Selective Removal of Toxic Metals for Abandoned Mine Water Remediation

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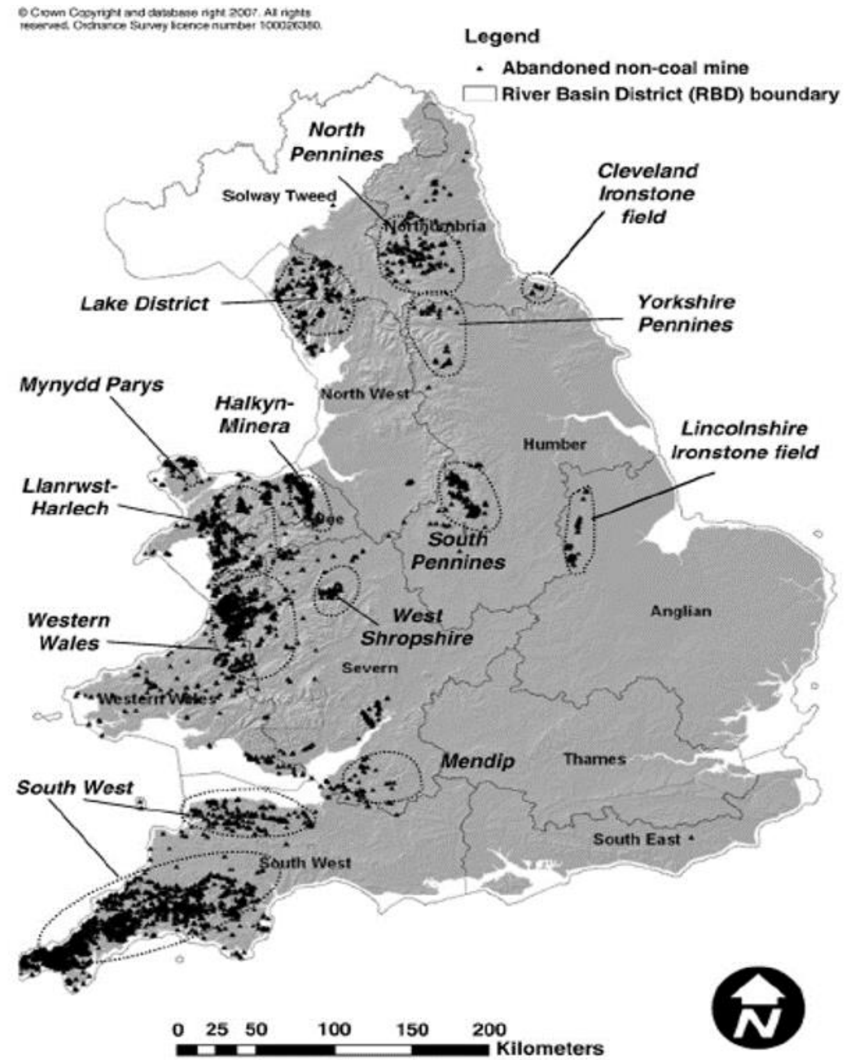
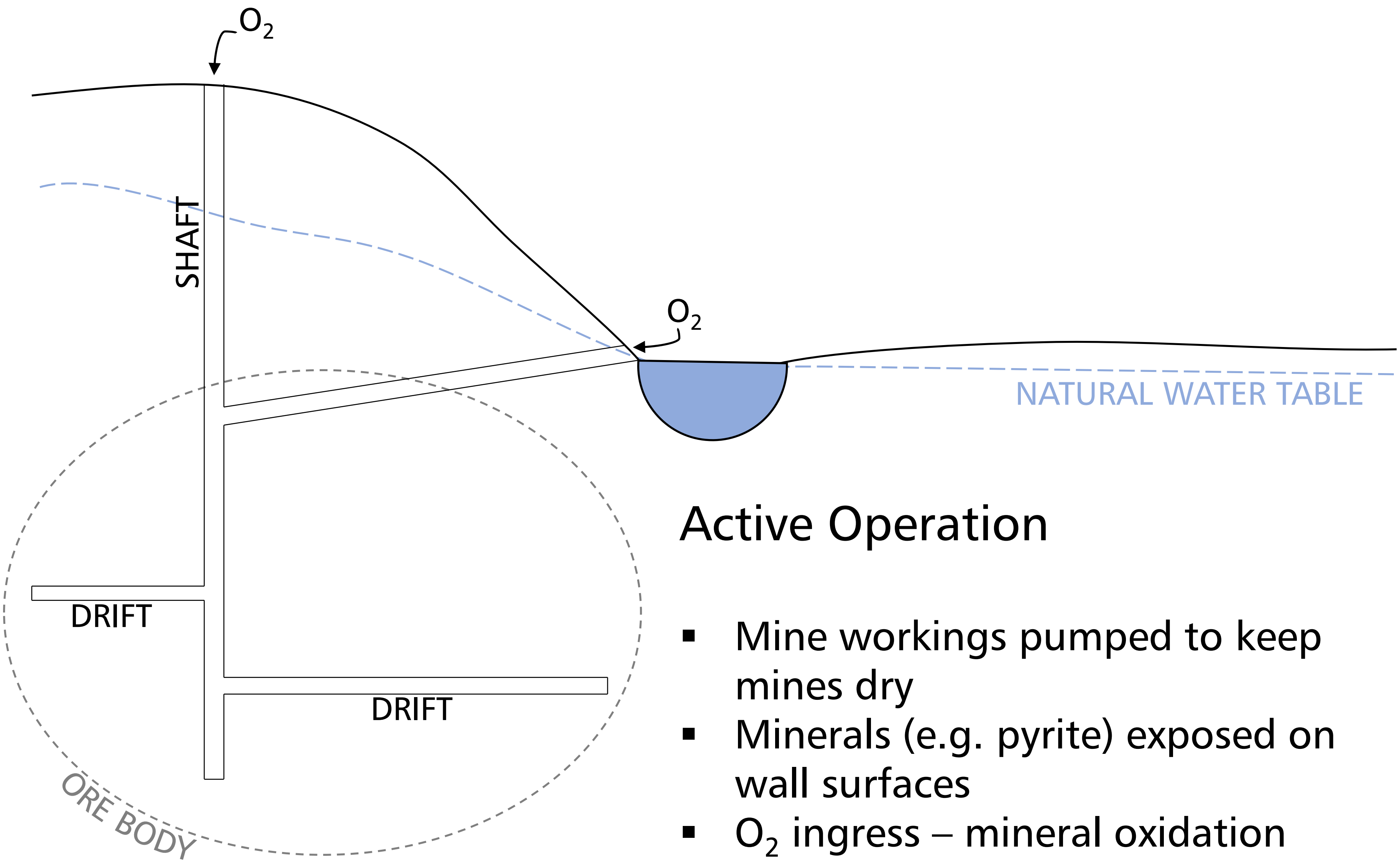
Mine Water Pollution | Scale of Problem

