CME 324 Mini-Project Report

May 1, 2025

Group Members: L.C, K.G., CJ Nesbit, N.P.

Tarnishing of Metal Surfaces: Technical Report

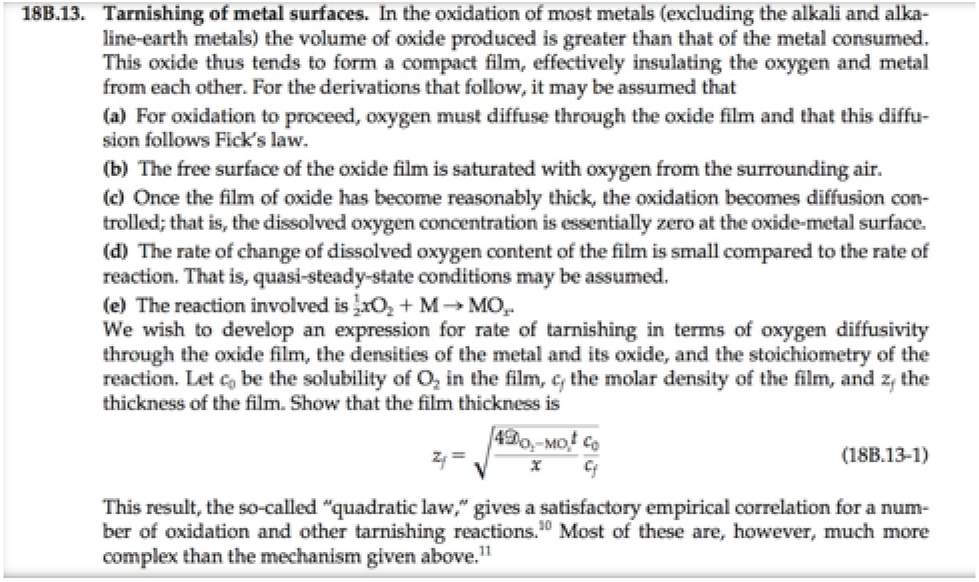
Dr. Erick Vasquez

Table of Contents

Section I: Problem Statement and Objectives

Problem Statement:

Our mass transport project studies the tarnishing of metal surfaces through oxidation mechanisms. Our project focuses on studying the effects of oxidation within cylindrical pipes, and the theoretical applications for momentum and heat transfer, as well as real-world applications. Our studies are based on this problem in the Transport Phenomena textbook:



18B.13. Tarnishing of metal surfaces. In the oxidation of most metals (excluding the alkali and alkaline-earth metals) the volume of oxide produced is greater than that of the metal consumed. This oxide thus tends to form a compact film, effectively insulating the oxygen and metal from each other. For the derivations that follow, it may be assumed that

(a) For oxidation to proceed, oxygen must diffuse through the oxide film and that this diffusion follows Fick's law.

(b) The free surface of the oxide film is saturated with oxygen from the surrounding air.

(c) Once the film of oxide has become reasonably thick, the oxidation becomes diffusion controlled; that is, the dissolved oxygen concentration is essentially zero at the oxide-metal surface.

(d) The rate of change of dissolved oxygen content of the film is small compared to the rate of reaction. That is, quasi-steady-state conditions may be assumed.

(e) The reaction involved is $\frac{1}{2}xO_2 + M \rightarrow MO_x$.

We wish to develop an expression for rate of tarnishing in terms of oxygen diffusivity through the oxide film, the densities of the metal and its oxide, and the stoichiometry of the reaction. Let c_0 be the solubility of O_2 in the film, c_f the molar density of the film, and z_f the thickness of the film. Show that the film thickness is

$$z_f = \sqrt{\frac{4\mathscr{D}_{O_2-MO_x} t}{x} \frac{c_0}{c_f}} \qquad (18B.13\text{-}1)$$

This result, the so-called "quadratic law," gives a satisfactory empirical correlation for a number of oxidation and other tarnishing reactions.[10] Most of these are, however, much more complex than the mechanism given above.[11]

Objectives:

- Prove that Equation 18B.13-1 is true for simple Cartesian and Cylindrical systems, by representing diffusion in the z direction (Cartesian) and the r direction (Cylindrical).
- Create basic models for mass transport using Equation 18B.13-1.
- Compare two common metals to visualize the difference between them under the same conditions.
- Create basic models for flow rate reduction based on film buildup.
- Create basic models for heat flux reduction based on film buildup.
- Create basic models for temperature reduction based on film buildup.
- Connect the problems to real-world applications.

