

Additional Mechanisms and Measurements to Improve ARD/ML Prediction

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Outline

- **Introduction of NRC**
- **Sulfide Minerals Oxidation Reactions/
Electrochemical Reactions**
- **3-D Microscopic Observation of
Secondary Mineral Formation**
- **Metal Leaching**

The National Research Council (NRC) at a Glance

NRC Activities:

Strategic research & development

Scientific and technical services

Science and technology infrastructure

Industrial Research Assistance Program (IRAP)

- 3,700 scientists, engineers, technicians, and other specialists, including 255 industrial technology advisors
- 178 buildings in 72 locations
- \$1.1B annual budget: \$271M to SMEs



We work with

- 8,000 SMEs (advice & funding)
- 1,000 companies (R&D)
- 150 hospitals
- 70 colleges and universities
- 35 federal departments
- 36 countries

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Sulfide Minerals Oxidation Reactions

- Particle-level Water Film Model

Unsaturated water flow

Matrix flow under capillary forces:

rock surface covered with thin film of stagnant water (1-100 μm)

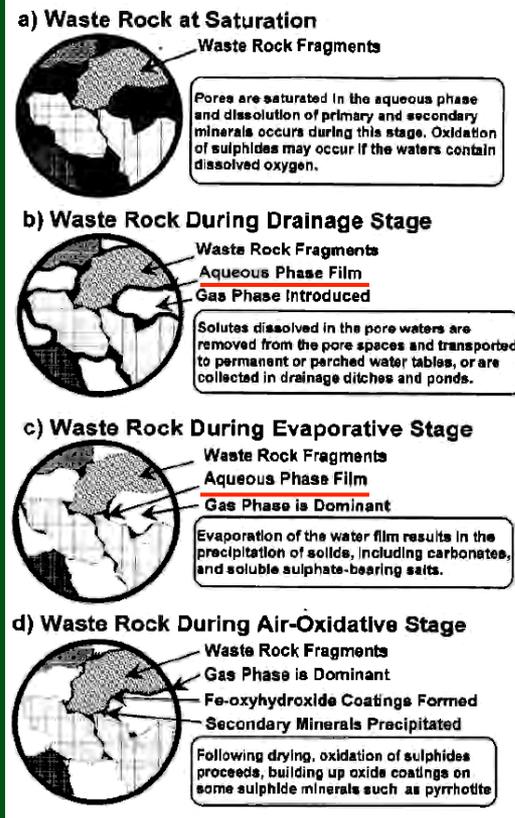
Function: chemical reaction sites/storage for H^+ , metal ions

Preferential flow: rapid and channelized

Function: metal leaching processes

Importance of Water film model vs. existing core models:

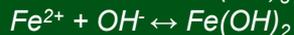
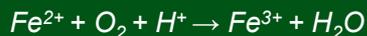
1. Count for the **water content** on the surface of pyrite
2. Count for the **history** of oxidation reactions
3. Complex **oxidation/neutralization** reactions, reaction rates are not only controlled by **oxygen** concentration, but also by **other specie** concentrations



Sulfide Minerals Oxidation Reactions

- Particle-level Water Film Model

Reactions in the water film:



Reactions on the interface:



NP dissolution (pH dependent)

