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# Development of a HTHP Logging Tool for Downhole pH Measurements

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## ABSTRACT

Sandia National Laboratories has developed technology enabling novel downhole electrochemical assessment in extreme downhole environments. High-temperature high-pressure (HTHP) electrodes selectively sensitive to hydrogen ($H^+$), chloride ($Cl^-$), iodide ($I^-$) and overall ionic strength (Reference Electrode$^{+-}$) have been demonstrated in representative geothermal environments (225°C at 1500 psi in surrogate geothermal brine). This 2-year program is a collaboration effort between Sandia and Thermochem, Inc. with the goal of taking the prototype sensors and developing them into a commercial product that is operable up to 300°C and 5000 psi. While other sensors may prove useful in the future, the focus of this collaboration is the pH and reference probe.

The National Technology and Engineering Solutions of Sandia (NTESS)-developed prototype HTHP chemical sensor package creates a capability that has never been possible to date. This technology is desired by the geothermal industry to fill a gap in available downhole real-time measurements. Only limited sensors are available that operate at the extreme temperatures and pressures found in geothermal wells. The existing Thermochem two-phase downhole sampling tool (rated to 350 °C) will be re-configured to accept the sensors. A downhole tool with an integrated pH real-time sensor capable of operation at 300°C and 5000 psi does not exist and as such, the developed technology will provide the geothermal industry with data that would otherwise not be possible such as vertical in-situ pH-profiling of HT geothermal wells. The pH measurement was chosen as the first chemical sensor focus since it is one of the fundamental measurements required to understand downhole chemistry and it directly affects installation longevity.

## 1. Introduction

The Sandia-developed prototype high-temperature high pressure (HTHP) chemical sensor package creates a capability that has never been possible to date. This technology is desired by the geothermal industry to fill a gap in available downhole real-time measurements. Only limited sensors are available that operate at the extreme temperatures and pressures found in geothermal wells. A downhole tool with an integrated pH real-time sensor capable of operation at 300°C and 5000 psi does not exist and as such, the developed technology will provide the geothermal industry with data that would otherwise not be possible such as in-situ vertical pH profiling of HT geothermal wells. The pH of fluids is one of the fundamental measurements required to understand downhole chemistry, is critical to geochemical modeling simulations and understanding of scaling and corrosion processes. Initial laboratory testing shows that the Sandia chemical sensor package functions at high temperature and pressure while maintaining necessary sensitivity and selectivity. Thermochem is positioned to advance the current prototype probes into a commercial logging tool. Furthermore, Thermochem's existing downhole sampler (DHS) tool can be retrofitted to integrate the Sandia HTHP chemical sensor package within the payload of the tool. While other sensors may prove useful in the future, the focus of this collaboration is the pH and reference probe.

The goals of this collaboration include optimizing the probe internal assembly components, increasing the operating temperature to 300°C and pressure to 5000 psi and enhancing the packaging of the device to ease the implementation of the sensors into a downhole tool. By the end of the second year of this project, it is anticipated that a series of downhole field tests will be conducted to validate the accuracy and repeatability of the developed sensors. The field tests will use the pH sensor and reference probe integrated into Sandia's HT Tool along with fielding of Thermochem's DHS. This will permit the tests to include sampling of the downhole fluid which will enable direct pH comparison between the downhole sample and the real-time pH sensor. Several downhole zones will be sampled as part of this field work.

At the completion of this effort, the design for integrating the pH and other sensors into Thermochem's sampling tool and surface equipment will be complete. In addition to a downhole pH sensor, measuring pH at high temperatures will enable the monitoring of surface brine pH in chemical process applications including corrosion mitigation and scale inhibition at the actual process temperature. These systems potentially can be enhanced with the developed sensors by providing real-time measurements of produced high temperature geothermal fluids and using these measurements to control and optimize the treatment required. This real-time optimization can potentially lower production costs.

