High Temperature Vaporization into Different Environments

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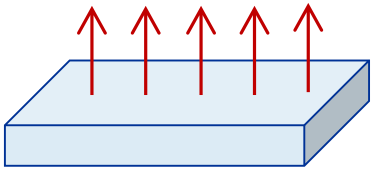
Vaporization

- At the appropriate temperature, all materials exhibit some degree of vaporization

- May be the limiting factor at high temperatures

- How does the amount of vaporization (net vapor flux) depend on the environment above the sample?
  - Vacuum (e.g. heat treatment)
  - Static Gas (e.g. heat treatment, processing)
  - Flowing Gas (e.g. gas turbine)
    - Laminar Flow
    - Turbulent Flow



- Model SiO_2 vaporization $\rightarrow$ $SiO(g) + \frac{1}{2} O_2(g)$ (primary route)

  $\rightarrow$ $SiO_2(g)$

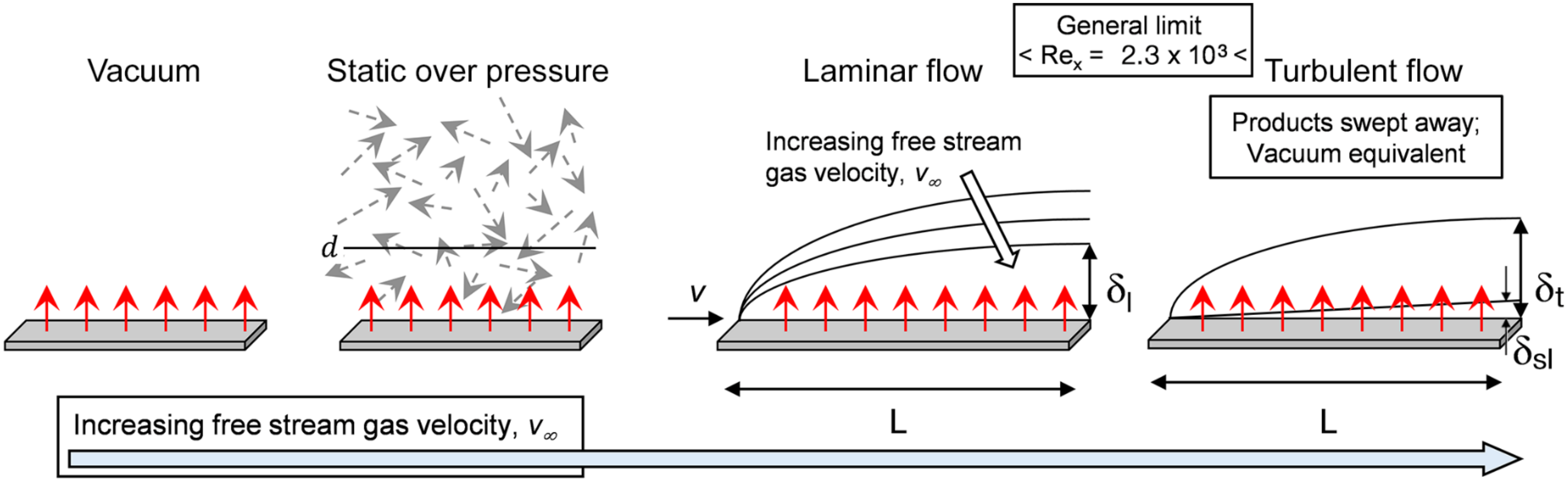
- Model each with equations from kinetic theory, fluid flow

  Flowing gases can also be modeled with Computational Fluid Dynamics (CFD)

Quantify Vaporization

- Thermochemical: Use partial pressure
- Focus on Vapor: Use *J*, vapor flux (mole/unit area-unit time) or (weight/unit area-unit time)
  - $J_i = \frac{h_i}{RT}\left(P_{i,s} - P_{i,\infty}\right)$ h_i = Mass transfer coefficient
- Focus on oxidation/corrosion issues of structural materials, use R, recession rate (unit length/unit time)
  - $R_i = \frac{\sum_i J_i}{\rho}$ ρ = Density of oxide

Vaporization into a Vacuum, Static Gas, Flowing Gas



HKL equation

$$J_v = \frac{\alpha_v [P_{eq}(MO)]}{\sqrt{2\pi MRT}}$$

Fick's first law

$$J = -\frac{D}{RT}\frac{P_{surf}}{d}$$

Laminar flow

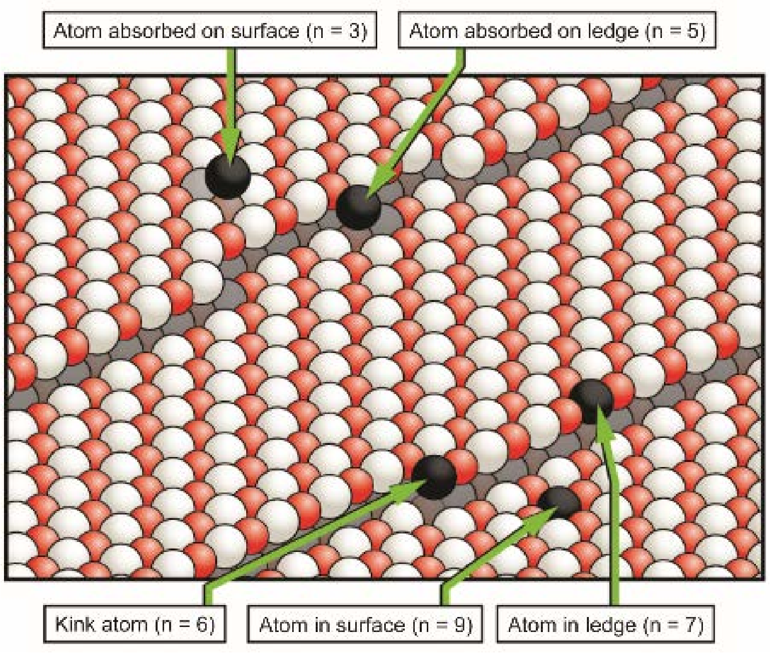
$$J_i = 0.665(Re)^{0.5}(Sc)^{0.33}\frac{D_i(\rho_{i,s})}{L}$$

