

## Development of a Downhole Tool for Measuring Enthalpy in Geothermal Reservoirs

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**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.

## 2. EXPERIMENTAL

### 2.1 Electrochemical Sensor Construction

The downhole electrochemical sensor consists of two ruggedized electrodes: a chloride ion selective electrode (Cl-ISE) and a reference electrode. Also included in the tool are the high temperature stable electronic components necessary for data acquisition and processing.

The Cl-ISE is composed of three main parts: an ion selective membrane (ISM) that is selective for only chloride ions ( $\text{Cl}^-$ ), 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 chloride ( $\text{Ag}_2\text{S}/\text{AgCl}$ ). The purpose of the membrane is to selectively conduct  $\text{Cl}^-$  ions. The use of  $\text{Ag}_2\text{S}/\text{AgCl}$  as a chloride ion selective material has been demonstrated by Nyachhyon et. al. (2012). 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 FEP and PTFE tube, respectively.

The reference electrode consists of a FEP/PTFE tube open on both ends. The end of the tube exposed to the reservoir contains a porous alumina frit attached to the tube using a shrinkable Teflon sleeve and fittings. The tube is filled with either a 1 M  $\text{CuSO}_4$  and copper wire or 3 M KCl solution and a silver wire coated with AgCl. Figure 1 contains schematics and pictures of our ruggedized Cl-ISE and reference electrodes. Figure 2 contains a schematic of our wireline tool design incorporating our electrochemical sensor.

