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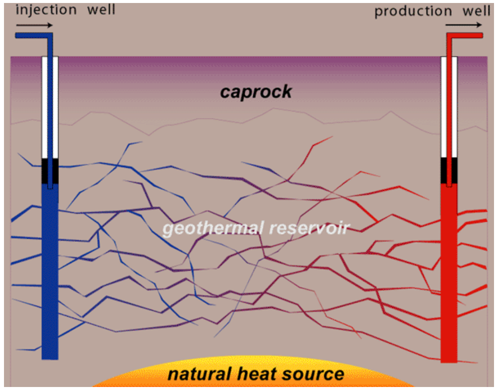

Measuring Real-time Concentration of Ionic Tracers and pH in Geothermal Reservoirs Using a Ruggedized Downhole Tool

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Sandia National Laboratories

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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

SAND2014-18262

Goals

- **Develop a downhole instrument to measure:**

  tracer concentration pH temperature pressure

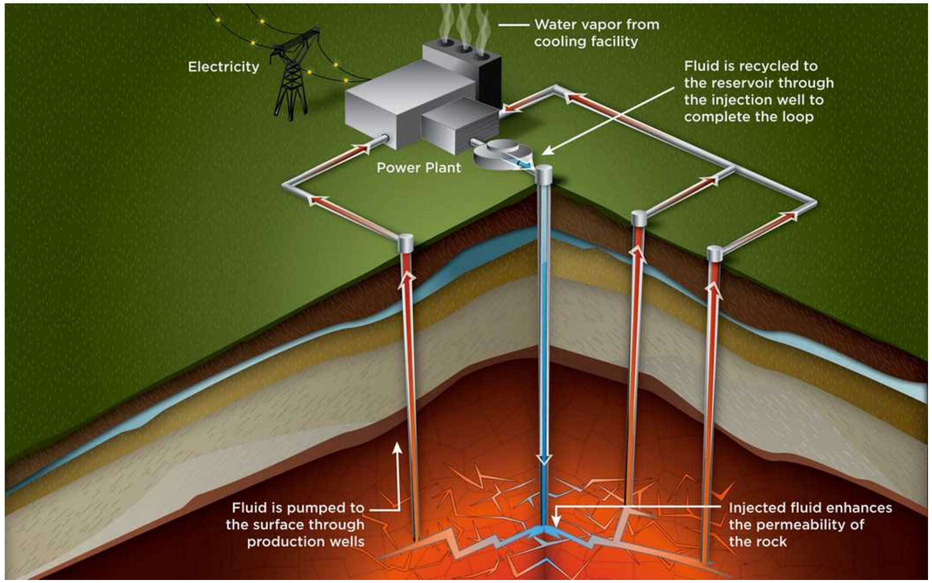
  ….in wells up to 225 °C and 3000 psi in real-time

- Want to generate tracer concentration (and pH) versus depth and time inside geothermal wells

- Which tracers?
  - Initial goals include: **Li^+ Cs^+ F^- I^-**

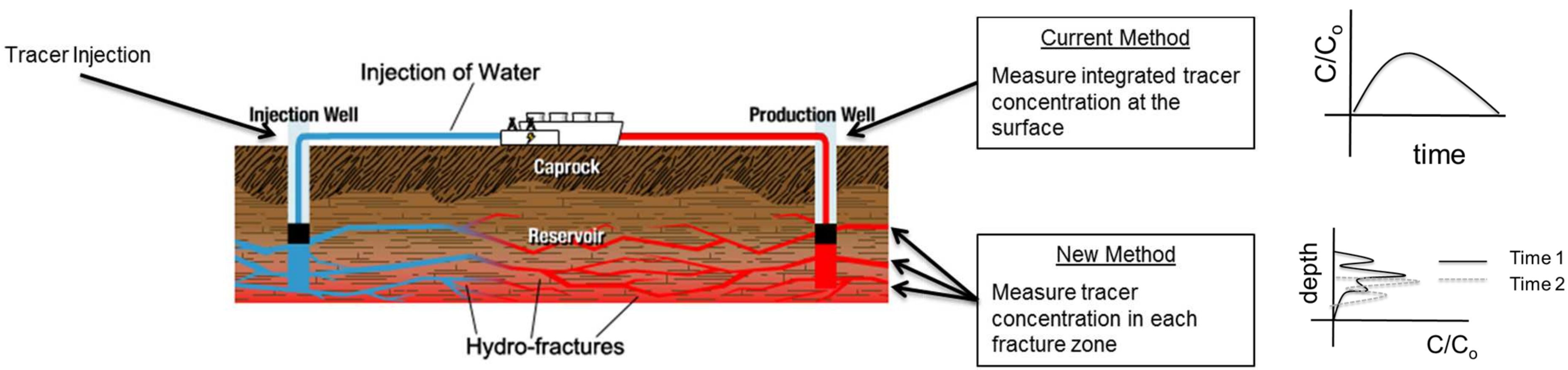
- How will it work?
  - We are developing a series of high temperature and pressure ion selective electrodes to work in conjunction with pH, T, and P probes to enable the generation of tracer concentration and pH versus depth and time data

Enhanced Geothermal Systems (EGS)



Tracers provide valuable information on fracture network but….

Current methods do not provide information on depth of key fractures



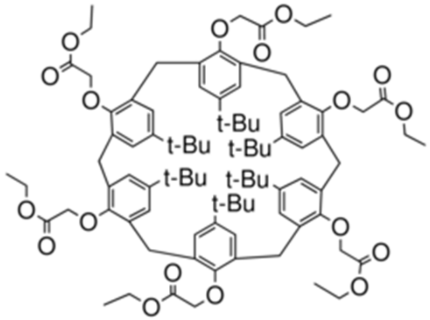
http://www1.eere.energy.gov/geothermal/presentations.html (Eric Haas, Geothermal Technology Office Review)

Materials Compatibility Challenges

- Brine temperature from 100 – 350 °C
- Pressure in the 1000s psi range
- Depth in the 1000 – 10,000 ft range
- Brine pH 2 – 11, with many in the 6 – 7 range
- Well operators….

