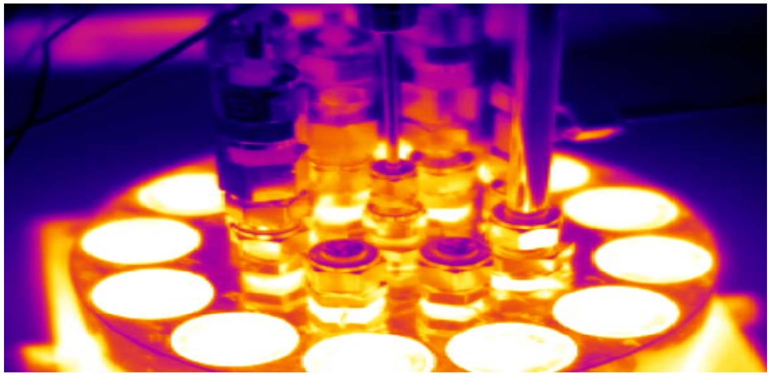
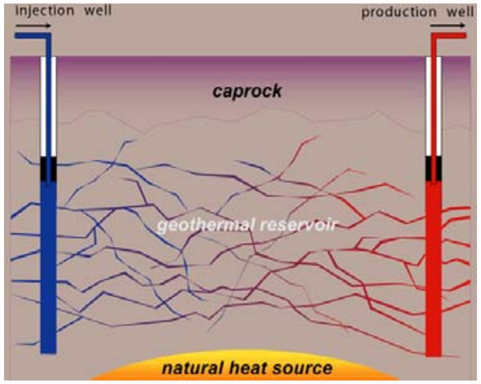
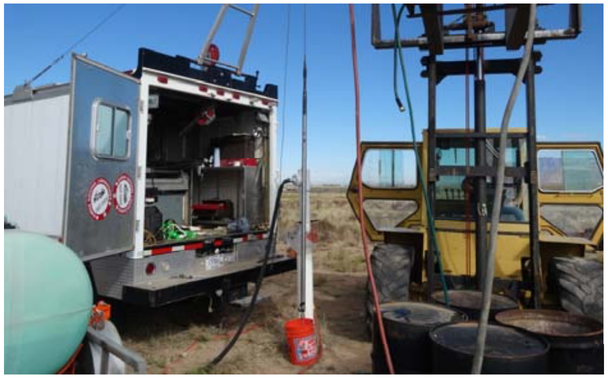
Geothermal Technologies Office 2017 Peer Review

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy







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

Project Officer: Lauren Boyd

Total Project Funding: $2184k

November 15, 2017

Avery "Zack" Cashion

Sandia National Laboratories

EGS Tools

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Relevance to Industry Needs and GTO Objectives