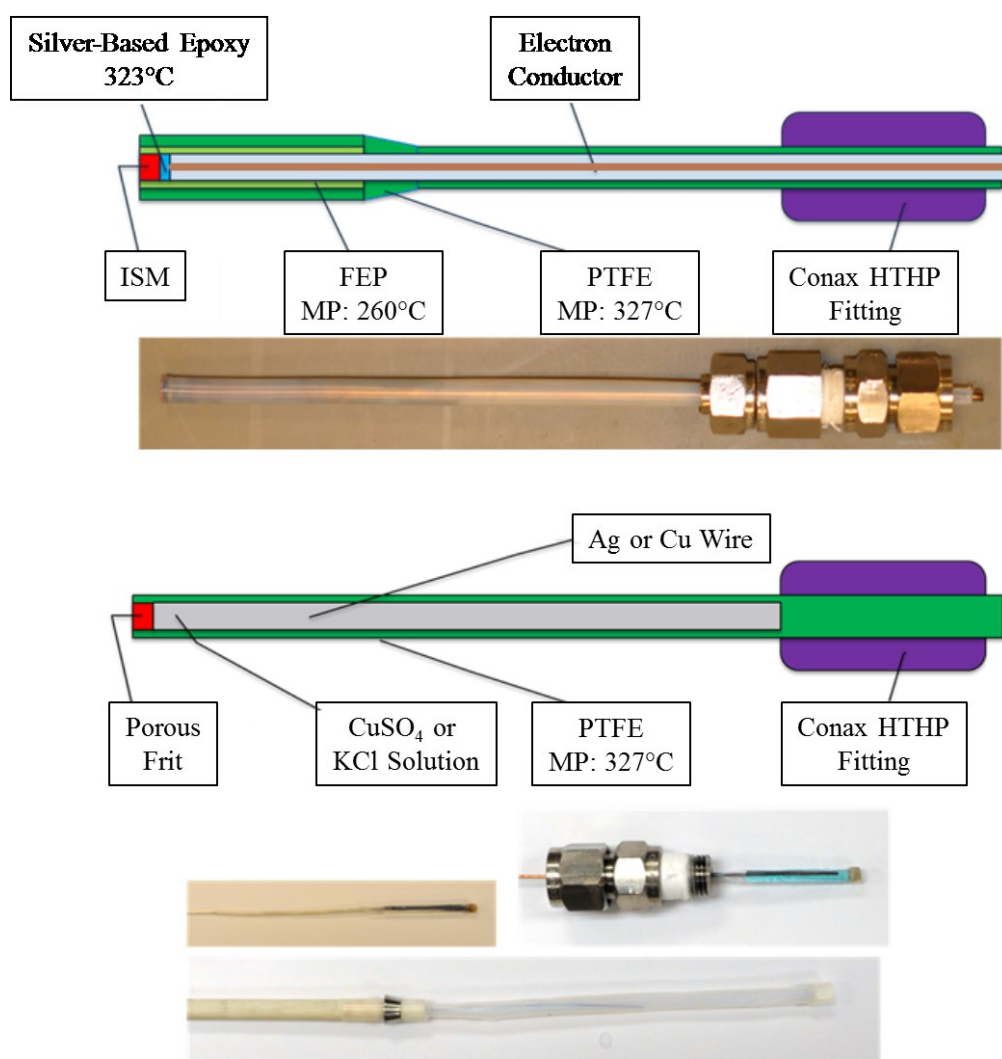


Figure 1: Schematic drawing and photograph of the ruggedized Cl-ISE electrode (top) and reference electrode (bottom).

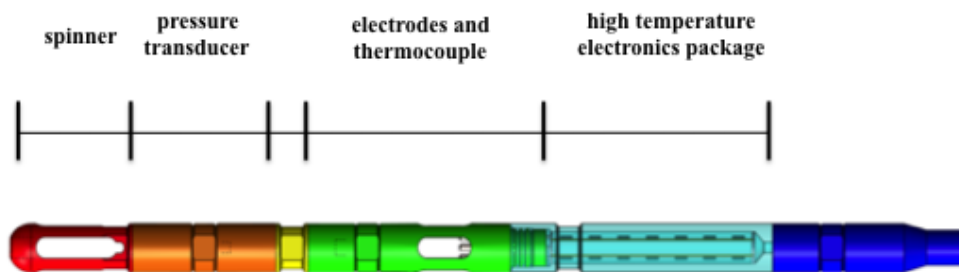


Figure 2: Schematic drawing of the wireline tool incorporating the new Cl<sup>-</sup> electrochemical sensor.

Extreme temperature electronics components are extremely limited compared to the available components at standard temperature. As a relevant example, currently available high temperature (>220°C) analog-to-digital converters typically only operate in the positive voltage range, typically 0V to +5V. Electrical potentials generated by the sensors in this project can range from approximately negative 2 volts to positive 2 volts. To make the sensor voltage compatible with the selected ADC and multiplexer electronics, a negative supply rail and a level shifter are required (Figure 3). The negative supply rail is accomplished using a diode network and switched capacitor design clocked by a high temperature 555 timer in an astable multivibrator configuration. The level shifter is accomplished using buffer and summing high temperature operational amplifier circuits. Each electrode potential is sampled through a separate channel of a high temperature multiplexer and the potential difference between the reference electrode and sample electrode are computed either in software up hole or downhole on the high temperature microcontroller. Other envisioned implementations can measure the working electrode and reference electrodes differentially or monitor by current injection with a custom high temperature potentiostat.