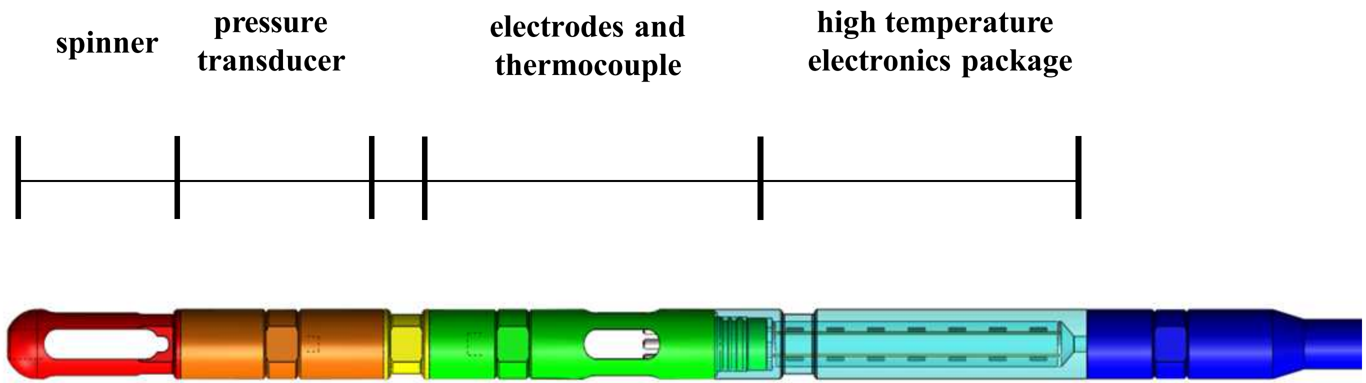
Consequences

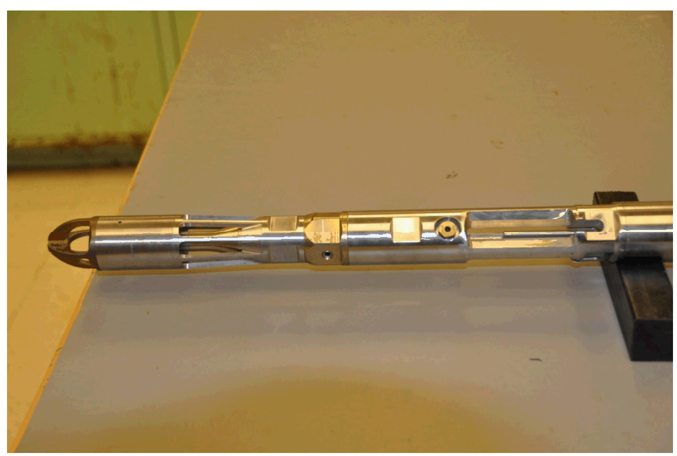
- We can't use most organic ionophores
- Teflon will likely be too soft, need PEEK or ceramics
- Need high temperature epoxies and solder
- Have to use specialty electronics for data acquisition
  - No fun collecting data over 5,000 feet of wire….