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

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

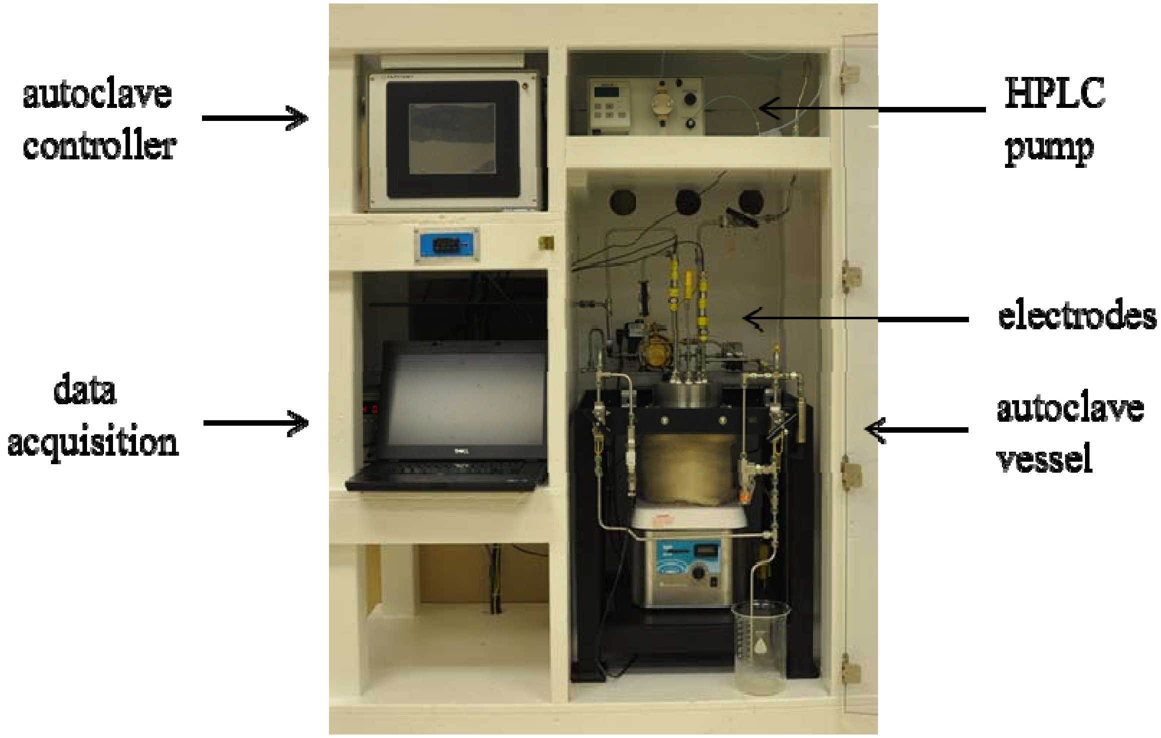
Goals

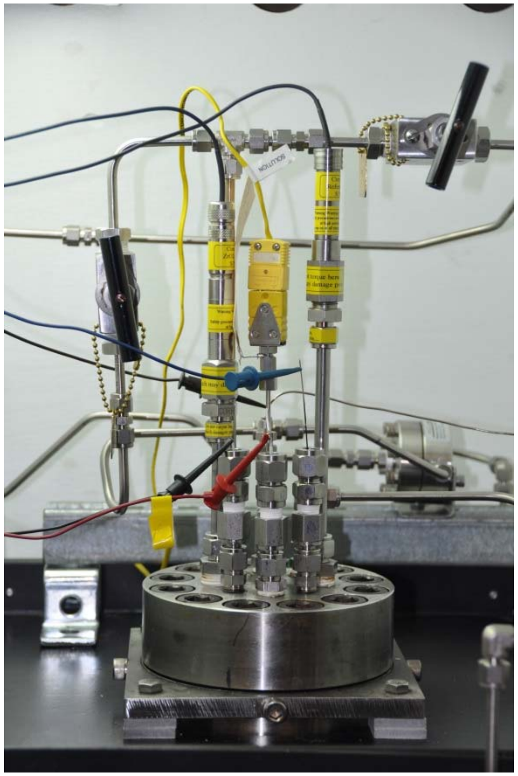
- Develop a wireline tool capable of measuring ionic tracer concentration and pH downhole in real time at temperatures up to 225 °C and pressures up to 3000 psi
- The primary ionic tracer of interest is iodide with lithium, cesium, and fluoride also desired

Methods/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



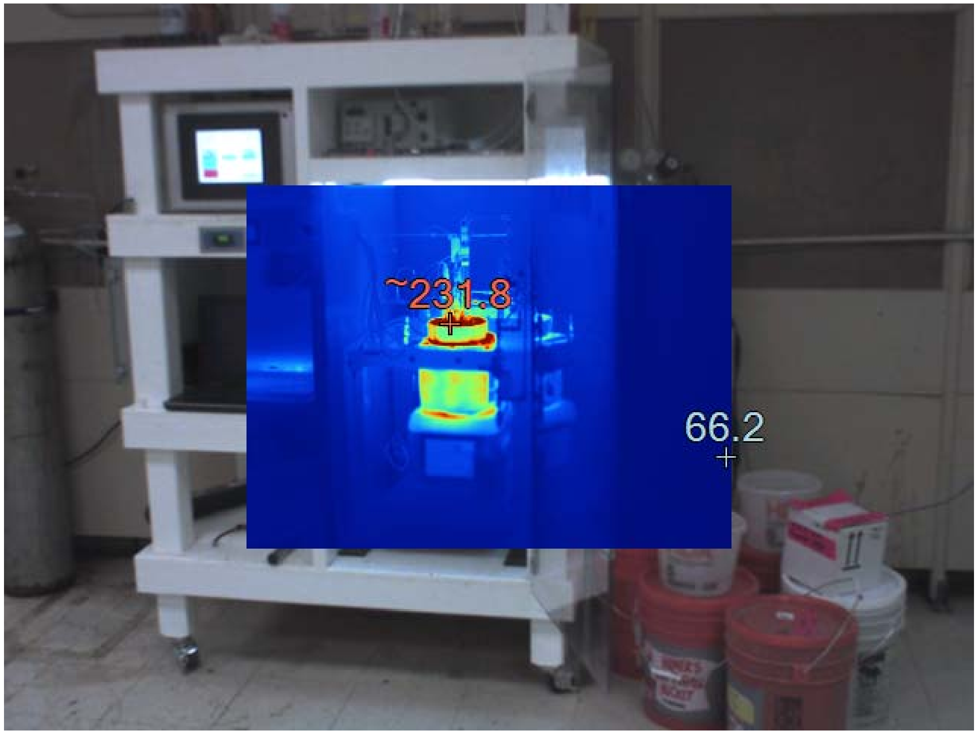


- 1 liter autoclave and a SSI Series 3 HPLC pump
- Corr Instruments High Model A2 pH electrode and Ag/AgCl internal balance reference electrode
- Data collected using a NI-9234 16-bit analog to digital converter to monitor the potential of the I-ISE, pH, and reference electrodes

