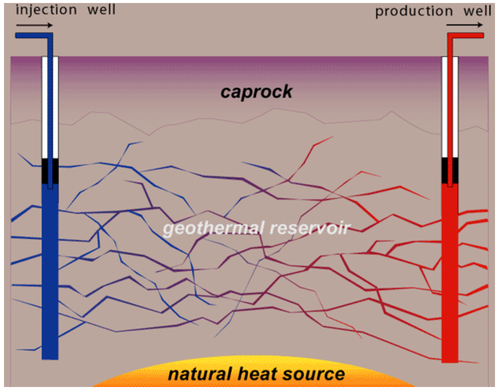

Development of a downhole tracer and pH measurement instrument for application in geothermal wells: Toward real-time chemical well logging

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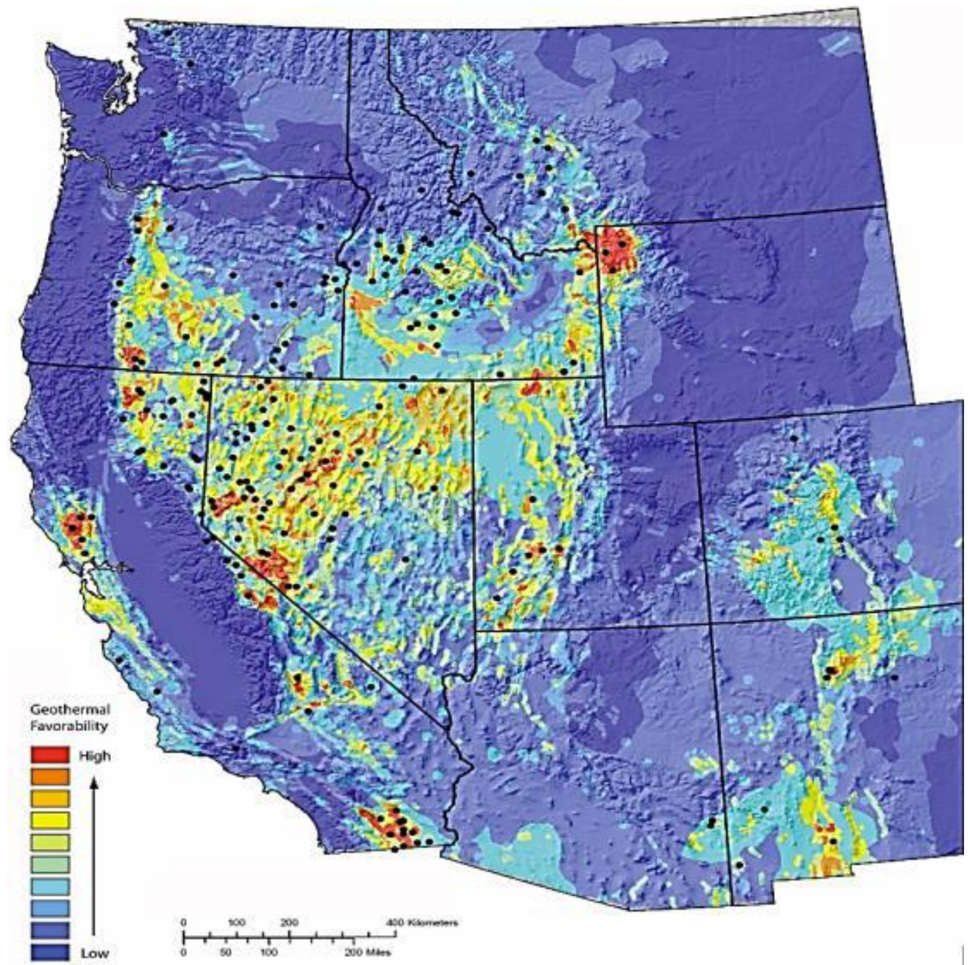
Microsystems-Enabled Detection Department