- Considered one of the most severe pollutant sources in the UK
  - 6% of surface water bodies affected in England/Wales[1]
  - 2nd most important freshwater pollutant source in Scotland (behind sewage)[2]
  - Over 700 km of waterways affected nationally[3]
- 'Hotspot' distribution of abandoned mines



(Figure from Mayes et al. (2009))

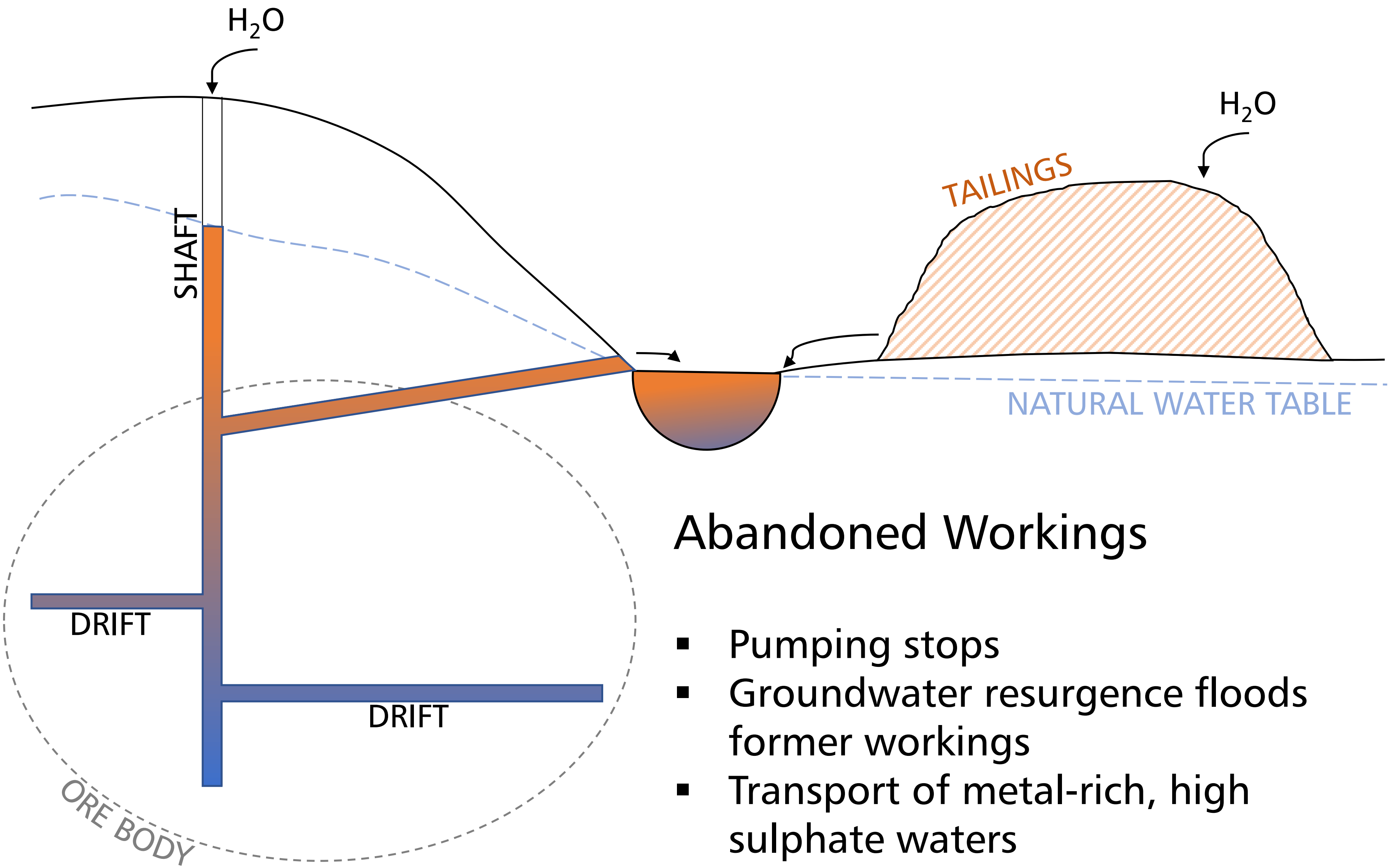
Mine Water Pollution | Sources



Active Operation

- Mine workings pumped to keep mines dry
- Minerals (e.g. pyrite) exposed on wall surfaces
- O_2 ingress – mineral oxidation

