

Development of a downhole tool measuring real-time concentration of ionic tracers and pH in geothermal reservoirs

Ryan F. Hess¹, Timothy J. Boyle¹, Steven Limmer¹, William G. Yelton¹, Samuel Bingham¹, Greg Stillman², Grzegorz Cieslewski¹

- 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-OES), Ion Chromatography (IC), High Performance Liquid Chromatography (HPLC) with fluorescence detection.

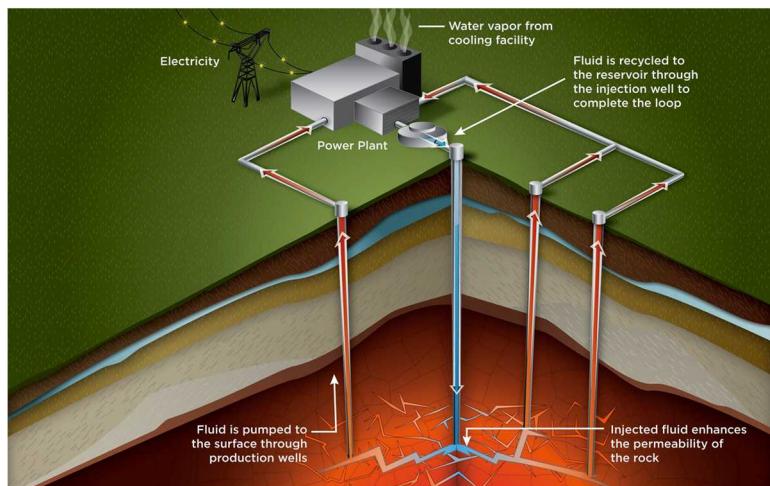


Figure 1. Department of Energy drawing showing the relationship between injection and production wells in an Engineered Geothermal System.¹)

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.

Any sensor designed to operate inside a geothermal well must be able to survive a number of exceptionally harsh conditions: (i) high temperatures (100 – 350 °C), high pressures (1000s psi range), varied pH conditions (pH 2 -11), varied sediments (total dissolved solids (TDS) range from 100 to 100,000 ppm), and chemistries that vary from site to site. Further, all these conditions can change drastically over a short amount of time. Our design goal for this new downhole tool is for successful operation up to 225 °C and 3000 psi. Table 1 contains information on the surrogate brine that was used to measure the ambient temperature behavior of our I-ISE. This paper describes our initial foray into developing a sensor that can operate at a range of geothermal sites.

Table 1. Surrogate brine chemistry used for ambient temperature I-ISE testing.

Species	Concentration (mM)
Na ⁺	77.44
K ⁺	5.57
Cl ⁻	65.18
HCO ₃ ⁻	17.83

EXPERIMENTAL

Tool Overview

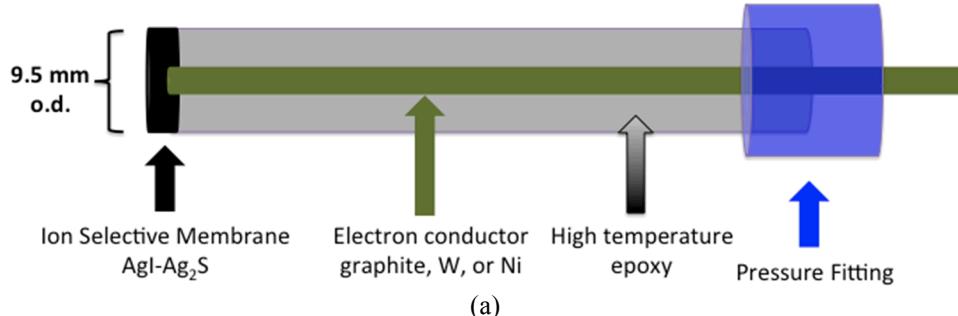
Our downhole geothermal tracer concentration and pH tool consists of following major components:

- Temperature sensor
- Pressure sensor
- Flow rate sensor
- Ruggedized high temperature stable iodide ion selective electrode
- Ruggedized high temperature stable reference electrode
- Ruggedized high temperature stable pH electrode

Iodide Ion Selective Electrode (I-ISE)