Sandia National Laboratories

Diagram from: http://egs.egi.utah.edu/images/egsmain/EGSstage3.gif

Outline

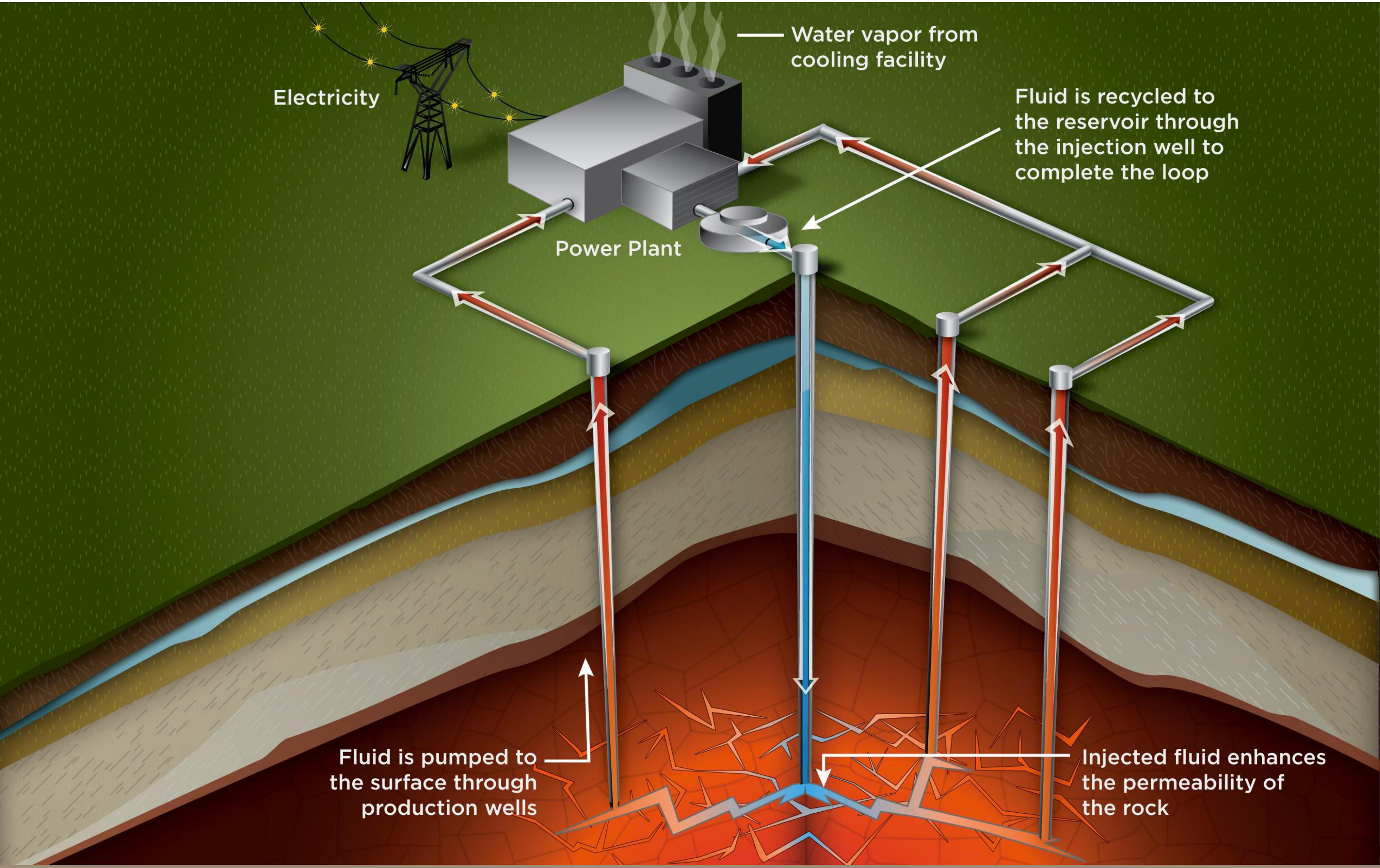
- Geothermal tracer studies
- Materials compatibility challenges
- Current downhole measurement capabilities
- Investigation into high temperature ion selective electrodes and reference electrodes



Red is hot, high geothermal potential
Blue is cold, lower potential

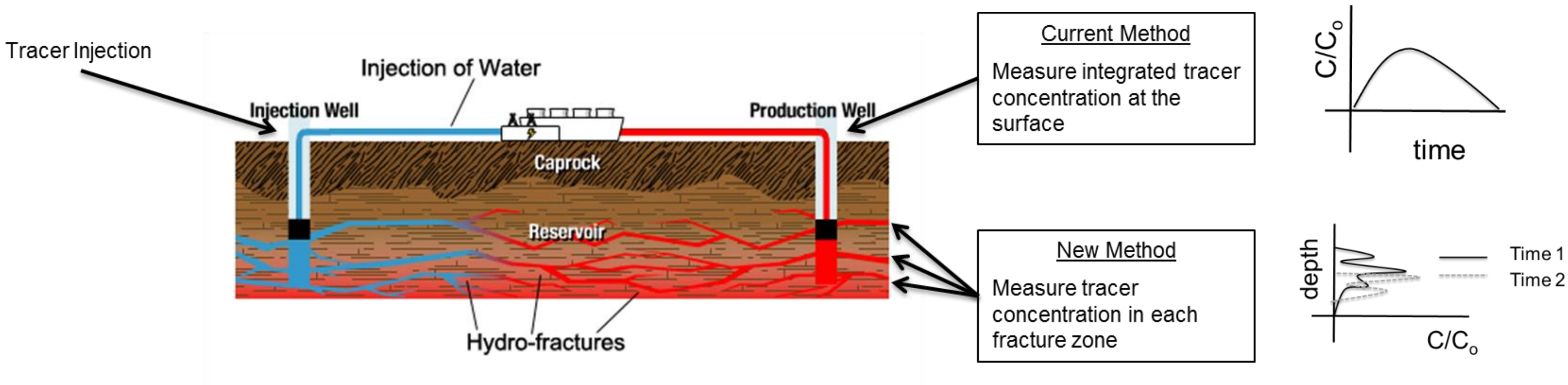
http://www1.eere.energy.gov/geothermal/presentations.html (Eric Haas, Geothermal Technology Office Review)

Enhanced Geothermal Systems (EGS)



http://www1.eere.energy.gov/geothermal/presentations.html (Eric Haas, Geothermal Technology Office Review)

Why Collect Downhole Tracer Data?



- The location of the injection well with respect to the production well is critical to the efficient operation of a geothermal power plant
- Information related to the reservoir fracture network plays a key role in planning well locations
- Tracer tests provide a great way to learn about flow patterns in the reservoir

Goals

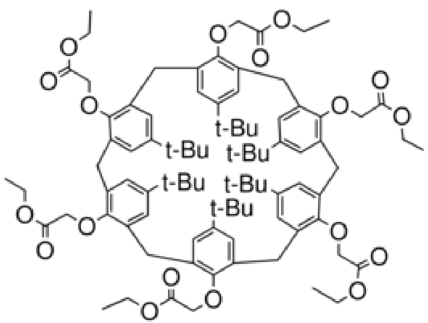
- Develop a downhole instrument that will measure tracer concentration, pH, temperature and pressure in wells up to 225 °C and 5000 psi
- Want to generate tracer concentration (and pH) versus depth and time inside geothermal wells
- Which tracers?
  - Initial goals include: **Cs^+ and I^-**
- How will it work?
  - We are developing a series of high temperature and pressure ion selective electrodes to work in conjunction with pH, T, and P probes to enable the generation of tracer concentration and pH versus depth and time

Materials Compatibility Challenges

- Brine temperatures from 100 – 350 °C
- Pressures in the 5000 psi range
- Depths in the 1000 – 10,000 ft range
- Brine pH 2 – 11, with many in the 6 – 7 range
- Well operators….