Section II: BSL 18B.13 Solution

Assumptions:

- Steady State
- No Convection
- Diffusion obeys Fick's Law
- One-dimensional diffusion as a function of z/r
- Constant Molar Film Density
- Constant diffusivity
- Oxygen concentration is zero at oxide/metal interface
- Oxidation reaction is heterogeneous, that is, not in the bulk

Boundary Conditions:

- B.C. 1: At z/r = 0, or the oxide/gas interface, concentration = c_0
- B.C. 2: At z/r = z_f/r_f, or the oxide/metal interface, concentration = 0.

Combined Flux (Equation 18.0-1)

*Note: Fick's law for z/r is equivalent, so for the rest of the solution, z will be used

- $N_{O_2,z} = -c\mathfrak{D}_{O_2-MO_x}\frac{\partial x_{O_2}}{\partial z} + x_{O_2}(N_{O_2,z} + N_{MO_x,z})$

Assuming no convection and short handing mass diffusivity constant gives:

- $N_{O_2,z} = -\mathfrak{D}\frac{\partial c_{O_2}}{\partial z}$

There are three ways to obtain the concentration gradient. One is by use of shell balances, another is to use the equation of change, the final is a 'shortcut' using our boundary conditions. The shortcut method is shown in the slides to save both time and slides. However, in this report, the shell balance solution and equation of change is shown here:

Shell Balance/Equation of Change Solution

It is redundant to list the first steps of the shell balance, and it is intuitive based on the simplicity of the problem statement to recognize that the shell balance equation will reduce to:

- $\frac{dN_{O_2,z}}{dz} = 0$

Using the equation of change will give us the exact same result, as we assume diffusion only as a function of z, steady state, no convection, and heterogeneous reaction.

Integrating both sides is a familiar process to arrive at:

- $N_{O_2,z} = C_1$

We can substitute the combined flux term for the simplified expression we found from Equation 18.0-1 to arrive at:

- $-\mathfrak{D}\frac{\partial c_{O_2}}{\partial z} = C_1$
- $\frac{\partial c_{O_2}}{\partial z} = \frac{C_1}{-\mathfrak{D}}$ (Rearranging)

Integrating again gives us an expression for the concentration profile:

- $c_{O_2} = -\frac{C_1}{\mathfrak{D}}z + C_2$

Applying Boundary Condition 1 results in:

- $c_0 = C_2$

Applying Boundary Condition 2 results in:

- $C_1 = \frac{\mathfrak{D}c_0}{z_f}$

The overall concentration profile then becomes:

- $c_{O_2} = -\frac{c_0}{z_f}z + c_0$

Taking the derivative yields our desired term:

- $\frac{\partial c_{O_2}}{\partial z} = -\frac{c_0}{z_f}$

Solution using Boundary Condition Shortcuts

If we recognize that we already have the boundaries of the system solved, we can arrive at the desired term much quicker. This is the solution shown in the slides.

- $\frac{\partial c_{O_2}}{\partial z} = \frac{0-c_0}{z_f-0} = -\frac{c_0}{z_f}$

So, our total flux becomes:

- $N_{O_2,z} = \mathfrak{D}\frac{c_0}{z_f}$

Relating the Combined Flux to Diffusion

The logical ‘leap of faith’ to solve this problem lies within the reaction stoichiometry. Remember from the problem statement that the oxidation reaction is:

- $\frac{1}{2}xO_2 + M \rightarrow MO_x$

Our combined molar flux solved for oxygen diffusion, but we can use this reaction stoichiometry to relate to our oxide molar formation, which we can then relate to our film thickness.

We can see that the oxide is related to the oxygen by $\frac{2}{x}$. Applying this to our total flux:

- $MO_x \propto \frac{2\mathfrak{D}c_0}{xz_f}$

To further continue, we must have a way to relate our film thickness to molar flux. That relationship is found using molar density. Letting c_f be our molar density, we can divide both sides of the equation to get:

- $\frac{MO_x}{c_f} = \frac{2\mathfrak{D}c_0}{xz_fc_f}$

Intuitively it can be seen that our left-hand side term is dimensionally equivalent to our film thickness per time. Converting into differential form gives us:

- $d\frac{MO_x}{c_f} = \frac{dz}{dt} = \frac{2\mathfrak{D}c_0}{xzc_f}$

Separating like terms and integrating will yield an expression for film thickness. Observe that our coordinate system is defined from 0 to some arbitrary thickness z_f, and our system must range in time from the start 0 to some arbitrary time t.

