A robust solid-state reference electrode and its application in environmental monitoring

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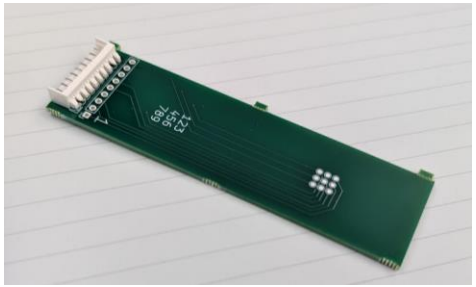
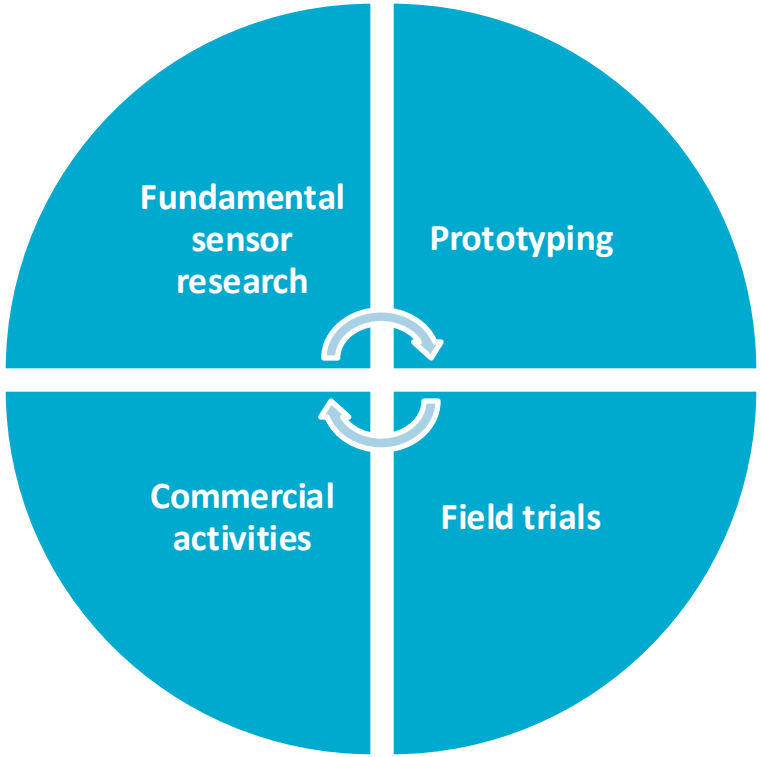
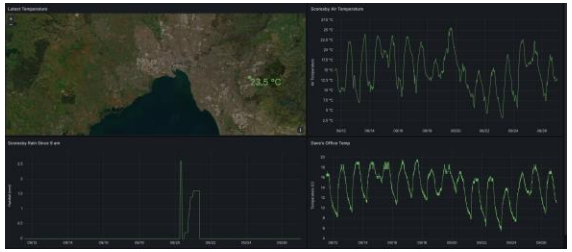
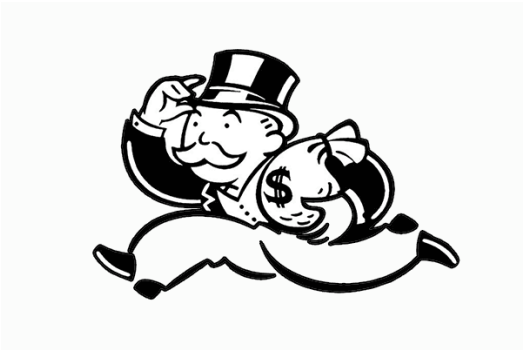
Sensor Development Team (Mineral Resources)



