



# Development of a High Temperature, High Pressure Logging Tool for Downhole pH Measurements

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# Outline

- Introduction
- Background
- Probe Assembly
- Obstacles
- Summary



# Introduction

- The Sandia-developed prototype high-temperature high pressure (HTHP) chemical sensor package creates a capability that has never been possible to date
- 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 345 bar does not exist
  - Developed sensor enables in-situ vertical pH profiling of geothermal wells
    - The pH of fluids is one of the fundamental measurements required to understand downhole chemistry
    - Critical to geochemical modeling simulations and understanding of scaling and corrosion processes
  - Thermochem is positioned to advance the current prototype probes into a commercial logging tool



# Background

- The technology to be enhanced for industry adoption through this collaborative effort has been developed by Sandia during the period of FY13-FY18
- 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
- FY15 Sandia focused on refining and calibrating the three 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
- FY18 The solid-state reference electrode technologies were refined and calibrated in representative geothermal environments (225°C and 103 bar in surrogate geothermal brine)



# Goals

- Year 1 Goals
  - Optimize the probe internal assembly components
  - Increase the operating temperature to 300°C and pressure to 345 bar
  - Enhance the packaging of the probes to ease the implementation into a downhole tool
- Year 2 Goals
  - Further optimization and lab testing of probes
  - Field tests
    - Conduct series of downhole field tests 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 high-temperature (HT) tool and fielded with Thermochem's DownHole Sampler (DHS) tool
    - 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

