Transient Modeling of an Electrochemical Printer using COMSOL Multiphysics

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Introduction

The Department of Chemical Engineering at the University of Washington desired to model an electrochemical printer head under transient analysis. The primary goal of this research was to develop a model that simulated the deposition of metal onto a substrate. The computer program, COMSOL Multiphysics (v 3.4) was the primary tool of research. The scope of this investigation was limited to modeling copper solutions.

This paper will describe the methods and procedures used to model the electrochemical printer head in a transient state. Then, results will be presented and discussed. Those results focus on three primary transient analysis areas: development of the velocity profile, development of the concentration profile, and finally, the implementation of a moving boundary, which represents the deposition of metal onto a substrate.

The symmetry and properties of the electrochemical printer head in this research are based off the paper "Electrochemical Printing: Mass Transfer Effects" by Jeffrey B Nelson, Zudtky Wisecarver, and Daniel T Schwartz [1].

Moving Mesh Theory

According to Fick's law of diffusion, the molecular flux, N_i, is proportional to the negative gradient of molecule concentration, C_i, and the diffusive coefficient, D_i. This relationship is expressed below in Equation 1.

$$N_i = -D\frac{dC_i}{dy}\bigg|_{y=0} \qquad \text{(Eqn 1)}$$

As seen in Equation 1, Fick's law of diffusion is evaluated at y=0. This will correspond to the inward flux of molecules, in our case Cu^{2+} ions, at the surface of the charged substrate. As copper molecules are deposited onto the substrate, they form a time dependent boundary layer.

This boundary layer can be modeled by evaluating the local change in height with respect to time. This is accomplished when the diffusive flux is divided by the molecular weight of the ion and its density, shown as Equation 2.

$$\frac{N_i}{M_i\rho_i} = \frac{Volume_{purei}}{Area * Second} = \frac{dy}{dt} \qquad \text{(Eqn 2)}$$

Equation 3 is a result of manipulating Equations 1 and 2.

$$\left.\frac{dy}{dt}\right|_{y=0} = -\frac{D}{M_i \rho_i}\left.\frac{dC_i}{dy}\right|_{y=0} \qquad \text{(Eqn 3)}$$

Equation 3 can be imposed as the boundary condition of the substrate. When the concentration is set to zero (at the boundary layer), the boundary layer will grow as a function of the concentration gradient. This concentration gradient is evaluated by COMSOL at every point along the substrate allowing the gradient to vary, and thus simulate variant growth.

Procedures

This section of the report will describe the symmetry used in COMSOL Multiphysics to model the electrochemical printer head. Then, it will give detail on several modules used to model the printer and list the options that were chosen. Once again, the simulations described are only for the modeling of Cu^{2+} ions in the printer solution.

Analysis of the electrochemical printer head in a transient state requires the integration of three transient COMSOL modules: Convection and Diffusion, Incompressible Navier-Stokes, and the Moving Mesh (ALE).

Printer Symmetry and Subdomain Settings

The printer fly height to diameter ratio (h/D) was .062 . In addition, the Reynolds number of the incoming flow was assumed to be 14. See Figure 1 for the dimensions of the printer and fluid properties. Shown also are the properties used for the subdomain settings. The viscosity of the fluid was assumed to be .0013 Pa*s and the molecular diffusivity of the copper ion was set to 2.07e-10 m^2/s.

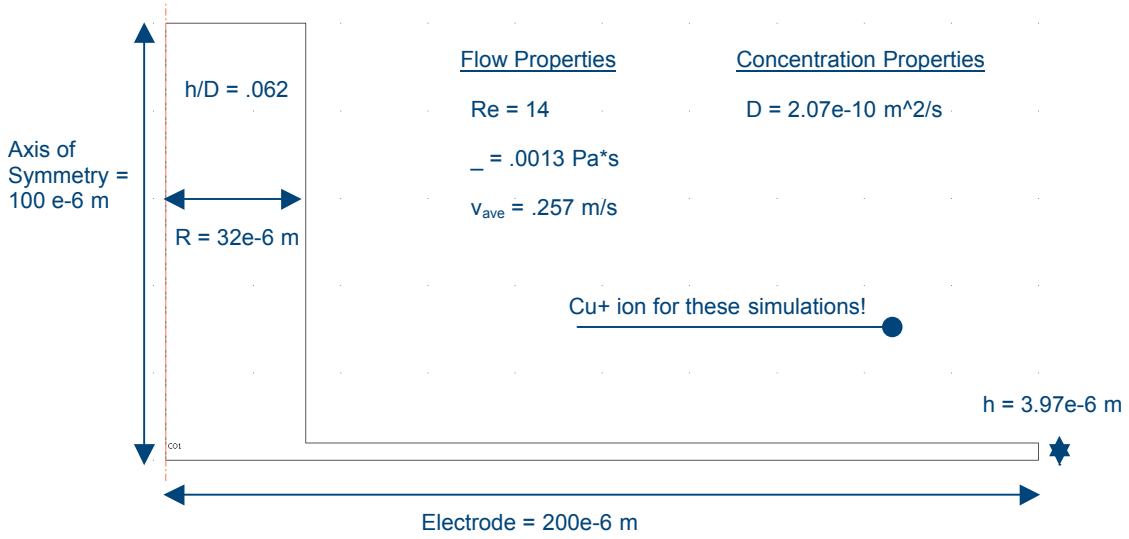

Figure 1: Electrochemical printer head symmetry with a fly height to diameter ratio of .062 .

It is important to note that this symmetry was established in COMSOL as a two dimensional problem with axial symmetry (the symmetric boundary to the left).

Boundary Conditions

This section will explain the boundary conditions placed on the model. See figure 2 for a detailed depiction.

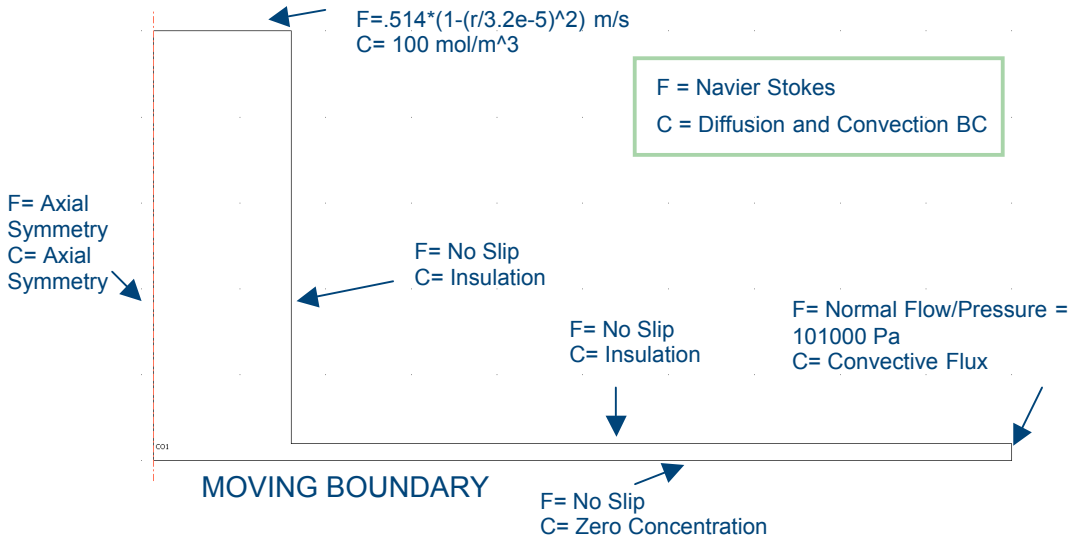

Figure 2: Boundary conditions placed in COMSOL. The 'F' and 'C' represent the incompressible Navier-Stokes' module and the convection and diffusion's module boundary conditions, respectively.