Consequences

- We can't use most organic ionophores
- Teflon will likely be too soft, need PEEK or ceramics
- Need high temperature epoxies and solder
- Have to use specialty electronics for data acquisition
  - No fun collecting data over 5,000 feet of wire….



Cs ionophore II
Sigma-aldrich

Current Downhole Diagnostics

- Nuclear well logging
- Seismic and ultrasonic analysis
- Borehole imaging
- Temperature, pressure, and flowrate

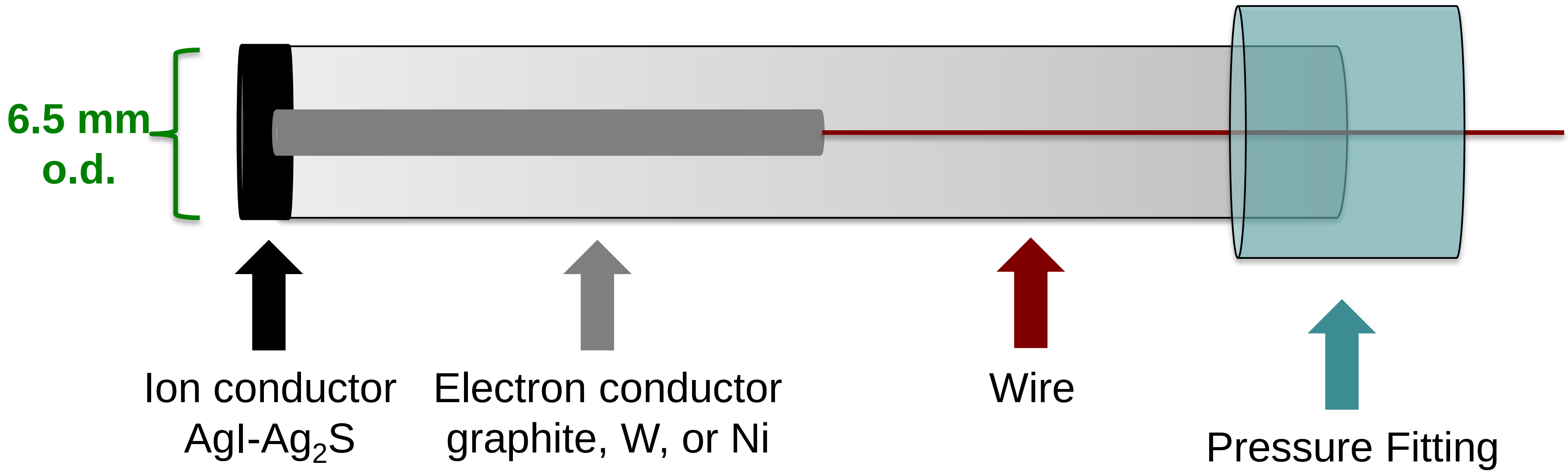
T and P Tool
240 °C unshielded
400 °C shielded

Iodide Ion Selective Electrode

- Our goal is to use an all solid state design to enable stability at temperatures greater than 100 °C
- Chose $AgI\text{-}Ag_2S$ pellet as the ion selective material
- Working on optimizing membrane dimensions

10 – 12 cm length

Currently using PTFE bodies but will shift to PEEK



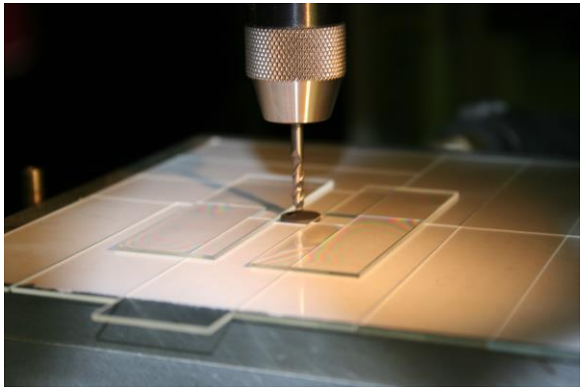
Solid State I-ISE Construction

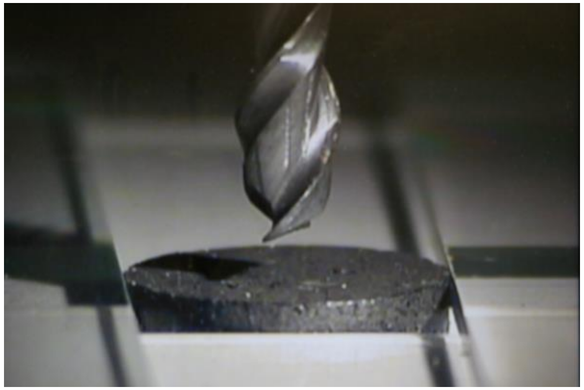
Ion selective membrane: AgI-Ag_2S (50/50), 0.5g total