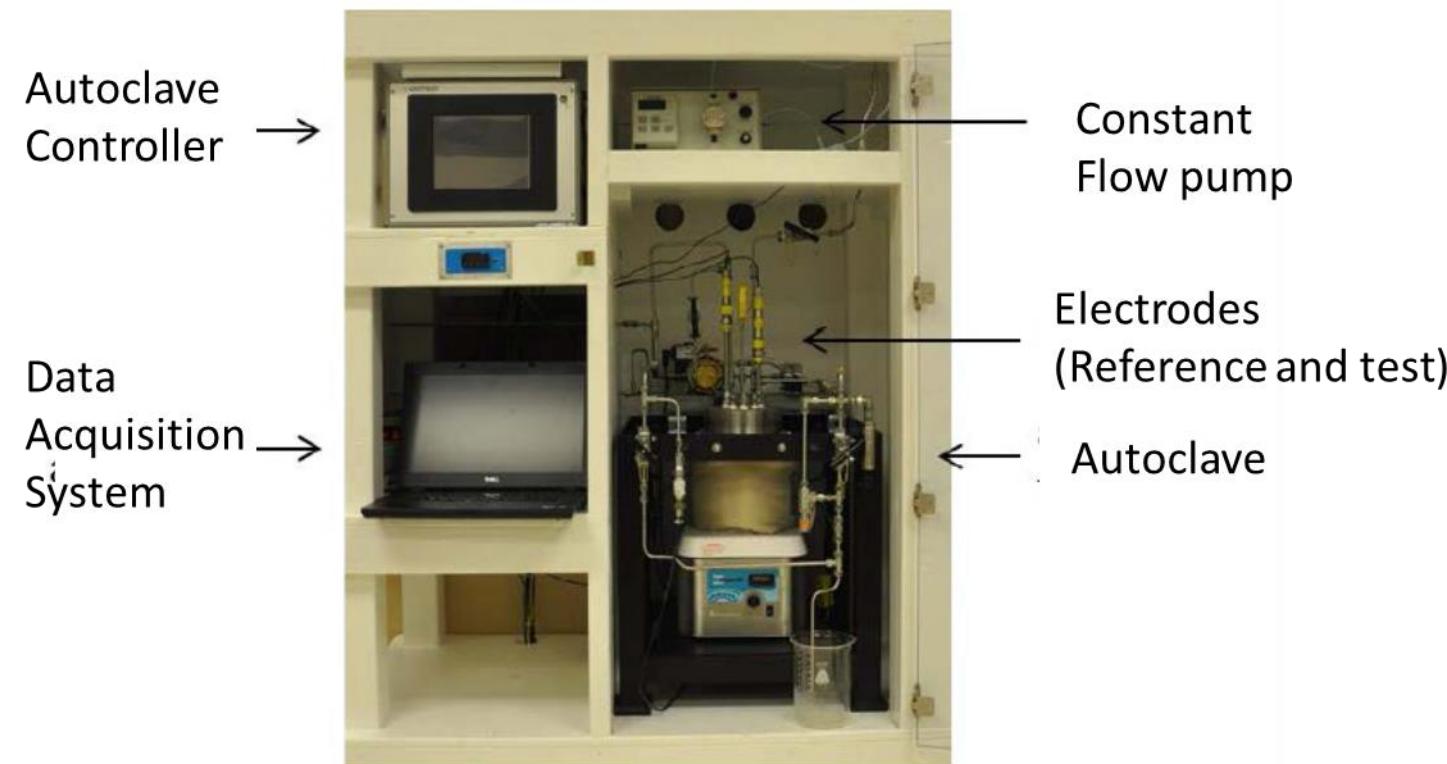


# Obstacles

- The key obstacles that need to be overcome to ensure commercial success include:
  - Optimizing the internal components to ensure the probes can be fabricated at a commercially viable cost
  - Increasing the operating parameters to 300°C and 345 bar
    - Preliminary lab test results indicate these parameters are reasonable and achievable
  - 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



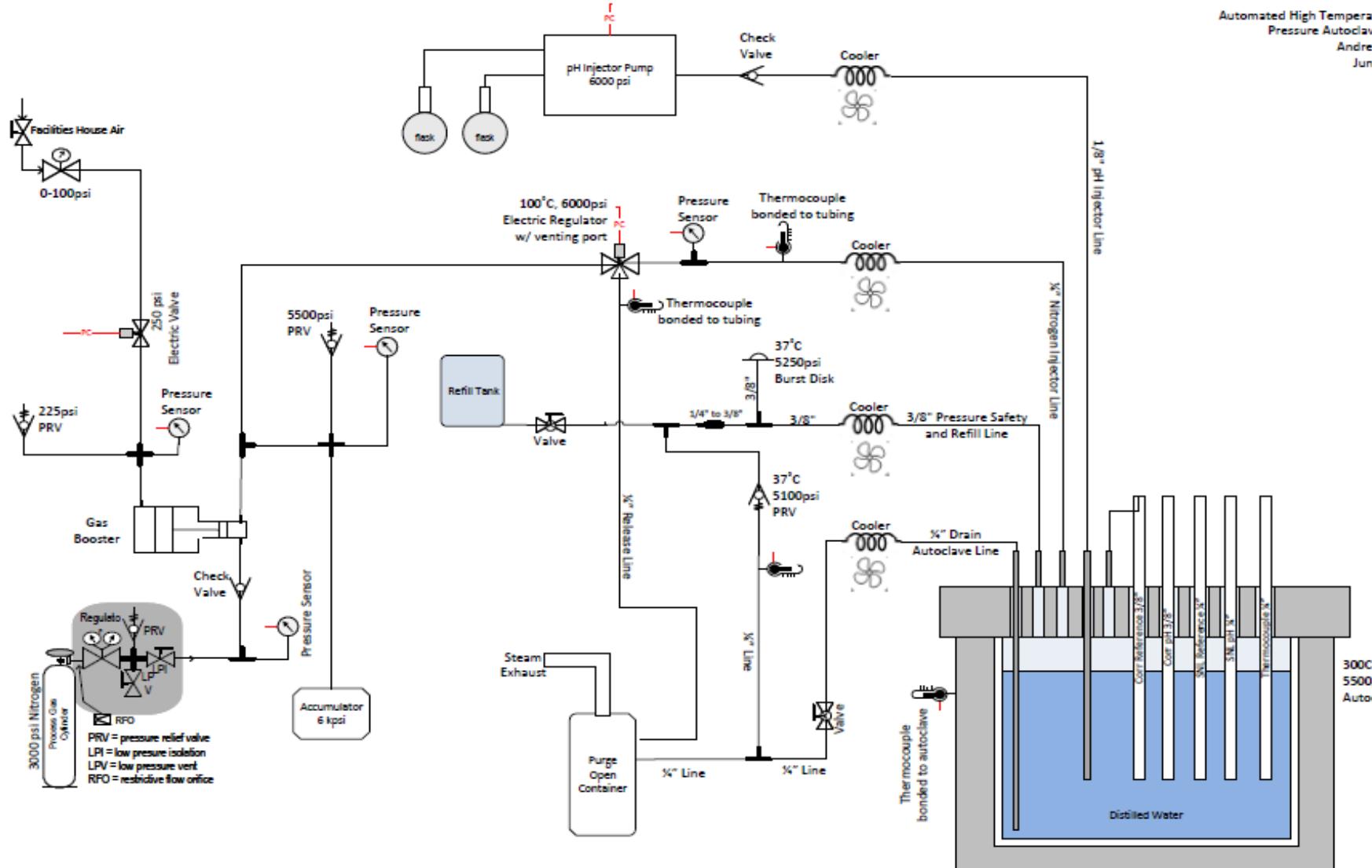
# Initial Lab Testing



# Enhanced Autoclave Design



Automated High Temperature High Pressure Autoclave System  
Andrew Wright  
June 7, 2022





