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

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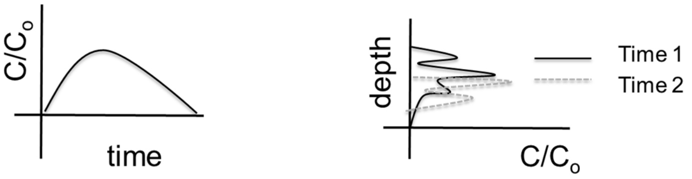
ABSTRACT

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.



a.) b.)

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.

The electrochemical 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. Therefore, at each depth a measurement is taken, tracer concentration, pH, temperature, pressure, and flowrate data will be acquired.

2. EXPERIMENTAL

2.1 Electrochemical sensor construction

The downhole tracer and pH sensors consist of three ruggedized electrodes: an iodide ion selective electrode (I-ISE), a pH electrode, and a reference electrode. Also included in the tool are the high temperature stable electronic components necessary for data acquisition and processing.

The 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.

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. Figure 3 contains a schematic of our wireline tool design incorporating our electrochemical sensor.

2.2 Material Characterization

Ag_2S/AgI pellets were characterized by powder X-ray diffraction (PXRD) on a PANalytical X'Pert Pro diffractometer using CuKα radiation with step size 0.0167 degree, with 0.152 ^{o}/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 Ag_2S in the ISM pellet. Thermal analysis was used to determine the temperature stability of the ISM pellet and was conducted in air.

2.3 Laboratory Autoclave System

High temperature and pressure experiments were conducted in a 1 L autoclave shown in Figure 4. An 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-9207 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.