The key obstacles that need to be overcome to ensure commercial success include: 1) optimizing the internal components to ensure the probes can be fabricated commercially at a reasonable cost. 2) increasing the operating parameters to 300°C and 5000 psi. Preliminary lab test results indicate these parameters are reasonable and achievable. Further lab testing is required for validation. 3) packaging of the sensor to enable integration into a downhole tool. The present design is close to what is needed, but an improvement such as a redundant seal is needed. A path to solve these key obstacles is outlined in the technical section of this document.

## 2. Background

The technology to be enhanced for industry adoption through the proposed work has been developed by Sandia during the period of FY13-FY18. Sandia was initially funded to develop a high-temperature chemical sensing tool for distributed mapping of fracture flow in enhanced geothermal systems. The effort continued through FY18. The initial goal of the project was 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. Below are highlights of the project development timeline. The test apparatus used for the initial tests is shown in figure 1.

FY13-14 Sandia Geothermal worked with the Sandia Advanced Materials Laboratory to develop and test prototype electrochemical sensors consisting of a HT stable ion-selective electrode for detecting iodide, a HT reference electrode, and a HT pH electrode which would enable measurement of tracer concentrations and pH downhole on a wireline tool. An HT potentiostat electronic system was designed and constructed to enable downhole tool instrumentation. Initial testing was performed using a high-temperature high-pressure autoclave in water, while subsequent tests used representative geothermal brine.

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.

FY16 Sandia integrated the electrodes and HT signal conditioning electronics into a 2-inch diameter high-temperature wireline logging tool.

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 halfway 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 eliminating the liquid junction by developing a solid-state materials approach.

FY18, the solid-state reference electrode technologies were refined and calibrated in representative geothermal environments (225°C and 1500 psi in surrogate geothermal brine).

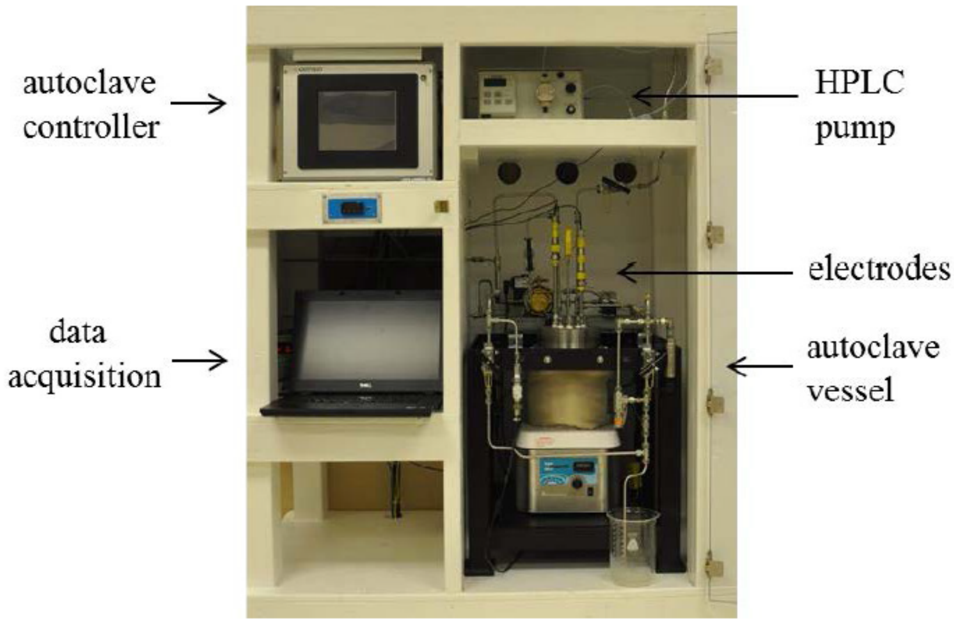


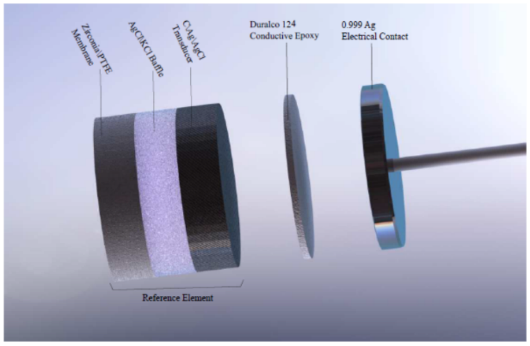

**Figure 1: Autoclave and associated components used in the initial development effort**

## 3. Probe assemblies

Each probe has a unique material makeup and specific assembly techniques. The basic details follow:

The pH sensor is comprised of an yttria (10%)-stabilized zirconia tube that is closed on the sensor end. The 10% yttria acts as an oxygen ion conductor and contains an internal reference consisting of metal-metal oxide pair (both nickel-nickel oxide and copper-copper oxide has been lab tested). The pair of choice is the nickel-nickel oxide and is the configuration for the probes to be re-tested to validate the previous probe assembly and test results. To complete the electron conductive path for the sensor, a nickel rod will be submerged into the nickel-nickel oxide powder and will exit the top of the zirconia tube for connection into the measurement system.

The reference probe is an alumina tube (shell) comprised of four internal layers that serve functions to enable a stable reference for the pH measurement, namely an electrical contact, a transducer, a baffle or reference membrane and a hydrophobic ion-permeable ceramic membrane composite (Figure 2). The layers are compressed and sintered into a solid crystalline body (pellet) and housed within a low porosity alumina shell when assembled. Within the shell, an electrode is attached to the pellet using a conductive epoxy where it exits the top of the alumina tube for connection into the measurement system (Figure 3 and Figure 4).



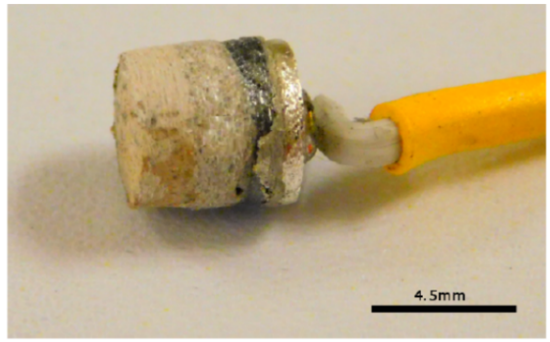




**Figure 2: Reference Probe Internal Makeup** **Figure 3: Assembled Reference prior to shell**

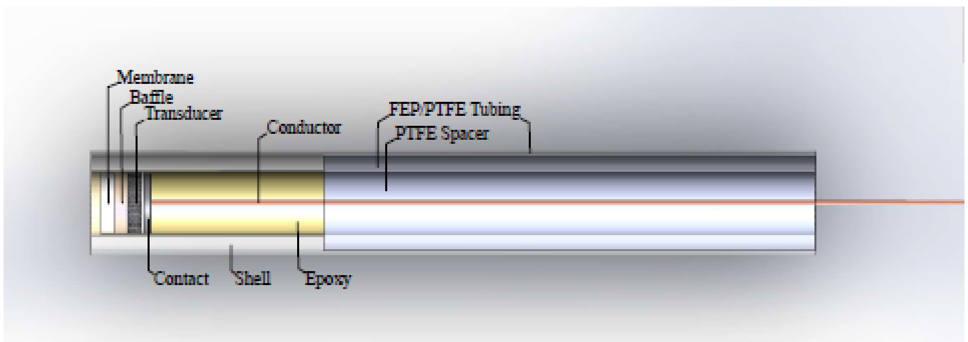



Figure 4: Sketch of reference probe overall layout

## 4. Path to Solving Obstacles

As stated earlier, the success of this project hinges on addressing three key obstacles, namely: 1) optimizing the internal components to ensure the probes can be made commercially at a reasonable cost. 2) increasing the operating parameters to 300°C and 5000 psi. 3) packaging of the sensor to enable integration into a downhole tool. Details of the required tasks to overcome the key obstacles are outlined below:

### *4.1 Optimizing Internal Components*

Before optimalization, the Sandia-developed probes and testing details will be discussed, probes will be assembled using prior techniques and laboratory tested to assure the same results are obtained to verify the probe assembly techniques. Thermochem will provide input to Sandia about the needs for deployment and successful commercialization as an adaptation to their current sampling system. In parallel with the verification of the probes using prior techniques, the team will address the required changes to optimize the assembly process and to achieve the goal of manufacturing the probes outside of Sandia. To achieve market success, the developed systems must eventually meet Thermochem's cost- based metrics for profitability. The Sandia build procedure will be worked through to identify areas that could be enhanced to improve efficiency, and/or simplify the build procedure to ultimately lower the cost of production. Material sources external to Sandia will be identified for all necessary components. The identification and implementation of an external source to build the probes is a critical step in the commercialization process. Without a method of manufacturing the probe outside Sandia at a reasonable cost, the commercialization value would be significantly diminished.