Turbulent flow

$$J_i = 0.0365\,(Re)^{0.8}(Sc)^{0.33}\frac{DiP_i}{RTL}$$

Also model with CFD

Vaporization of Clean Surface into a Vacuum

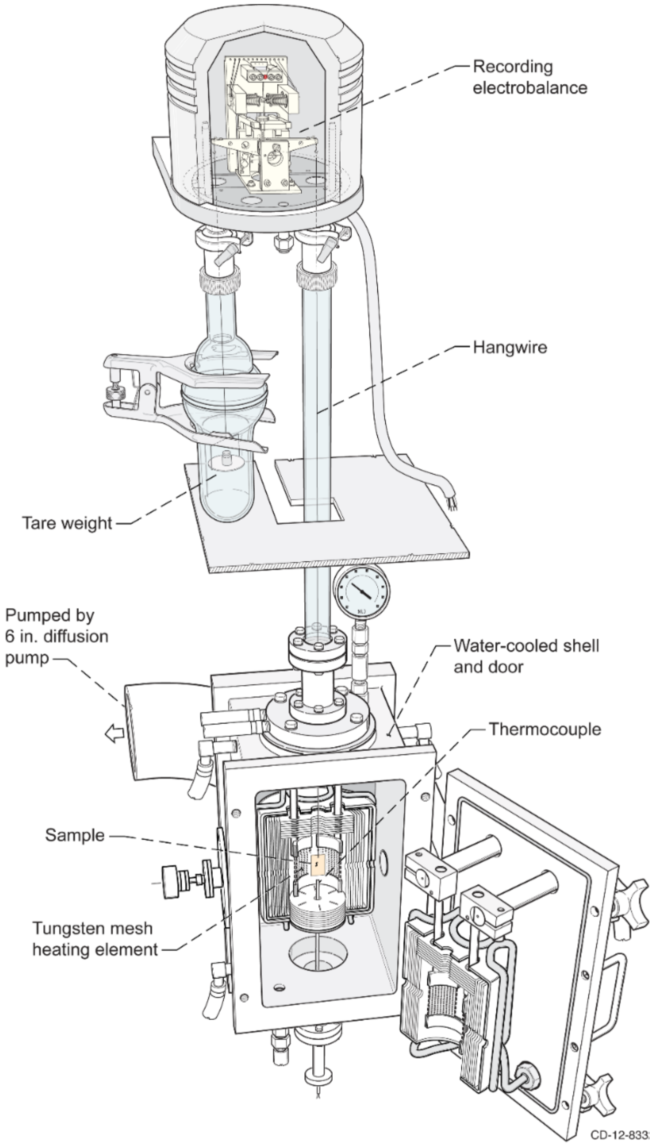


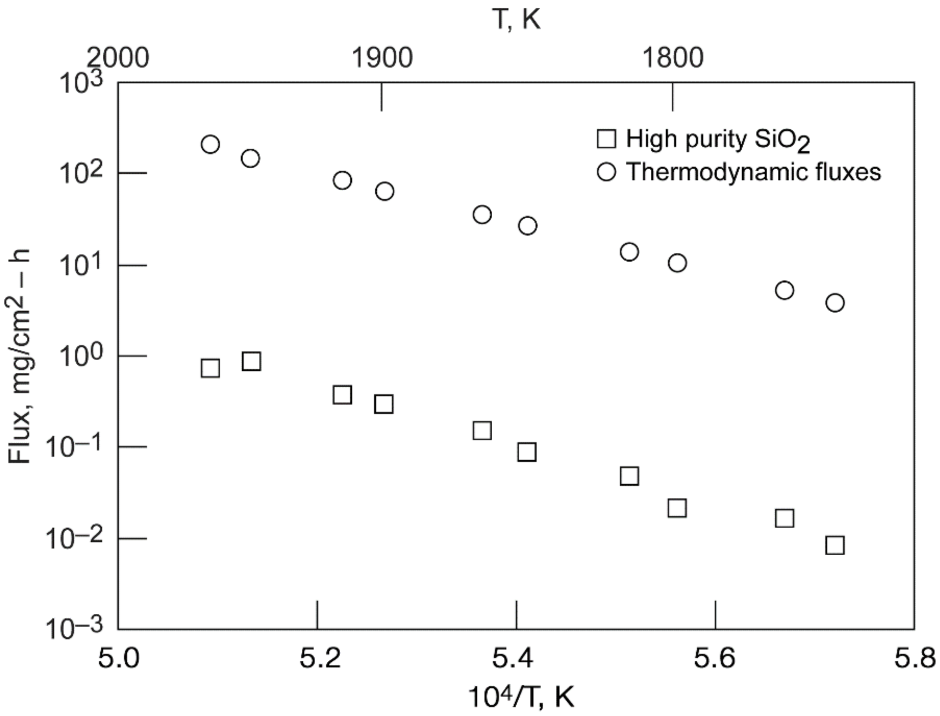
- Derive flux from kinetic theory of gases
  - $J = \alpha P/(2\pi MRT)^{0.5}$
  - α = vaporization coefficient (kinetic factor)

- Fundamental models* of vaporization developed from these conditions
  - Terrace-Ledge-Kink model
  - Vaporizing species moves to smaller coordination number site
  - $A(s) \rightarrow A(l) \rightarrow A(a) \rightarrow A(g)$

*1, O. Knacke and I. N. Stranski, The mechanism of evaporation. In *Progress in Metal Physics*: 6, 1956 (181-235).
2. W. Hirschwald and I. Stranski, Theoretical considerations and experiments on evaporation of solids. In *Condensation and Evaporation of Solids*, Gordon & Breach, New York, 1964 (59-85).