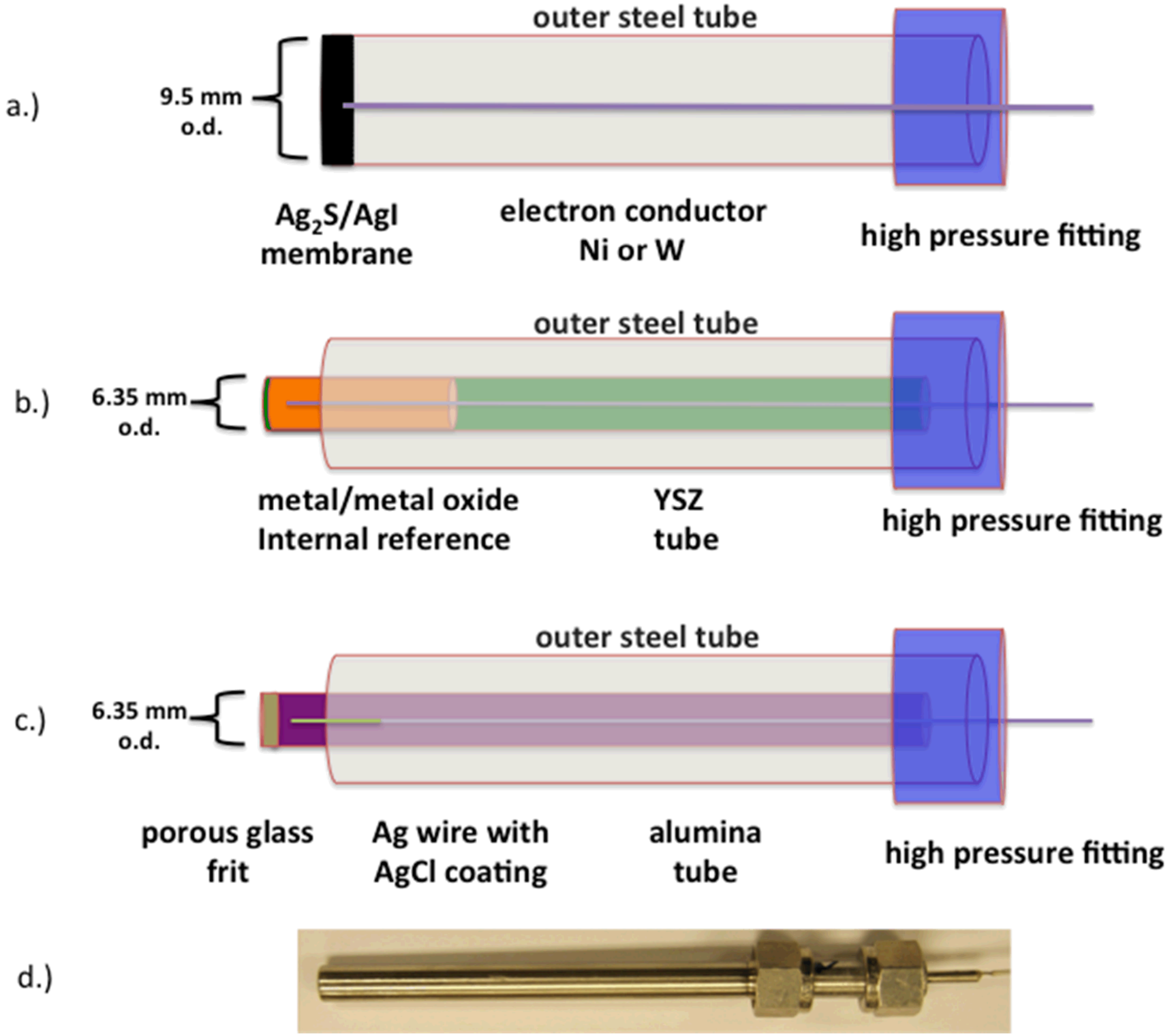


Figure 2: Schematic drawing of the ruggedized: a.) I-ISE electrode, b.) solid state YSZ pH electrode, c.) solid state Ag/AgCl reference electrode, and d.) photograph of the I-ISE using a stainless steel electrode body and high pressure fittings.

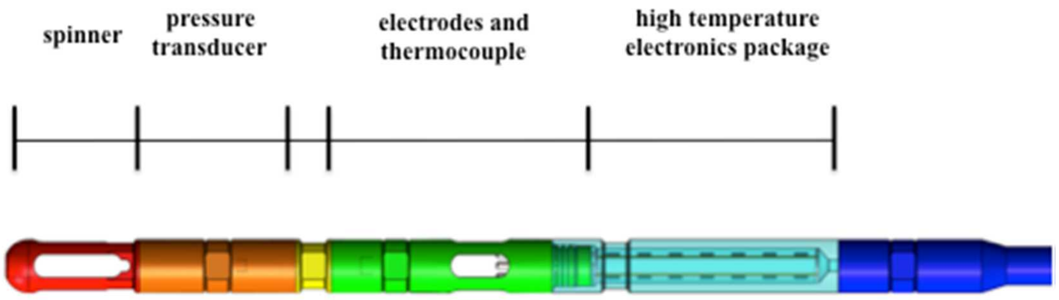


Figure 3: Schematic drawing of the wireline tool incorporating the new electrochemical sensor.

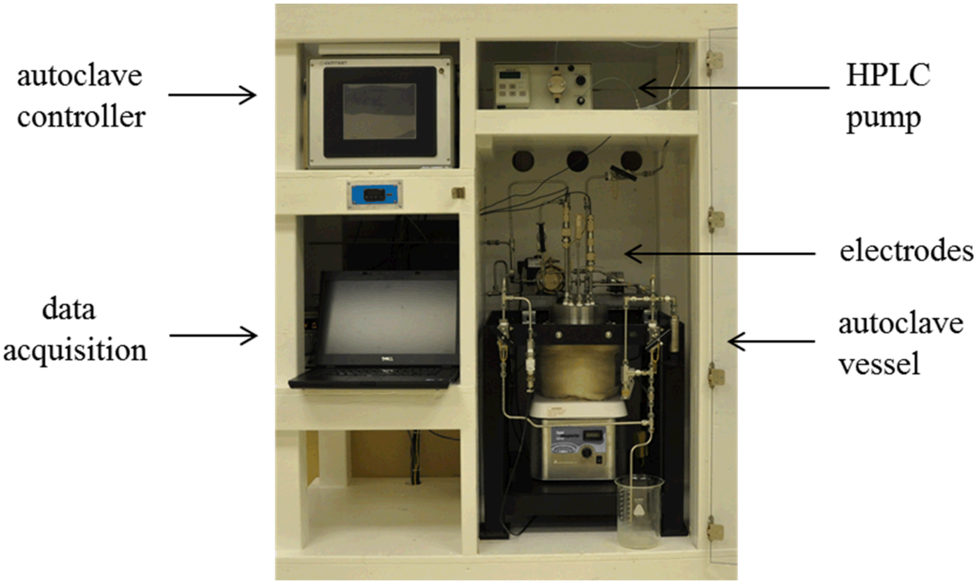


Figure 4: Photograph of the one liter autoclave and solution delivery system used in our high temperature and pressure measurements