Technical Accomplishments and Progress

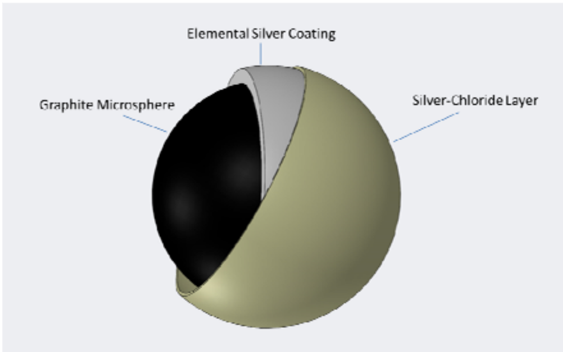
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

- Electrodes are assembled in pressure vessel port hardware
- PTFE liner in the pressure vessel is filled with test solution
- Pressure vessel is pressurized to up to 1700psi and heated to up to 230°C
- pH, reference, and ion selective electrode potentials are recorded on National Instruments DAQ hardware



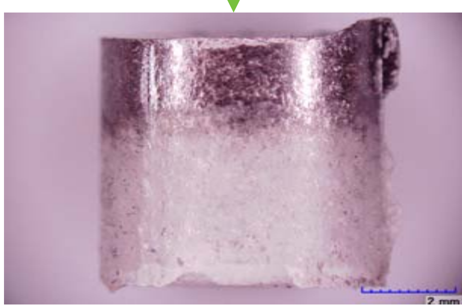
Thermal image of heating pressure vessel (°F)

Technical Accomplishments and Progress

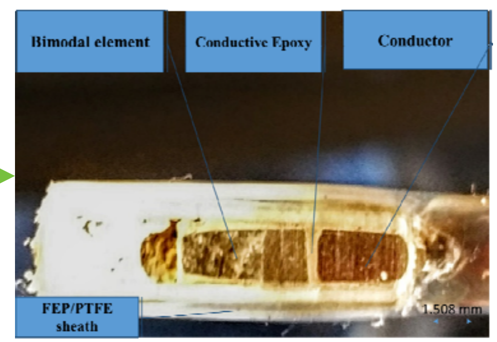


Engineered Particles (powder)

Press 8h @5 Tons



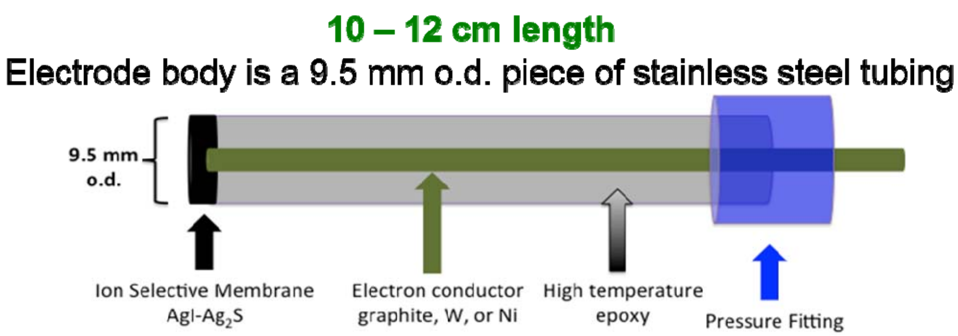
Electrode Pellet

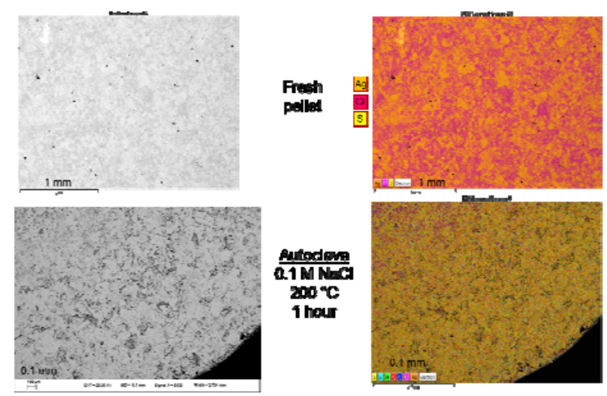


Electrode Assembly

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 for iodide
  - Explored various compositions and dimensions of the pellet
  - Thermogravimetric analysis shows pellet stability up to ~500 °C
  - Initial design below showed leak failures due to CTE mismatch



