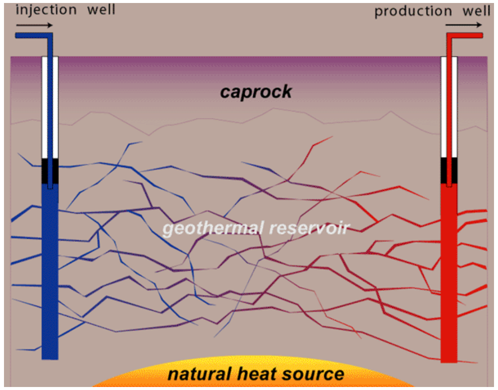
SAND2014-2114C

Exceptional service in the national interest

Sandia National Laboratories



Development of a downhole instrument for measuring real-time concentration of ionic species in geothermal wells

Ryan Hess, G. Cieslewski, T. Boyle, W.G. Yelton, S.J. Limmer, S. Lindblom, G. Stillman, S.P. Bingham

Microsystems-Enabled Detection Department

Sandia National Laboratories

U.S. DEPARTMENT OF ENERGY

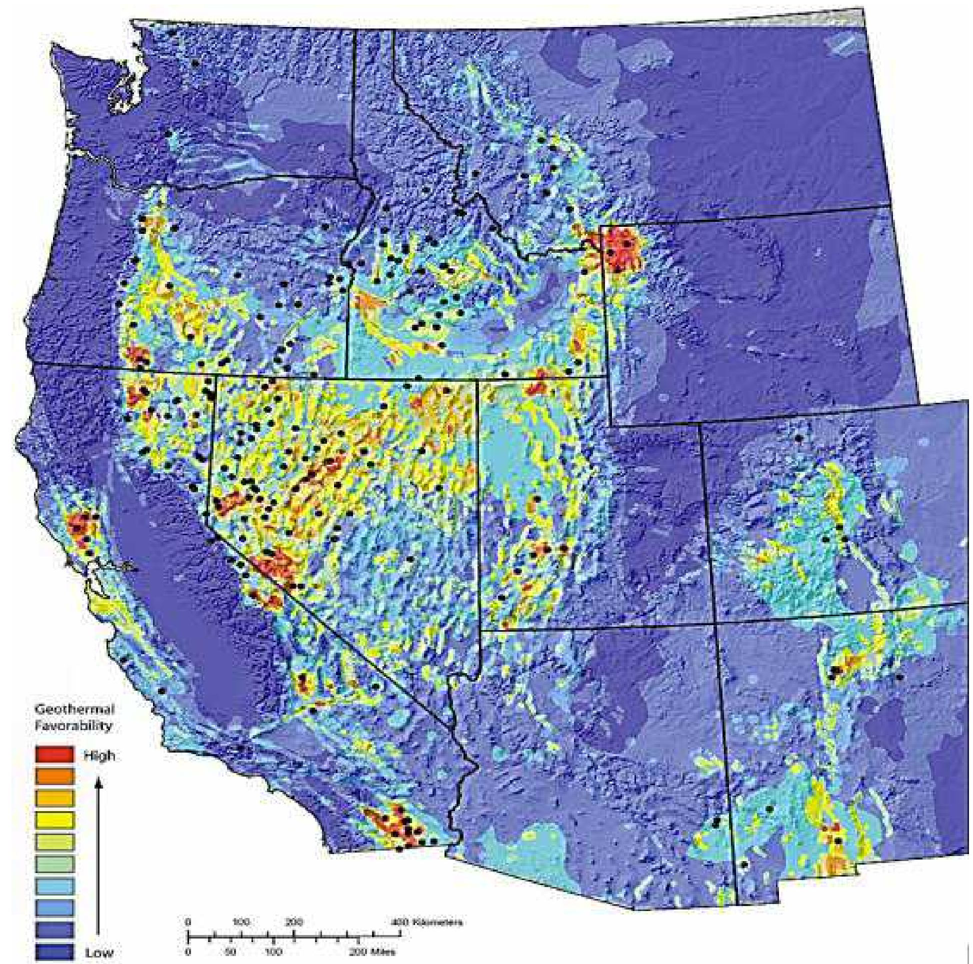
NNSA National Nuclear Security Administration

