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Development of a Wireline Tool Containing an Electrochemical Sensor for Real-time pH and Tracer Concentration Measurement

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KEYWORDS

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ABSTRACT

Understanding the connectivity of fracture networks in a reservoir and obtaining an accurate chemical characterization of the geothermal fluid are vital for the successful operation of a geothermal power plant. Tracer experiments can be used to elucidate fracture connectivity and in most cases are conducted by 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. This method does not identify which specific fractures are the ones producing the tracer; it is only a depth-averaged value over the entire wellbore. Sandia is developing a high-temperature wireline tool capable of measuring ionic 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.

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 often by inductively coupled plasma – mass spectrometry (ICP-MS), ICP-Optical Emission Spectroscopy (ICP-OEC), Ion Chromatography (IC), or High Performance Liquid Chromatography (HPLC) with fluorescence detection. These analytical techniques provide very low limits of detection, often in the parts per billion range, but the concentration data collected does not provide any information regarding the depth of the fractures which produced the tracer. Because the data is collected at the wellhead, the measured tracer concentration represents a depth-averaged value. Additional information on the fracture connectivity could be obtained if the specific fractures producing the tracer could be identified within the wellbore. To accomplish this objective Sandia National Laboratories has been developing a wireline tool containing a ruggedized electrochemical sensor 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 and lithium ion tracers and pH under conditions up to 225 °C and 3000 psi are discussed.

Traditionally, the pH of a reservoir fluid is measured by collecting a liquid sample at the surface after passing through a cooling coil and sending it to an off-site laboratory for analysis. Alternatively, a sampling device may be lowered on a wireline that captures a liquid sample and returns it to the surface for laboratory analysis. In both cases the sample will have to be cooled and depressurized which alters the pH of the sample compared to its original state inside the reservoir. By collecting pH data in real-time and continuously at depth a more accurate profile of the reservoir fluid chemistry may be obtained.

2. EXPERIMENTAL

The electrochemical iodide tracer sensor section of our wireline tool will consist of three ruggedized electrodes: an iodide ion selective electrode (I-ISE), a pH electrode, 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, temperature, pressure and flowrate sensors currently in use in other tools will be incorporated into the new tool shown in Figure 1. Therefore, at each depth a measurement is taken, tracer concentration, pH, temperature, pressure, and flowrate data will be acquired.

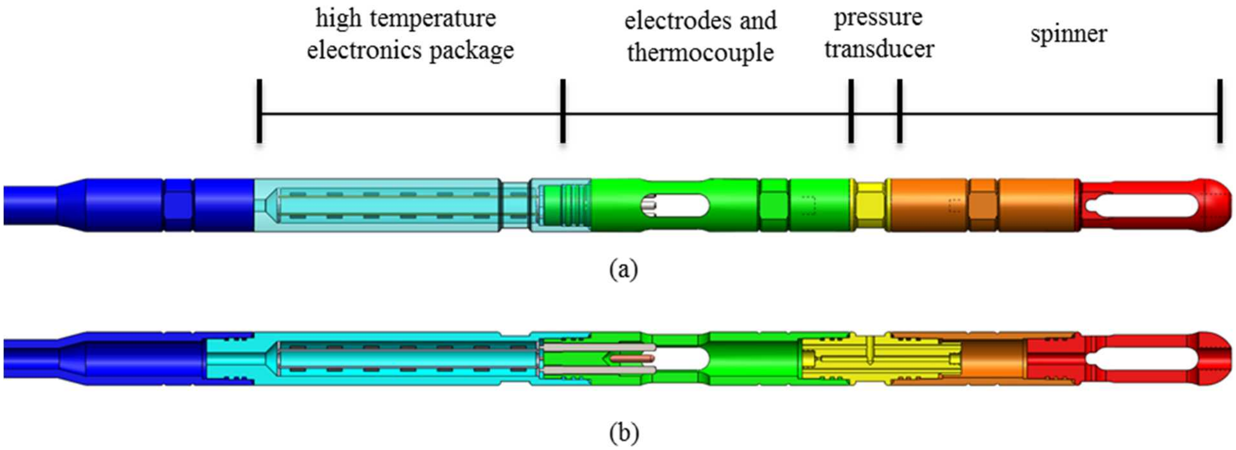

Figure 1. Diagram of the downhole tool capable of measuring temperature, pressure, and flowrate. The ruggedized I-ISE, pH, and reference electrodes will be housed in the green (middle) section.

