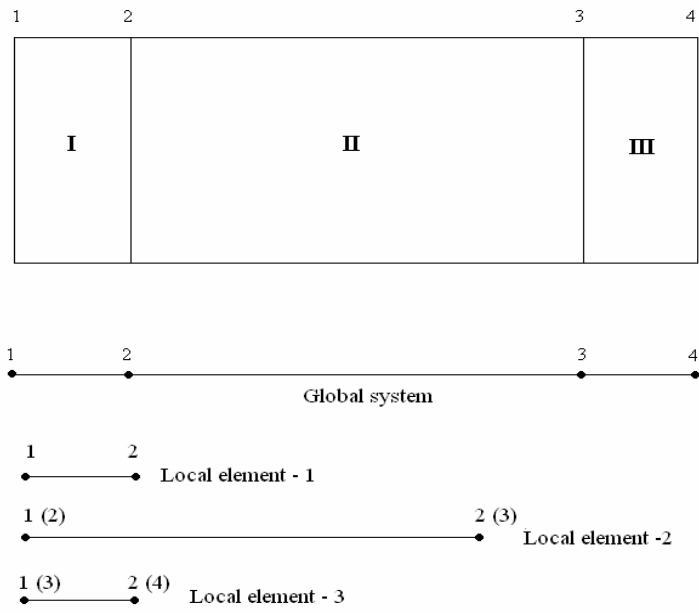
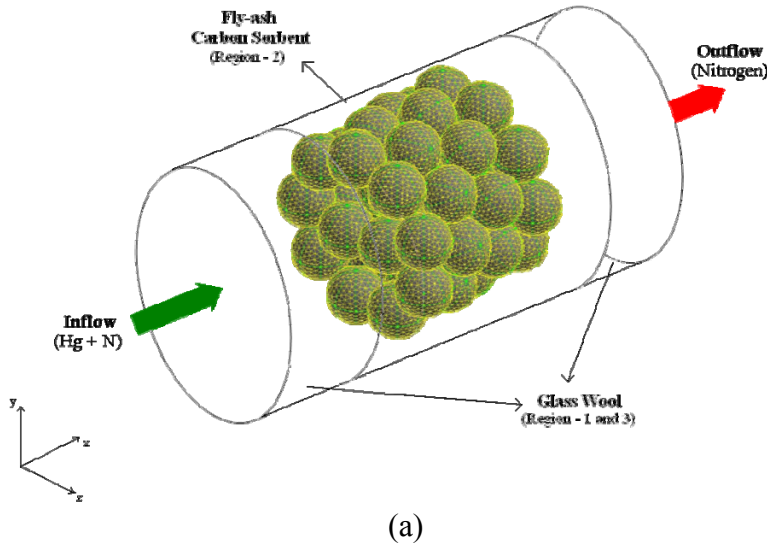


Figure 2.1: Diagram of the sample tube system (a) and global and local node identification (b).

For this project system, shown in figure 2.1, the 3-D graphic indicates the real system where carbon sorbent is packed into a glass tube with glass wool at each end to hold the sample in place. Fluid (gas mixture) flow is in the “x” direction. The rectangular shape below this represents the global system with global nodes 1, 2, 3, and 4. There are three regions within the global system. Region – 1 and Region – 3 have the same physical properties, such as the same diffusion coefficient, as these regions are both filled with glass wool. Region – 2 is filled with fly-ash carbon sorbent with a much higher diffusion coefficient. In the overall system, there are three local elements which are shown by straight lines and dots which refer to nodes. Local elements have both local nodes (1, 2) and their corresponding global nodes in parentheses.

2.2. Initial Formulation and Solution

Three geometries with multiphysical properties were determined for the identification of boundary and subdomain settings, as shown in figure 2.2.1. Global node-2, which is shared by geometry-1 and 2, and global node-3, which is shared by geometry-2 and 3, are connected by “*identity boundary conditions*” as both nodes are to have the same concentration component “*c*” in the system. Subsequently, in each geometry the boundary conditions are identified individually. For geometry one, the local node-1 (global-1, local boundary-1) is adjusted to “*concentration*” with $C = C_0 = 10 \text{ mol/m}^3$. Local node-2 (global-2, local boundary-4) is adjusted to “*convective flux*” since the concentration component of the system for this boundary is not predictable. Also part of geometry-2, local node-1 (global-2, local boundary-1) and local node-2 (global-3, local boundary-4) which is the same as local node-1 in geometry-3 (global-3, local boundary-1) are identified as “*convective flux*” for similar reasons. For geometry-3, the final concentration of local node-2 (global-4, local boundary-4) is identified initially to be $C = C_f = 0 \text{ mol/m}^3$. A discussion on the validity of this can be found in the Validation section (section 3) and a revised solution follows. The boundaries found at the top and bottom (local boundary-2 and 3) in the overall system are insulated.