1. O_2 consumption rate to "oxygen transport"
2. O_2 concentration from "oxygen transport"
3. Surface to volume ratio

Water/Air Interface



O_2

Film thickness

1. Film thickness/water content from "water flow"
2. Integration of ions generation to "ions transport"

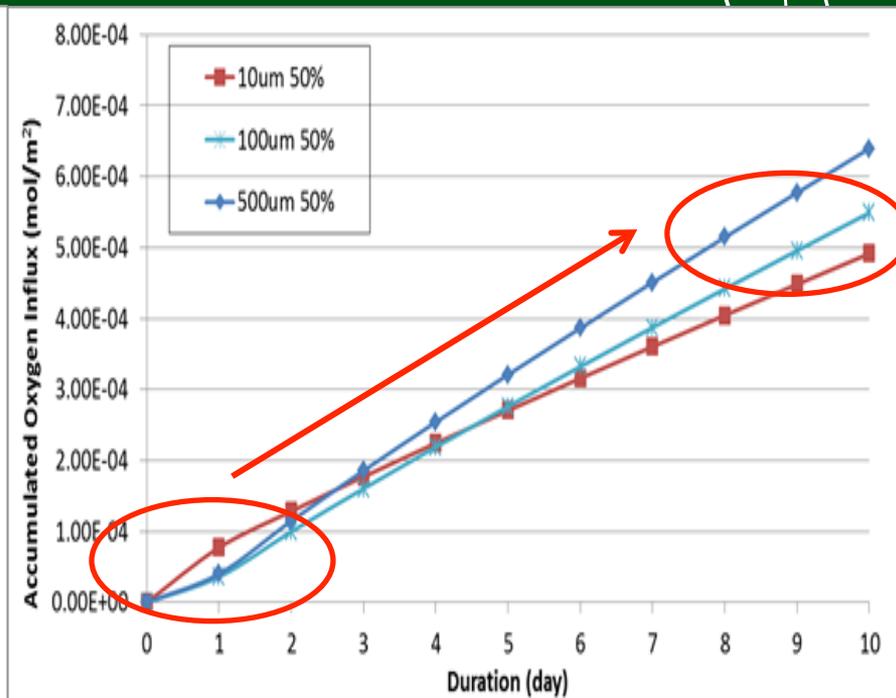
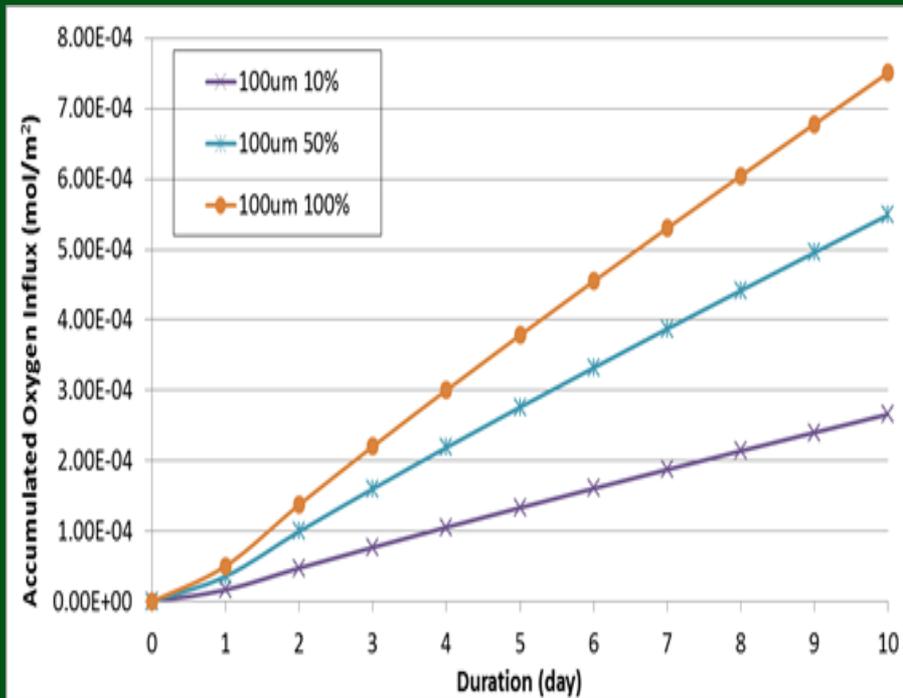
Water/Rock Interface

(ARD generated here)

1. Water covered surface ratio from "water flow"
2. Heat generation rate to "heat transfer"
3. Surface to volume ratio
4. Pyrite surface ratio

Sulfide Minerals Oxidation Reactions

- Particle-level Water Film Model



Oxygen Concentration and Water Content

Sulfide Minerals Oxidation Reactions

- Gas transport coupled with O_2 consumption

Diffusion flow (slowest)

(21% O_2 \rightarrow 0-2% O_2)

Convection flow

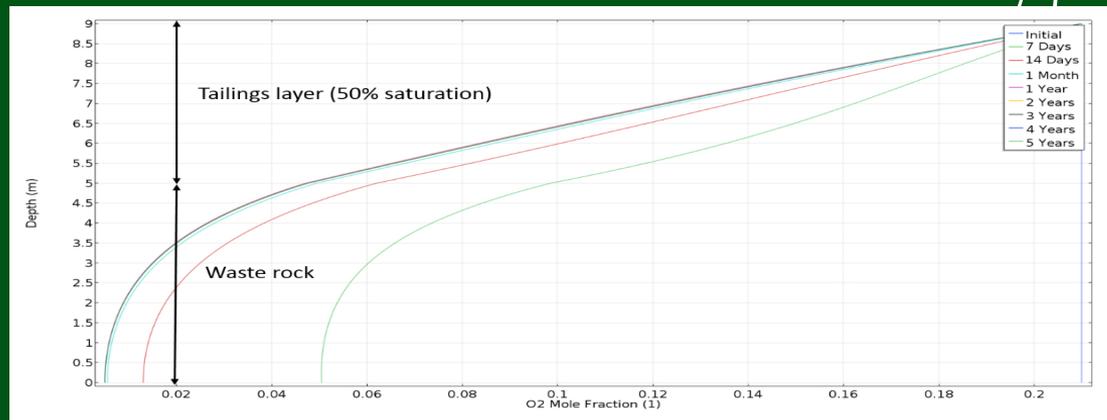
- temperature change

(exothermic reactions)

- partial vacuum

(21% O_2 \rightarrow 0-2% O_2)