Vaporization from a SiO_2 coupon in a Vacuum





$$J = \frac{\alpha P_{eq}(MO)}{\sqrt{2\pi MRT}}$$

α = vaporization coefficient (kinetic factor)

- α(Pure metals) ~ 1
- α(Oxides) 1 to 10^{-6} !
- $\alpha(SiO_2) = (5 - 22) \times 10^{-3}$

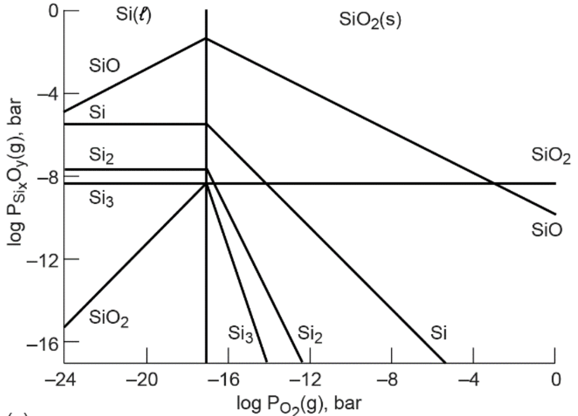
Vaporization into a Static Gas

- Inert Gas: Kinetic effect only
  - Fick’s first law

$$J_i = -D_i \frac{dc_i}{dx} = \frac{-D_i}{RT}\frac{dP_i}{dx} \approx \frac{-D_i}{RT}\frac{P_o}{x}$$

  - Flux $\propto$ 1/x

- Reactive Gas
  - Kinetic effect
  - Thermodynamic Effect
    - Suppress vaporization
      - $SiO_2(s) = SiO(g) + ½\ O_2(g)$
    - Enhance vaporization
      - $Cr_2O_3(s) + 3/2\ O_2(g\} = 2CrO_3(g)$



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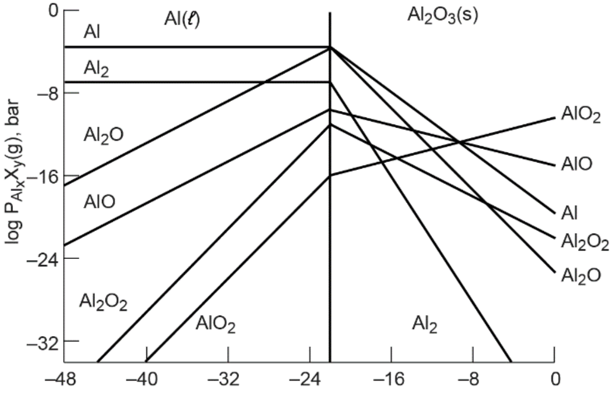

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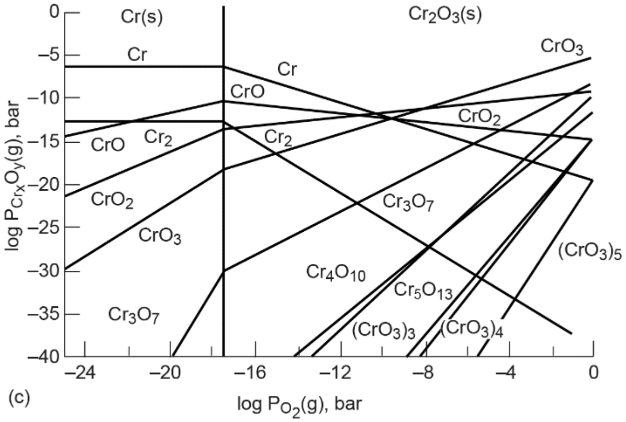


(c)

Reactive Gas Over Pressure

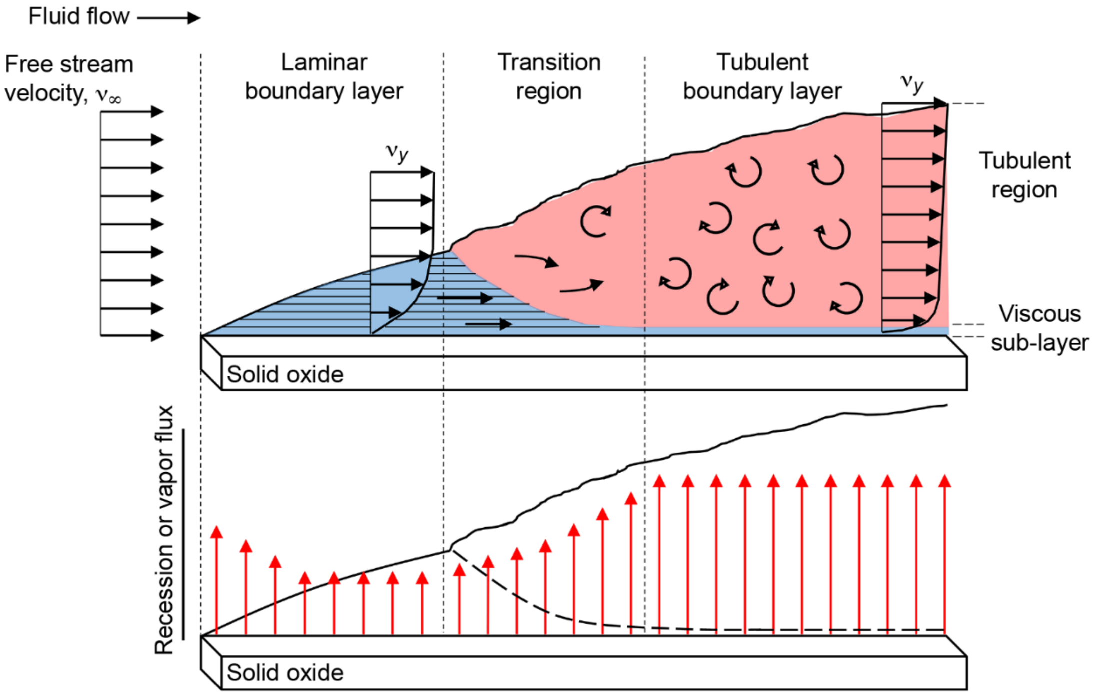
Best shown with volatility diagrams (Kellogg 1966)