Fully developed laminar flow was placed as a boundary condition at the top of the printer head. Shown in Figure 2, is a commonly known flow equation where the maximum velocity in the printer head is twice the average velocity. The average velocity was calculated using the Reynolds number, viscosity, and density of the fluid as well as the diameter of the channel, D.

The bottom boundary in Figure 2 represents a moving mesh boundary, or ALE, that requires the integration of the 'Moving Mesh (ALE)' COMSOL module. Boundary conditions and subdomain settings for the moving mesh will be discussed next.

The Moving Mesh (ALE) Module

The moving mesh module had all boundary conditions set to zero displacement in the radial direction. The only boundary condition mathematically imposed was for the substrate boundary where the mesh velocity in the z- upward direction was set to '2.7e-10*cZ/(63.5e-3*8920)'. The 'cZ' is the designated variable for the concentration gradient in the z- direction in COMSOL. As for the subdomain settings, the main domain was set to 'free displacement.

Executing Simulations

When two or more modules were simultaneously solved, many times their integration caused very complicated solutions. For that reason, some solutions were found by using properties of the fluid that would allow them to be more easily solved. Then, the simulation would be re-run using the solution of the previous run while stepping towards a real solution. For example, all incompressible Navier-Stokes simulations were solved

first with the viscosity set to 1.0. Then, the simulation was re-solved with a viscosity of, say, .01. The process was repeated until the final viscosity of fluid was .0013 Pa*s and the problem converged.

In addition, the solver parameter's time-stepping option was used. For example, because the velocity profile was found to develop very quickly (to be discussed later), the default time stepping value of .1 seconds to a final time of 1 second is much to long to observe the velocity profile develop. For that simulation, the time stepping was set to the order of 10^{-6} seconds.

Another way to make the solving process simpler was to be selective where the mesh was refined. Near the substrate, the flow and concentration dynamics were modeled more accurately than near the fluid entrance. For that reason, the mesh was refined in those areas. However, near the top of the model the mesh was initialized and left at its default value.

Because the simulations were complicated, many took upwards of 30 minutes to solve. It was important to reduce the complication of the model in ways previously described. Then, the model could be stepwise updated to simulate an actual scenario.

Results and Discussion

Computational results will be shown and discussed here. Because the electrochemical printer head was modeled under transient analysis, several pictures will be shown at various times within each solution to illustrate findings.

First, the development of the velocity profile inside the printer head will be discussed. Then, a molecular transport model with and without the convective terms will be compared. Finally, simulation of metallic deposition onto a substrate using a moving boundary will be shown and discussed.

Development of Velocity Profile

This part of the research focused on understanding how quickly the velocity profile of the electrochemical printer approached steady state. This was simulated using the incompressible Navier-Stokes module only. Refer to Figures 3 through 5 for the simulation.

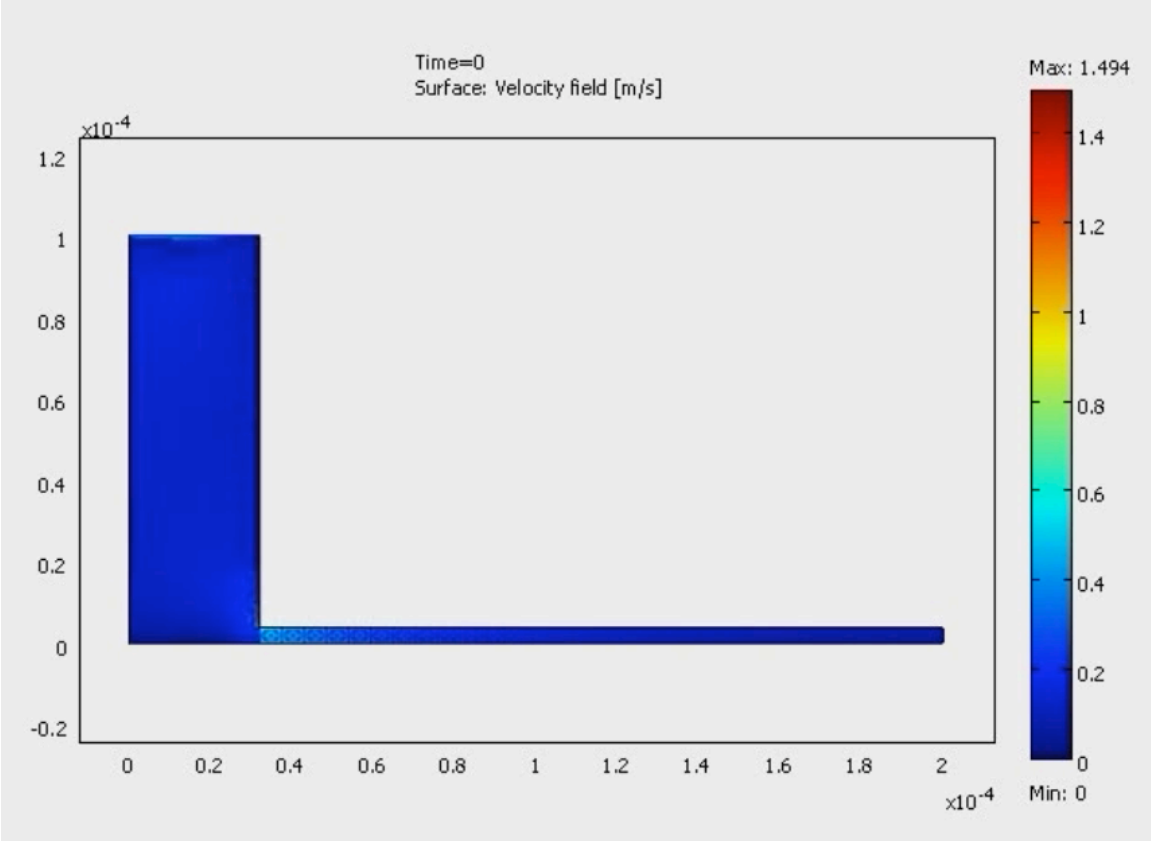

Figure 3: Velocity profile at zero time- notice that the majority of the profile is zero, with the exception of a few deviations that are a result of model inaccuracies.

