



# Laboratory Characterization of Aquifer Attenuation Mechanisms for Acidic Groundwater at a Copper Mine in Arizona: **Experimental Design, Results and Development of Supporting Models**

Laura Volden, MSc, PGeo  
Dirk Kirste, PhD  
Kelly Sexsmith, MSc, PGeo



# Outline

- Site Description and History
- Geology
- Conceptual Model
- Objectives
- Hypotheses
- Study Approach
- Experimental Design & Results
- Summary of Findings
- Applications of Results

# Site Description and History

- Open pit copper porphyry operation
- Mining throughout the mid 20<sup>th</sup> century followed by acid leaching of waste facilities
- Relevant facilities include an open pit, leach dumps, tailings and waste rock
- The pit is used to manage acidic leach solutions and water levels are controlled by enhanced evaporation (sprayers)
- Mine is in pre-closure with limited reclamation to date

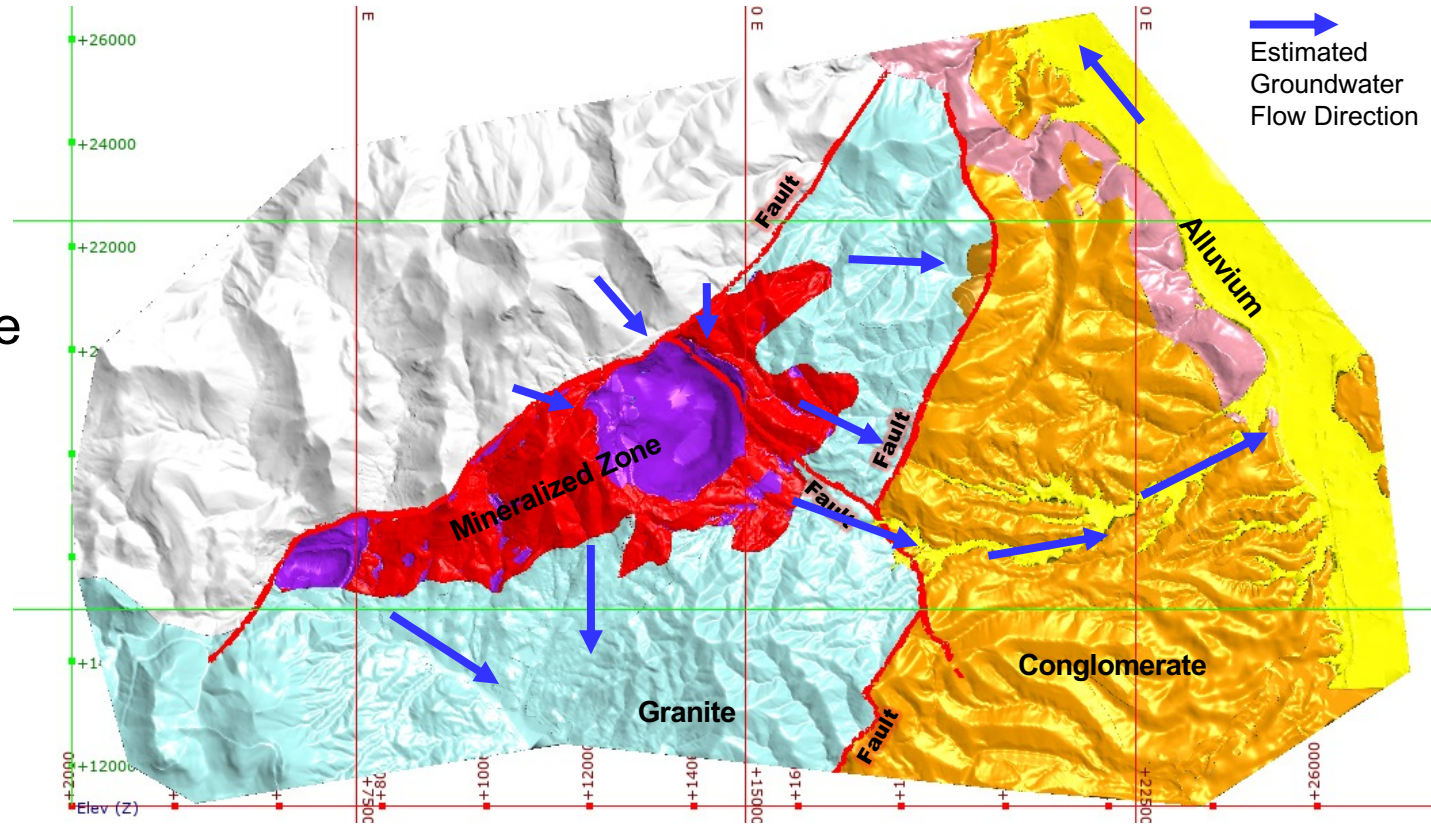




# Geology

Three major lithologies:

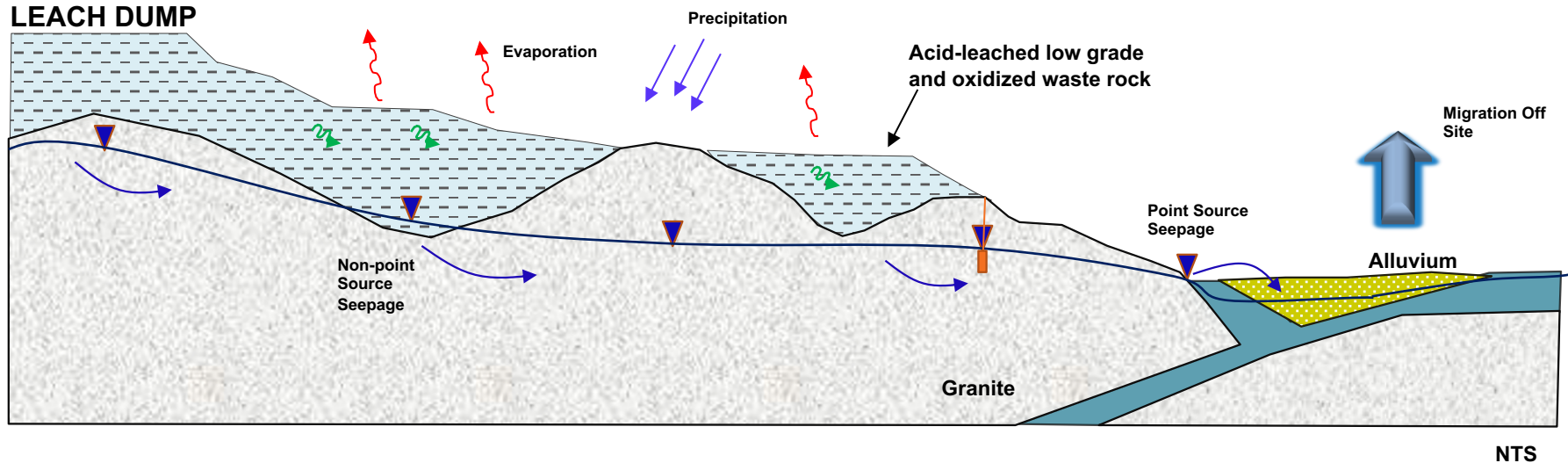
1. Alluvium
2. Conglomerate
3. Granite



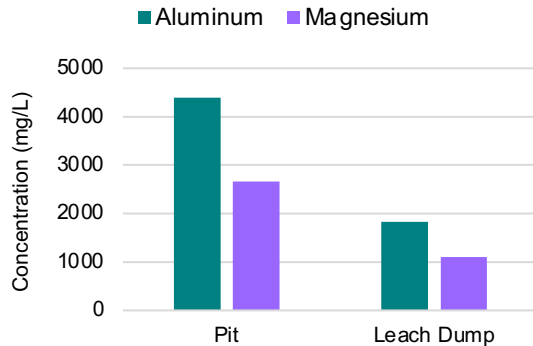
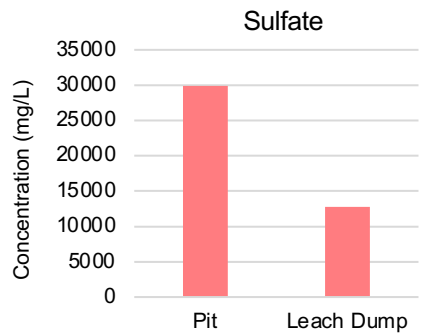
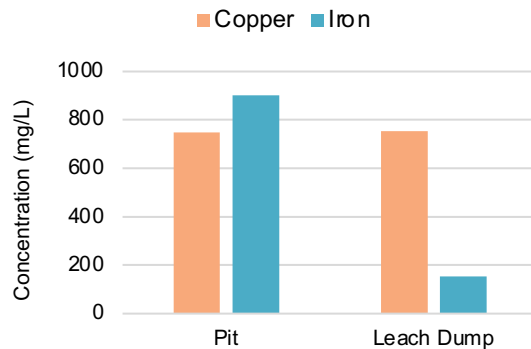
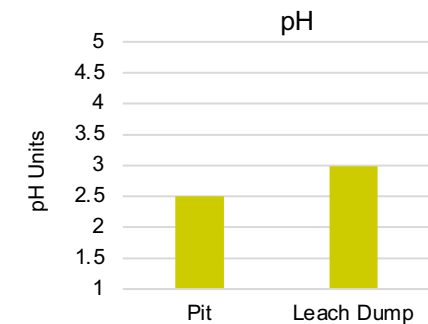


# Conceptual Model

- Potential for point and non-point seepage sources to contribute leach dump leachate to the groundwater system
- Alluvial material provides a transport pathway offsite and downgradient to surface receptors