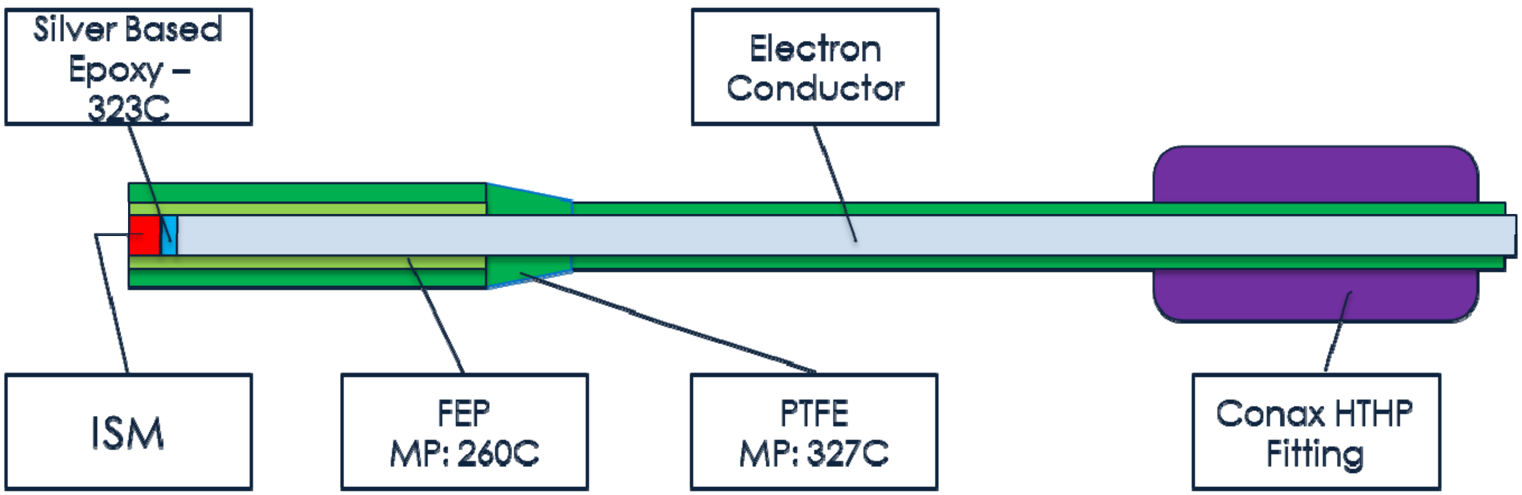


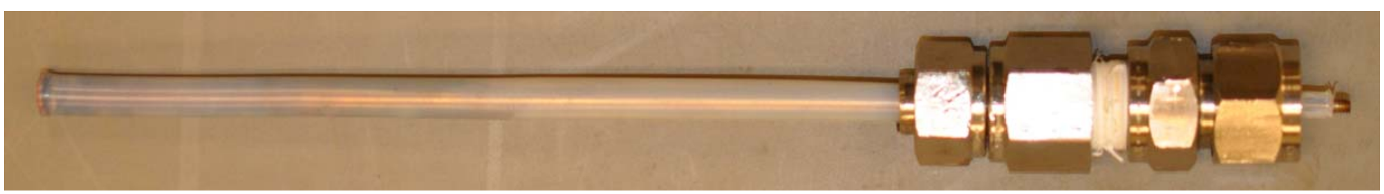
Scanning electron microscopy (SEM) images of a 1:1 AgCl/Ag_2S pellet surface. Colored images represent electron dispersive spectroscopic (EDS) results and indicate elemental homogeneity