A ruggedized version of an I-ISE has been designed that is able to survive the geothermal well environment. The I-ISE consists of an ion selective membrane (ISM), an electron conductor, the electrode tube body, and a high-pressure fitting. Figure 2 contains a schematic drawing and a photograph of the I-ISE design used in this study. The ion selective membrane is a pellet containing silver iodide (AgI) and silver sulfide (Ag₂S) in various ratios. For example, for an ISM containing a 1:1 iodide to sulfur ratio, 0.250g of AgI was combined with 0.250g of Ag₂S and mixed using a mortar and pestle. The powder was then pressed at 1.8 metric tons using a hydraulic press. The ISM pellet was then fired at 375 °C in air for one hour. Iodide ISMs based on AgI/Ag₂S mixtures have been demonstrated to have the sensitivity needed for this application which is on the order of one ppm iodide.^{4,5}

In order to better establish electrical connectivity to the ISM a small hole was drilled to approximately 1/3 the thickness of the pellet. The electron conductor used in this study was a 3.2 mm diameter rod. The rod was bonded to the ISM using a high temperature silver-based conductive epoxy. The I-ISE body was constructed of stainless steel with an outer diameter of 9.5 mm and an inner diameter of 7.6 mm. The ISM pellet and rod were placed inside the steel tube and sealed using a high-temperature non-conductive epoxy.



(a)



(b)

Figure 2. (a) Schematic drawing of a ruggedized high temperature and pressure stable iodide ion selective electrode (I-ISE). (b) Photograph of the I-ISE.

High Temperature and Pressure Stable pH and Reference Electrodes

High temperature and pressure stable pH and reference electrodes suitable for use in an autoclave were purchased from Corr Instruments. The High Model A2 pH electrode is a solid-state design using a ZrO_2 membrane. The $Ag-AgCl$ reference electrode is an internal pressure balanced design containing potassium chloride solution. These electrodes contain some parts that reside outside the autoclave and cannot be exposed to temperatures above 100 °C. For this reason, the development of an in-house pH and reference electrodes that can be used in the downhole environment where the entire tool will be at 225 °C is in progress.

Electrochemical Experiment Design

For ambient and near-ambient testing electrochemical measurements were made using a Gamry Reference 3000 potentiostat. I-ISE response was established by measuring the open circuit potential difference between the I-ISE and a silver/silver chloride reference electrode produced by Radiometer.

High temperature and pressure experiments were conducted in a 1 L autoclave shown in Figure 3. A HPLC pump (SSI Series 3) was used to deliver test solution to the autoclave. I-ISE measurements were conducted using 0.01 M KNO_3 as the electrolyte. Iodide concentration was adjusted using the method of standard additions while under continuous stirring. The measurements were made using the NI-9234 16-bit analog to digital converter which simultaneously monitors the potential of I-ISE, pH and reference electrodes. The autoclave itself is grounded and all the potential measurements are referenced to it. The potential difference is obtained by subtracting the reference electrode potential from the I-ISE potential.