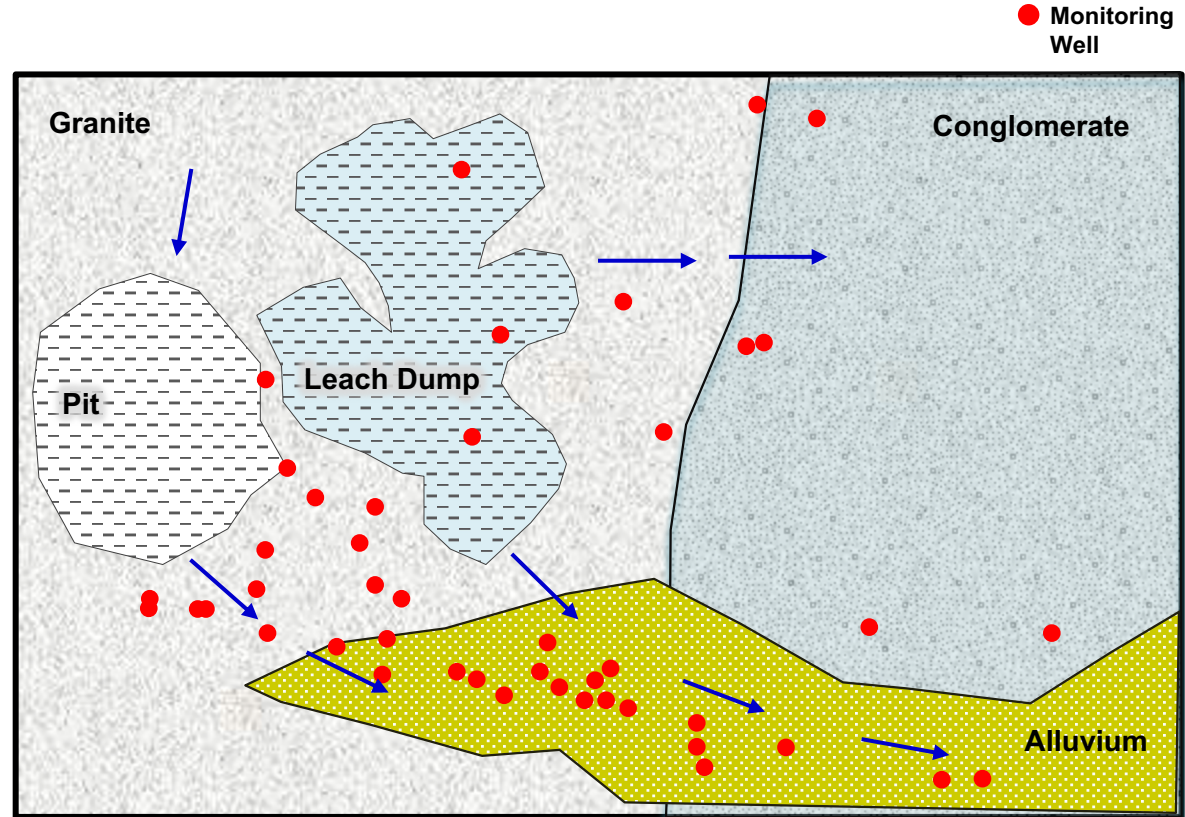
# Source Chemistry





# Water Quality Monitoring

- Numerous downgradient monitoring locations that have been monitored for up to 35 years
- Limited evidence of contaminant breakthrough at any of these locations suggesting that rates of groundwater flow are very small or that attenuation reactions are limiting breakthrough





# Objective

**Identify attenuation mechanisms along groundwater flow paths between sources of leachate and downgradient receptors**

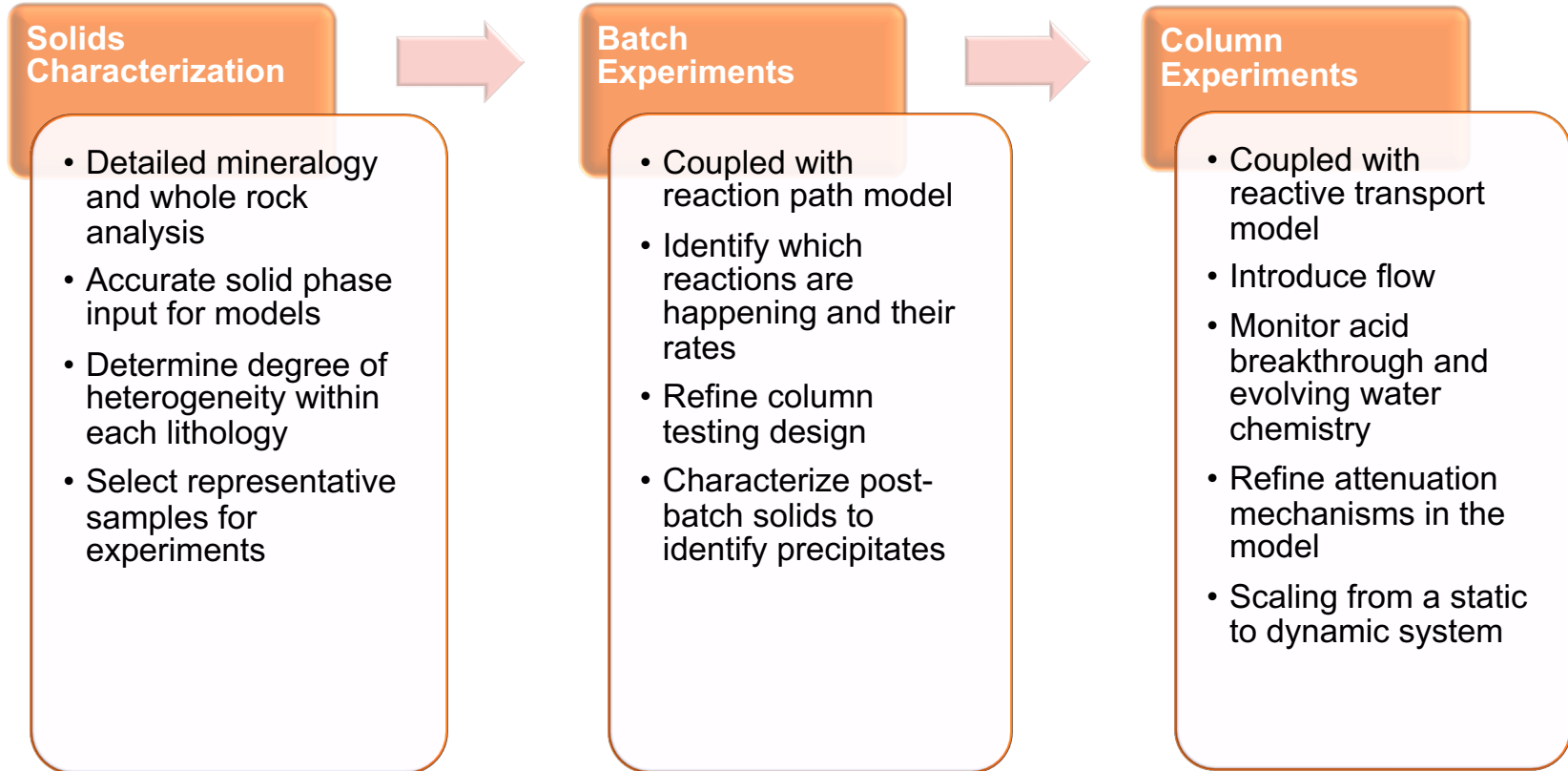
To Support:

- Understanding of reactions that occur in the groundwater system
- Interpretation of water quality monitoring results
- Contribution to risk assessments involving water quality
- Support closure design

# Hypotheses

1. Carbonate minerals in the aquifer will buffer pH
2. Change in pH will facilitate mineral precipitation and dissolution reactions
3. Trace elements will be attenuated by adsorption
4. Cation exchange will act as a (temporary) sink
5. Co-precipitation of trace elements with authigenic minerals

# Study Approach





# Solids Characterization – Methods

- Acid Base Accounting
- Trace Elements by Aqua Regia Digest
- Whole rock chemistry
  - Lithium Borate Fusion – Summation of Oxides, XRF Finish
  - Sodium Peroxide Fusion – ICP-MS Finish
- Mineralogy (XRD/QEMSCAN)
- LPNORM (linear programming normative analysis)
  - Allows geochemical accounting of elements to minerals by linking bulk chemistry and mineralogy
  - Carbonate minerals are constrained using TIC

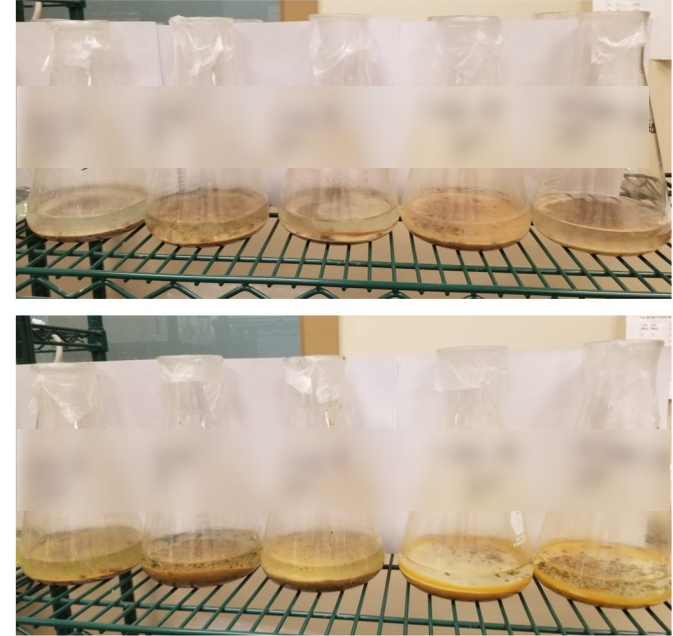
# Solids Characterization – Results

- Mostly quartz and other silicates
- Calcite is the main carbonate
- More calcite in conglomerate than alluvium
- Heterogeneity within the same aquifers
- Few iron oxides/oxyhydroxides present

Mineral Group	Mineral	Alluvium				Conglomerate			
Framework Silicates	Quartz	48	48	52	40	57	37	42	40
	Orthoclase	24	21	22	23	14	15	19	16
	Albite	8.0	11	7.5	14	7.1	8.8	8.1	7.1
	Andesine	5.6	6.0	3.9	8.1	6.4	8.1	8.3	8.9
	Labradorite	0.91	0.37	0.34	0.39	0.18	1.5	0.08	2.0
	Anorthite	0.04	0.03	0.07	0.03	0.06	0.08	0.01	0.05
Sheet Silicates	Muscovite	5.4	4.6	3.8	3.9	2.9	2.2	1.2	2.3
	Biotite	1.1	1.0	0.8	1.3	0.38	2.9	0.54	1.9
	Illite	2.8	2.8	2.2	3.4	2.5	3.6	8.9	4.6
	Smectite	1.9	1.5	1.9	2.3	2.3	6.2	8.5	5.1
	Kaolinite	0.2	0.2	0.17	0.13	0.07	0.19	0.06	0.07
	Chlorite	0.4	0.22	0.18	0.16	0.75	2.2	0.54	1.7
Carbonates	Talc	-	0.02	0.02	0.1	0.01	0.18	-	0.01
	Calcite	0.04	0.29	0.02	0.19	2.1	2.2	1.8	3.2
	Dolomite	-	0.15	-	0.1	-	-	-	0.03
Oxides	Hematite	0.25	0.58	0.2	0.34	1.2	1.7	0.82	3.5
	Goethite	0.02	0.28	0.23	0.07	0.02	0.15	0.05	0.05
	Magnetite	0.01	0.02	0.01	0.02	0.05	0.27	0.18	0.21
	Ilmenite	0.24	0.24	0.64	0.25	1.6	2.6	0.07	1.8
	Rutile	0.13	0.04	0.27	0.06	0.49	0.15	-	0.05
Amphiboles	Actinolite	0.59	0.8	0.58	0.51	0.49	3.2	-	1.2
	Augite	0.36	0.15	2.2	0.41	0.02	0.9	-	0.11
	Ferrohornblende	-	-	-	-	0.06	0.1	-	0.05
Orthosilicates	Zircon	0.11	0.01	0.01	0.02	0.12	0.01	-	0.06
	Fayalite	-	-	-	-	0.02	0.26	0.01	0.06
Pyroxene	Jadeite	0.08	0.13	0.08	0.13	0.15	0.16	0.14	0.12
Sulfates	Jarosite	0.21	0.26	0.28	0.27	-	-	-	-
Phosphate	Apatite	0.13	0.04	0.12	0.13	0.14	0.25	0.24	0.19
Others	Others	0.08	0.09	0.12	0.11	0.08	0.19	0.08	0.08
Unidentified	Unclassified	0.22	0.25	0.19	0.21	0.16	0.2	0.15	0.18
Total Inorganic C %		<0.02	0.14	<0.02	0.05	1.0	0.42	0.35	0.47
LPNORM Calcite		0.17	1.16	0.17	0.41	9.3	4.4	4.1	4.5