4.1.1 Current Status

The status for the work pertaining to optimizing the internal components are heighted below:

The internal parts for both the pH and reference probes are ordered. The original die design required for fabricating the pellets is being reviewed and will be updated if necessary to enable the fabrication of the pellets.

The assembly procedures for the probes are being reviewed.

The electrodes for each probe are being evaluated to enable a common material to be used for both.

### *4.2 Increasing Probe's Operating Parameters*

Thermochem has determined that 300°C at 5000 psi is a broadly useful environmental characterization for geothermal customers. While risks exist to extend the operating temperature and pressure of the probes, the data from previous tests suggest this task is achievable. If the outcome of this task results in a lower temperature and/or pressure than desired, it will be documented and discussed with Thermochem. Between the two factors, an operating temperature of 300°C is more important compared to the pressure. As such, increasing the operating temperature will be the highest priority.

4.2.1 Performance Evaluation

After optimizing the probes for higher temperatures and pressures, Sandia will conduct performance tests to validate the sensors for sensitivity, accuracy, and repeatability. Thermochem will provide the representative geothermal fluids for the tests, analytical lab support and their own in-house high-temperature reaction vessel with chemical dosing and constant gas partial pressures ($CO_2$ and $H_2S$) capability. It will also be a goal of this step to evaluate the sensors for long-term drift and determine an estimation of sensor life under the extreme geothermal environmental conditions. Due to time constrains of the project and the broad scope of work, comprehensive analysis may not be possible, but this subtask will serve as a good step towards commercializing the sensors. At the completion of the project, Thermochem will continue testing the sensors, using this baseline data for reference.

4.2.2 Current Status

Sandia now has a higher pressure and temperature autoclave and HPLC pump. Sandia and Thermochem are working together to identify the components necessary to enable the developed probes to be tested at temperatures up to 300°C and pressures up to 5000 psi. The system should be online for testing probes by the end of May. In addition, the probes (both pH and reference) utilized as the reference for the Sandia developed probes are no longer operational. Thermochem has reviewed the available options for the probes that will be used for reference and have identified probes that should serve well for the planned testing both at Sandia and Thermochem.

### *4.3 Packaging for Downhole Tool*

Mechanical and electrical design support from both Thermochem and Sandia will work together from the beginning of the project to establish a planned implementation of the probes into the existing Thermochem tool. While this collaboration will be limited to mechanical and electrical design only, the future integration of the pH and reference probe will complement the present measurements of well temperature, pressure, flow (spinner) and 2 phase flow sampling. If funding permits, the pH and reference probes will be integrated into the Sandia HT Tool and together with Thermochem's sampling tool, will be fielded for direct comparison between collected samples and measured pH.

#### 4.3.1 Current Status

To enable the probes to be integrated into downhole tools, the probes must have resilient seals to prevent possible leaks within the tool and must be small in diameter to enable integration into the tool's sub. As such, we are currently working on eliminating the outer layer of Teflon and replacing with an outer ceramic shell. The outer shell will be metalized on the upper end of the tube and brazed into the tool's sub, thereby eliminating the bulky fittings utilized for the initial tests. The braze effort is being conducted in parallel since it is not required for evaluating the probes using the autoclave.

## 5. Summary

While this project is just getting underway, based on the years Sandia has invested into the material selection, assembly procedure and test results, commercializing the pH and reference probes for use both for downhole and high temperature surface applications look promising. Optimizing the probes for both higher temperature and pressure operation will likely entail changes in hardware, assembly procedure and material selection, but is believed to be technically achievable.

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