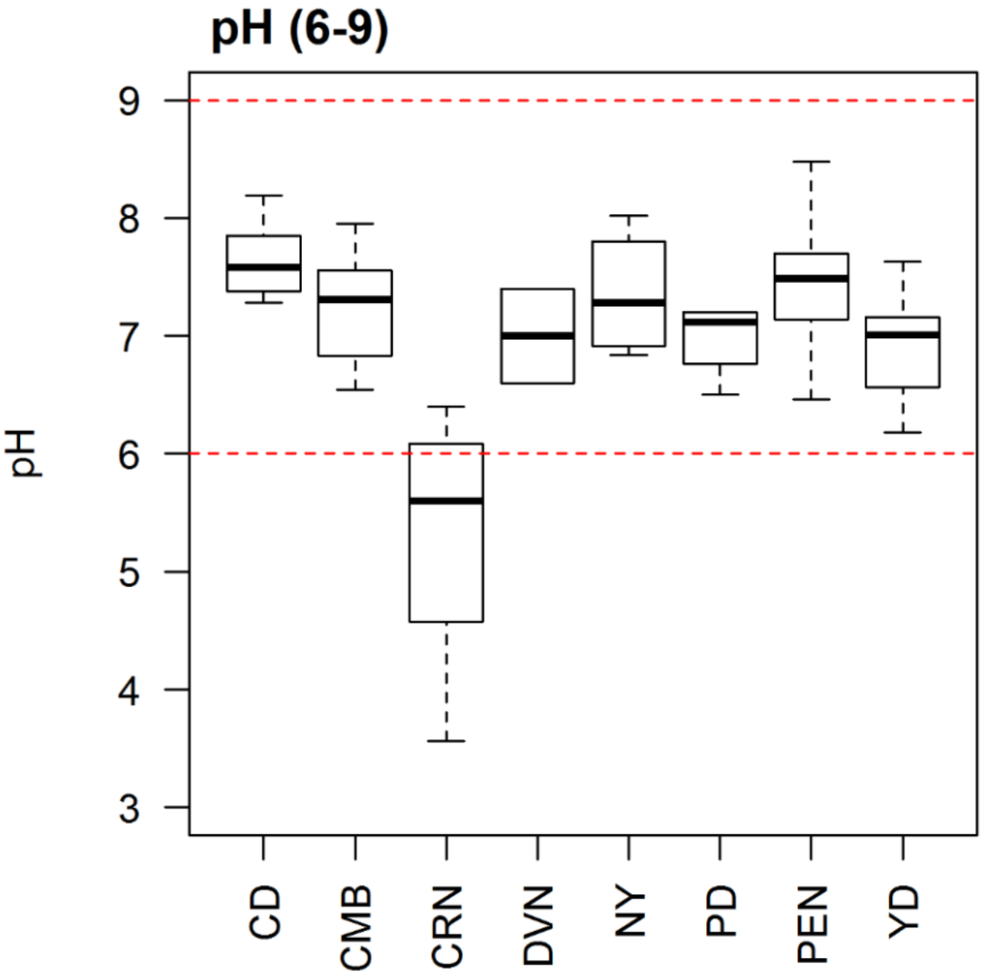
Mine Water Pollution | Sources



Abandoned Workings

- Pumping stops
- Groundwater resurgence floods former workings
- Transport of metal-rich, high sulphate waters

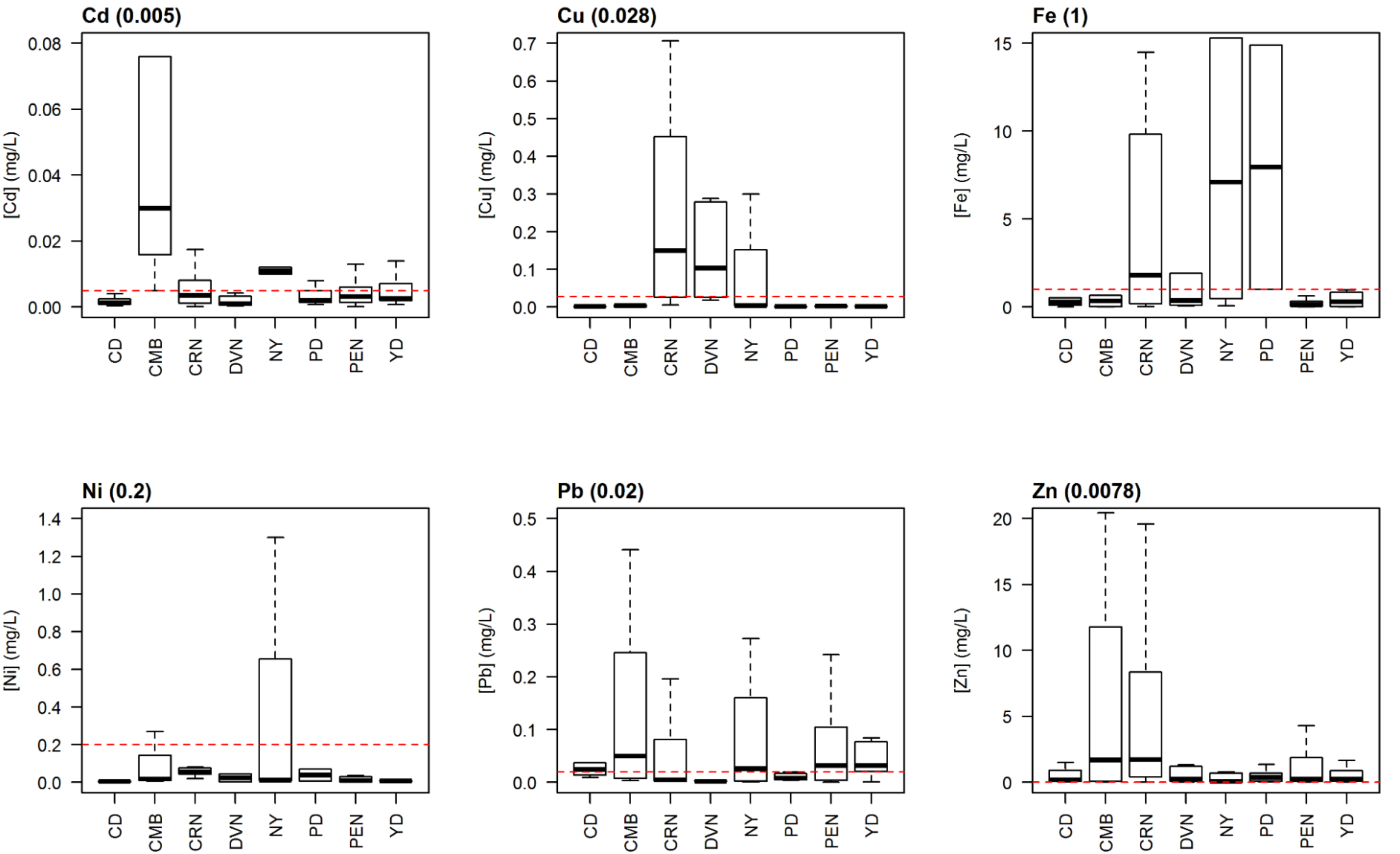
Mine Water Pollution | Geochemistry



CD = County Durham
CMB = Cumbria
CRN = Cornwall
DVN = Devon
NY = North Yorkshire
PD = Peak District
PEN = Pennines
YD = Yorkshire Dales