- $\int_0^{z_f} zdz = \int_0^t \frac{2\mathfrak{D}c_0}{xc_f}dt$
- $\frac{1}{2}z_f^2 = \frac{2\mathfrak{D}c_0t}{xc_f}$

Solving for z_f gives:

- $z_f = \sqrt{\frac{4\mathfrak{D}_{O_2-MO_x}t}{x}\frac{c_0}{c_f}}$

The $\pm$ is omitted because it is not reasonable to have a negative film thickness within the context of this problem.

Section III: Studies of Two Different Metals: Film Thickness, Mass Flow Rate, Heat Flux, and Temperature Effects

A publication from 1999 has diffusivity estimates for Aluminum Oxide (alumina) and Magnesium Oxide. These diffusivities were measured at 1325 K, which should be considered when analyzing the results of this section, as well as the other transport measurements. In addition, the purpose of comparing these two metals is to show how diffusivity affects the differences in measured variables, not necessarily to show precise data measurements.

All values used for these calculations can be found in Appendix: Supporting Calculations, Constants, and Dimensional Analysis.

Film Thickness Graphs

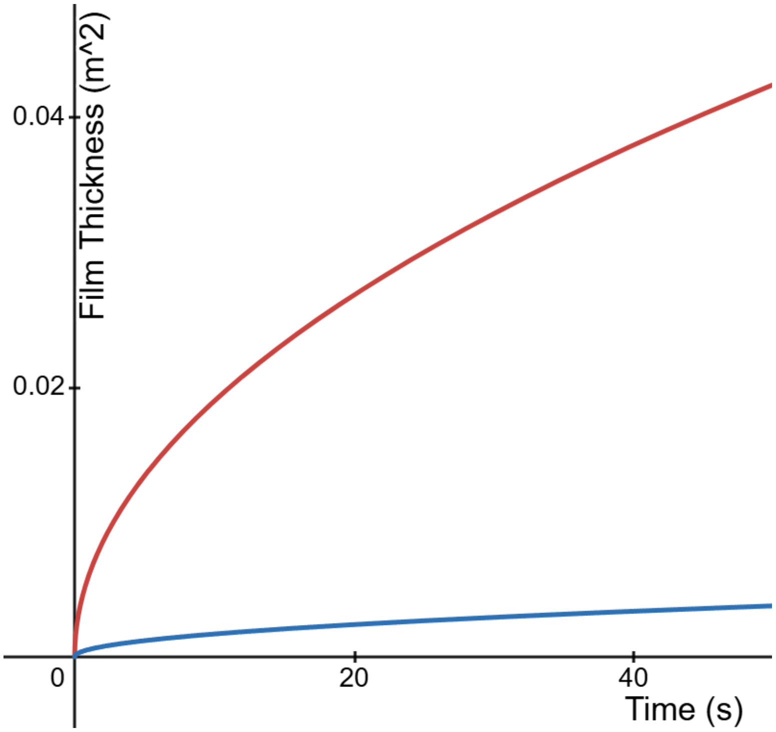


Figure 1: Film Thickness of Al_2O_3 *and MgO over time*

Substituting in mass diffusivities from the Journal of Applied Physics for alumina and magnesium oxide, we can graph film thickness as a function of time.

Alumina is shown in red while magnesium oxide is shown in blue in Figure 1.

Film thickness grows much quicker with alumina than with magnesium oxide. Other metals, such as titanium, have even lower diffusivities.