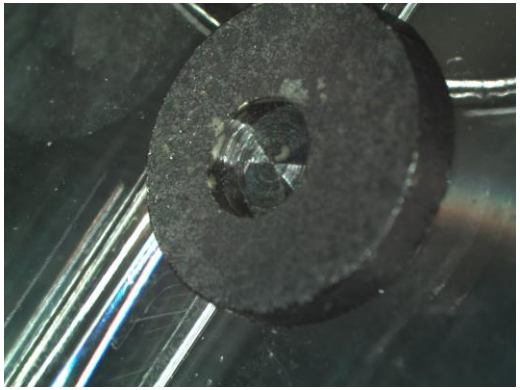
Electrode body: Teflon

Epoxy: Silver two part mix and UV curable compound

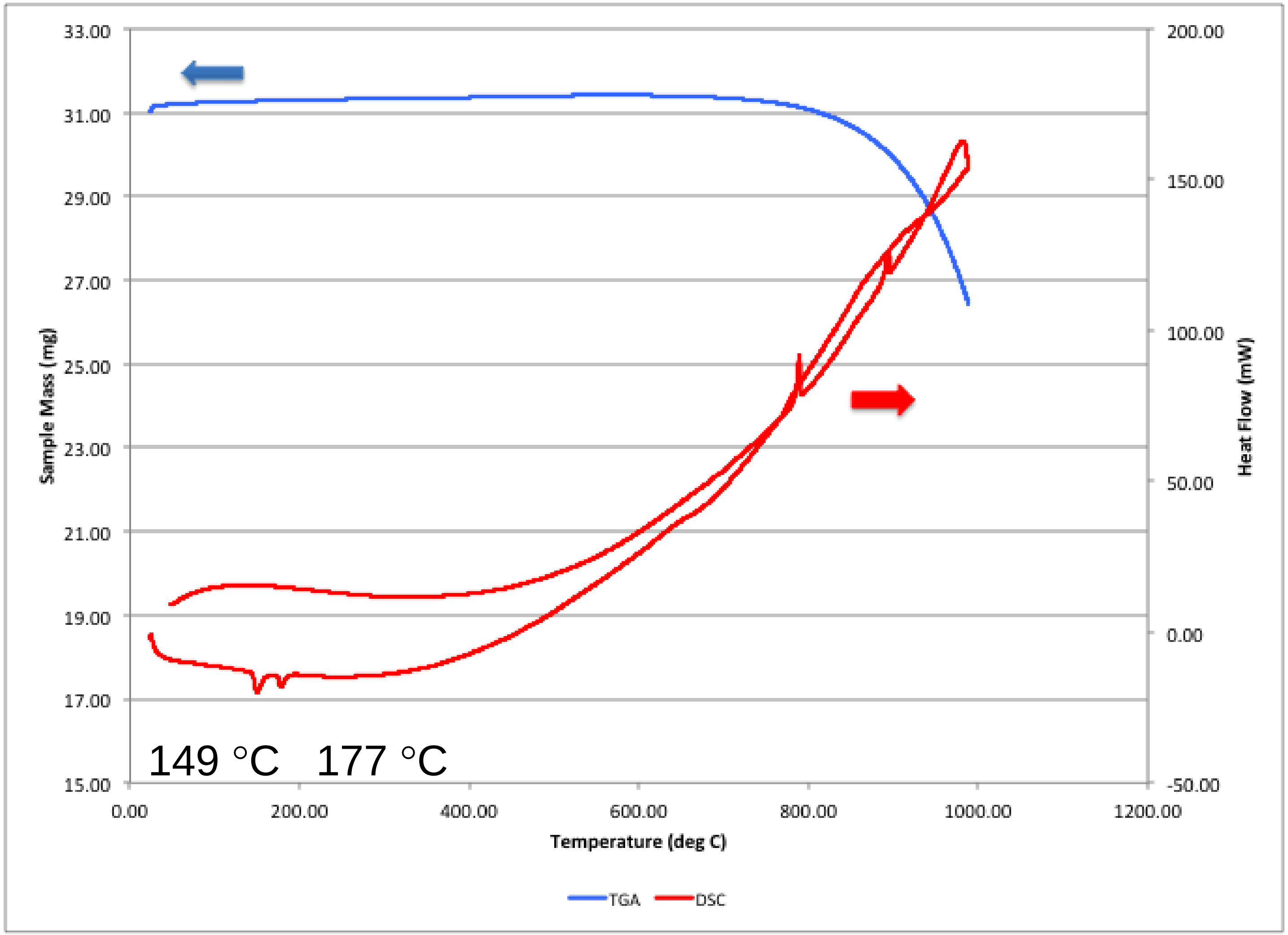
Electron Conductor: Graphite rod (3 mm diameter) to copper wire