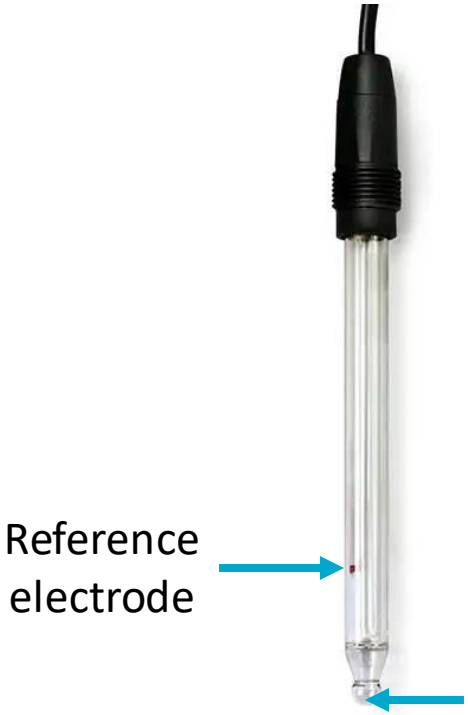






Potentiometric sensor background

Combination sensor (pH, ISE, ORP)



$E_{indicator}$

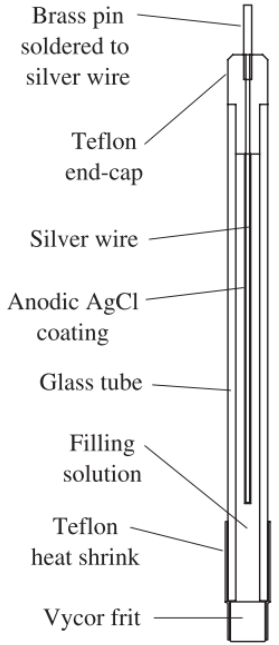
Response to analyte
Interference/poor selectivity
Fouling

$E_{cell} = E_{indicator} - E_{reference}$

$E_{reference}$

Stable regardless of solution chemistry
Electrolyte leakage
Poisoning (sulphide, OH^-, etc.)

Reference electrode background



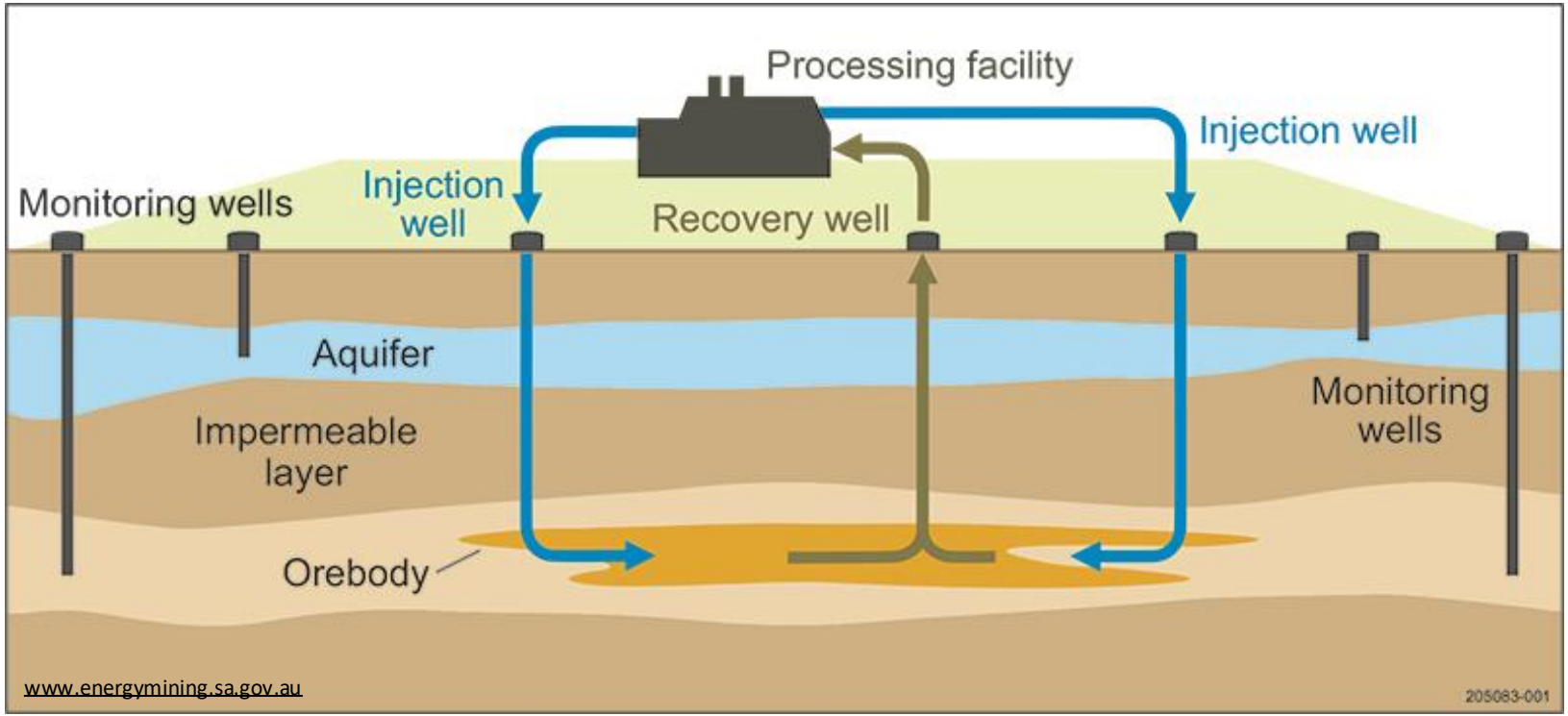
Smith and Stevenson, Handbook of Electrochemistry (2007)