While many different ion selective electrodes and reference electrodes are commercially available in almost all cases they have upper temperature limits of approximately 80 °C. This is due to a number of factors include the thermal stability of the ion selective membrane and the sealants used to ensure water does not enter the electrode body.

The Sandia iodide ion selective electrode (I-ISE) is composed of three main parts: an ion selective membrane (ISM) that is selective for only iodide ions (I^-), an electron conductor, and the electrode body and high-pressure fitting. The ion selective membrane is a 0.25 in diameter pellet containing an equimolar mixture of silver sulfide and silver iodide (Ag_2S/AgI). The purpose of the membrane is to selectively conduct I^- ions. The use of Ag_2S/AgI as an iodide ion selective material has been demonstrated by Nyachhyon et. al. (2010) and Abdel-Latif et. al. (2007). The ISM is connected to an electron conductor such as a nickel rod using a small amount of silver-based conducting epoxy. The ISM and nickel rod are encapsulated inside a stainless steel rod using a high temperature epoxy. In addition to I^-, we have also constructed prototype ISE's that are selective for Li^+, Cl^-, and S^{2-} ions.

The pH electrode is based on the yttria-stabilized zirconia design such as those used by Ding and Seyfried (2007), Neidrach (1980), and Neidrach and Stoddard (1984). In this design a tube, open on only on end, made of zirconia-10% yttria acts as an oxygen ion conductor and contains an internal reference consisting of a metal-metal oxide pair such as nickel-nickel oxide or copper-cupreous oxide. Electron conductivity is established using a nickel or copper wire immersed on the metal/metal oxide powder at the closed end of the YSZ tube. The YSZ tube is sealed using high temperature epoxy.

The reference electrode consists of an alumina tube open on both ends. The end of the tube exposed to the reservoir contains a porous glass frit attached to the tube using a shrinkable Teflon sleeve and fittings. The tube is filled with a 3M potassium chloride-silver chloride solution and a silver wire that has a thin layer of silver chloride coating on one end. Figure 2 contains schematics of our ruggedized I-ISE, pH, and reference electrodes.

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.