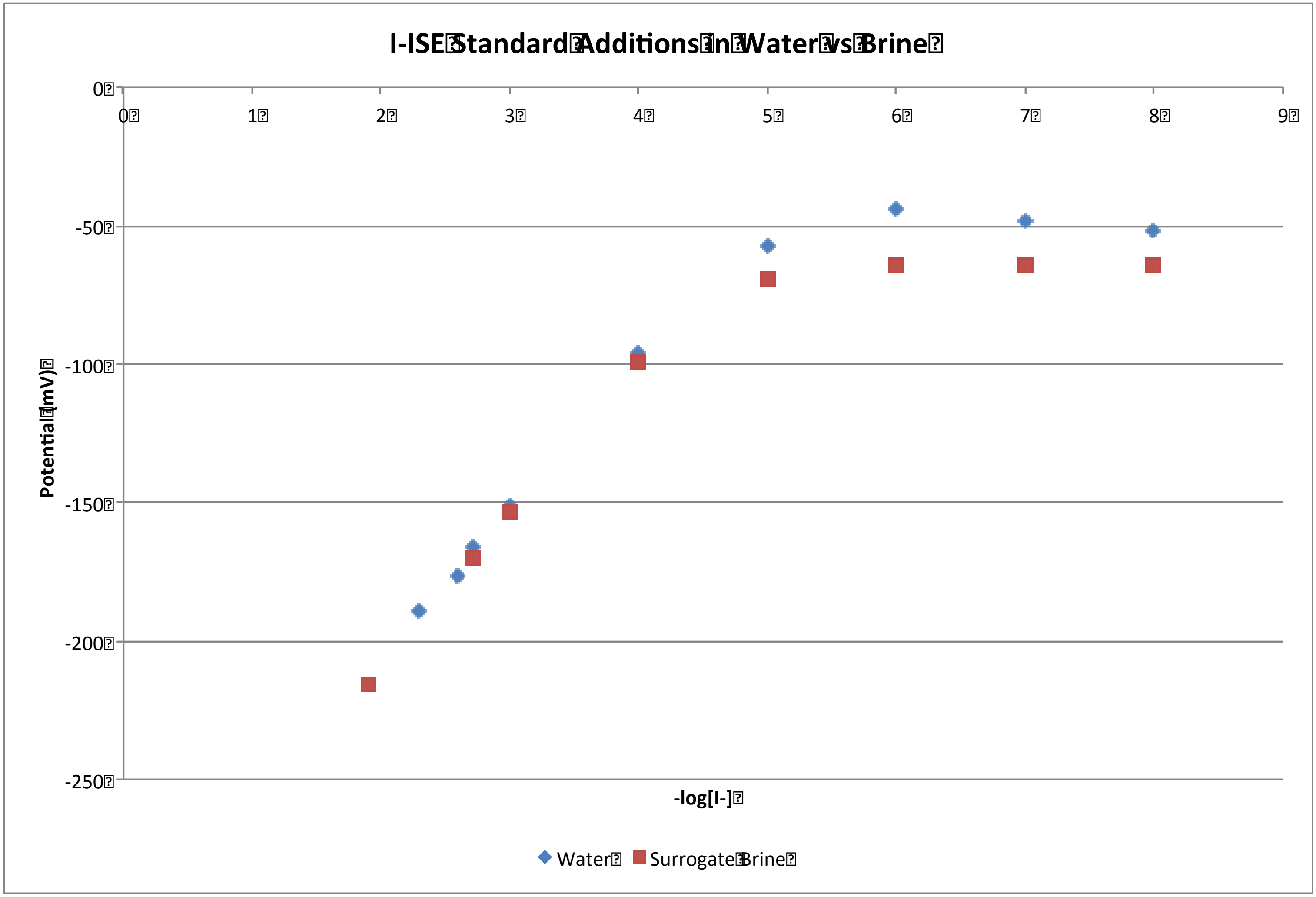
Thermal Analysis of AgI-Ag_2S



AgI polymorphs: β-phase and γ-phase (<149 °C) and α–phase (>149 °C)

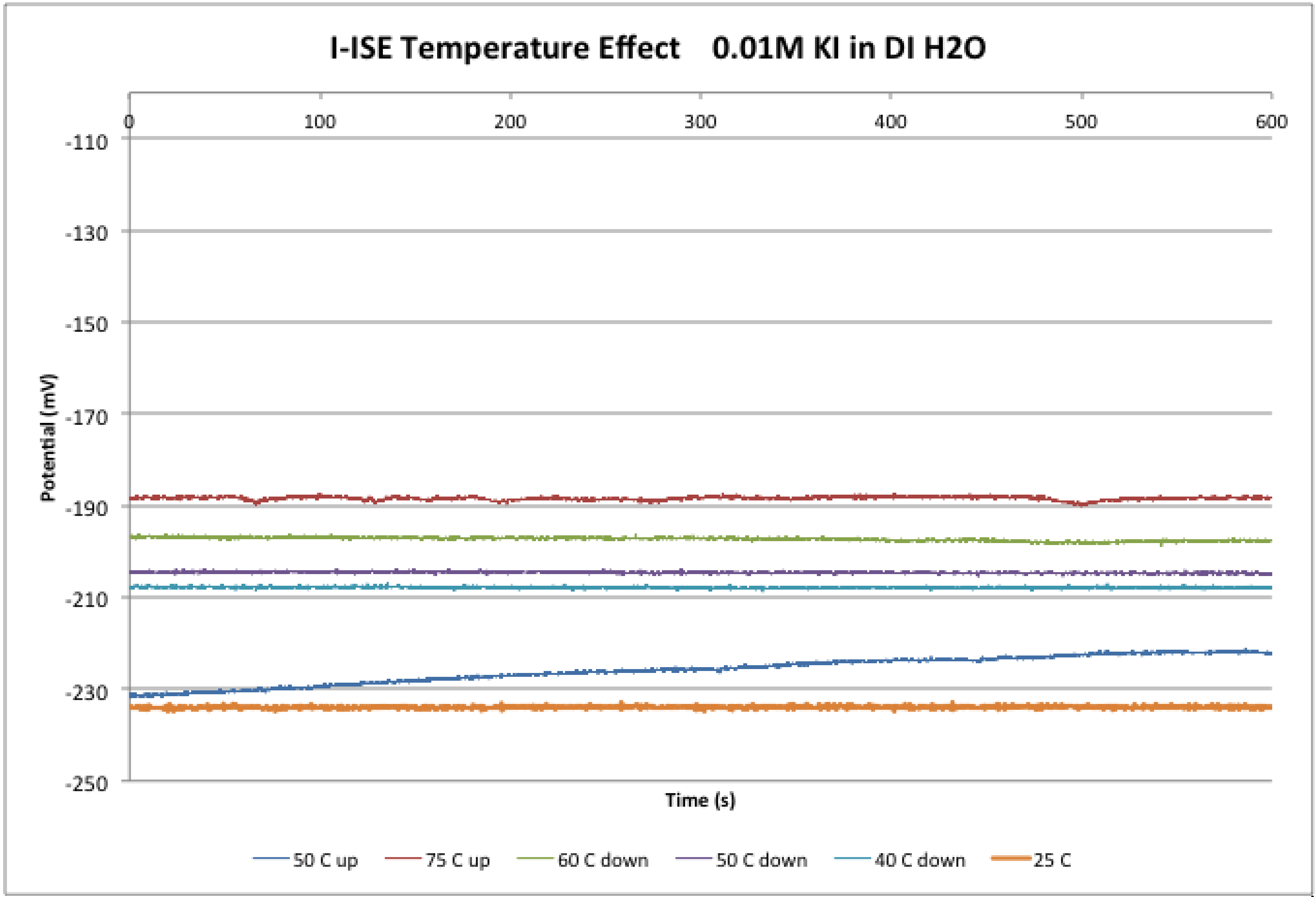
Ag_2S polymorphs: α-phase (< 179 °C) and β-phase (179 – 586 °C)