- Plot of log $P(M_xO_y(g))$ vs log $P(O_2)$
- Negative slope means: ↑ $P(O_2)$, ↓ $P(M_xO_y)$
  - SiO_2, Al_2O_3
- Positive slope means: ↑ $P(O_2)$, ↑ $P(M_xO_y)$
  - Cr_2O_3

Kohl et al.,NASA TM-X-73682

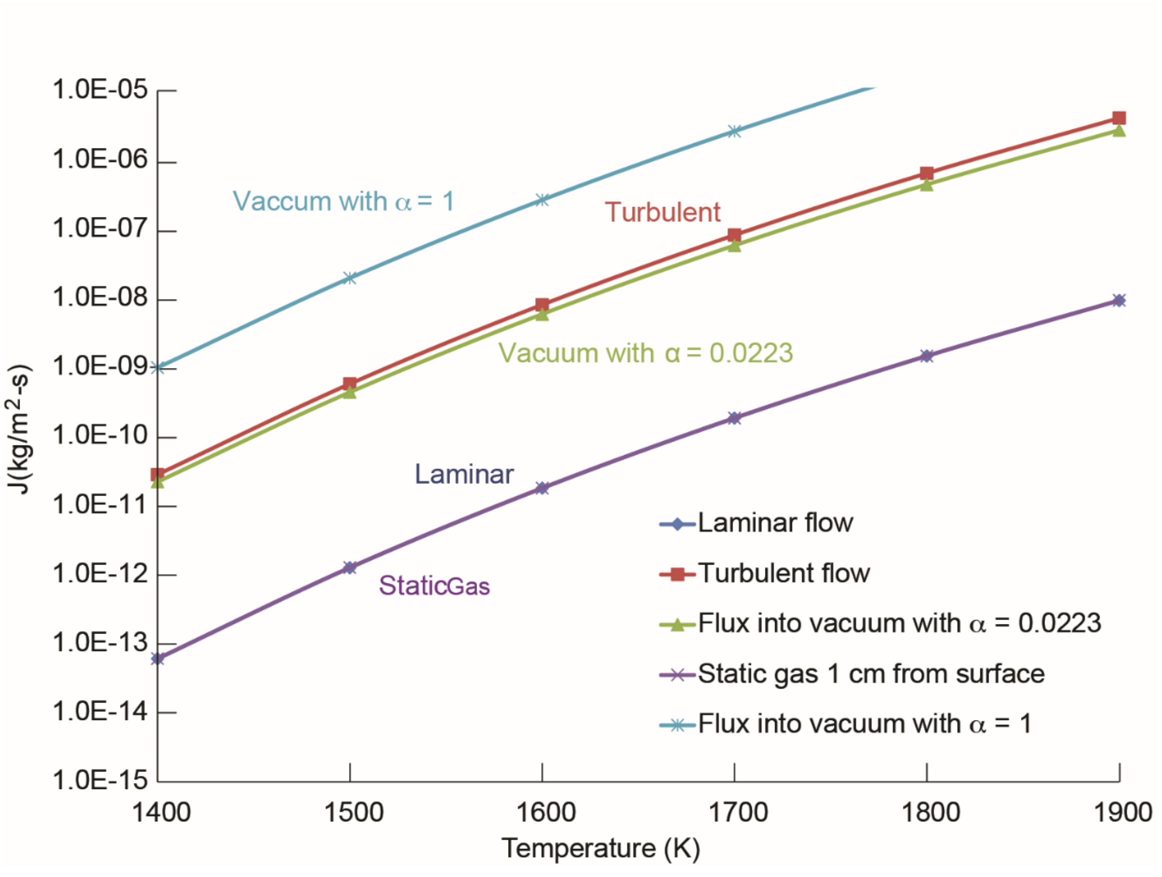
Flowing Gas: Developing Boundary Layer

- Laminar → Turbulent by increasing Reynolds number
- $Re_x = \frac{\rho v L}{\mu}$ Increases with increasing ρ, v, L



- Velocity boundary layer: Edge at 99% of free stream velocity
- Turbulent region has steep gradient in velocity near surface: viscous sublayer
- Viscous sub-layer limits vapor flux; Flux in rapidly flowing inert gas = Flux in vacuum

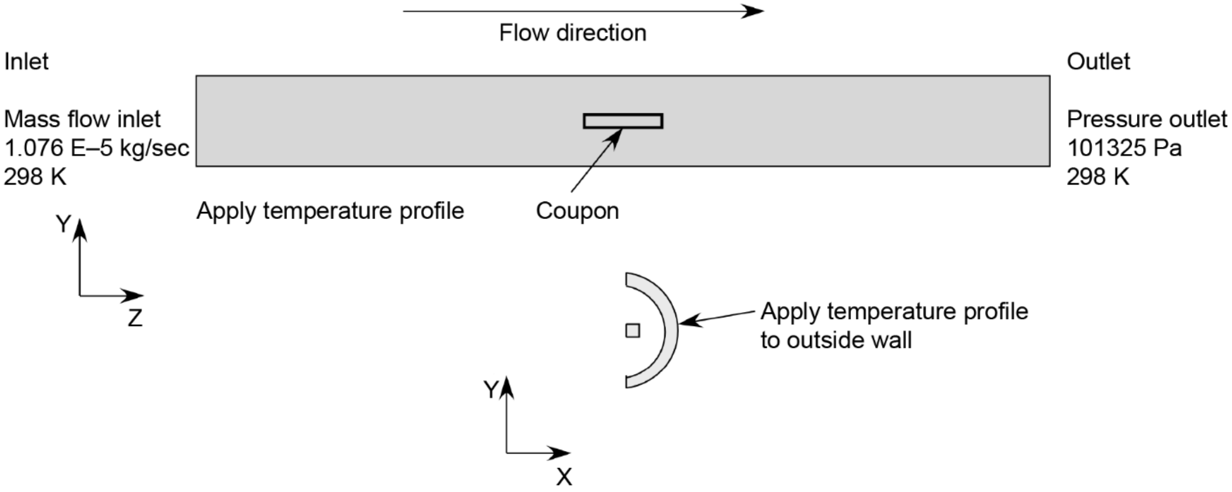
Comparison of Fluxes for each Condition



J(vacuum with $\alpha = 1$) > J(vacuum with $\alpha = 0.02$, turbulent) > J(Laminar, static)