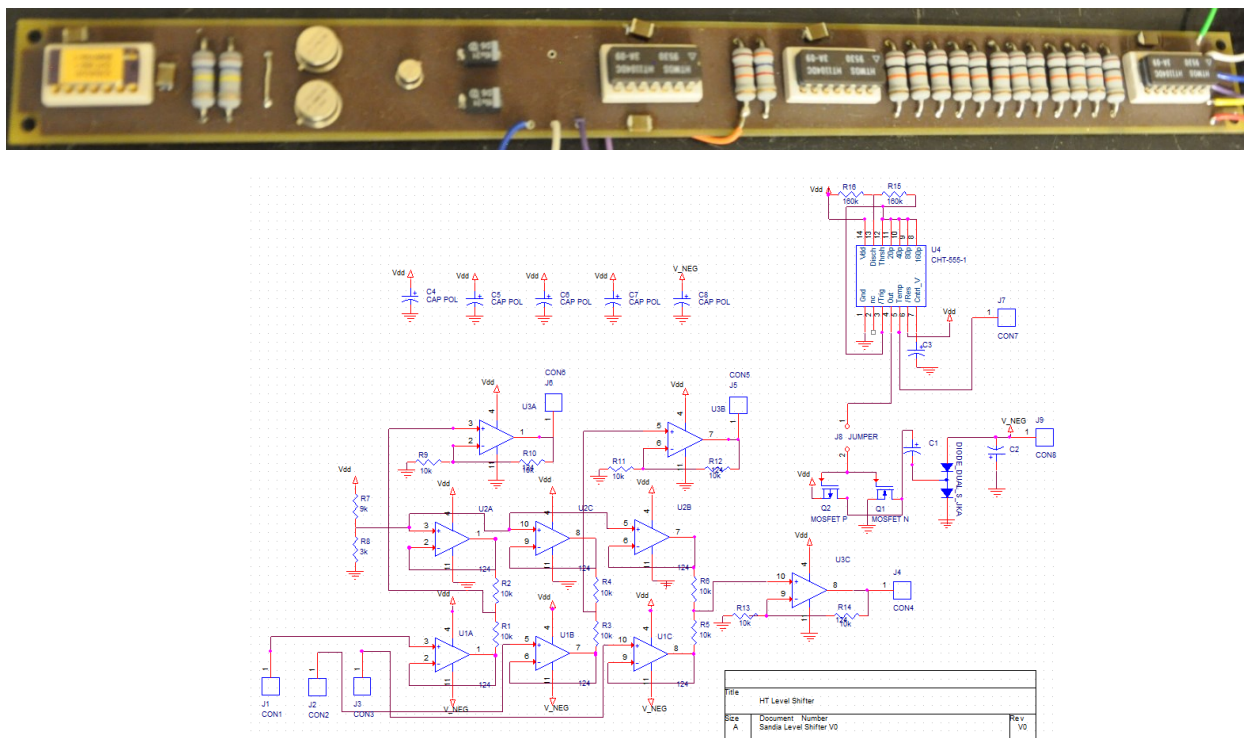


Figure 3: (Top) Populated printed circuit board of the electrochemical sensor signal conditioning circuitry. (Bottom) Circuit schematic of the high temperature signal conditioning circuitry

In addition to component performance challenges with high temperature circuitry, careful consideration must be given to the board design itself. Electrical trace work can delaminate from the printed circuit board (PCB) substrate material due to adhesive degradation, material oxidation, or thermal expansion rate mismatch between PCB materials. Surface mount components can often completely separate from the board. High temperature polyimide substrate material is used as the PCB base. To address surface mount component issues, surface mount PCB footprints are designed with a plated through-hole and mirror PCB footprint on the opposing side of the board. This costs space on both sides of the board but provides mechanical support to keep the pads in place. Where possible, trace work

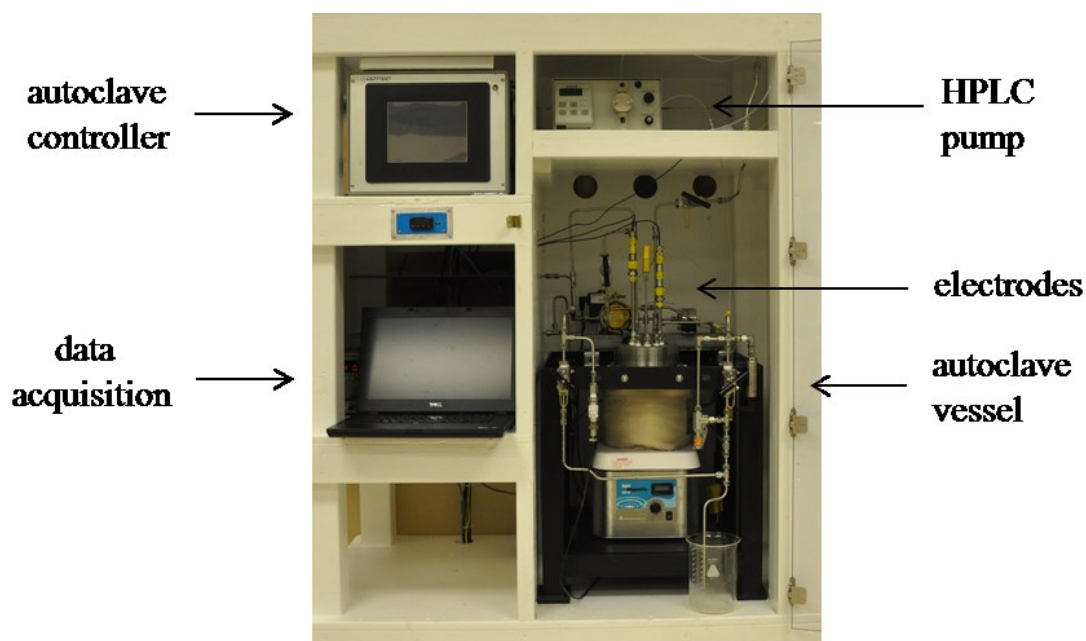
is laid in internal PCB layers to prevent degradation and delamination. Exposed copper on the PCB surface is plated with gold to prevent oxidation.