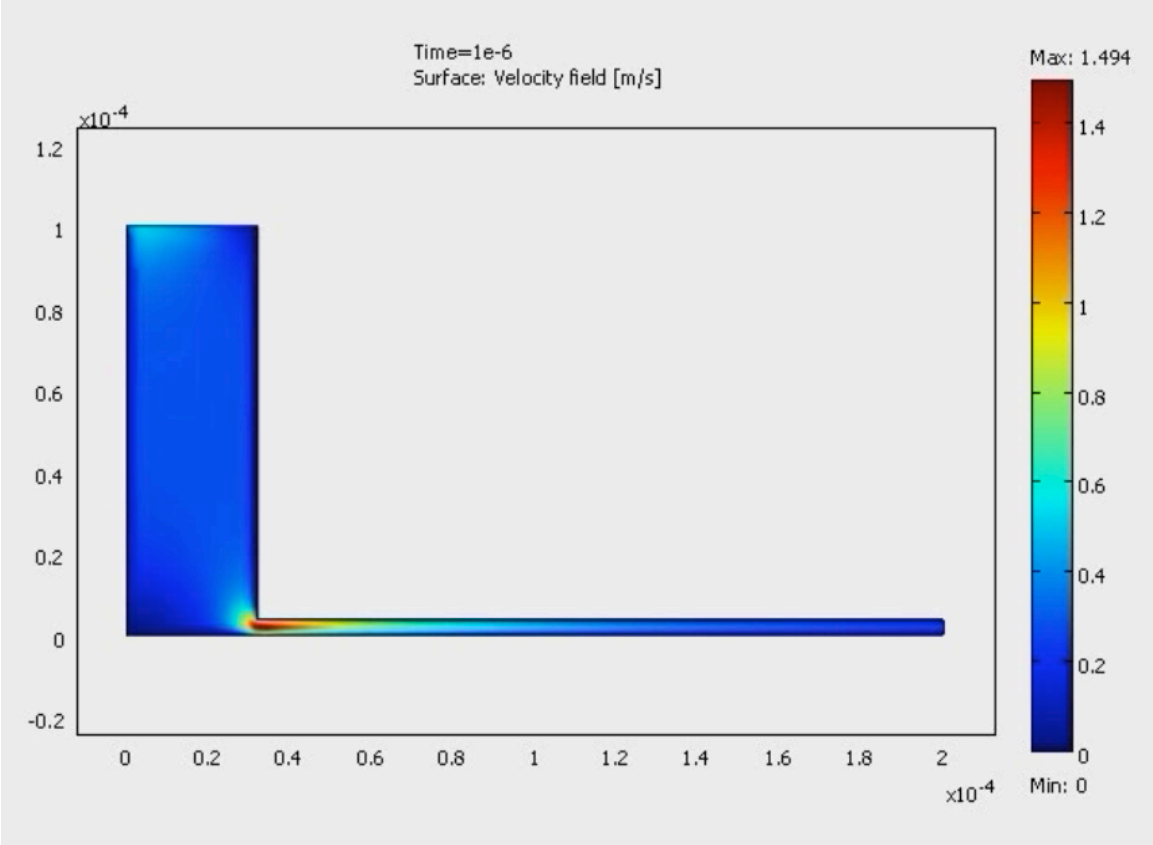

Figure 4: Velocity profile at 1e-6 seconds.

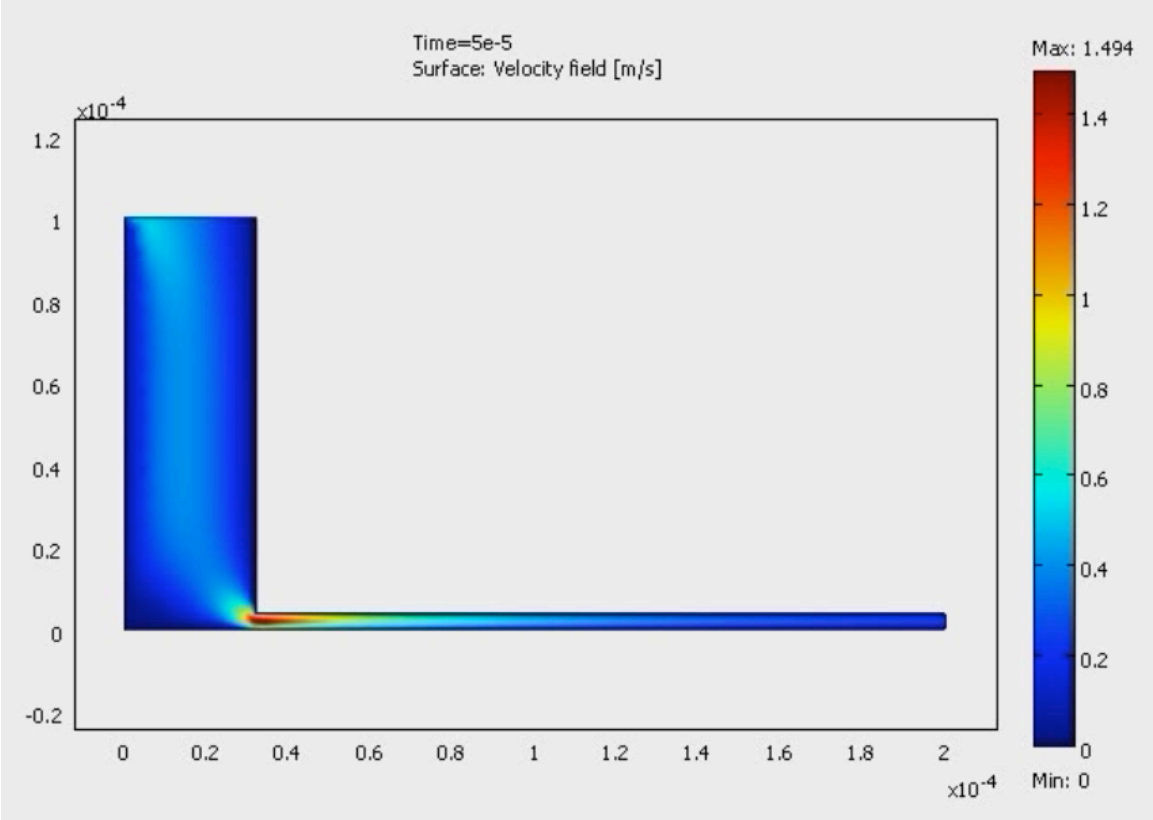

Figure 5: Flow approaches steady state in only fractions of a second, 5e-5 seconds.

It can be seen from the figures above that steady state flow is achieved extremely quickly- 50 microseconds. This is an important discovery because it shows that the steady state and transient models of velocity only differ in the very first microseconds of printer head operation.

Copper Concentration Development: Diffusive Term Only

This simulation was run disregarding the convective term in the diffusive and convective COMSOL module by setting the velocity equal to zero at all boundaries. The top of the electrochemical printer, at time zero, is brought to a 100 mol/m^3 copper concentration. Figures 6 through 8 illustrate the diffusive concentration of the copper through the printer head.