Flow Rate Loss Graphs

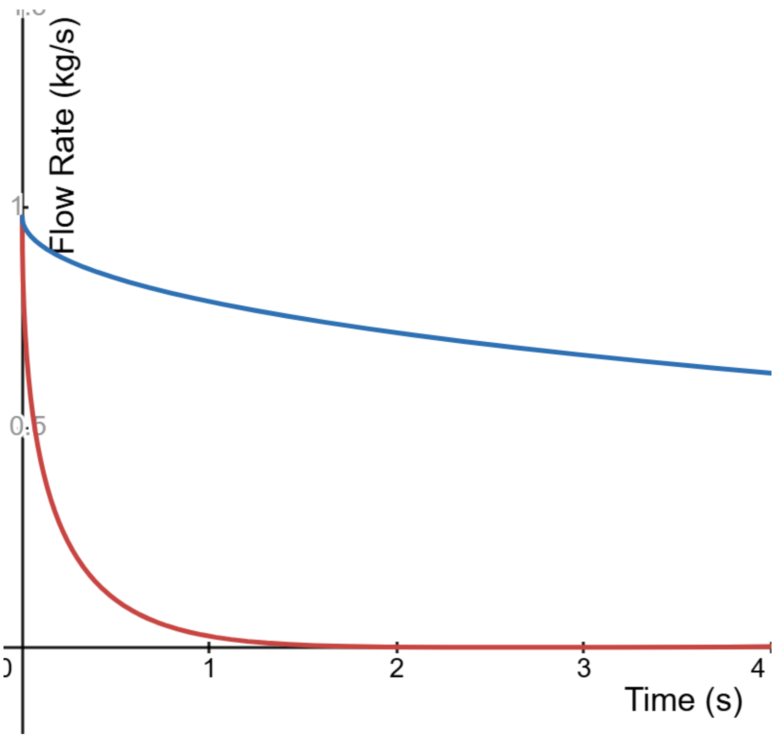


Figure 2: Flow Rates of Al_2O_3 *and MgO over time*

Choosing a cylindrical coordinate system and using the Hagen–Poiseuille equation yields the following surprising result for flow rate reduction.

Aluminum Oxide forms a film so quickly that the flow rate is virtually nothing after only a second. Magnesium oxide retains around ~60% of its initial flow rate after five seconds and tapers off to zero around five minutes.

This has interesting implications for corrosion engineering: Your selected metal or alloy could have massive implications for flow assurance. A seemingly small difference in diffusivities can quickly get out of hand, considering flow rate in a pipe depends on radius raised to the fourth power. That loss will propagate extremely fast, as visually demonstrated in Figure 2.

Heat Flux Loss Graphs

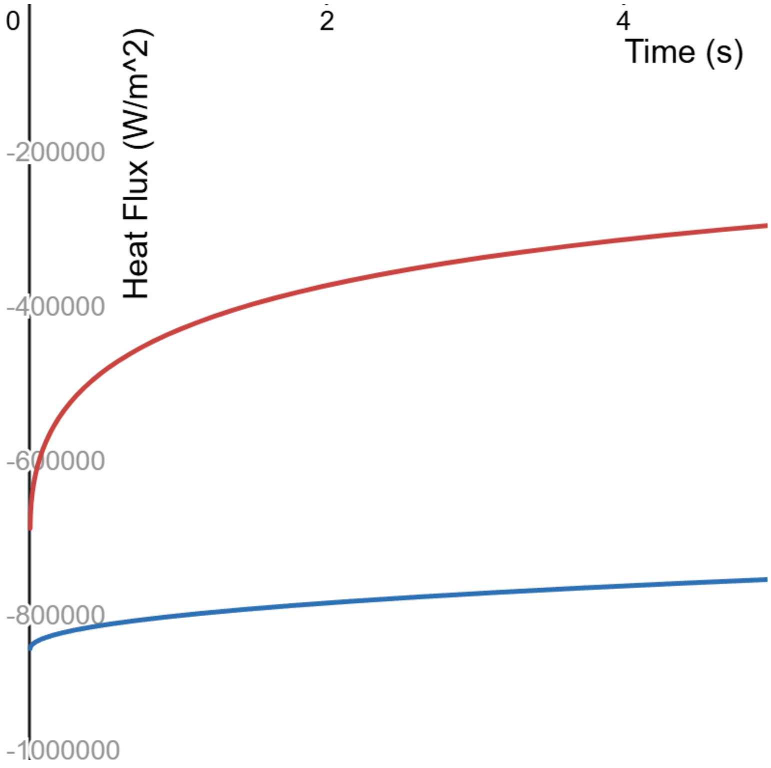


Figure 3: Heat Flux of Al_2O_3 *and MgO over time*

The same pattern continues when examining heat flux. Using the heat transfer example of a steam pipe provided in CME 324 notes, we obtain the following curves in Figure 3.

These graphs provide an excellent model to understand how the oxide film affects the heat flux loss, but they are nowhere near reality.

Fourier's Law of Thermal Conductivity tells us that temperature drop is related to heat flux, so the temperature distribution would change as time goes on. Thermal conductivity is also a strong function of temperature as you approach absolute zero, so this analysis has reasonable limits.

However, no industry can operate steam at temperatures near absolute zero without unrealistically high pressures, so it is safe to assume that this model paints a semi-complete picture of the energy transport model.

Aluminum loses over 50% of the initial heat flux within five seconds under these conditions.

Magnesium oxide strongly retains the initial heat flux for over five minutes. Magnesium Oxide also takes almost eight hours to reach ~10% of the initial heat flux due to the natural logarithmic nature of this scenario.