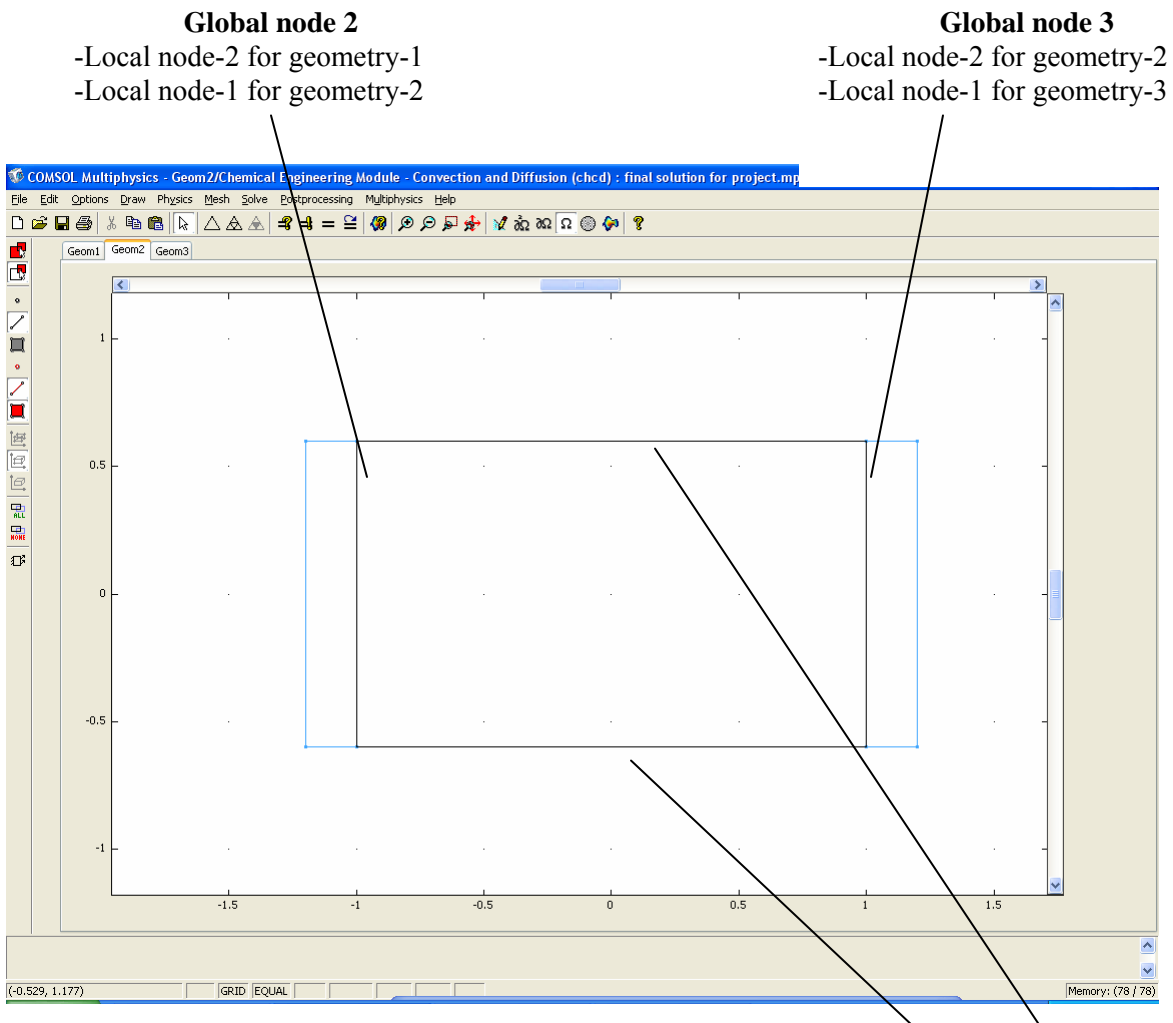


Figure 2.2.1: Defined Geometries

Since our system has three geometries, where 1 and 3 are identical, the “*diffusion coefficients*” are defined according to the component’s behavior in these medias. Element-1 and 3 are comprised of “*glass wool*” and the diffusion coefficient in these mediums is identified as $10 \text{ cm}^2\text{s}^{-1}$, accordingly. The fly-ash carbon media is located in element-2 and its diffusion coefficient is defined as $1 \text{ cm}^2\text{s}^{-1}$. The magnitudes of the diffusion coefficients were chosen simply to demonstrate the different behaviors of the media based on how they were known to perform from experimental observation. Glass wool does not have any significant effect on the overall adsorption capacity of this system; therefore, the very small decrease in mercury concentration observed in element-1 and 3 is expected. Substantial amounts of Hg are adsorbed in element-2, where the sorbent is located. Results for each element are shown in figures 2.2.2 to 2.2.4 below. The system begins with a concentration of 10 mol/m^3 Hg and as the vapor flows from

geometry-1 to 3, the concentration change is easily obtainable until it reaches zero at the end of the system. Ultimately, this is a snapshot of the instant just before the breakthrough point of mercury adsorption by the fly ash carbon sorbent. The breakthrough point, as mentioned previously, is the instant at which the mercury vapor has finally progressed the entire way through the sample tube and is observed or measured exiting the sample tube at its outlet. It usually occurs just after the sorbent becomes fully saturated with mercury vapor. When it can no longer adsorb, the sorbent will allow the mercury vapor to pass through the sample tube uninhibited.