Solid State I-ISE Response



For pI 1 – 5 in water, slope of 50.0 mV/pI
For pI 1 – 5 in brine, slope of 48.0 mV/pI

I-ISE Temperature Stability



Solid State Cs-ISE Construction

- Goal was to make a Cs-12-molybdophosphate phase identified in the literature and determine if it would work at high temperature
  - Synthesis: $CsNO_3 + H_3Mo_{12}PO_{40} \rightarrow Cs_3Mo_{12}PO_{40} + 3\ HNO_3$
  - C.J. Coetzee; A.J. Basson; *Anal. Chim. Acta;* 56, (1971), 321-324.

- Options for the electrode include pellets and coatings
  - Tried pressing pellets without using any binder with no success
  - We have been making membranes using a procedure developed by Arida's group at the Egyptian Atomic Energy Authority

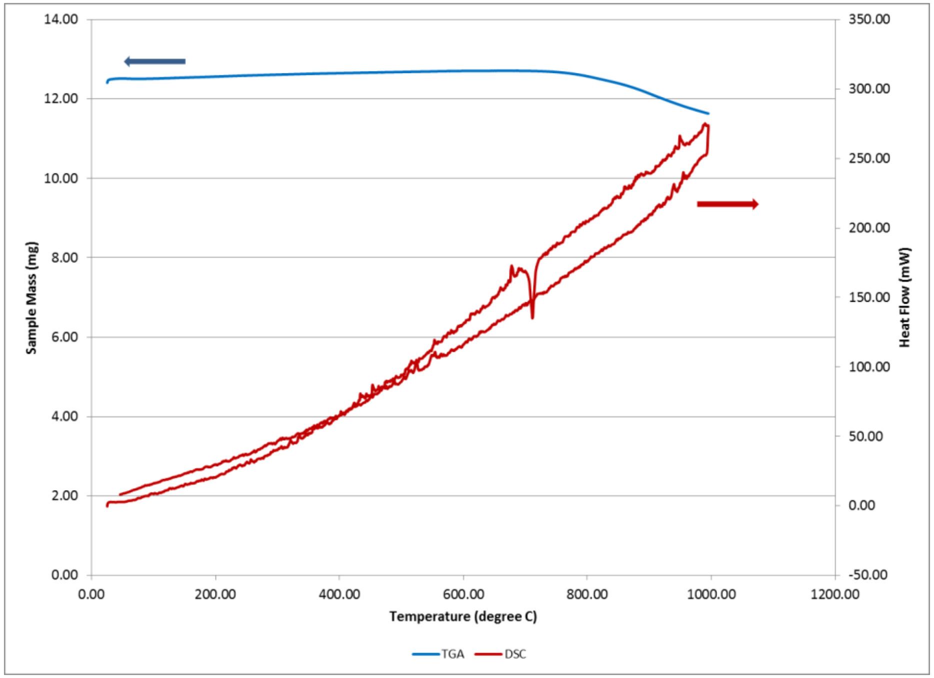
- 10 mg Cs-12-MPO + 350 mg dibutylphthalate + 190 mg PVC in 6 mL THF
  - Makes a yellow membrane when cast or dip coated onto a rod
  - Made thin disks that withstand brine at 120 °C in an autoclave
  - Made electrodes using graphite rods and a tungsten rods. These were then loaded into a Teflon body and connected via Ni wires.

H.A. Arida, R.F. Aglan, S.A. El-Reefy; Analytical Letters; V37, no1, (2004), 21-33.