$$AgCl_{(s)} + e^- \rightleftharpoons Ag_{(s)} + Cl^-_{(aq)}$$

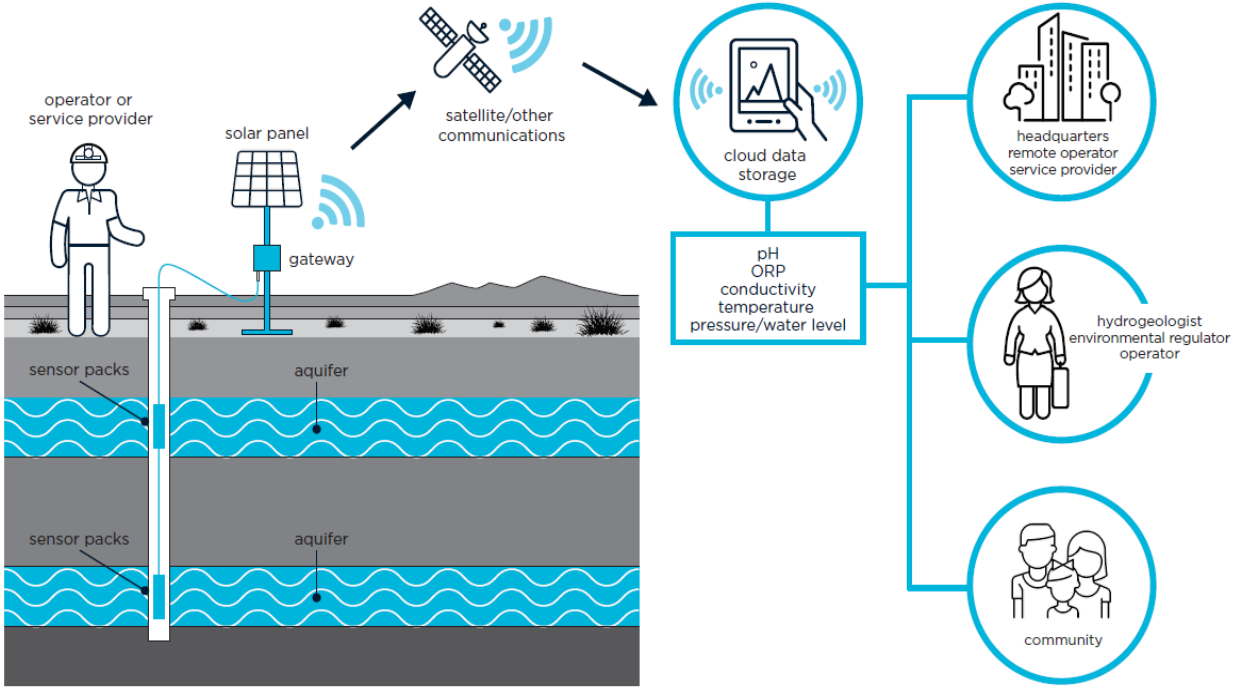
$$E_{Ag|AgCl} = E^{\circ}_{Ag|AgCl} - \frac{RT}{F} \ln a_{Cl^-}$$

- Potential dependent on chloride activity (concentration)
- Potential can also be affected contamination (S^{2-}, OH^-, etc.)
- Frit needs to enable ionic conductivity, but shouldn't be too permeable!