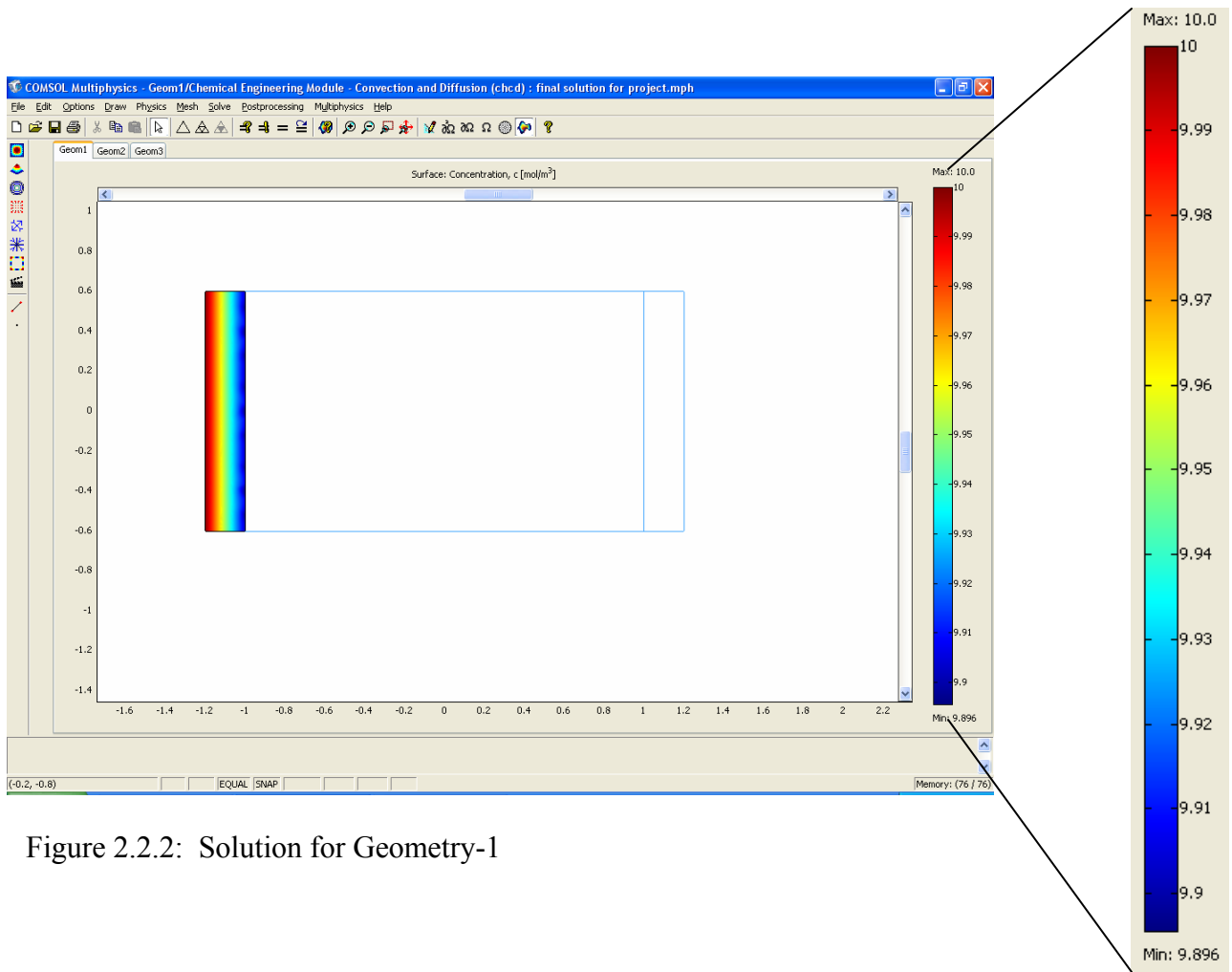


Figure 2.2.2: Solution for Geometry-1

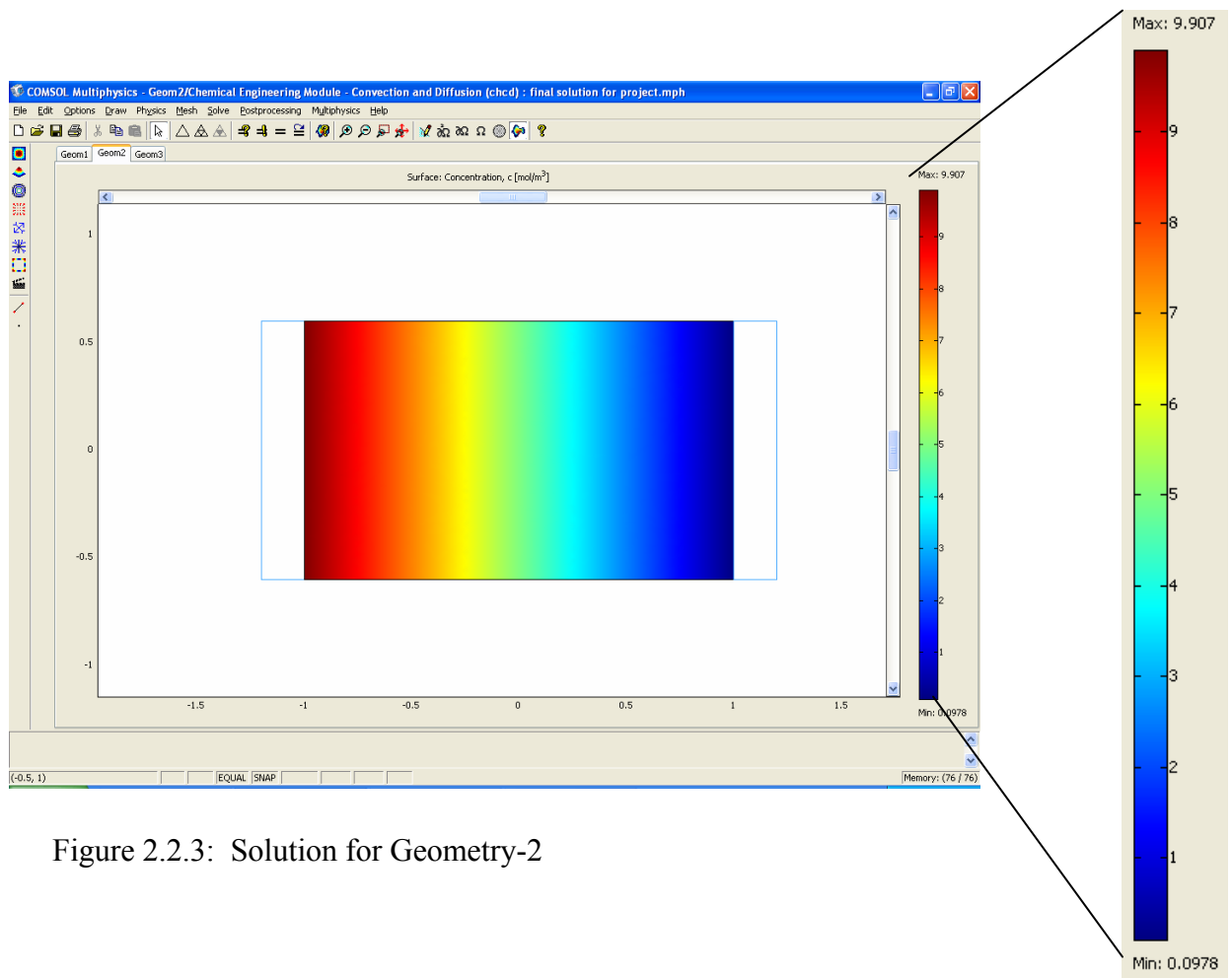


Figure 2.2.3: Solution for Geometry-2

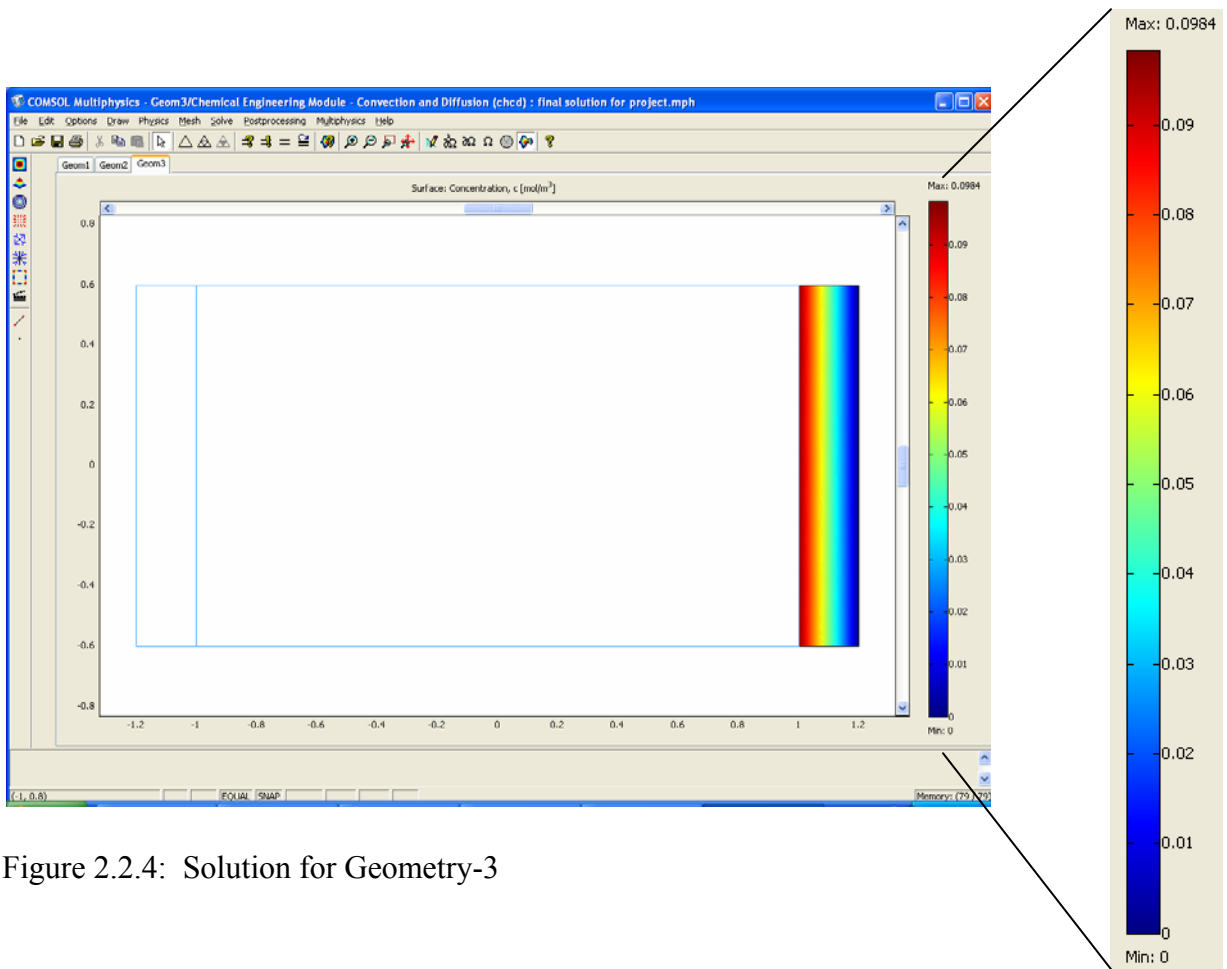


Figure 2.2.4: Solution for Geometry-3

3. Initial Solution Validation

To validate the accurateness and workability of our project's solution derived from COMSOL, the concentration values at the input (boundary 1, global) were varied from 10 to 20 and then to 100 mol/m³. After comparing the *cross-section plots* of the resulting solutions, it became apparent that adjustments needed to be made to the original solution which is consistent with the comments given with the grading of our original solution. In each case, the concentration decreases slightly through the glass-wool section of the system, but then drops off rapidly to nearly zero in the adsorbent section of the system (see Figures 3.1, 3.2, and 3.3). This happens conversely to what is expected in a real-world scenario. With all other things held constant (e.g. fly ash sorbent volume, mass flow rates, and diffusion coefficients), it would make sense that as the concentration of

