2017 PROJECT PEER REVIEW
U.S. DEPARTMENT OF ENERGY
GEOTHERMAL TECHNOLOGIES OFFICE

SAND2017-11000R

Summary: High Temperature Chemical Sensing Tool

1. **High Temperature Chemical Sensing Tool for Distributed Mapping of Fracture Flow in EGS**

   - Organization or Affiliation: Sandia National Laboratories[1], Albuquerque NM
   - Principal Investigator: Avery "Zack" Cashion
   - Contact information: atcashi@sandia.gov
   - Project Team: Grzegorz Cieslewski, Ryan Hess, Cody Corbin, Sasha Egan, Timothy Boyle, Steven Limmer, William Yelton, Samuel Bingham, Douglas Blankenship

   - Project Start and End Date: 10/2012– 09/2018
2. **Project Objectives and Purpose**
   Chemical tracers are commonly used to characterize fracture networks and to 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, it does not provide information regarding the location of the fractures conducting the tracer between wellbores.
   The goal of this project is to develop chemical sensors and design a prototype tool to help understand the fracture properties of a geothermal reservoir by monitoring tracer concentrations along the depth of the well. The sensors will be able to detect certain species of the ionic tracers (mainly iodide) and pH in-situ during the tracer experiment. The proposed high-temperature (HT) tool will house the chemical sensors as well as a standard logging sensor package of pressure, temperature, and flow sensors in order to provide additional information on the state of the geothermal reservoir. The sensors and the tool will be able to survive extended deployments at temperatures up to 225 °C and high pressures to provide real-time temporal and spatial feedback of tracer concentration. Data collected from this tool will allow for the real-time identification of the fractures conducting chemical tracers between wellbores along with the pH of the reservoir fluid at various depths.
3. **Project Timeline (with milestones and/or decision points, as applicable)**
   During the first year to this project (FY13) Sandia investigated multiple technologies which could be used to detect tracers of interest. The first focus was the ionic tracers and using electrochemical methods for detection. The second focus was on naphthalene sulfonate tracers in conjunction with surface acoustic wave (SAW) technology for detection. The selection of appropriate ionic tracers and the proper sensing membrane for electrodes continued into the beginning of FY14 when an inorganic sensing membrane capable of sensing iodide was selected for further development. The detection of naphthalene sulfonates via SAW technology has been shown to be nearly impossible for both downhole and surface applications.
   Throughout the remainder of FY14, Sandia developed and tested a prototype electrochemical sensor consisting of a HT stable ion-selective electrode for detecting iodide, a HT reference electrode, and a HT pH electrode which will allow measuring tracer concentrations and pH downhole on a wireline tool. The initial testing was performed using a high-temperature high-pressure autoclave in water, while subsequent tests used representative geothermal brine. In FY15 Sandia focused on refining and calibrating the three electrodes, developing the materials necessary to construct electrodes selective for other ions of interest, and developing the logging tool which will house the electrodes.
   In FY16 Sandia integrated the electrodes and HT signal conditioning electronics into a 2 inch diameter high temperature wireline logging tool. In early FY17, the tool was mounted to a wireline truck and run in a 44 foot mock well at Sandia. An iodide feed zone fracture was emulated half way down the mock well and was located with the prototype tool. While the liquid reference electrode was proven in laboratory HTHP environments, it is prone to leakage failures in pressure cycles. Because the reference electrode is critical, the remainder of FY17 focused on

[1]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.

eliminating the liquid junction by developing a solid state materials approach. In FY18, the solid state reference electrode technologies will be refined and calibrated in representative geothermal environments. All three electrodes will be tested with a new autoclave system in surrogate geothermal brine up to 225°C and 3000 psi.

4. Technical Barriers and Targets

- Determine the depth/location of the specific fractures that are conducting chemical tracers during typical tracer studies as well as provide concentration of tracer with respect to depth.
- Provide more accurate pH measurements for specific inflow zones in real-time without the need to collect cooled and depressurized samples at the wellhead.

Both of these goals are difficult to achieve because very few materials and sensor technologies exist that can perform accurate measurements of ion concentration and pH at the extreme conditions found in geothermal reservoirs. Additionally, the development of HT signal conditioning electronics and selection of passive materials (housing, sealing, insulation) for the constructions of the electrodes is crucial in order to provide a reliable operation.

5. Technical Approach

To achieve our goals of downhole ionic tracer concentration and pH measurements we chose an electrochemical sensor approach. The chemical sensor consists of three ruggedized high temperature and pressure stable electrodes (ion selective, pH, and reference) and the high temperature sample electronics necessary for data acquisition and processing. The majority of our efforts have focused on the measurement of iodide ion tracers. Key issues that needed to be addressed for this project to be successful include the identification and synthesis of ion selective materials capable of withstanding harsh conditions, developing a reference electrode rugged enough to withstand the environment found in wellbores and generate only minimal drift in brine, and a pH electrode that responds well through a pH range of at least 4 to 8. Currently, no downhole tools exist for measuring ionic tracer concentration and pH in the narrow diameter boreholes and harsh environments found in geothermal systems.