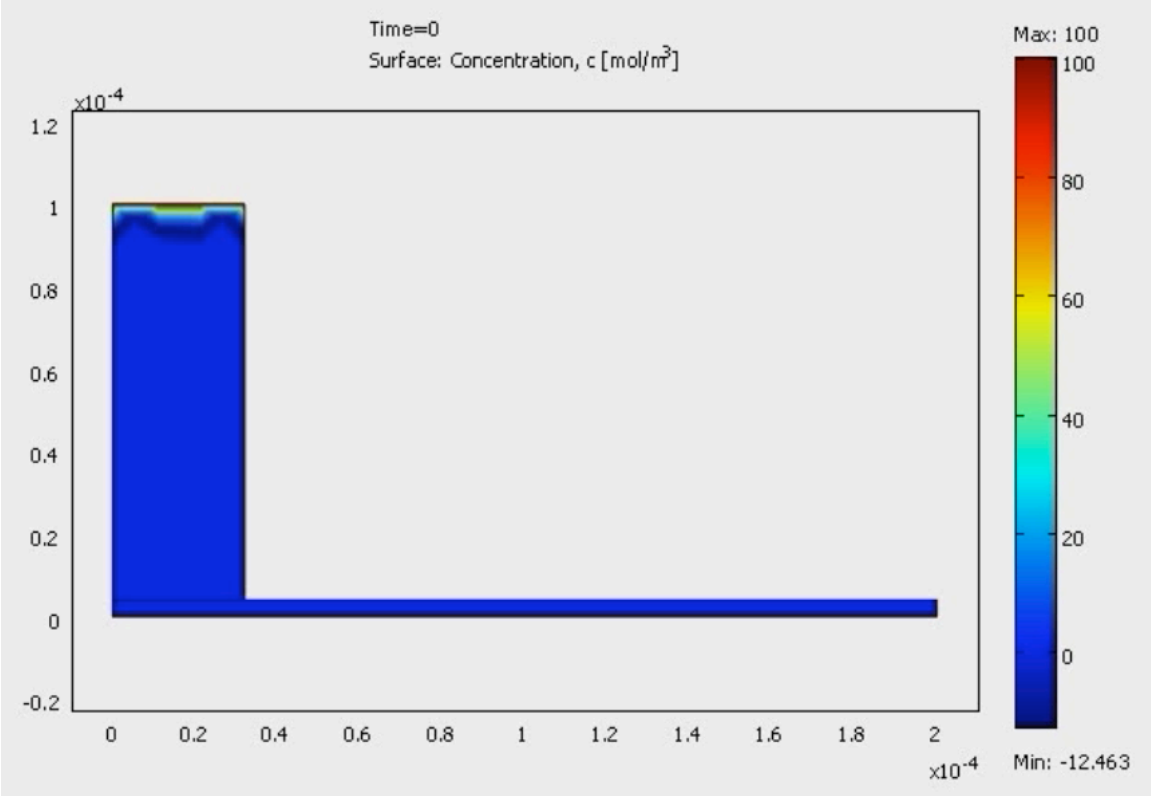

Figure 6: Development of concentration profile with only diffusive term at time zero. The top of the model has a boundary condition of 100 mol/m^3.

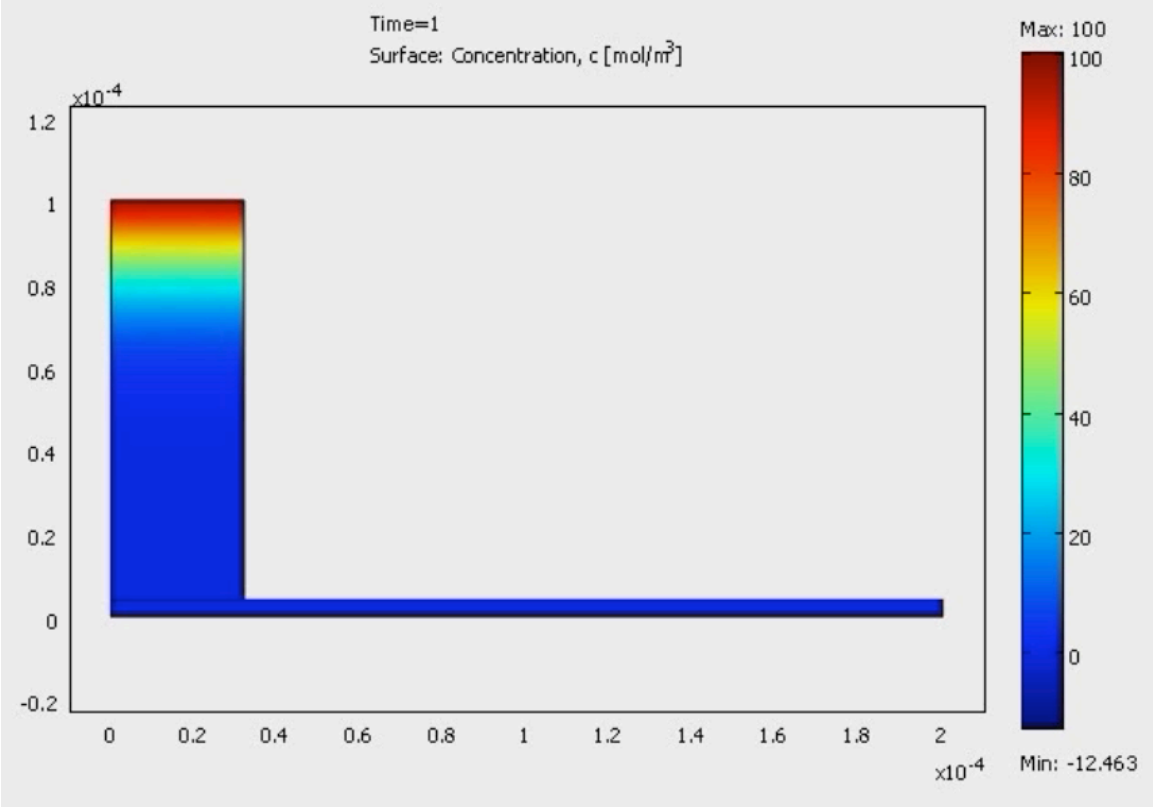

Figure 7: Diffusive concentration at 1 second.

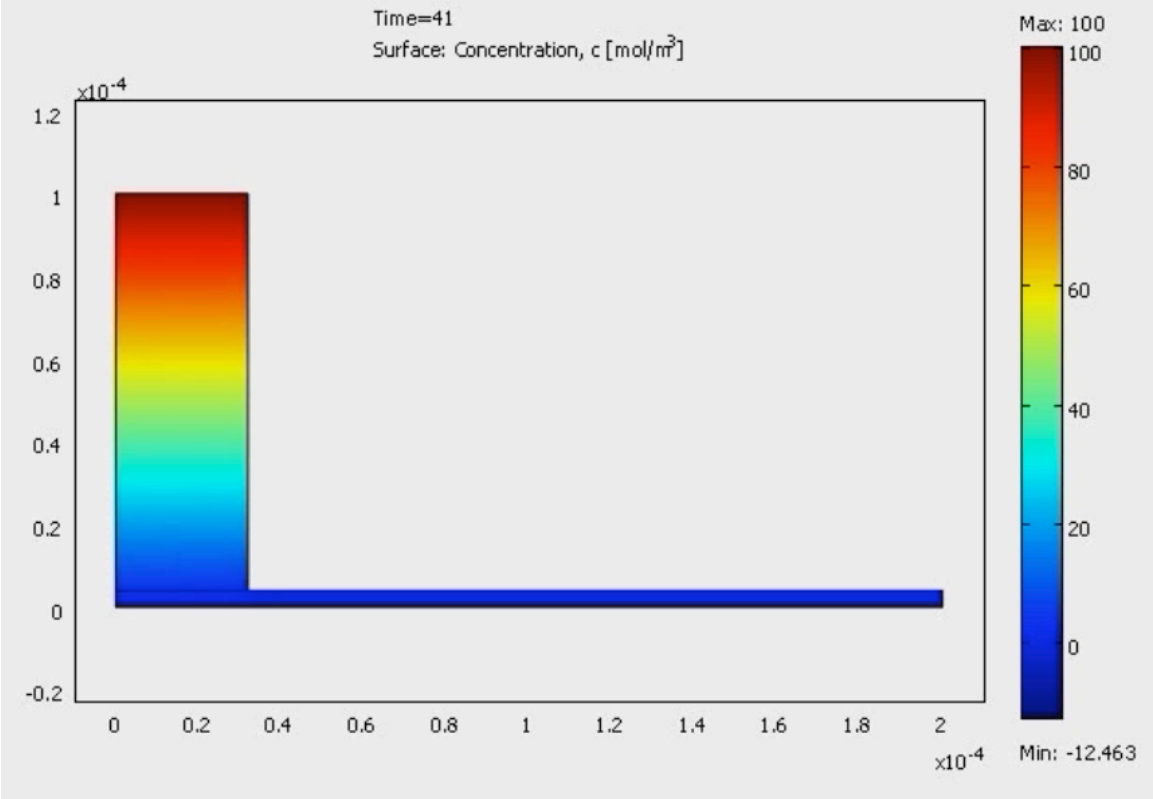

Figure 8: Diffusive concentration profile at 41 seconds where the simulation approaches steady state and some of the copper ions have diffused towards the bottom of the substrate.

