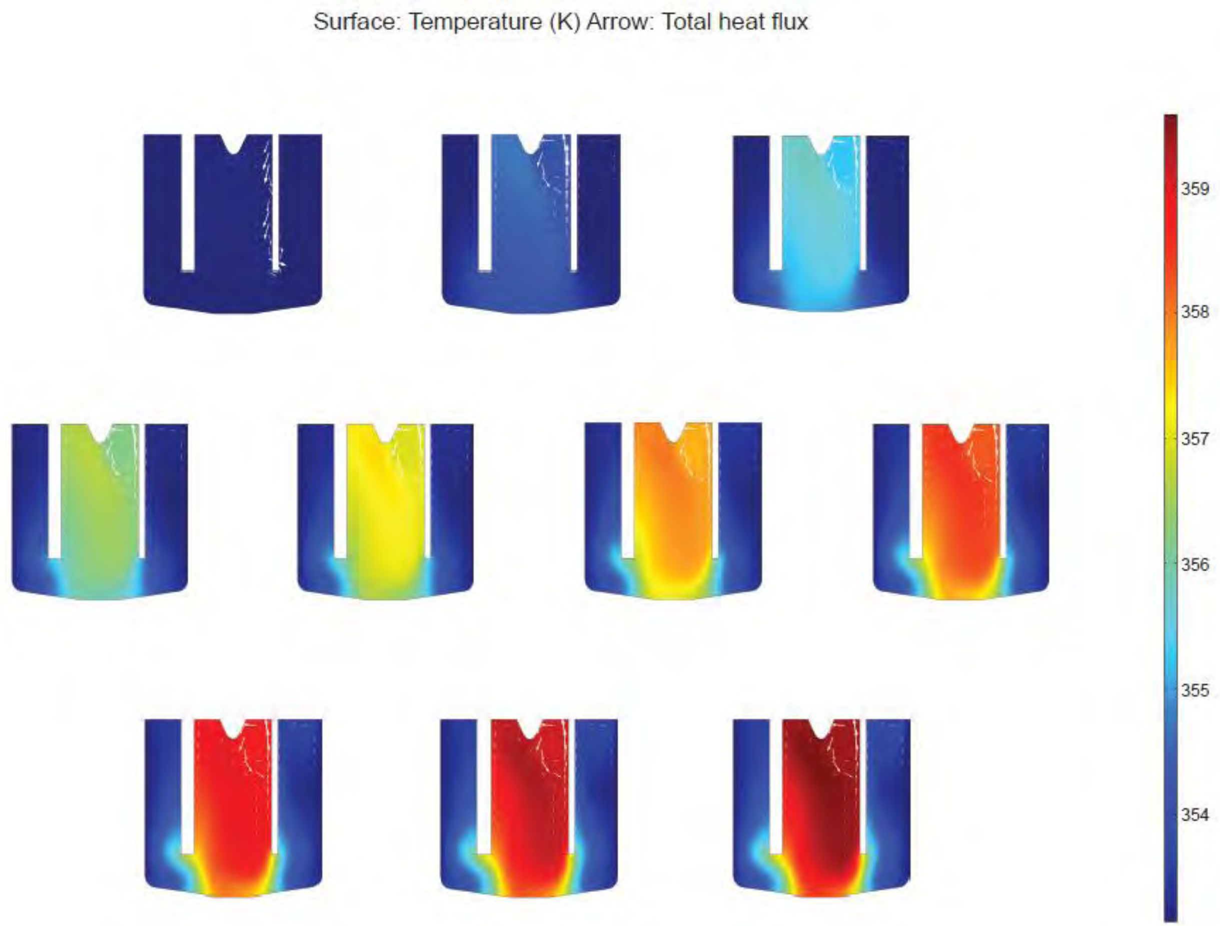
A TRANSIENT COMPUTATIONAL FLUID DYNAMIC STUDY OF A LABORATORY-SCALE FLUORINE ELECTROLYSIS CELL



A TRANSIENT COMPUTATIONAL FLUID DYNAMIC STUDY OF A LABORATORY-SCALE FLUORINE ELECTROLYSIS CELL

RYNO PRETORIUS

UNIVERSITY OF PRETORIA

FLUORO-MATERIALS GROUP

Objective/Problem Statement

- Construct a model that predicts the physical processes during the production of fluorine by electrolysis.

- Simulation will be validated by comparing COMSOL simulations to published simulations.

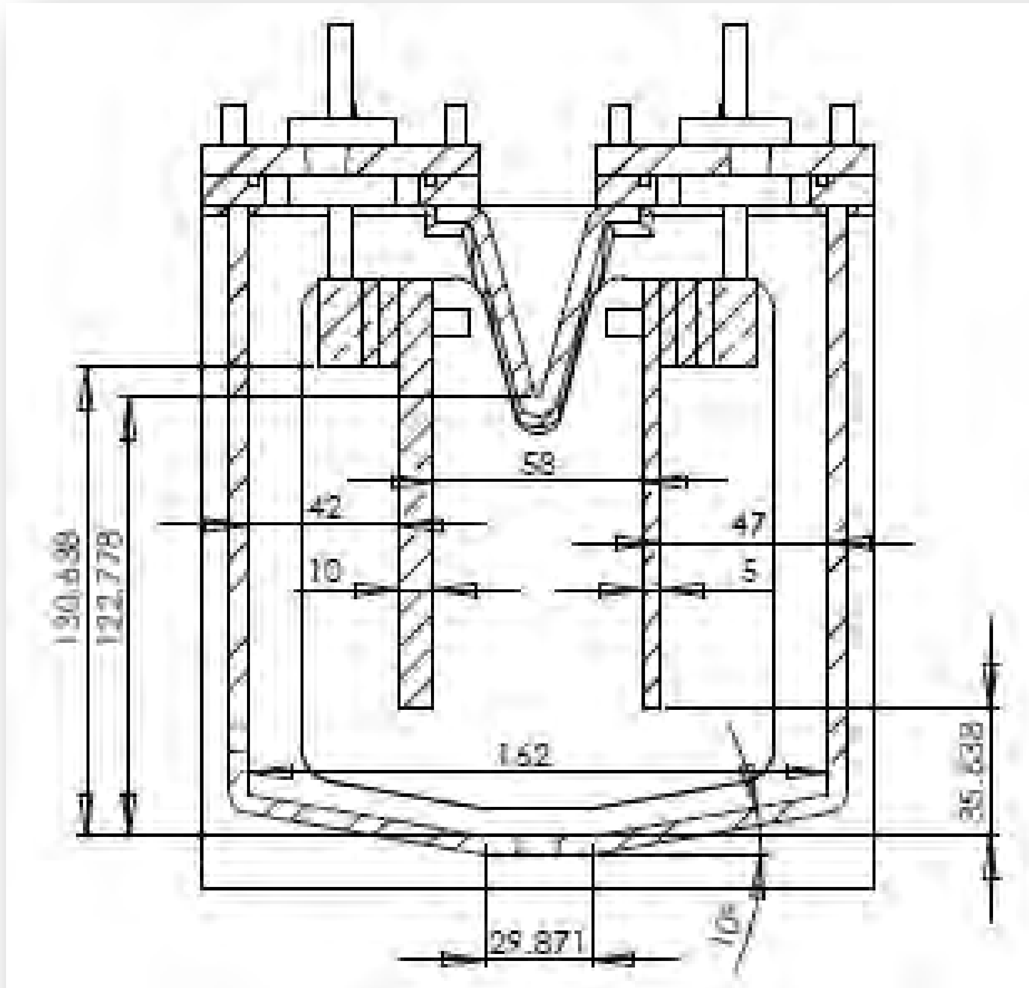
- Upon completion of the reactor under construction, experimental findings will be compared to the simulations.

Background

- Uses were initially limited to the nuclear industry where it was used for uranium enrichment.
- Fluorine finds a wide range of uses today from non-stick cookware to HydroFluoroCarbons used during refrigeration.
- Electrolysis of hydrogen fluoride in molten potassium acid fluoride facilitates the formation of fluorine gas.

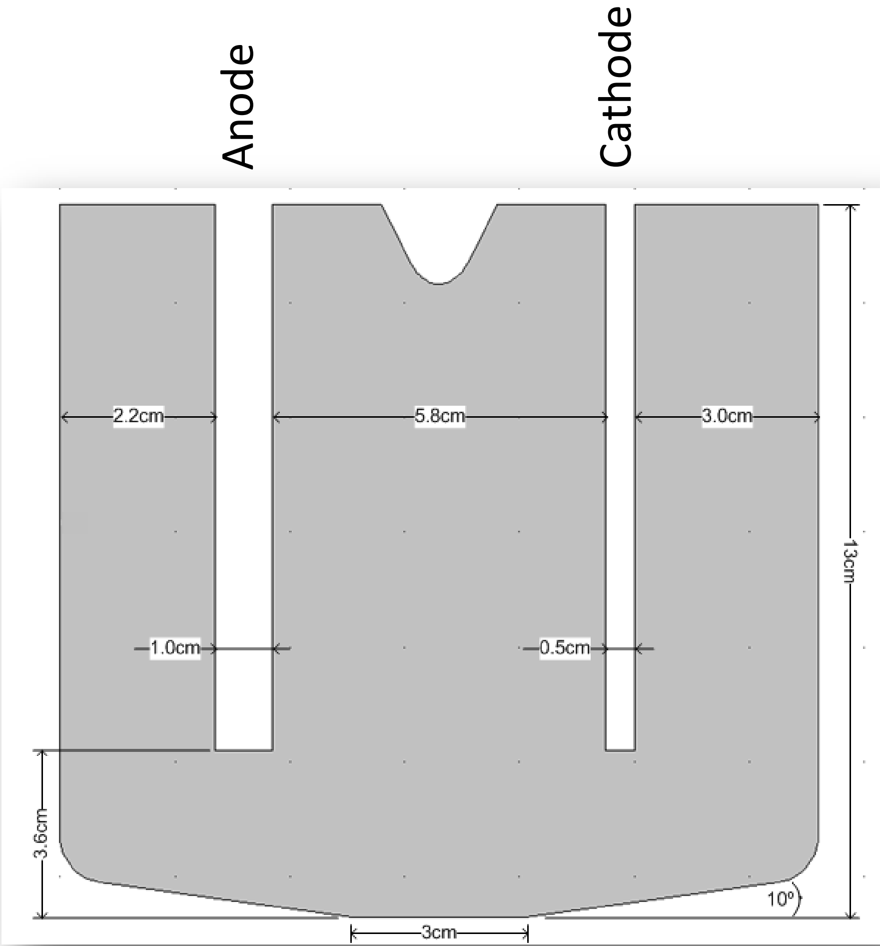
$$2HF \rightarrow H_2 + F_2$$

Simulation Procedure



Reactor cross-section

Simulation Procedure (Continued)