# Probe Assemblies

## Reference Probe

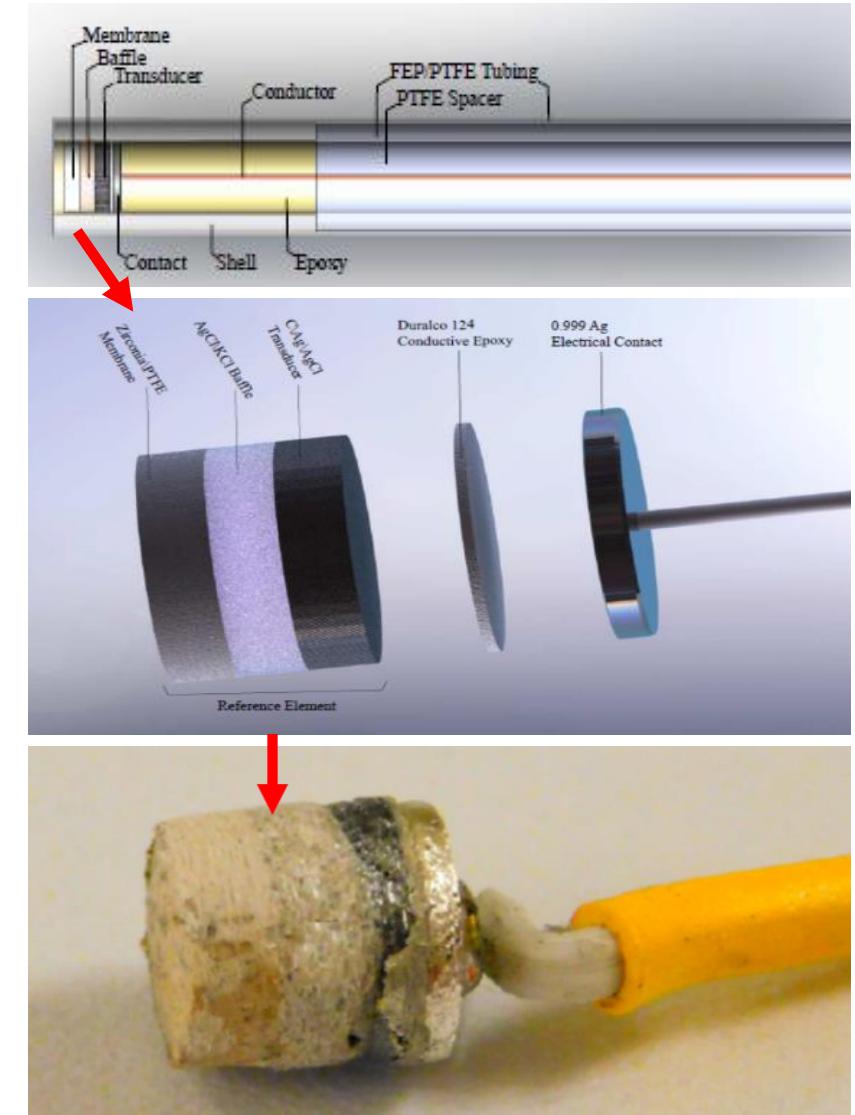
- Characteristics of an ideal reference probe include:
  - Remain constant and stable over the duration of the experiment (tool deployment)
  - Be compatible with the solution under study
  - Demonstrate that it behaves in a proper thermodynamic manner
  - Respond to changes in activities (concentrations) of the electroactive components involved in the electrode reaction in accordance with the Nernst equation
  - Activity of the potential-determinate ion must be known at the temperature, pressure and concentrations of interest
- Added for our application of operating at high temperature and pressures
  - Rugged to withstand high temperatures at high pressures and rapid heat-up and cool-down cycles
  - Reasonable long service life
    - Design to enable calibration checks and replacement