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

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

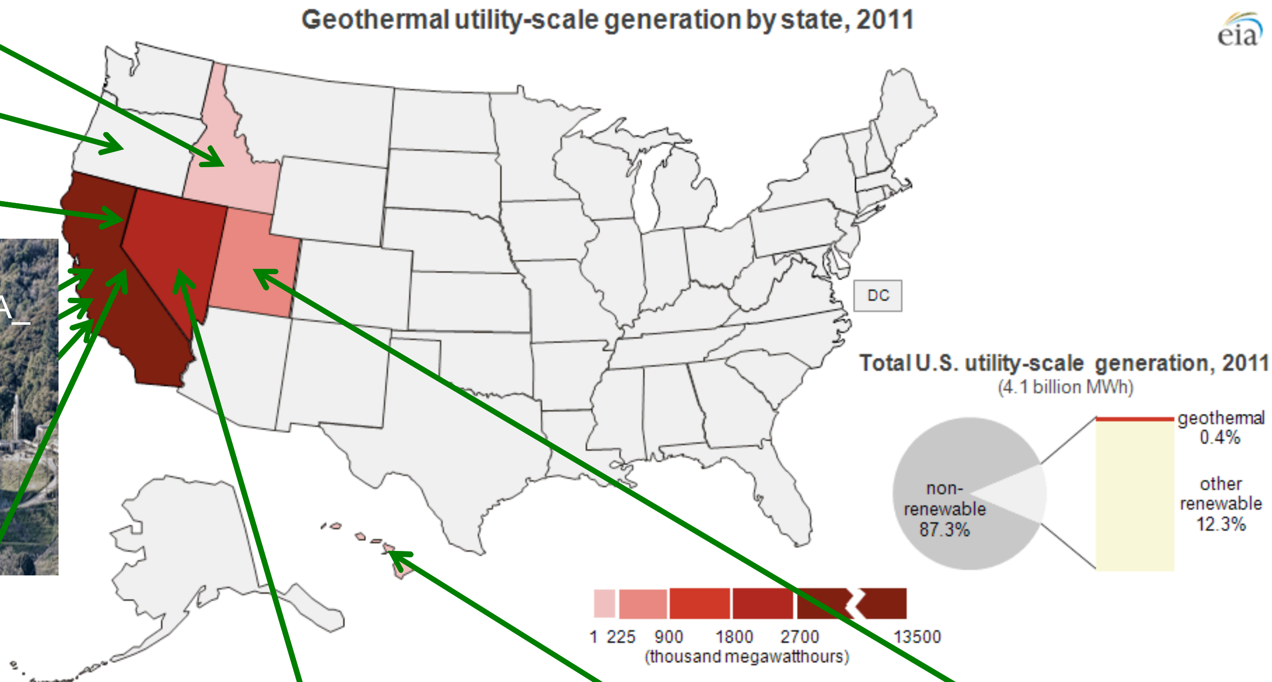
Outline

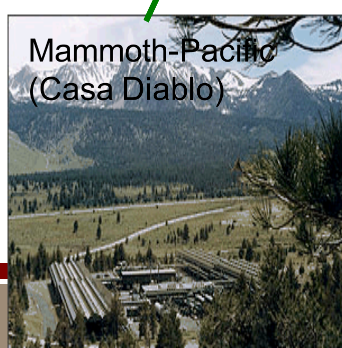
- Geothermal tracer studies
- Materials compatibility challenges
- Current downhole measurement capabilities
- Investigation into high temperature ion selective electrodes and reference electrodes

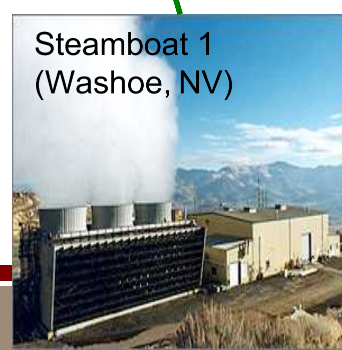


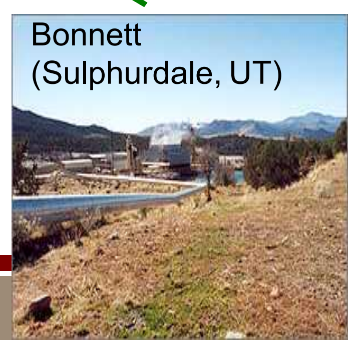
Red is hot, high geothermal potential
Blue is cold, lower potential