We initially also explored the use of Sandia developed microfabricated gas chromatography (GC) instrumentation for the detection of naphthalene sulfonate (NS) tracers. The microfabricated GC unit uses a surface acoustic wave (SAW) detector, is rugged and runs at low power. Unfortunately, our results indicated that the volatility of the NS tracers is too low for GC-based methods that could be readily carried out in the field. We explored a number of chemical derivitization approaches to increase the volatility of the incoming NS tracer but none of those approaches were amenable to the autonomous field operations and work on autonomous detection of NS tracers was abandoned.

6. Technical Accomplishments

- Iodide Ion Selective Electrode - Successful HT and pressure testing in an autoclave in a form suitable for integration in a downhole wireline tool. Current limit of detection is approximately 16 ppm iodide. Testing has been conducted at temperatures up to 200 °C and pressure up to 1500 psi.
- pH Electrode – Successful HT and pressure testing in an autoclave of pH electrode based on an yttria-stabilized zirconia design using a nickel-nickel oxide internal reference. Testing has been conducted at temperatures up to 225 °C and pressure up to 1500 psi. This pH electrode design showed highly linear behavior (R2 = 0.999) and a slope of -87 mV/decade over a pH range of 3 to 8.
- Reference electrode – Successful HT and pressure test at temperatures up to 225 °C and pressure up to 1500 psi. The electrode has shown to be stable over the pressure and temperature range, but drifts predictably with temperature. While the drift can be addressed with calibration, the technology still depends on a liquid junction which can lead to mechanical instabilities. An all solid state reference electrode has been recently developed and shows promise. Testing is on-going.
- Tool design – Leveraged previous PTS tool design. Completed design of new housing which will be used for chemical sensor.

- HT electronics – Designed and tested HT electronics capable of interfacing and recording the data from the chemical sensors.

7. Challenges to Date

- Iodide Ion Selective Electrode – Lower the limit of detection from 16 ppm to single digit ppm levels. To address this issue we intend to explore the use of a transduction layer between the ion selective membrane and the electron conductor.
- Reference Electrode – The 100% solid state electrode design originally envisioned proved to be unreliable at HT and pressure environment due to pressure gradient across the junction under the initial approach. To address this, we switched to liquid reference electrode with pressure compensation. Recently, we have continued development of a solid state electrode and initial tests indicate stability.
- pH Electrode – Initial testing at HT and pressure showed that the electrode was not sensitive above pH 7. To address this we heat-treated the electrode prior to use to resolve the issue.
- NS tracers – Not volatile enough to vaporize for use in the field portable GC-SAW based detectors developed at Sandia. We identified some approaches for chemically derivitizing the tracers to increase volatility that would potentially work for human-enabled field operations but not for the desired autonomous operations.
- HT electrode construction – Sealing the electrodes has proven to be a challenge throughout this project as the various materials used in the electrodes have significantly different CTEs. To resolve this a different sealing approach was needed for each electrode.

8. Conclusion and Plans for the Future

Sandia has developed a prototype HT chemical sensor package capable of sensing iodide, chloride, and pH in simulated geothermal environments. Laboratory testing shows that the developed electrodes function well at high temperature and pressure while maintaining necessary sensitivity and selectivity. The sensors and HT signal conditioning electronics were integrated into a wireline tool and verified to identify a conducting fracture zone in a mock well bore field test. For the remainder of this year we will focus on eliminating the weakest link of the liquid reference electrode and improving manufacturability of all three electrodes.

9. DOE Geothermal Data Repository

- Preliminary pH and reference electrode test results
- FY17 field test and laboratory data will be uploaded
- Electrode manufacturing approach documentation

10. Other Dissemination of Research

- Collaboration with Stanford University for an electrochemical sensor enabled enthalpy measurement came out of this project. This collaboration led to two papers/presentations at Stanford Geothermal Workshop (2/17), a poster at American Chemical Society (4/17), a paper/presentation at GRC (10/17), and a provisional patent application 62454194.

11. Publications and Presentations, Intellectual Property (IP), Licenses, etc.

- "Development of a Wireline Tool Containing an Electrochemical Sensor for Real-time pH and Tracer Concentration Measurement," Geothermal Resources Council, October 2016
- "Measuring real-time concentration of ionic tracers and pH in geothermal reservoirs using a ruggedized downhole tool," Stanford Geothermal Workshop, February 2015
- US Patent and Trademark Office Provisional Application 61983234 , April 2014
- "Real-time downhole measurement of ionic tracer concentration and pH in geothermal reservoirs," GRC Annual Meeting, October 2014
- "Development of a downhole tool measuring real-time concentration of ionic tracers and pH in geothermal reservoirs," SPIE Sensing Technology + Applications Conference, May 2014
  - "Development of a downhole tracer and pH measurement instrument for application in geothermal wells: Toward real-time chemical well logging", ACS National Meeting, September 2013