mercury at the inlet to the sample tube increases, the mercury concentration at the end of the sample tube would also increase – that the same volume of fly ash would adsorb the same amount of mercury then allow the excess to pass through and out of the sample tube, especially when the inlet concentration is increased ten-fold. The problem is a result of the ending global boundary of the system being set to a concentration of 0 mol/m^3 . This was originally done to simulate the system conditions at the point just before mercury breakthrough, or at the point where the sample becomes fully saturated and the incoming mercury vapor is not adsorbed, thereby passing through and out of the system.

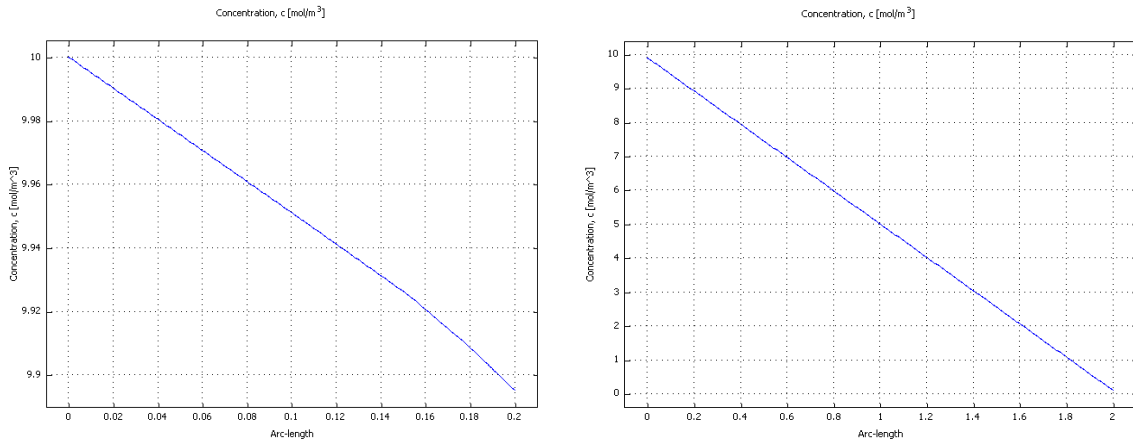


Figure 3.1: Concentration 10 mol/m^3 with $D = 10 \text{ m}^2/\text{s}$ (left) and $D = 1 \text{ m}^2/\text{s}$ (right).

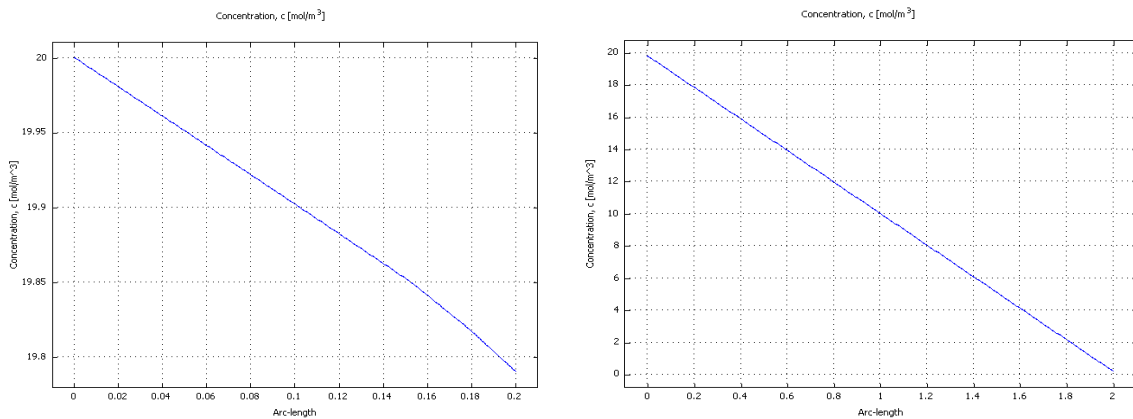


Figure 3.2: Concentration 20 mol/m^3 with $D = 10 \text{ m}^2/\text{s}$ (left) and $D = 1 \text{ m}^2/\text{s}$ (right).