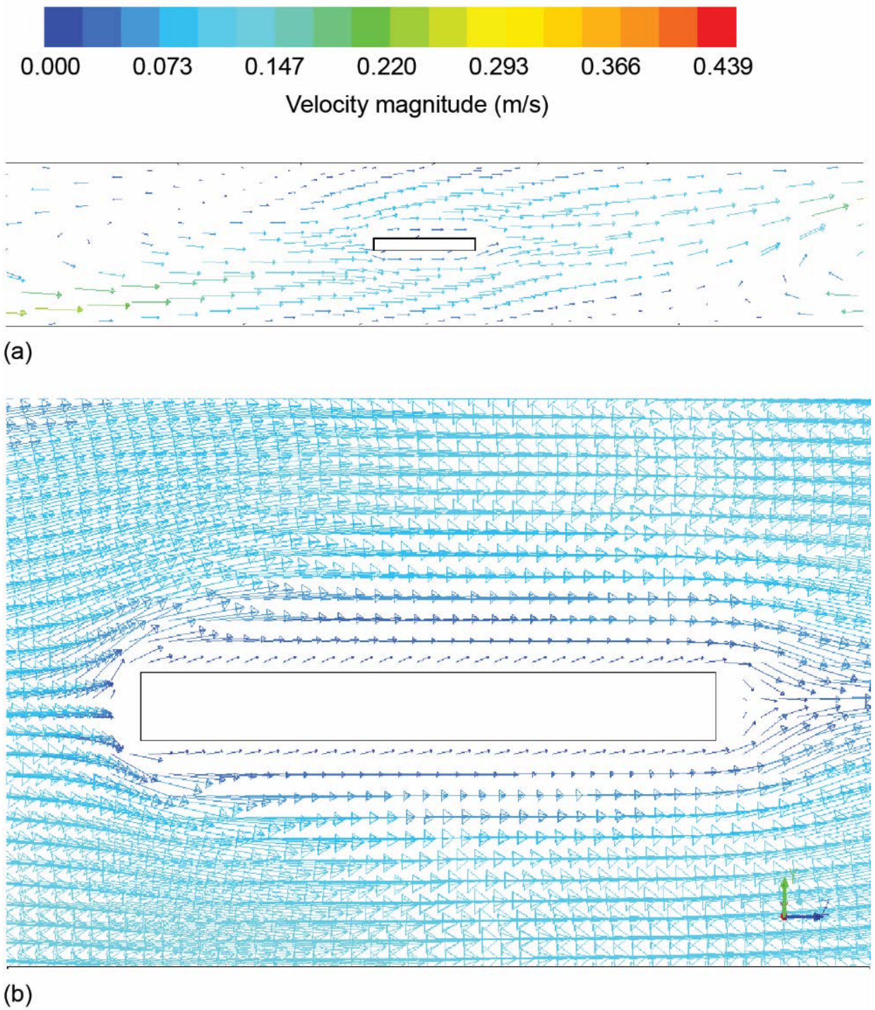
Computational Fluid Dynamics (CFD): Maria Kuczmarski

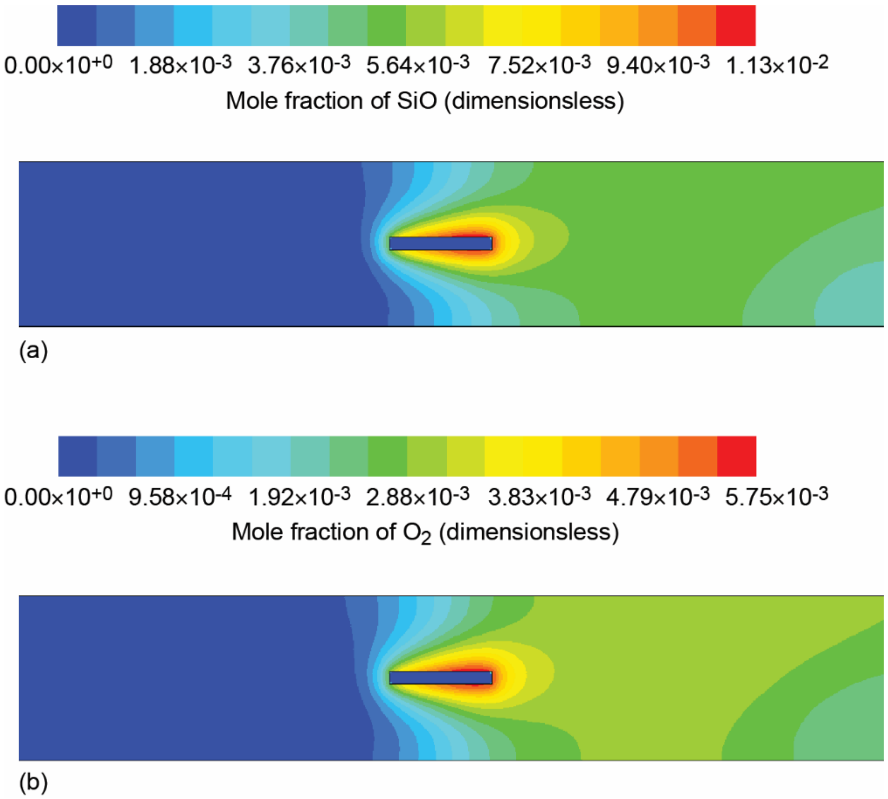
- Set up small cells around samples
- Conservation of mass, momentum, energy within each cell.
- Define the problem
  - – Coupon in a furnace: Model half the system to utilize symmetry