## 2.2 Material Characterization

Ag<sub>2</sub>S/AgCl pellets were characterized by powder X-ray diffraction (PXRD) on a PANalytical X'Pert Pro diffractometer using CuK $\alpha$  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 heating. PXRD was used to verify the presence of AgCl and Ag<sub>2</sub>S in the ISM pellet. Thermal analysis was used to determine the temperature stability of the ISM pellet and was conducted in air. Ion chromatography was performed on a Dionex Ion Chromatograph with an EG 50 Eluent Generator and ED 50 Electrochemical Detector, AS20 column and EGC III KOH eluent cartridge for anion analysis (method ASRS\_4mm), and a CS16 column with EGC II MSA eluent cartridge for cation analysis (method CS16\_iso\_30).

## 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. Cl-ISE measurements were conducted using 0.1 M KNO<sub>3</sub> as the supporting electrolyte. Chloride concentration was adjusted using the method of standard additions while under continuous stirring. The measurements were made using a NI-9207 16-bit analog to digital converter that simultaneously monitors the potential of Cl-ISE and reference electrodes. The autoclave itself was grounded and all the potential measurements are referenced to it. The potential difference was obtained by subtracting the reference electrode potential from the Cl-ISE potential.

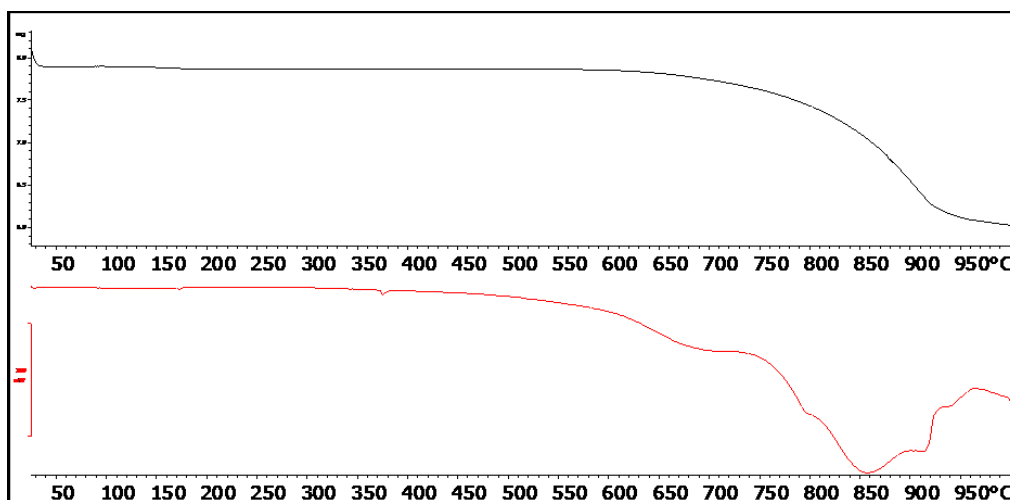


**Figure 4: Photograph of the one liter autoclave and solution delivery system used in our high temperature and pressure measurements**