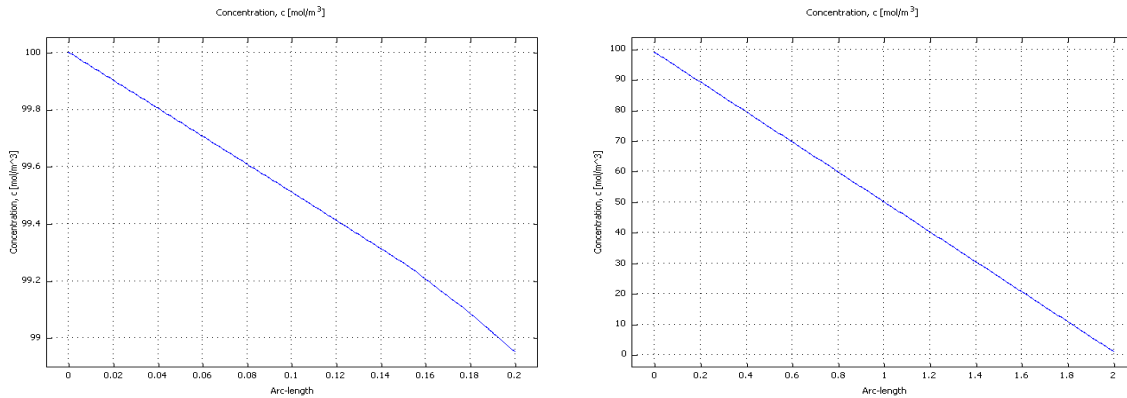


Figure 3.3: Concentration 100 mol/m^3 with $D = 10 \text{ m}^2/\text{s}$ (left) and $D = 1 \text{ m}^2/\text{s}$ (right).

To correct this problem, incompressible Navier-Stokes equations needed to be added to each geometry. The reaction rate was adjusted and a free-convective condition was added at the downstream end, or outlet of the sample tube rather than prescribing a concentration for this point.

4. Revised Solution

The revisions made included utilizing the *transient analysis* of a *reacting flow* under *Fluid-Chemical Reactions Interaction* in the *Predefined Multiphysics Couplings* application mode in COMSOL. This mode allows for the incorporation of incompressible Navier-Stokes equations as well as convection and diffusion equations into the model geometries.

For this solution, the central element (where the fly ash sorbent is located) was focused on. The minimal effect the glass wool has on the system can be observed in the initial solution where the effect of varying diffusion coefficients was examined. The adsorption modeled through this element shows the velocity field as well as the concentration change during adsorption. The progress of the mercury vapor through the element is modeled as it reaches saturation at the outlet of the sample tube.

The results of the COMSOL modeling show a curve-shaped progression of adsorptive flow through the element, as can be seen in figure 4.1. The first time this system was evaluated, a negative concentration was observed as the minimum in the concentration range, which is known as “overshooting” and is an unrealistic result. Re-meshing the system to a very fine mesh (meshing three more times) produced non-negative, more believable results that were incorporated into the revised solution. The vapor flow is shown to move most quickly through the sample tube at the center where the flow develops most quickly, see figure 4.2.

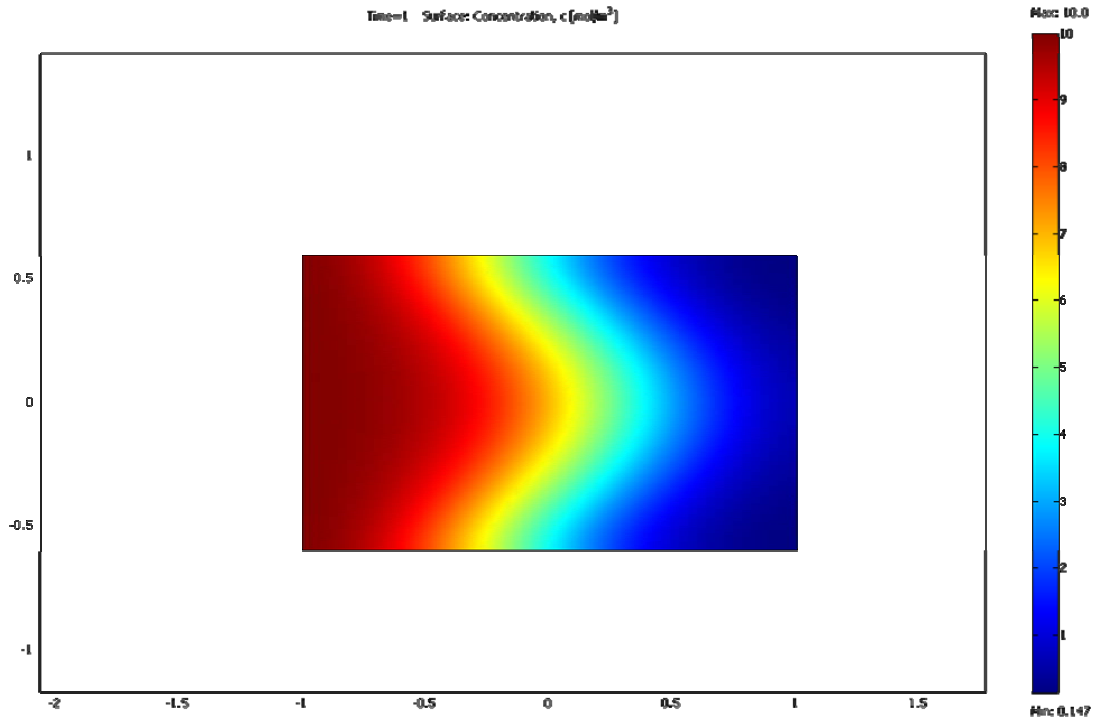


Figure 4.1: A snapshot of the revised solution plot of mercury concentration movement over time.