The above figures show that the copper ions take a long time to diffuse through the printer channel towards the substrate- 20 seconds in this simulation. This is can be primarily related to the small diffusive coefficient of copper ions, which is 2.07 e-10 m^2/s.

After approximately 40 seconds, the copper ions approach steady state. It is also important to note that the substrate has a boundary condition of zero concentration- that is why it remains blue.

Copper Concentration Development: Convective and Diffusive

This experiment was conducted to understand the effect of adding a convective term to the diffusive experiment previously discussed. This was accomplished by using the same model, but imposing the velocity boundary condition at the top of the printer head to be fully developed laminar flow. Figures 9 through 12 show how the velocity term effects the concentration of copper as it approaches steady state.

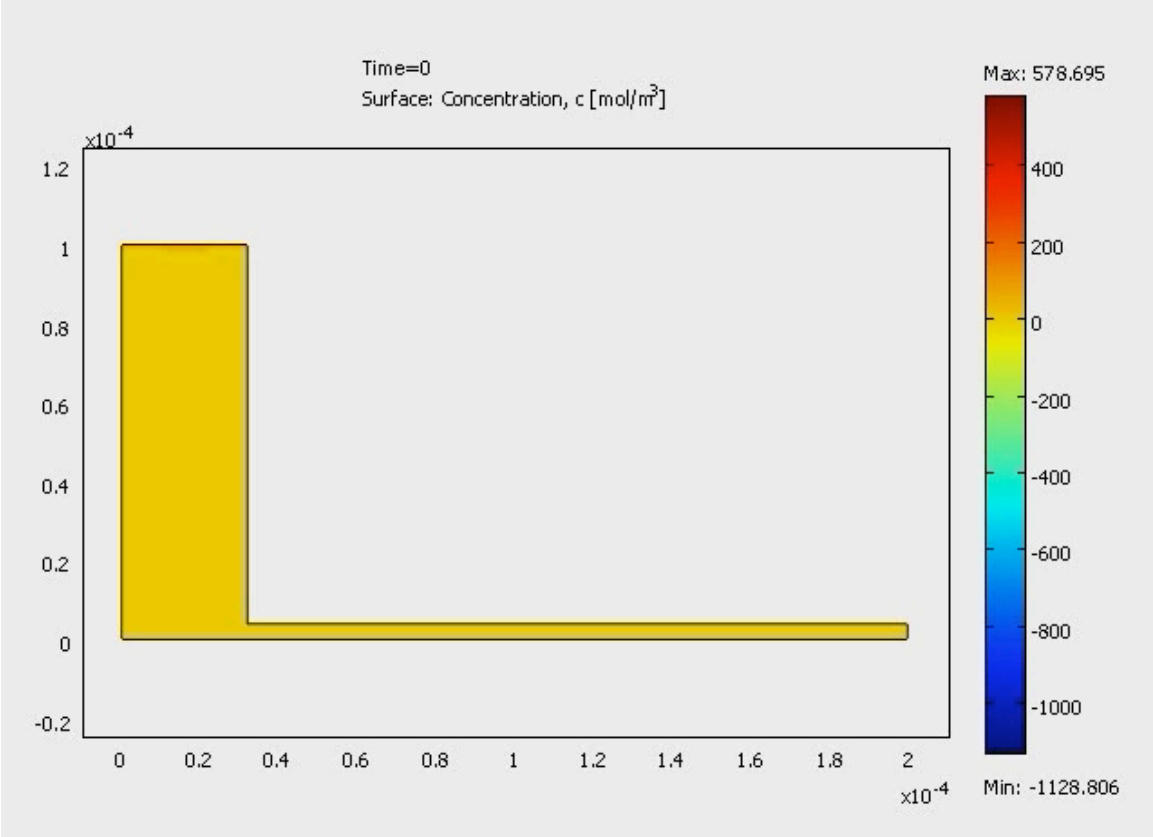

Figure 9: Concentration profile development with convective and diffusive terms at time zero.

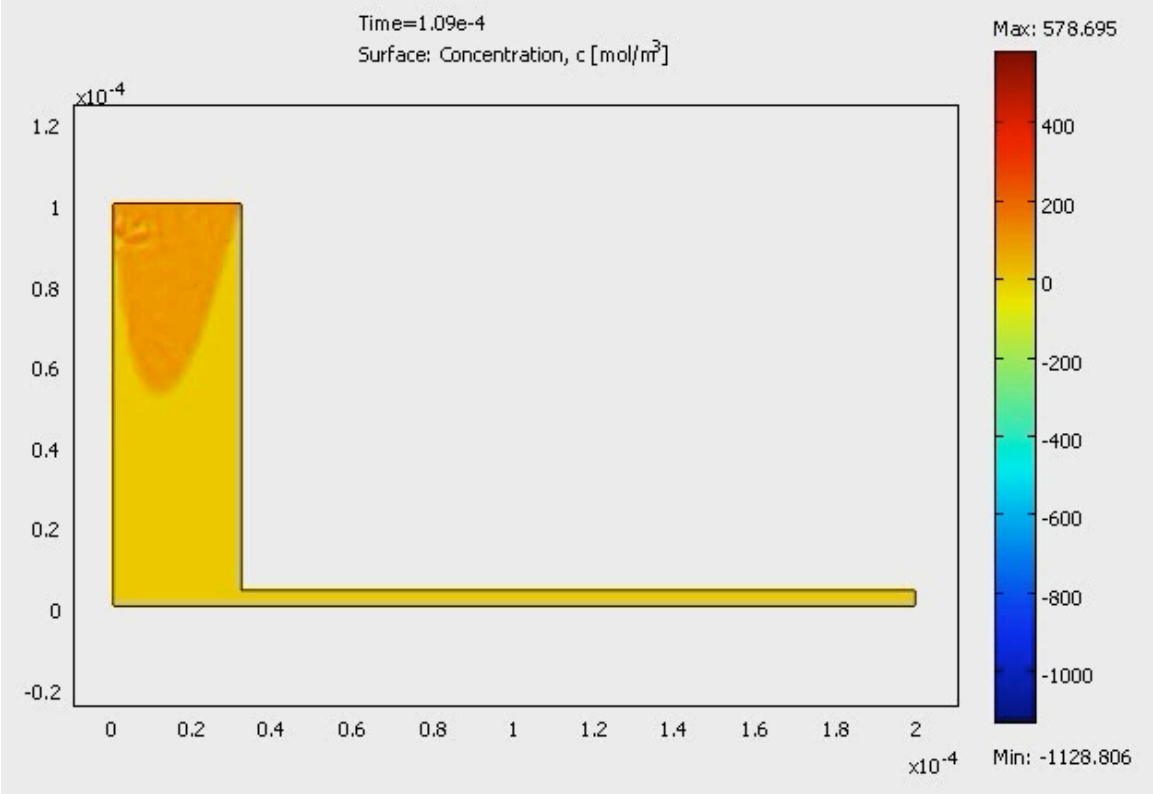

Figure 10: Concentration profile at 1.09e-4 seconds. Notice the sharp contrast in concentration, yellow representing 0 and orange representing 100 mol/m^3.