Cs ionophore II
Sigma-aldrich

Tool Design





T and P Tool

240 °C unshielded

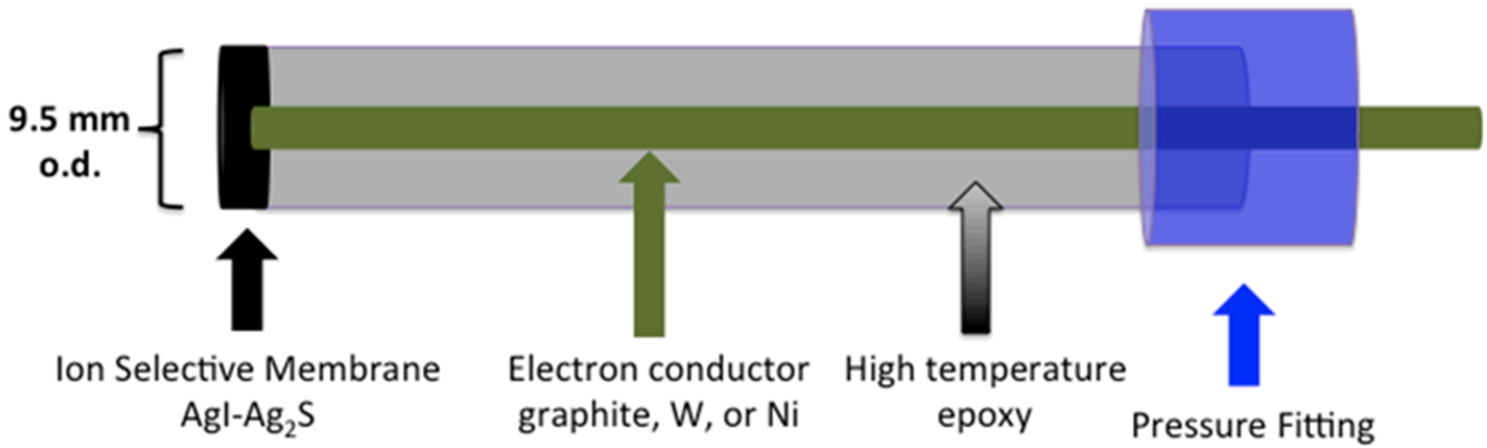
400 °C shielded

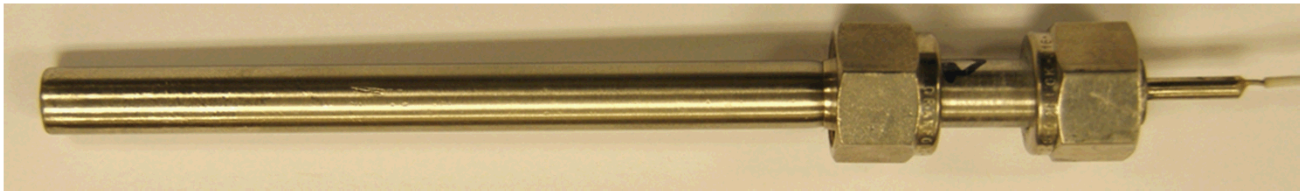
Iodide Ion Selective Electrode

- 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

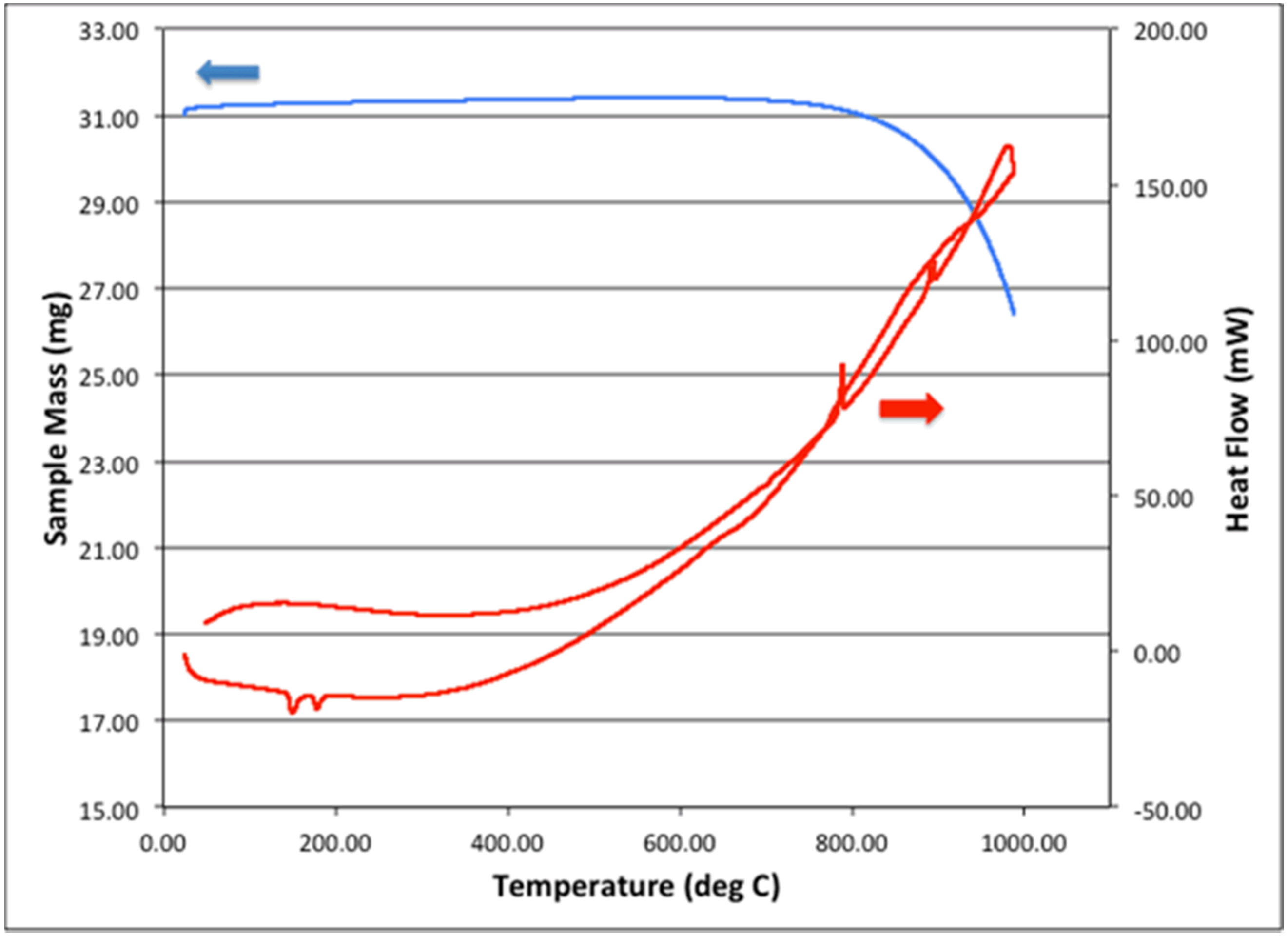
10 – 12 cm length

Electrode body is a 9.5 mm o.d. piece of stainless steel tubing





Thermal Analysis of AgI-Ag_2S



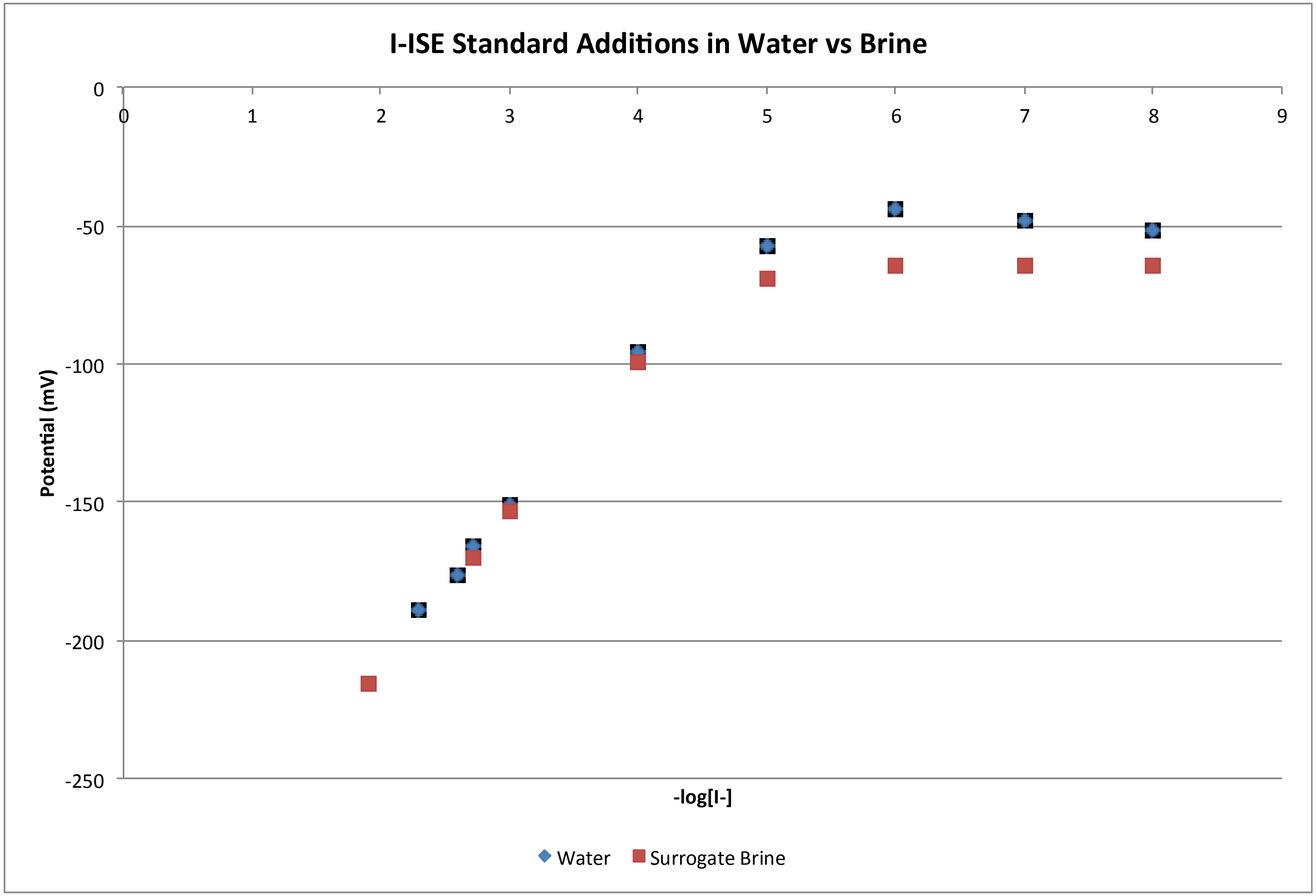
Blue – weight change at at a given T

Red – phase changes at a given T

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)