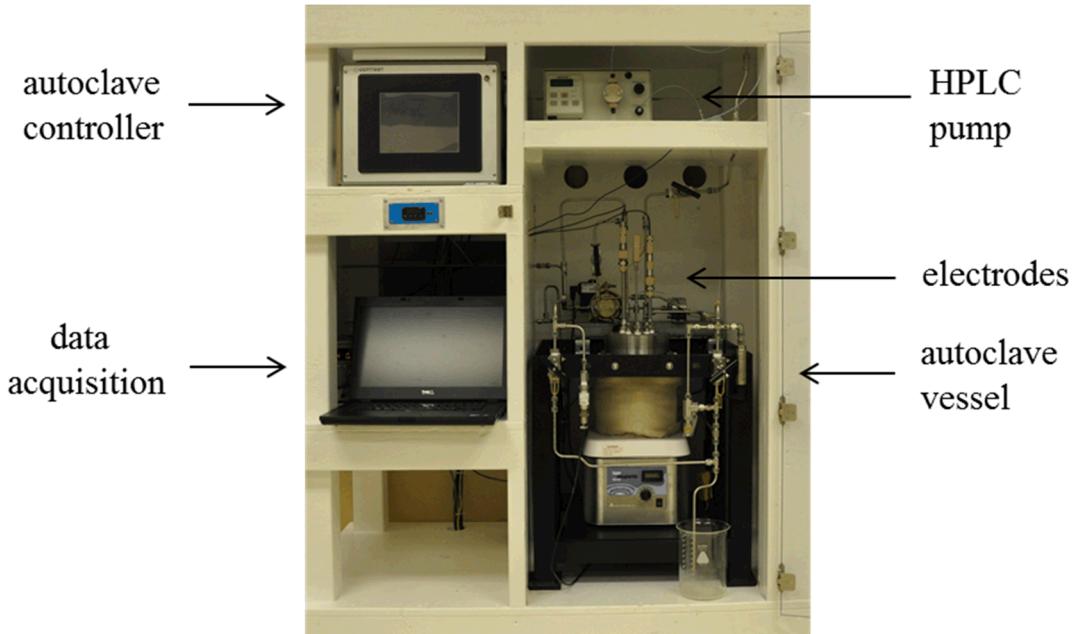


Figure 3. Photograph of the one liter autoclave and solution delivery system used in our high temperature and pressure measurements.

Tool Construction

The high-temperature tool will consist of pressure transducer, temperature sensor, flow sensor, ISE electrode, pH electrode, reference electrode, and high-temperature electronics package as shown in Figure 4. The red and orange sections of the tool will house the spinner which will be used as a flow sensor. To calculate the rotation speed of the spinner the shaft of the spinner will have an integrated magnet which will open and close a reed switch. The yellow section will house a pressure transducer. The green section will house three electrodes (pH, reference, and I-ISE) and a thermocouple. The light blue section will house the electronic package. All the sensors will be connected to a HT 12-bit ADC via an HT analog multiplexer. In case of the electrodes an additional analog stage will be required to shift the potentials into the range which can be recorded by the ADC. The ADC and the multiplexer will be controlled by the HT micro-processor. The micro-processor will communicate the recorded data via the single conductor (inter conductor and shield) logging wireline to the surface using PSK encoding.

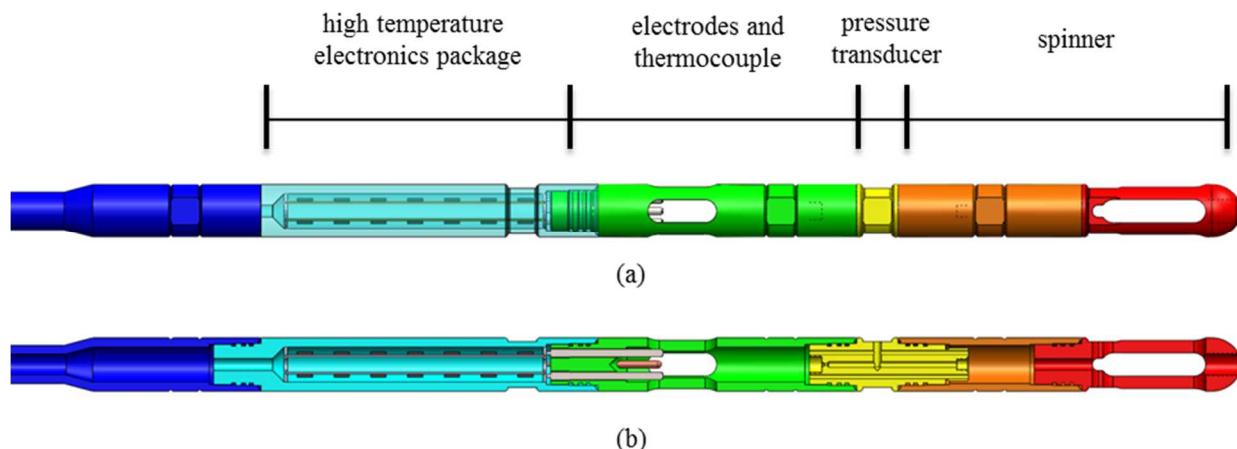


Figure 4. Diagram of the downhole tool capable of measuring temperature, pressure, and flow rate. The ruggedized I-ISE, pH, and reference electrodes will be housed in the green (middle) section.

Chemicals and Solutions

The chemicals used in this study were of analytical grade from Aldrich and used as received: potassium iodide (KI), potassium chloride (KCl), sodium chloride (NaCl), potassium nitrate (KNO₃), sodium bicarbonate (NaHCO₃), and hydrochloric acid ((aq) HCl), sodium hydroxide (NaOH), silver chloride, silver sulfide, lithium manganese oxide, lithium iron phosphate, cesium nitrate, and molybdochosphoric acid. All solutions of these compounds were made from distilled water.

