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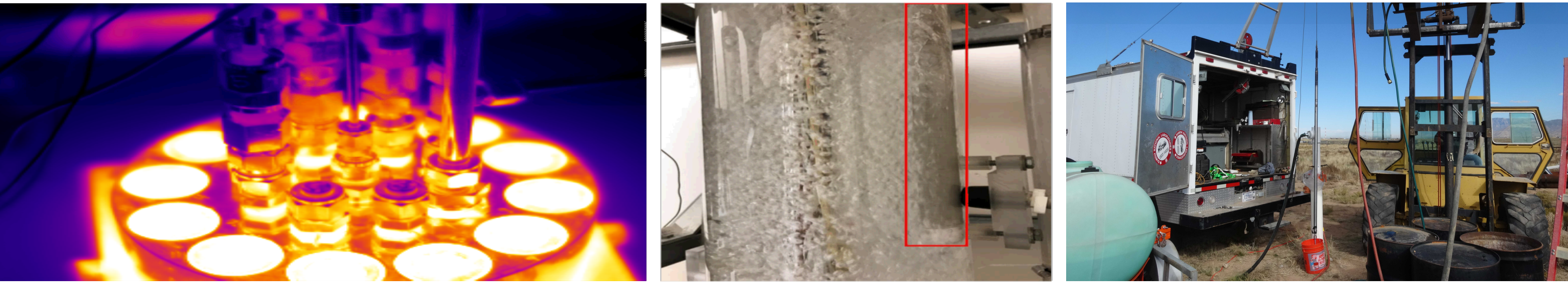

Extreme Environment Electrochemical Sensing Materials

Sasha Egan, William C. Corbin, Ryan Hess,

and Avery T. Cashion

Introduction

- Who are we, what are we doing, and why are we doing it?
  - Sandia National Laboratories
    - Geothermal Research and Development Division
    - Advanced Materials Laboratory
  - Stanford University
    - Department of Energy Resources Engineering

Introduction

GRC *Transactions*, Vol. 38, 2014

Real-Time Downhole Measurement of Ionic Tracer Concentration and pH in Geothermal Reservoirs

Ryan F. Hess[1], Timothy J. Boyle[1], Steven Limmer[1], William G. Yelton[1],
Samuel Bingham[1], Greg Stillman[2], and Grzegorz Cieslewski[1]

[1]Sandia National Laboratories, Albuquerque, NM
[2]Department of Energy, Washington, DC

ABSTRACT

Chemical tracers are commonly used to characterize the fracture network and determine the connectivity between the injection and production wells. Currently, most tracer experiments involve injecting the tracer at the injection well, manually collecting liquid samples at the wellhead of the production well, and sending the samples off for laboratory analysis. While this method provides accurate tracer concentration data at very low levels of detection, it does not provide information regarding the depth of the fractures which were conducting the tracer between wellbores. Sandia is developing a high-temperature electrochemical sensor capable of measuring ionic tracer concentration and pH downhole on a wireline tool. The goal of this effort is to collect real-time pH and ionic tracer concentration data at temperatures up to 225 °C and pressures up to 3000 psi. In this paper, a prototype electrochemical sensor and the initial data obtained will be presented detailing the measurement of iodide tracer concentrations at high temperature and pressure in a newly developed laboratory scale autoclave. Efforts to expand this tool to measure lithium, cesium, and fluoride ion tracers will be discussed as well.

Introduction

Successful development of geothermal power plants is dependent on understanding the underground reservoir properties such as the extent and interconnectivity of rock fractures. One method employed to elucidate the fracture network between production and injection wells is to monitor the flow of tracers between the wells. Figure 1 contains a notional diagram of how three wells might be interconnected. Currently, tracer return curves are measured by collected samples from the wellhead manually. These samples are then sent to a laboratory where the tracer concentration is measured by techniques such as inductively coupled plasma – mass spectrometry (ICP-MS), ICP-Optical Emission Spectroscopy (ICP-OEC), Ion Chromatography (IC), High Performance Liquid Chromatography (HPLC) with fluorescence detection.

While this method of tracer sampling and detection is able to achieve very low limits of detection (LOD), on the order of parts per billion, it has two drawbacks. One is that it provides a depth-averaged value for tracer concentration, the operator does not know which fractures are the ones producing that tracer response. The other drawback is that while lab-based techniques have great LODs it often takes days to weeks for the operator to receive all of the data necessary to build tracer response curves.

A downhole, real-time tool that is capable of measuring the pressure-temperature dependent concentration of ionic geothermal tracers (i.e., as iodide) is being developed. This sensor will allow for a more accurate generation of tracer return curves with depth information as well as measuring the pH of the fluid under actual temperature and pressure conditions. This is important since it is difficult to accurately reconstruct what the actual pH at depth based on samples which have been cooled and depressurized because the solution pH is highly dependent on localized chemical species, which in turn are dependent on temperature and pressure. Iodide ions have been used in a number of geothermal tracer tests including studies in Iceland and Japan.[2,3] In the test conducted in Iceland, 45.3 kg was injected in one well and samples were collected in production wells nearby. The authors of that study measured production well iodide tracer concentrations on the order of 10's ppm.

Figure 1. Department of Energy drawing showing the relationship between injection and production wells in an Engineered Geothermal System.[1])

- 2014: Development and characterization of an iodide ion selective electrode for use in reservoir tracer experiments (I-ISE) (polycrystalline silver iodide – silver sulfide)[1,2] US Patent and Trademark Office Provisional Application 61983234 , April 2014

Introduction

PROCEEDINGS, Fourtieth Workshop on Geothermal Reservoir Engineering
Stanford University, Stanford, California, January 26-28, 2015
SGP-TR-204

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

Ryan F. Hess, Timothy J. Boyle, Steven Limmer, William G. Yelton, Samuel Bingham, Greg Stillman, and Grzegorz Cieslewski
Sandia National Laboratories, P.O. Box 5800, Albuquerque, NM 87185
rfhess@sandia.gov

Keywords: tracer, pH, tool, sensor, instrument, high temperature electronics

ABSTRACT

Chemical tracers are commonly used to characterize the fracture network and determine the connectivity between the injection and production wells in geothermal reservoirs. Currently, most tracer experiments involve injecting the tracer at the injection well, manually collecting liquid samples at the wellhead of the production well, and sending the samples off for laboratory analysis. While this method provides accurate tracer concentration data at very low levels of detection, it does not provide information regarding the location of the fractures which were conducting the tracer between wellbores. Sandia is developing a high-temperature wireline tool capable of measuring tracer concentrations and pH downhole using electrochemical sensors. The goal of this effort is to collect real-time pH and ionic tracer concentration data at temperatures up to 225 °C and pressures up to 3000 psi. A prototype electrochemical sensor and the initial data obtained will be presented detailing the measurement of iodide tracer concentrations and pH at high temperature and pressure in a recently developed laboratory scale autoclave.