Electrolyte cross-section

Electron Transfer Boundaries

- Current density specified on electrodes
- Insulation all other boundaries

Heat Transfer Boundaries

- Temperature specified on side walls
- Insulation all other boundaries

Mass Transfer Boundaries

- Movement allow in and out of electrodes
- No flow of dissolved species through any boundaries

Momentum Transfer Boundaries

- Gas inlets at electrodes
- Gas outlet at top of electrolyte
- No flow of electrolyte through any boundaries

Simulation Procedure (Continued)

- Electron Transfer

$$-\nabla \cdot d(\sigma \nabla \Phi) = 0$$

$$\nabla \Phi^2 = 0$$

- Heat Transfer

$$\rho C_p \frac{\partial T}{\partial t} + \nabla \cdot (-k \nabla T) = Q - \rho C_p \vec{u} \nabla T$$

$$Q = i \cdot \left(\Phi - \Phi_{RV}\right) + i \cdot \left[2.81 \left(100 - E\right) / 100 \right]$$

Simulation Procedure (Continued)

- Mass Transfer

$$\frac{\partial C_i}{\partial t} + \nabla \cdot (-D_i \nabla C_i - z_i \mu_{m,i} F C_i \nabla \Phi + C_i \vec{u}) = r_i$$

$$KF \cdot 2HF \rightarrow K^+ + HF + HF_2^-$$

$$HF_2^- \rightarrow HF + \frac{1}{2} F_2 + e^-$$

$$2HF + e^- \rightarrow HF_2^- + \frac{1}{2} H_2$$

Simulation Procedure (Continued)

- Momentum Transfer

$$\phi_l \rho_l \frac{\partial \vec{u}}{\partial t} + \phi_l \rho_l \cdot \nabla \vec{u}_l = -\nabla P + \nabla \cdot \left[\phi_l (\eta_l + \eta_T) \left(\nabla \vec{u}_l + \nabla \vec{u}_l^{\ T} - \frac{2}{3} (\nabla \cdot \vec{u}_l) \vec{I} \right) \right] + \phi_l \rho_l g + \vec{F}$$

$$\nabla \cdot \vec{u}_l = 0$$

$$\frac{\partial \rho_g \phi_g}{\partial t} + \nabla \left(\phi_g \rho_g \vec{u}_g \right) = 0$$

Simulation Procedure (Continued)

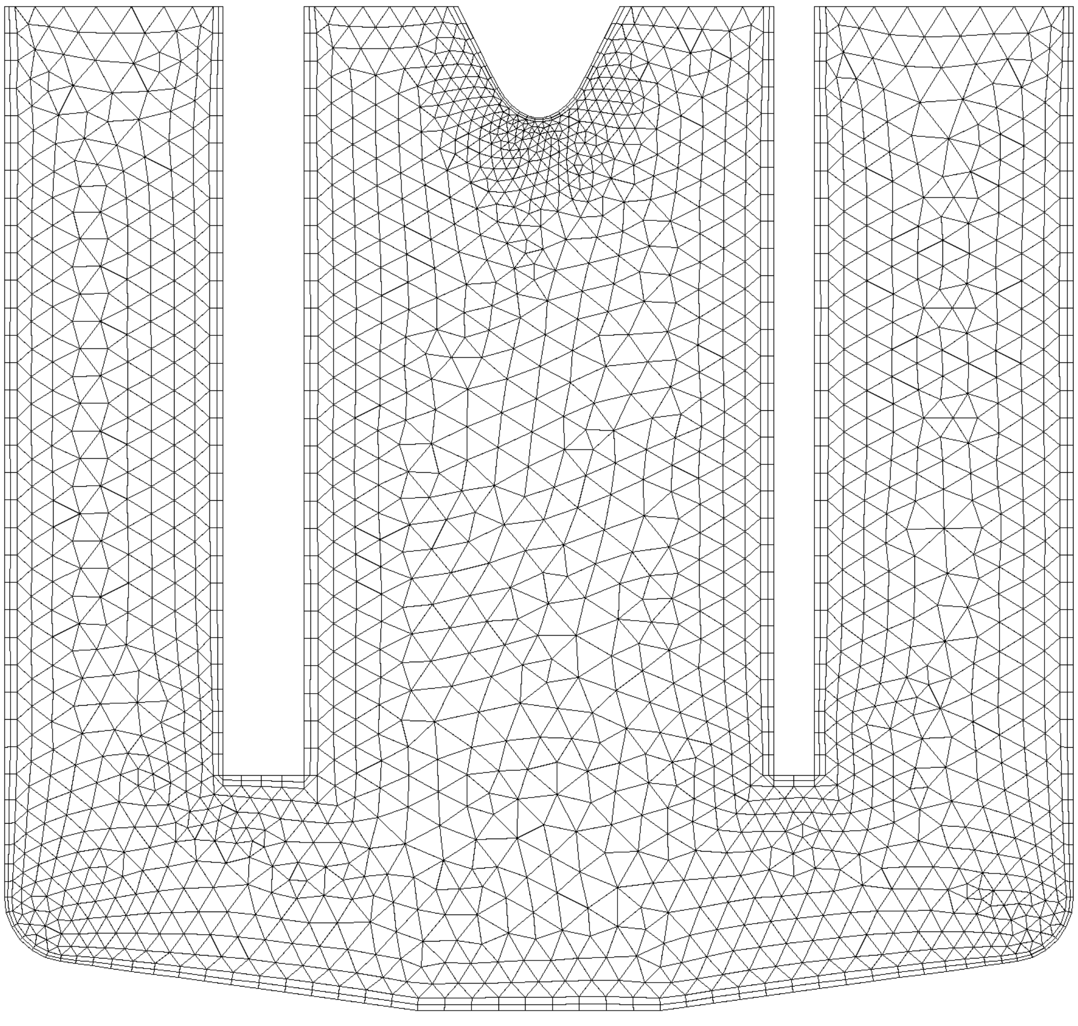
$$i_A = i_0 \left[\exp\left(\frac{\alpha_A F}{R_g T} \eta_s \right) - \exp\left(\frac{\alpha_C F}{R_g T} \eta_s \right) \right] \qquad i_C = -i_0 \left[\exp\left(-\frac{\alpha_A F}{R_g T} \eta_s \right) - \exp\left(-\frac{\alpha_C F}{R_g T} \eta_s \right) \right]$$

$$i_0 = F k_c^{0.5} k_a^{0.5} C_{HF_2^-}^{0.5} C_{HF}^{0.5}$$

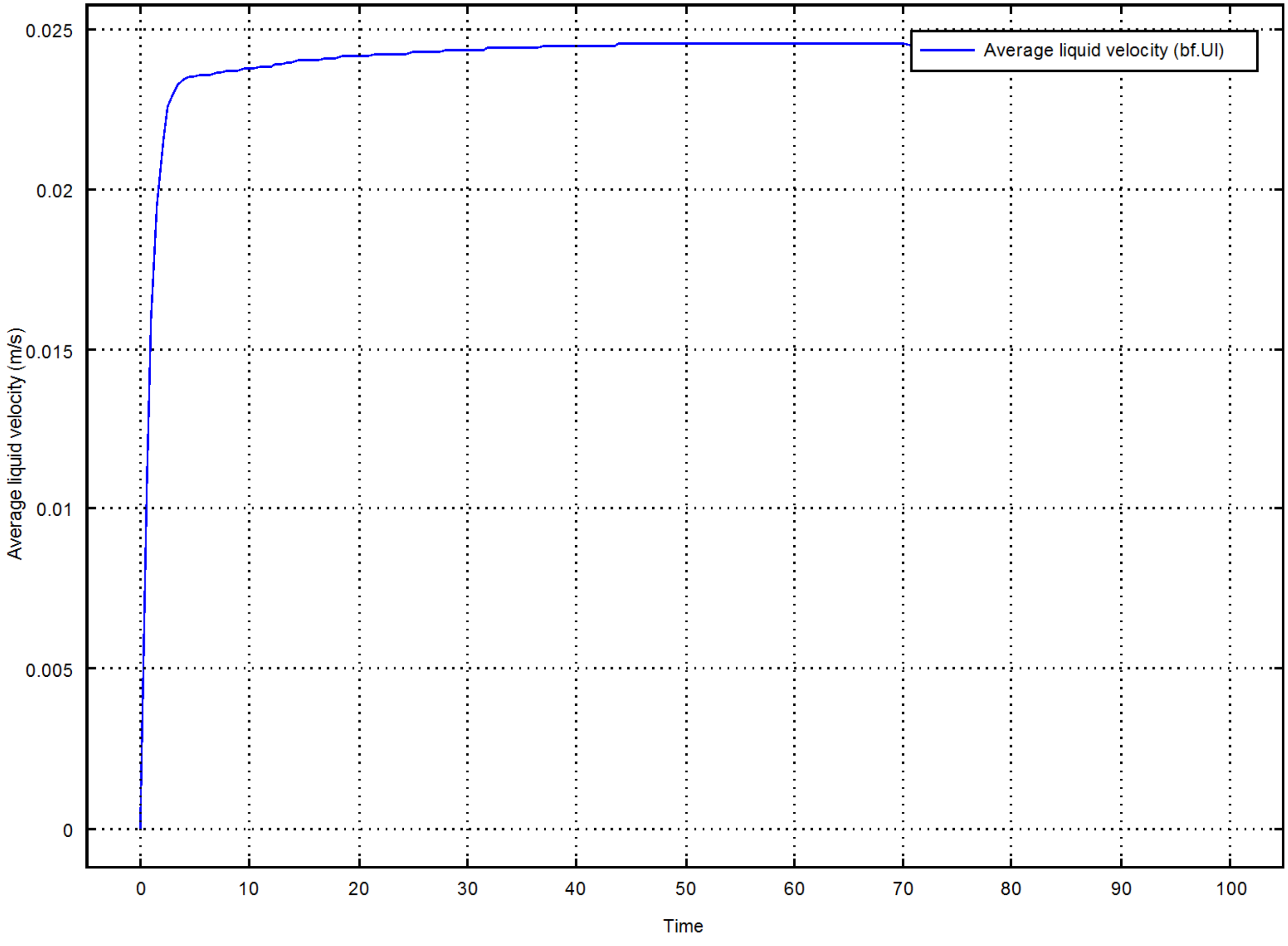
$$\eta_{s,A} = \Phi - \Phi_{0,A} \qquad \eta_{s,C} = -\Phi - \Phi_{0,C}$$