# Batch Experiments – Methods

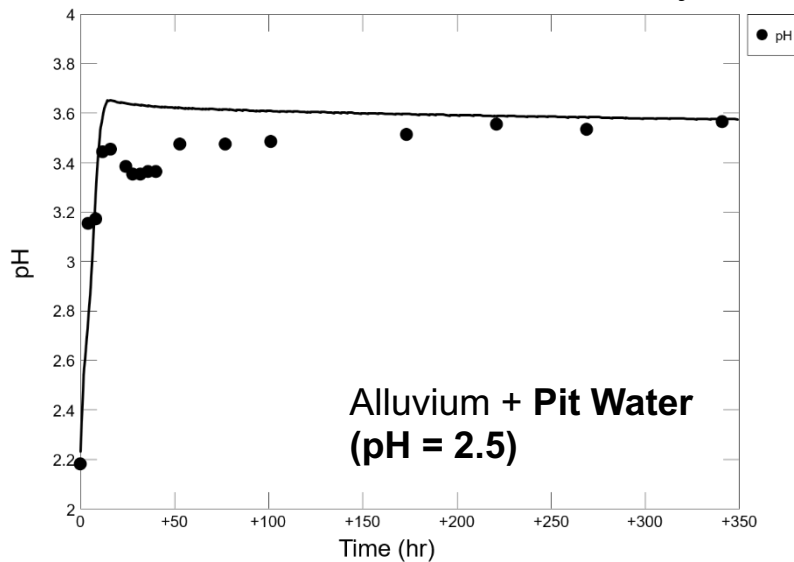
- Combination of aquifer materials with leachate solutions
- Run for 15 days with 8-10 samples throughout and frequent pH/EC monitoring
- Built an accompanying reaction path model to simulate the experiments
- Post-batch mineralogy on precipitates to constrain model inputs
  - Shows chemical evolution of solution composition as minerals dissolve/precipitate and exchange and adsorption reactions happen
  - Reduce uncertainty in reactive surface area of carbonate minerals



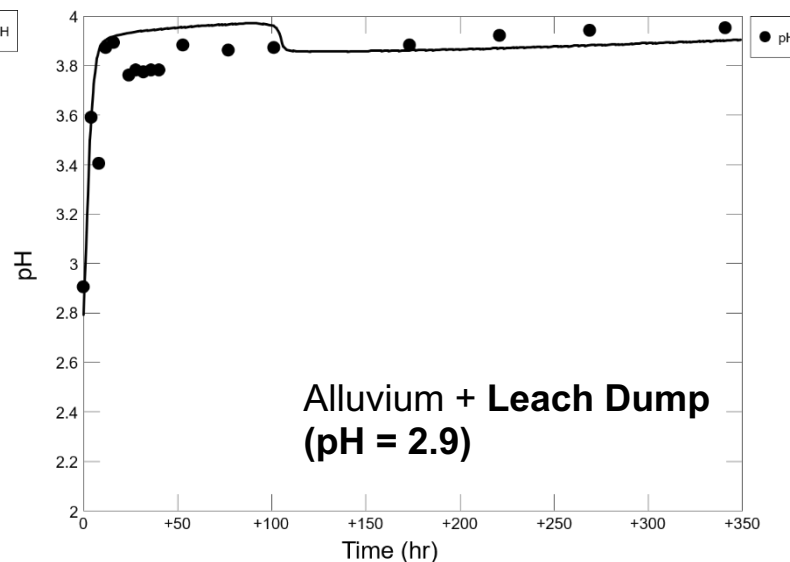


# Reaction Path Models & Batch Results

- Model pH is too high early on, reflecting Calcite dissolution but not enough Aluminite precipitation
- Model uses transition state theory