Geothermal Power in the US

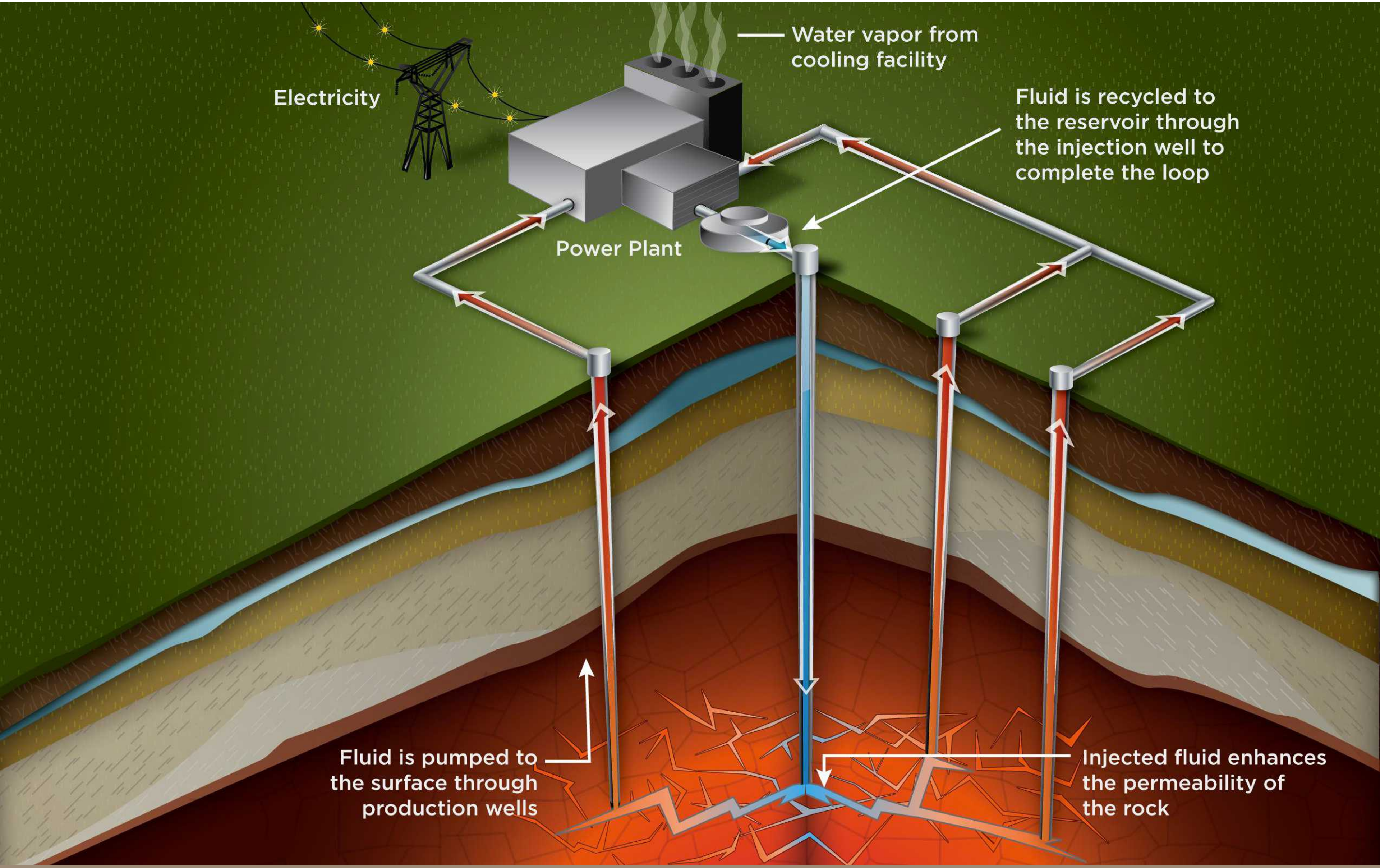






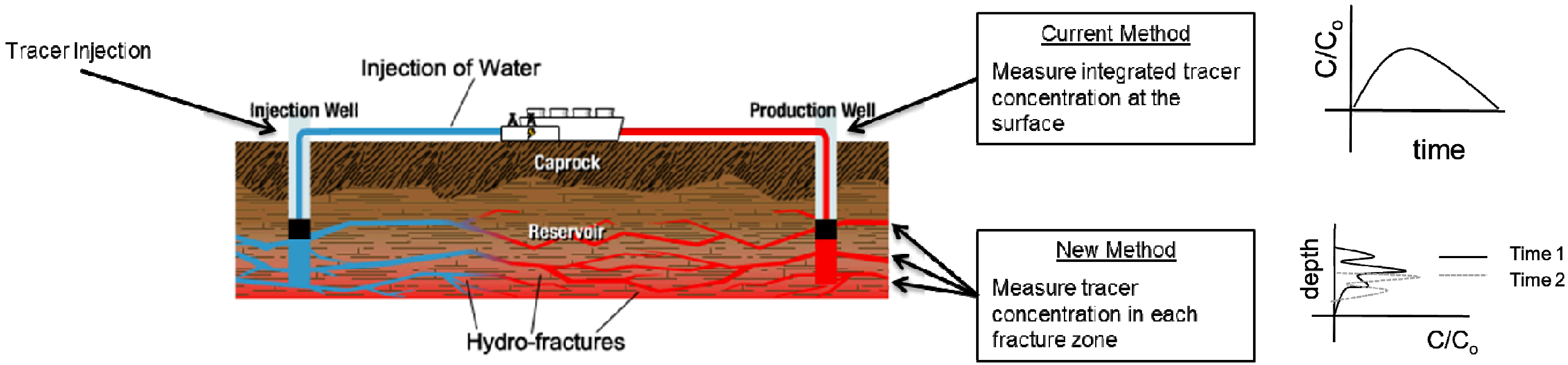


Enhanced Geothermal Systems (EGS)



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

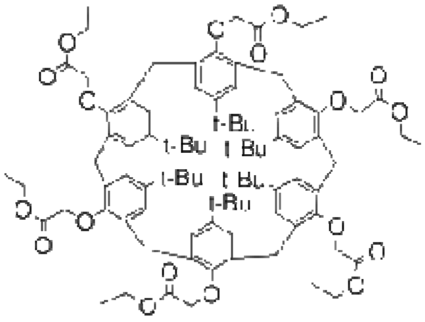
- Develop a downhole instrument that will measure tracer concentration, pH, temperature and pressure in wells up to 225 °C and 5000 psi
- Want to generate tracer concentration (and pH) versus depth and time inside geothermal wells
- Which tracers?
  - Initial goals include: **Li^{+} Cs^{+} F^{-} I^{-}**
- 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

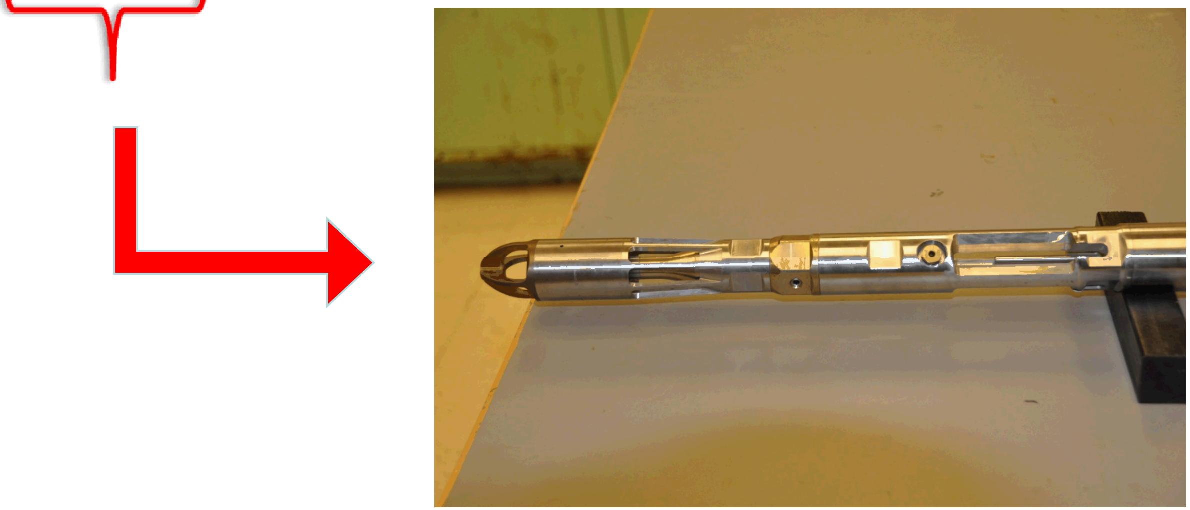
- We can't use most organic ionophores
- Teflon will likely be too soft, need PEEK or ceramics
- Need high temperature epoxies and solder
- Have to use specialty electronics for data acquisition
  - No fun collecting data over 5,000 feet of wire….