1. INTRODUCTION

Tracer tests can be used to elucidate key properties of geothermal reservoirs such as the connectivity of fractures between injection and production wells. A typical tracer test involves injecting a know quantity of tracer in one well and monitoring both the time it takes for the tracer to appear in a recovery well and the quantity of tracer recovered at that well. Currently, the tracer recovered at nearby wells is measured by collecting a liquid or gas sample at the wellhead after passing through a cooling coil. The sample is then sent to an off-site laboratory for analysis, which may take days to weeks depending on location. While this approach does provide valuable data it does not allow one to determine the depth of the fractures actually producing fluid between the injection and recovery wells. Because the data is collected at the wellhead, the measured tracer concentration represents a depth-averaged value. One approach that may allow for the identification of specific fractures linking the injection and recovery wells together is to measure the tracer concentration downhole and in real-time. The resulting data would allow one to plot the concentration of the tracer recovered versus the depth the measurement was taken thereby identifying the specific fractures connecting the wells together. Figure 1 contains notional tracer response curves generated when data is collected at the wellhead and what is expected from data collected downhole.

Figure 1: a.) Notional depth-averaged tracer response curve generated when tracer concentration is measured at the wellhead, b.) Notional tracer response curve generated when tracer concentration data is collected a various depths using a wireline tool. C is the concentration of tracer sampled at the recovery wellhead and C_o is the initial concentration of the tracer injected.

To accomplish our goal we have been developing a wireline tool containing a ruggedized electrochemical ion selective electrode capable of measuring certain ionic tracers in real-time along with in-situ pH, temperature, pressure, and flowrate measurements. Efforts to develop a downhole tool to measure iodide ions used as tracers and pH under conditions up to 225 °C and 3000 psi is discussed. Given the harsh environment found in typical geothermal reservoirs – corrosive brine at high temperatures and pressures – many typical analytical detection methods would not be suitable. Using ion selective and pH electrodes has the advantage of needing no moving parts and requires relatively straightforward data processing that can be accomplished downhole. However, ion selective membranes capable of surviving high temperatures have to be identified and modified for use downhole.

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543

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- 2015: Wireline tool with high-temperature electronics is under development while lab tests are continued to assess the capabilities of measuring other ions.[3]

- 2015: Related partnership with Stanford University (LDRD funded) began for measuring wellbore chloride concentrations and relating them to enthalpy.
- US Patent and Trademark Office Provisional Application 62454194 , Feb 2017

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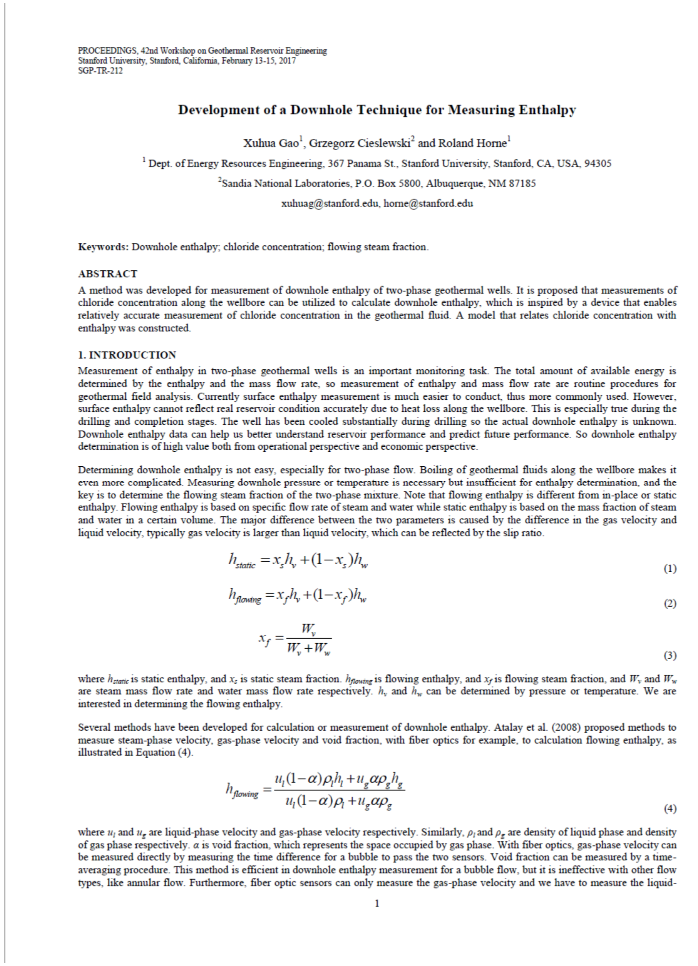
- 2016: Successful field test of a full-scale wireline tool which implemented the I-ISE sensor.

Enthalpy Measurement

2017: Stanford develops the model for measuring the enthalpy of two-phase flow using a chloride selective electrode (Cl-ISE) and Sandia develops the sensors and tool. [4,5]



PROCEEDINGS, 42nd Workshop on Geothermal Reservoir Engineering
Stanford University, Stanford, California, February 13-15, 2017
SGP-TR-212

Development of a Downhole Technique for Measuring Enthalpy

Xuhua Gao[1], Grzegorz Cieslewski[2] and Roland Horne[1]

[1] Dept. of Energy Resources Engineering, 367 Panama St., Stanford University, Stanford, CA, USA, 94305

[2]Sandia National Laboratories, P.O. Box 5800, Albuquerque, NM 87185

xuhuag@stanford.edu, horne@stanford.edu

Keywords: Downhole enthalpy; chloride concentration; flowing steam fraction.

ABSTRACT

A method was developed for measurement of downhole enthalpy of two-phase geothermal wells. It is proposed that measurements of chloride concentration along the wellbore can be utilized to calculate downhole enthalpy, which is inspired by a device that enables relatively accurate measurement of chloride concentration in the geothermal fluid. A model that relates chloride concentration with enthalpy was constructed.

1. INTRODUCTION

Measurement of enthalpy in two-phase geothermal wells is an important monitoring task. The total amount of available energy is determined by the enthalpy and the mass flow rate, so measurement of enthalpy and mass flow rate are routine procedures for geothermal field analysis. Currently surface enthalpy measurement is much easier to conduct, thus more commonly used. However, surface enthalpy cannot reflect real reservoir condition accurately due to heat loss along the wellbore. This is especially true during the drilling and completion stages. The well has been cooled substantially during drilling so the actual downhole enthalpy is unknown. Downhole enthalpy data can help us better understand reservoir performance and predict future performance. So downhole enthalpy determination is of high value both from operational perspective and economic perspective.