$$R_A = -\frac{1}{F} i_A \qquad R_C = -\frac{2}{F} i_C$$

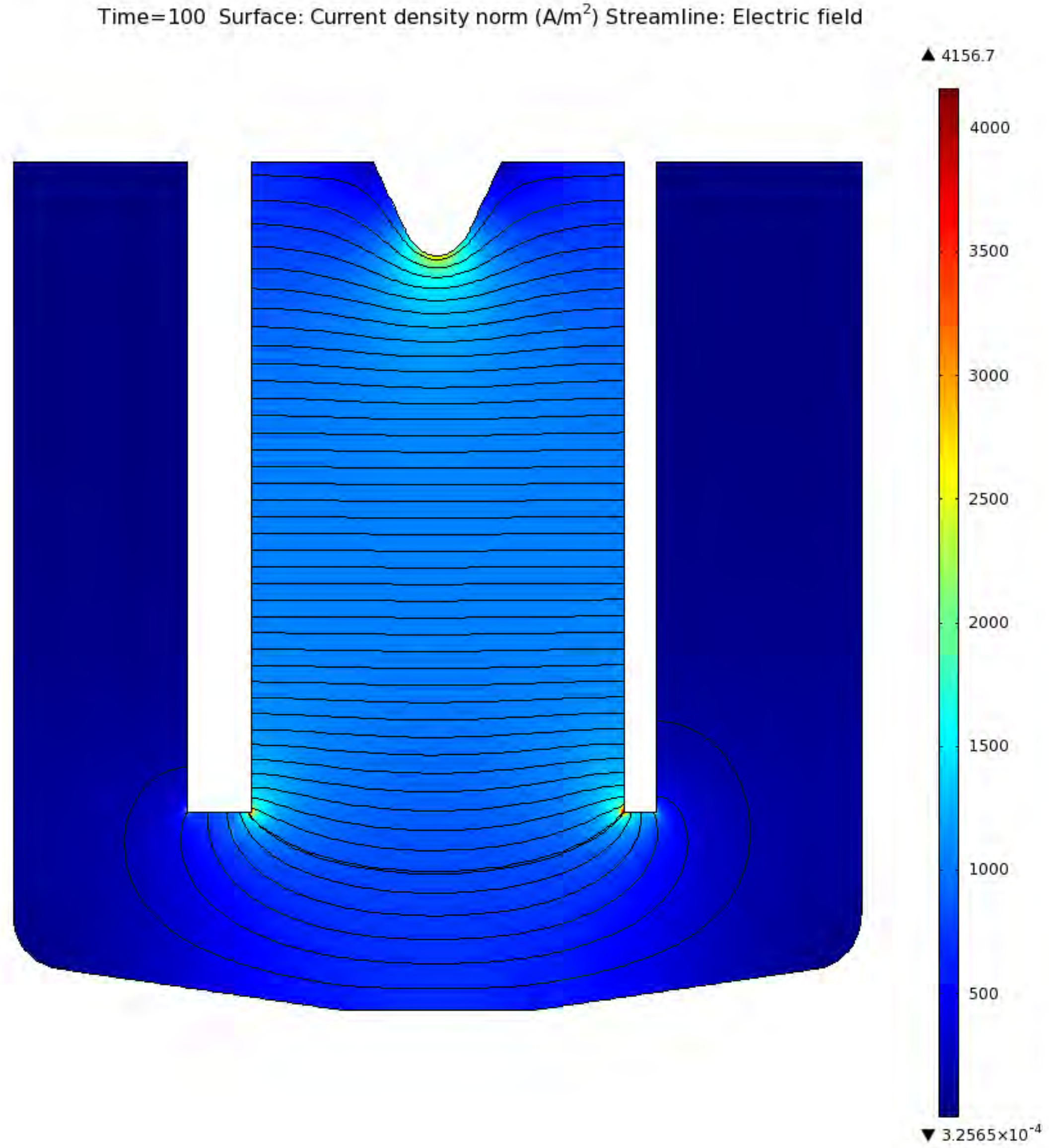
Simulation Procedure (Continued)