Cs ionophore II
Sigma-aldrich

Current Downhole Diagnostics

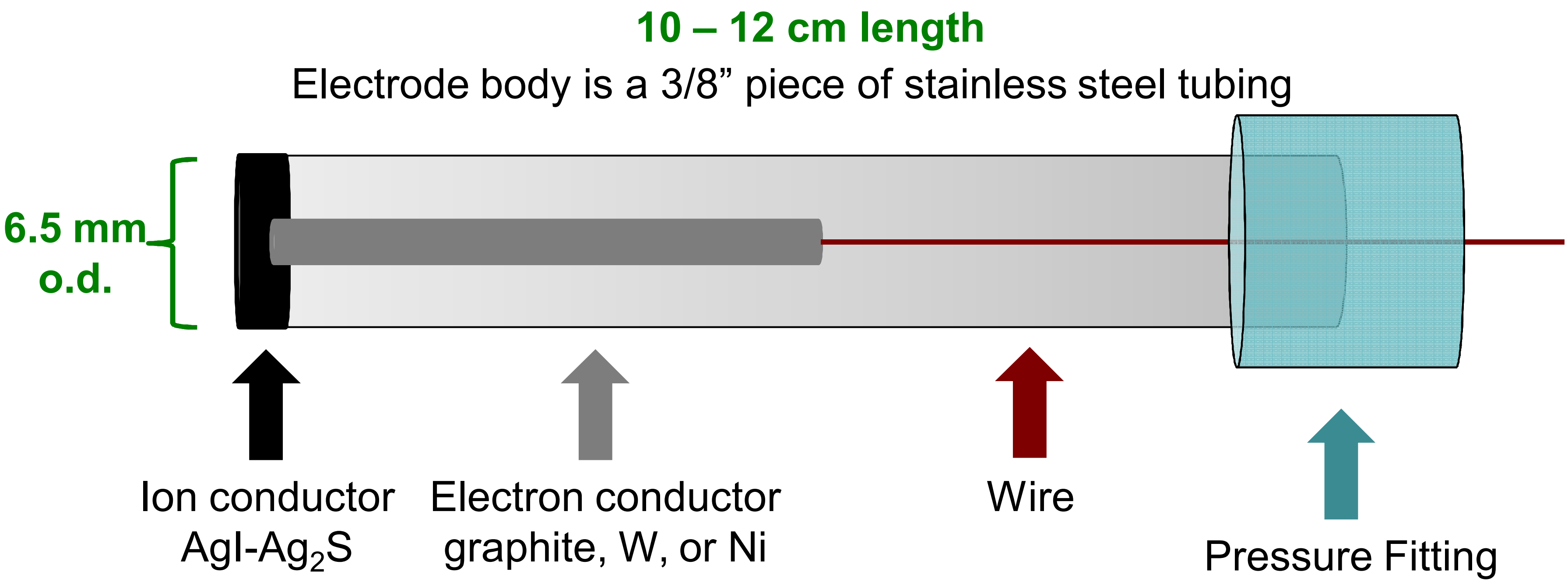
- Nuclear well logging
- Seismic and ultrasonic analysis
- Borehole imaging
- Temperature, pressure, and flowrate



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-Ag_2S pellet as the ion selective material
- Working on optimizing membrane dimensions



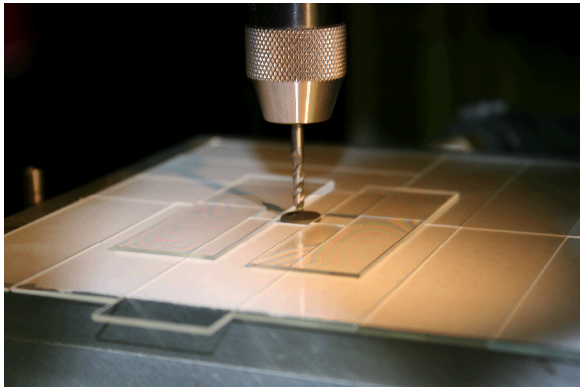
Solid State I-ISE Construction

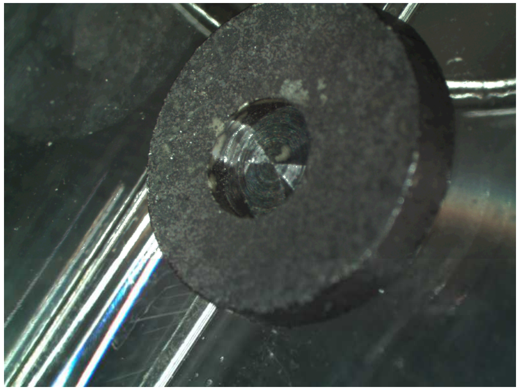
Ion selective membrane: AgI-Ag_2S (50/50), 0.5g total

Electrode body: Stainless steel

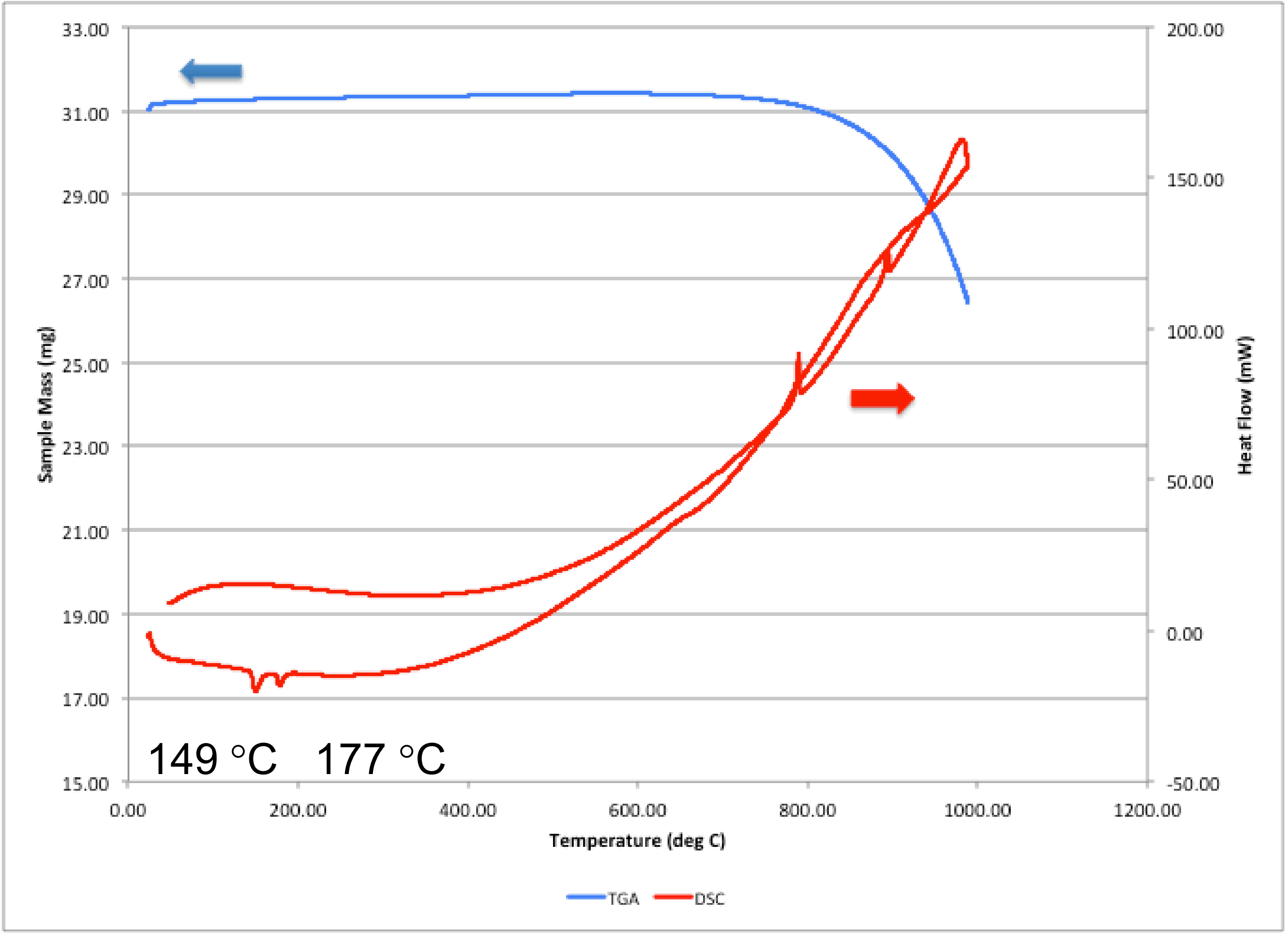
Epoxy: Silver two part mix and high temperature ceramic adhesive