# Probe Assemblies

## Reference Probe

- 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. They are:
  - Electrical contact
  - Transducer
  - Baffle or reference membrane
  - Hydrophobic ion-permeable ceramic membrane composite
- The layers are compressed and sintered into a solid crystalline body (pellet)





# Probe Assemblies

## Reference Probe-pellet element fabrication





# Probe Assemblies

## pH Probe

- 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
  - Contains an internal reference consisting of nickel-nickel oxide
  - To complete the electron conductive path for the sensor, a nickel rod is bonded to metal pair and exits top of the zirconia tube for connection into the measurement system

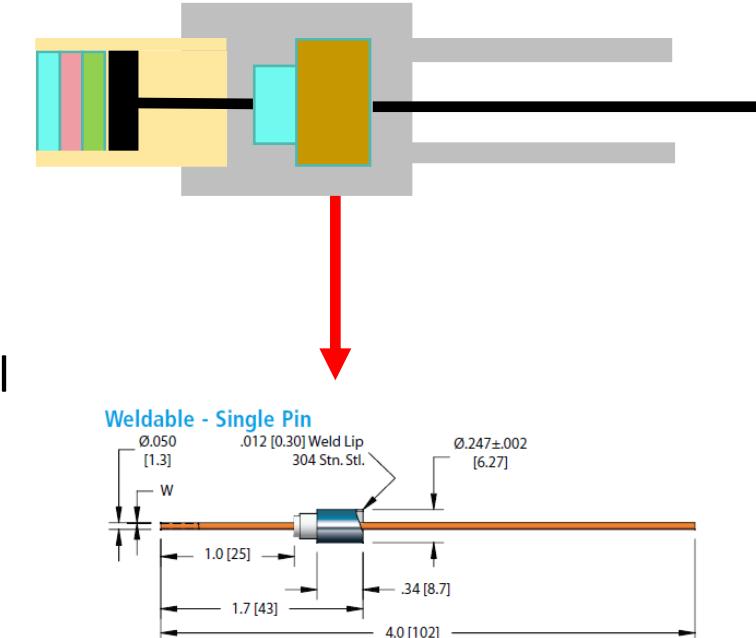




# Probe Assemblies

## Increasing Pressure Capabilities of Reference Probe

- Original design relied on Teflon as seal for pellet, electrical isolation and was part of the pressure seal
- Redesign to increase pressure capabilities includes
  - Eliminating Teflon as the sealing mechanism
  - Integrating high pressure/high temperature electrical feedthrough as primary seal to help ensure no leaks into tool
  - Pellet will be pressed directly into ceramic tube
  - Ceramic bonded to pellet

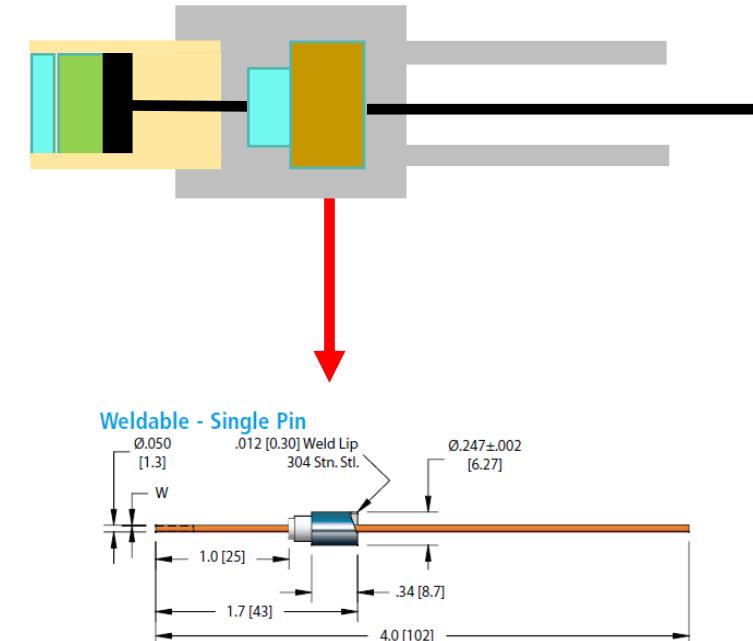




# Probe Assemblies

## Increasing Pressure Capabilities of pH Probe

- Original design relied on sealing zirconia tube into tool's pressure housing, possible leaks when temperature cycled
- Redesign to increase pressure capabilities includes
  - Integrating high pressure/high temperature electrical feedthrough as primary seal to help ensure no leaks into tool
  - Pellet approach with alumina shell (consistent with reference probe)
    - Powdered yttria stabilized zirconia
    - Metal-metal oxide
    - Ceramic bonded to pellet