- 'Acid' Mine Drainage?
  - Environment Agency data for mine impacted streams (surface)
  - Low pH leachates within mines, but generally not at surface
  - Buffering of pH by carbonate-rich bedrock
  - UK streams usually within environmental quality standards

Mine Water Pollution | Geochemistry



Mine Water Pollution | Environmental Impact

- Metal Release
  - Fish mortalities, particularly salmonids[4]
  - Reduced diversity of invertebrate species
  - Barrier to legislative targets
- Mineral Precipitation
  - Benthic smothering
  - Loss of spawning gravels[4]
  - Important habitat loss
  - Aesthetic issues

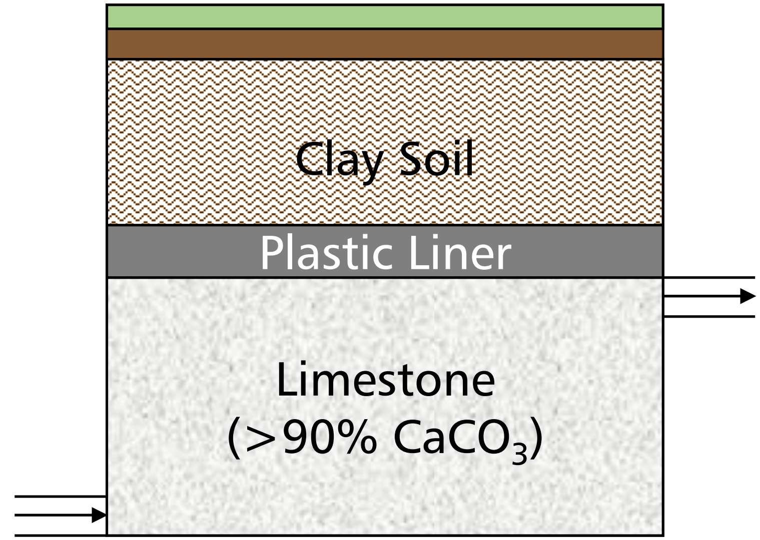
Damage to ecological community structure[5,6]

Mine Water Pollution | Remediation

- Active – e.g. alkali dosing
- Passive – e.g. aerobic wetland
  - Remove metals through oxidation and hydrolysis ⟶ metal hydroxides
  - High initial cost but remediate pollution at lower-long term cost[8]
  - Well suited to Fe removal
  - High area required ⟶ low area-adjusted removal rates[9,10]
  - Require periodic dredging/ dewatering of precipitate ⟶ extra cost

Mine Water Pollution | Remediation

- Other remediation options;
  - Anoxic limestone drains (ALDs)
  - Pelletised inorganic waste media[11]
  - Vertical flow reactors[12]



- Current drawbacks:
  - High capital/resource cost of active dosing
  - High area requirement of wetlands
    - Also requires low topography (not always available)
    - Well suited for Fe removal, less so for other metals
  - Mineral precipitation ⟶ loss of capacity in sorption systems
  - Limited potential for resource recovery

Project Aim | Overview

Remains a need for a low-footprint, affordable, treatment system capable of selective, metal removal and recovery.

↓

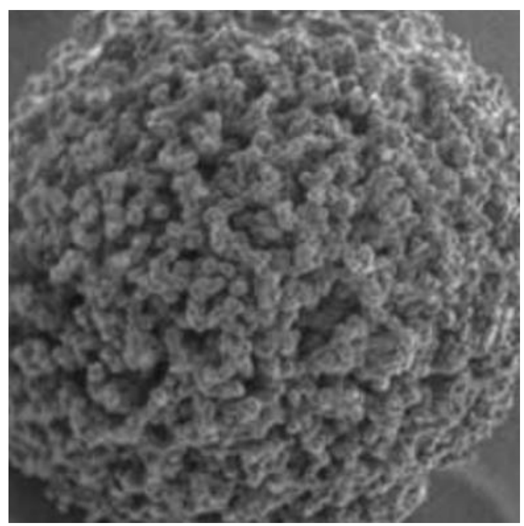
Develop a laboratory-scale system using simulated and real mine waters.

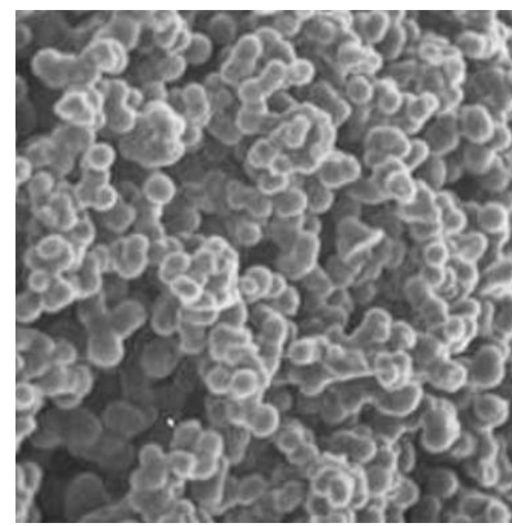
↓

Explore potential for process valorisation to offset remediation costs

Ion Exchange Resins | Introduction

- Small crosslinked polymer beads (often Polystyrene-DVB)
- Commercially available augmented with a range of functional groups
- Macroporous structure ensures high surface area and porosity

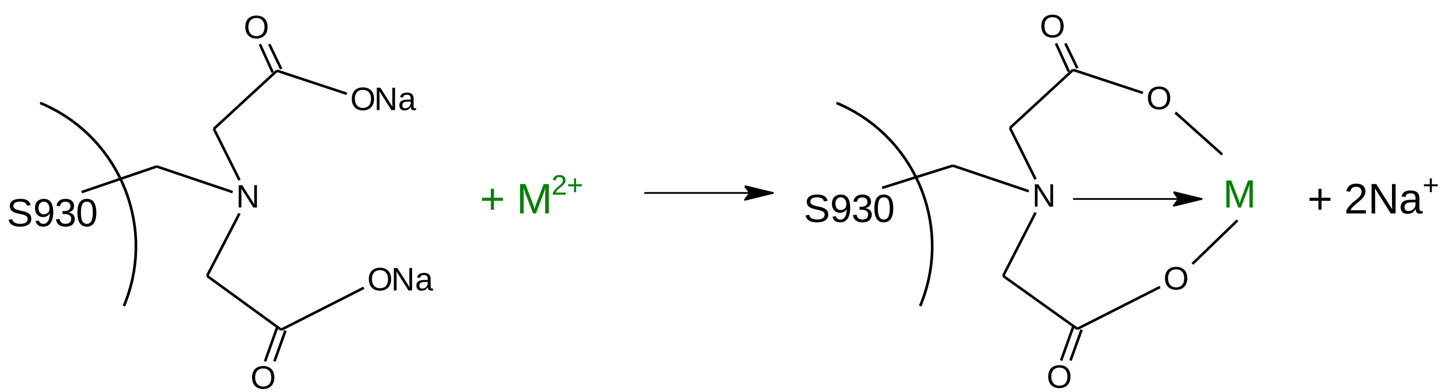




(Images from Hubicki et al. (2012))