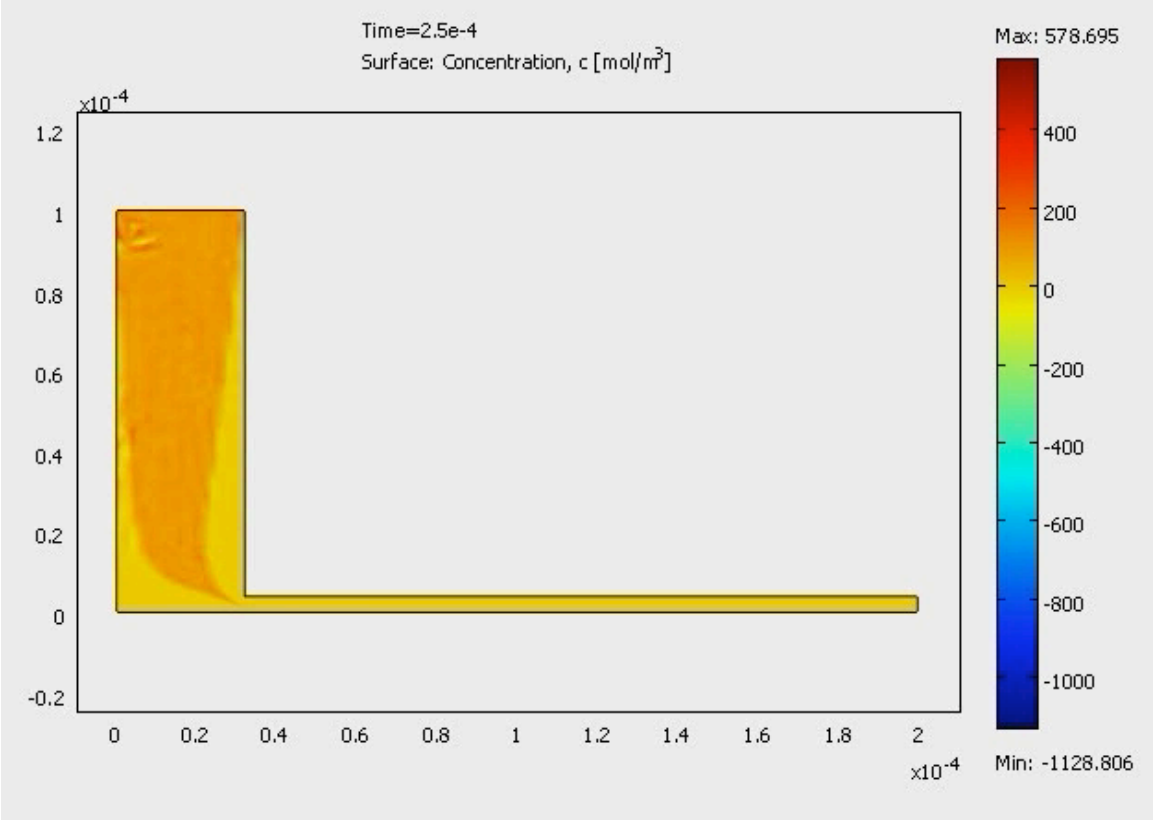

Figure 11: Concentration profile at 2.5 e-4 seconds. Concentration front nears the bend of the printer head.

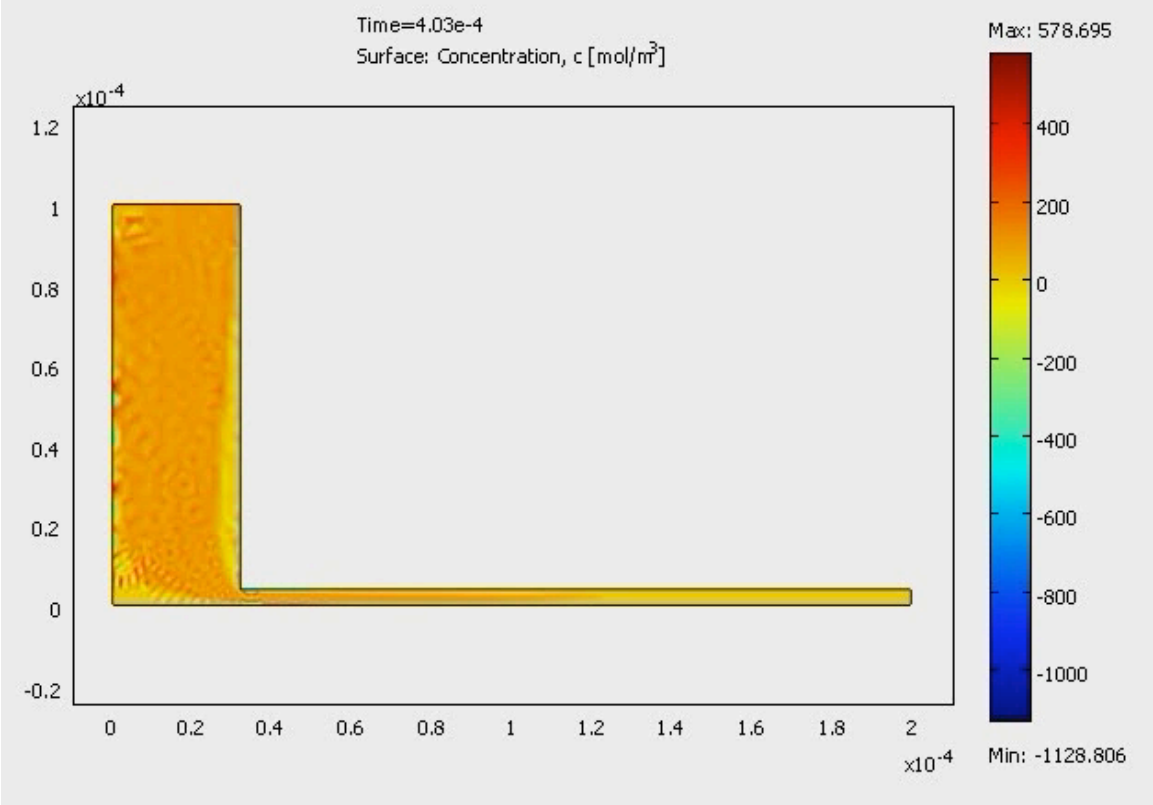

Figure 12: Concentration profile at 4.03e-4 seconds. The concentration front has penetrated the bend of the printer head and moves outward.

Figures 9 through 12 show how quickly the concentration of copper spreads when the convective term is added to the model. The speed at which the concentration front spreads to the substrate is indeed coupled with fluid's velocity. For instance, when only the diffusive terms are used to model concentration, it required approximately 20 seconds for the molecules to transport through the fluid to the substrate. On the other hand, it required only a fraction of a second to bring 100 mol/m^3 concentrated solution to the substrate- 4e-4 seconds. This is five orders of magnitude difference. This illustrates the massive effect that the convective term has on the development of the concentration profile.

It is also interesting to note, and can be seen clearly in Figure 9, the contrast of the solution's concentration front. The front forms sort of a concentration bubble, at 100 mol/m^3, and moves through the printer head and does not mix. A very distinct color contrast can be seen between the concentration front and the rest of the solution within the printer head. This also illustrates the dominance of convective terms in molecular transport because the front moves so fast through the fluid that the diffusive term does not have time to smudge the concentration in areas of no velocity. That is why a sharp color contrast can be seen.