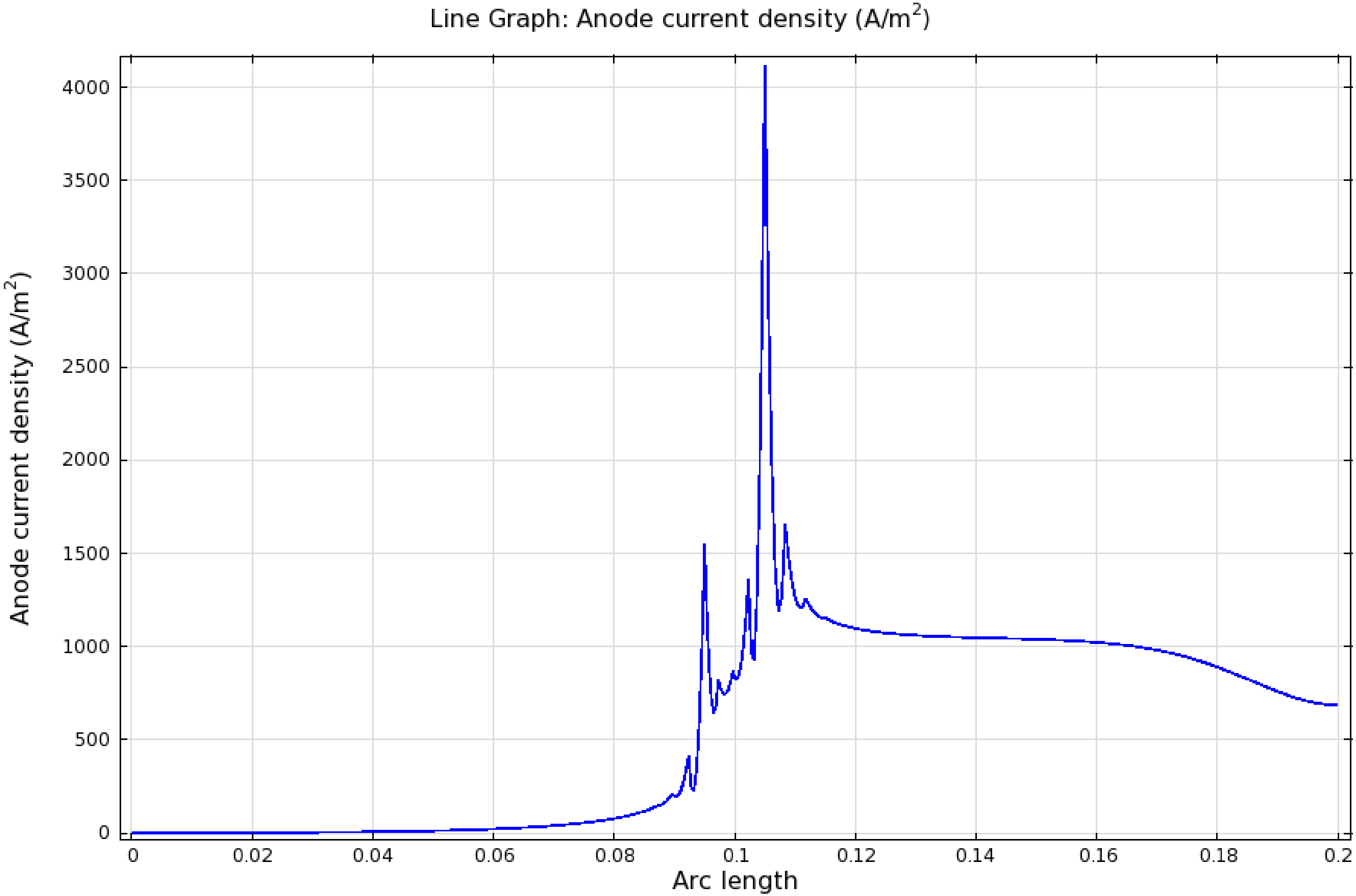
Results & Discussion



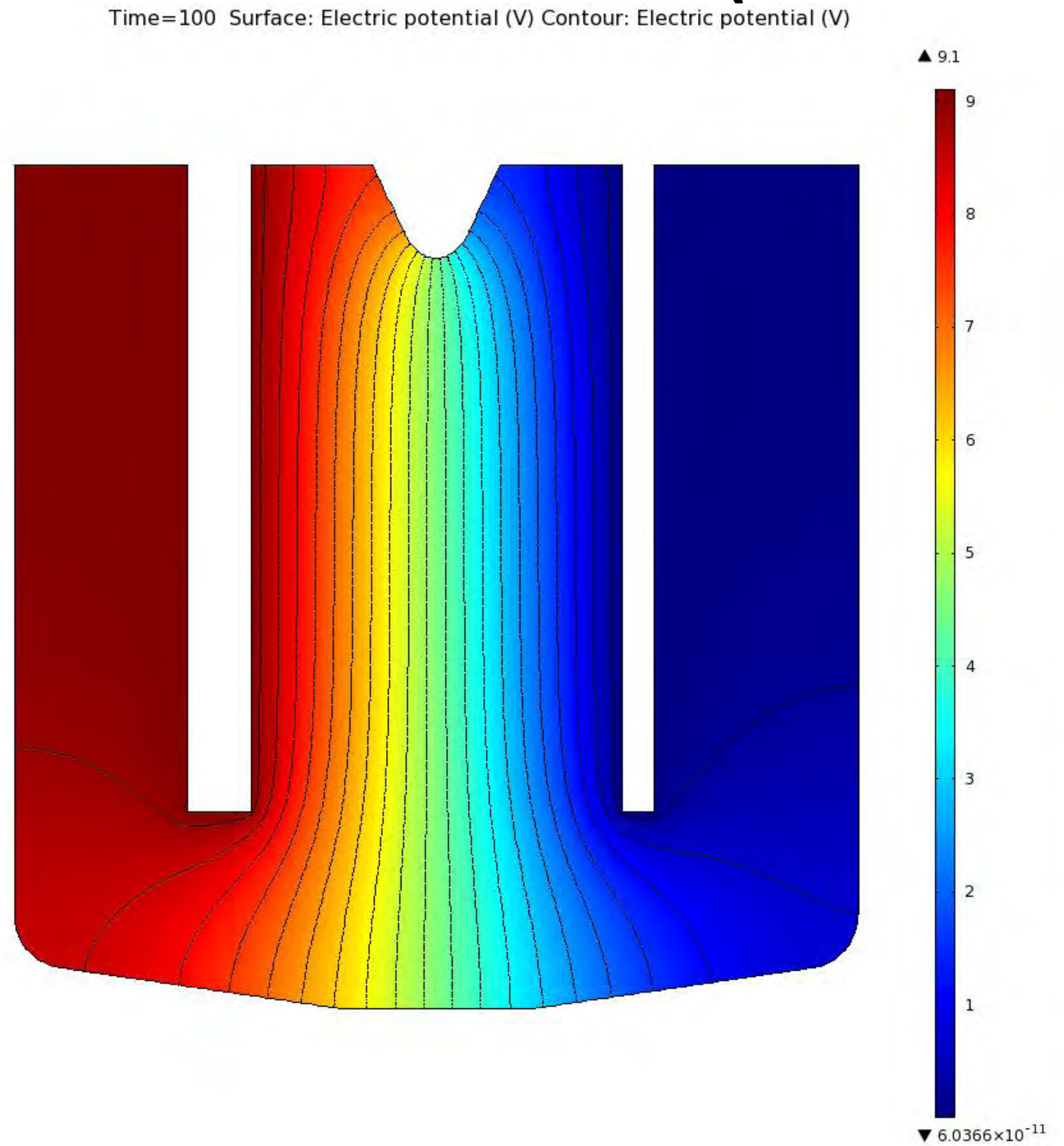
Results and Discussion (Continued)



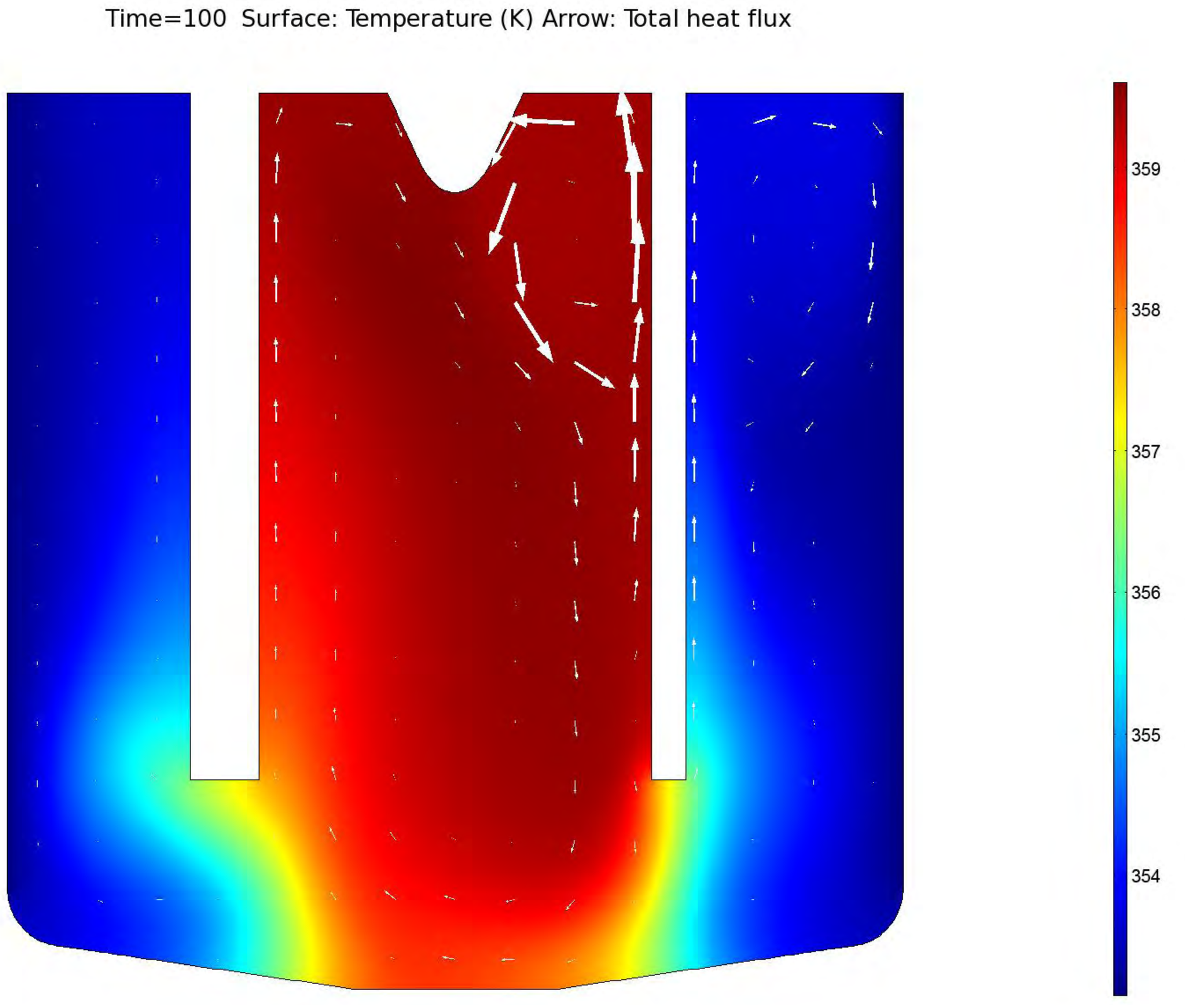
Results and Discussion (Continued)



Results and Discussion (Continued)

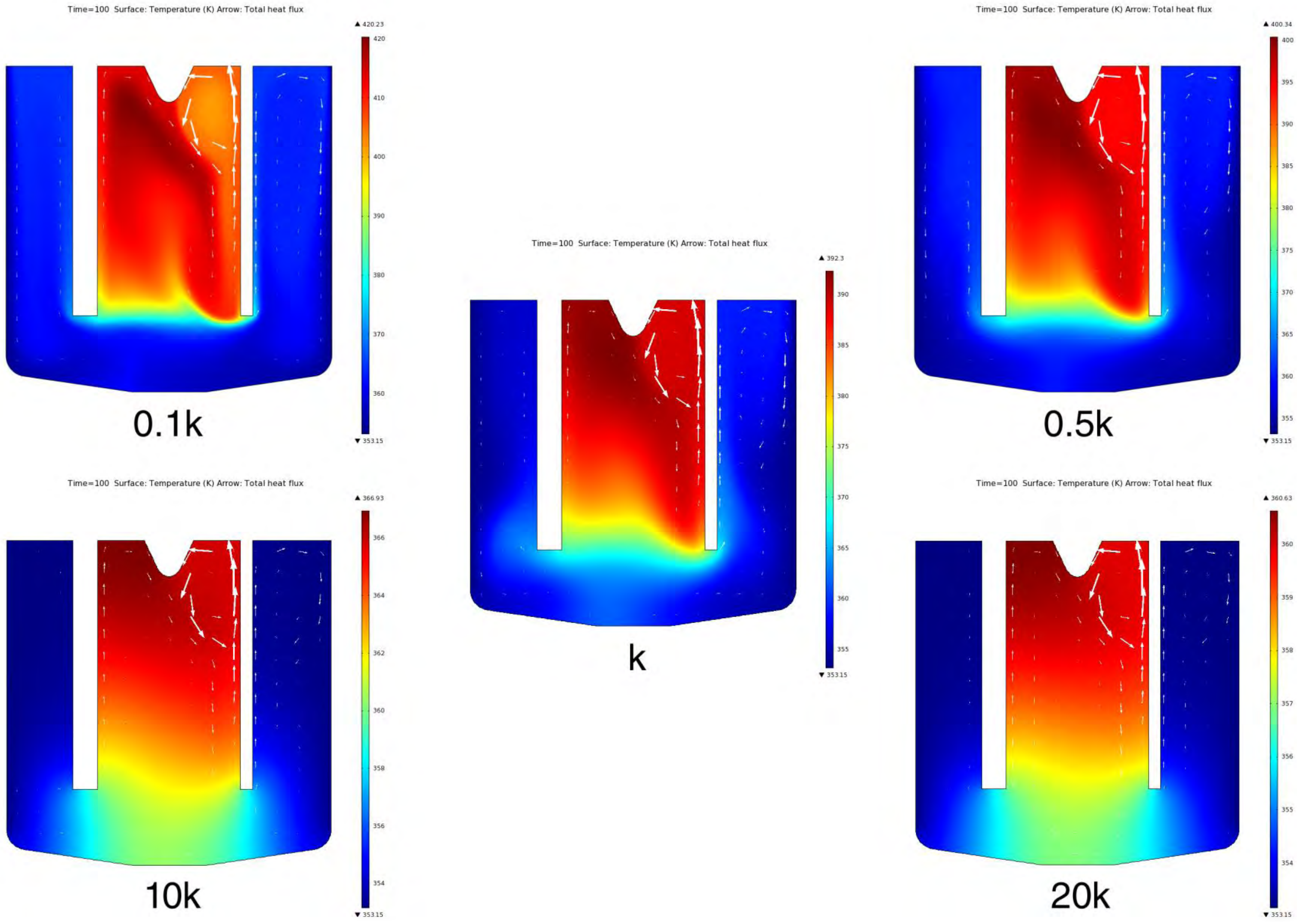


Results and Discussion (Continued)