Material Characterization

AgI/Ag₂S pellets were characterized by powder X-ray diffraction (PXRD) on a PANalytical X'Pert Pro diffractometer using CuK α radiation with step size 0.0167 degree, with 0.152 %/sec dwelling time. Thermal properties characterization using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) was carried out on a Mettler instrument. The material was heated to 1000 °C at a rate of 5 °C/min and data was collected during both heating and cooling back to ambient temperature. PXRD was used to verify the presence of AgI and Ag₂S in the ISM pellet. Thermal analysis was used to determine the temperature stability of the ISM pellet and was conducted in air. The techniques listed above were also used to characterize lithium manganese oxide and cesium molybdochosphosphate membranes.

IODIDE ION SELECTIVE ELECTRODE PERFORMANCE

The iodide ion selective membranes used in this study consisted of mixtures of AgI and Ag₂S powders pressed into pellets with cylindrical geometries. In order to efficiently screen a number of different I-ISE designs, the majority of experiments are conducted under ambient temperature and pressure conditions. The thermal stability of the ISM was studied by TGA and DSC analyses and is shown in Figure 5 for a mixture of AgI and Ag₂S in a 1:1 ratio. These data show that there is no significant mass loss below 500 °C. The DSC data shows to phase transitions at relatively low temperature. The first peak at 149 °C is the AgI beta to alpha phase transition. The second peak at 177 °C is the Ag₂S alpha to beta phase transition.

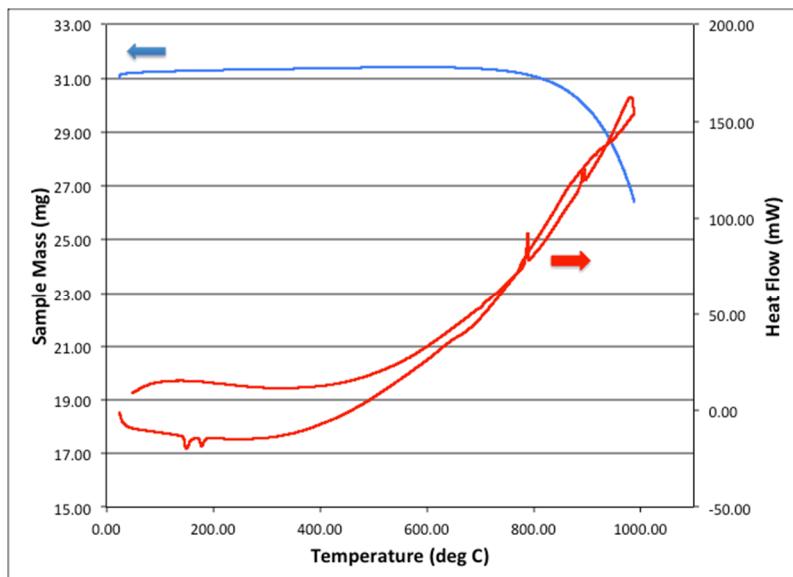


Figure 5. Thermal analysis of a 1:1 AgI-Ag₂S mixture. The primary y-axis contains Thermo Gravimetric Analysis (TGA) data while the secondary y-axis contains Differential Scanning Calorimetry (DSC) data.

This data is considered preliminary since testing using the I-ISEs under elevated temperature and pressure conditions in a laboratory-scale autoclave has only just begun. However, based on these results, it appears the AgI/Ag₂S is stable up to the necessary temperatures.