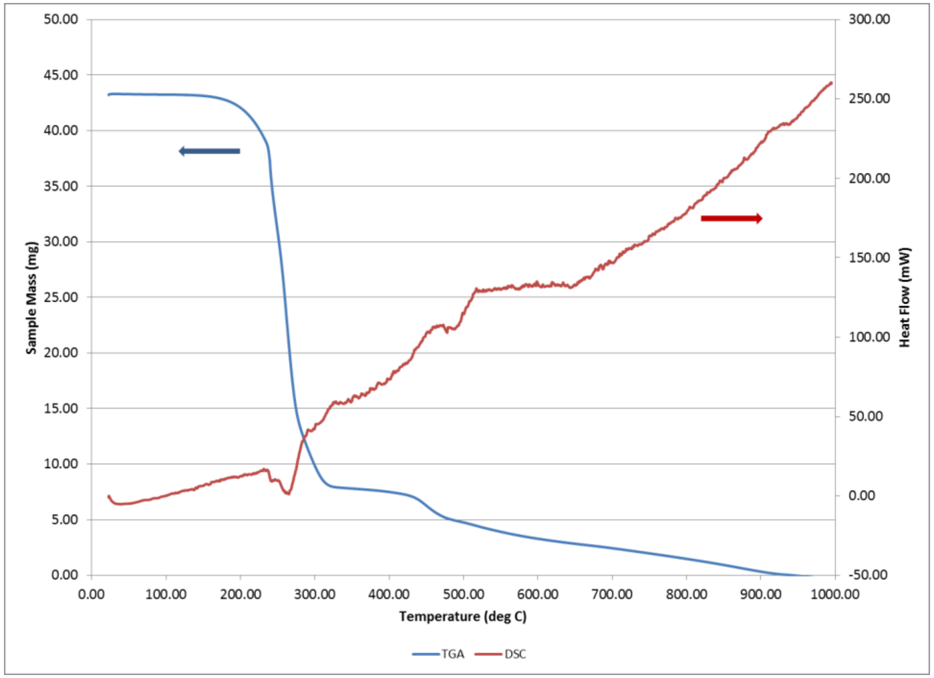
Cs-ISE Material: Thermal Stability

Sandia National Laboratories

Selective Material:
Nominally $Cs_3PMo_{12}O_{40}$

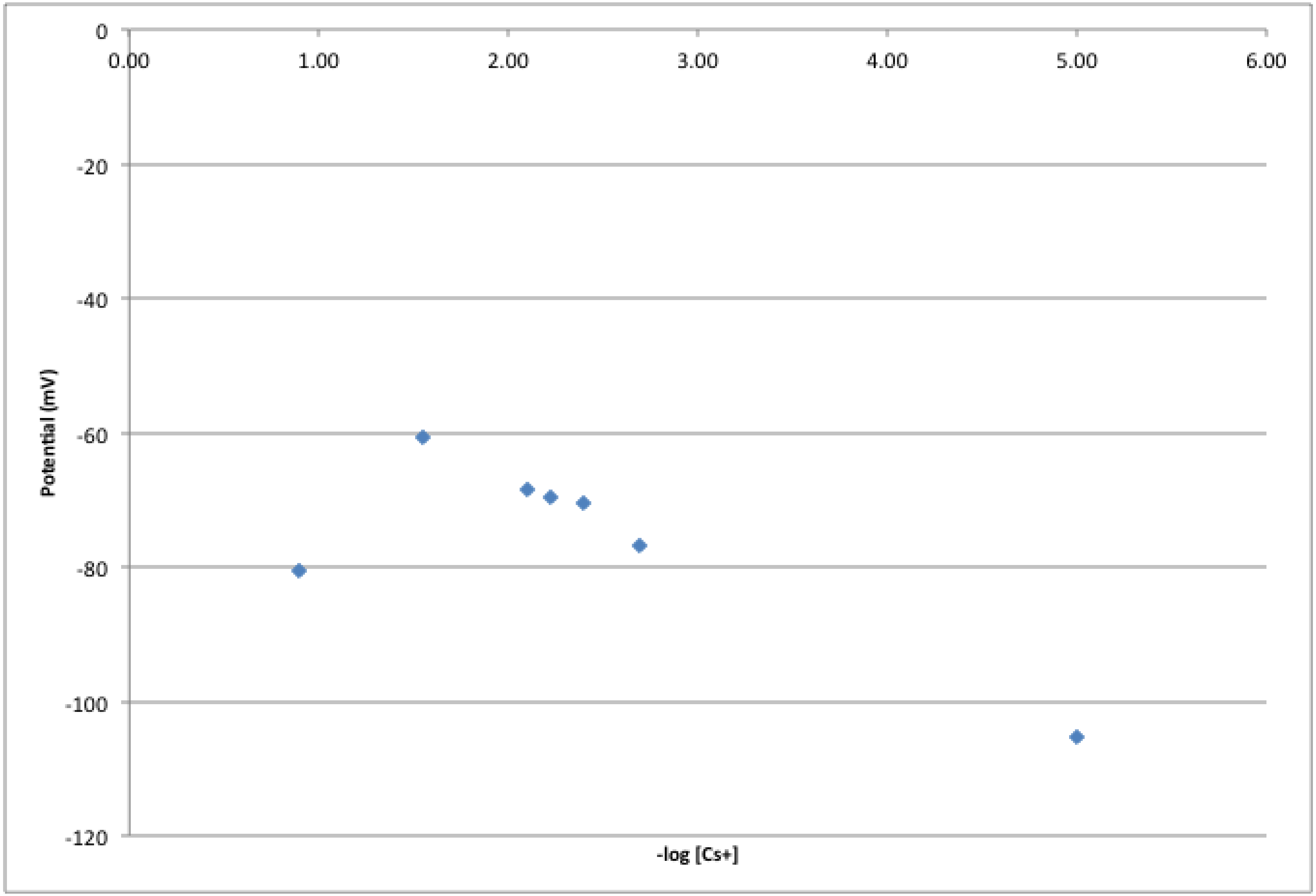


Electrode Membrane:
$Cs_3PMo_{12}O_{40}$ – dibutylphthalate-PVC



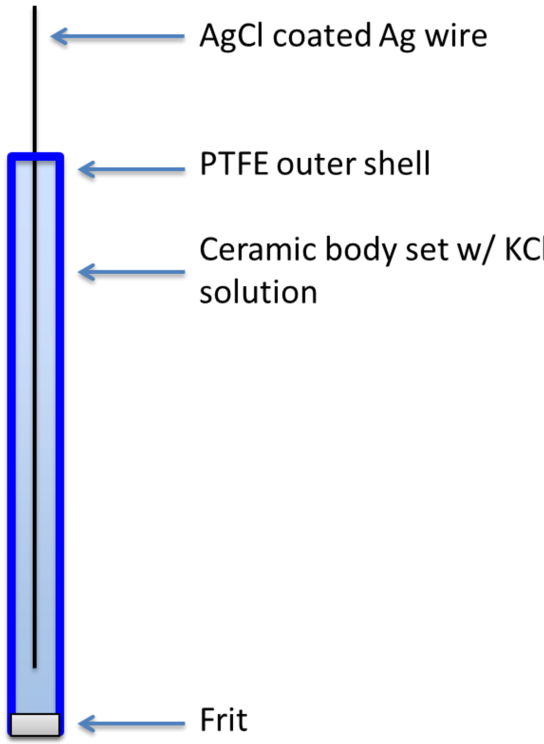
The selective material is stable to > 225 °C but the membrane is only stable to 150 °C