Temperature Gradient Loss Graphs

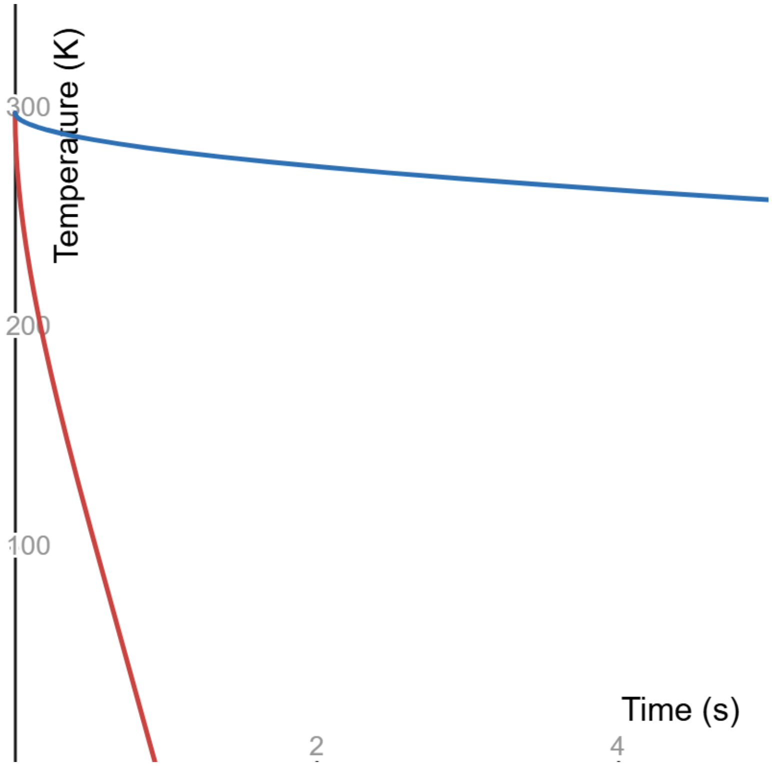


Figure 4: Temperature of inside surface of Al_2O_3 *and MgO over time*

Using the same system as the previous system, Figure 4 displays the temperature on the boundary of the pipe, assuming that the ambient temperature is 298.15 K.

Yet again, the limits of these models are quickly realized. Thermal conductivity becomes a strong function of temperature approaching absolute zero, and the limits of this analysis are shown.

This model, assuming constant thermal conductivity, gives the absurd result that the aluminum pipe surface hits absolute zero in under a second.

More realistically, thermal conductivity would increase massively, and the curve would deviate from absolute zero.

The model still shows the drastic difference between the two oxides however, with magnesium oxide taking yet again over five minutes to display the same absolute zero drop off behavior.

Appendix: Supporting Calculations, Constants, and Dimensional Analysis

Molar Density of Aluminum (III) Oxide: $3.987\frac{g}{cm^3} = \frac{3{,}987\frac{kg}{m^3}}{0.10196\frac{kg}{mol}} = 39{,}103.57\frac{mol}{m^3}$

Molar Density of Magnesium (I) Oxide: $3.600\frac{g}{cm^3} = \frac{3{,}600\frac{kg}{m^3}}{0.040304\frac{kg}{mol}} = 89{,}321.16\frac{mol}{m^3}$

Diffusivity of Aluminum (III) Oxide: $5.62 * 10^{-2}\frac{m^2}{s}$

Diffusivity of Magnesium (I) Oxide: $6.76 * 10^{-4}\frac{m^2}{s}$

Diffusivity data: https://physics.uwo.ca/~lgonchar/courses/p9826/Lecture12_oxidation.pdf

Film Thickness Coefficient Aluminum (III) Oxide: $\sqrt{\frac{4*5.62*10^{-2}}{1.5} * \frac{9.4}{39103.57}} = 6.002 * 10^{-3}$

Film Thickness Coefficient Magnesium (I) Oxide: $\sqrt{\frac{4*6.76*10^{-4}}{1} * \frac{9.4}{89321.16}} = 5.334 * 10^{-3}$

Thermal Conductivity of Aluminum (III) Oxide at 500K: $20\frac{W}{m^2*K}$ (Perry's Handbook)

Thermal Conductivity of Magnesium (I) Oxide at 500K: $27\frac{W}{m^2*K}$ (Perry's Handbook)

Film Thickness Graph: https://www.desmos.com/calculator/dmvjcdl3pe

Flow Rate Graph: https://www.desmos.com/calculator/79fqdmm8cl

Heat/Temperature Graph: https://www.desmos.com/calculator/6oytiv7mft