  - – Steady state, incompressible fluid, include thermal diffusion

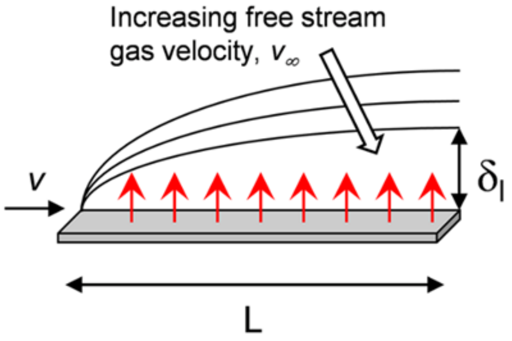
Laminar Flow CFD Results with Temperature Fixed: Velocities and x(SiO), x(O_2)

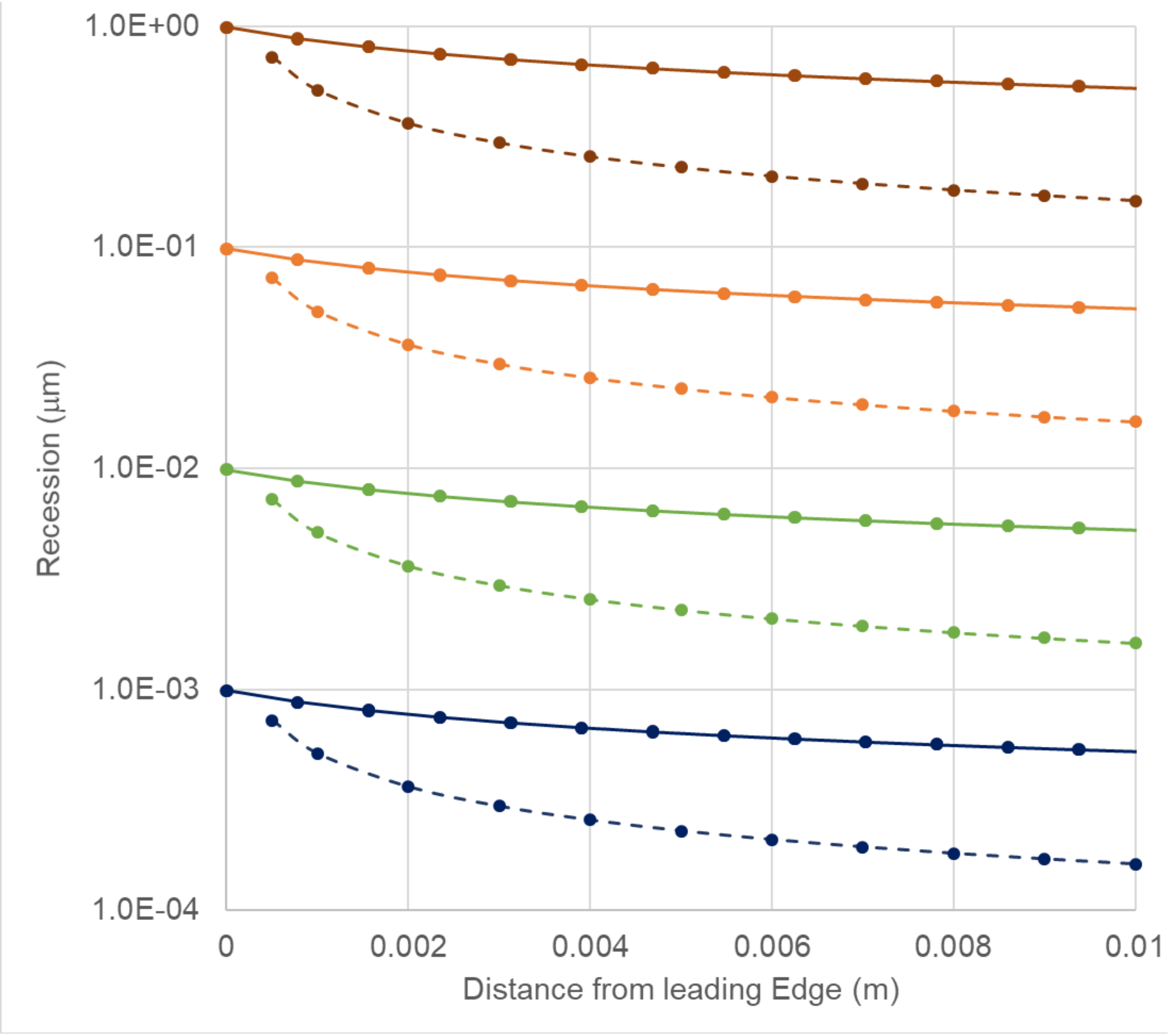




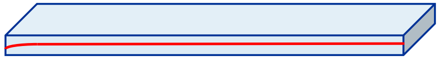
- Coupon disturbs flow: Boundary layer
- Distribution of SiO, O_2 after coupon

Recession for Laminar Flow





10000 s



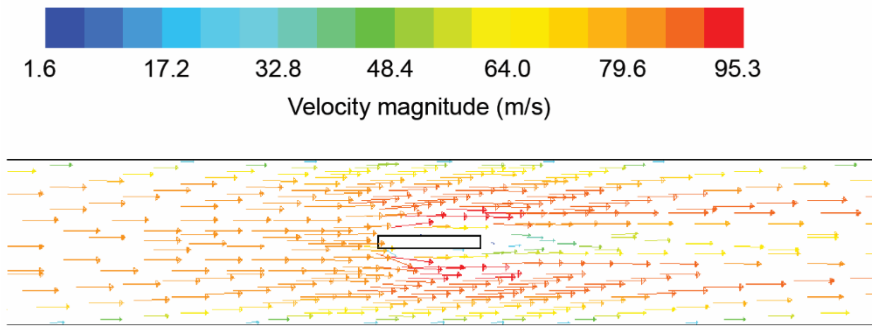
1000 s

100 s

10 s

Solid line: Analytic
Dashed line: CFD

Turbulent Flow: CFD Results with Temperature Fixed Velocities and x(SiO), x(O_2)



