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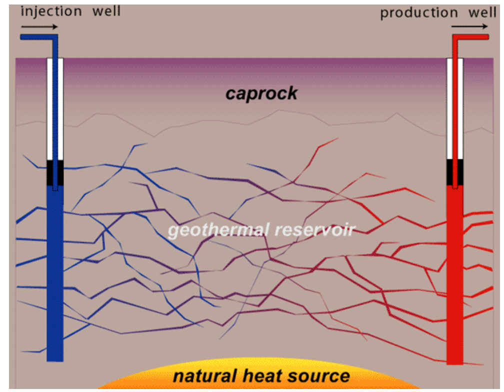

High Temperature Chemical Sensing Tool for the Distributed of Fracture Flow in EGS

Project Officer: Lauren Boyd
Total Project Funding: $1758k
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EGS: High Temp Tools, Drilling Systems

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Relevance/Impact of Research

Background

- Current chemical tracer tests are conducted by measuring the tracer concentration at the recovery/production wellhead.
  - While this provides the transit time between wells it only provides a "depth-averaged" concentration value. pH measurements are also conducted at the surface after depressurizing and reaching ambient temperature – this is not necessarily an accurate representation of pH in the reservoir
- The ability to accurately measure ionic tracer concentration and pH at depth in geothermal wells will allow for the identification of specific fractures actually producing the tracer of interest and for a more accurate pH measurement. The measurement of pH downhole will also allow for the identification of specific inflow zones based on changes in pH with depth