Determining downhole enthalpy is not easy, especially for two-phase flow. Boiling of geothermal fluids along the wellbore makes it even more complicated. Measuring downhole pressure or temperature is necessary but insufficient for enthalpy determination, and the key is to determine the flowing steam fraction of the two-phase mixture. Note that flowing enthalpy is different from in-place or static enthalpy. Flowing enthalpy is based on specific flow rate of steam and water while static enthalpy is based on the mass fraction of steam and water in a certain volume. The major difference between the two parameters is caused by the difference in the gas velocity and liquid velocity, typically gas velocity is larger than liquid velocity, which can be reflected by the slip ratio.

$$h_{static} = x_s h_v + (1 - x_s) h_w \tag{1}$$

$$h_{flowing} = x_f h_v + (1 - x_f) h_w \tag{2}$$

$$x_f = \frac{W_v}{W_v + W_w} \tag{3}$$

where h_{static} is static enthalpy, and x_s is static steam fraction. $h_{flowing}$ is flowing enthalpy, and x_f is flowing steam fraction, and W_v and W_w are steam mass flow rate and water mass flow rate respectively. h_v and h_w can be determined by pressure or temperature. We are interested in determining the flowing enthalpy.

Several methods have been developed for calculation or measurement of downhole enthalpy. Atalay et al. (2008) proposed methods to measure steam-phase velocity, gas-phase velocity and void fraction, with fiber optics for example, to calculation flowing enthalpy, as illustrated in Equation (4).

$$h_{flowing} = \frac{u_l(1-\alpha)\rho_l h_l + u_g \alpha \rho_g h_g}{u_l(1-\alpha)\rho_l + u_g \alpha \rho_g} \tag{4}$$

where u_l and u_g are liquid-phase velocity and gas-phase velocity respectively. Similarly, ρ_l and ρ_g are density of liquid phase and density of gas phase respectively. α is void fraction, which represents the space occupied by gas phase. With fiber optics, gas-phase velocity can be measured directly by measuring the time difference for a bubble to pass the two sensors. Void fraction can be measured by a time-averaging procedure. This method is efficient in downhole enthalpy measurement for a bubble flow, but it is ineffective with other flow types, like annular flow. Furthermore, fiber optic sensors can only measure the gas-phase velocity and we have to measure the liquid-

PROCEEDINGS, 42nd Workshop on Geothermal Reservoir Engineering
Stanford University, Stanford, California, February 13-15, 2017
SGP-TR-212

Development of a Downhole Tool for Measuring Enthalpy in Geothermal Reservoirs

William C. Corbin, Grzegorz Cieslewski, Ryan F. Hess, Bonnie E. Klamm, Lauren Goldfarb, Timothy J. Boyle, William G. Yelton, Avery T. Cashion

Sandia National Laboratories, Advanced Materials Laboratory, 1001 University Blvd. SE, Albuquerque, New Mexico, 87106

rfhess@sandia.gov

Keywords: enthalpy, geothermal reservoirs, tool, sensor, instrument, high temperature electronics

ABSTRACT

The amount of thermal energy (enthalpy) contained in geothermal fluid is one of the key parameters used to determine the value of a geothermal resource and vital in understanding the performance of existing reservoirs. The enthalpy of a single-phase fluid can be determined from the temperature, pressure and flow rate of the fluid; however, geothermal fluid flow often is multi-phased and enthalpy calculations require knowledge of the steam fraction and flow rate of each phase. Current surface-based methods for measuring enthalpy are expensive and complicated while providing an incomplete view of the wellbore. Downhole measurement of enthalpy would provide a better understanding of the geothermal resource and allow for improved measurement of energy produced from different fracture zones.

We are developing a method and apparatus for measuring the downhole enthalpy of a flowing geothermal fluid in real-time at high-temperature and pressure. Our method involves measuring the concentration of selected naturally occurring ions found in the liquid phase of the geothermal fluid throughout the wellbore using a novel electrochemical sensor technologies. Capabilities developed by Sandia for robust electrochemical sensing of geothermal environments (funded by DOE-GTO) are leveraged in support of enthalpy measurements. The change in liquid-phase ion concentration will be used to calculate the proportion of liquid to steam and allow for accurate enthalpy measurements. While benchtop instrumentation exists for routinely measuring ion concentration under ambient conditions, the sensing materials and supporting electronic components in these devices are unable to survive in the harsh environments found downhole. Results of the electrochemical sensor development effort will be discussed. Beyond enthalpy assessment, many techniques and technologies described here can be applied to any application of electrochemical sensing in extreme environments.

1. INTRODUCTION

The determination of downhole enthalpy is of major interest due to the renewable energy of associated with geothermal reservoirs. Investigating the practicality and accuracy of enthalpy measurements requires evaluation of two-phase, steam-water distribution and flow in the wellbore. The location and extent of boiling will exert a significant influence on the concentration of ions in the liquid phase. Similarly, wellbore heat loss will cause condensation which will also influence the steam-water ratio and hence the ion concentration. This fraction is a key parameter for calculating enthalpy in a multiphase flow.

Current methods for measuring the total enthalpy (H) of geothermal fluids are conducted using surface based instrumentation and have a number of drawbacks. A common method used by the industry is the tracer dilution technique and involves precise continuous injection of tracers into the surface pipeline and concurrent sampling downstream from the injection point. The samples then have to be cooled and depressurized to be analyzed in an off-site laboratory. Cooling and pressure change can cause errors in measurement of tracers. Other methods for measuring enthalpy at the surface involve measuring resistivity and acoustic waves. The resistivity method measures resistance of the flowing two-phased fluid and correlates it to the steam-water present. While this approach can yield meaningful results it is not suitable for all types of two-phase flow. The acoustic method involves generating and recording acoustic waves at a particular chosen frequency. The received amplitude is then correlated with the two-phase flow rate. The results published show good correlation; however, a careful calibration is required as well as selection of the optimal frequency. Finally, there have been attempts at measuring the downhole enthalpy in the past using optical methods. Optical methods involve measuring the refractive index at of the fluid at the tip of a very thin fiber optic probe. As steam bubbles pass by the tip of the probe, a change in refractive index is observed. Based on this measurement, the steam-water ratio can be determined. While this technique showed promise in a laboratory setting it would have limited utility in a downhole setting due to effects of geothermal fluid on the probe and fiber optic cable. Such a tool would be susceptible to hydrogen darkening making the fiber measurement more difficult. Additionally the method needs to be calibrated with flow velocity.

The electrochemical sensor section of our wireline tool will consist of two ruggedized electrodes: a chloride ion selective electrode (Cl-ISE) and a reference electrode. In addition to the electrodes themselves we developed a data acquisition and processing system capable of functioning at high temperatures without the use of a Dewar. Finally, technologies and methods associated with a previously developed electrochemical tool at Sandia will be incorporated into the new tool. Therefore, at each depth a measurement is taken, chloride concentration, temperature, pressure, and flowrate data will be acquired allowing the determination of enthalpy in the geothermal fluid. For detailed analysis of application of this technique to improving wellbore measurements of enthalpy, see recent work published by Gao and Horne from Stanford, whom with we are currently collaborating.