Technical Accomplishments and Progress

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

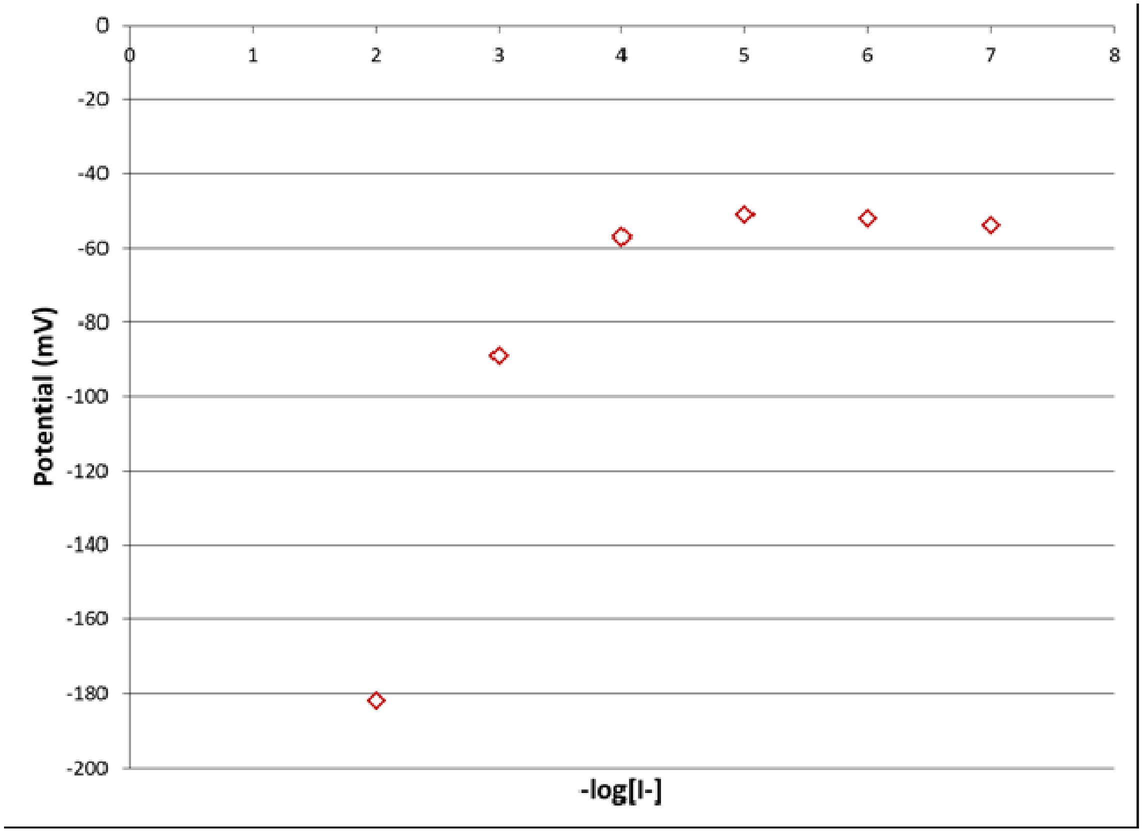
- Uses dual fluoropolymer construction (FEP, PTFE)
  - Heat cure at 342C
    - ISM consists of pressed silver-sulfide/silver-iodide powders
    - FEP melts around the lower part of electrode
    - PTFE shrinks around to form tight protective sheath
- Tested up to 225C in the autoclave with no leaks.





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

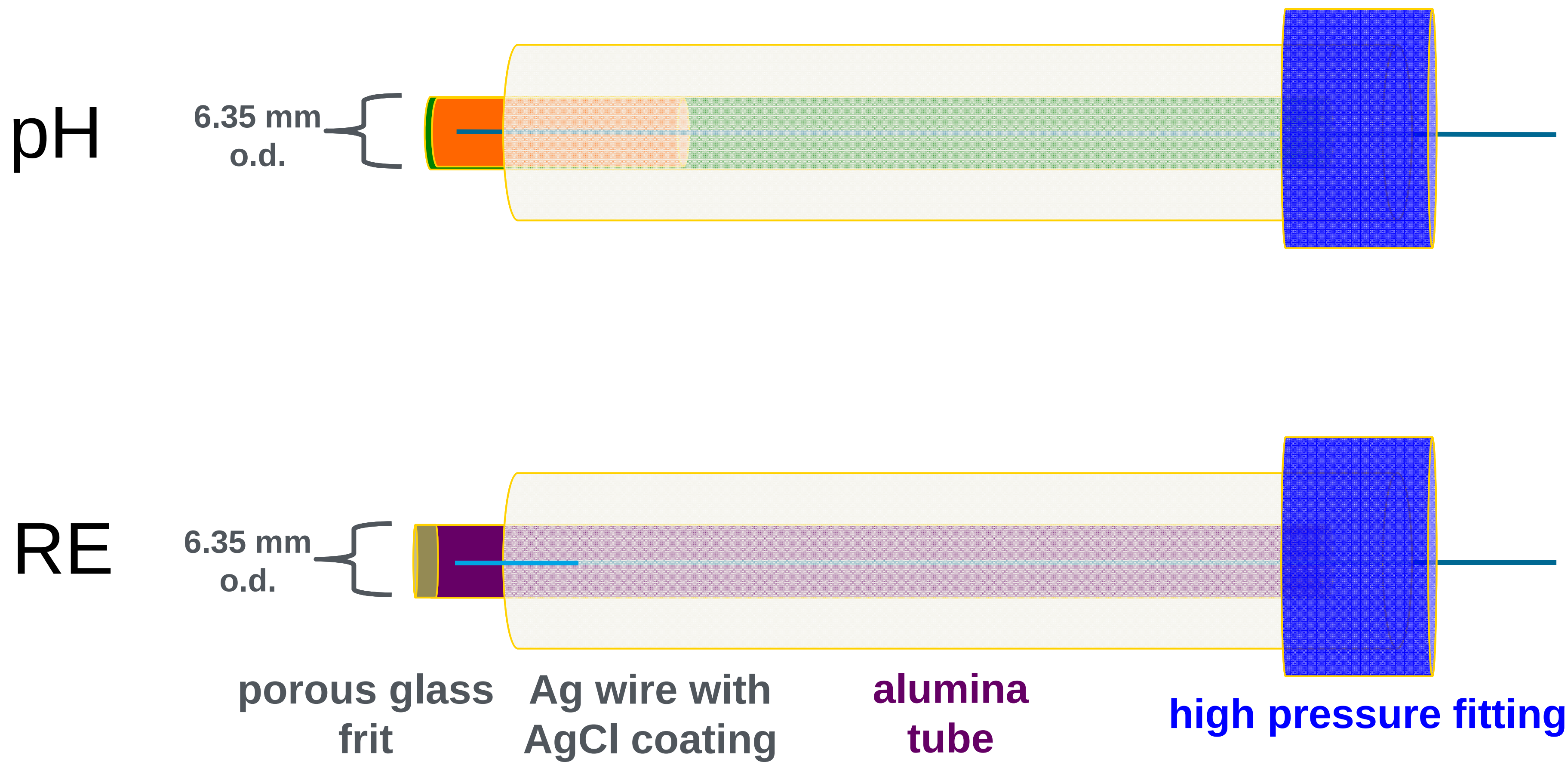
- Temperature **200 °C**
- Pressure **1171 psi**
- Supporting electrolyte 0.01 M KNO_3