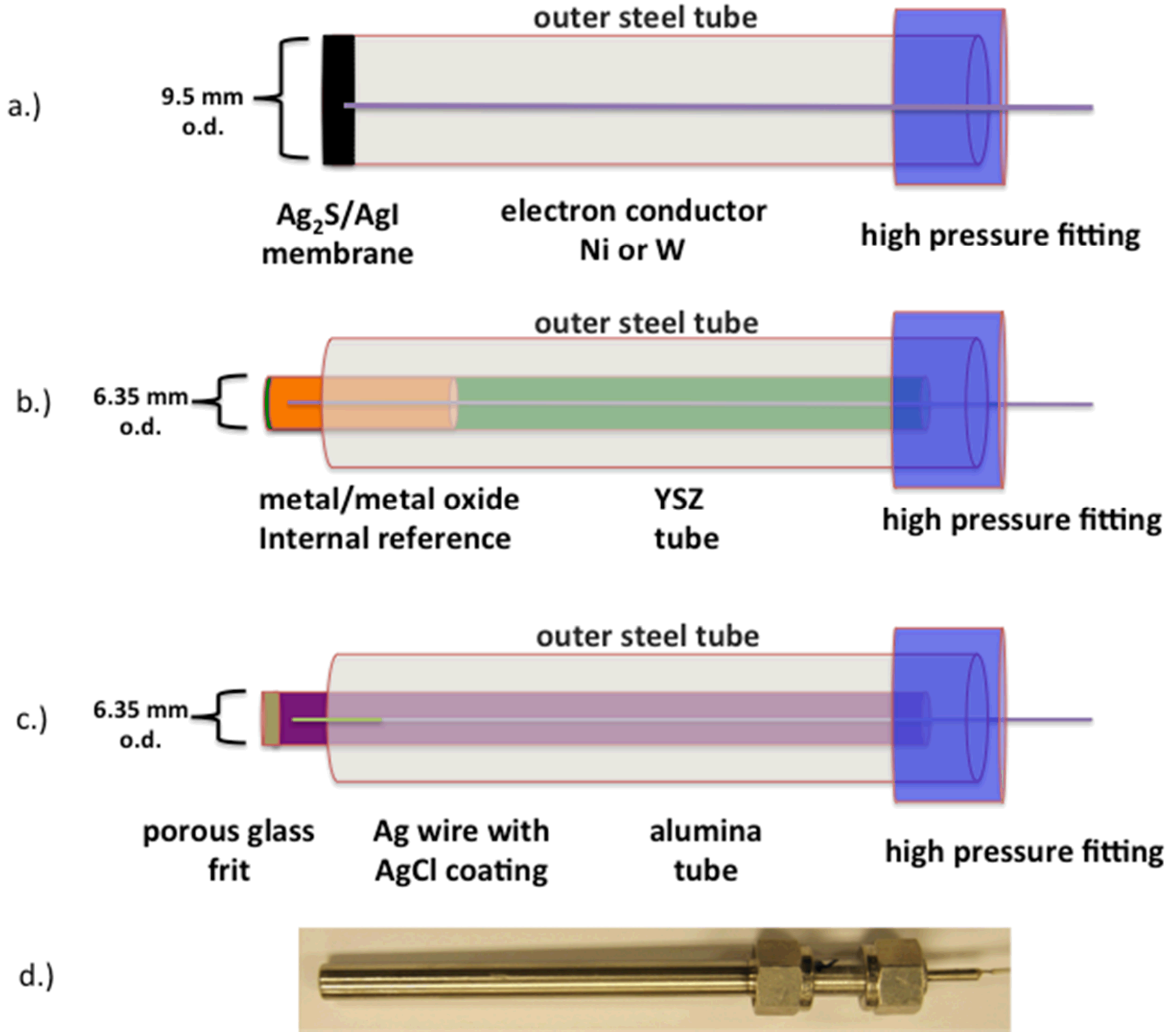

Figure 2: Schematic drawing of the ruggedized: a.) I-ISE electrode, b.) solid state YSZ pH electrode, c.) solid state Ag/AgCl reference electrode, and d.) photograph of the I-ISE using a stainless steel electrode body and high pressure fittings.