Electron Conductor: Nickel rod (3 mm diameter) to nickel wire





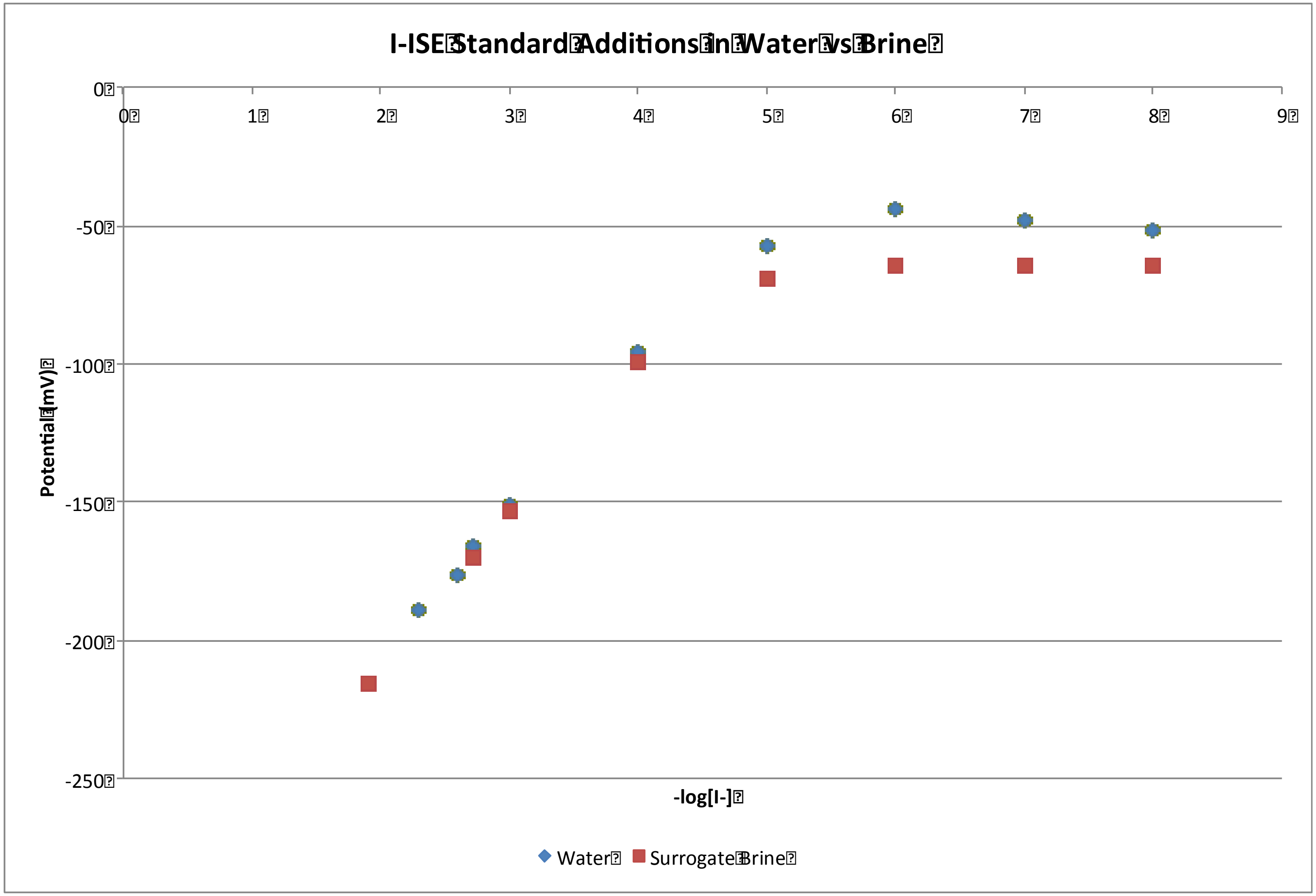
Thermal Analysis of AgI-Ag_2S



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

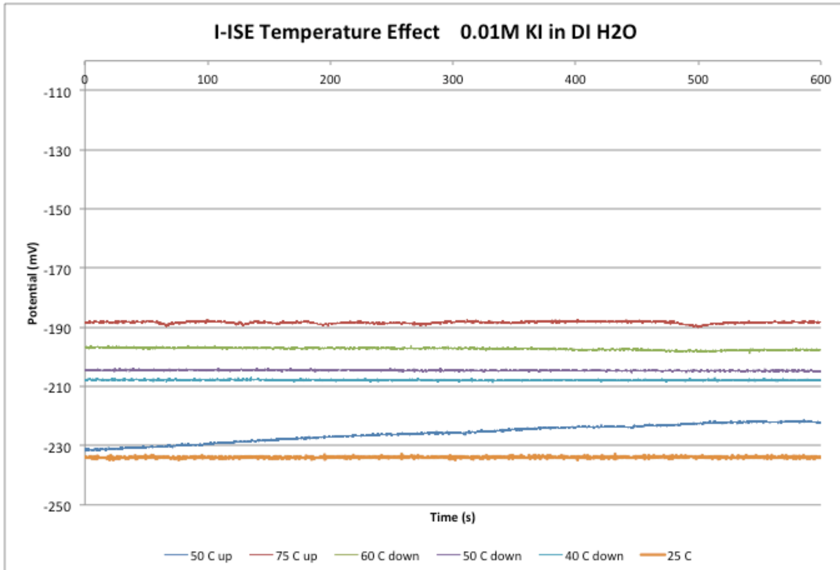
Ag_2S polymorphs: α-phase (< 179 °C) and β-phase (179 – 586 °C)

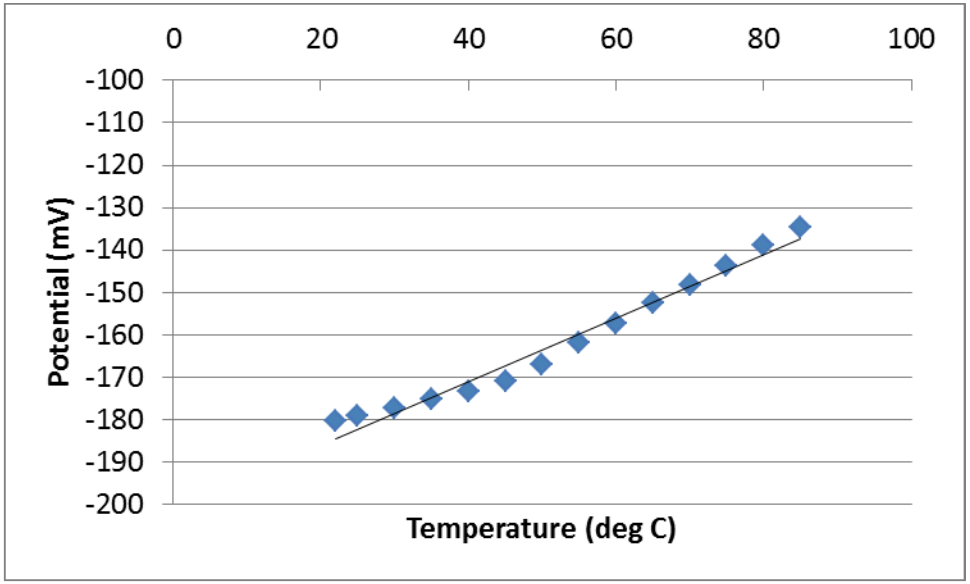
Solid State I-ISE Response



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





0.001M KI in DI water
+44.6mV over 60°C increase

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.

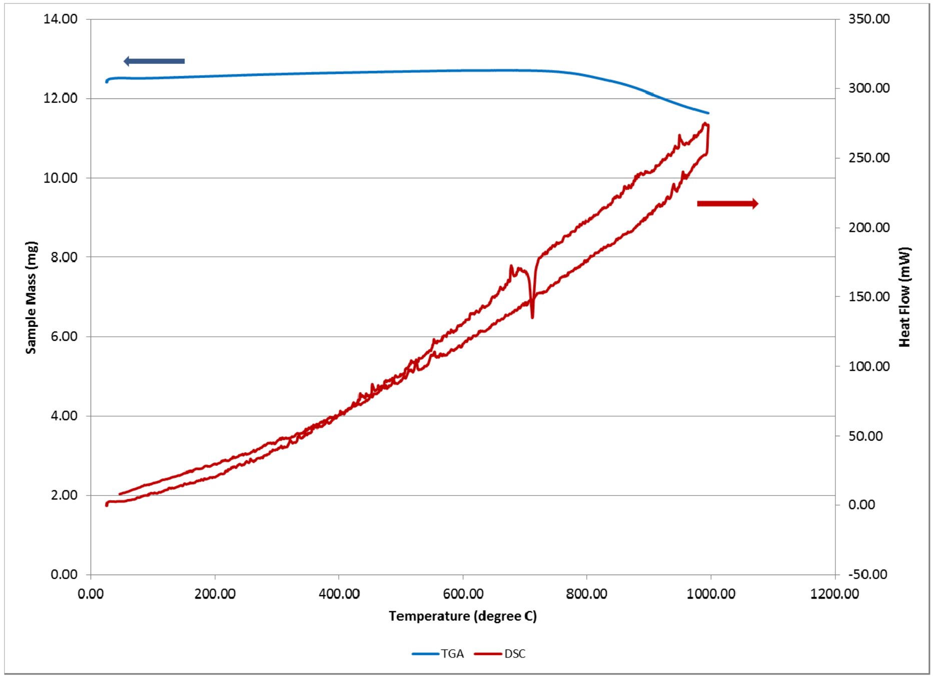
- Options for the ion selective membrane include pellets and coatings
  - Tried pressing pellets with and without using any binder with no success
  - We have been making membranes using a procedure developed by Arida's group at the Egyptian Atomic Energy Authority

- 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.