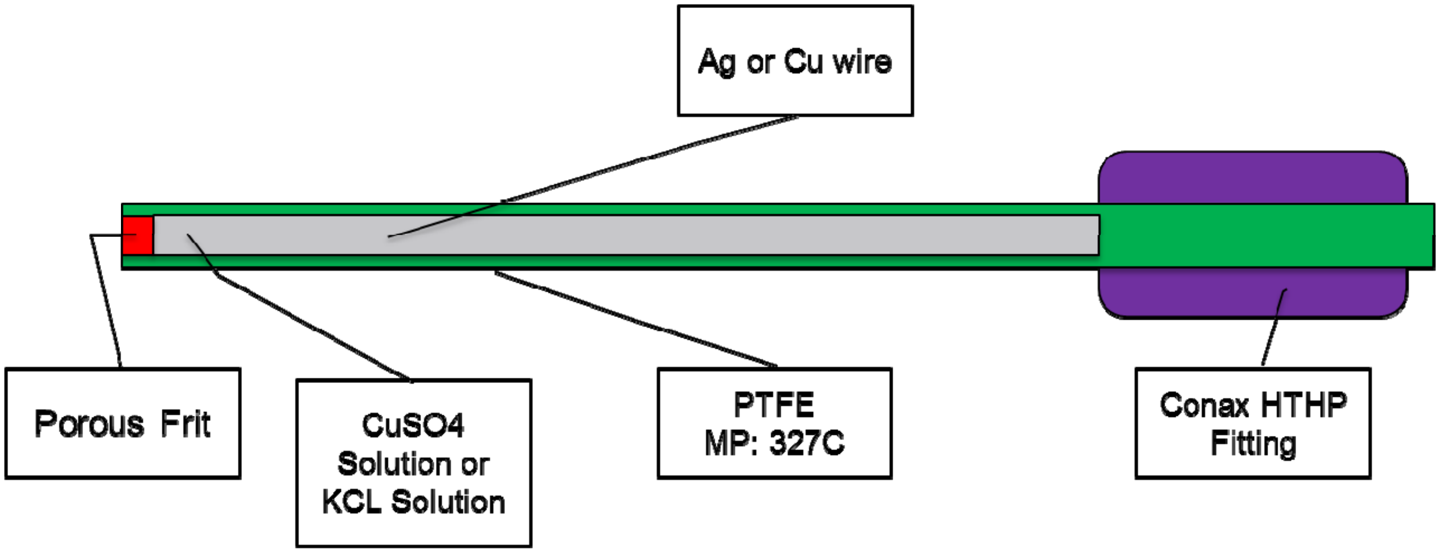
- Linear response between 10^{-4} M and 10^{-2} M iodide
- R^2 of 0.926 and a slope of 63 mV/decade

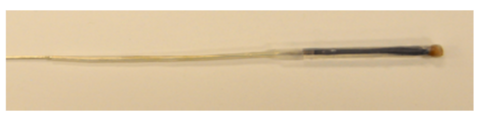
Ruggedized pH and Reference Electrode Design

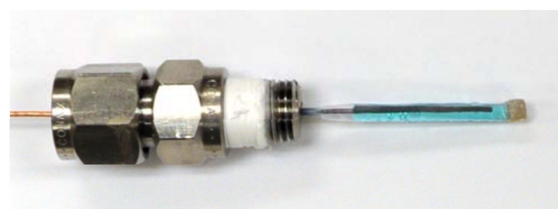
Leveraging work done by Niedrach at GE, Macdonald & Lvov at PSU,
Ding & Seyfried at U of Minnesota, & Jung at the Korea Atomic Energy Research Institute



