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Diffusion-Dominated Flux of Poregases and Aqueous Ions in Minesite Components - Commonly Modelled but Rarely Applicable Because Realistic Fluxes are Much Faster

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Abstract

For fine-grained mined materials like unsaturated tailings and for fine-grained covers over minesite components, the movements of poregases like oxygen are typically simulated by diffusion using Fick's First Law. For submerged tailings monitored by diffusive gradients in thin films (DGT), again diffusion is invoked as the primary transport mechanism for aqueous ions. In reality, diffusion is the slowest possible “transport” mechanism in minesite components, and is not even true transport because there is no net mass movement.

Moreover, variations and cycles in temperature, pressure, precipitation, and electrical potential initiate transport that exceeds and overrides that of diffusion. Additionally, for sulphidic mined materials, the consumption of oxygen can create up to a 21% partial vacuum from air, “sucking in” oxygen much faster than predicted by diffusion.

Therefore, in virtually all cases, diffusion is unlikely to be the primary transport mechanism for poregases and aqueous ions in minesite components. In turn, transport will often be much higher than predicted by models focussed on diffusion, providing another reason why predictions of ML-ARD frequently underestimate reality.

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1. Introduction

Studies abound for minesite components that consider diffusion to be the main transport mechanism. For example, oxygen fluxes into fine-grained soil covers and unsaturated tailings are often considered to be diffusion controlled. Aqueous-ion fluxes through very-fine-grained tailings and submerged tailings have been considered diffusion controlled and measurable by diffusive gradients in thin films (DGT).

This MDAG Case Study first reviews the concept of diffusion in Chapter 2, which by itself is the slowest possible transport mechanism for minesite components and literally is not even true transport. Diffusion in porous media is then shown to be “anomalous diffusion” which can lead to much greater flux.

Moreover, as discussed in Chapter 3, there are many other transport mechanisms in minesite components driven by differences in variables like pressure, temperature, precipitation, and electrical potential. Fluxes caused by these other mechanisms can greatly exceed or override the relatively slow flux by diffusion.

2. Diffusion

Wikipedia (2021a) explains,

“Bulk flow’ is the movement/flow of an entire body due to a pressure gradient (for example, water coming out of a tap). ‘Diffusion’ is the gradual movement/dispersion of concentration within a body, due to a concentration gradient, with no net movement of matter.”

Thus, by definition, there is “no net movement of matter” with diffusion. In turn, diffusion is not a true transport mechanism. Furthermore, diffusion requires isothermal, adiabatic, and isobaric conditions (discussed in Chapter 3 below). Otherwise, other transport processes like convection arise that can far exceed the net effect of diffusion.

Classic diffusion is often characterized and modelled using the First and/or Second of “Fick’s Laws” (Wikipedia, 2021b), derived by Adolf Fick in the mid-1800’s.

$$\text{Fick's First Law: } J = -D \, dC/dx \quad (\text{Eq. 2-1})$$

where J = diffusive flux
 D = diffusion coefficient
 C = concentration
 x = length

$$\text{Fick's Second Law} = \partial C/\partial t = D \, \partial^2 C/\partial x^2 \quad (\text{Eq. 2-2})$$

where t = time

It has been pointed out that Fick’s First Law is similar in form to others, like Darcy’s Law, Ohm’s Law, and Fourier’s Law derived about the same time. This is likely not coincidental. However, it hides the fact that diffusion is very different in nature.

There is no net movement by diffusion. Random walk or Brownian motion cause diffusion to continue indefinitely in a stagnant fluid; it never stops (above a temperature of absolute zero).

The chemical effect of diffusion becomes apparently only when there is a concentration gradient between two locations. The concentration gradient (dC/dx) does not cause the diffusive movement of chemical species like a hydraulic gradient causes water movement, because Brownian motion is always occurring. However, a concentration gradient allows diffusion to be chemically observed by humans.

There is no net mass movement. Diffusion is the slowest “transport” mechanism in minesite components with all others being faster. Yet minesite-component simulations typically use diffusion for fine-grained materials with little to no evidence to justify it.

There is no net mass movement. For whatever chemical species diffusing in one direction, there must be by definition one or more chemical species equally diffusing in the opposite. How many

simulations of diffusion in minesite components consider the other chemical species diffusing in the opposite direction? I haven't seen any. That leads to accumulating mass imbalances in the models.

As discussed in Chapter 3 below, this becomes critical when a chemical species, such as oxygen in poregas or an aqueous ion in water, is "consumed" by the solid phase. In poregas, this creates a partial vacuum that "sucks in" outside gases much faster compared with diffusion of the consumed species would in stagnant poregas.

Finally,

"It has been found that equations describing normal diffusion are not capable of characterizing some complex diffusion processes, for instance, diffusion process in inhomogeneous or heterogeneous medium, e.g. porous media." (Wikipedia, 2021c).