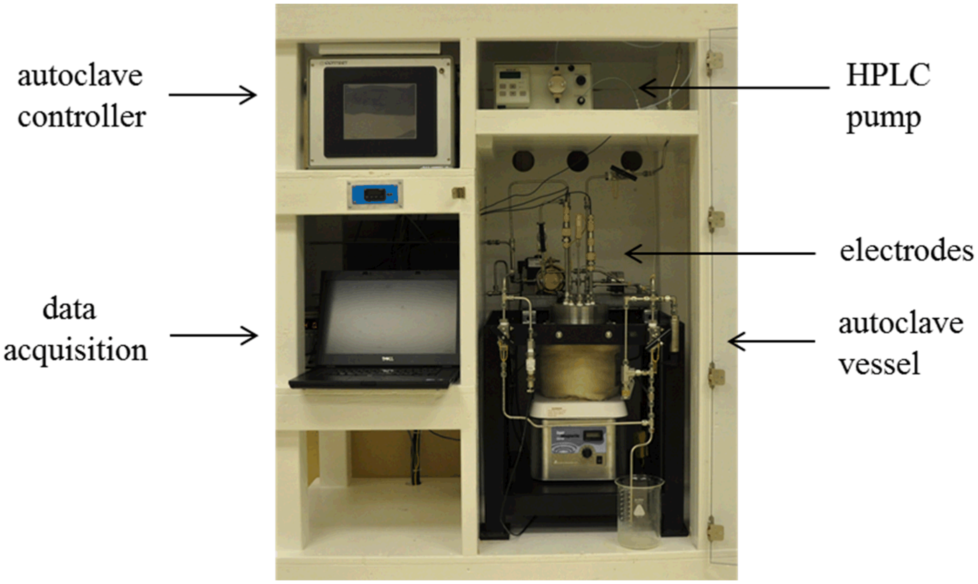

Figure 3: Photograph of the one liter autoclave and solution delivery system used in our high temperature and pressure measurements

3. ION SELECTIVE ELECTRODE MESUREMENTS

An electrochemical approach was used to measure iodide ion concentration based on its ability to ruggedize the sensor hardware for operation in harsh environments and the relatively straightforward data processing used to make open circuit potential measurements.

The iodide ion selective membrane used in this study consisted of a mixture of AgI and Ag_2S 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 for a mixture of AgI and Ag_2S 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 Ag_2S alpha to beta phase transition. Based on the thermal analysis of the membrane material we expect it to survive the high temperature conditions found in many geothermal reservoirs.

A ruggedized I-ISE design has been 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 4 contains a plot showing electrode response at temperatures ranging 155 °C to 177 °C with an average value of 161 °C. The pressure in the autoclave ranged from 702 to 738 psi with an average value of 719 psi. The supporting electrolyte was 0.01 M KNO_3. Modifications to our autoclave and chemical delivery system are underway to increase the temperature and pressure stability during the course of the experiment. This experiment shows our I-ISE design has approximately Nernstian response for iodide concentrations in the 10^{-4} M to 10^{-2} M range with a slope of 70 mV/decade and a R^2 of 0.993. The estimated limit of detection for this design is ~16 ppm.

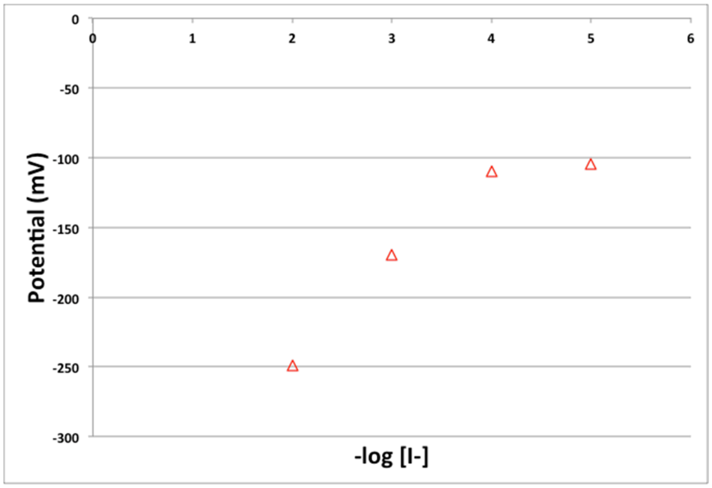

Figure 4: I-ISE response at temperature between 155 °C and 177 °C and pressure between 702 and 738 psi. Linear response was found between 10^{-4} and 10^{-2} M iodide with a R^2 of 0.993 and a slope of 70 mV/decade. The solution had a pH of 6.

This I-ISE design was tested up to 200 °C with similar results. Figure 5 contains a plot of electrode response at 200 °C and an average pressure of 1171 psi. The supporting electrolyte was 0.01M KNO_3. At 200 °C we found a slope of 63 mV/decade and a R^2 of 0.926 for iodide concentration in the 10^{-4} to 10^{-2} M range. Figure 6 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.