O_2 consumption rate



Sulfide Minerals Oxidation Reactions

- Oxygen Consumption Rate

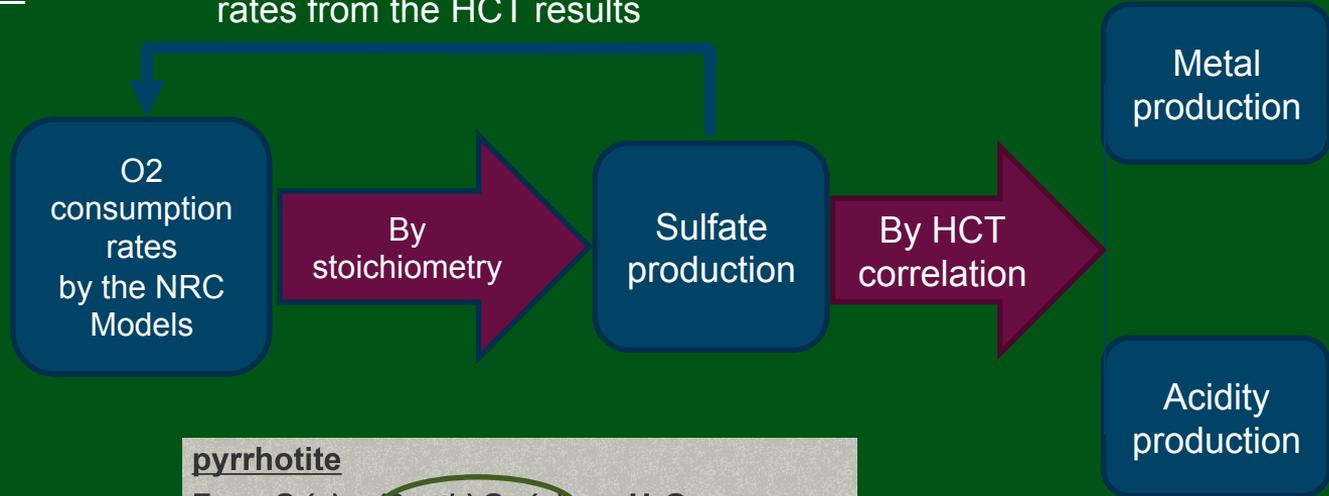
O₂ consumption rate:

$$= \lambda * k_*$$

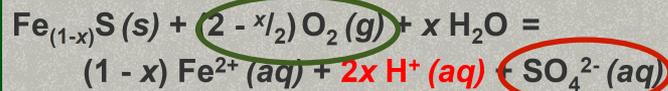
λ, specific surface area

k_{*}, kinetic constant of sulfide oxidation

Extract O₂ consumption rates from the HCT results



pyrrhotite



where x ranges between 0.000 and 0.125

Sulfide Minerals Oxidation Reactions

- Oxygen Consumption Rate

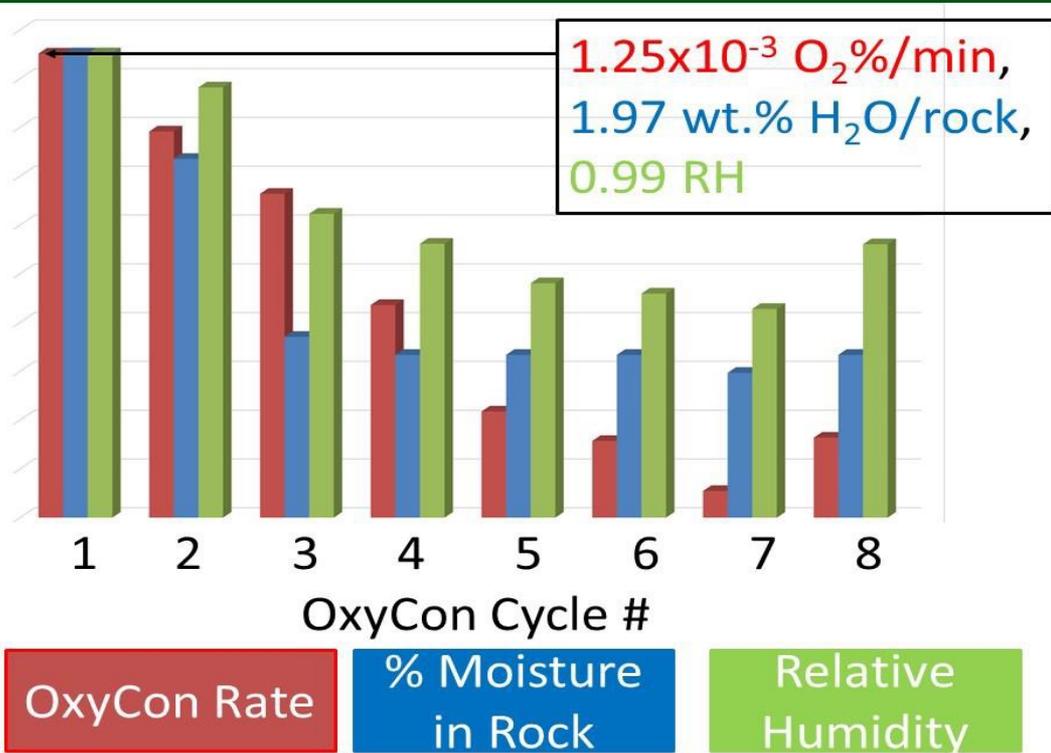
- Influence of negative pore-water pressure (PWP) in waste rock on metal leaching and acid rock drainage
- Oxygen consumption (OxyCon): direct measure of sulfide oxidation rate
- PWP (suction) calculated from RH



Customized test columns for waste rock developed in-house with O_2 , CO_2 , RH & temperature sensors