## 3. CHLORIDE ION SELECTIVE ELECTRODE MEASUREMENTS

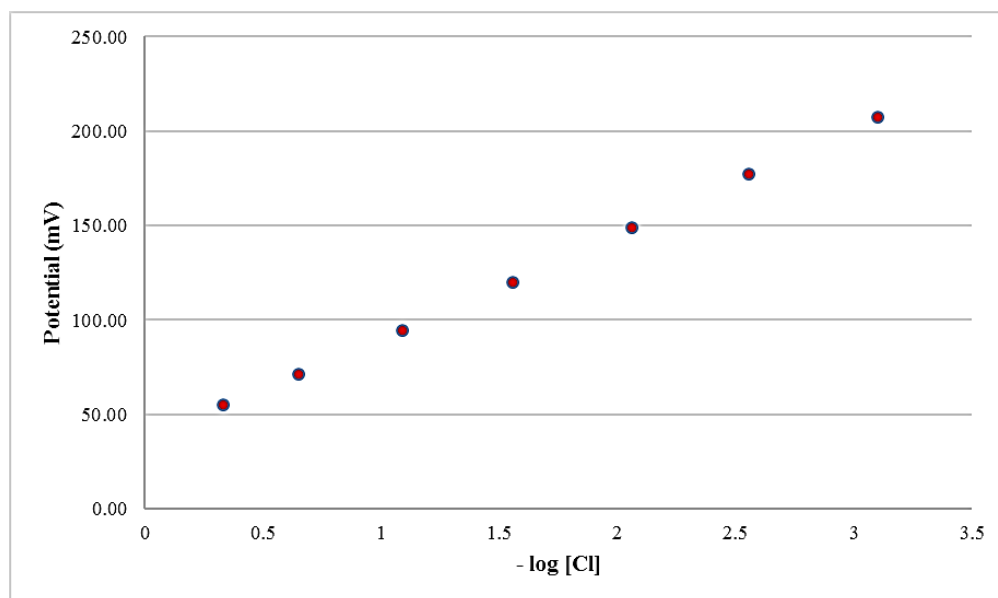
An electrochemical approach was used to measure chloride ion concentration based on its ability to ruggedize the sensor hardware for operation in harsh environments and the relatively straightforward data processing used to make open circuit potential measurements.

The chloride ion selective membrane used in this study consisted of a mixture of AgCl and Ag<sub>2</sub>S powders pressed into pellets with cylindrical geometries. In order to efficiently screen a number of different Cl-ISE designs, the majority of experiments were 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 AgCl and Ag<sub>2</sub>S in a 1:1 ratio. These data show that there is no significant mass loss below 750°C. The DSC data shows a single phase transition at relatively low temperature. This small peak, at 177°C, is the Ag<sub>2</sub>S 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.

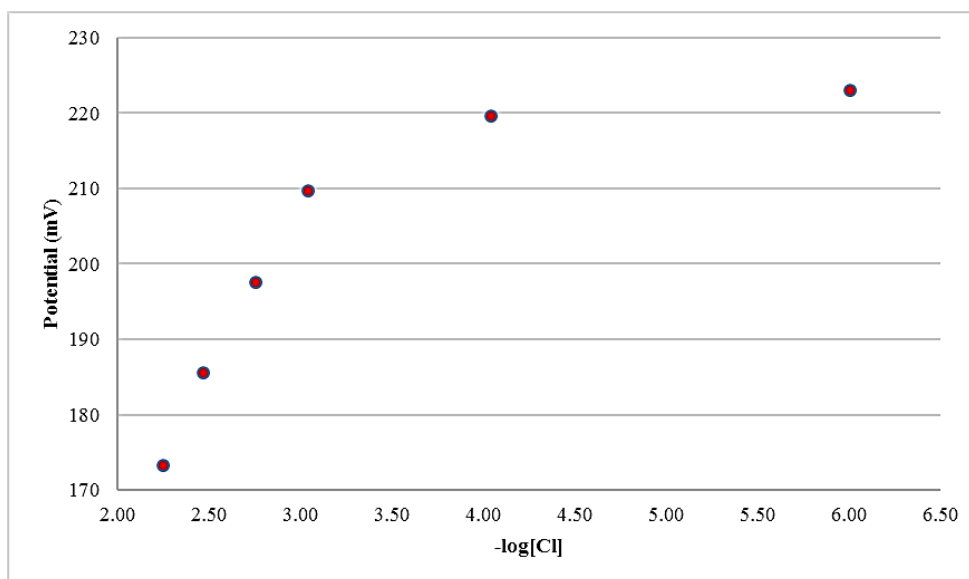


**Figure 5: Thermal analysis of a 1:1 AgCl-Ag<sub>2</sub>S mixture. (Top) Thermogravimetric Analysis (TGA) data and (bottom) Differential Scanning Calorimetry (DSC) data.**