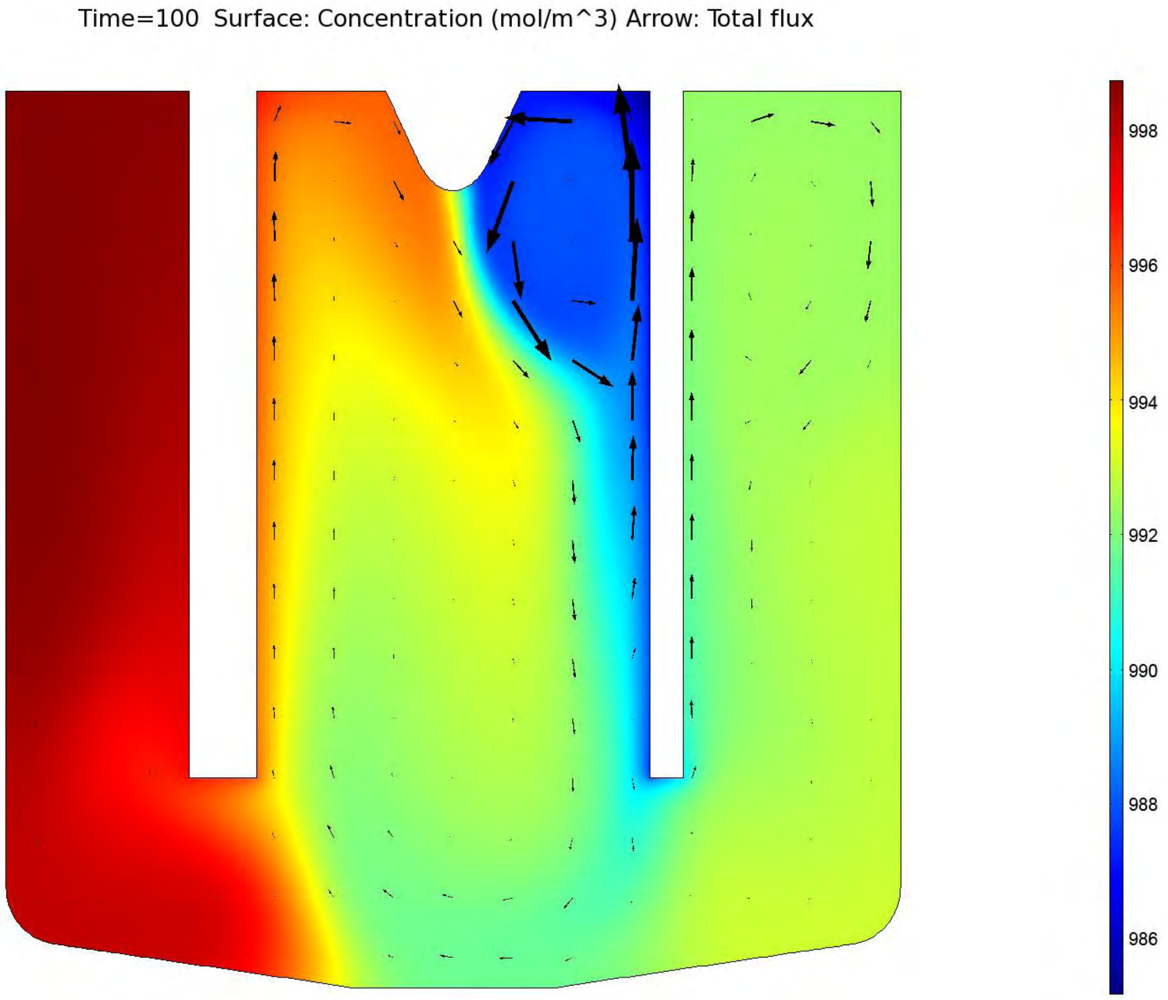
Play

Results and Discussion (Continued)

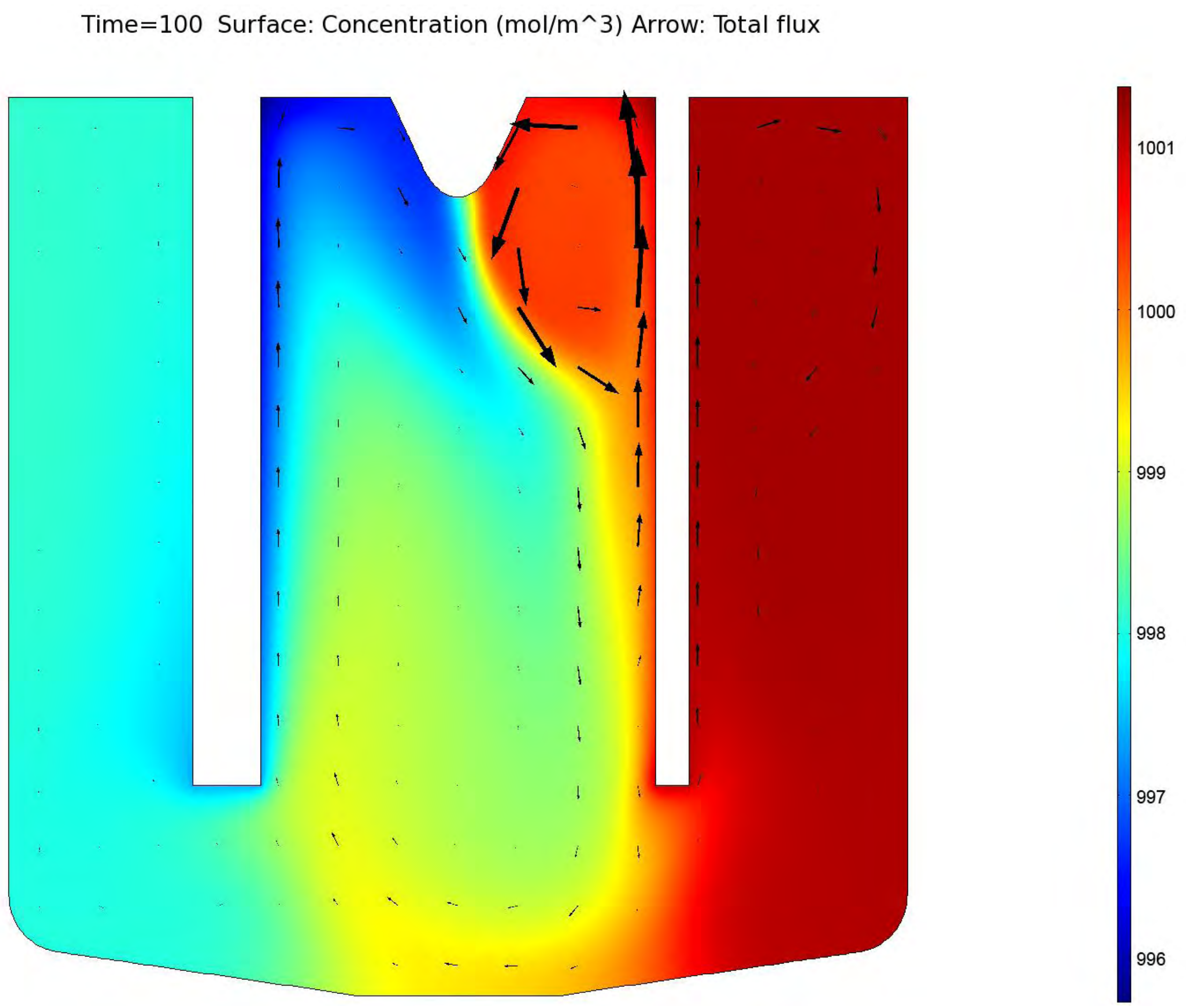


Results and Discussion (Continued)