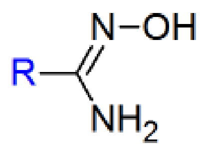
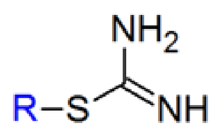
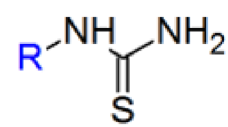
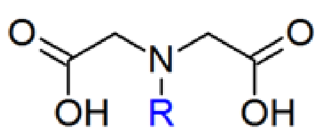
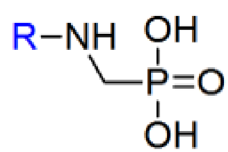
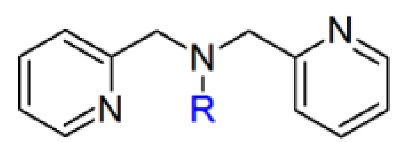
Ion Exchange Resins | Characteristics

- High physical and chemical stability
- High exchange capacity
  - Many functional sites on bead and pore surfaces
  - High metal uptake per resin mass
- Chelate formation ability
  - Enables strong bonding with specific metal species/complexes
  - Exhibit preferential selectivity towards certain ionic species
  - Effective when target ion at low concentrations



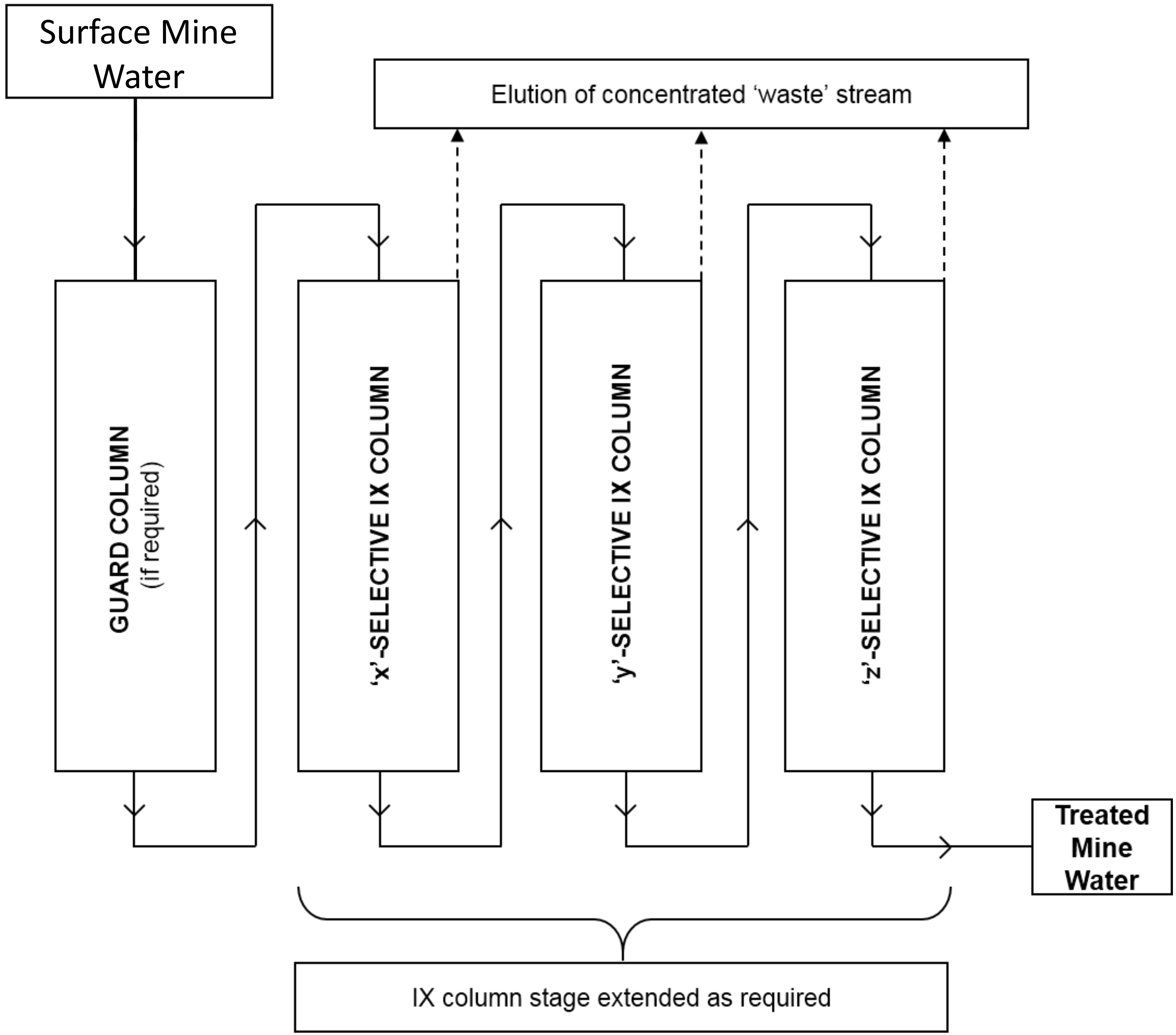
Ion Exchange Resins | Applications

- Extensive application in industrial processes
  - e.g. hydrometallurgy, nuclear industry
    - Base metal recovery
    - Precious metal recovery
    - Uranium enrichment