In-situ recovery (ISR)

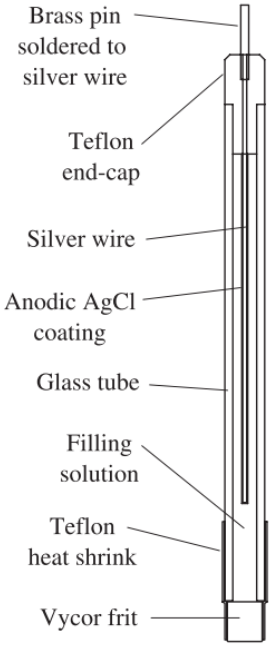


Sensor system overview



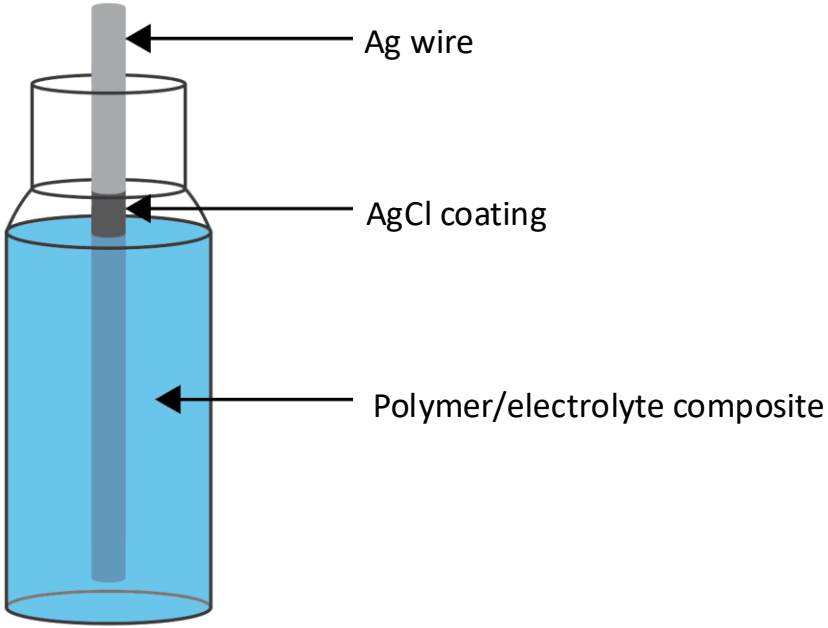
Reference electrode design

Liquid filled RE



Smith and Stevenson, Handbook of Electrochemistry (2007)

"Solid state" RE

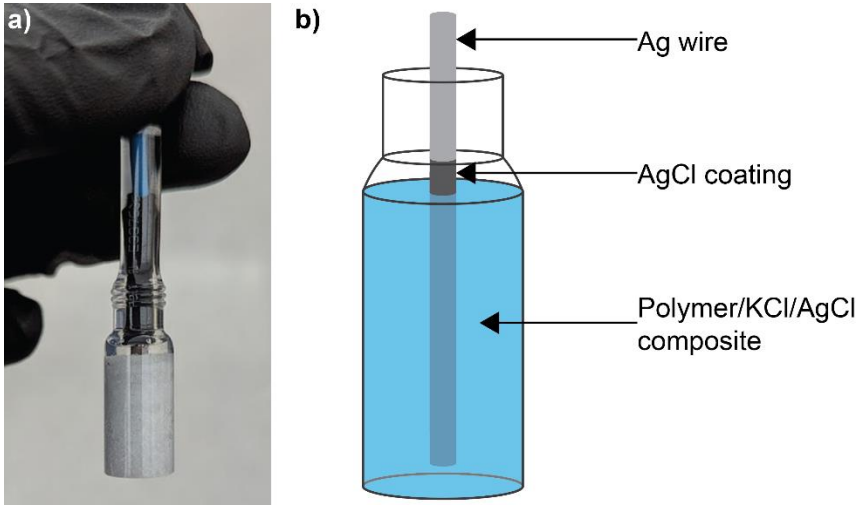


ISR trials revealed issues

- Poor polymer strength/electrolyte retention
- Poor adhesion between polymer composite and case
- Potential poisoning from sulphide species in reducing environment