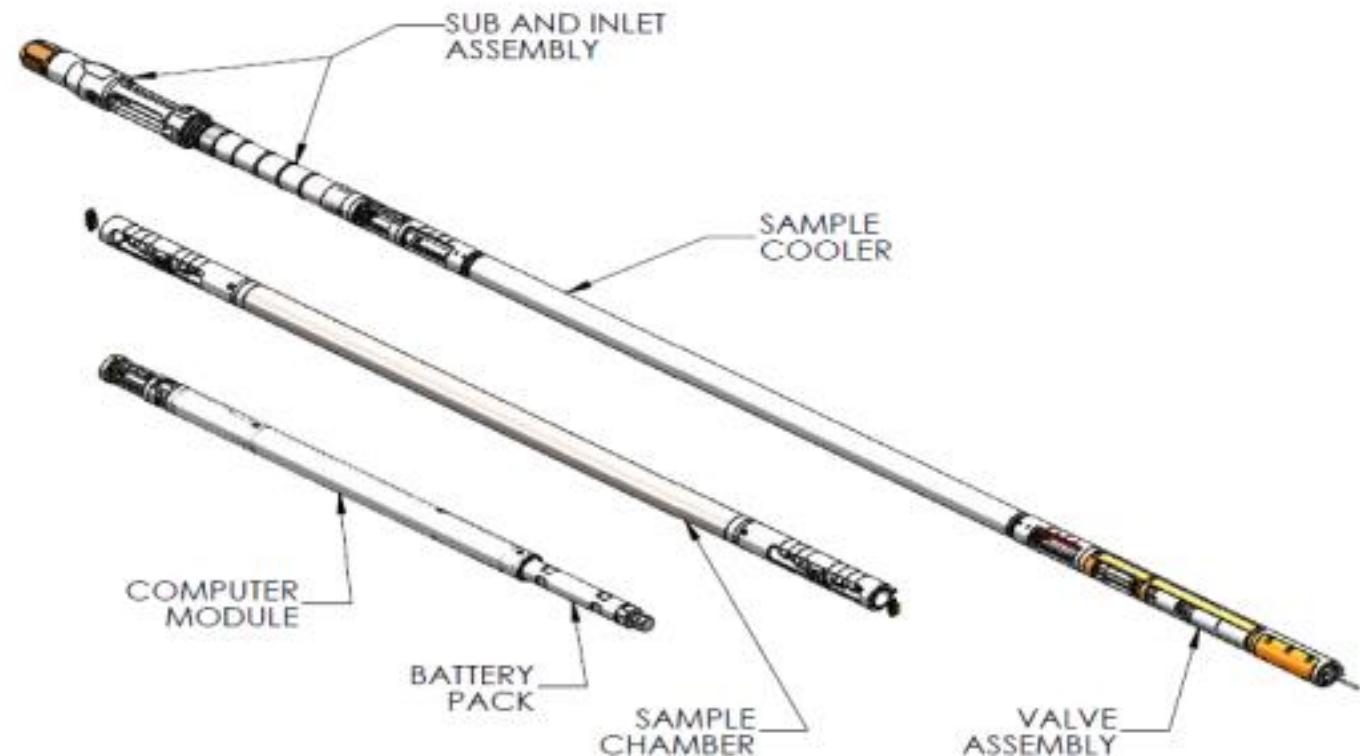




# Downhole Tool Implementation

## Integration into Thermochem's DownHole Sampler (DHS) tool

- Tool's bottom sub will be modified to enable implementation of probes in addition to sample port, pressure and temperature measurements





# Current Status

- Higher pressure and temperature (300C and 345 bar) autoclave near completion
  - Design complete
  - Parts on order
  - Initial safety review, final scheduled in October
- Powders and related materials are on hand
- Reference probe pellets have been fabricated
- pH probes have been assembled
- Discussions underway to determine path forward in hardware design to field test



# Summary

- Downhole tool capable of vertical profiling pH in wells look technically achievable
  - While this project is just getting underway, combining the years Sandia has invested into the material selection, assembly procedure and test results with Thermochem's extensive experience with well chemistry and tool development, 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
  - Year 2 downhole field tests will help 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 high-temperature (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



# Funding Statement

This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

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# Thank You!