		
S910 - Amidoxime	S914 - Thiourea	S920 - Isothiouronium
		
S930 - Iminodiacetic	S950 - Aminophosphonic	M4195 – Bis-picolylamine

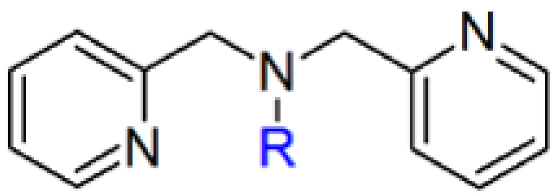
R = resin matrix

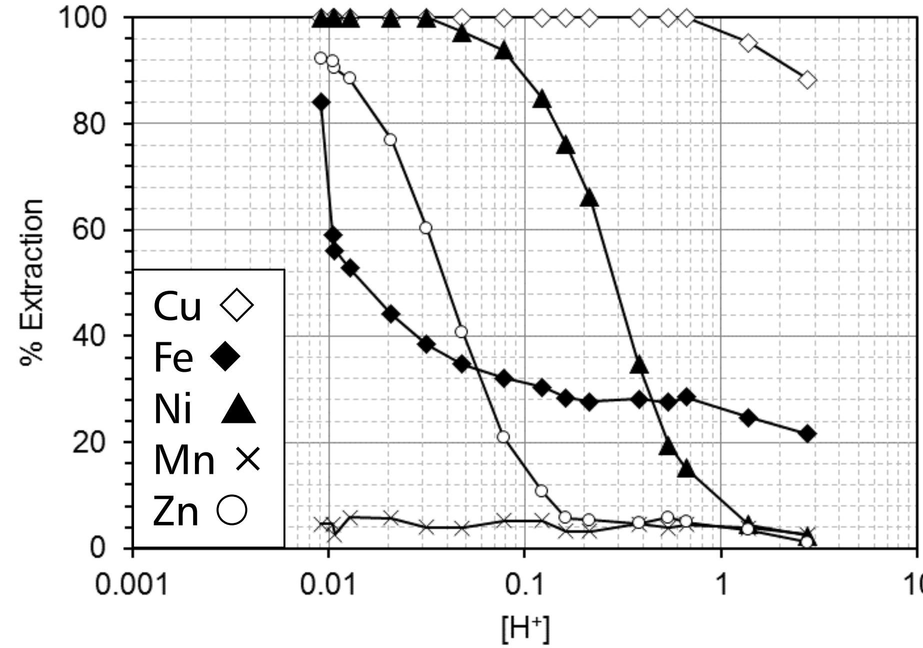
- IX system never successfully used for the remediation of legacy mine waters

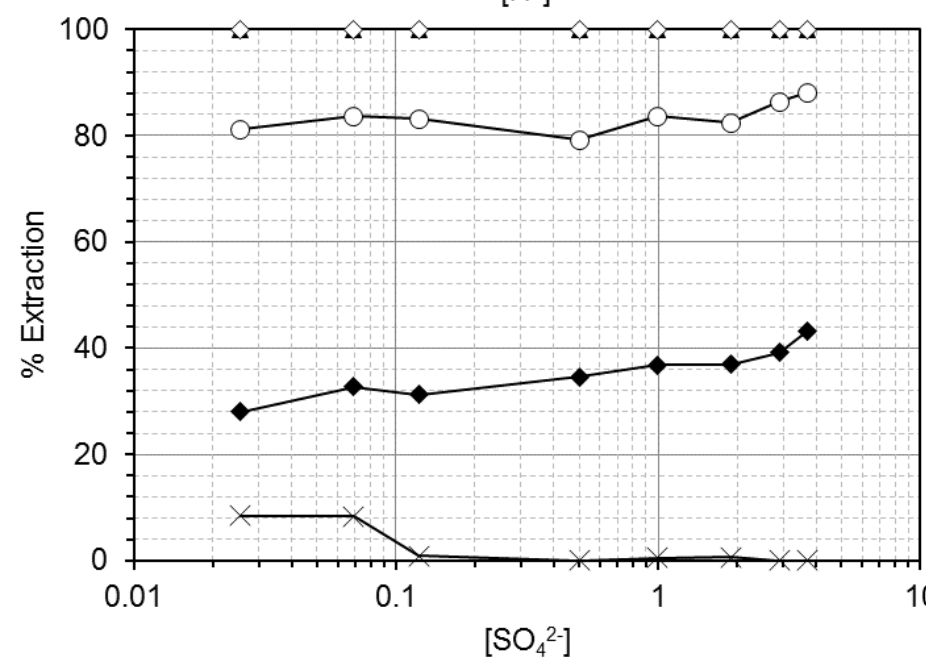

Surface Mine Water
Elution of concentrated 'waste' stream
GUARD COLUMN
(if required)
'x'-SELECTIVE IX COLUMN
'y'-SELECTIVE IX COLUMN
'z'-SELECTIVE IX COLUMN
Treated Mine Water
IX column stage extended as required

Preliminary Results | pH Screening

- Batch contacts – 2000ppm
- M4195 (Bis-picolylamine)



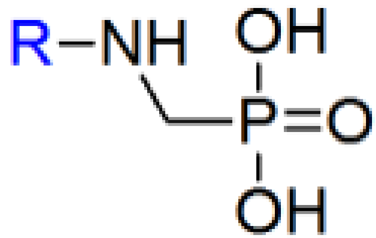




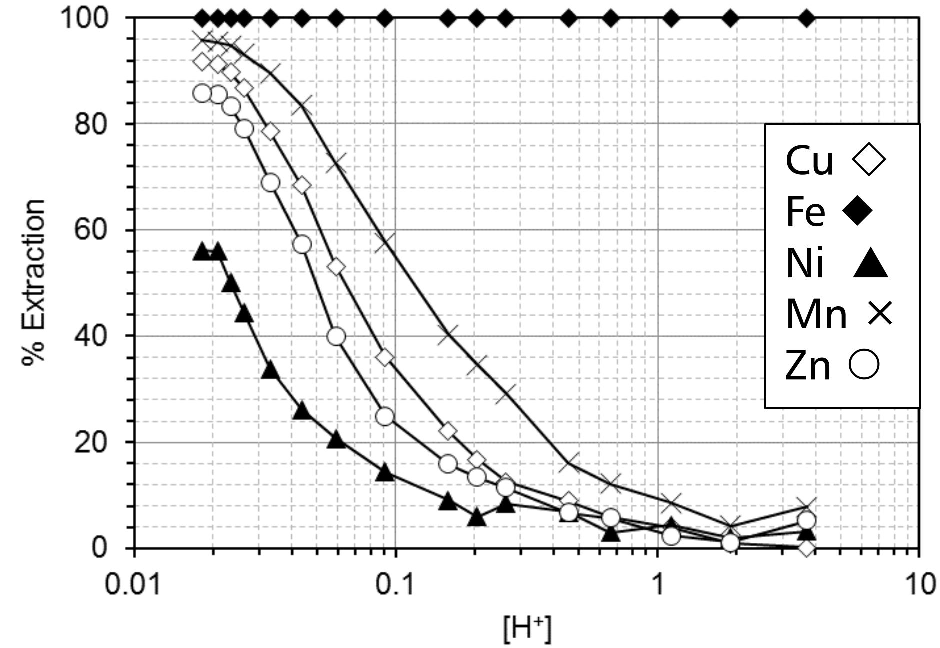
- Effective Cu removal over pH range
- Uptake of other metals suppressed with increased $[H^+]$
- Removal relatively unaffected by high $[SO_4]$