Sulfide Minerals Oxidation Reactions

- Oxygen Consumption Rate



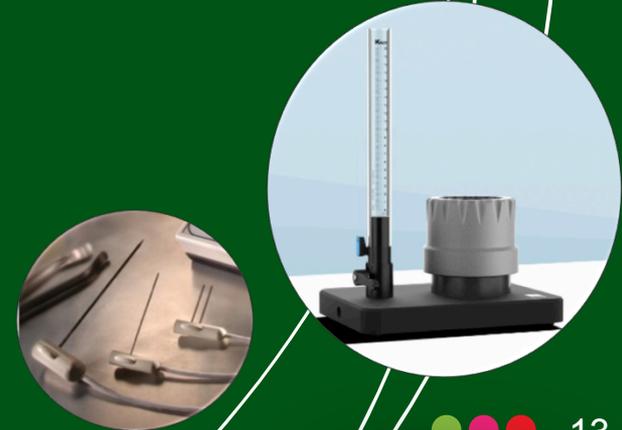
- ✓ Strong positive correlations between oxygen consumption rate, the moisture content of the waste rock and RH of the surrounding air when RH is <0.99 and the moisture content is <2.0%.
- ✓ Pyrite oxidation did not slow appreciably until the moisture content of the rock was around **0.6% wt.** and the RH of the headspace above the rock was **0.44.**

Sulfide Minerals Oxidation Reactions

- Important Transport Properties

Measurement of Important Transport Properties at NRC EME

- **Heat Transfer**
 - Heat Capacity (Modulated DSC, 3-run isothermal DSC, probe method)
 - Thermal Conductivity (probe method, ASTM D5334-14)
- **Water Transport**
 - Saturated Hydraulic Conductivity (Falling Head Method, Constant Head Method)



Sulfide Minerals Oxidation Reactions

- Important Transport Properties

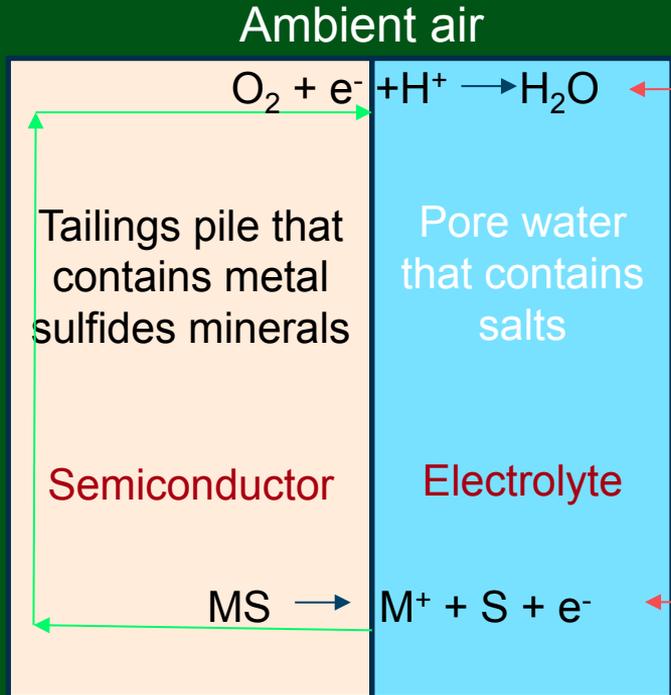
- Water Retention Curve (Evaporation method)
- Water Content/Loss Behaviour
(Moisture balance method, TGA method, Karl Fisher titration)
- **Gas Transport**
 - Air Permeability (In-house test method)
 - Gas diffusion (In-house test method)
 - Oxygen Consumption and CO₂ generation test



Electrochemical Mechanism of Metal Sulfides Oxidation: Facts

1. Sulfur and/or metals of metal sulfides are oxidized and in the same time oxygen and/or ferric ions and/or hydrogen ions are reduced. It is a redox reaction;
2. The redox reaction couple do not have to happen at the same physical site, and can happen **at different physical sites** as long as there are electronic pathways and ionic pathways;
3. Wet conditions (moisture air and/or water solution) can provide ionic pathways; metal sulfides as semiconductors can provide electronic pathways;
4. Tailings piles, tailing ponds and waste rock piles can naturally provide the wet conditions, and as a consequence, the redox reaction can be electrochemical, and the oxidation and the reduction can happen **at different physical sites.**

Electrochemical Mechanism of Metal Sulfides Oxidation: Illustration



The top zone with higher oxygen concentration/more noble metal sulfides, acts as the cathodic zone, with $O_2/Fe^{3+}/H^+$ being reduced

Vertical downward

The lower zone with lower oxygen concentration/less noble metal sulfides, acts as anodic zone, with metal sulfides being oxidized

Electrochemical Mechanism of Metal Sulfides Oxidation: Implications

- The conventional assumption: metal sulfides tailings that are not in direct contact with oxygen gas are not oxidized and is regarded as being chemically safe;
- The conventional assumption may not hold true when the solid phase tailings acts as electronic conductor and the liquid phase (pore water) acts as electrolyte. In this situation metal sulfides can be oxidized without direct contact with oxygen gas.