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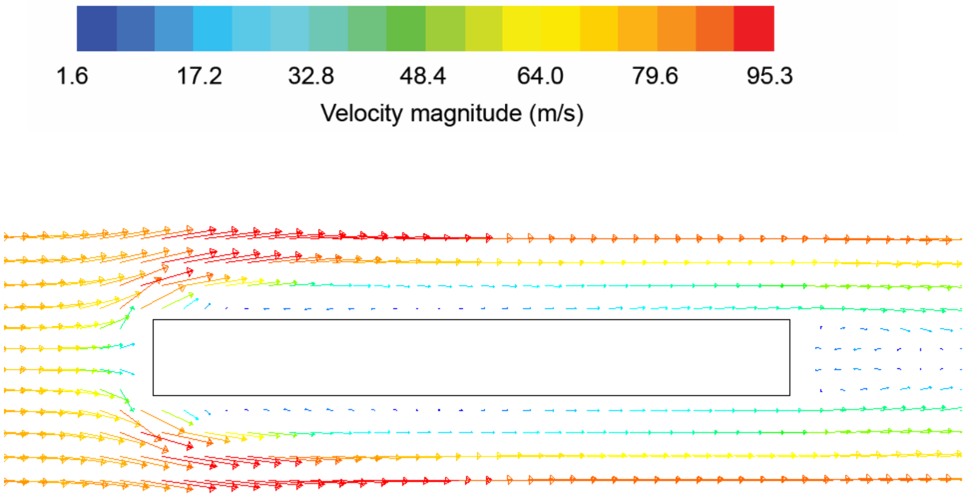

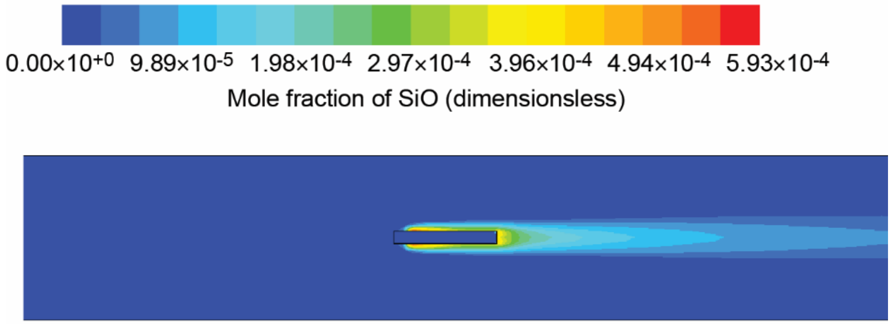

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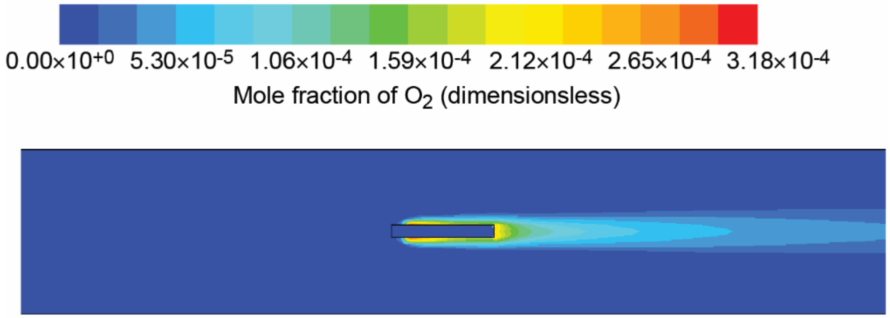
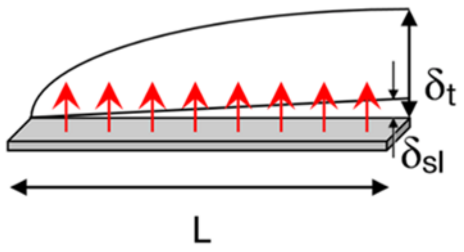