Moving Boundary (ALE)

This experiment was completed using the diffusive and convective module and the moving boundary (ALE) module only. Repeated attempts to integrate all three modules (the third being the incompressible Navier-Stokes module) but all failed due to inability to converge to a real solution. For that reason, the results shown below do not have a convective term.

The theory that was developed in the introduction was applied to the substrate boundary. Figures 12 through 16 show how the moving boundary module can be used to simulate the metal deposition of copper ions onto a substrate.

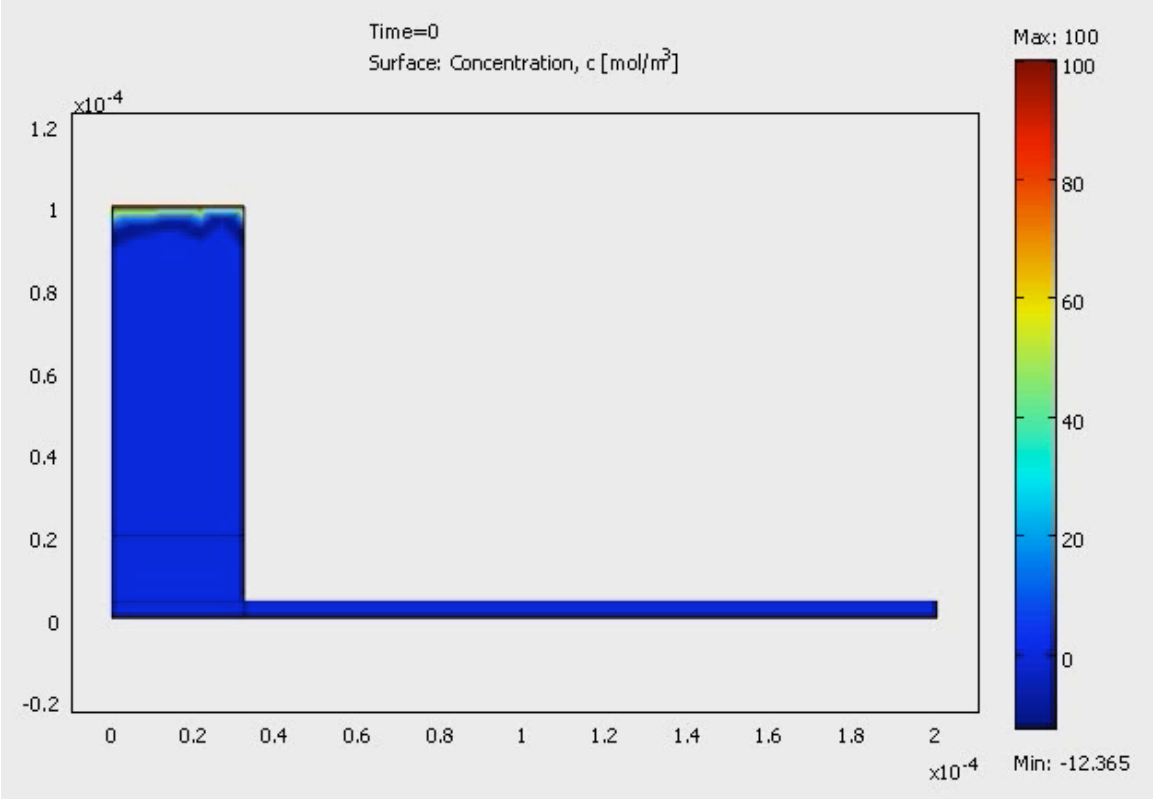

Figure 13: Moving boundary simulation at time zero.

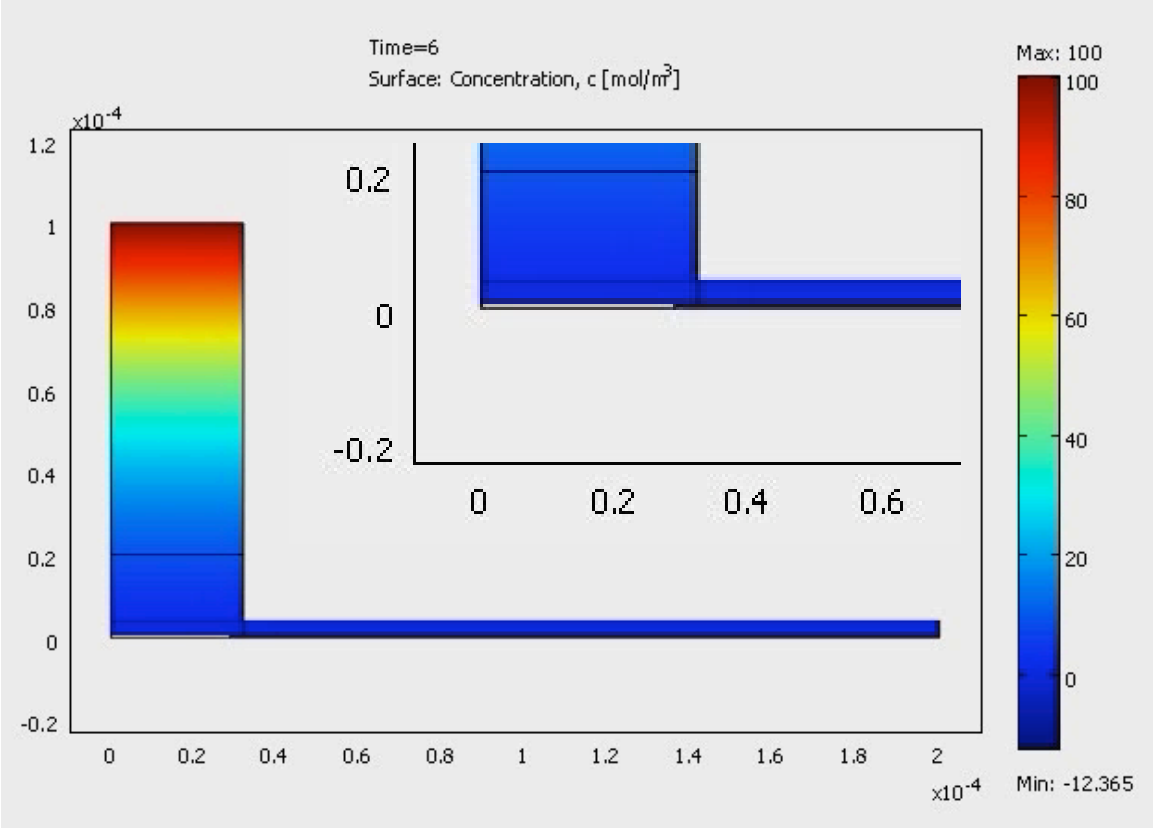

Figure 14: Moving boundary simulation at 6 seconds. At this point, the substrate boundary begins to move upward.