Electrochemical Mechanism of Metal Sulfides Oxidation: Our on-going research

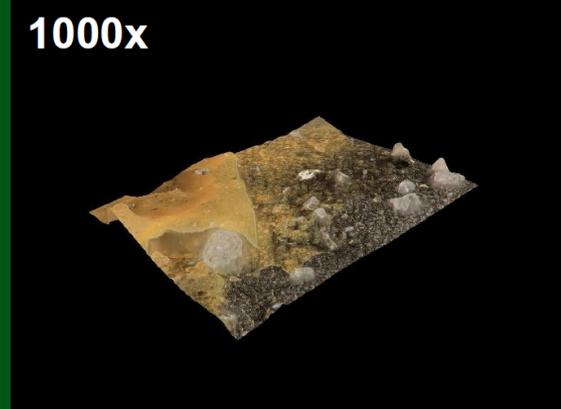
- Find evidences about whether the electrochemical mechanism plays an important role in actual tailings piles and/or tailings ponds and/or waste rock piles through lab testing, mine-site observations and mathematical models;
- Metal sulfides oxidation processes;
- Enhance our lab facility for characterization of important electrochemical properties of metal sulfides tailings.

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Secondary Mineral Formation

- 3-D Microscopic Observation (pyrite)



Surface topography:
20~2500x 4K zoom
microscopic imaging

Instrument

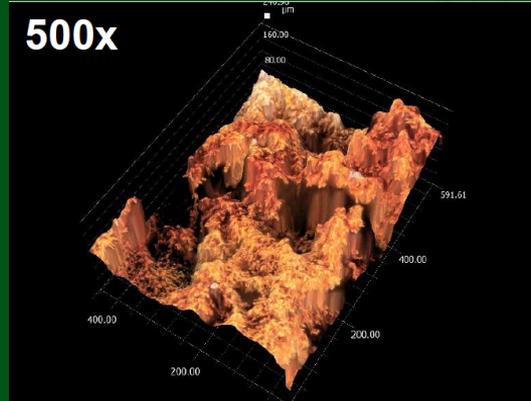
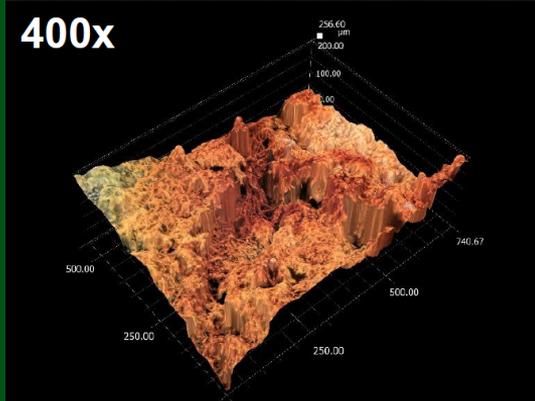
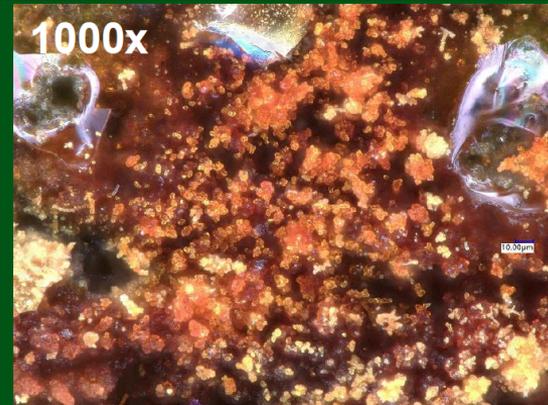
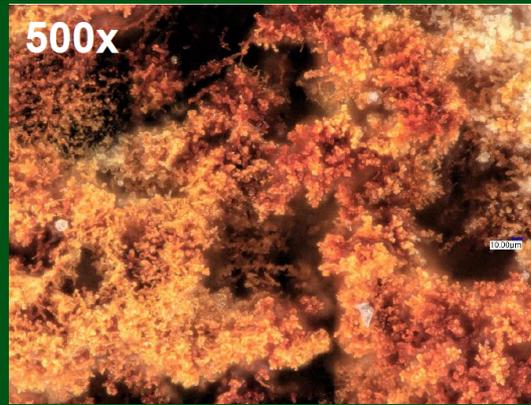
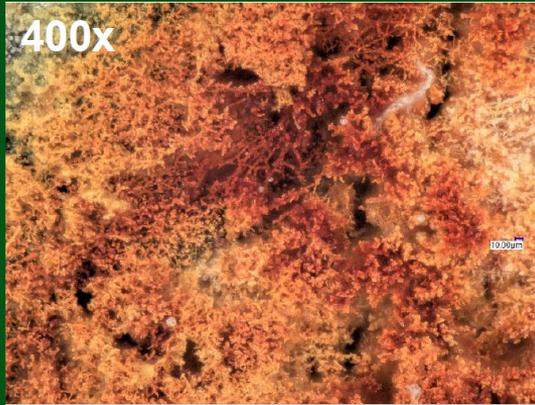
Viking Laser Profilometer

NANOVEA Laser Profilometer

Keyence VHX-7000-7100 Digital Microscope

Secondary Mineral Formation

- 3-D Microscopic Observation (Rock Samples)