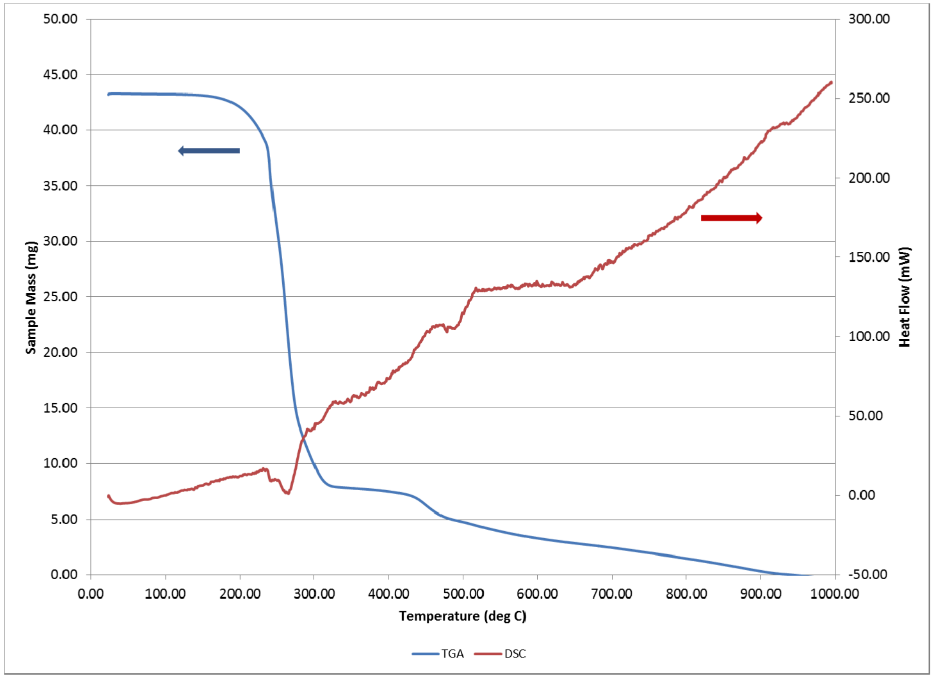
H.A. Arida, R.F. Aglan, S.A. El-Reefy; Analytical Letters; V37, no1, (2004), 21-33.