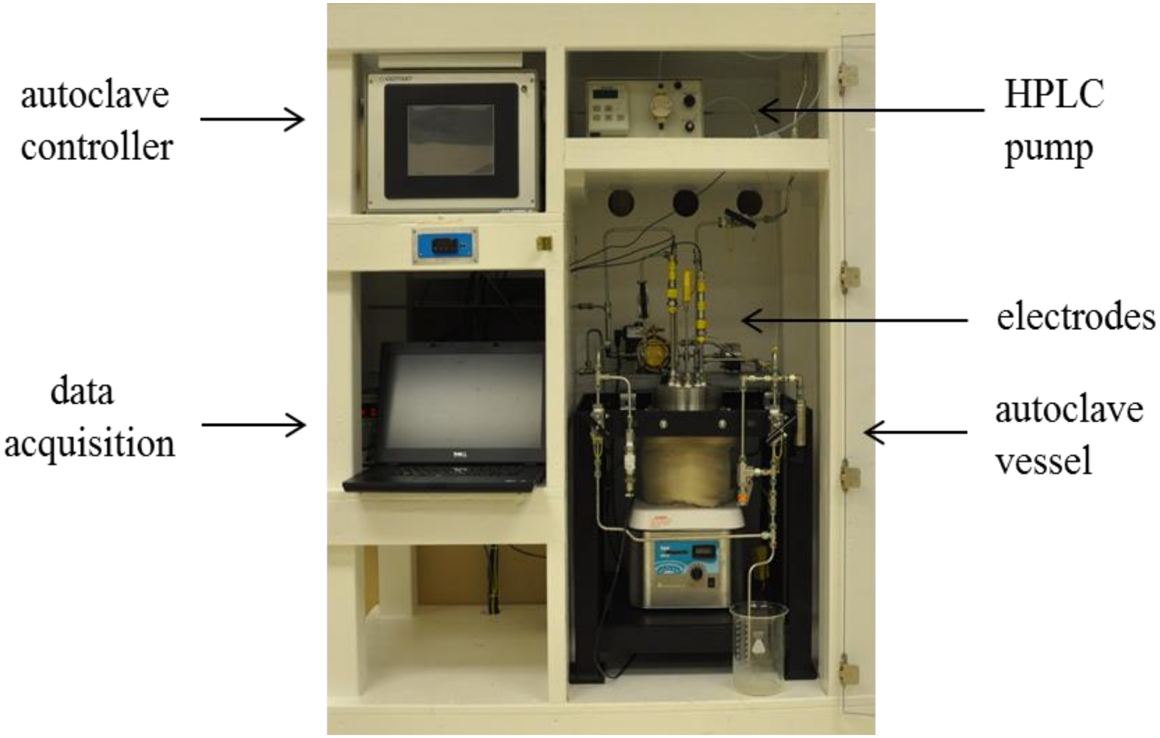
Goals

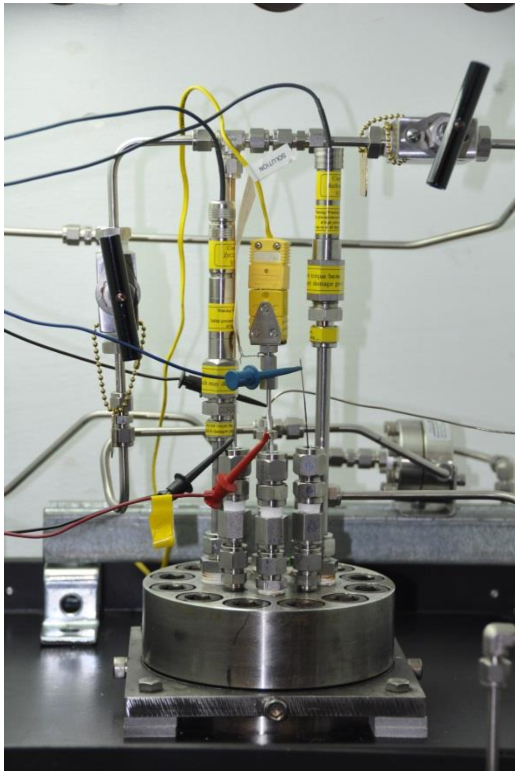
- Develop a wireline tool capable of measuring ionic tracer concentration and pH downhole in real time at temperatures up to 225 °C and pressures up to 3000 psi
- The primary ionic tracer of interest is iodide with lithium, cesium, and fluoride also desired

Scientific/Technical Approach

- Explored various approaches to detecting tracers downhole and uphole
  - Primary focus on naphthalene sulphonates (NS) and ionic tracers
  - Explored use of micro-fabricated GC coupled with SAW sensor
    - NS tracers were not volatile enough to allow for detection
  - Chose an electrochemical approach for measuring ionic tracer concentration and pH on a downhole wireline tool
- The sensor consists of three ruggedized electrodes and the high temperature stable electronics needed for processing the data downhole
  - Iodide ion selective electrode
  - pH electrode
  - Reference electrode
- The tool also contains instrumentation for measuring temperature, pressure, and flow rate using existing technology
- Key challenges include identifying ion selective materials capable of surviving downhole and remaining selective for the ion of interest and developing a reference electrode that is stable and leak proof at high temperature and pressure

High Temperature and Pressure Testing





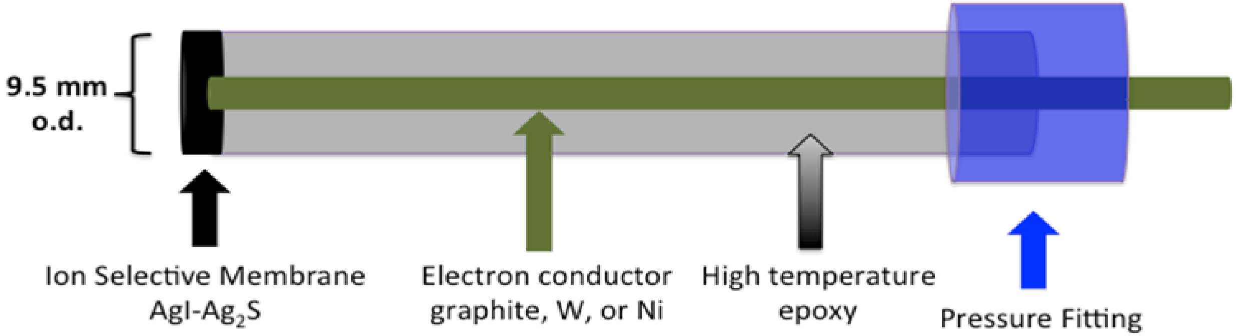
- 1 liter autoclave and a SSI Series 3 HPLC pump
- Corr Instruments High Model A2 pH electrode and Ag/AgCl internal balance reference electrode
- Data collected using a NI-9234 16-bit analog to digital converter to monitor the potential of the I-ISE, pH, and reference electrodes