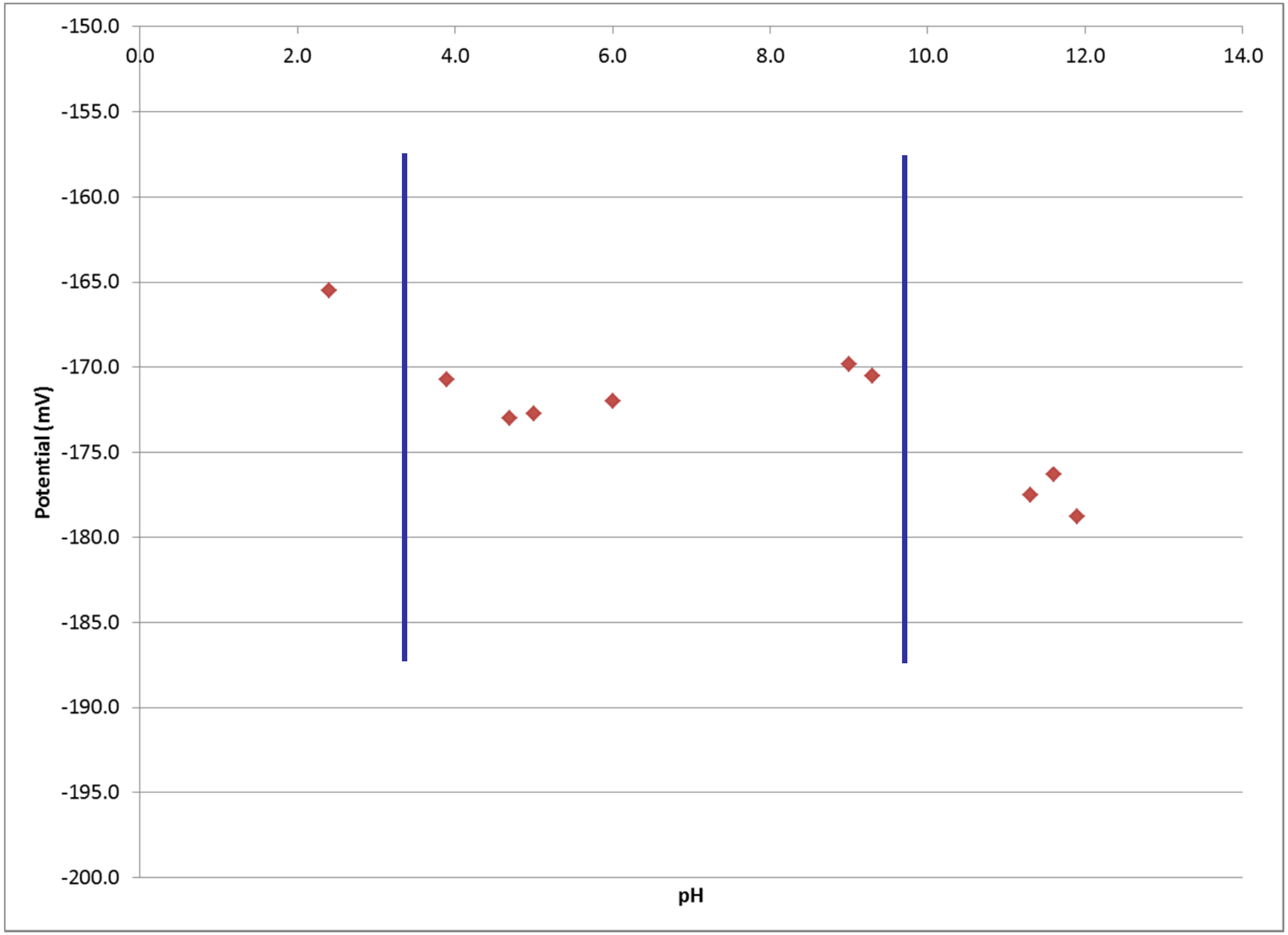
Solid State I-ISE Response - Ambient



pI = - log [I$^-$]