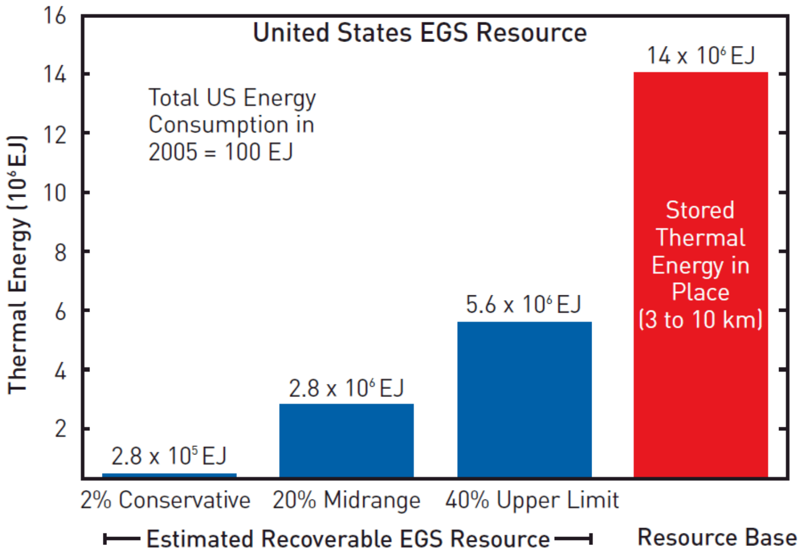
Borehole Enthalpy

- The amount of thermal energy available is a critical parameter to determining the value of a geothermal resource. (Enthalpy)
- Downhole enthalpy and real-time monitoring is considered high value/critical data. (Production predictions, reservoir performance, fracture mapping, flow mapping)
- Enhanced Geothermal Systems (EGS)
  - 2006 U.S. Department of Energy funded a comprehensive report

"The Future of Geothermal Energy – Impact of Enhanced Geothermal Systems (EGS) on the United States in the 21st *Century"*

Introduction

- Enhanced Geothermal Systems (EGS) (cont'd):
  - The 18-member panel concluded:



1. 2,800 times more energy consumed in all of 2005 is available at the most conservative level of estimation.
2. Electricity production for as low as 3.9 cents per kWh.
3. R&D investment potential of about $1 billion dollars over 15 years.

Goals, Development and Application

- Polycrystalline membranes
  - Iodide Selective Electrode (I-ISE)[6]
    - Not really a new technology (Orion, 1966)
    - Still highly relevant to practical application

- Requirements:
  - Solid-state material must be
    1. a good ionic conductor
    2. chemically inert in solution

       (Ag2S: Insoluble in acids/bases/NH+)
    3. possess low-solubility

       (Ag2S: Ksp = 6.1x10^50)

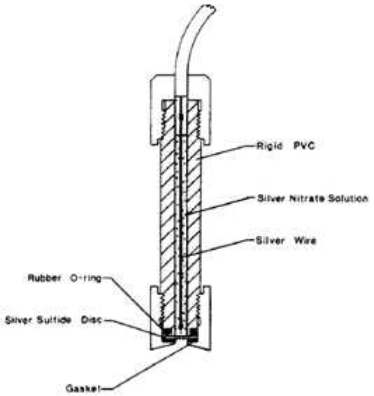
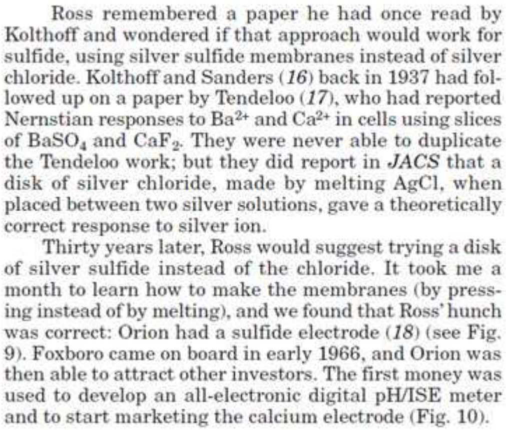


Figure 9. The first sulfide electrodes were made as shown above. This schematic drawing was used for a paper at the Eastern Analytical Conference in 1966, describing the new electrode.



Ross remembered a paper he had once read by Kolthoff and wondered if that approach would work for sulfide, using silver sulfide membranes instead of silver chloride. Kolthoff and Sanders (*16*) back in 1937 had followed up on a paper by Tendeloo (*17*), who had reported Nernstian responses to Ba^{2+} and Ca^{2+} in cells using slices of $BaSO_4$ and CaF_2. They were never able to duplicate the Tendeloo work; but they did report in *JACS* that a disk of silver chloride, made by melting AgCl, when placed between two silver solutions, gave a theoretically correct response to silver ion.

Thirty years later, Ross would suggest trying a disk of silver sulfide instead of the chloride. It took me a month to learn how to make the membranes (by pressing instead of by melting), and we found that Ross' hunch was correct: Orion had a sulfide electrode (*18*) (see Fig. 9). Foxboro came on board in early 1966, and Orion was then able to attract other investors. The first money was used to develop an all-electronic digital pH/ISE meter and to start marketing the calcium electrode (Fig. 10).

Goals, Development and Application

- Polycrystalline membranes (continued)
  - Chloride Selective Electrode (Cl-ISE)
  - Currently evaluating two other silver chalcogenides

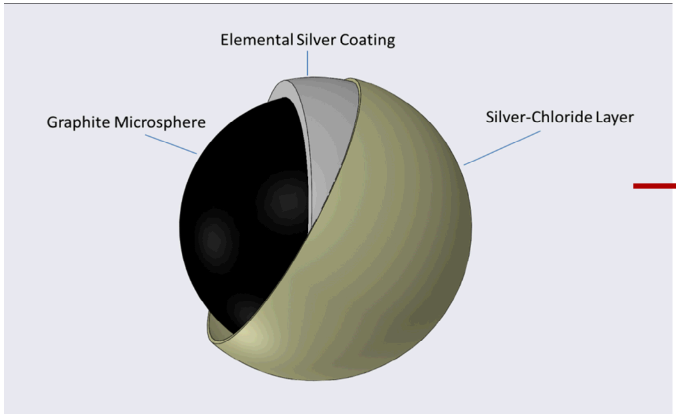
So… what is going on at the fundamental level?

Theoretical Mechanism

- Frenkel defects are a type of point defect
  - Overall neutrality has to be maintained
  - Density does not decrease
  - Cation is highly mobile
    - Anion lattice remains relatively rigid
    - Cation jumps into interstitial location
    - Electron remains associated to the interstitial void
  - These defects make it possible for atoms or ions to move through diffusion through the lattice.
    - Ionic conductivity

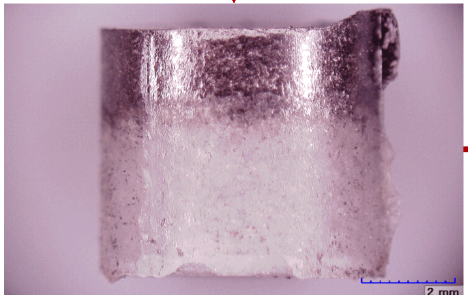
- So what does this lead to?