While other ratios of I:S were tested, it was found that the best results were obtained using a 1:1 ratio of AgI to Ag_2S . Figure 6 contains the response found for an electrode using a 1:1 AgI/ Ag_2S ISM and a 1.5 mm outer diameter tungsten rod conductor potted inside a Teflon™ outer tube using a UV-curable epoxy. The electrode was found to behave almost identically in water as it did in our surrogate brine. The surrogate brine used in this experiment had an ionic strength of 0.0830 M. The slope of line generated from a plot of potential versus the log of the iodide concentration is a good diagnostic for the performance of an ISE. The theoretical Nernst value for the slope of an ISE response curve is reported to be 59.16 mV per decade change in ion concentration. Figure 6 shows little to no response upon increasing the iodide concentration from zero through approximately 10^{-6} M. Between 10^{-6} to 10^{-5} M, a linear response to changing iodide concentration through 10^{-2} M iodide was noted. The slope of this linear portion of the response curve is 50 mV/decade with an R^2 of 0.994 for iodide in distilled water. The slope for the same electrode in surrogate brine is 48 mV/decade with an R^2 of 0.984. This response is close enough to the Nernst value of 59.16 mV/decade to indicate that this is a viable means of measuring iodide concentration in our geothermal fluid at least under ambient conditions. Because the slopes were so close in value between water and surrogate brine, no significant interference issues for this system is expected. However, as the fluid chemistry varies from well to well further investigation of response in the presence of interreferents is continuing. Our best limit of detection to data, as defined by the intersection of the flat portion and linear portions of the response curve, is on the order of 1 ppm iodide in surrogate brine under ambient conditions.

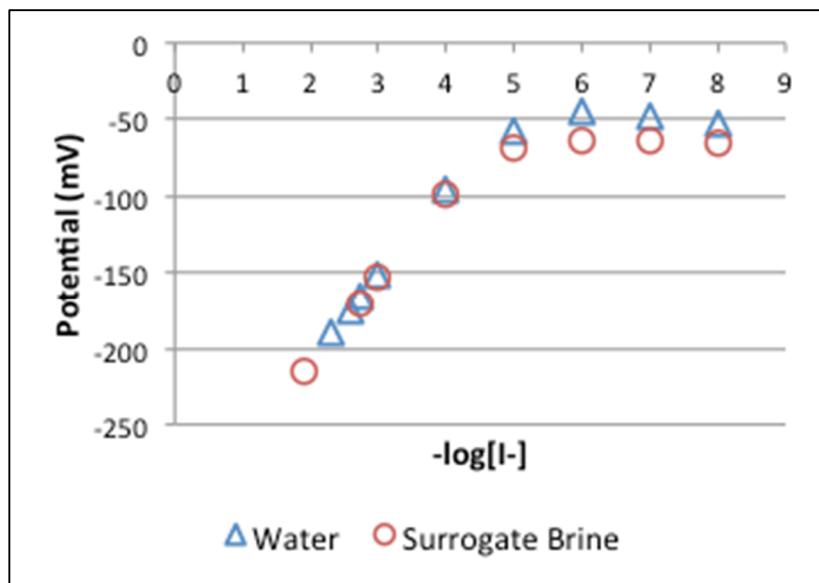


Figure 6. I-ISE response in water and in surrogate brine. This electrode consisted of a ISM using 1:1 I/S pellet and a 1.5mm diameter tungsten rod conductor in a Teflon body. The I-ISE responds to changes in iodide concentration in a predictable manner in both water and the surrogate brine which contains high amounts of chloride ion. For $-\log[\text{I}^-]$ 1– 5 the slope in water is 50 mV per decade iodide concentration with a R^2 of 0.994, in surrogate brine the slope is 48 mV per decade iodide concentration with a R^2 of 0.984.

While the Teflon™ body design described above is easy to build and useful for screening ISM candidates, it is not very rugged. Our next generation design involved using the same ISM pellet composition and a 3.2 mm outer diameter nickel rod conductor potted inside a steel tube using high temperature stable conductive and non-conductive adhesives. The response of this ruggedized electrode design is shown in Figure 7. From the linear portion of this plot, a slope of 61 mV/decade with an R^2 of 0.998 in surrogate brine was calculated. The limit of detection is therefore calculated to be 0.4 ppm iodide in surrogate brine under ambient conditions. Prior to the autoclave experiments, the performance of this electrode was tested at elevated temperature though still below the boiling point of water. Figure 8 contains a plot showing the change in potential with increasing temperature at a fixed iodide concentration in water of 0.001M. Increasing the temperature from 25 °C to 85 °C resulted in an increase in potential of 44.6 mV or a temperature coefficient of +0.74 mV/°C.