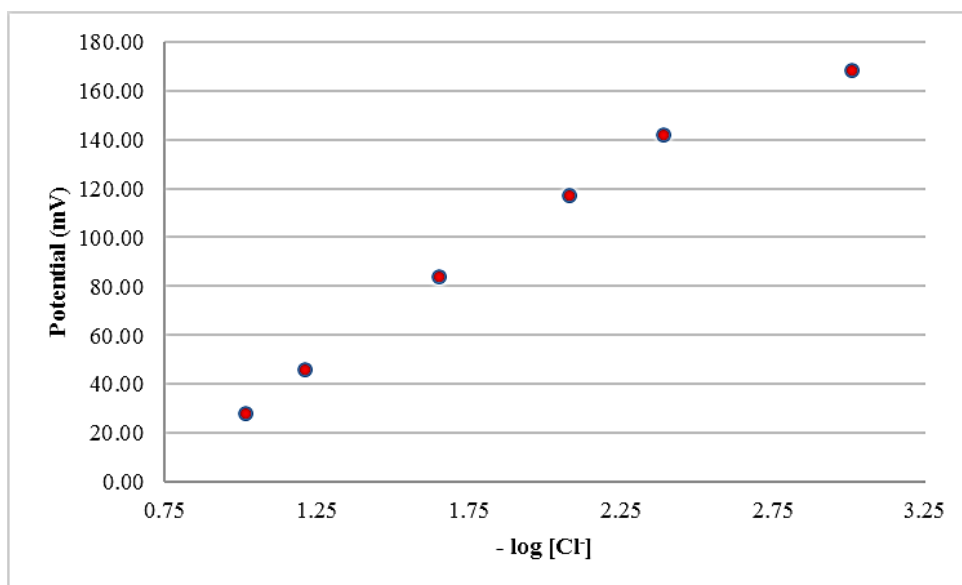
A ruggedized Cl-ISE design has been tested under elevated temperature and pressure conditions similar to those found in some geothermal wells. It is of note that because these experiments have only recently begun these results are still considered preliminary. Figures 6-8 contain plots showing electrode responses at ambient temperature, 70°C, and 200°C, respectively. The 200°C experiment was performed in the autoclave with an average pressure of 1279 psi. The supporting electrolyte was 0.1 M KNO<sub>3</sub>. This experiment shows our Cl-ISE design has approximately Nernstian response for chloride concentrations in the 10<sup>-3</sup> M to 10<sup>-1</sup> M range with a slope of 55 mV/decade and 72-82 mV/decade for the two low temperature runs and 200°C run, respectively, with R<sup>2</sup> values of 0.99 and 0.98 – 0.99. From this, it can be observed that there is a shift to less positive 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 chloride concentration under geothermal-relevant conditions.



**Figure 6. Cl-ISE response at ambient temperature and pressure using 0.1 M KNO<sub>3</sub> as a supporting electrolyte. A linear response was seen with a R<sup>2</sup> of 0.9997 and a slope of 55.3 mV/decade.**



**Figure 7.** Cl-ISE response at 70°C and ambient pressure using 0.1 M KNO<sub>3</sub> as supporting electrolyte. The linear response is seen between a pCl of 1.0 – 3.0 with a R<sup>2</sup> of 0.9924 and a slope of 55.617 mV/decade.



**Figure 8.** Cl-ISE response at 200°C and 1279 psi using 0.1 M KNO<sub>3</sub> as a supporting electrolyte. The linear response seen between a pCl of 1.00 – 2.4 had a R<sup>2</sup> of 0.9993 and a slope of 82.4 mV/decade. The linear response seen for the entire set has a R<sup>2</sup> of 0.983 and a slope of 72.382 mV/decade.