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 pH Stability



Our AgI/Ag_2S electrode should work for fluids with pH between 3.5 and 9.5

High Temperature and Pressure Testing

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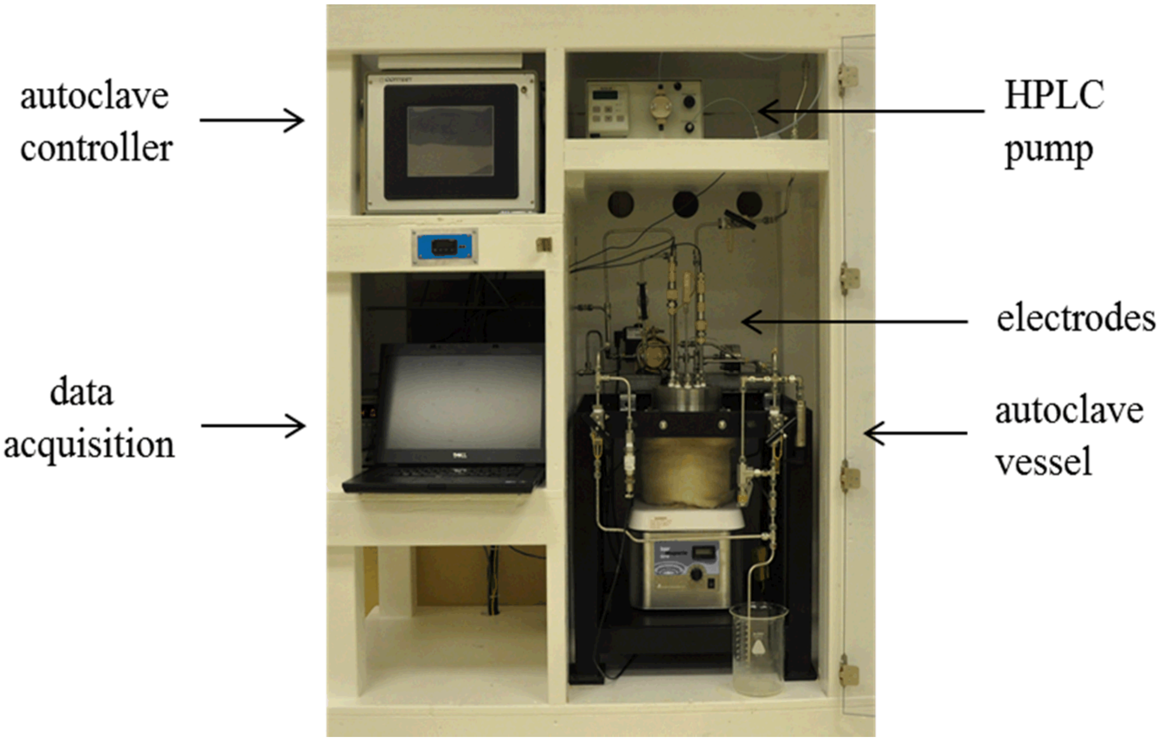
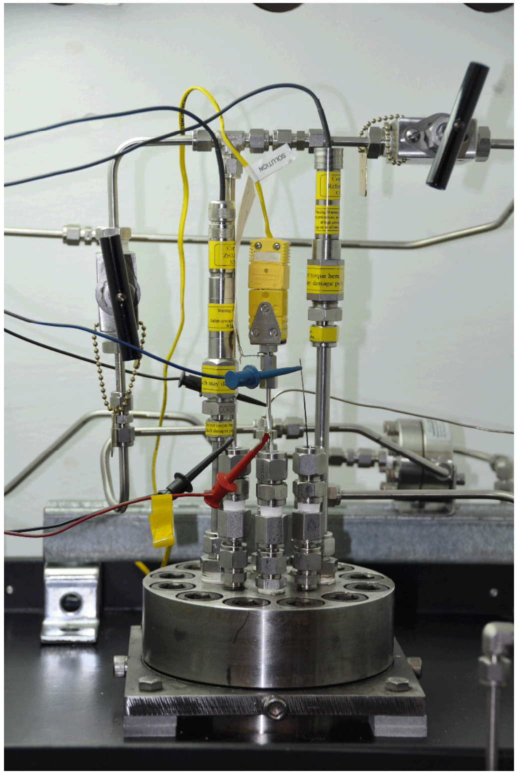
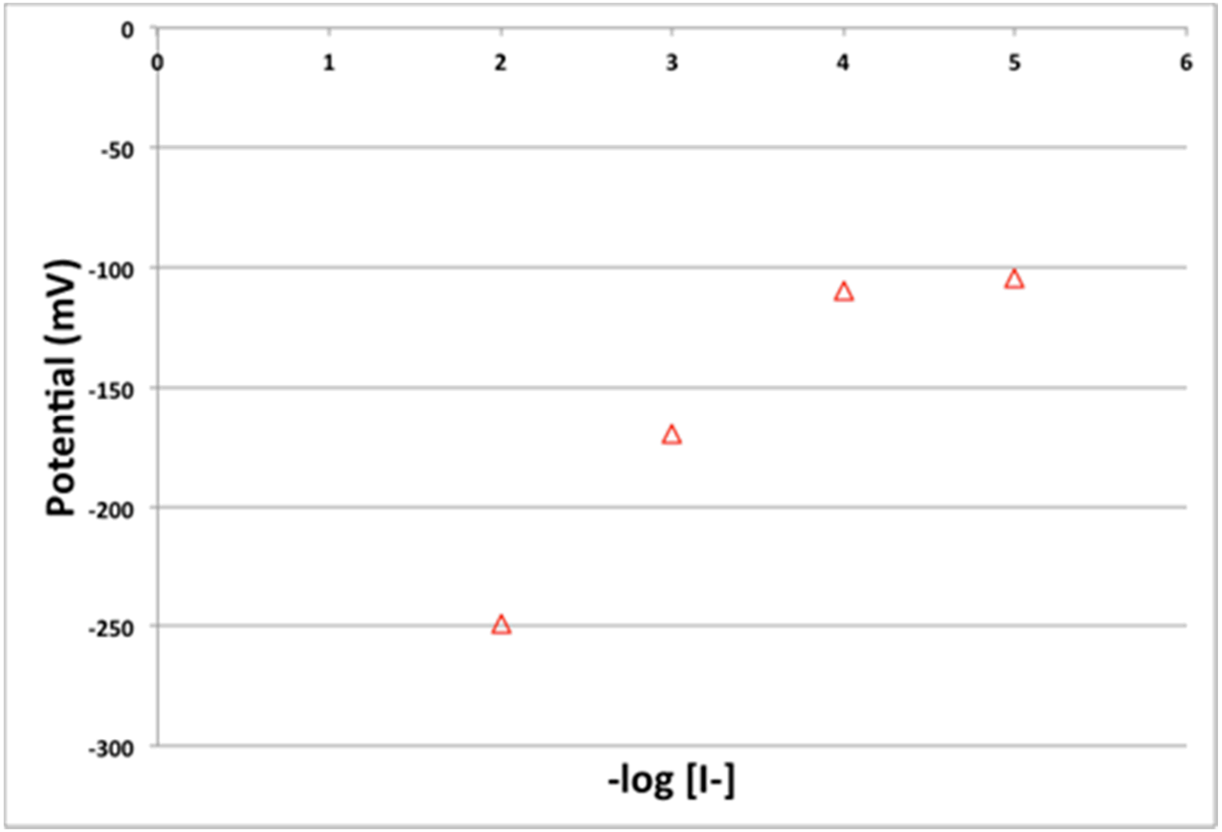




- 1 liter autoclave
- SSI Series 3 HPLC pump
- Corr Instruments High Model A2 pH electrode and Ag/AgCl internal balance reference electrode
- Data collected using a NI-9234 16-bit analog to digital converter to monitor the potential of the I-ISE, pH, and reference electrodes