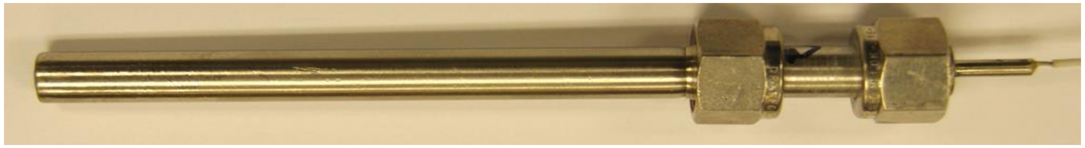
Iodide Ion Selective Electrode

- All solid state design to enable stability at temperatures up to 225 °C
- Chose AgI-Ag_2S pellet as the ion selective material
  - Explored various compositions and dimensions of the pellet

10 – 12 cm length

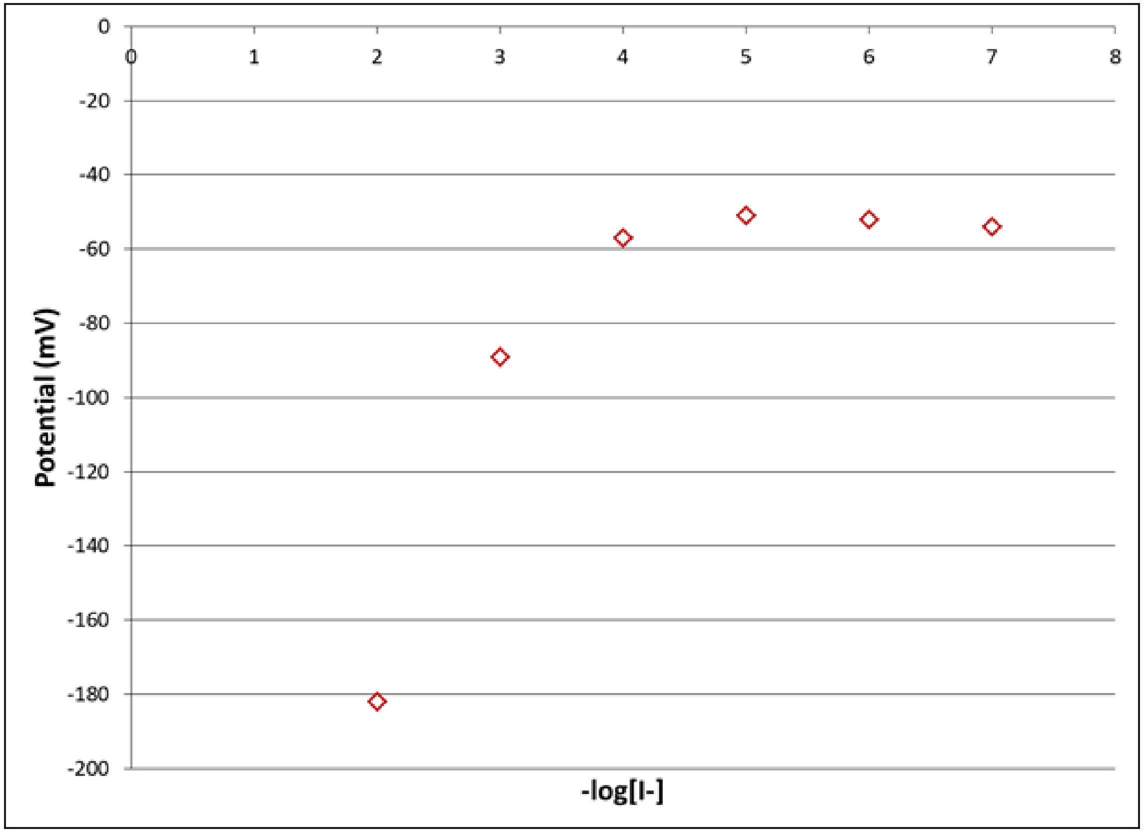
Electrode body is a 9.5 mm o.d. piece of stainless steel tubing