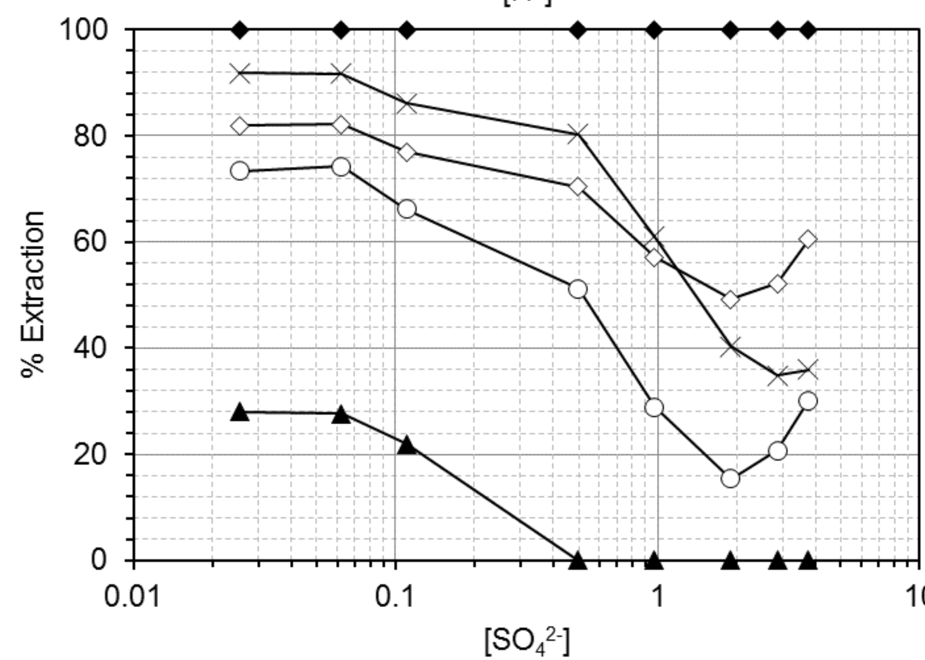
Preliminary Results | pH Screening

- S950 (Aminophosphonic)



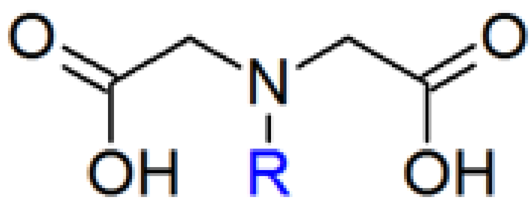
- Highly selective for Fe over other metals regardless of pH
- Suppression of other species at higher [H+] ⟶ weak acid functionalised
- Reduced metal uptake with higher sulphate concentration, with exception of Fe