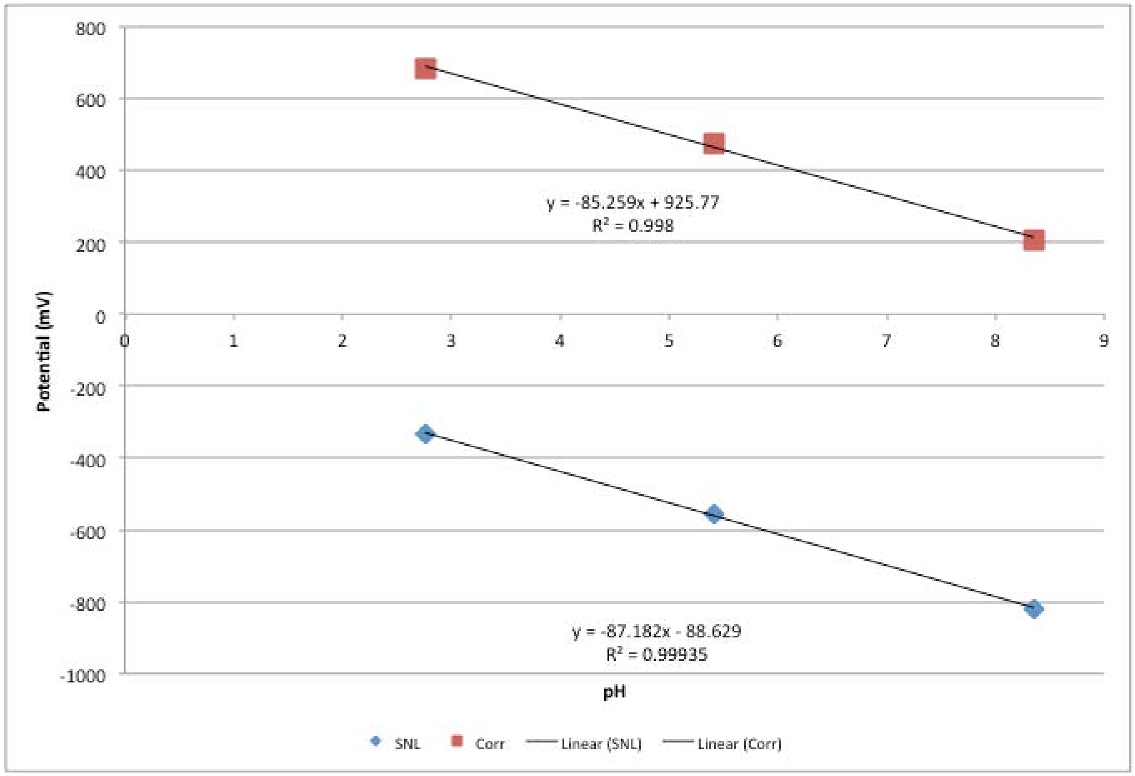
Technical Accomplishments and Progress







pH Electrode at 225ºC and 1500psi

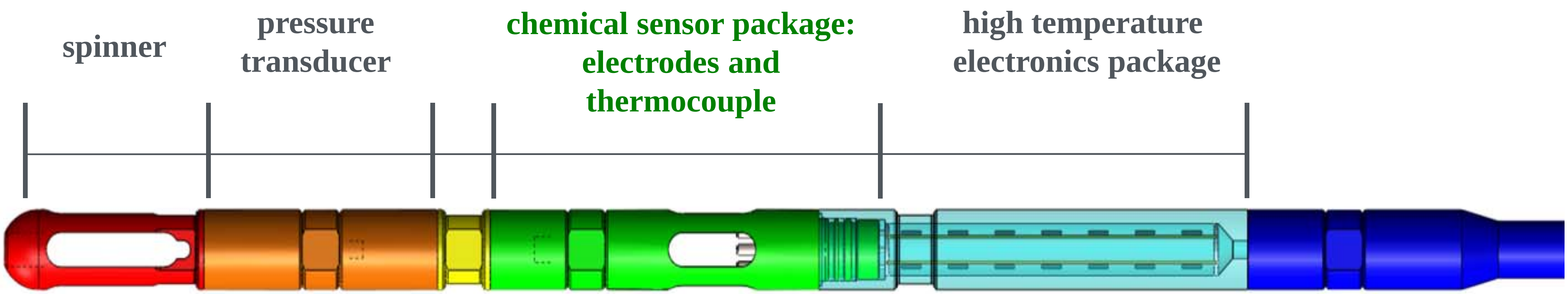


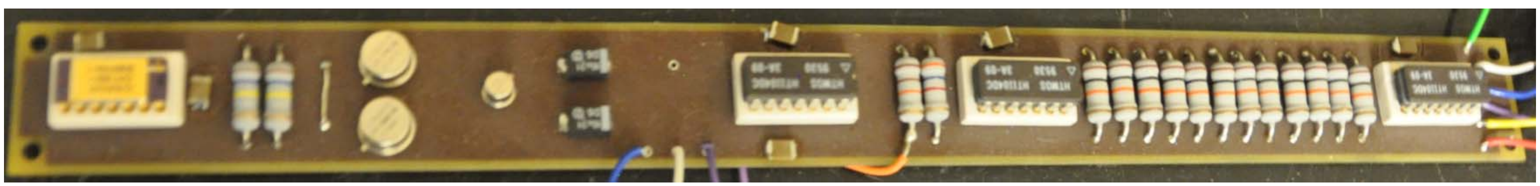
Commercial and Sandia reference electrodes used

pH electrode

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

Technical Accomplishments and Progress





- 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

Technical Accomplishments and Progress

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

- The HT signal conditioning electronics were integrated with Sandia's existing HT logging tool.