Sandia Ion-Selective and Reference Electrodes

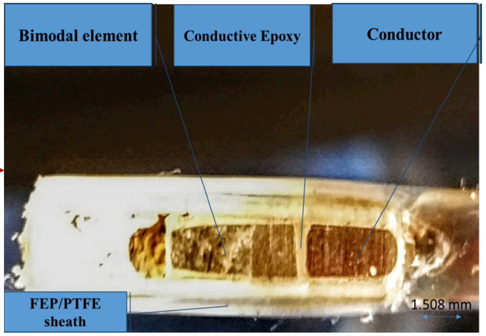


Engineered Particles (powder)

Press 8h @5 Tons



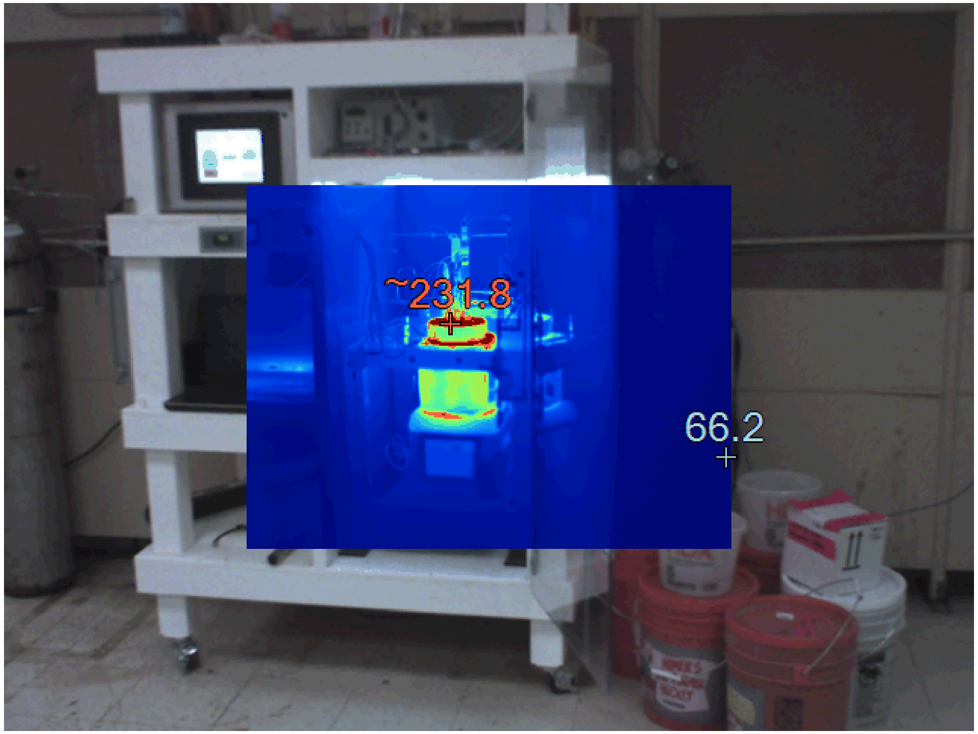
Electrode Pellet



Electrode Assembly

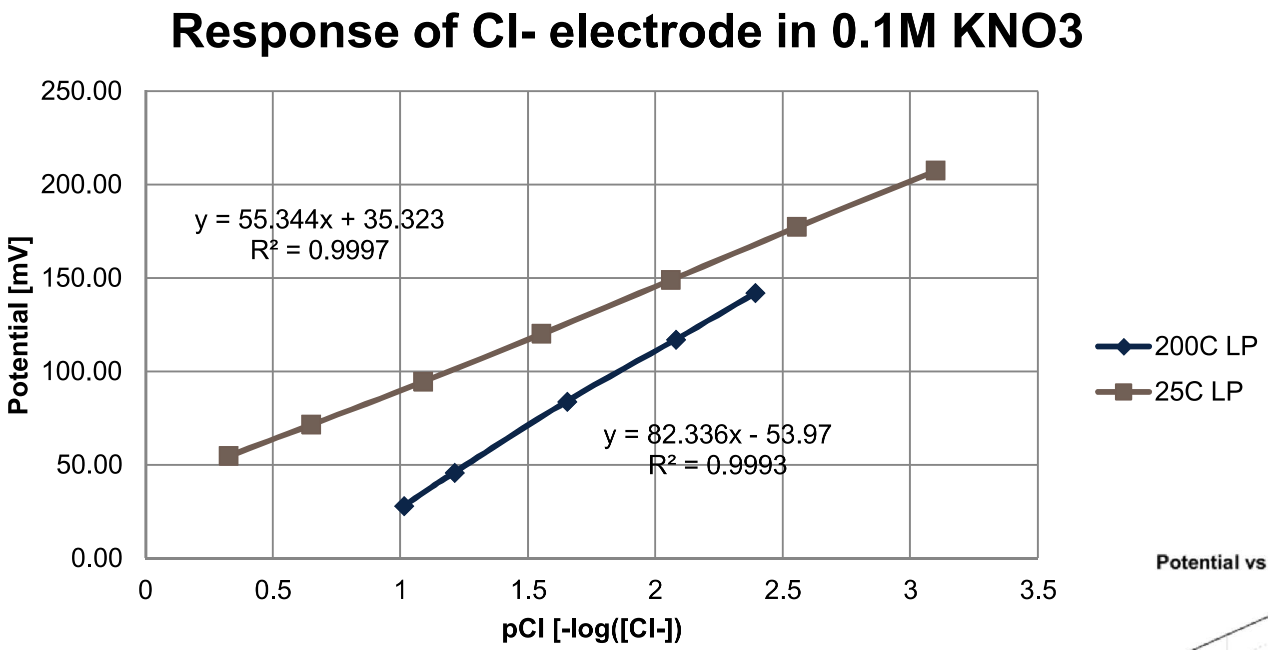
Sandia Pressure Vessel Test

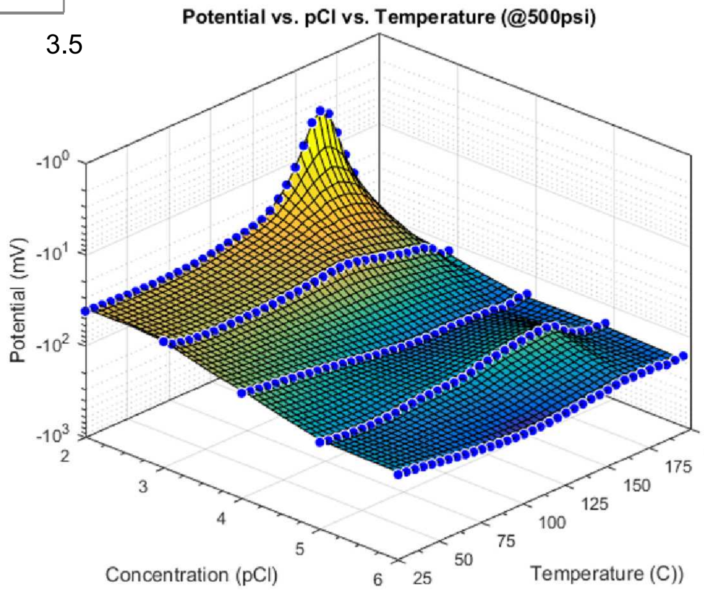
- Electrodes are assembled in pressure vessel port hardware
- PTFE liner in the pressure vessel is filled with test solution
- Pressure vessel is pressurized to up to 1700psi and heated to up to 210°C
- Ion-Selective electrode potentials are recorded on National Instruments DAQ hardware