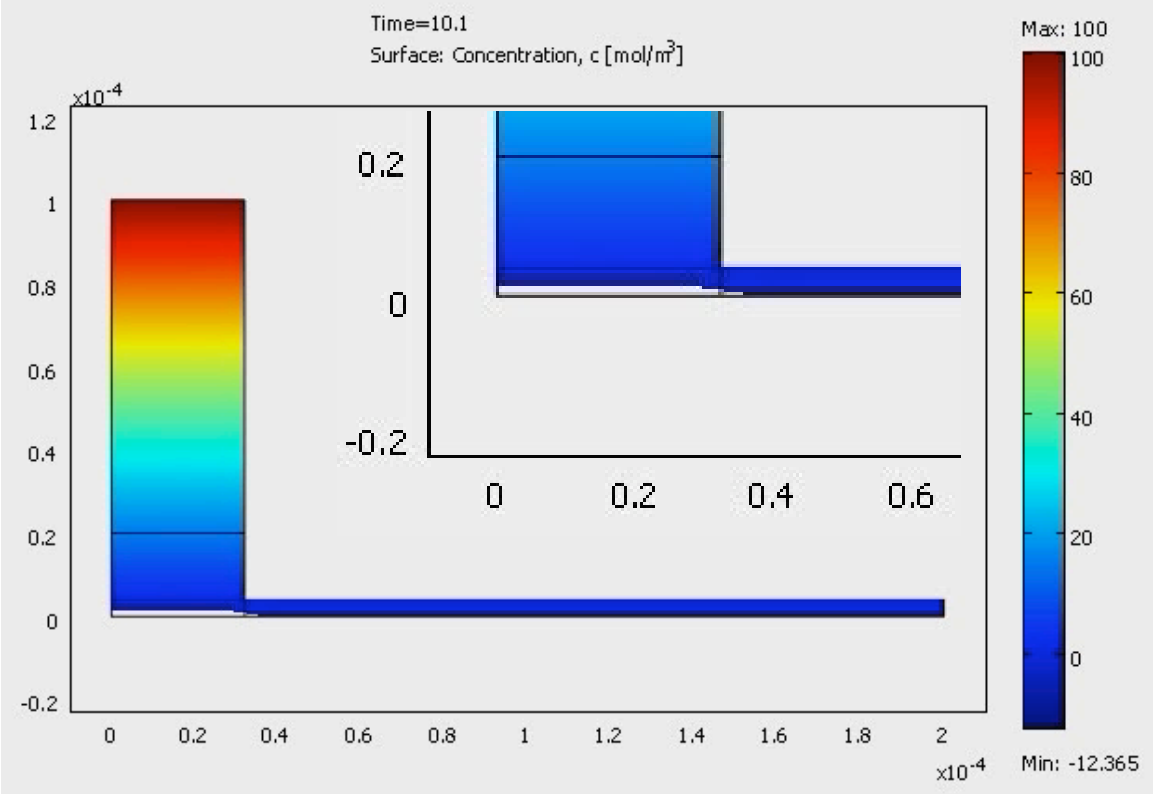

Figure 15: Moving boundary simulation at 10.1 seconds. The substrate boundary continues to move and forms a curved surface near the printer head's bend.

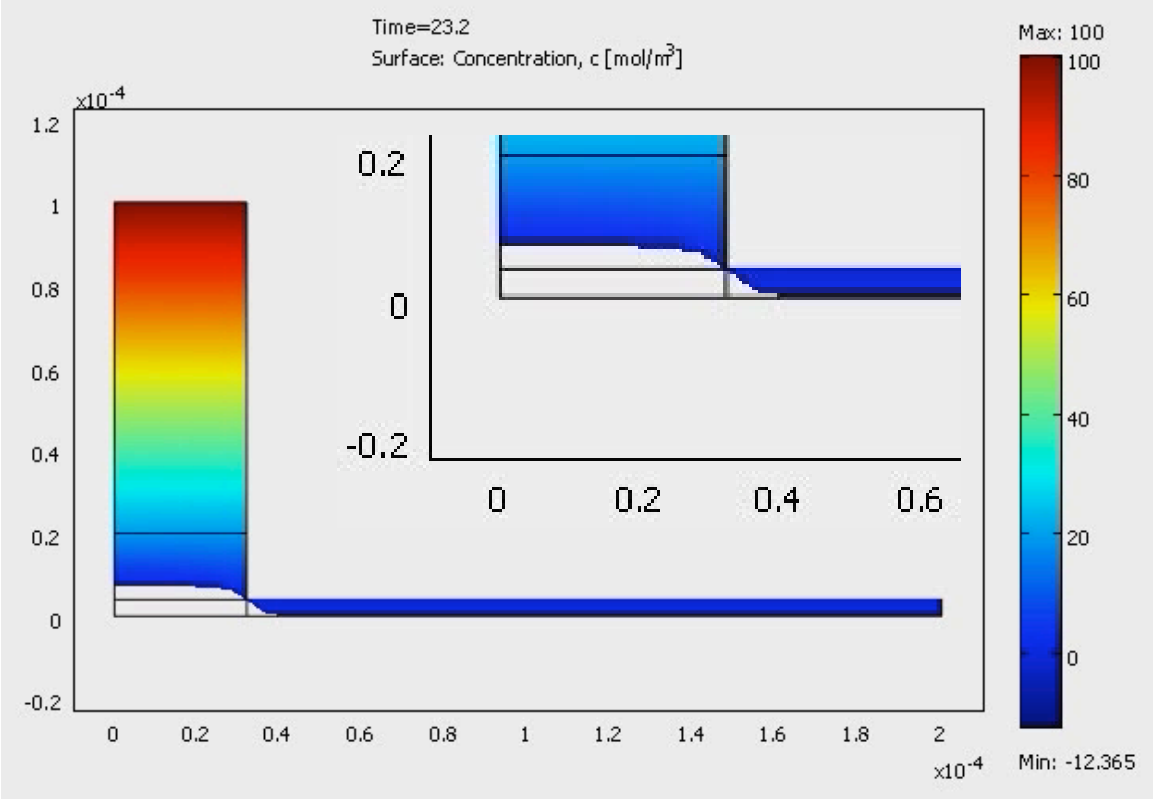

Figure 16: Moving boundary simulation at 23.2 seconds. The deposition of copper metal has been fully simulated. At this point in time, the deposited copper has built up passed the fly height of the printer so a later time in this simulation would yield unrealistic results.

The figures above illustrate that the theory developed in the introduction predict the deposition of metal onto a substrate without any convective transport terms present. However, as previously shown, these convective terms have a large impact on the concentration profile and cannot be neglected in a real simulation.

If the convective terms were added to this simulation, it would be interesting to see how the moving boundary responds to the concentration front, shown in Figures 9 through 12. The moving boundary's velocity, according to Equation 3, is a function of the concentration gradient. The sharp gradient produced by the concentration front would cause the boundary to suddenly grow at a high rate once the front reached the substrate. For that reason, an updated model would require a large amount of mesh refinement near the boundary layer to accurately compute the concentration gradient there.

With that said, it is important that this model be updated with the incompressible Navier-Stokes module. While this could not be achieved previously, a unique approach to solving the problem could be developed and possibly yield real answers.

Conclusions

The velocity profile of the electrochemical printer developed in only a fraction of a second. At that point, the profile resembled steady state flow.

As for the concentration profile, the convective term of molecular transport was found to have a great impact on the profile. When added to the diffusive term, the convective term produced a concentration wave front that reached the substrate in only fractions of a second (about 300 microseconds). In addition, a sharp concentration gradient surrounded the concentration front showing minimal molecular diffusion on the microsecond timescale. The diffusive term by itself required around 20 seconds for the copper concentration to reach the substrate.

Equation 3, when integrated into the moving boundary (ALE) module, accurately predicted the deposition of metal onto a substrate. However, this simulation was completed with only the diffusive term of molecular transport due to difficulty getting simulations to converge. To accurately model the printer head, the convective term should be integrated into the simulation.

References

[1] Nelson, Jeffrey B., Zudtky Wisecarver, and Daniel T. Schwartz. Electrochemical Printing: Mass Transfer Effects. University of Washington. Seattle, Wa: IOP, 2007. 1192-1199.