First field trial prototype after one month underground

Recent reference electrode work



Patents

Solid state reference electrode
WO2018201200A1
M Vepsäläinen, C Wood, M Chen, D Acharya, D Macedo

Interference resistant reference electrode
WO2021087572A1
D Macedo, M Vepsäläinen

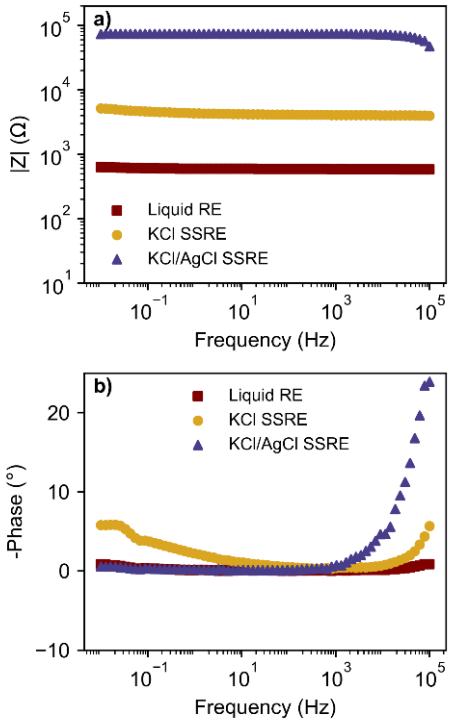
Publications

An unusually stable solid state Ag|AgCl reference electrode for long term continuous measurements based on a crosslinked poly(vinyl acetate)/KCl composite
D Macedo, M Vepsäläinen, et al. *Electrochimica Acta* (2020)

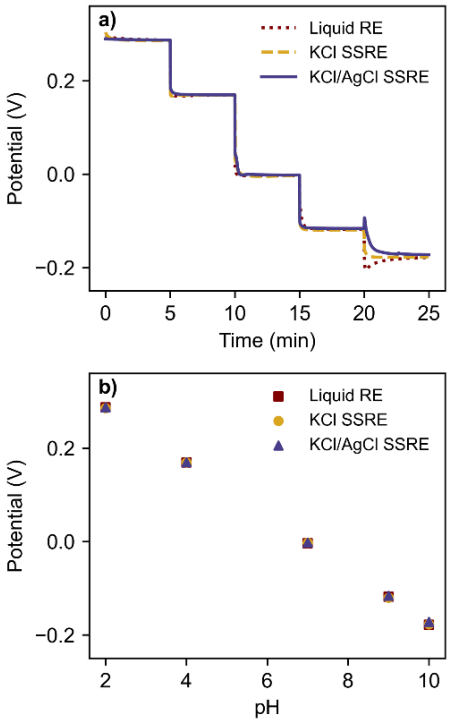
A sulphide resistant Ag|AgCl reference electrode for long-term monitoring
D Macedo, M Vepsäläinen, et al. *Analyst* (2024)