This leads to "superdiffusion" (faster than normal) or "subdiffusion", where porous media apparently lead to the former. This means diffusion in the absence of all other processes and mechanisms can still be faster in porous media than predicted by minesite-component models using Fick's Law.

3. Other Processes in Minesite Components Overriding Diffusion

As explained in Chapter 2 above, diffusion is the slowest possible “transport” process in minesite components and, in fact, is not even a true transport process because there is no net movement. Only when a concentration gradient exists between two locations can the effect of diffusion be observed chemically by humans, but it is always occurring in a stagnant fluid.

In reality, minesite components are open systems (Morin, 2021) with gradients of many variables like temperature, pressure, and electrical fields (Morin, 2020). These can drive the movement of poregases and aqueous ions much faster than the no-net-movement of diffusion. The fluids are not truly stagnant.

For example:

- natural variations in barometric pressure cyclically drive air and poregas periodically into and from minesite components;
- natural variations in precipitation cause proportional volumes of water and poregas inside minesite components to vary with time; and
- natural variations in temperature, like daily and annually, create thermal convection of poregases and cyclical condensation-evaporation of water vapour inside minesite components.

Additionally, for minesite components containing sulphide minerals like pyrite and pyrrhotite:

- oxygen can be “consumed” from the poregas through sulphide oxidation, causing up to a 21% partial vacuum from air, creating pressure-driven convection of poregases and air;
- water vapour from the poregas and water from the aqueous phase are “consumed” through sulphide oxidation,
 - (a) creating gradients in poregas partial pressure and in aqueous electrochemical potentials that lead to transport faster than diffusion, and
 - (b) creating solid-phase secondary minerals that “swell” in volume by taking in O and H from poregas and water/vapour and thereby affecting the volumes of the aqueous and gas phases; and
- the heat generated by exothermic sulphide oxidation causes the expansion of local poregas and creates thermal convection currents driving poregas and air movements faster than diffusion.

Therefore, there are many reasons to expect diffusion-based predictions to underestimate the movements of poregas and aqueous ions in minesite components virtually every time. Yet diffusion remains the basis of many predictions for fine-grained materials in or over minesite components. Is this another explanation for why sulphide oxidation and ARD are underestimated most times?

Currently, the only sulphide-oxidation transport model that considers many of these processes and solves them simultaneously is discussed in Ma et al. (2020) and Huang et al. (2020). Most other models simply assume slow diffusion controls the rates of transport and reaction. As a minimum,

thorough characterization and data should be presented to justify the usage of only diffusion as the dominant transport mechanism for a minesite component.

It is worthwhile to note that full-scale minesite components are not the only places where diffusion is often incorrectly applied. For biological organisms, Agutter et al. (2000) observed,

“Diffusion is a poor explanation for many examples of molecular motion in biological organisms . . . Nor have we acknowledged the crucial effect of mass flow, a key aspect of molecular movement. The non-universality of diffusive properties has led to ideological attacks on biology.”

4. References

- Agutter, P.S., P.C. Malone, D.N. Wheatley. Diffusive and Advective Transport. *Journal of the History of Biology*, 33, p. 71-111.
- Huang, C., L. Ma, Z-S. Liu, E. Dy, K. Tufa, E. Fisher, J. Zhou, M. Goulet, K. Morin, and M. Paradis. 2020. Gas Transport inside Co-disposal of Desulfurized Tailings and Sulfidic Waste Rocks. IN: Tailings and Mine Waste 2020 Virtual Event, November 15-18, Colorado State University, Colorado, USA., p. 541-550.
- Ma, L., Z-S Liu, E. Dy, K. Tufa, J-Q. Zhou, E. Fisher, M. Goulet, C. Huang, and K. Morin. 2020. Additional Mechanisms and Measurements to Improve ARD/ML Prediction. IN: 2020 BC MEND ML/ARD Virtual Workshop, Challenges and Best Practices, December 1-3.
- Morin, K.A. 2021. MDAG-com Case Study 65 - Thermodynamics - Not Designed for Minesite Components and Their Drainages. MDAG Internet Case Study #65, www.mdag.com/case_studies.html
- Morin, K.A. 2020. MDAG-com Case Study 63 - Planetary and large-scale processes affecting minesite-drainage flows and chemistries. MDAG Internet Case Study #63, www.mdag.com/case_studies.html
- Wikipedia. 2021a. Diffusion. Accessed February 2021 at: <https://en.wikipedia.org/wiki/Diffusion>
- Wikipedia. 2021b. Fick's laws of diffusion. Accessed February 2021 at: https://en.wikipedia.org/wiki/Fick%27s_laws_of_diffusion
- Wikipedia, 2021c. Anomalous diffusion. Accessed February 2021 at: https://en.wikipedia.org/wiki/Anomalous_diffusion