The Cl-ISE potential was tested in the presence of an assortment of ions that are common in a geothermal reservoir. Shown in Figure 9, the purpose of this study was to determine if any such ion interferes with the selective measurement of chloride. The cations Ca<sup>2+</sup> and Mg<sup>2+</sup> shows a single response at all concentrations indicating no interference to the electrode. The anions S<sup>2-</sup> and I<sup>-</sup>, however, show a significant potential drop with increased concentration. These results are reflected in the calculated value associated with these measurements, known as the selectivity coefficient, and describes the extent of interference of a specific ion. The larger the coefficient, the greater the interference. I<sup>-</sup> was determined to have the greatest impact on the potential while the cations had little to no effect.

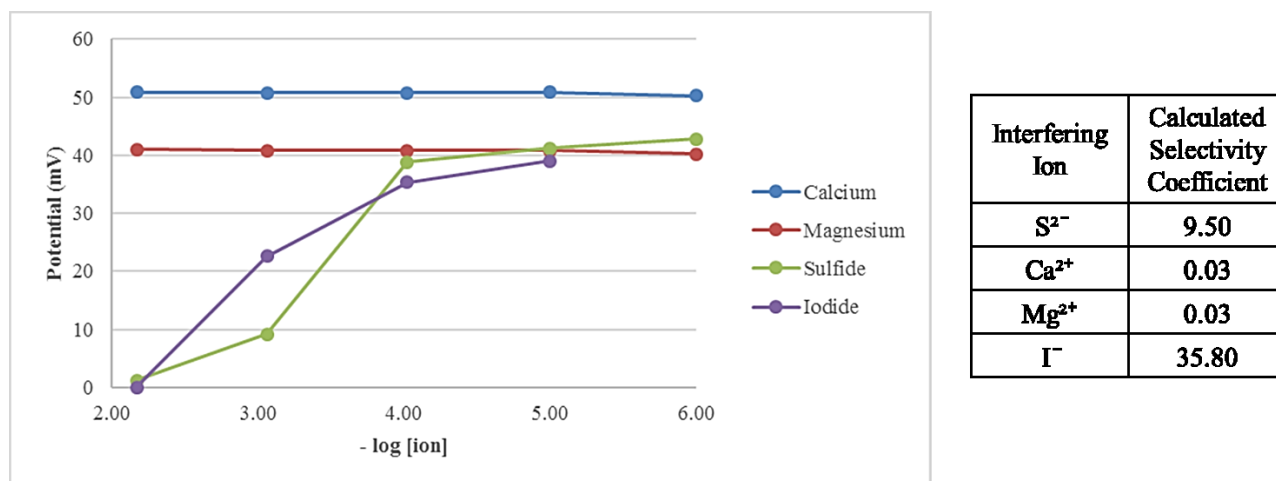


Figure 9: Cl-ISE potential response with different ions at ambient temperature and pressure.

Based on the above data it was suspected that the interference effect comes from anion exchange between chloride in the ISM and iodide/sulfide in solution. Such exchange would be due to the difference in silver halide solubility. Qualitative and quantitative tests were performed to confirm this hypothesis. First, a small amount of AgCl(s) was added to solutions of KI and Li<sub>2</sub>S to colorimetrically determine anion exchange. Shown in Figure 10, the off-white AgCl(s) turned to yellow in the iodide solution and black in the sulfide solution. These colors match commercial AgI and Ag<sub>2</sub>S, respectively, supporting anion exchange.