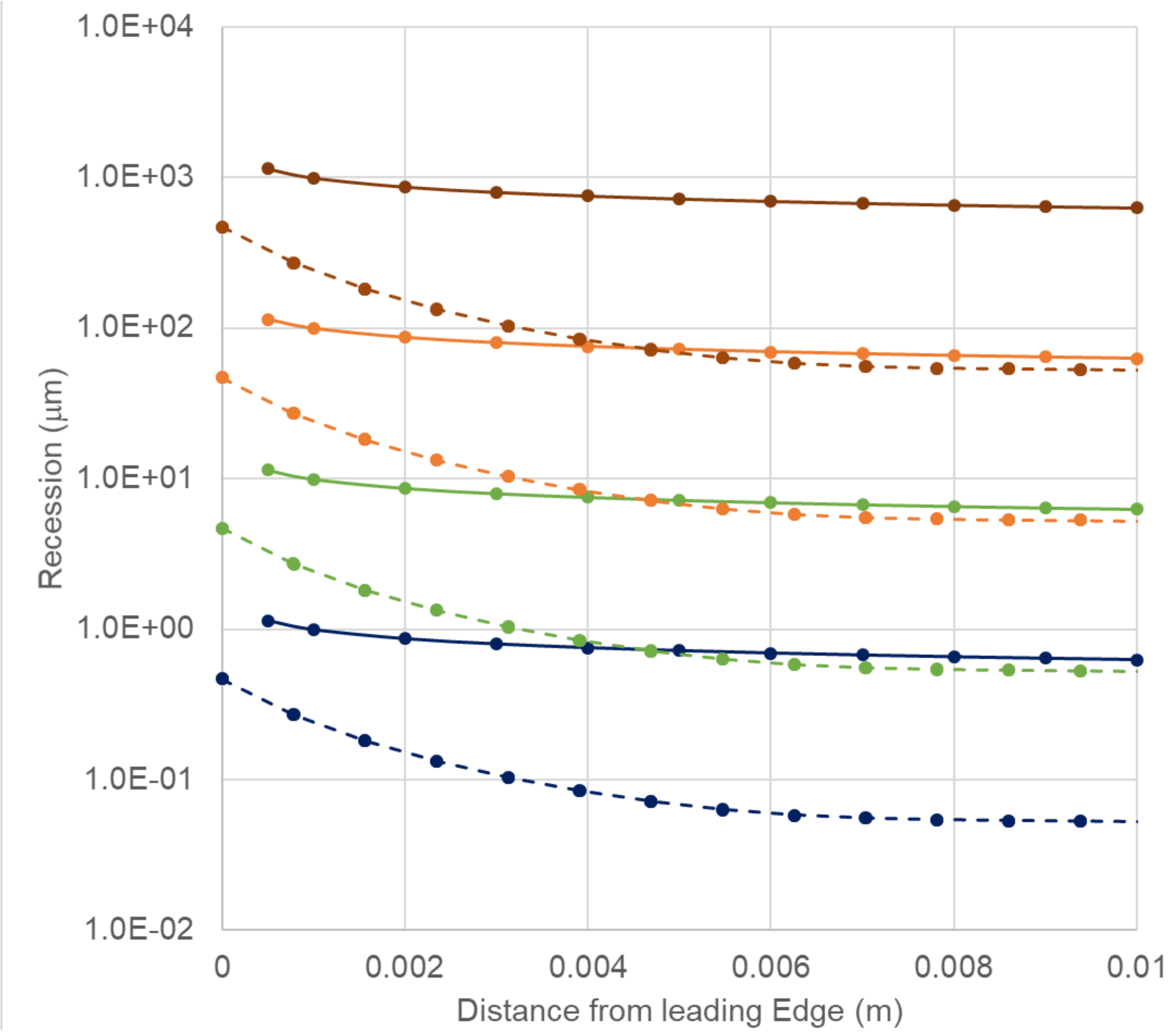
(b)

Note boundary layer, flow changes on trailing edge

- Coupon disturbs flow: Boundary layer
- Distribution of SiO, O_2 after coupon more localized

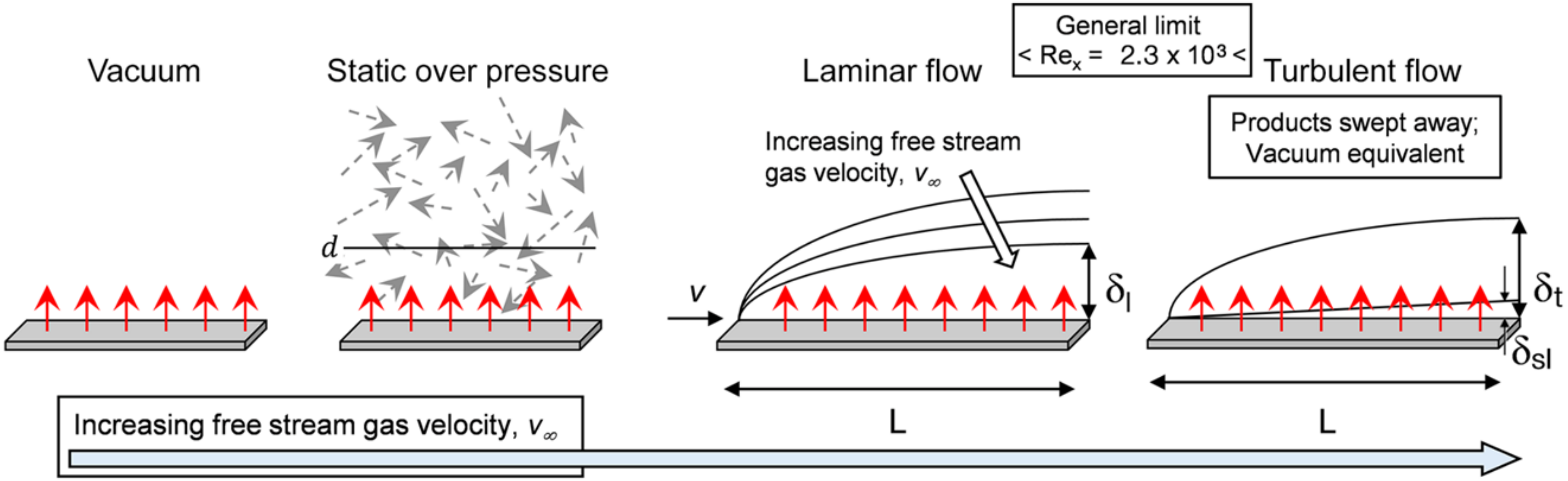
Recession for Turbulent Flow





Solid line: Analytic
Dashed line: CFD

Summary and Conclusions: Effect of Gas Atmosphere on Vaporization



- Vacuum: HKL equation from kinetic theory; modified by vaporization coefficient

- Static over pressure
  - Inert gas: Kinetic effect limits diffusion of vapor species, Fick’s first law
  - Reactive gas: May suppress or enhance reaction products

Summary and Conclusions: Effect of Gas Atmosphere on Vaporization

- Use analytic and CFD approach for laminar and turbulent flow
    - Both show more recession at leading edge; rates through turbulent flow approach rates through a vacuum
    - Laminar flow CFD about ¼ of recession predicted with analytic methods
    - Turbulent flow close near leading edge, but about an order of magnitude lower than that predicted with analytic methods
    - Differences likely due to heat transfer issues
        - We had to fix coupon temperature to avoid dramatic coupon cooling
- The analytical expressions provide good results which are easily obtained
- CFD offers a more comprehensive model of the process