3. IODIDE 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 and is shown in Figure 5 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 two 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.

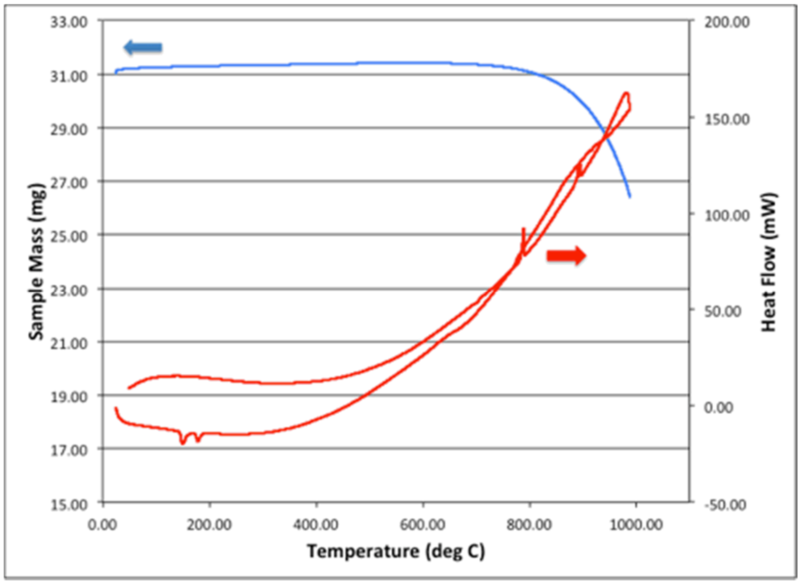


Figure 5: Thermal analysis of a 1:1 AgI-Ag_2S mixture. The primary y-axis contains Thermo Gravimetric Analysis (TGA) data while the secondary y-axis contains Differential Scanning Calorimetry (DSC) data.

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 6 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.

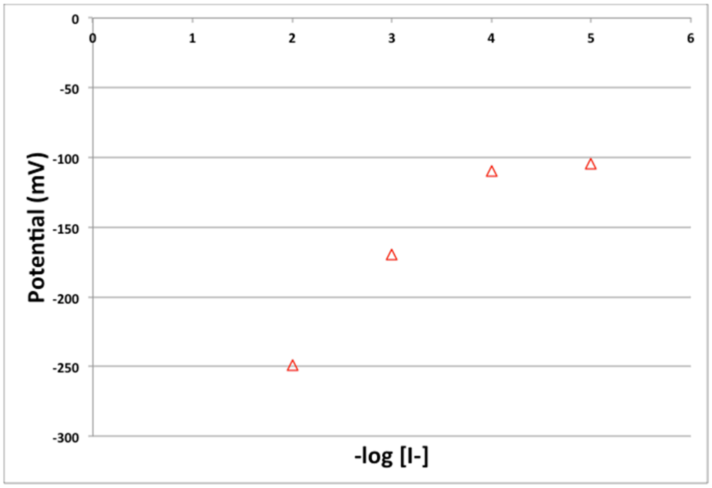


Figure 6: I-ISE response at temperature between 155 °C and 177 °C and pressure between 702 and 738 psi. Linear response was found between 10^{-4} and 10^{-2} M iodide with a R^2 of 0.993 and a slope of 70 mV/decade. The solution had a pH of 6.

This I-ISE design was tested up to 200 °C with similar results. Figure 7 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 8 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.