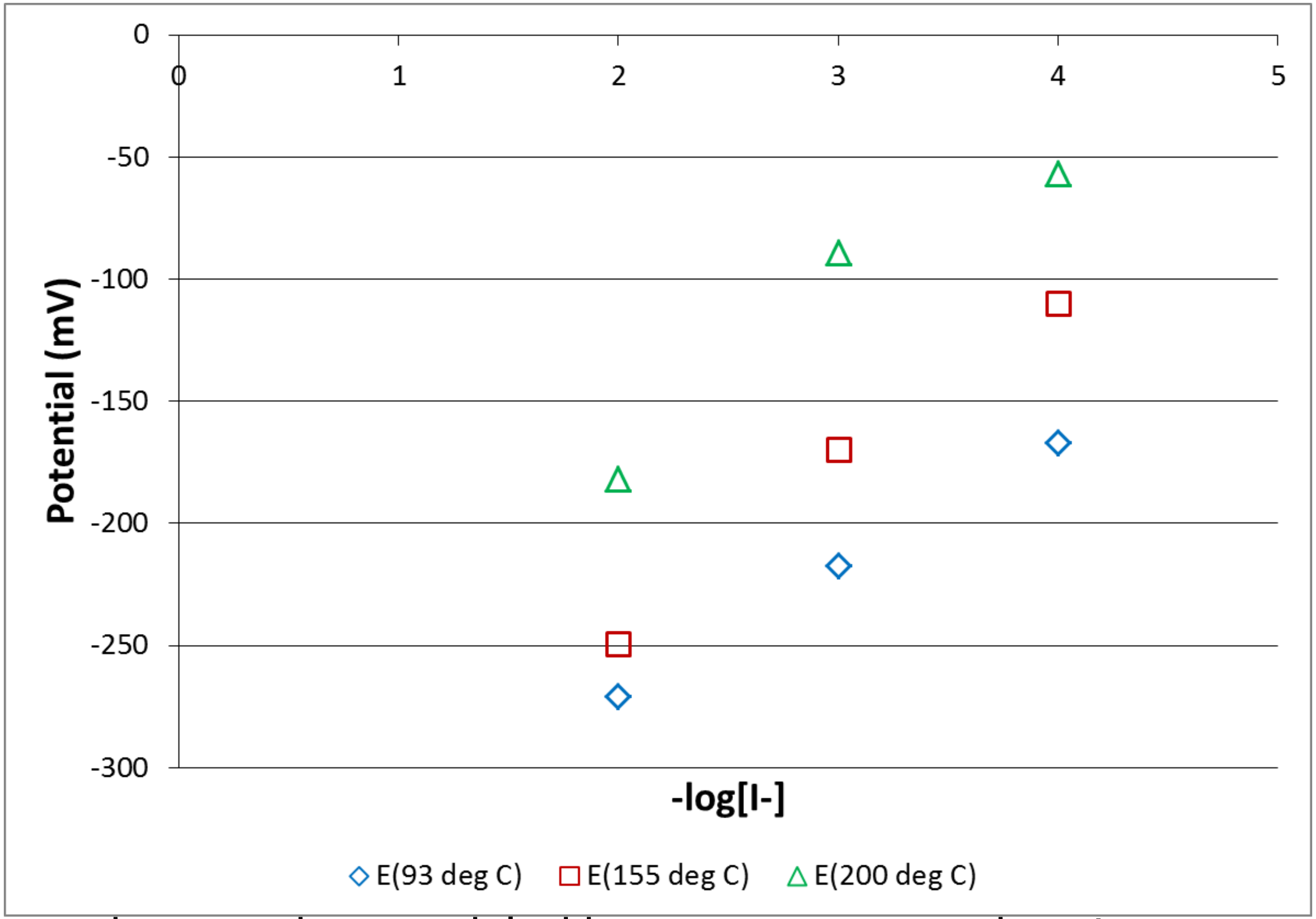
High Temperature Iodide Ion Selective Electrode (I-ISE) Performance