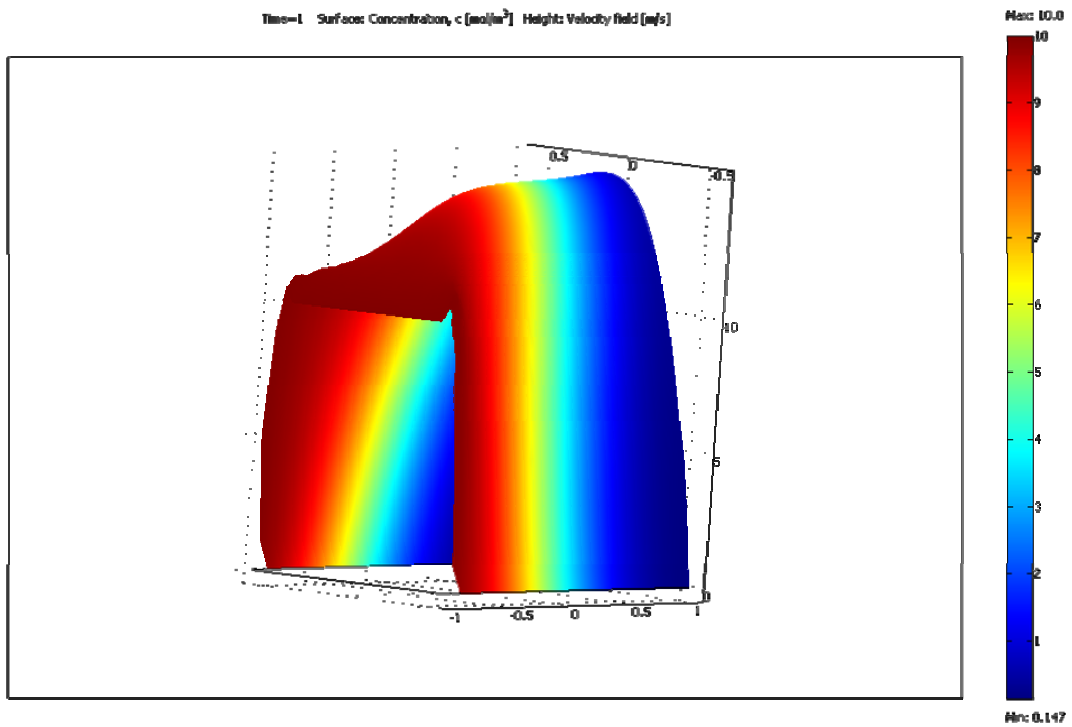


Figure 4.2: A 3-D snapshot of the revised solution showing development of velocity and the movement of mercury concentration over time.

The velocity profile obtained by the COMSOL model shows that the flow through the sample tube develops most quickly at the center of the tube and more slowly near the sides of the tube, as displayed in figures 4.3 and 4.4. As expected, this flow closely resembles the behavior of developing laminar flow through a tube or pipe [23].

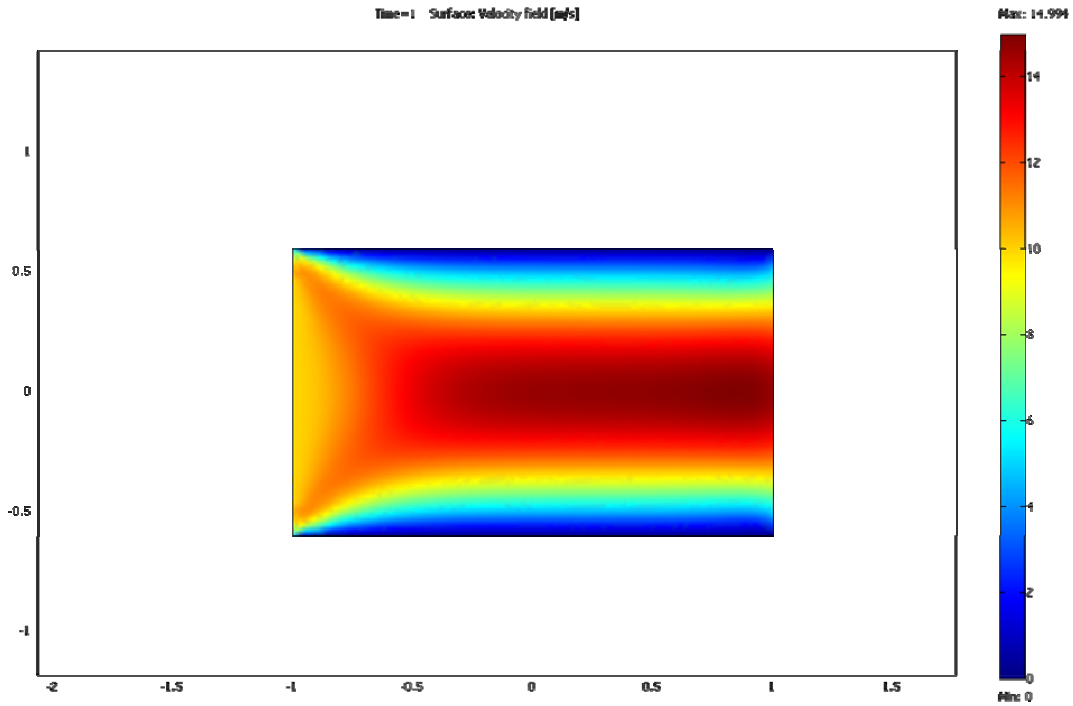


Figure 4.3: The surface velocity field of the revised solution.

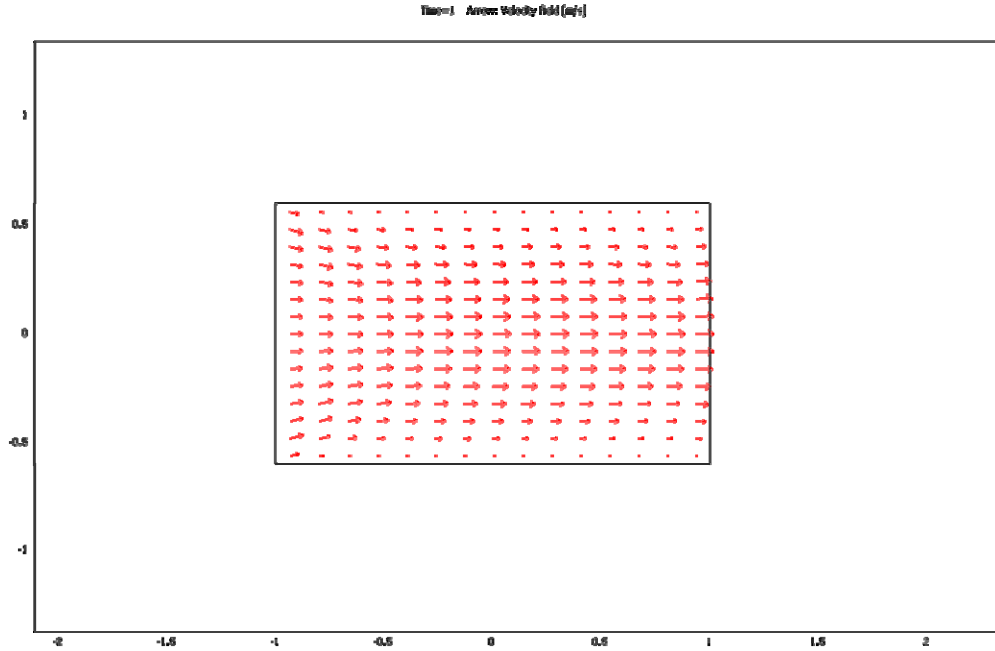


Figure 4.4: The surface velocity field of the revised solution in vector representation.