Solid State Cs-ISE Response in Water

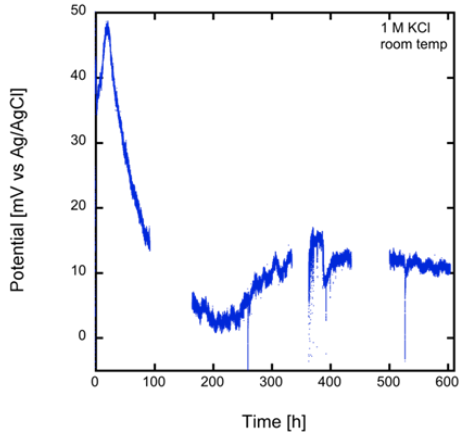


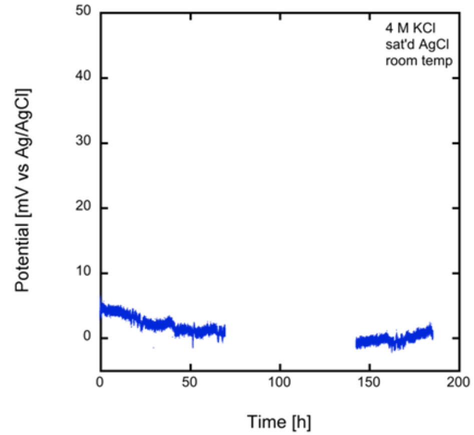
New High Temperature Reference Electrode

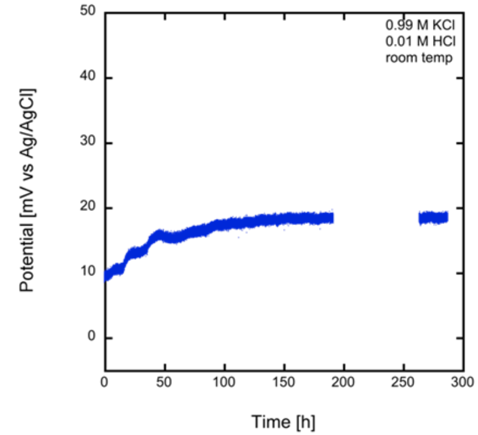
- Given the high pressure and temperature found in geothermal wells we want to avoid liquid based electrodes
- Using epoxies at high temperatures is tricky as well
- Found that an alumina potting compound works at these high temperatures



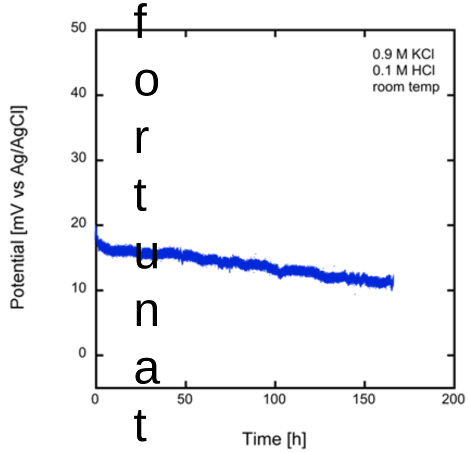
Reference Electrode Data

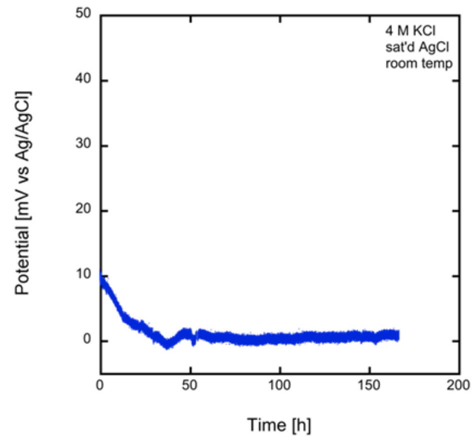


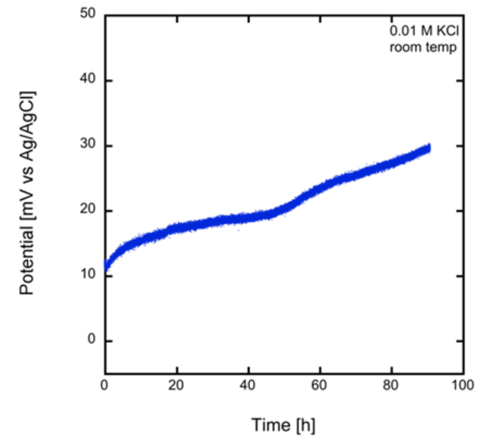




Unfortunately







Summary

- We have developed a series of iodide and cesium solid state ion selective electrodes that should be stable at 225 °C and 5000 psi
  - I-ISE data at 70 °C shows good stability, waiting on high temperature autoclave to arrive

- Demonstrated construction of a solid state reference electrode that is relatively stable to at least 90 °C without using epoxies that run and outgas

- Future work:
  - testing at high temperature and pressure in an autoclave
  - looking at the effect of a conducting polymer (PEDOT:PSS) transducer layer
  - building high temperature pH electrodes – similar to the designs used by Niedrach and co-workers in the 1980s YSZ and metal/metal oxides

L.W. Niedrach; et. al; *J. Electrochem. Soc.;* V127, (1980); 2122

Acknowledgements

- Scott Lindblom (PI) – high temperature electronics
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