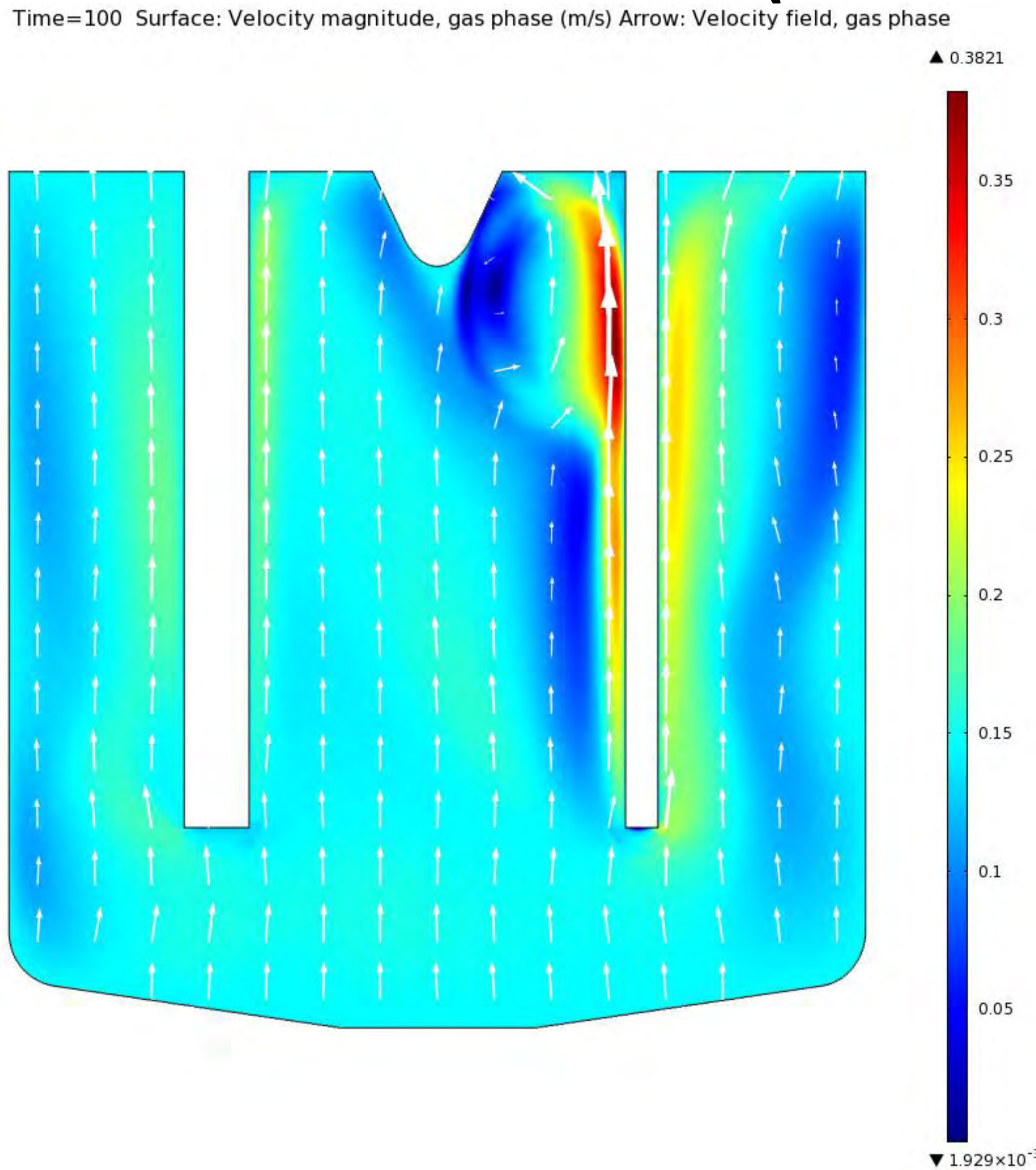
Play



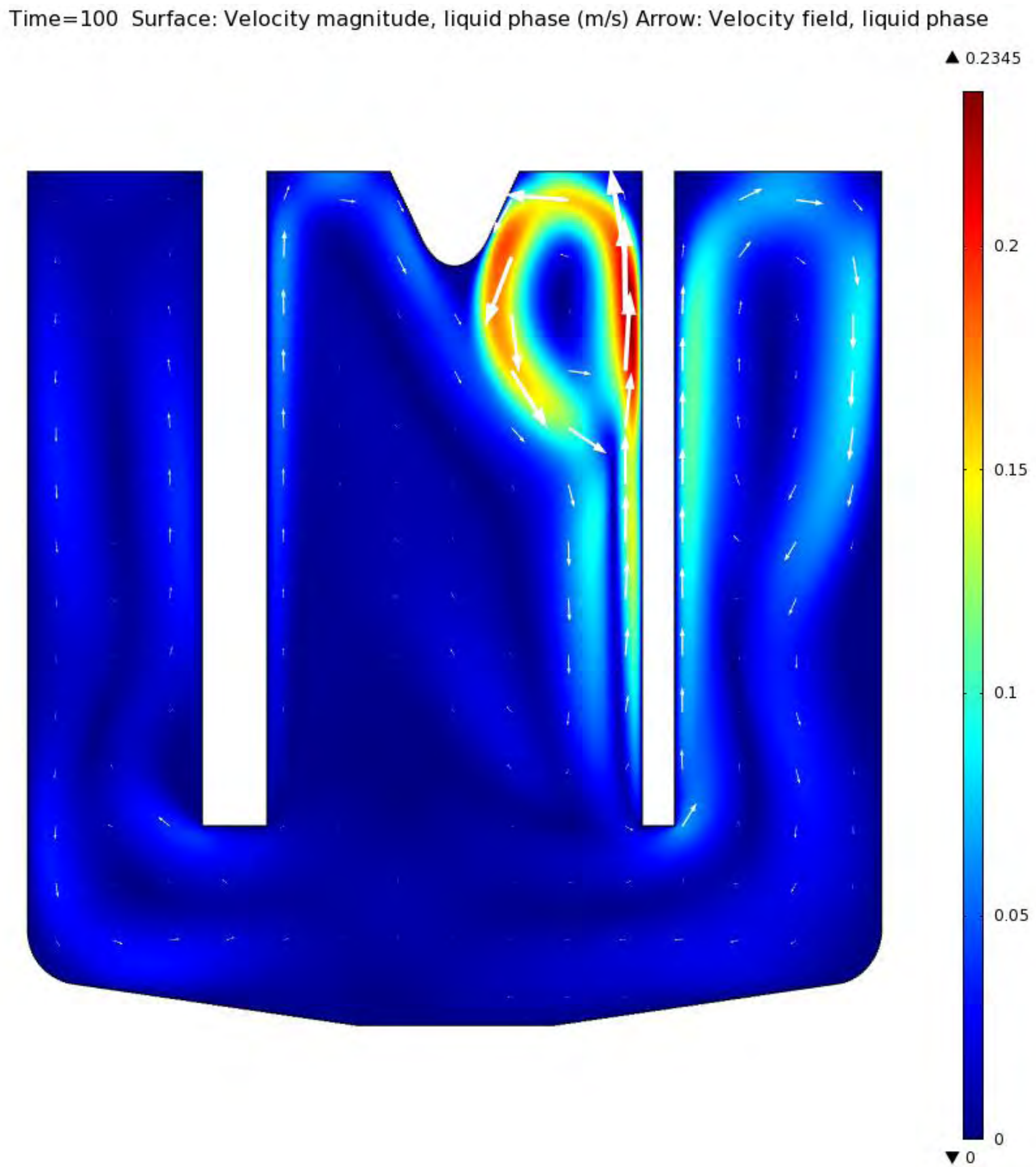
Results and Discussion (Continued)



Results and Discussion (Continued)

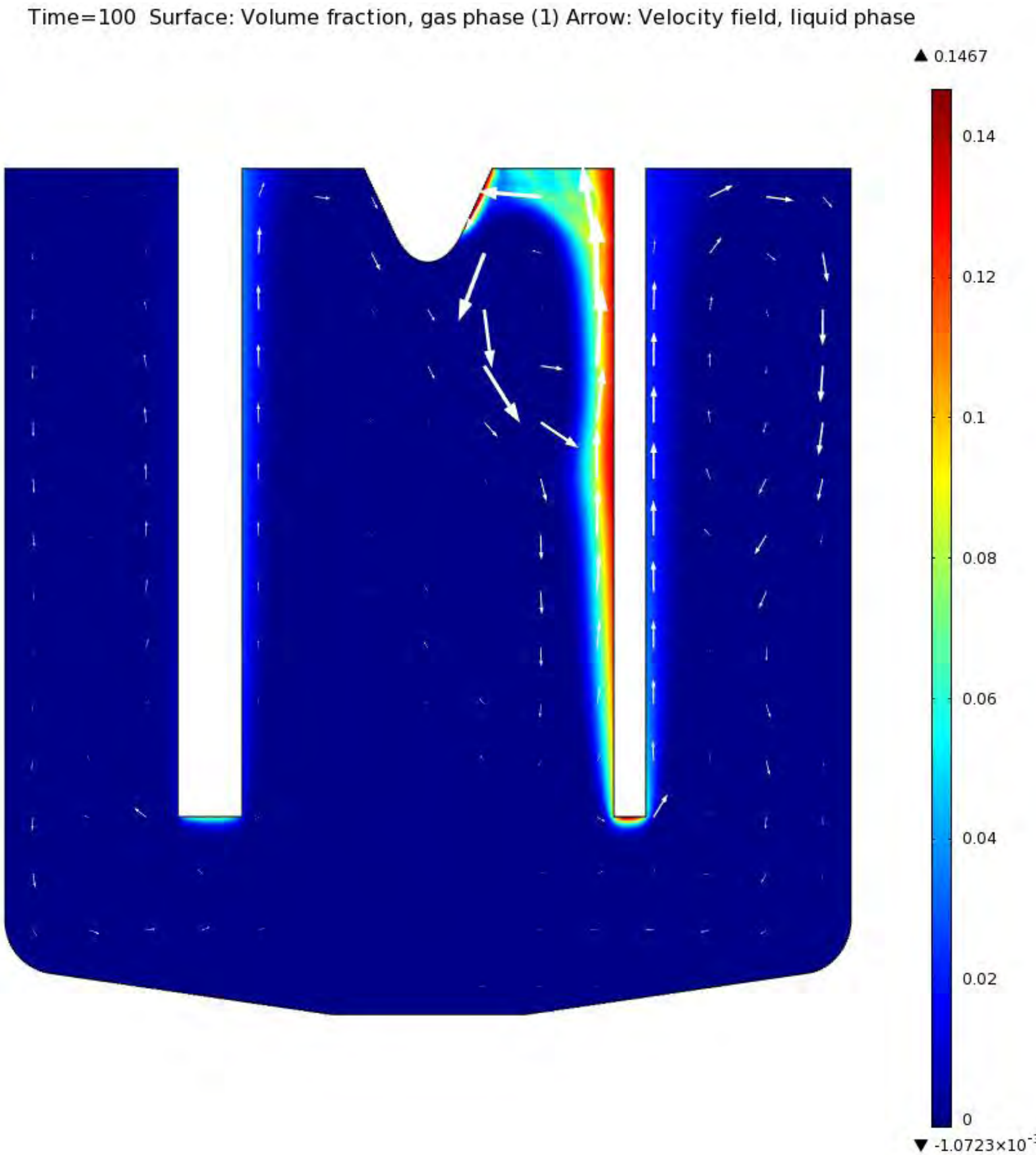


Results and Discussion (Continued)