- 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

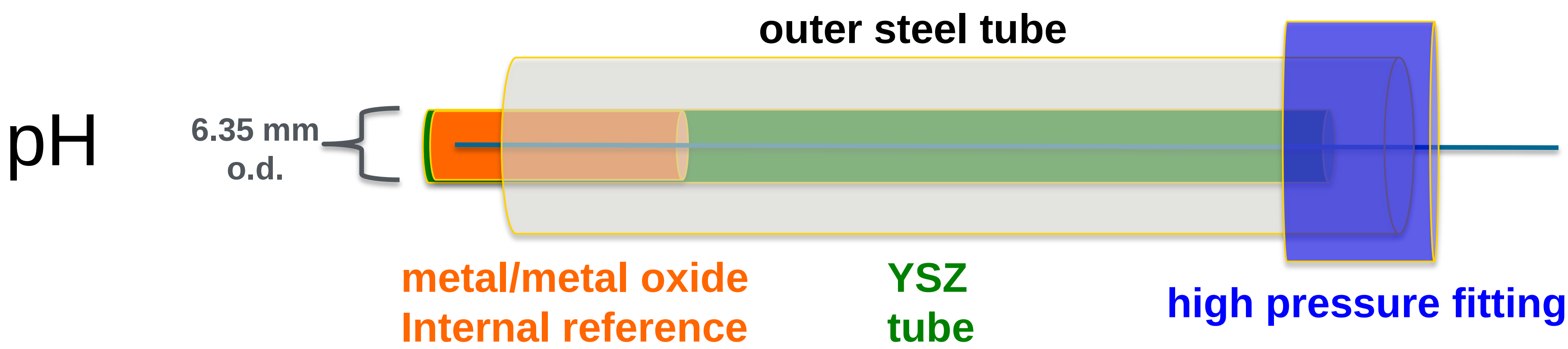
I-ISE Performance at a Range of Temperatures

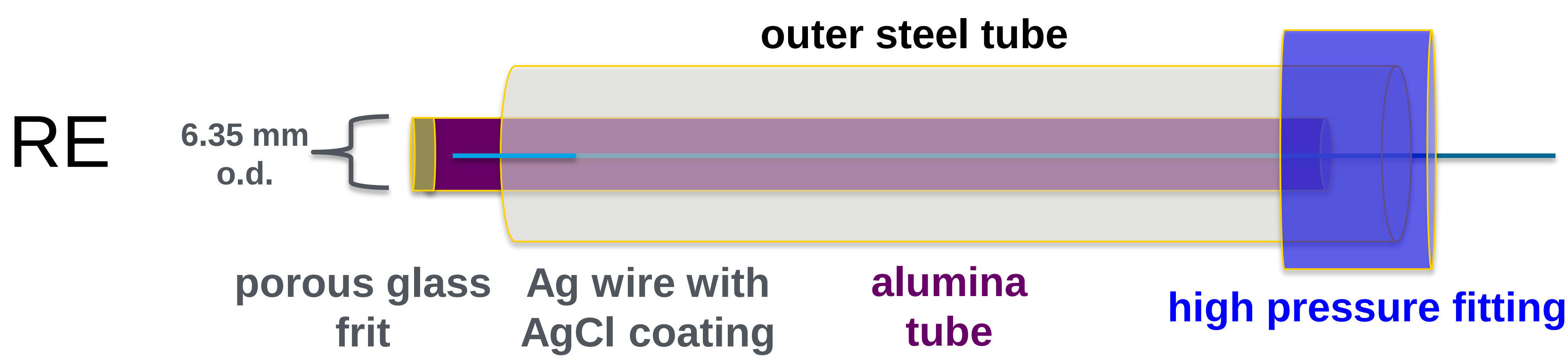


We see an increase in potential with temperature at a given I^- concentration which agrees with electrochemical theory