High Temperature and Pressure Testing

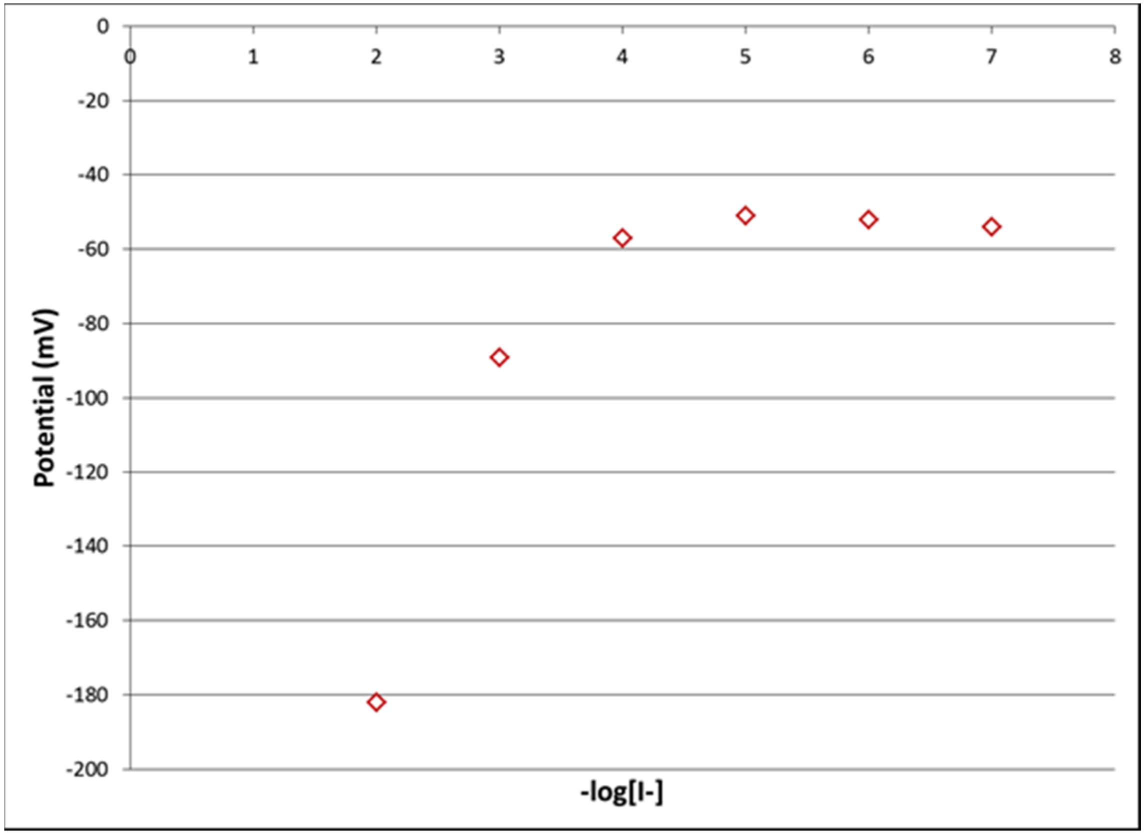
- Temperature **155 °C - 177 °C**
- Pressure **702 psi - 738 psi**



- Linear response between 10^{-4} M and 10^{-2} M iodide
- R^2 of 0.993 and a slope of 70 mV/decade

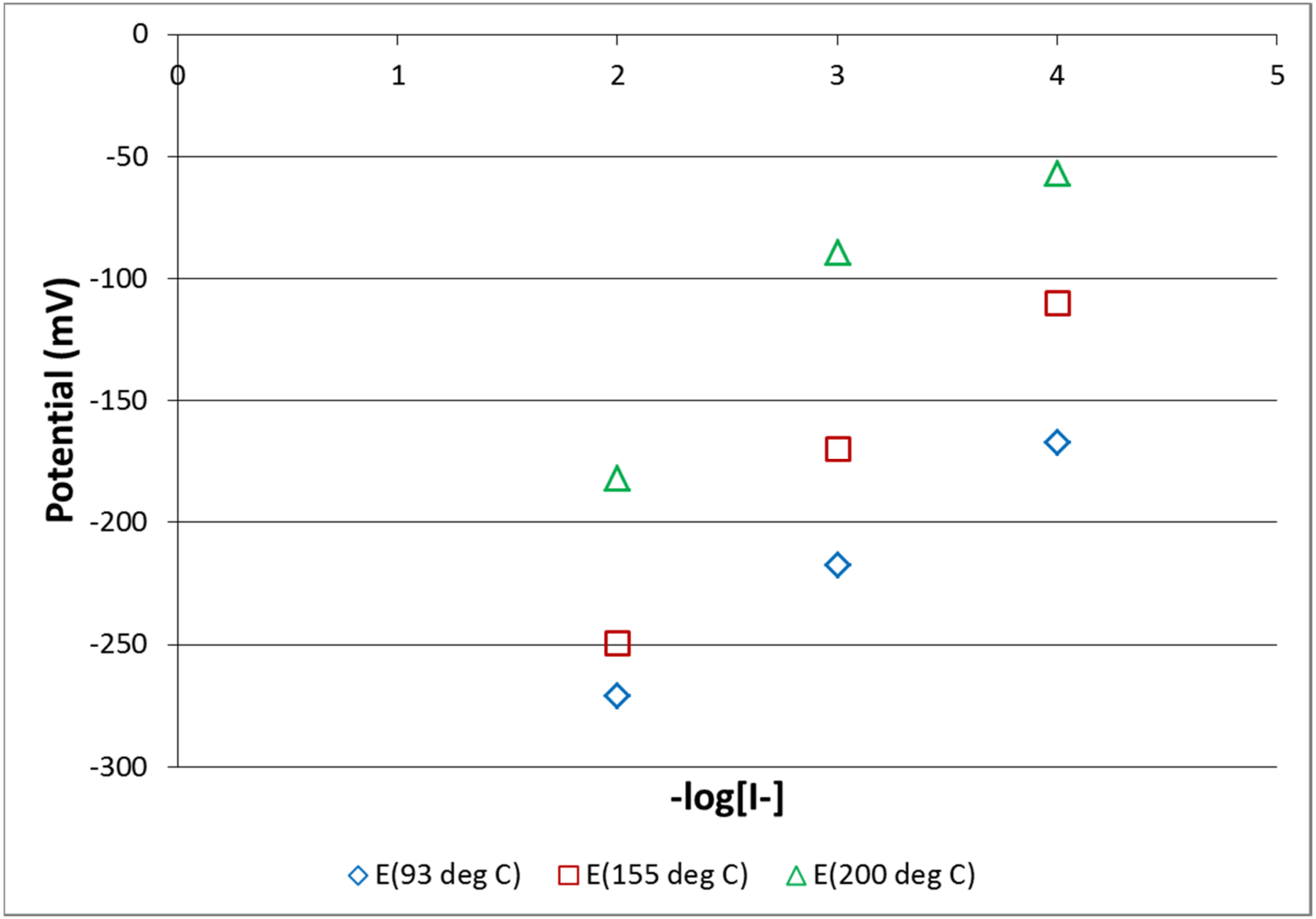
High Temperature and Pressure Testing

- Temperature **200 °C**
- Pressure **1171 psi**
- Supporting electrolyte 0.01 M KNO_3



- Linear response between 10^{-4} M and 10^{-2} M iodide
- R^2 of 0.926 and a slope of 63 mV/decade