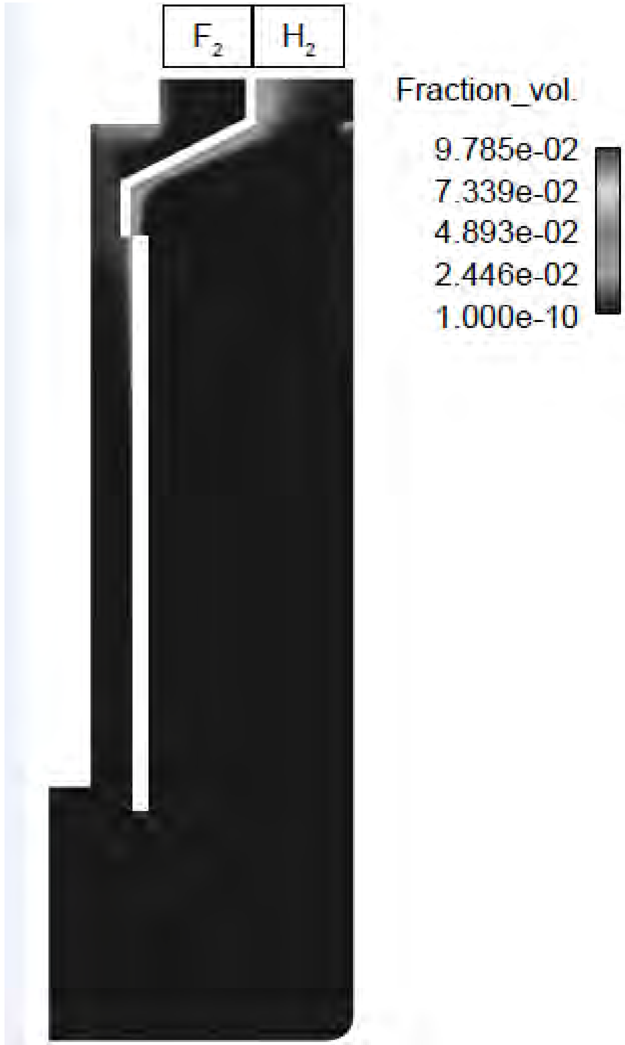


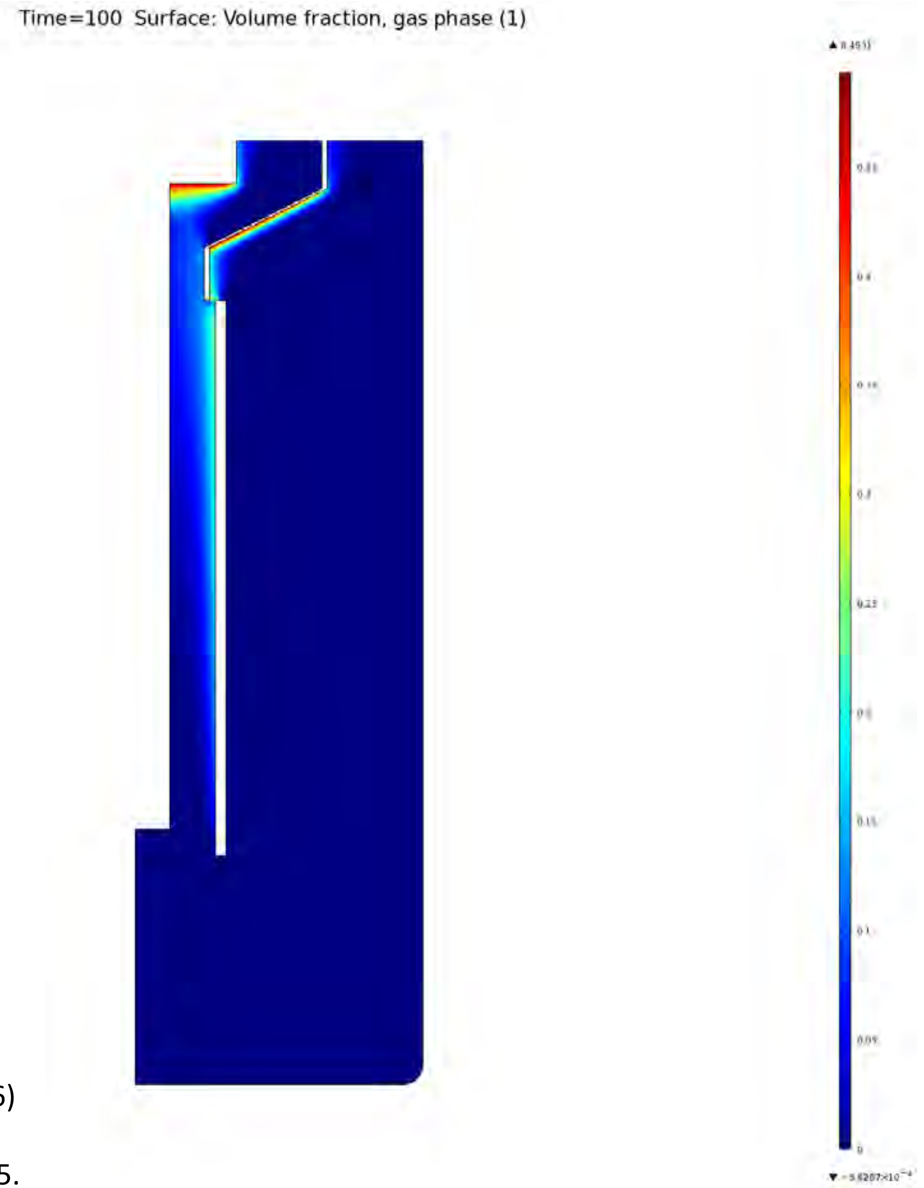
Results and Discussion (Continued)

Play



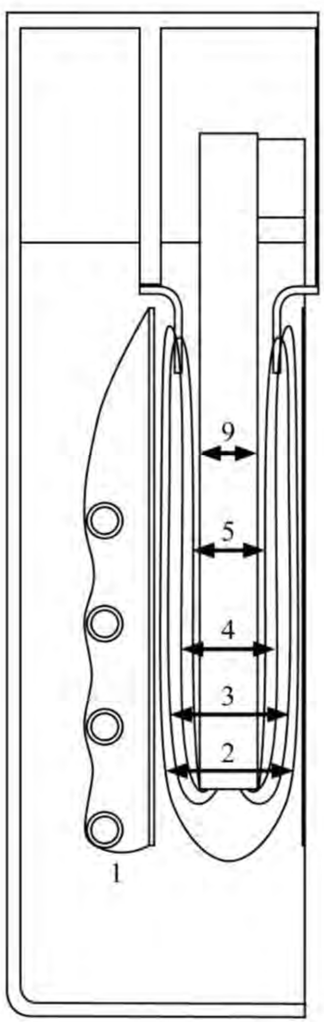
Results and Discussion (Continued)





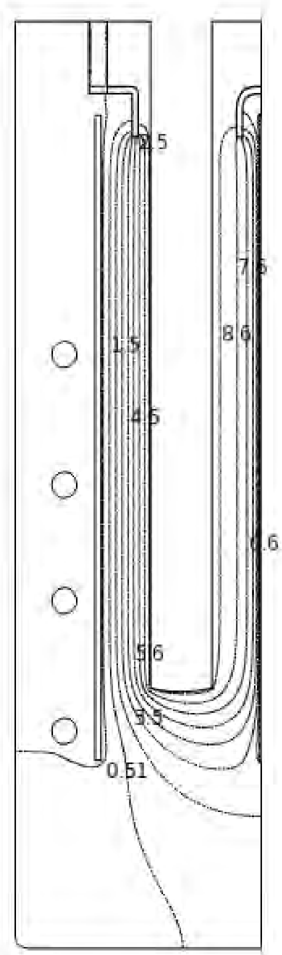
Reproduced from Espinasse, G, Peyrard, M, Nicolas, F and Caire JP (2006) “Effects of hydrodynamics on Faradaic current efficiency in a fluorine electrolyser” Journal of Applied Electrochemistry (2007) 37:77-85.