Thermal image of heating pressure vessel (°F)

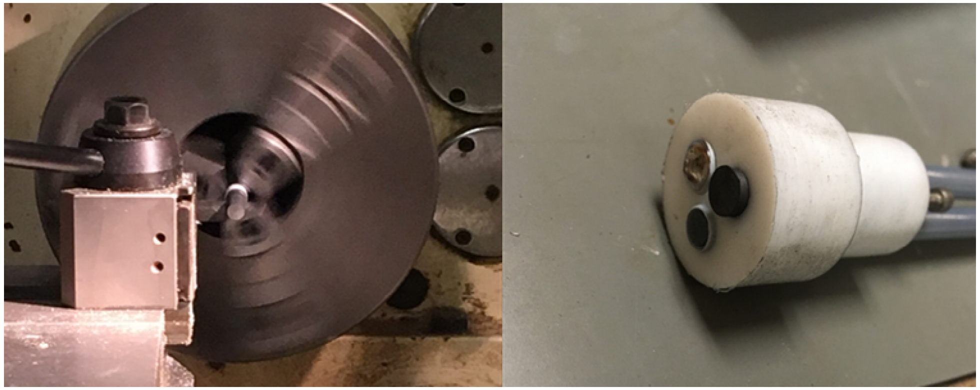
HT Cl- Electrode at 25˚C and 200˚C

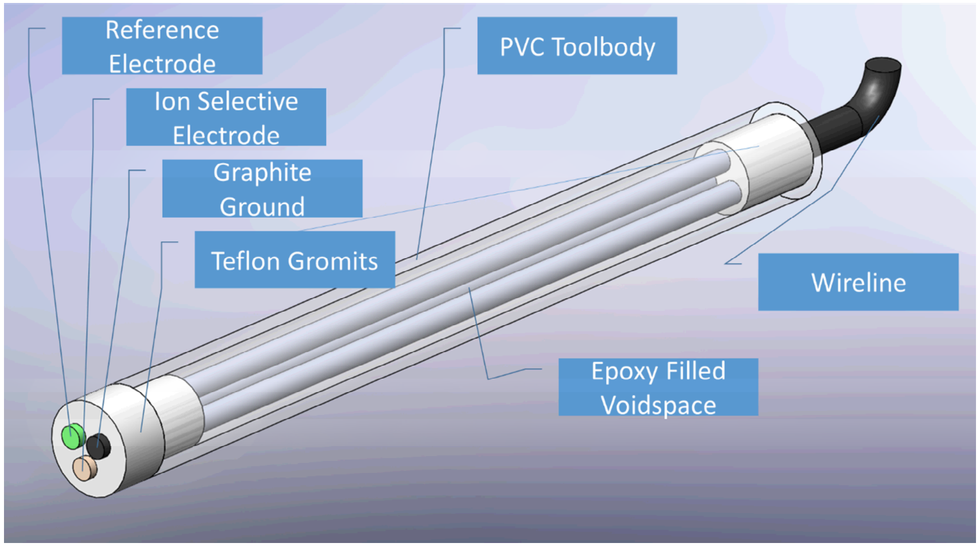




- Repeatable response (low hysteresis)
- Theoretical max slope @25C = 59.1mV/decade
- Theoretical max slope @200C = 93.92mV/decade
- Calibration for temperature is necessary.