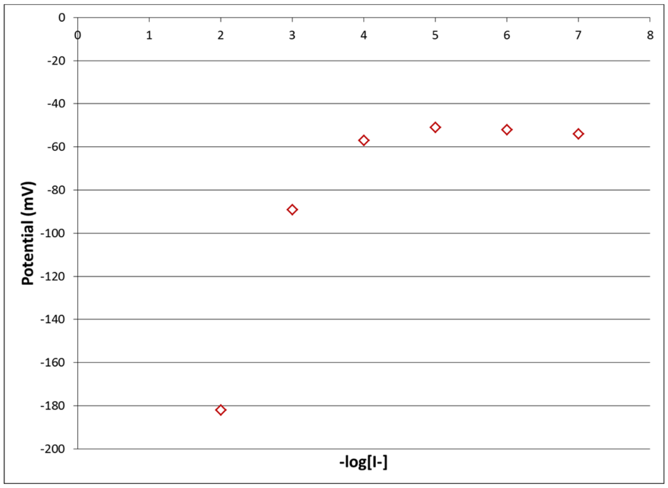

Figure 5: I-ISE response at 200 °C and an average pressure of 1171 psi. Linear response was found between 10^{-4} and 10^{-2} M I^- with a R^2 of 0.926 and a slope of 63 mV/decade. The solution had a pH of 6.

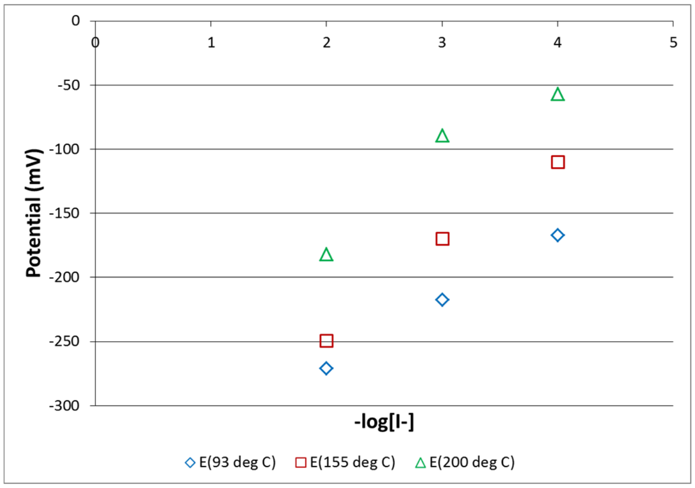

Figure 6. Plot showing the I-ISE response as a function of iodide concentration and temperature. These results show that for a given iodide concentration there is a positive increase in potential with increasing temperature as expected from electrochemical theory.

In addition to developing an ISE for iodide ion tracers efforts have been made to develop a corresponding cationic tracer sensor. Preliminary ambient temperature testing has shown that a Li-ISE consisting of a $LiMn_2O_4$ film deposited on a Pt substrate is selective for Li^+ even in solutions containing high concentrations of Na^+ and K^+ similar to those found in many geothermal reservoirs as show in Figure 7.

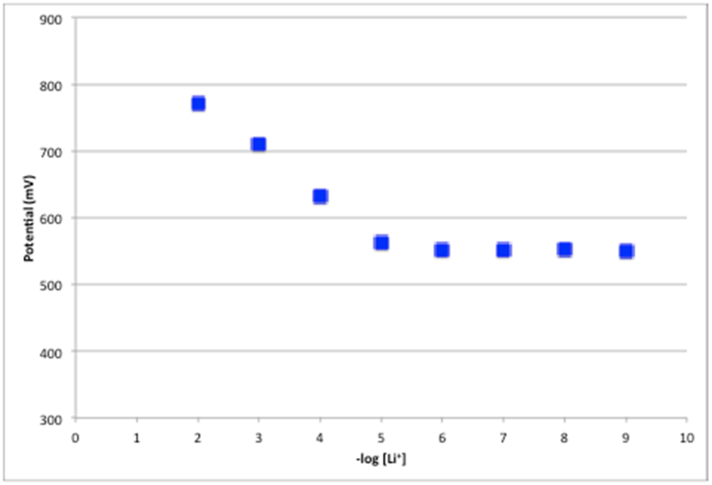

Figure 7. Li-ISE response at ambient temperature and pressure. Linear response was found between 10^{-5} and 10^{-2} M lithium with a slope of -70.6 mV/decade. The solution had a pH of 6 and consisted of 0.1M NaCl-KCl.