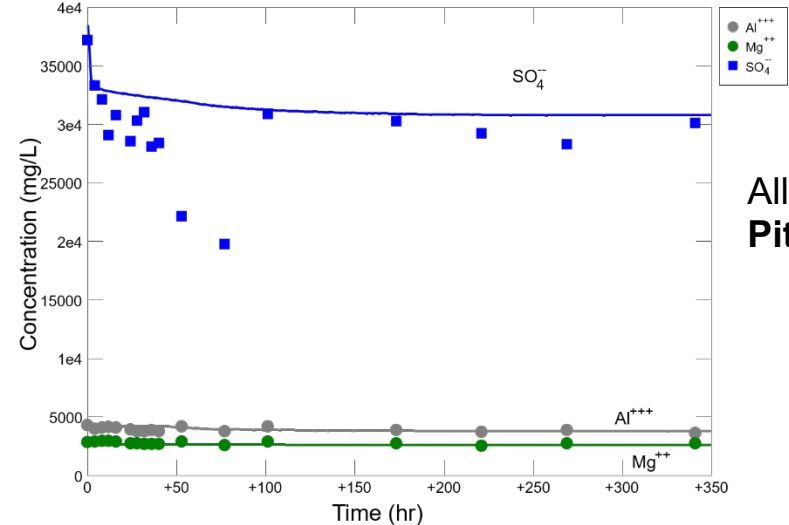
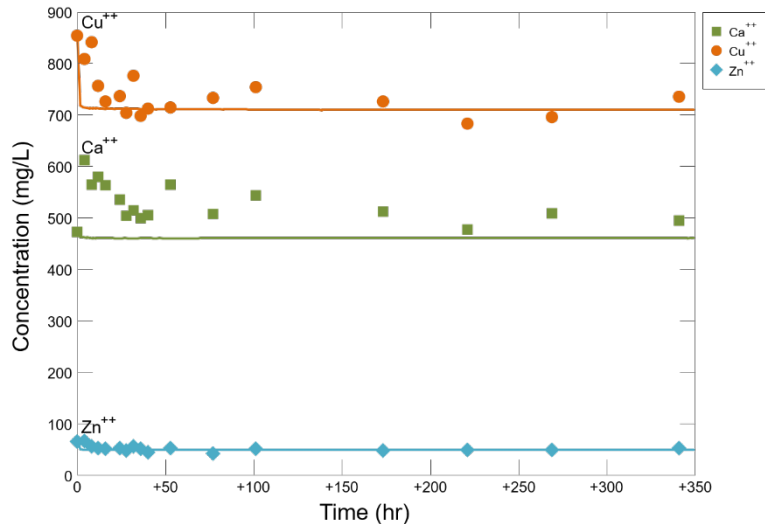


- Model pH increases initially due to Calcite dissolution and drops at the onset of Aluminite precipitation
- Model nucleation and crystal growth



# Reaction Path Models & Batch Results

- Initial increase in  $\text{Ca}^{2+}$  due to calcite dissolution and cation exchange
- Decrease in  $\text{Cu}^{2+}$  modelled as adsorption on newly formed sites associated with Aluminite (may also be in crystal structure)
- Sulfate decrease due to Gypsum and Aluminite ( $\text{Al}_2\text{SO}_4(\text{OH})_4 \cdot 7\text{H}_2\text{O}$ ) precipitation



# Column Experiments – Methods

	Conglomerate	Granite	Alluvium
Leach Dump	2	2	2
Pit Water	2	2	2

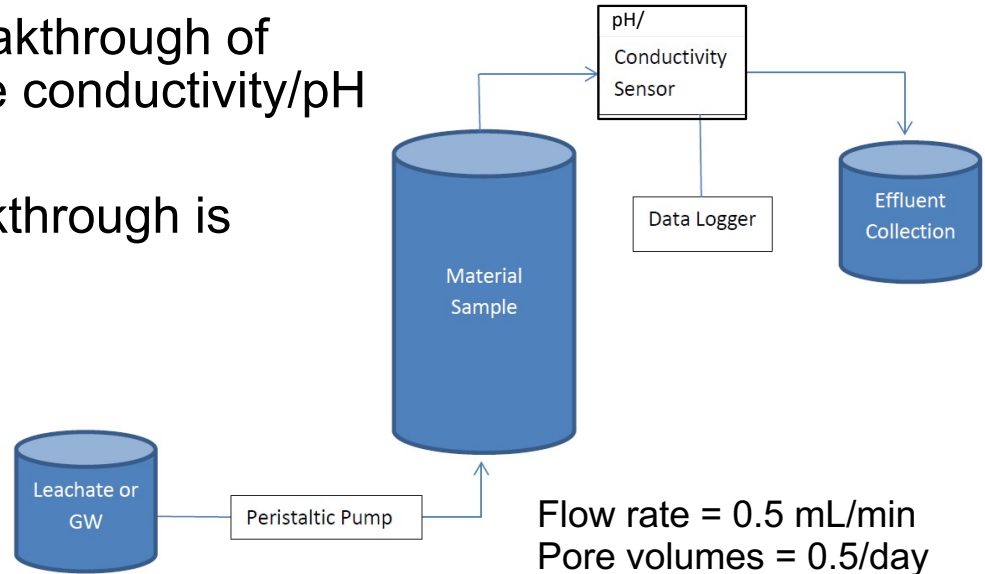
- Total of 12 columns representing a range of conditions
- Two different carbonate contents for alluvium and conglomerate
- Two different grain sizes for granite