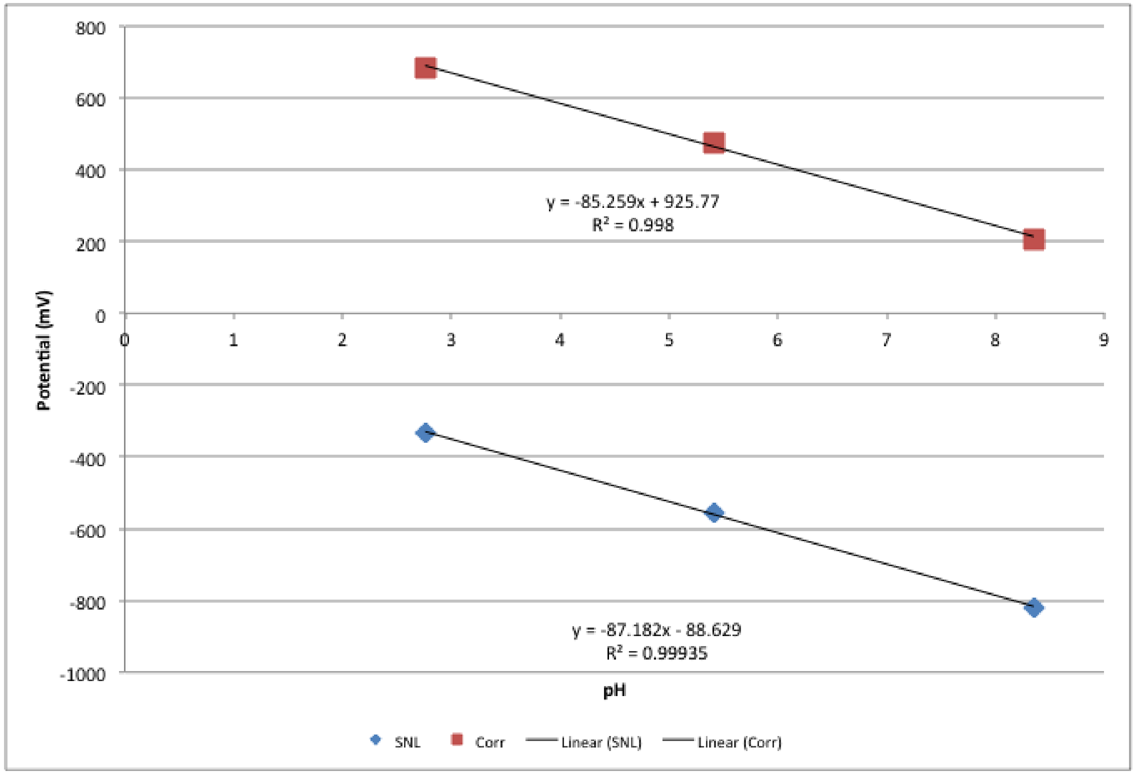
Ruggedized pH and Reference Electrode Design