Temperature Dependence



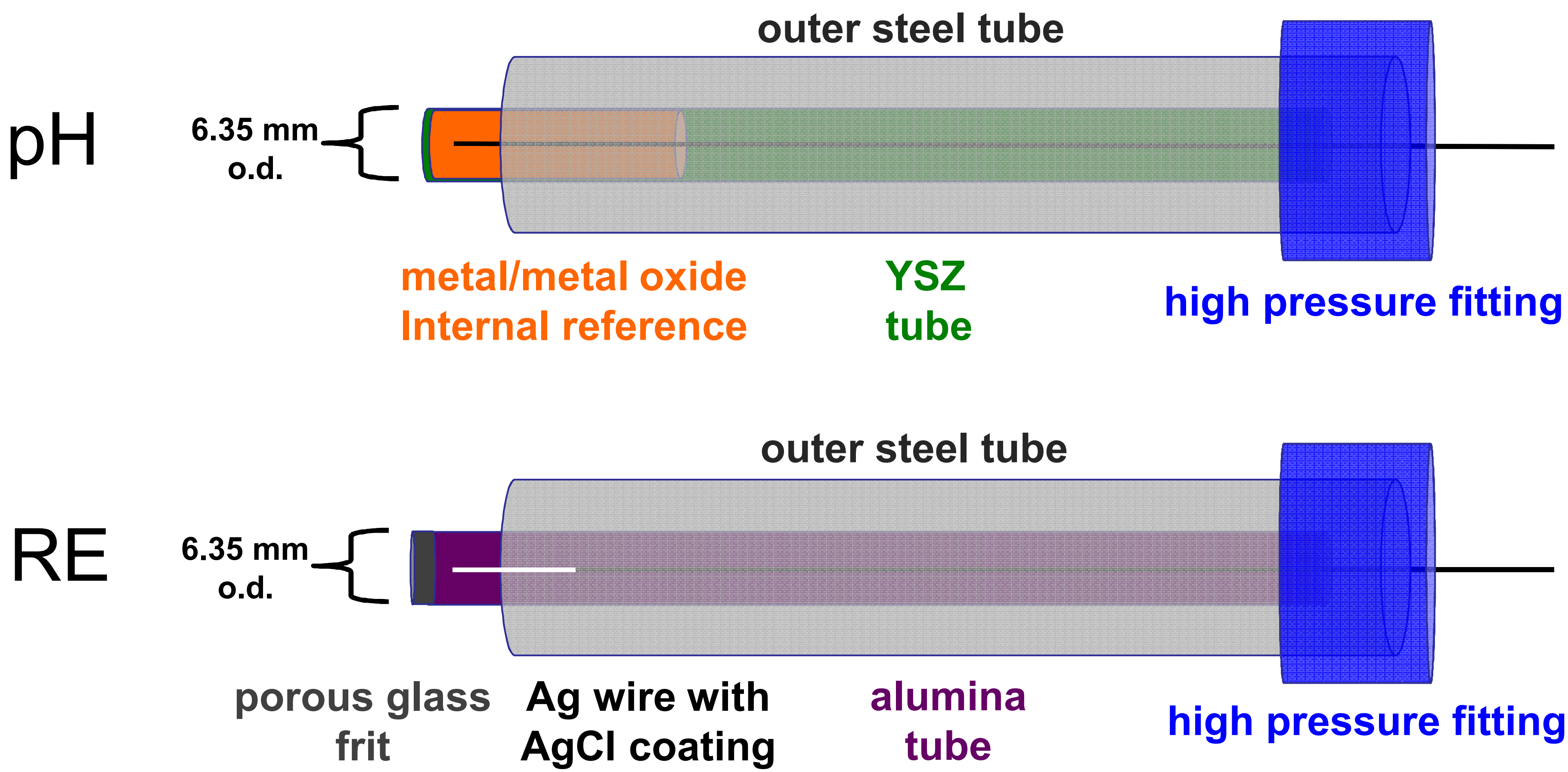
We see an increase in potential with temperature at a given I^- concentration which agrees with electrochemical theory

Potential for other downhole ISEs

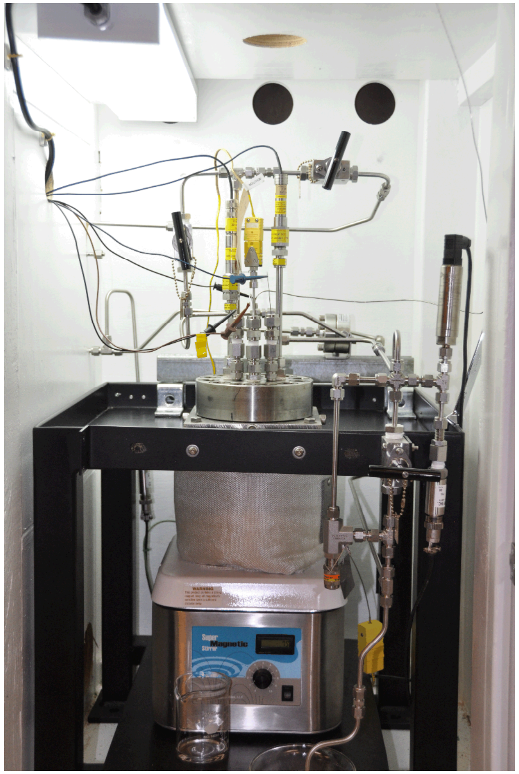
- **Sulfide-ISE:** uses a 100% Ag2S pellet as the membrane
  - Ambient results indicate a bimodal response
- **Fluoride-ISE**: uses a LaF3:Eu single crystal from Goodfellow
  - Ambient results show a slope close to theoretical but R^2 needs improvement
- **Lithium-ISE:** membrane consists of a piece of palladium coating with a LiMn2O4 thin film that has been "delithiated"
  - Ambient results show a slope greater than theoretical but close enough to probably be useful