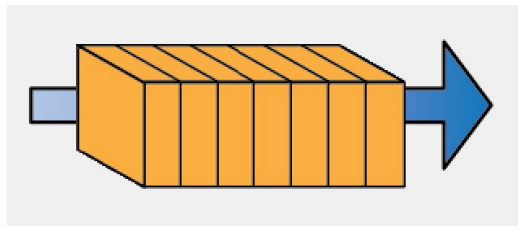
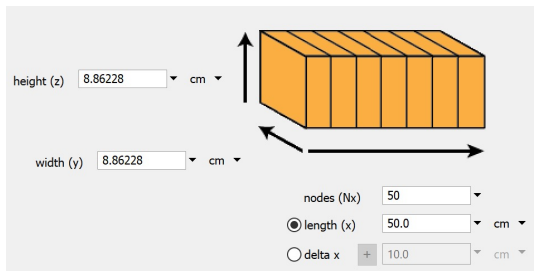


# Column Experiments – Methods

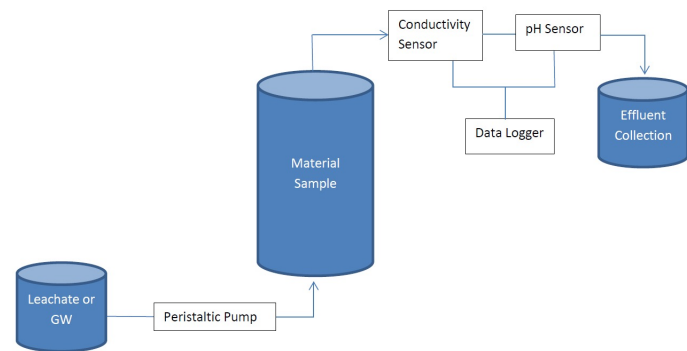
- Background groundwater is circulated through to establish baseline conditions
- NaCl tracer is introduced to measure dispersivity
- Leachate is introduced and breakthrough of leachate is measured with inline conductivity/pH probes
- Sampling increases when breakthrough is detected
- Monitoring evolution of water composition after breakthrough to evaluate reaction mechanisms and element mobility



# Reactive Transport Models



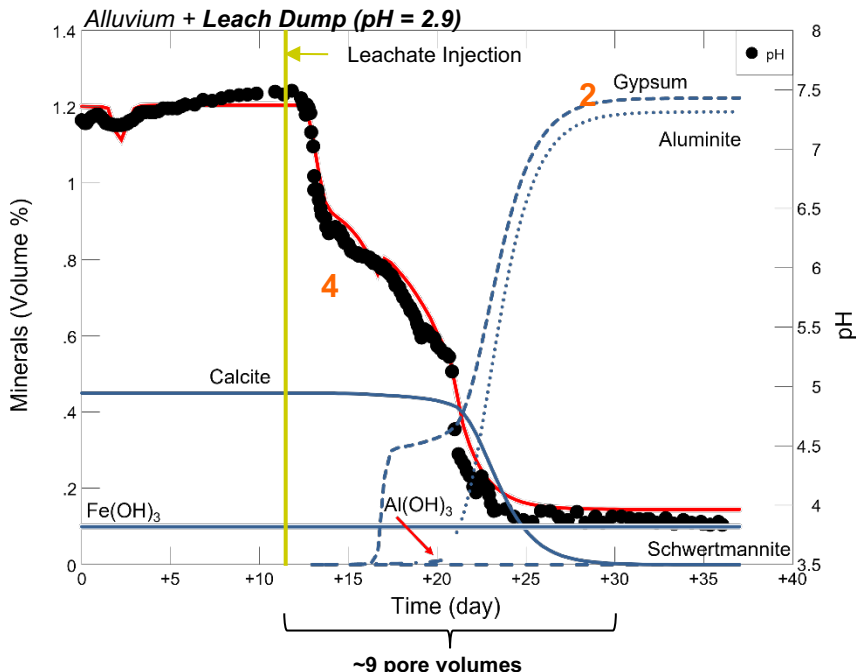
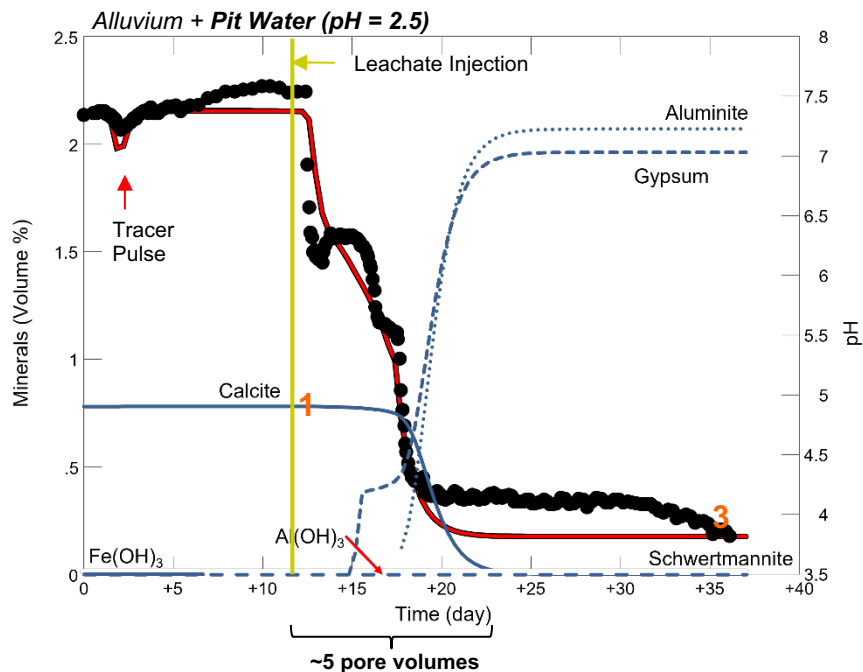
- Set up to simulate a 50 cm tall column with 10 cm diameter
- Flow rate of 0.5 mL/min and porosity as measured before columns are flooded
- Dispersivity – curve fit to NaCl pulse
- Populated with mineralogy and kinetic reactants identified in the reaction path modelling/post-batch characterization
- Refinement of adsorption and cation exchange sites and reactive surface areas as experimental results are history matched to the models