Electrochemical characterisation

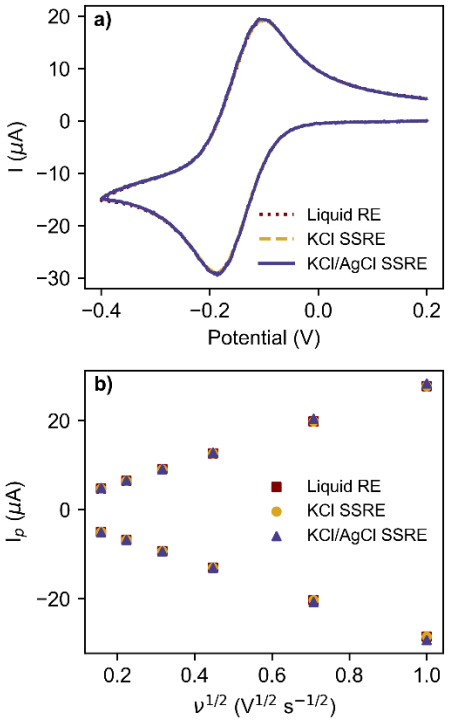
Electrochemical Impedance Spectroscopy



Potentiometric pH sensing

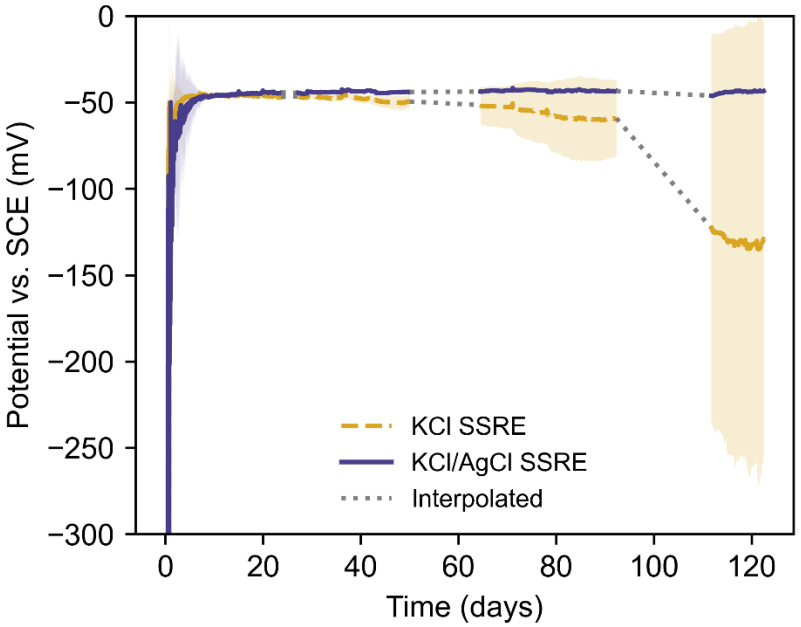


$[Ru(NH_3)_6]Cl_3$ voltammetry

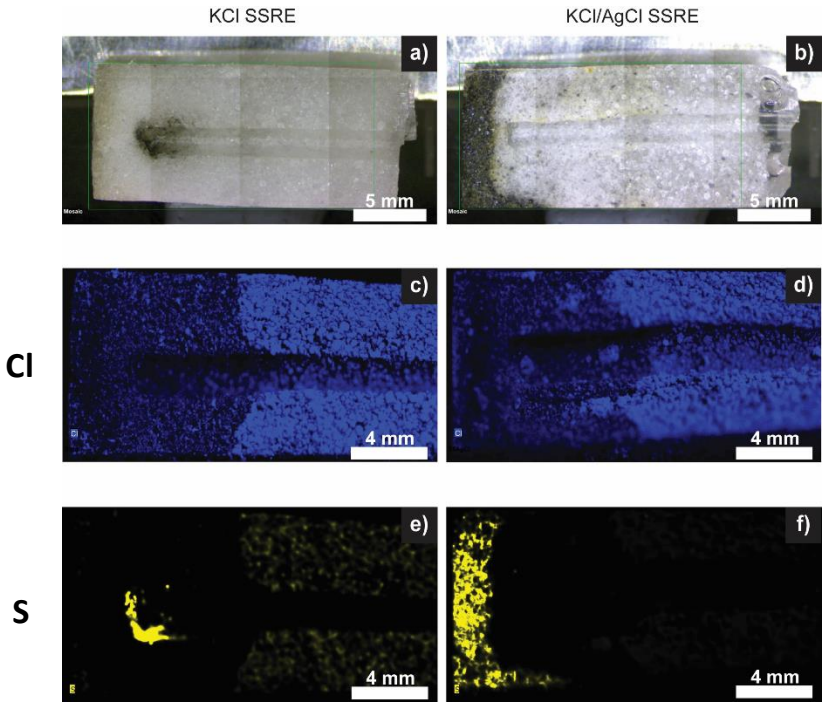


Sulphide resistance

Mean potential (n=5) in 1 g L^{-1} Na_2S



µXRF of electrode cross-sections



Revised Vesi™ prototype

Solution parameters

ORP

pH

Conductivity

Temperature

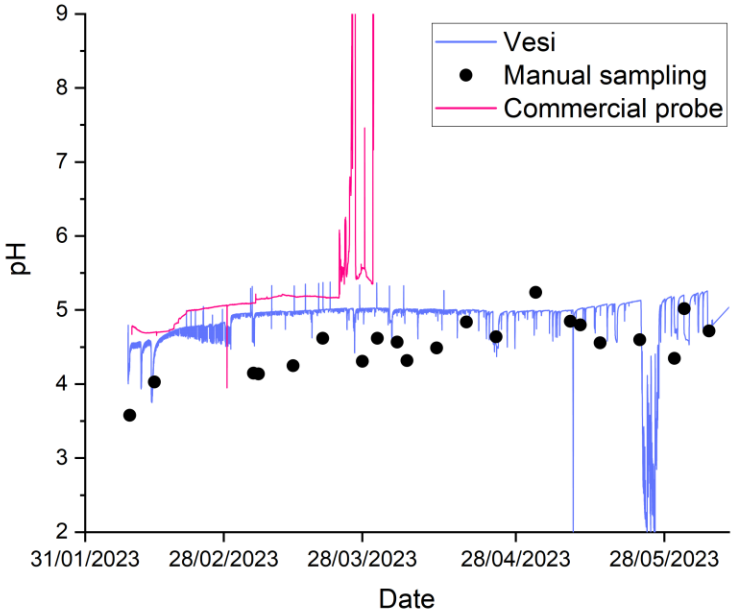
Field trials

Ground water

Surface water

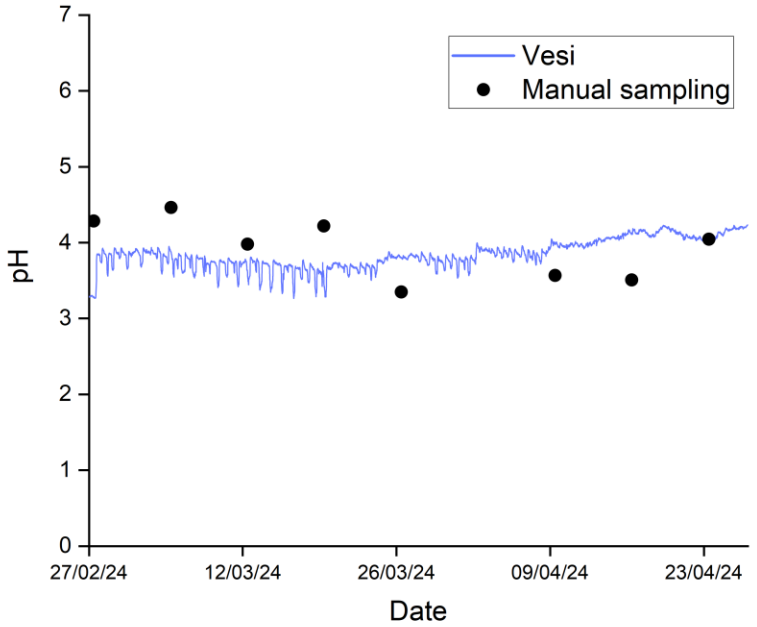
Seasonal creeks

Application in Monitoring Wells – Cu ISR



Comparison graph of VESI™ pH data compared to commercial pH probe and manual sampling

Acid mine drainage – Mt Lyell



pH measurement comparison between Vesi™ and manual sampling after ~6 months without calibration

Conclusions

- Sacrificial AgCl significantly improves RE longevity in challenging sulphide solutions
- Demonstrates a more general approach to improve reference electrode resistance to various interferant species
- Enables long-term monitoring with limited maintenance, improving feasibility of continuous monitoring

Other work

Residential waterways for water utilities

Rumen monitoring

Miniaturised modular prototype

Thank you

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