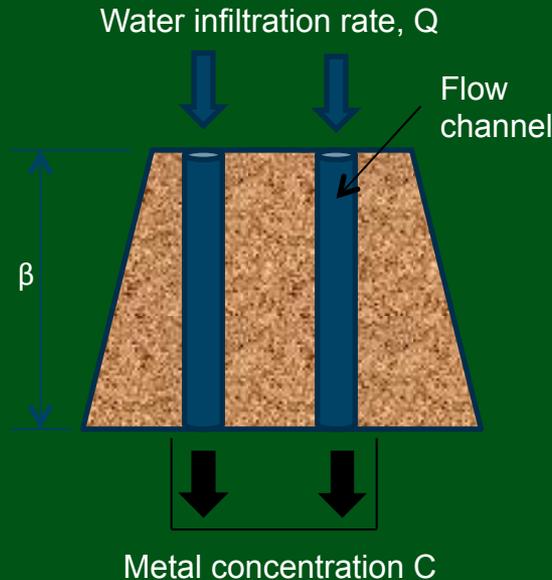


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Scaling Law and Rate Control Mechanisms of Metal Leaching

Similitude approach vs. scaling factors



$$C = C_s \left(1 - e^{-\lambda \beta k \psi / Q} \right)$$

$$= C_s \left(1 - e^{-\alpha} \right)$$

1. α is the scaling law
2. α is the rate control quotient
3. $\lambda \beta k \psi$ is solute production potential, the intrinsic property of a rock pile, rather than individual quantities of λ, β, k , and ψ .

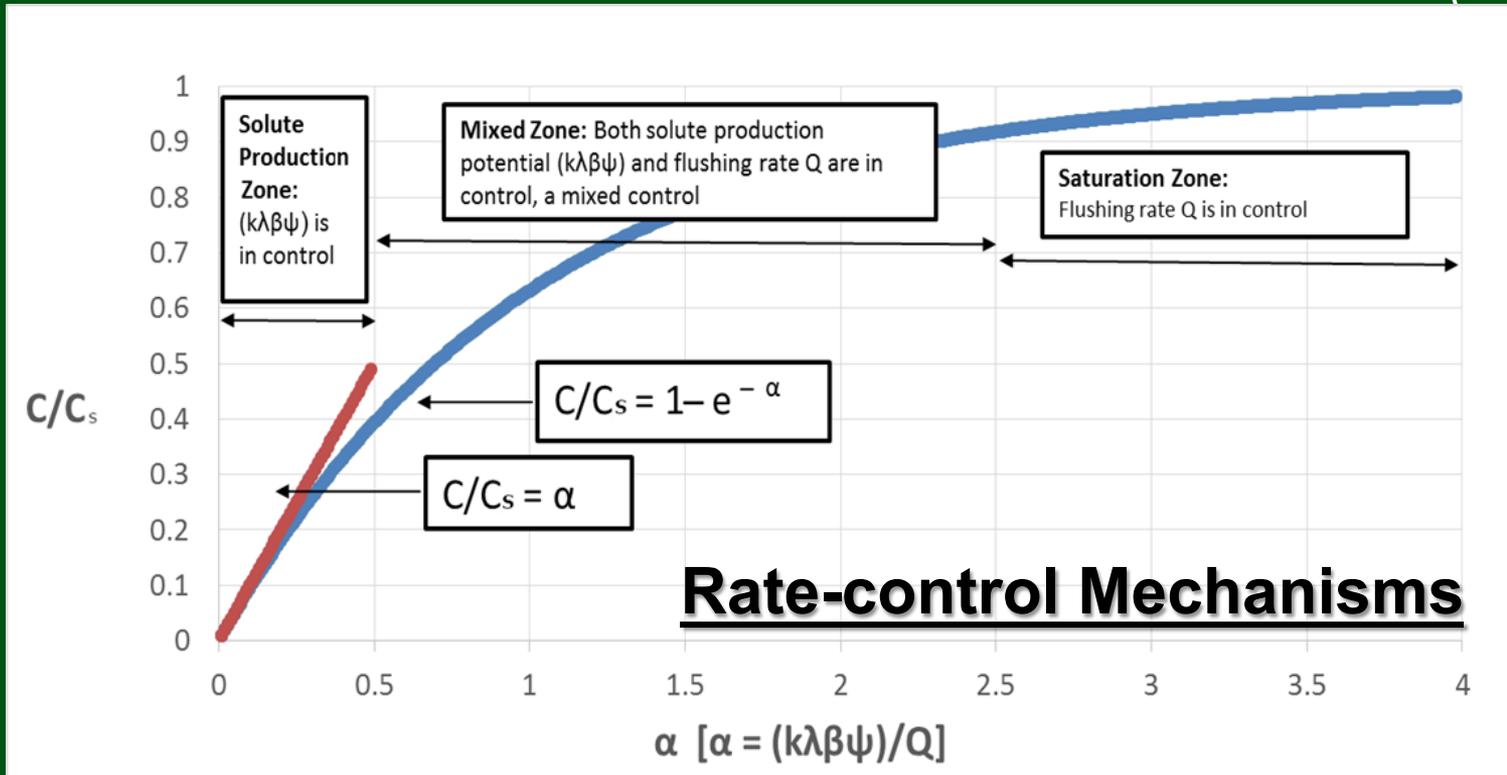
k is defined by $dM/dt = -Ak(C - C_e)$

C_e is saturation concentration

λ is the specific surface area, sum of rock surface areas divided by their volume

Ψ is sum of the areas of the cross-sections of flow channels in a waste rock pile