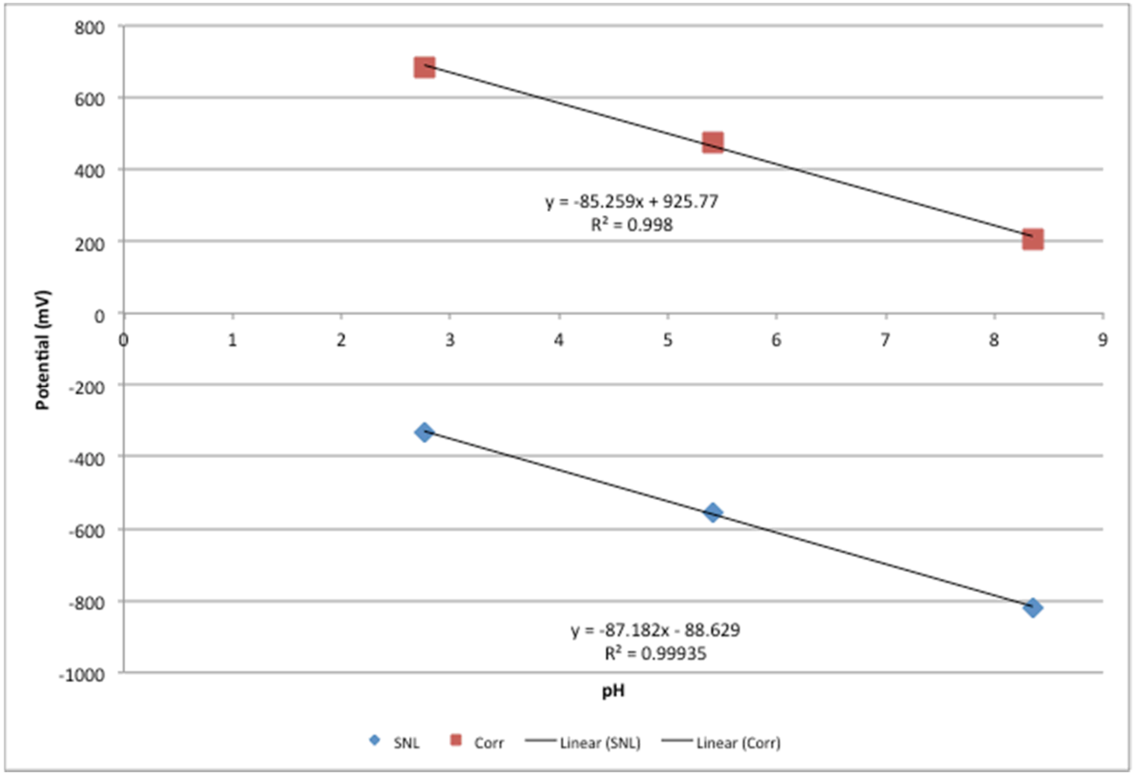
pH and Reference Electrodes

Leveraging work done by Niedrach at GE, Macdonald & Lvov at PSU, Ding & Seyfried at U of Minnesota, & Jung at the Korea Atomic Energy Research Institute



pH Electrode Response at 220° C and 1500 psi





Commercial and Sandia reference electrodes used

pH electrode

yttria-stabilized zirconia membrane, Ni/NiO internal reference, Ni wire, high temperature epoxy

Summary

- We have developed a ruggedized iodide ion selective electrode that should be stable at 225 °C and 3000 psi
- Preliminary I-ISE data shows stable response up to 200 °C and 1171 psi with an estimated limit of detection (LOD) of 16 ppm iodide
  - Below 100 °C this design has a LOD of 0.4 ppm iodide
- Demonstrated construction of solid state reference and pH electrodes that are relatively stable to at least 90 °C without using epoxies that run and outgas
- Currently working on selective materials for Li^+ and F^- that work in brine
  - $LiMn_2O_4$ and nano-LaF_3:EuF_3

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, now at Stanford), 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

A Little Electrochemistry…

$$\Delta G^\circ = -RT \ln K = -nFE^\circ_{cell}$$

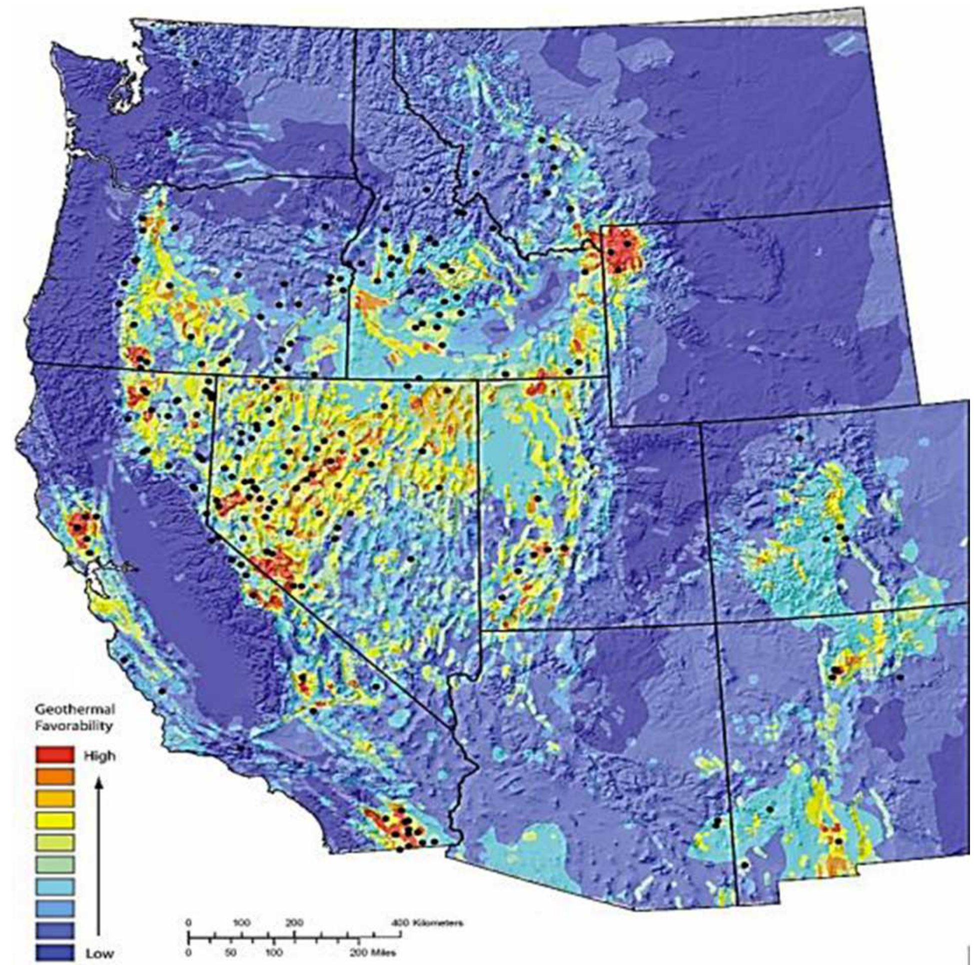
$$E^o_{cell} = \frac{RT}{nF} \ln K$$

$$E^o_{cell} = \frac{0.0591\,\mathrm{V}}{n} \log K$$

For every order of magnitude change in target ion concentration we should get a 59.16 mV change in potential

Outline

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



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