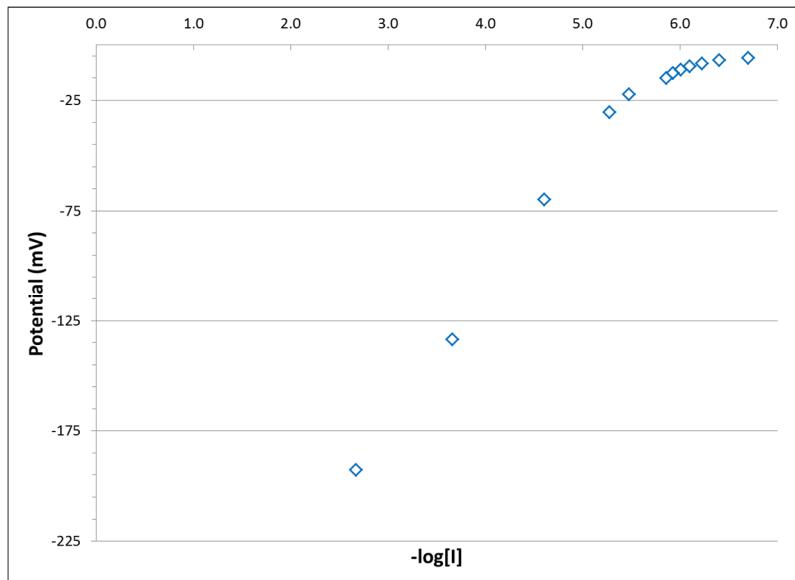


Figure 7. Response of a ruggedized I-ISE at ambient temperature and pressure. The limit of detection is estimated at 3.4×10^{-6} M iodide or a pH of 5.48. For data between pH of 5.48 and 2.67 with a measured slope of 61 mV/decade and a R^2 of 0.998.

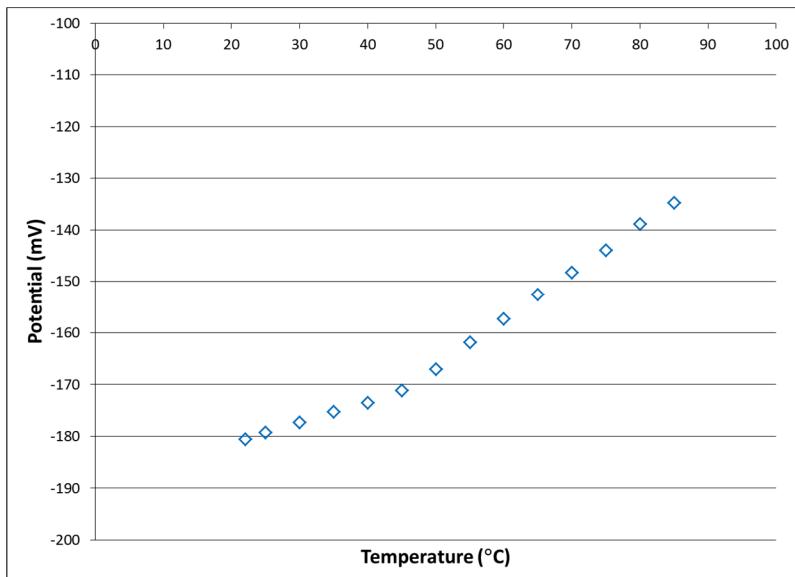


Figure 8. Effect of temperature on an IISE consisting of a 1:1 I/S ISM, a 3.2mm diameter nickel conductor in a steel body. The potential increased by +44.6 mV over a 60 °C increase in temperature.

Because the pH value of geothermal fluid varies greatly from location to location it is important to determine the useful pH range for our ruggedized I-ISE. Figure 9 contains a plot of potential versus pH at a fixed iodide in water concentration of 0.001M at ambient temperature. From these data it is believed that this electrode design should work well for fluids with a pH between 3 – 9. Below and above this range, it was noted that the potential begins to deviate significantly from that found around neutral pH making calibration difficult.