Scaling Law and Rate Control Mechanisms of Metal Leaching



Heterogeneous Preferential Water Flow

Finer pore zone vs Coarser pore zone: the distribution of permeability is controlled by a Probability Density Function (PDF):

$$f(x) = \begin{cases} \frac{e}{(b-a)} & a \leq x \leq b \\ \frac{1-e}{(c-b)} & b \leq x \leq c \\ 0 & x < a \text{ \& } x > c \end{cases}$$

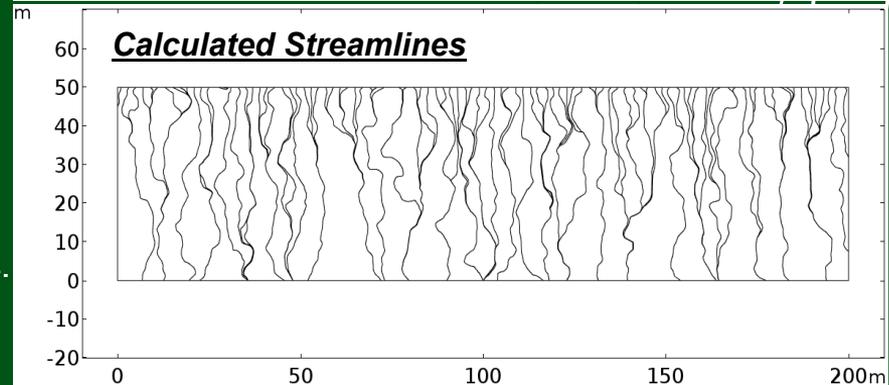
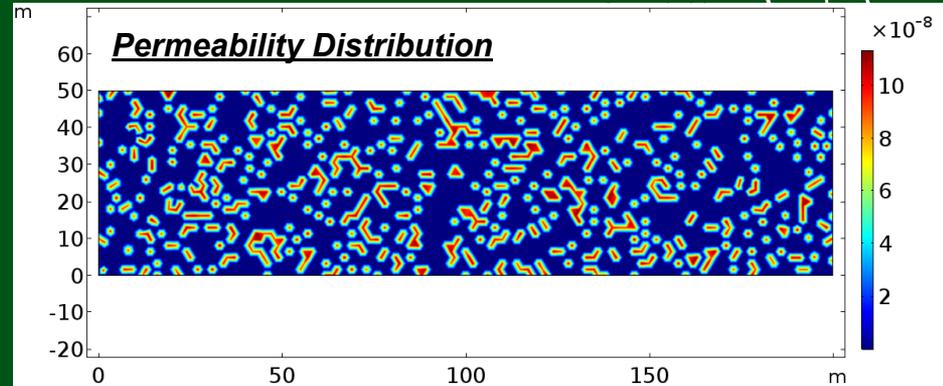
a is the lower boundary of permeability for finer pore zone.

b is the transition boundary of permeability between two zones.

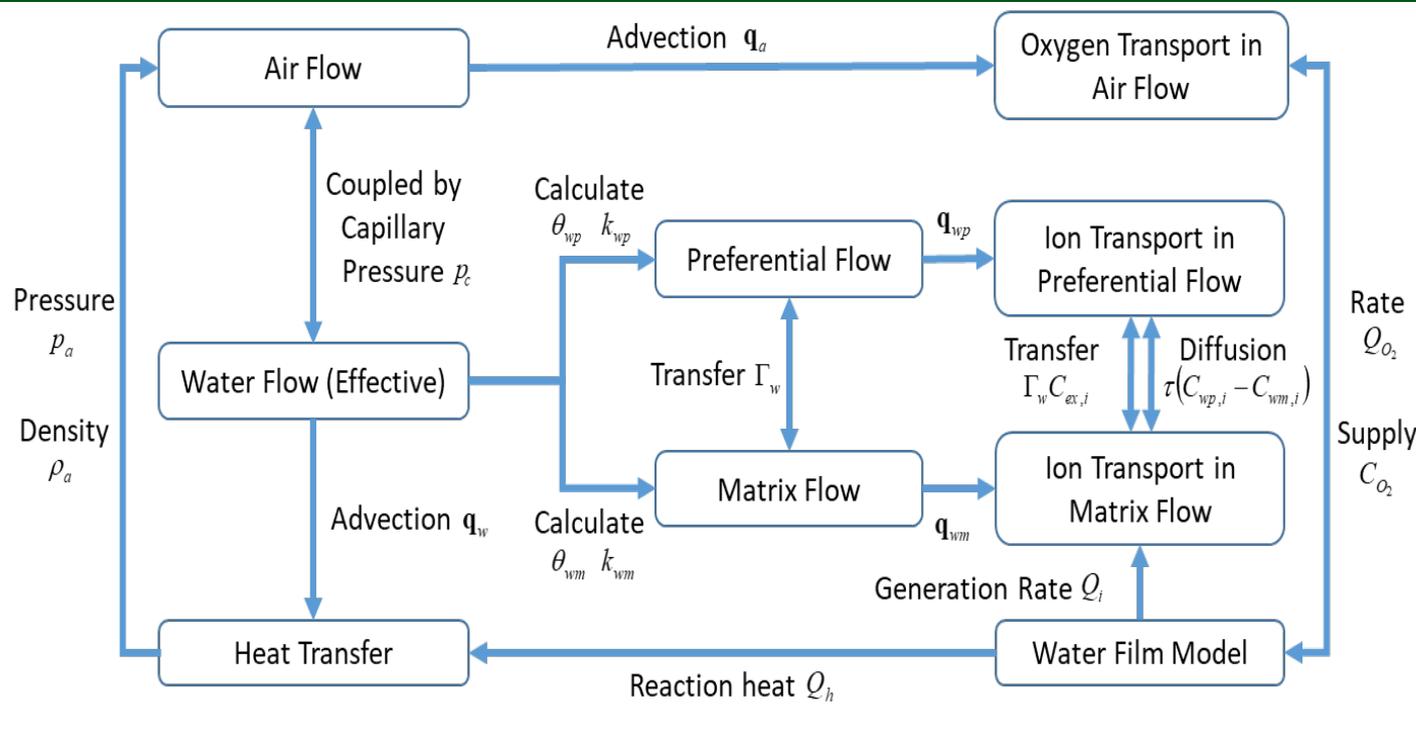
c is the higher boundary of permeability for coarser pore zone.