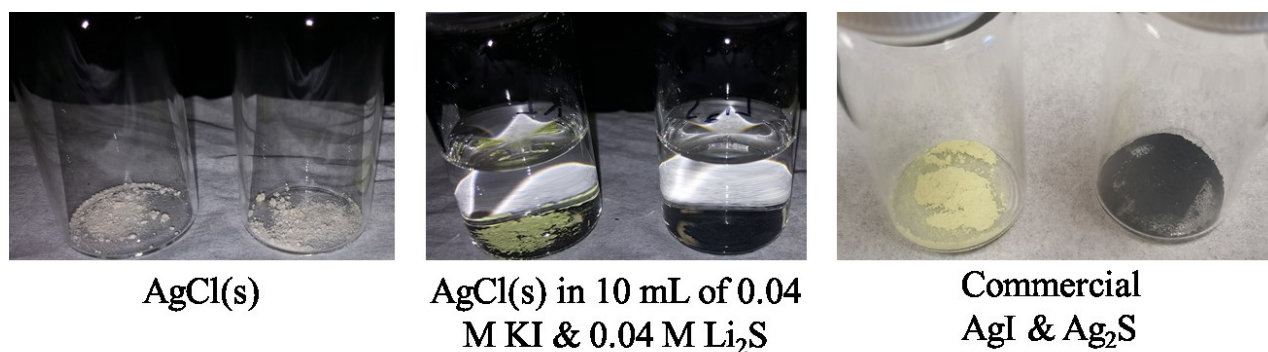


Figure 10. Qualitative observations when commercial AgCl(s) is added to solutions of I<sup>-</sup>(aq) and S<sup>2-</sup>(aq). Anion exchange occurs due to the difference in solubility product constants ( $K_{sp}$ ).  $K_{sp}$  for AgCl =  $1.77e^{-10}$ , AgI =  $8.52e^{-17}$ , Ag<sub>2</sub>S =  $8.0e^{-51}$ .

Finally, once the qualitative measurements of anion exchange were confirmed, the quantitative extent of the exchange was of interest, as degradation of the ISM was expected to increase with greater exchange. Three solutions (0.1, 0.01, and 0.001 M) were made for both iodide and sulfide using KI and Li<sub>2</sub>S, respectively. A precise amount of AgCl(s) was added to each of these vials and allowed to stir overnight followed by solution analysis using ion chromatography. The results, given in Table 1 below, indicate the majority of mixtures completely exchange the Cl<sup>-</sup> in the ISM for the solution anion. These results support the claim of surface anion surface exchange on the ISM pellet and thus the observed interference.

**Table 1: Quantitative results of ion chromatography analysis for potassium and lithium salts. Estimated limit of detection for the ions: Li ~ 7.1e<sup>-5</sup> M; K ~ 1.3e<sup>-5</sup> M; Cl ~ 1.4e<sup>-5</sup> M. Samples were diluted to optimal concentrations for chromatographic analysis.**

Dilution factor	Expected Concentration	Lithium (moles/L)	Potassium (moles/L)	Chloride (moles/L)
964	0.1M KCl	--	0.1043	0.1025
103	0.01M KCl	--	0.0112	0.0101
10	0.001M KCl	--	0.0006	0.0005
103	0.2M LiCl	0.1939	--	0.1999
10	0.02M LiCl	0.0198	--	0.0171
1	0.002M LiCl	0.0022	--	0.0018

#### 4. CONCLUSIONS

While current surface methods of collecting data needed for downhole enthalpy provide valuable information regarding reservoir surroundings, the ability to collect that data in real-time may allow for the identification of specific fractures where optimal enthalpy conditions exist. These measurements rely on the capability to determine steam fractions and the flow rates associated with each phase. To accomplish this goal, the development of a wireline tool capable of measuring chloride ion concentration, temperature, pressure, and flowrate is underway. Chloride concentration determinations “throughout the wellbore provides a route to measure the steam-to-liquid fraction, as more liquid would result in a more dilute solution and more steam would result in a more concentrated solution. 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 chloride ions at the part per million level. Currently, the ruggedized Cl-ISE shows near Nernstian responses for chloride concentrations in the 10<sup>-3</sup> M to 10<sup>-1</sup> M range from ambient temperature to 200°C. Ion selectivity measurements revealed iodide/sulfide interference and ion chromatographic experiments confirmed the extent and cause. Efforts are underway to determine the selectivity coefficients of other ions seen in geothermal brine, lifetime stability of the ISE, and integration of the entire tool for an actual wellbore test.

#### ACKNOWLEDGEMENTS

Portions of this work were funded by the Sandia Laboratory Directed Research and Development (LDRD) Program and by the Department of Energy Geothermal Technologies Office. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000.

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