Wireline Tool for the Mock Well





Reference Electrode

Ion Selective Electrode

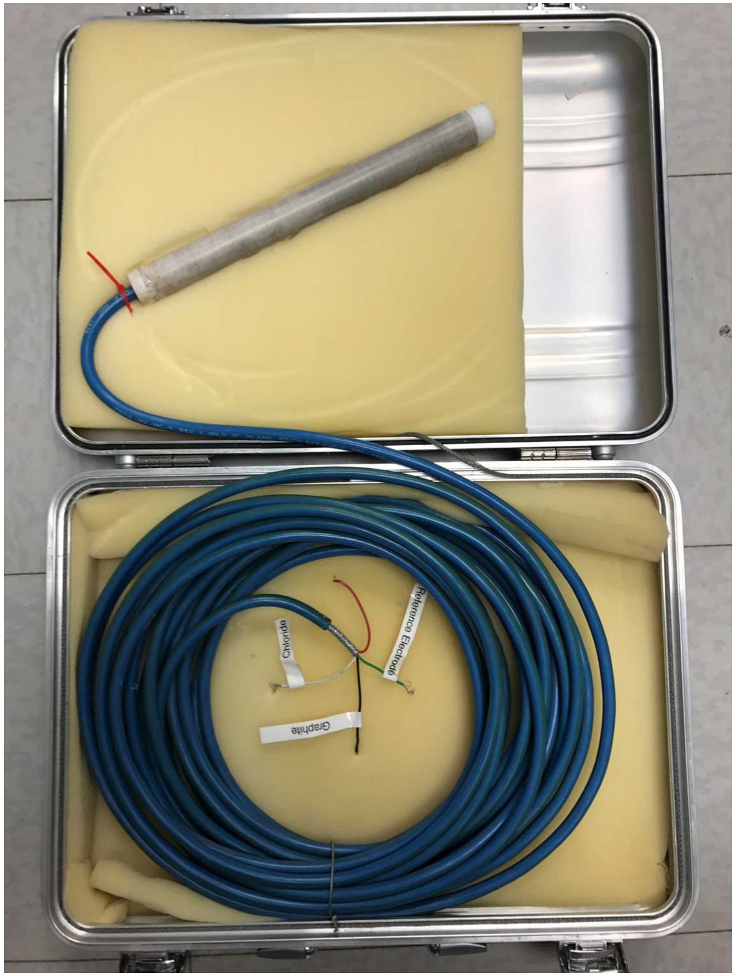
Graphite Ground

Teflon Gromits

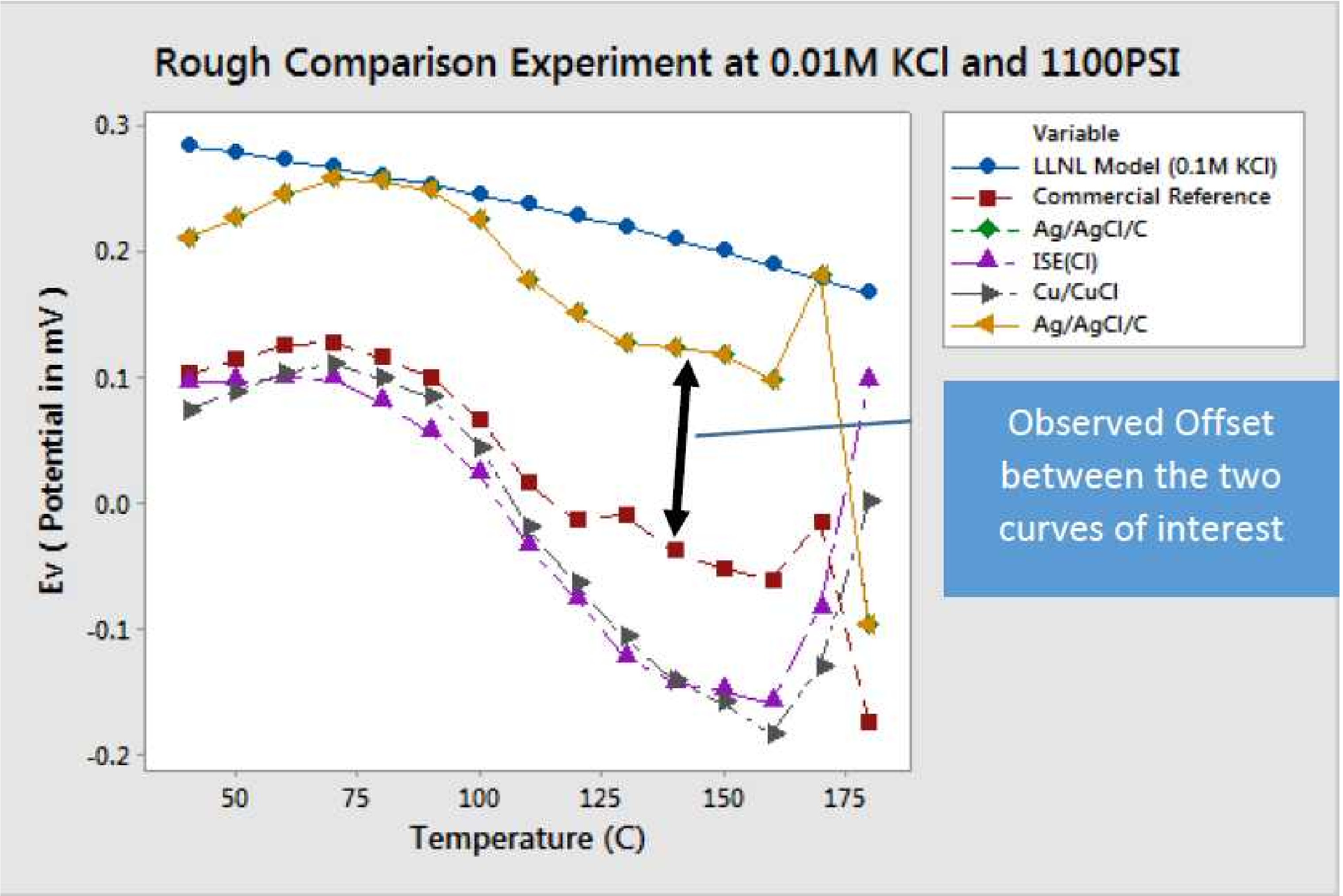
PVC Toolbody

Wireline

Epoxy Filled Voidspace



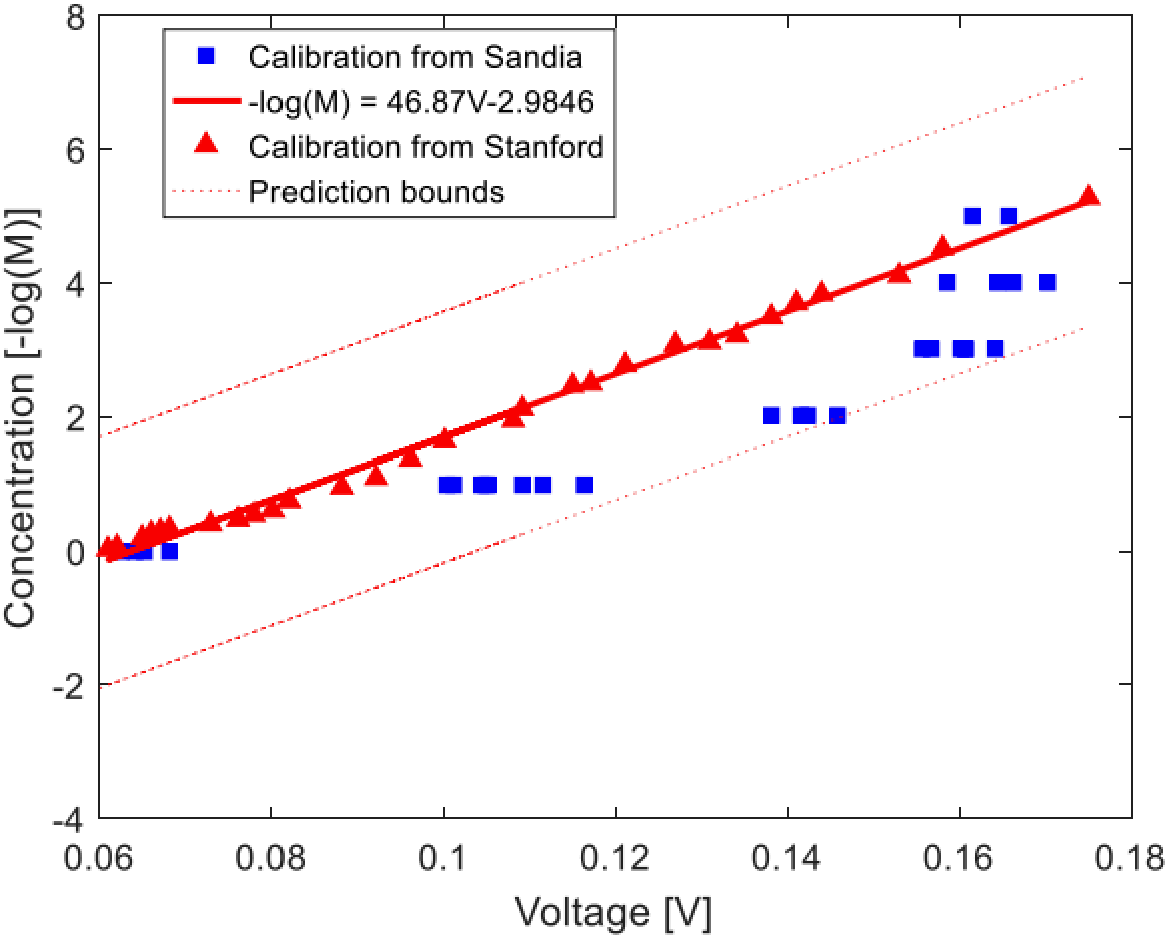
Solid State Reference Electrode



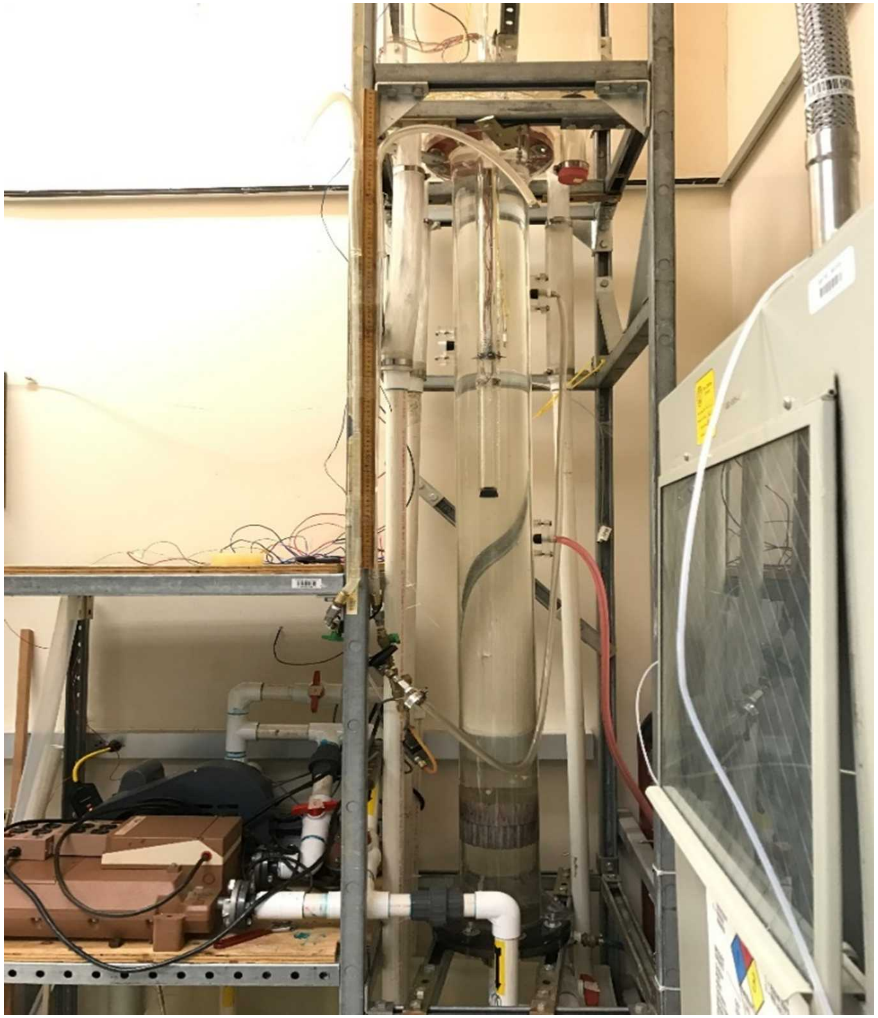
Observed Offset between the two curves of interest

Calibration at Stanford

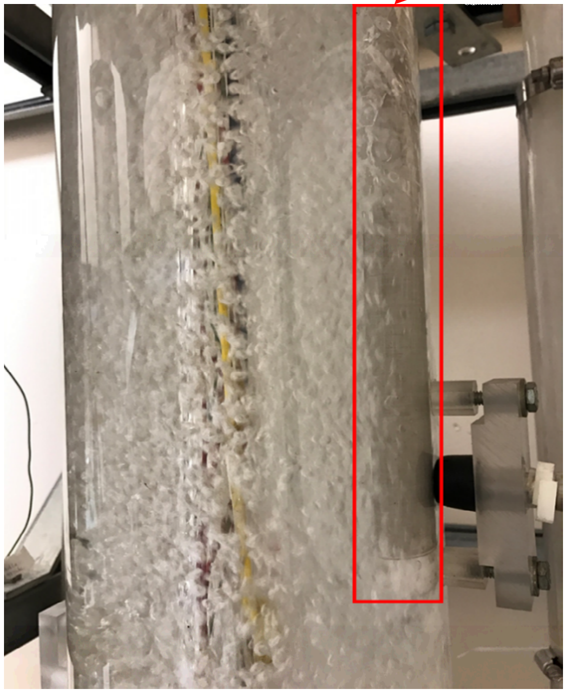
Concentration calibration curve for the tool obtained from Stanford prior to multiphasic flow experiment



Stanford Multiphase Flow Chamber



Wireline tool for mock well



Bibliography

1. F. Hess, Ryan & J. Boyle, Timothy & Limmer, Steven & Yelton, W & Bingham, Samuel & Stillman, Greg & Lindblom, Scott & Cieslewski, Grzegorz. (2014). Development of a downhole tool measuring real-time concentration of ionic tracers and pH in geothermal reservoirs. Proceedings of SPIE - The International Society for Optical Engineering. 9113. 91130J. 10.1117/12.2051151.