- Communication over wireline
  - The tool was programmed and successfully returned data from the electrodes.

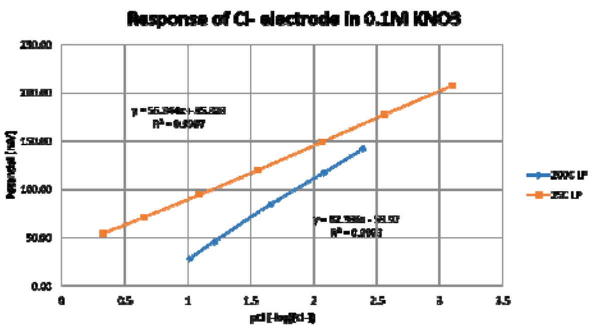
- Mock Borehole test
  - The tool was submerged in surrogate brine in a 44-foot mock borehole
  - 10^{-3} M iodide solution trickled in borehole at 20 ft depth
  - Successful data return and clear detection of leak location
  - No leaks

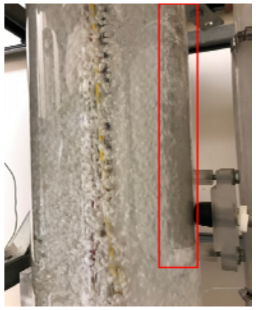
Technical Accomplishments and Progress

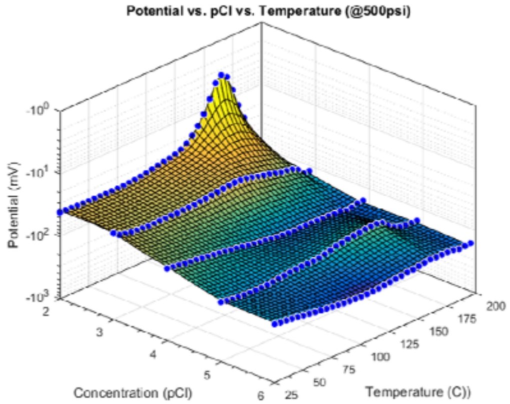
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Original 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	09/2013
FY(14) Exploration of GC-SAW detection for naphthalene sulfonate tracers	Unable to identify suitable approach for GC detection due to low volatility	09/2014
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, liquid reference electrode achieved (solid state on going)	09/2014 with advancements on-going
FY(14) Develop HT electronics capable of interfacing and monitoring developed electrodes	Developed and tested HT electronics which 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	09/2015 with advancements on-going
FY(15) Finalize design of 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	09/2015 with advancements on-going
FY(16) Integrate electrodes and interface electronics into a digitizing wireline tool	Systems were assembled into the existing PT tool and the software/hardware modified to record electrode potentials	09/2016
FY(17) Perform a field test of the completed High Temperature Chemical Sensing Tool (stretch)	Performed an integrated test using wireline truck and running tool in a 44 foot mock well at Sandia. Inlet flow of 10^{-3}M iodide detected at 20 foot depth.	12/2016
FY(17) Replace the pressure-balanced liquid electrode with an all solid-state design	All solid-state electrode designs conceived and tested but FY17 funding delay pushed completion to FY18	On-going (FY18)

- Presentation at Stanford Geothermal Workshop led to LDRD collaboration with Stanford University in development of a chloride sensing tool in application for enthalpy measurement.







Future Directions

Milestone or Go/No-Go	Status & Expected Completion Date
Complete solid-state reference electrode design and testing	(03/2018) Design iteration up to current design was completed in FY17. Current design shows promise up to 225°C.
Complete pH, solid reference, and ISE 3d surface calibration (potential vs. temperature vs. concentration) in autoclave. Complete interference ion analysis.	(06/2018) 3d surface calibration procedure was developed for the enthalpy chloride tool and can be modified for all electrodes
Integrate into final tool and perform mock wellbore test with new systems (stretch)	(09/2018) Electronics are integrated. Wireline truck available.
HT Geothermal Well Testing	(Future) Key potential collaborators have shown interest. Funding will be sought for 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 and drifts predictably with temperature but is still based on balanced liquid. Several solid state designs have been tested and failed. Solid state bimodal pellet design is promising.
- 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.
  - Tested tool on wireline truck in a mock well. Engineered iodide "fracture flow" detected successfully.