e is the fraction for finer pore zone.

$1-e$ is the fraction for coarser pore zone.



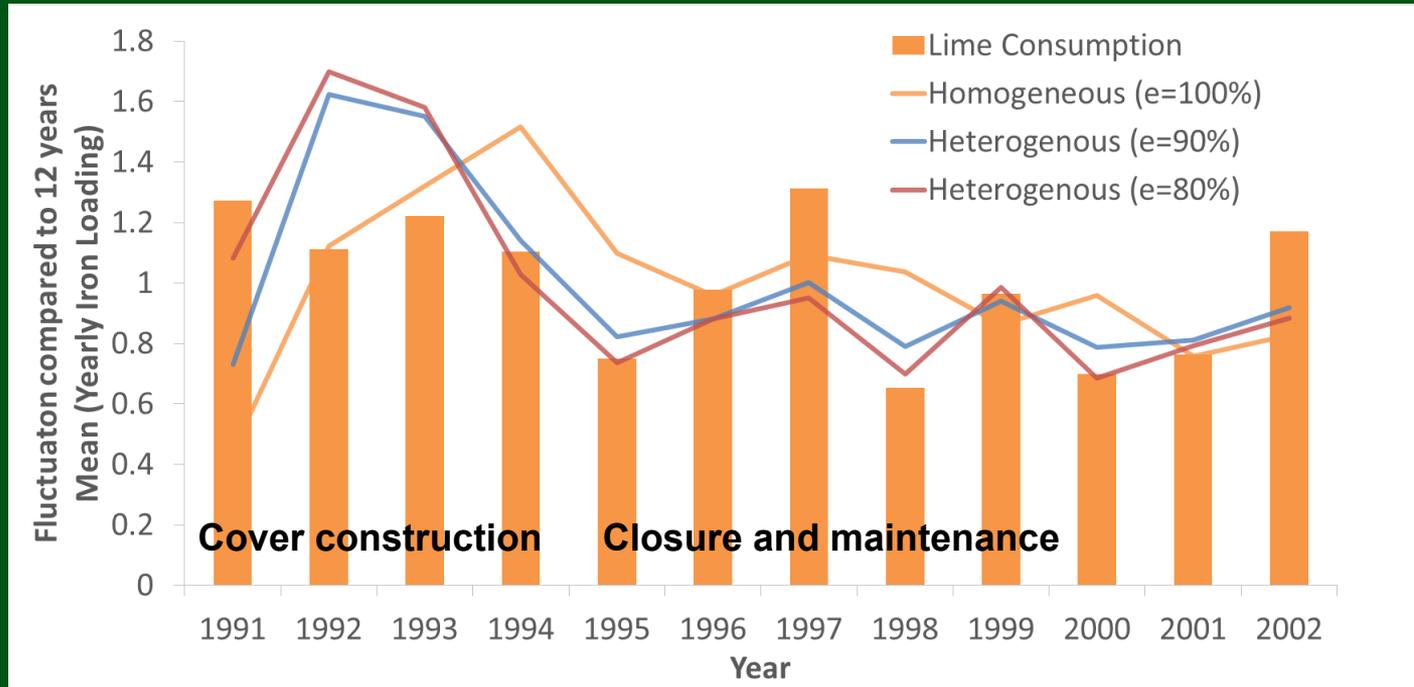
Coupling of the Mechanisms



- Water film
- Gas transport
- ✓ Convection
- ✓ Diffusion
- Oxygen consumption
- Heat transfer
- Water flow
- ✓ Matrix
- ✓ Preferential

Heterogeneous Preferential Water Flow

Prediction of long-term iron loading for a full-scale waste rock dump



Summary

- ❑ Research activities cover the mechanisms of ARD generation, secondary formation and metal leaching;
- ❑ ARD-ML is the synergy and competition of many factors and mechanisms;
- ❑ Through the fully coupled models of the linked factors and mechanisms, more accurately predict the ARD-ML from waste rock piles, dry-stack tailings and co-disposal of mine wastes;
- ❑ Optimize the configurations of waste rock pile, dry-stack tailings and co-disposal of mine wastes to minimize the ARD-ML.

Q & A

THANK YOU

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