2. Hess, R., Boyle, T., Limmer, S., Yelton, W., Bingham, S., Stillman, G., Lindblom, S. and Cieslewski, G. (2014). Development of a downhole tool measuring real-time concentration of ionic tracers and pH in geothermal reservoirs. Sensors for Extreme Harsh Environments. [online] Available at: https://www.osti.gov/scitech/servlets/purl/1241727 [Accessed 6 Oct. 2017].
3. Hess, R., Boyle, T., Limmer, S., Yelton, W., Bingham, S., Stillman, G., Lindblom, S. and Cieslewski, G. (2014). Measuring real-time concentration of ionic tracers and pH in geothermal reservoirs. Sensors for Extreme Harsh Environments. [online] Available at: https://www.osti.gov/scitech/servlets/purl/1244897 [Accessed 6 Oct. 2017].
4. Gao, X. (2017). Development of a Downhole Technique for Measuring Enthalpy in Geothermal Wells. [online] Stanford University. Available at: https://earth.stanford.edu/researchgroups/geothermal/sites/default/files/SGP-TR-210_0.pdf [Accessed 6 Oct. 2017].
5. Stanford University. (2017). Development of a Downhole Tool for Measuring Enthalpy in Geothermal Reservoirs. [online] Available at: https://pangea.stanford.edu/ERE/db/GeoConf/papers/SGW/2017/Corbin.pdf [Accessed 6 Oct. 2017].
6. Frant, M. (1997) "Where Did Ion Selective Electrodes Come From? The Story of Their Development and Commercialization", Journal of Chemical Education, 74(2), p. 159. doi: 10.1021/ed074p159.