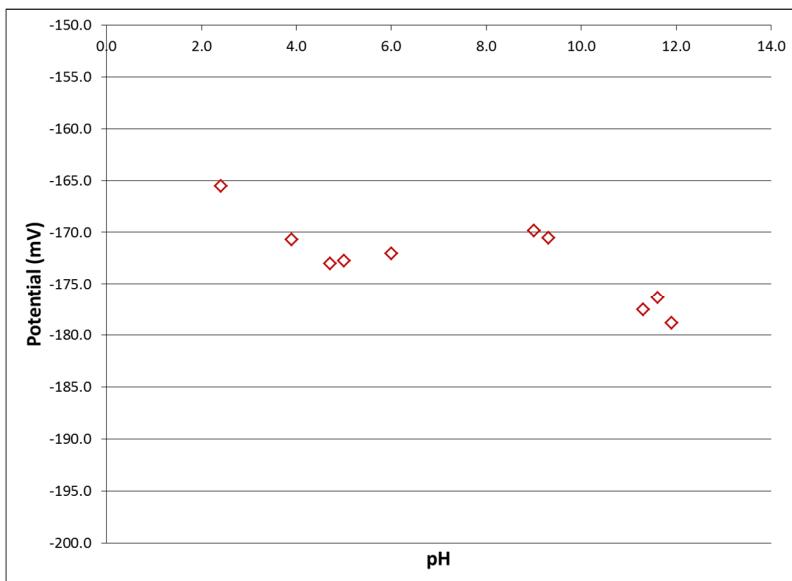


Figure 9. Effect of pH on I-ISE response at a constant iodide concentration of 0.001M in distilled water. These results indicate that this electrode design should work well in fluid with pH values in the 3–9 range.

High Temperature and Pressure Testing

The ruggedized I-ISE design was recently tested under elevated temperature and pressure conditions similar to those found in some geothermal wells. It is of note that because these experiments have only recently begun these results are still considered preliminary. Figure 10 contains a plot of electrode response at 200 °C and an average pressure of 1171 psi. The supporting electrolyte was 0.01M KNO₃. At 200 °C we found a slope of 63 mV/decade and a R² of 0.926 for iodide concentration in the 10⁻⁴ to 10⁻² M range. Figure 11 contains a plot that compares the linear portion of the I-ISE response at three different temperatures. From this, it can be observed that there is a shift to less negative electrode potential as the temperature increases. While more data is clearly needed, these results indicate that a stable enough response is available with this electrode design that will allow us to detect changes in iodide tracer concentration under geothermal-relevant conditions.

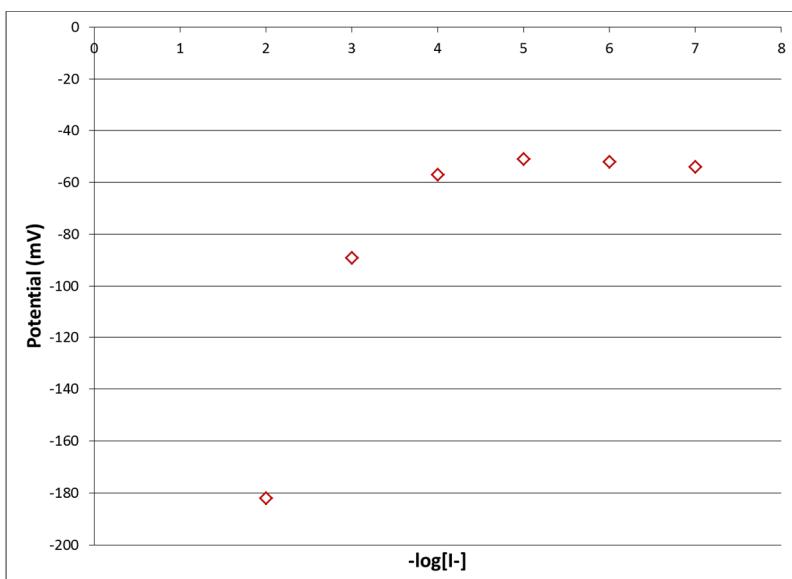


Figure 10. I-ISE response at 200 °C and an average pressure of 1171 psi. Linear response was found between 10^{-4} and 10^{-2} M I^- with a R^2 of 0.926 and a slope of 63 mV/decade. The pH of the test solution was 6.