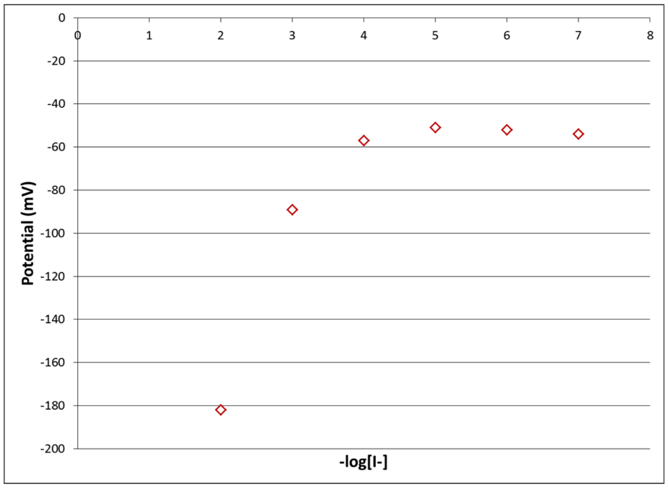


Figure 7: I-ISE response at 200 °C and an average pressure of 1171 psi. Linear response was found between 10^{4} and 10^{-2} M I^- with a R^2 of 0.926 and a slope of 63 mV/decade. The solution had a pH of 6.

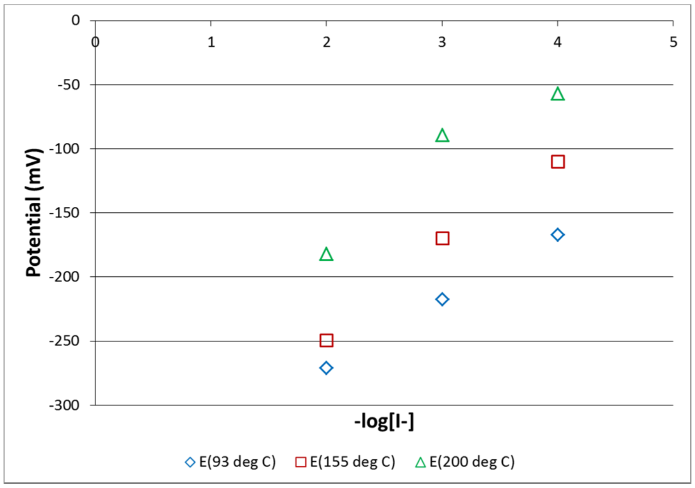


Figure 8. Plot showing the I-ISE response as a function of iodide concentration and temperature. These results show that for a given iodide concentration there is a positive increase in potential with increasing temperature as expected from electrochemical theory.

4. PH ELECTRODE PERFORMANCE

Standard laboratory pH electrodes typically use thin glass hydrogen ion membranes 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 9 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.

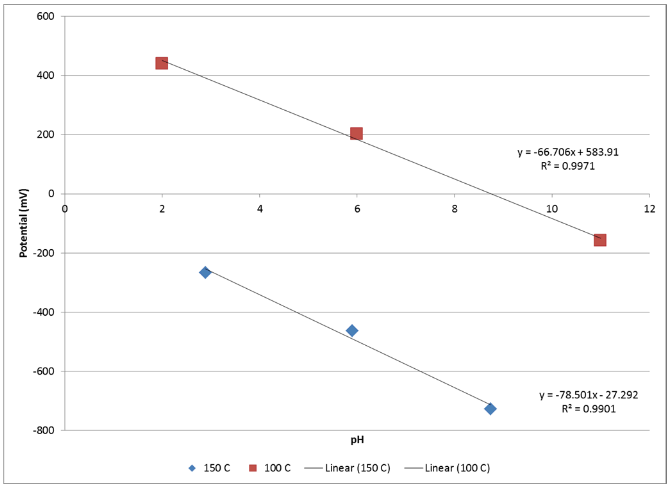


Figure 9: Plot of the Sandia pH electrode versus a commercial Ag/AgCl reference electrode (high temperature reference electrode from Corr Instruments) at 100 °C and 150 °C.

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 specifications 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. Ongoing work includes high temperature and pressure testing of a ruggedized reference electrode design and expansion of the electrochemical sensor's ability to measure other ionic species such as lithium, fluoride, and sulfide ions.

ACKNOWLEDGEMENTS

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