5. Revised Solution Validation

To validate the revised solution, two graphs were generated using COMSOL that display concentrations of mercury vapor vs. time at specific locations along the element (sample tube) outlet, see figures 5.1 and 5.2. In essence, these graphs represent the breakthrough curves of mercury vapor for the fly ash sorbent. The curves in figure 5.1 and 5.2 represent the time it takes for mercury to reach the center of the outlet tube and the top or side of the outlet tube, respectively. When comparing these two graphs, it can be seen that the mercury breakthrough point occurs earlier at the center of the sample tube than at the sides, which corresponds to previous diagrams and discussions (see section 4).

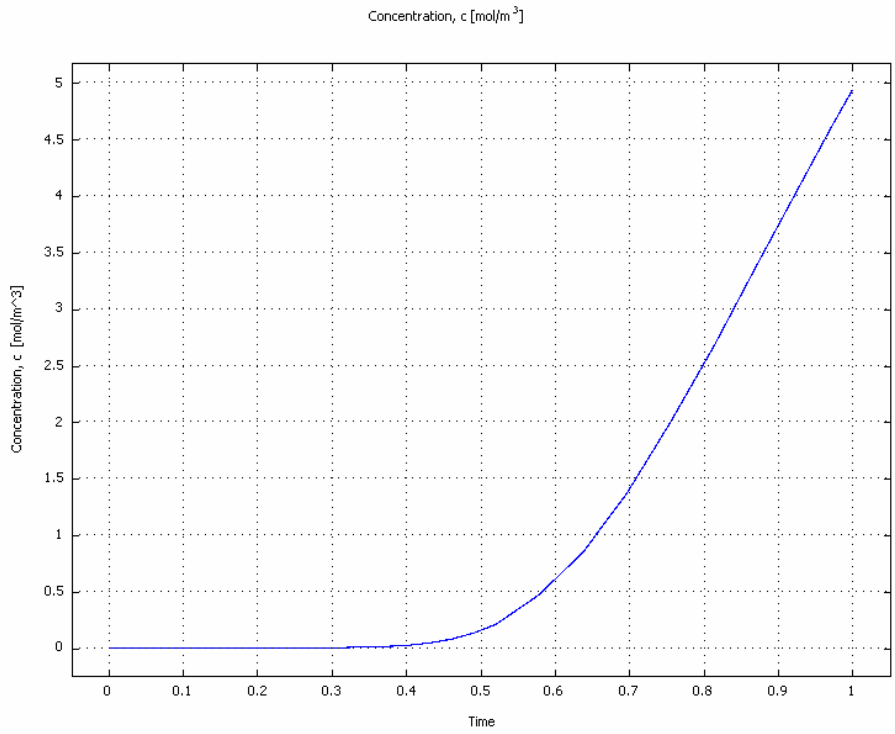


Figure 5.1: COMSOL breakthrough curve at center of sample tube outlet

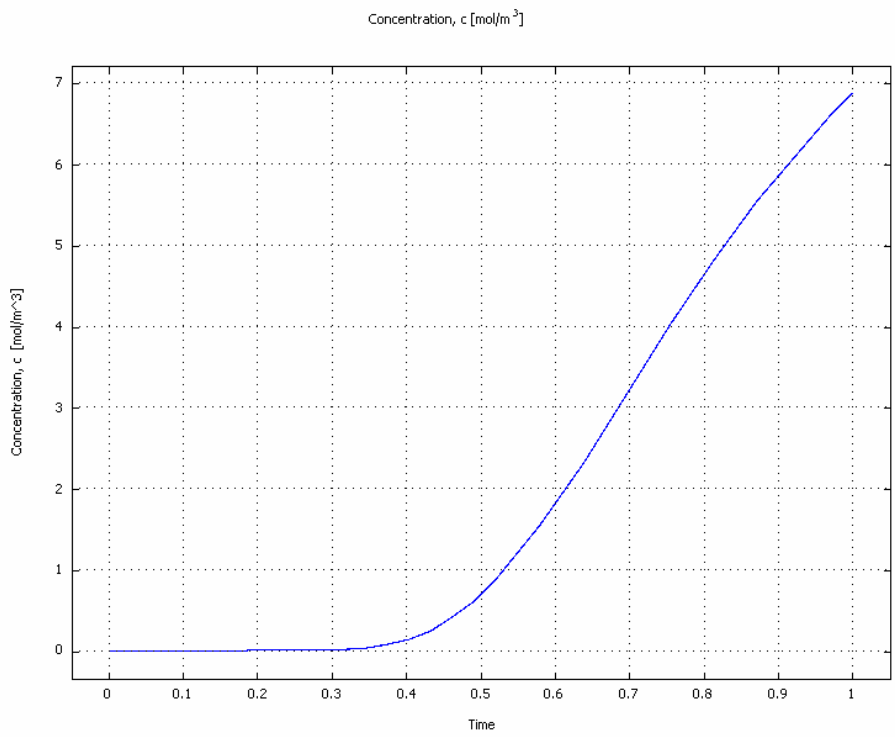


Figure 5.2: COMSOL breakthrough curve along the side of the sample tube outlet

The validation of this model is demonstrated by comparing the breakthrough curves in figures 5.1 and 5.2 to the experimentally obtained mercury adsorption data shown in figure 5.3. This experimental data shows an actual mercury breakthrough curve for a fly ash carbon sorbent obtained by one of the authors from a mercury generation/capture rig located at the University of Nottingham, UK. This curve shows the time to breakthrough as measured at the outlet of the sample tube holding the fly ash sorbent.

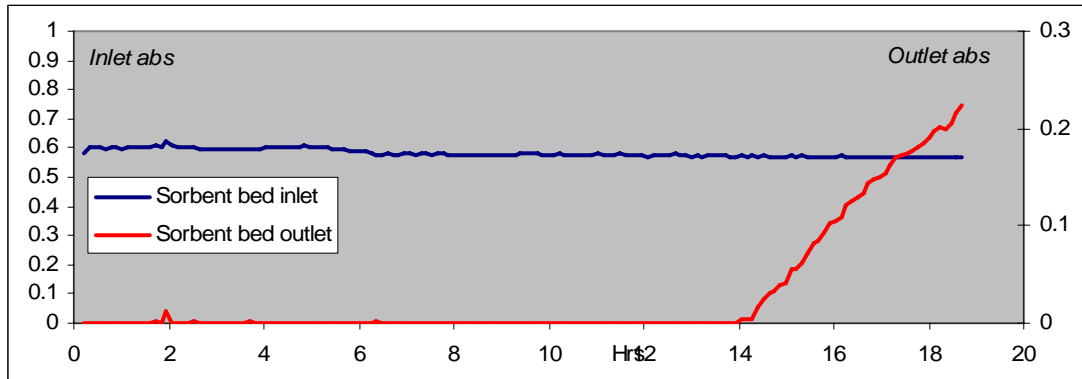


Figure 5.3: Experimental mercury breakthrough curve for fly ash sample FA1. Y-axis units correspond to the mercury concentration reading made by the Atomic Adsorption Spectrophotometer (AAS).