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 at 225ºC and 1500psi

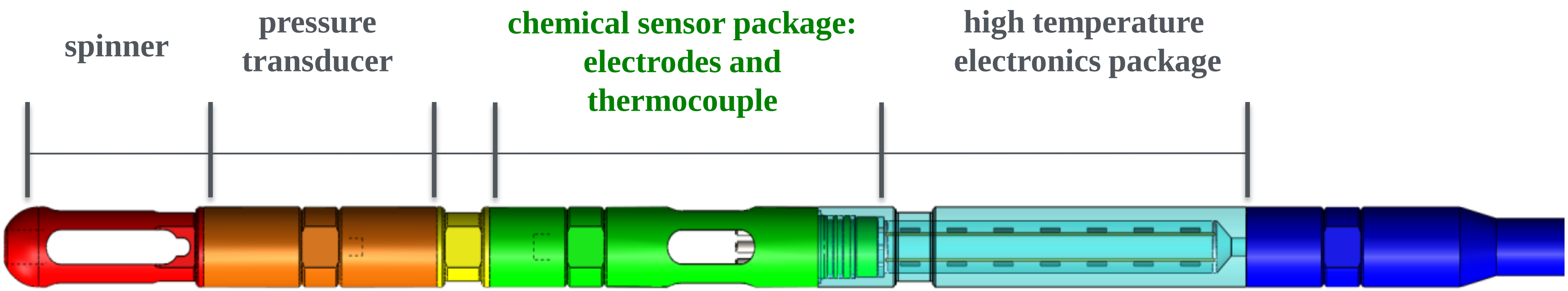


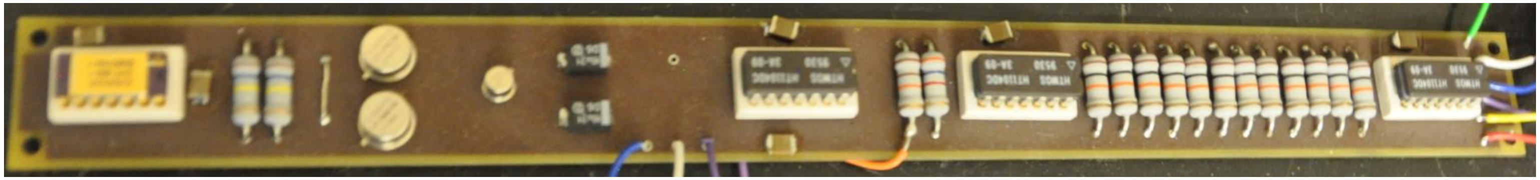
Commercial and Sandia reference electrodes used