4. PH ELECTRODE PERFORMANCE

Standard laboratory pH electrodes typically use a thin glass hydrogen ion membrane and other components that are not conducive to operation in a high temperature, pressure, and vibration environment. The pH electrode used in this work is an all solid-state design that has been used to measure pH in deep sea hydrothermal vents and should work well in a geothermal reservoir environment. The main components of this pH electrode are the YSZ membrane and the internal reference. To date, the best results we have obtained in our autoclave testing used an internal reference of nickel and nickel oxide mixed together in a 1:1 ratio by mass. Figure 8 contains a plot showing the response of a YSZ based pH electrode containing Ni-NiO powder as the internal reference at 100 °C and at 150 °C. The solution used was a surrogate brine containing 0.1M NaCl-KCl. In both cases the change in potential (versus commercial Ag/AgCl reference electrodes) versus pH is linear with R^2 of 0.99. The slope calculated from our data is expected to increase with temperature according to the Nernst equation and is close to the expected theoretical values of 75 mV/decade at 100 °C and 83.9 mV/decade at 150 °C.

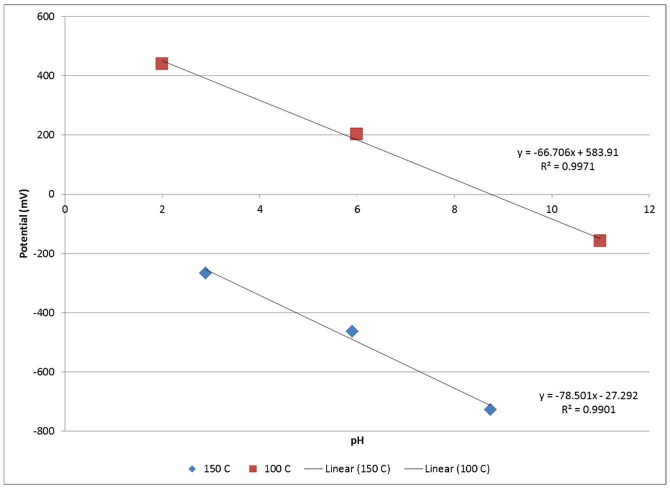

Figure 8. Plot of the Sandia pH electrode versus a commercial Ag/AgCl reference electrode (high temperature reference electrode from Corr Instruments) at 100 °C and 150 °C.

5. SUMMARY

While current methods of collecting tracer concentration and pH data at the surface provide valuable information regarding reservoir conditions, the ability to collect those data downhole in real-time may allow for the identification of the specific fractures actually producing the tracer. To accomplish this goal, the development of a wireline tool capable of measuring ionic tracer concentration, pH, temperature, pressure, and flowrate is underway. Initial specification for the tool include operation at temperatures up to 225 °C without the use of a Dewar, pressure up to 3000 psi, and measurement of iodide ion tracers at the parts per million level. Currently, the ruggedized iodide ion selective electrode 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 iodide ion 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. The current pH electrode design using a Ni-NiO internal reference has an acceptable response over pH values ranging from 3 to 9. At 150 °C the slope is -78.5 mV/decade, close to the theoretical value based on the Nernst equation and an R^2 value of 0.99. Though not yet as extensively tested as the I-ISE recent experiments have shown it should be possible to produce ISE's selective for other ions such as chloride, sulfide, and lithium even in the harsh environments found in geothermal reservoirs.

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