Cs-ISE Material: Thermal Stability

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

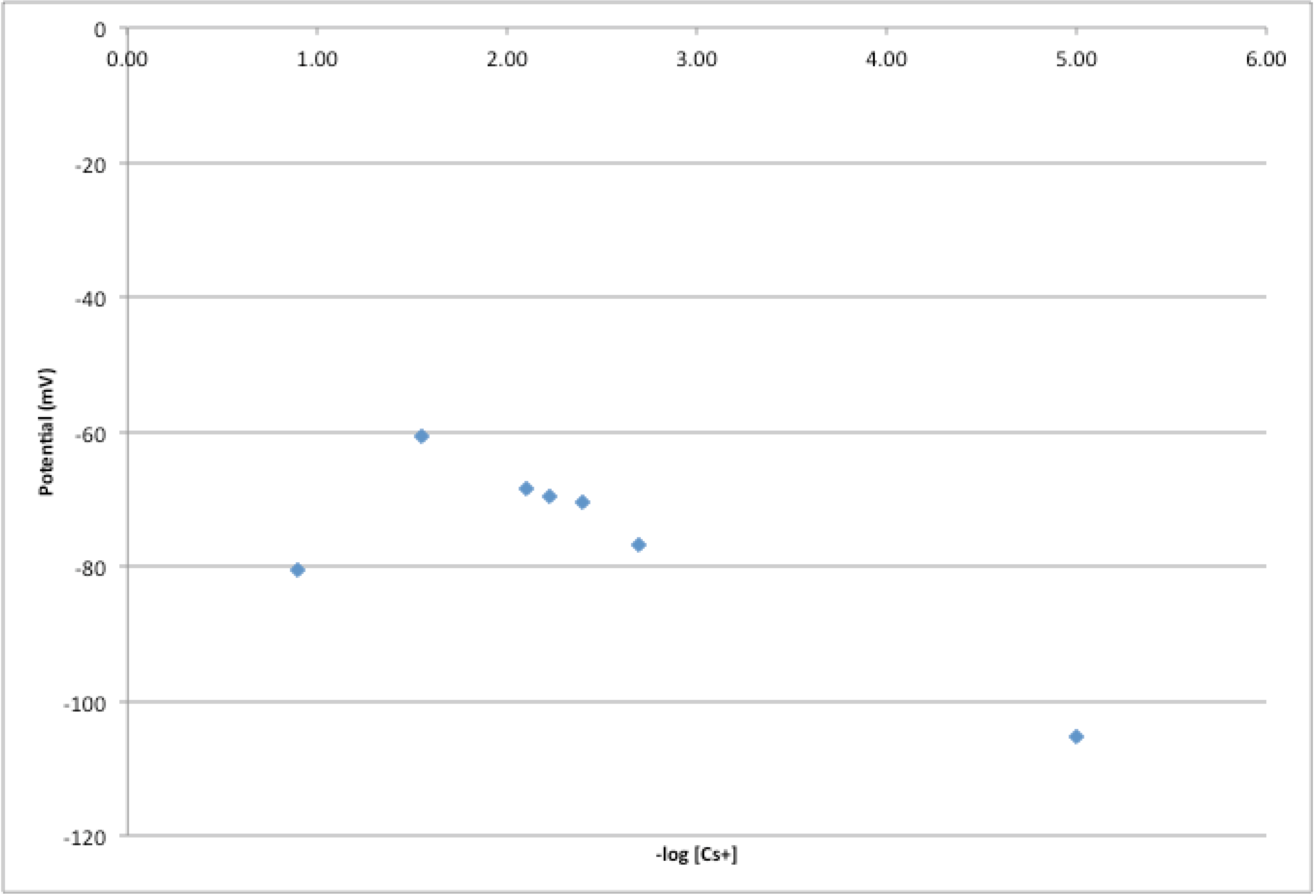


Electrode Membrane:
$Cs_3PMo_{12}O_{40}$ – dibutylphthalate-PVC



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

Solid State Cs-ISE Response in Water

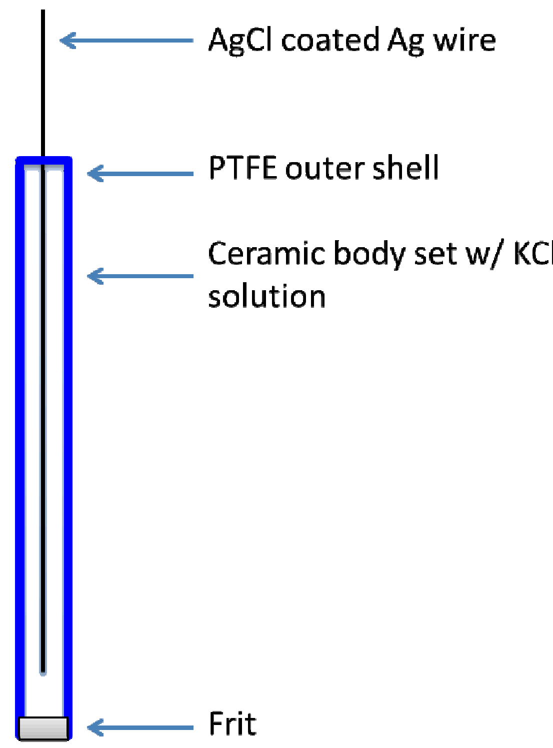


New High Temperature Reference Electrode

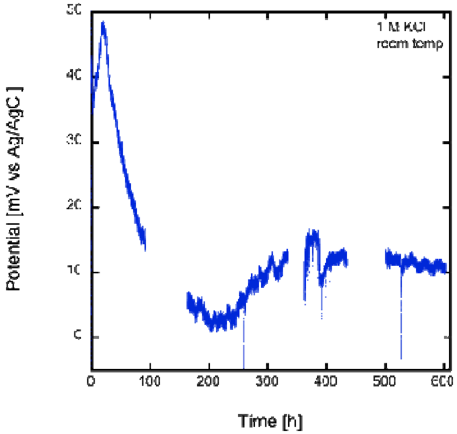
- Given the high pressure and temperature found in geothermal wells we want to avoid liquid based electrodes

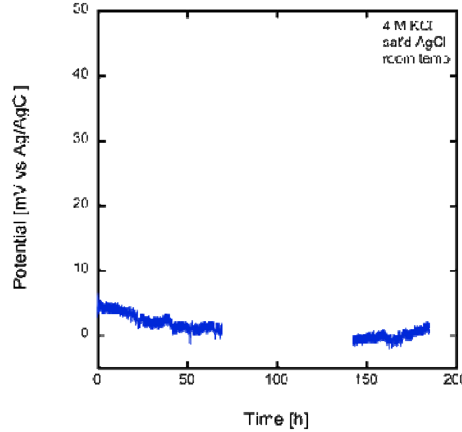
- Using epoxies at high temperatures is tricky as well

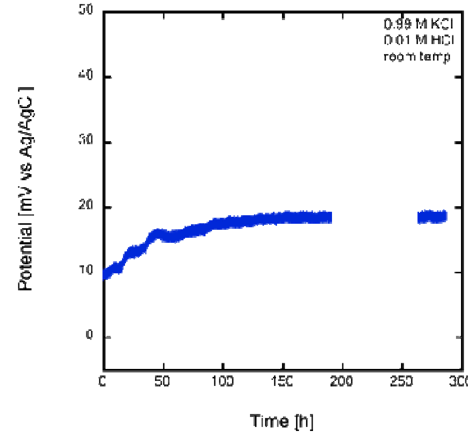
- Found that an alumina potting compound works at these high temperatures



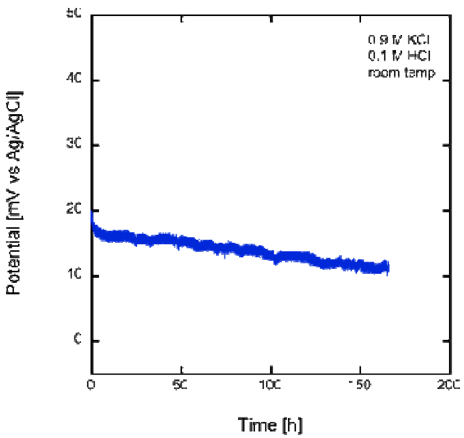
Reference Electrode Data

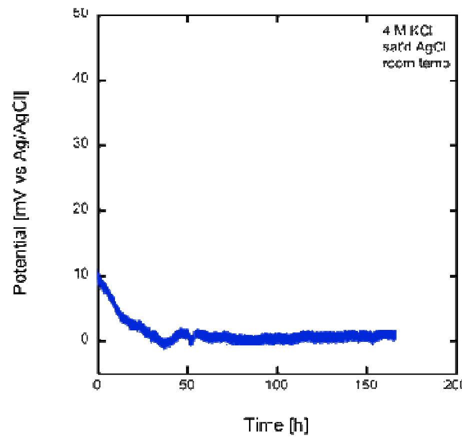


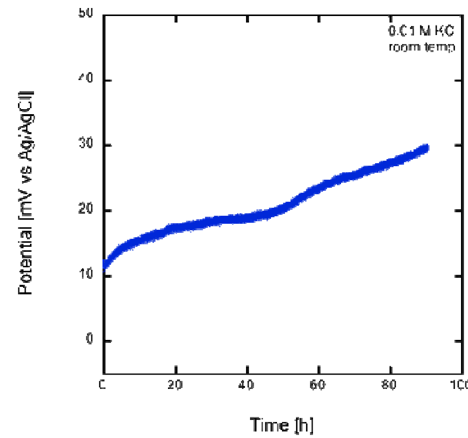




Unfortunately, we still have a weak [Cl$^-$] and pH dependence…







High Temperature pH Electrode

- Based on the design developed by L.W. Niedrach
- Uses either a Cu/CuO or Ni/NiO metal/metal oxide pair inside a YSZ tube
- Waiting on autoclave to become operational for testing, do not work very well below 100 C

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

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 be approved for operation

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

- Working on selective materials for Li+ and F- that work in brine
  - $LiMn_2O_4$ and nano-LaF_3:EuF_3

- Future work:
  - testing at high temperature and pressure in an autoclave

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

Acknowledgements

- Greg Cieslewski (PI) and Scott Lindblom – high temperature electronics
- Timothy Boyle, Greg Stillman (DOE-EERE), Sam Bingham, Michael Neville, and Adam Cook – ion selective material synthesis and characterization
- Steven Limmer and William G. Yelton – reference electrode development
- Funding: Department of Energy, Office of Energy Efficiency and Renewable Energy – Geothermal Technologies Office