pH electrode

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

Downhole tool and electronics



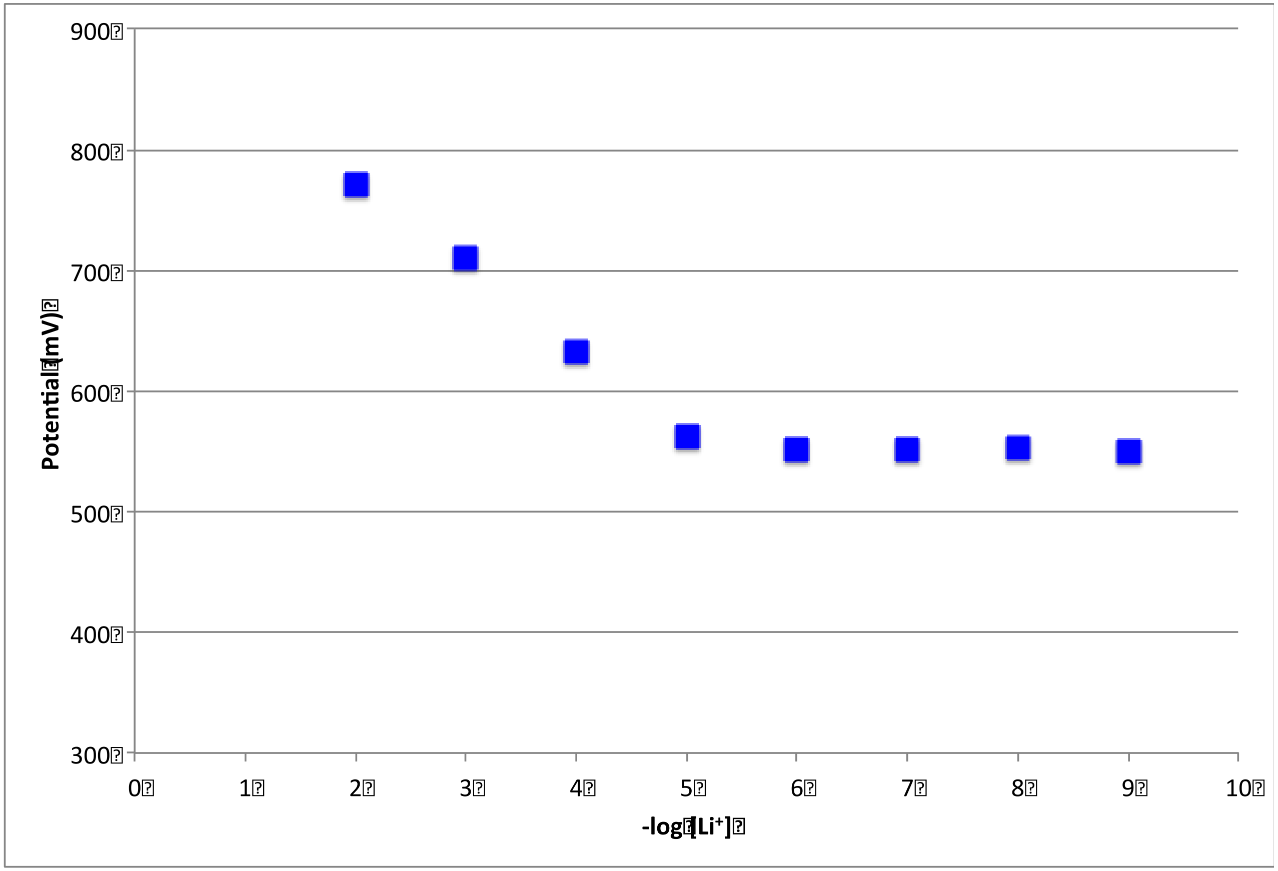


- Leveraged previously used PTS tool
  - Added new section which will house the electrodes
- High temperature level shifter circuit
  - HT switched capacitor voltage inverter for negative op-amp rail supply
  - Direct electrode buffers to isolate low current electrode signals
  - Summing amplifier for level shifting input signals

Potential for Other Downhole ISEs

- **Sulfide-ISE:** uses a 100% Ag_2S pellet as the membrane
  - Ambient results indicate a bimodal response
- **Fluoride-ISE**: uses a LaF_3:Eu single crystal
  - 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 $LiMn_2O_4$ thin film that has been "delithiated"
  - Ambient results show a slope slightly greater than theoretical but close enough to be useful

Performance of Li-ISE electrode using $LiMn_2O_4$ on Palladium Foil



Slope in the 10^{-5} to 10^{-2} M region = -70.6 mV/decade
Limit of Detection: $10^{-5.15}$ M in 0.1M NaCl-KCl

Accomplishments, Results and Progress

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Original Planned Milestone/ Technical Accomplishment	Actual Milestone/Technical Accomplishment	Date Completed
FY(13) Selection of ionic tracers and sensing membranes	Selected AgI-Ag2S for iodide and LiMn2O4 for lithium	On going for Cs and F
FY(14) Exploration of GC-SAW detection for naphthalene sulfonate tracers	Unable to identify suitable approach for GC detection due to low volatility	9/2014
FY(14) Development of the HT ion selective electrodes, pH electrodes and reference electrode; testing in the high pressure autoclave	I-ISE LOD at high temperature of 16 ppm, stable pH performance between 2.5 and 8.5 at 225°C	On going
FY(14) Develop HT electronics capable of interfacing and monitoring developed electrodes	Developed and tested HT electronics which will interface with the electrodes	9/2014
FY(15) Fabrication of mechanical components, electronics and ruggedized electrochemical sensor	Developed design and manufacturing techniques to construct leak proof electrodes	On going
FY(15) Finalize the downhole High Temperature Chemical Sensing Tool which can measure the concentration of iodide in and pH in-situ at temperatures of 225°C	Developed and tested designs for I-ISE, pH, and reference electrodes up to 225°C and 1500 psi	On going
FY(15) Perform a field test of the completed High Temperature Chemical Sensing Tool. The downhole concentration measurements should be in agreement with the integrated uphole measurement (stretch)	Looking for suitable partners and site.	

Future Directions

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- Conduct autoclave testing of all three electrodes simultaneously using the high temperature stable electronics package
  - Derive appropriate calibration curves
  - Measure the longevity of the complete sensor
- Continue development of Cs and F ISE’s
  - Selectivity is very difficult
- Explore methods to lower the limit of detection to 1 ppm for the ruggedized I-ISE
- Locate a partner and a field site to perform field test.

Summary Slide

- Evaluated various chemical detection methods for both uphole and downhole detection
- Developed ruggedized HT electrodes
  - I-ISE electrode - preliminary data shows stable response up to 200 °C and 1171 psi with an estimated limit of detection (LOD) of 16 ppm iodide
  - pH electrode - successful test up to 225 °C and 1500psi. Highly linear in pH range of 3 to 8
  - Reference electrode – successful test up to 225 °C and 1500psi. The electrode is stable over the pressure and range but drifts predictably with temperature
- Tool Design
  - Successfully leverage previous design to incorporate new sensors
  - Designed and tested HT electronics capable of interfacing and recording the data from chemical sensors.