# Reactive Transport Models & Column Results

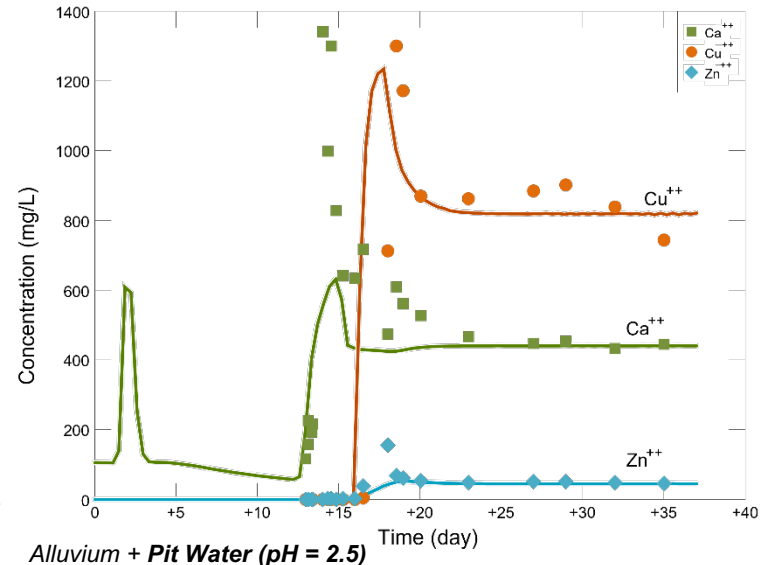
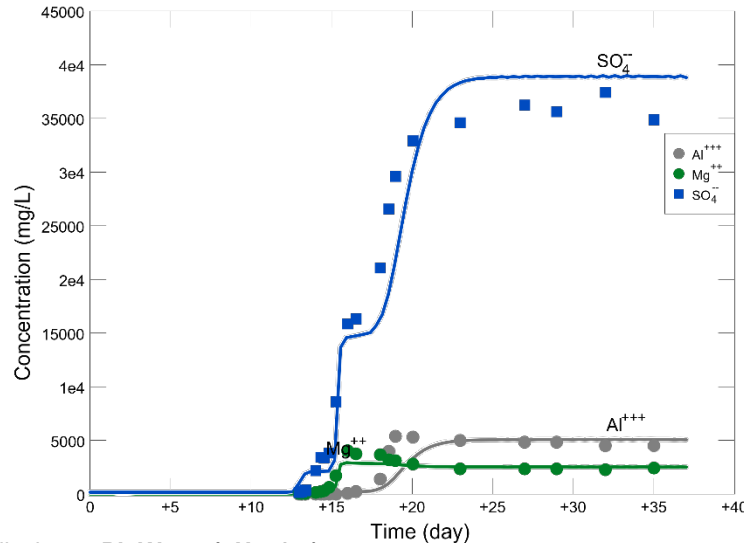
## Main Processes

1. Calcite dissolution
2. Gypsum,  $\text{Al}(\text{OH})_3$  and Aluminite precipitation
3. Aluminite ( $\text{Al}_2\text{SO}_4(\text{OH})_4 \cdot 7\text{H}_2\text{O}$ ) dissolution and Schwertmannite ( $\text{Fe}_8\text{O}_8(\text{OH})_{5.48}(\text{SO}_4)_{1.26} \cdot n\text{H}_2\text{O}$ ) precipitation near the end (earlier in the cell)
4. Cation exchange + adsorption/desorption



# Reactive Transport Models & Column Results

- Desorption/exchange result in pulse like peaks
- Chromatographic effect reflects the preference on exchange and adsorption sites as well as mineral precipitation/dissolution
- Attenuation of metals arrival (4-5 days) relative to  $\text{SO}_4$ , Ca and Mg



# Summary of Findings

- Carbonate content and the rate of calcite dissolution are controlling pH buffering – rates of subsequent mineral precipitation follow calcite
- Low carbonate content still plays an important role in buffering – abundances can't be accurately quantified with traditional methods
- Adsorption and cation exchange play a large role in trace element mobility and provide attenuation capacity
- Precipitation of aluminum and iron minerals provides buffering of pH values
- The study helps to explain why there has been limited evidence of contaminant breakthrough to the downgradient environment in the existing groundwater monitoring network



# Application of Results

- Solid mechanistic understanding will be used to explain current conditions at the site
- Results may eventually be used to support predictive modelling

Challenges and uncertainties in extrapolating these findings to the full scale system include:

1. Estimating reactive surface area of fractured bedrock
2. Representing variations in carbonate content and availability in aquifer materials
3. Uncertainties in the groundwater flow system (i.e. amount and rate of flow bypassing collection)
4. Contributions from mixing and dilution by freshwater sources

# Questions?

thank  
you

**AGAT** Labs 