6. Parametric Study

A parametric study was performed to show the reaction of the model to changes in certain variables. Firstly, the reaction rate was varied to demonstrate the change in behavior when the rate of adsorption was increased for the fly ash sorbent, as shown in figure 6.1. With an increase in how quickly the mercury adsorbs on the sorbent, an increase in breakthrough time was observed. As the reaction rate was increased from $0.001 \text{ mol/m}^3\text{s}$ to $10 \text{ mol/m}^3\text{s}$, the breakthrough of mercury vapor happened almost immediately after the start of adsorption.

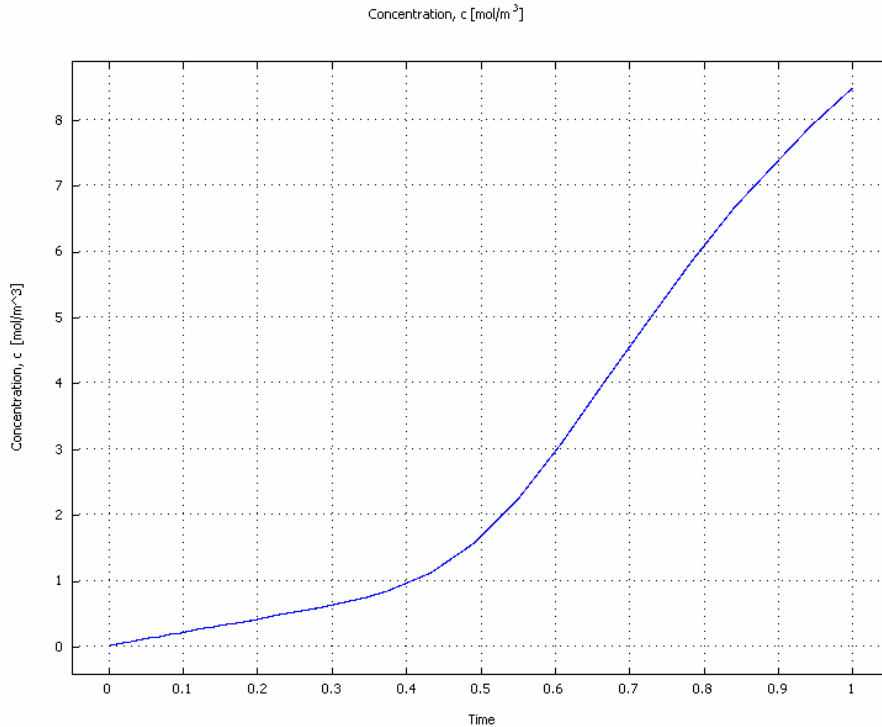


Figure 6.1: COMSOL breakthrough curve with reaction rate increased by 10^5 times

When the increased reaction rate breakthrough curve in figure 6.1 was compared with another experimentally obtained breakthrough curve in figure 6.2, they showed similar curve shapes. The graph depicted in figure 6.2 spans a much shorter time frame than that of the previous experimental graph due to its immediate breakthrough time. If given a longer experiment time, the graph would curve upwards exponentially as in figure 6.1; however, the purpose of the initial experiment was to determine only the time to breakthrough for the fly ash samples and not the shape of the experimental curve after the breakthrough point.

The fly ash sorbent used in figure 6.2 had a much higher carbon content than the sample in figure 5.3, and therefore, a much faster adsorption rate than that of the lower carbon content fly ash². This similarity can also be used as a further validation for the workability of COMSOL for this modeling scenario.

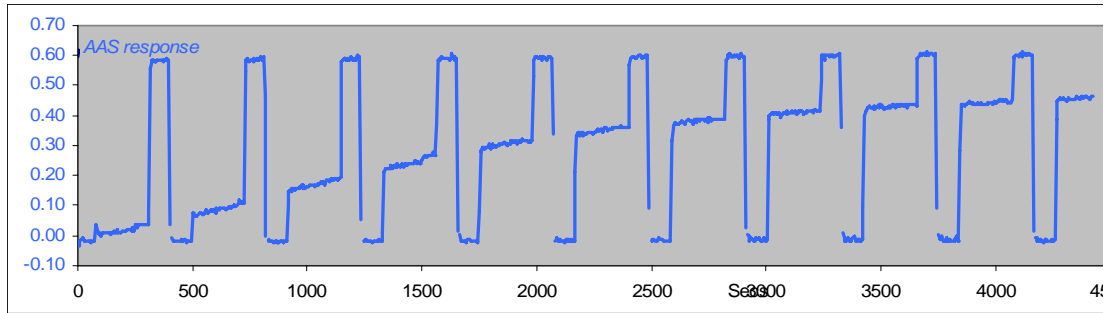


Figure 6.2: Experimental mercury breakthrough curve for fly ash sample CPC-Knockout. Y-axis units correspond to the mercury concentration reading made by the Atomic Adsorption Spectrophotometer (AAS).

7. Conclusions

This project focused on the modeling of mercury adsorption through a fixed bed of fly ash using the finite element method implemented in the COMSOL Multiphysics program. The results obtained from the program showed that velocity development and mercury breakthrough occurs more quickly at the center of the element (sample tube) than at any other point. The slowest velocity development and mercury breakthrough occurs along the sides of the sample tube.

The adsorption through the modeled element behaves as expected based on fully developed laminar flow through a tube or pipe. The adsorption breakthrough curve generated by COMSOL also closely resembles the results obtained via experimentally obtained data. With an increase in reaction rate, or rate of adsorption, breakthrough occurs much more quickly as expected. This behavior also resembles experimental data obtained from fly ash that has a faster adsorption rate.

Overall, COMSOL is an effective modeling tool for this application. It generates results that are consistent with experimentally obtained data and allows for the configuring of all important variables involved in convection and diffusion. Ultimately, more research and investigation would be needed to determine accurate parameter identification (e.g., force velocity, dynamic viscosity, diffusion coefficient) for the fly ash samples that have been tested to make the curves match identically.

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