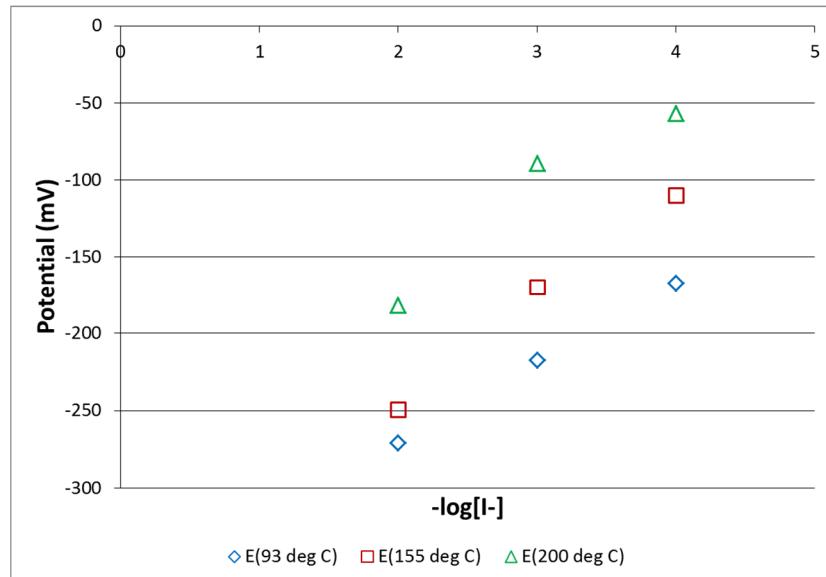


Figure 11. Plot showing the I-ISE response as a function of iodide concentration and temperature. These results show that for a given iodide concentration there is a positive increase in potential with increasing temperature as expected from electrochemical theory.

DEVELOPMENT OF Li^+ , Cs^+ , AND F^- ION SELECTIVE ELECTRODES

An effort to design similar ruggedized high temperature and pressure stable ISEs for Li^+ , Cs^+ , and F^- is underway. For these designs to be realized ISMs that are stable at high temperatures and selective for the target ion in a brine matrix must be fabricated. For F^- efforts in our laboratory have focused on the use of polycrystalline $\text{LaF}_3\text{:EuF}_3$ nanoparticles for the ISM. Experiments using a home-made F-ISE containing a single crystal $\text{LaF}_3\text{:Eu}$ disk (Goodfellow) showed a weak response to F^- in water but no F^- selectivity in surrogate brine. For the Li-ISE and Cs-ISE efforts in our laboratory have focused on the use of LiMn_2O_4 , a common lithium battery material as the ISM and a cesium molybdochosphate (Cs-12-MPO) compounds as the ISMs respectively. Work to characterize the performance of these ISMs is currently on going.

CONCLUSIONS

A ruggedized iodide ion selective electrode was developed for measuring changes in iodide concentration during geothermal reservoir tracer experiments. This electrode will be paired with ruggedized pH and reference electrodes and mounted on a wireline tool that already contains the capability to measure temperature, pressure, and flow rate in the harsh environments found in geothermal wells. Preliminary testing of our I-ISE design shows near Nernstian response for iodide concentrations in the 10^{-4} M to 10^{-2} M range at temperatures from 100 – 200 °C. At 200 °C the estimated limit of detection is 16 ppm. Below 100 °C the linear response range is extended and we calculate an estimated limit of detection of 0.4 ppm iodide. Efforts are underway to lower the limit of detection for our I-ISE design at elevated temperature and pressure.

REFERENCES

¹ Hass, E., Geothermal Technology Office Review, <http://www1.eere.energy.gov/geothermal/presentations.html> (Eric Haas, Geothermal Technology Office Review).

² Axelsson, G., Floenz, O.G., Hauksdottir, S., Hjartarson, A., Liu, J., "Analysis of tracer test data, and injection-induced cooling, in the Laugaland geothermal field, N-Iceland," *Geothermics*, 30, 697-725 (2001).

³ Kumagai, N., Tanaka, T., Kitao, K., "Characterization of geothermal fluid flows at Sumikawa geothermal area, Japan, using two types of tracers and an improved multi-path model," *Geothermics*, 33, 257-275 (2004).

⁴ Nyachhyon, A.R., Yadav, A.P., Manandhar, K., Pradhananga, R.R., "Characterization of home-made silver sulphide based iodide selective electrode," *Talanta*, 82, 1448-1454 (2010).

⁵ Abdel-Latif, M.S., Al-Saraj, M.R., "A Novel Potentiometric Solid-State Iodide Sensor," *Anal. Lett.*, 40, 729-736 (2007).