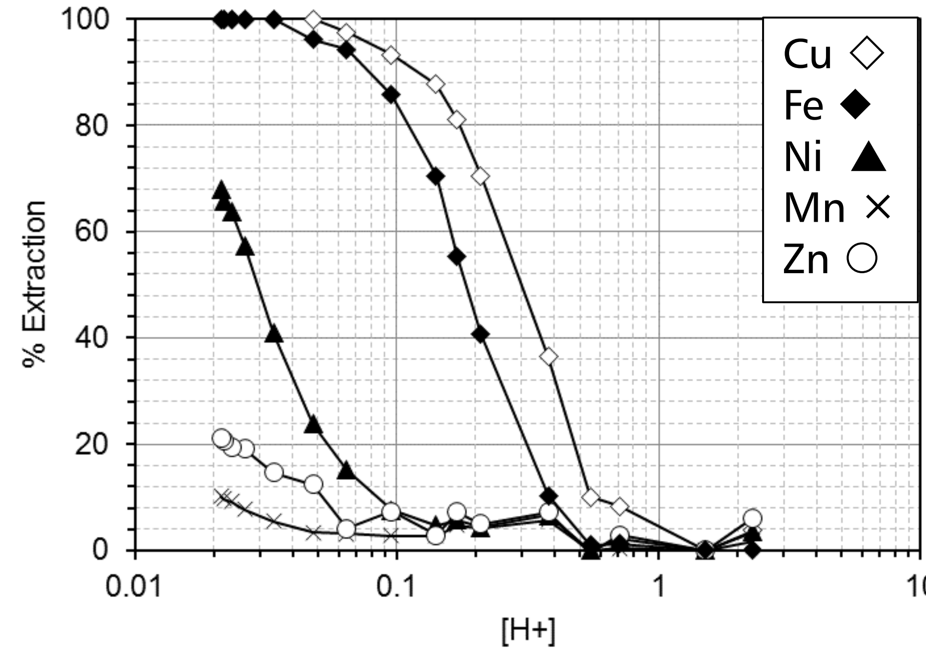


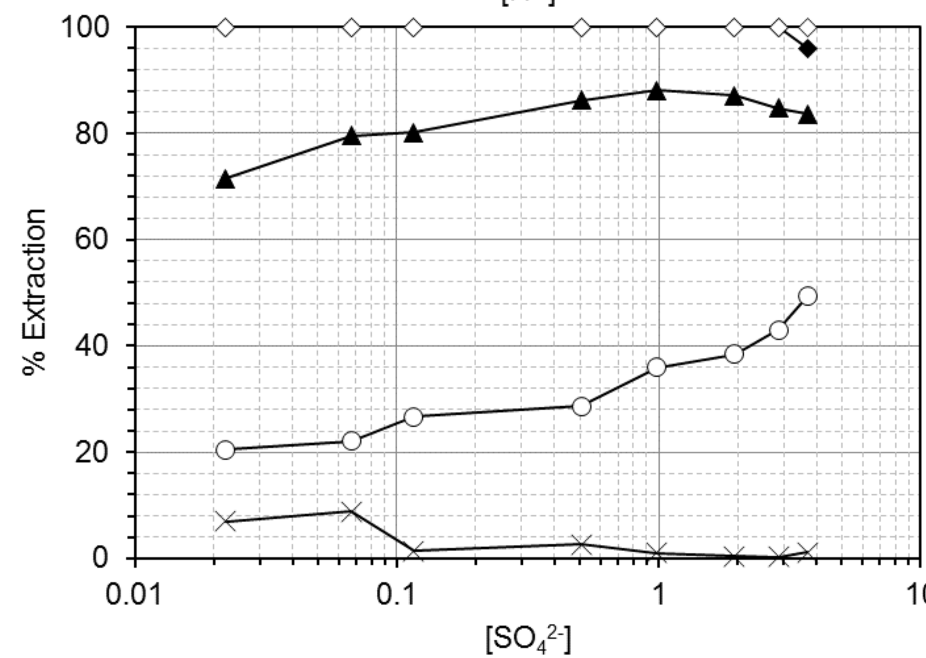
Preliminary Results | pH Screening

- S930 (Iminodiacetic acid)

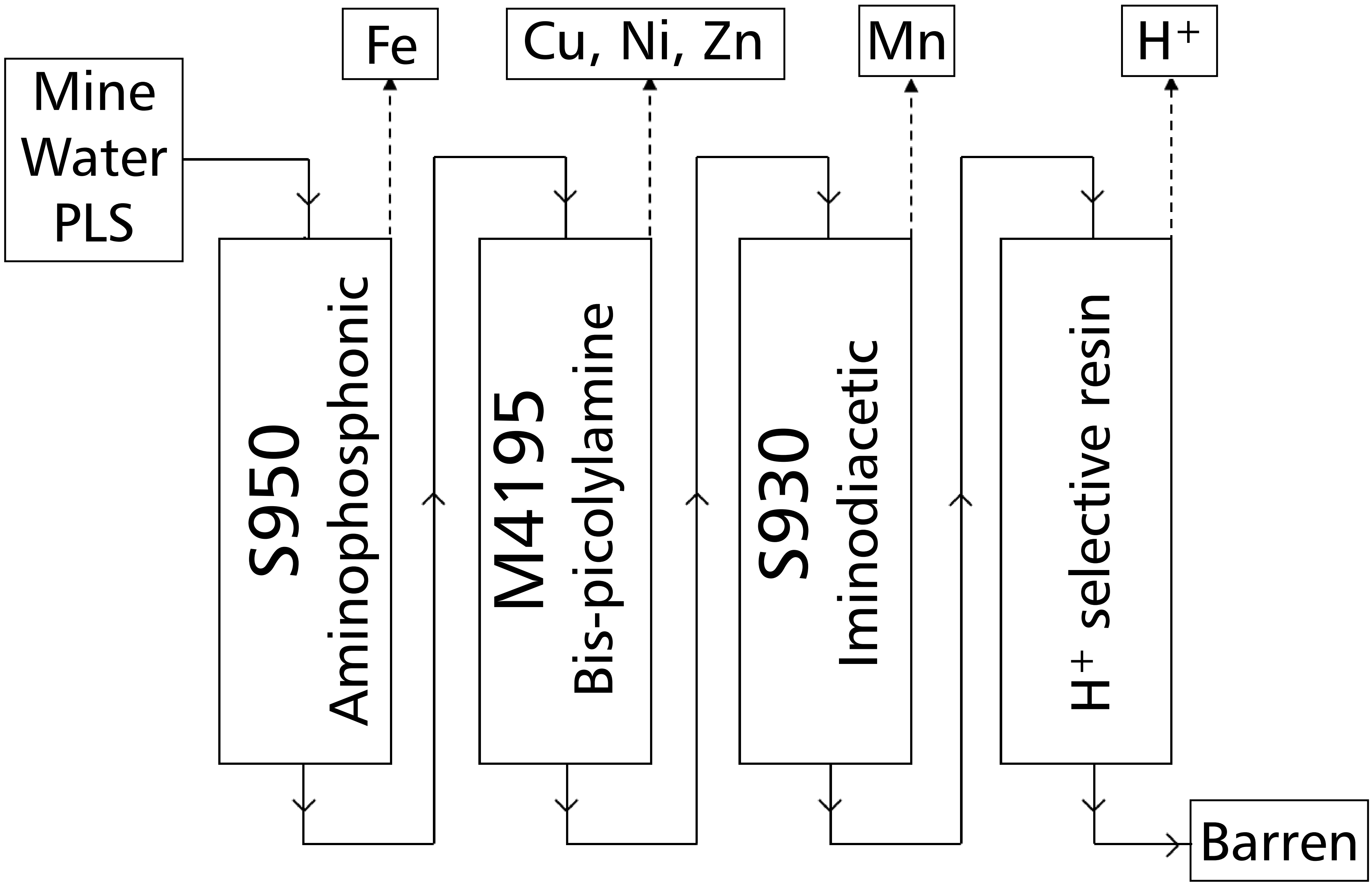


- Sharp suppression at higher pH
- Most selective for Fe and Cu, other metals extracted equally at ~pH 1-1.5
- Increased extraction with higher $[SO_4^{2-}]$ ⟶ stronger chelation with higher ionic strength





Preliminary Results | System Design



Further Work | References

SNUCER
Separations & Nuclear Chemical Engineering Research

- Continue static screening
  - More resin functionalities
  - Cu, Ni, Zn
- Isotherm loading experiments
  - Determine operating capacities
- Dynamic (column) experiments
  - Use real mine water samples
  - Metal recovery
- System design and scale-up

[1] Mayes, W.M., Johnson, D., Potter, H.A.B., & Jarvis, A.P. (2009). *Science of the Total Environment*, 407(21), pp. 5435-5447.

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