Results and Discussion (Continued)

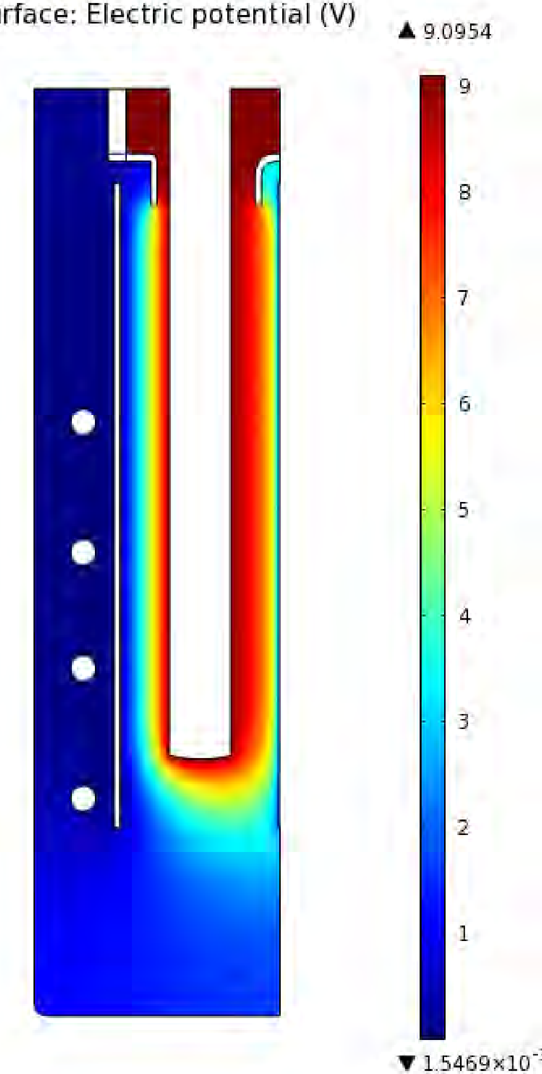


Key: (1) 0.0 V;
(2) 0.5 V;
(3) 1.0 V;
(4) 1.5 V;
(5) 7.5
...(9) 9.5 V.

Contour: Electric potential (V)

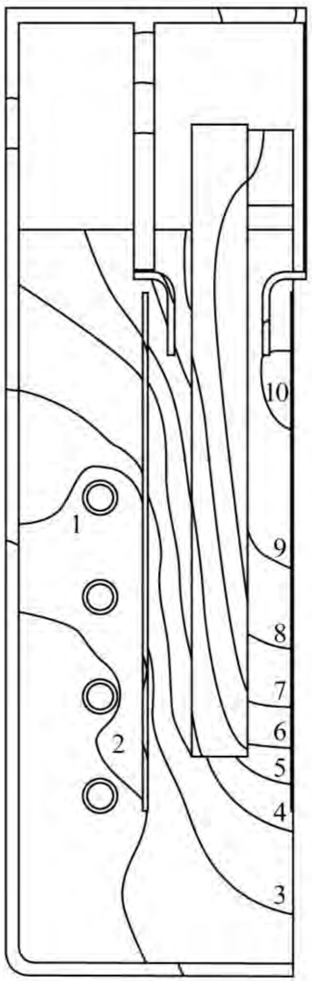


Surface: Electric potential (V)

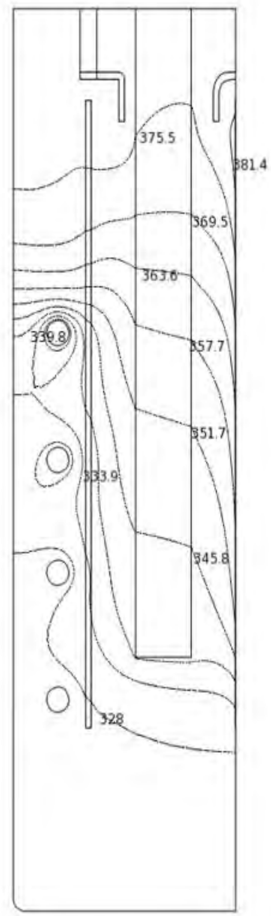


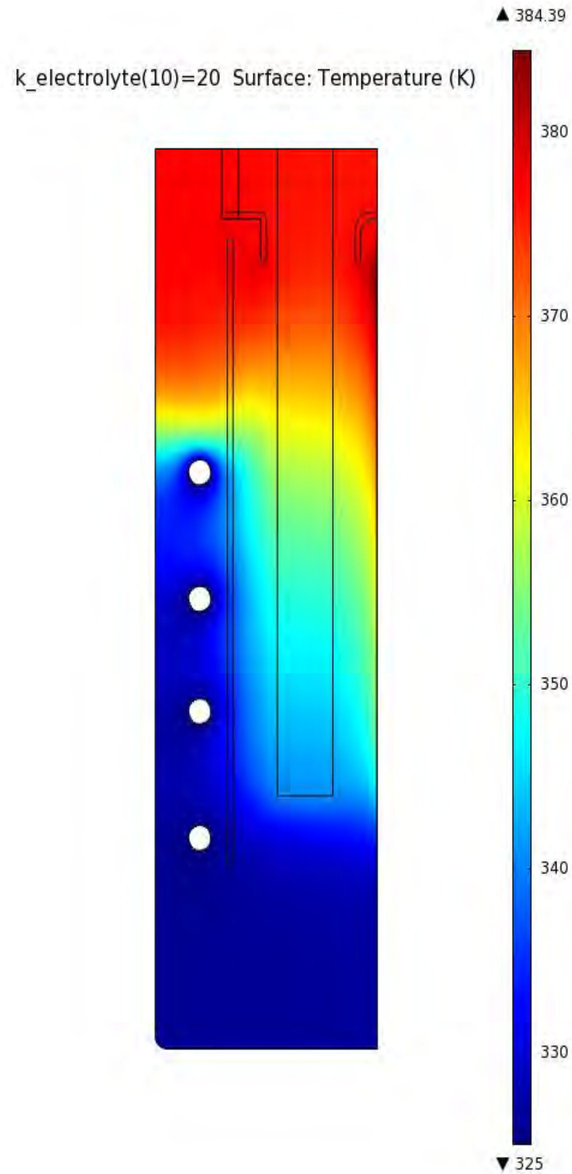
Reproduced from Rouston, H, Caire, JP, Nicolas, F, Pham, P (1997)
"Modelling coupled transfers in an industrial fluorine electrolyser"
Journal of Applied Chemistry, 28 (1998) 237-243.

Results and Discussion (Continued)



Key: (1) 325 K;
(2) 332 K;
(3) 339 K;
(4) 346 K;
(5) 353 K;
(6) 360 K;
(7) 367 K;
(8) 374 K;
(9) 381 K;
(10) 388 K.





Reproduced from Rouston, H, Caire, JP, Nicolas, F, Pham, P (1997) "Modelling coupled transfers in an industrial fluorine electrolyser" Journal of Applied Chemistry, 28 (1998) 237-243.

Conclusions

- The simulated results of the UP experimental reactor are reasonable and within expected limits.

- The COMSOL simulations of published experimental results compare favourably to the published results in most cases.

Recommendations

- Use of the simulated results as a guideline during the experimental investigation of the reactor performance
- Thorough investigation into physical constants used during simulation
- Investigation of equations used during simulation, specifically the Ohmic-heating equation

References

- Espinasse, G, Peyrard, M, Nicolas, F and Caire JP (2006) “Effects of hydrodynamics on Faradaic current efficiency in a fluorine electrolyser” Journal of Applied Electrochemistry (2007) 37:77-85.
- Roustan, H, Caire, JP, Nicolas, F, Pham, P (1997) “Modelling coupled transfers in an industrial fluorine electrolyser” Journal of Applied Electrochemistry, 28 (1998) 237-243.

Thank you

Boundary Conditions

- Heat Transfer Boundary Conditions

Boundary	***Boundary Condition***	***Description***	***Equation***
Walls in contact with heating/cooling jacket	Temperature specified	Wall temperature set to T_w, a constant 80 °C	$T = T_w$
All other boundaries	Thermal insulation	No heat flux allowed	$\vec{n} \cdot (-k\nabla T) = 0$

- Electron Transfer Boundary Conditions

Boundary	***Boundary Condition***	***Description***	***Equation***
Anode	Inward current density	Current density i_A as determined by the Butler-Volmer equation	$\vec{n} \cdot i_n = i_A$
Cathode	Inward current density	Current density i_C as determined by the Butler-Volmer equation	$\vec{n} \cdot i_n = i_C$
All other boundaries	Electric insulation	No current flow allowed	$\vec{n} \cdot i_n = 0$

Boundary Conditions

- Mass Transfer Boundary Conditions

Boundary	***Boundary Condition***	***Value/Expression***	***Equation***
Anode	Dual mass flux	Reactive species HF flows into electrode and HF_2^- out of electrode as defined by R_A	$\vec{n}\cdot(-D_i\nabla C_i + C_i\vec{u}) = -n\cdot R_A$
Cathode	Inward current flow	Reactive species HF_2^- flows into electrode and HF out of electrode as defined by R_C	$\vec{n}\cdot(-D_i\nabla C_i + C_i\vec{u}) = 0$
All other boundaries	Mass flow insulation	No mass flow allowed	$\vec{n}\cdot(-D_i\nabla C_i + C_i\vec{u}) = -n\cdot R_C$

Boundary Conditions

- Momentum Transfer Boundary Conditions

Boundary	***Boundary Condition***	***Description***	***Equation***
Electrolyte level	Liquid boundary condition: slip Gaseous boundary condition: gas outlet	Acts as a gas outlet and allows liquid slip.	$\frac{\partial \vec{u}_l}{\partial t} = 0$ $\frac{\partial \vec{u}_g}{\partial t} = \phi \cdot \rho \cdot \vec{u}_g$
Anode surface	Liquid boundary condition: no slip Gaseous boundary condition: gas flux	Allows gas production according to specified reaction rate (R_A). No liquid flow.	$\vec{u}_l = 0$ $\frac{\partial \vec{u}_g}{\partial t} = n \cdot \rho_g \cdot R_A$
Cathode surface	Liquid boundary condition: no slip Gaseous boundary condition: gas flux	Allows gas production according to specified reaction rate (R_C). No liquid flow	$\vec{u}_l = 0$ $\frac{\partial \vec{u}_g}{\partial t} = n \cdot \rho_g \cdot R_C$
All other boundaries	Liquid boundary condition: no slip Gaseous boundary condition: no gas flux	Allows neither gas or liquid flow, both without slip	$\frac{\partial \vec{u}_i}{\partial t} = 0$