

**Evaluations of Advanced Thermal Shock-Resistant Cement (TSRC)
Suitable to Withstand Frequent Thermal Cycling**

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Six-month Report

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Summary

This report documents additional evaluations of Thermal Shock-Resistant Cement (TSRC) developed by Brookhaven National Laboratory (BNL). Our work focused on thermal expansion, and fluid flow through the TSRC, and the application of thermal shock to a steel/TSRC sheathed sample. The key contributions of this work to the geothermal community are:

1-Development of a test system to make measurements of material properties at elevated temperature and pressure.

2-Measurements of thermal expansion and permeability of TSRC at elevated temperature and pressure conditions relevant to in situ geothermal conditions.

3- Development of a test system to thermally shock a steel/TSRC sheathed sample at elevated temperature and pressure conditions relevant to in situ geothermal conditions.

Herein we report the results of the study of repeated testing upon 3 cylindrical samples supplied by BNL, one steel, one TSRC, and one steel/TSRC sheathed sample.

1. Introduction

In Reservoir Thermal Energy Storage (RTES) systems the storage medium is at elevated pressures and temperatures of up to 300°C. The reservoir rocks and sands containing hot geo-steam and geofluids, and confined hot aquifer located above bedrock heated by magma, may provide a flexible source of energy for electricity generation on demand. Cold water is injected underground through an injection well and hot steam/water is recovered through a production well and used to generate electricity. The cold condensate is returned underground for makeup water heat recovery through the injection well. In RTES, repeated thermal shock (TS) conditions experienced by casing-cement sheaths is the major concern for the integrity of the wells. At the beginning of electricity generation, the near-the-surface, relatively cool cement sheath in the production well suffers from TS from hot geo-fluid, while the hot cement sheath deep in the injection well encounters TS with the sudden drop in temperature of >160°C as cold water passes through the casing. Furthermore, when electricity is no longer required, the cooled injection casing heats up to hot RTES temperatures. In contrast, hot production casing cools off. Thus, during frequent thermal cycles in injection and production wells, the cement sheath repeatedly undergoes thermal stresses by thermal expansion (microcrack development in sheath by compressive stress) and cool contraction of casing (micro-annulus development between the sheath and casing by tensile stress). Our work scope for the project involves study of steel, TSR cement and a TSR cement sheathed pipe.

2. Original scope of work

The original testing program included measurements on a steel cylinder, a cylinder of TSRC, and a TSR cement sheathed pipe. It was planned to measure thermal expansion of the steel at pressure, thermal expansion of the water-saturated TSRC at elevated temperature and pore water pressure, the permeability of the TSRC at elevated temperature and pore water pressure, and lastly to thermally shock water-saturated TSR cement sheathed pipe at elevated pressure and temperature. Included in the initial planning was for numerous thermal cycles; ultimately numerous cycles were

reduced to a few due to long durations of test, however our tests lasted for weeks as we had planned.

We achieved a measure of success in each of these tasks and report the results in the following.

We need to report that early on in our lab setup and testing of the steel, we had a never-before equipment malfunction and we melted the lead jacketing from the steel sample when it was at a high confining pressure. This caused a major time and budgetary setback in our efforts. The recovery was accomplished with delays in reporting.

3. Experimental

3.1 Samples Tested

Three samples were delivered for testing, a hollow cylinder of steel, a cement sample, and a sample of cement with a steel tube cemented inside it. The steel was cut to length and end ground perpendicular to length, the latter two samples were ground round on a wet lathe and then end ground perpendicular to length in a water bath. The cement and the cement sheathed steel samples were always stored in water prior to jacketing. The dimensions are given in Table 1, and images of the cement and cement sheathed steel are shown in Figure 1. Air bubbles were visible in the cement and some discontinuous cracks.

Table 1. Sample Dimensions

| | Steel | Cement | Cement Sheathed Steel |
|------------------------------|--------------|---------------|------------------------------|
| Diameter (OD cm) | 7.0 | 6.8 | 6.5 |
| Diameter (ID cm) | 4.4 | 0.0 | 2.2 |
| Area (cm²) | 5.2 | 36.3 | 14.2 |
| Length (cm) | 17.8 | 17.0 | 17.4 |
| Mass (g) | 3213.1 | 1162.4 | 1048.0 |

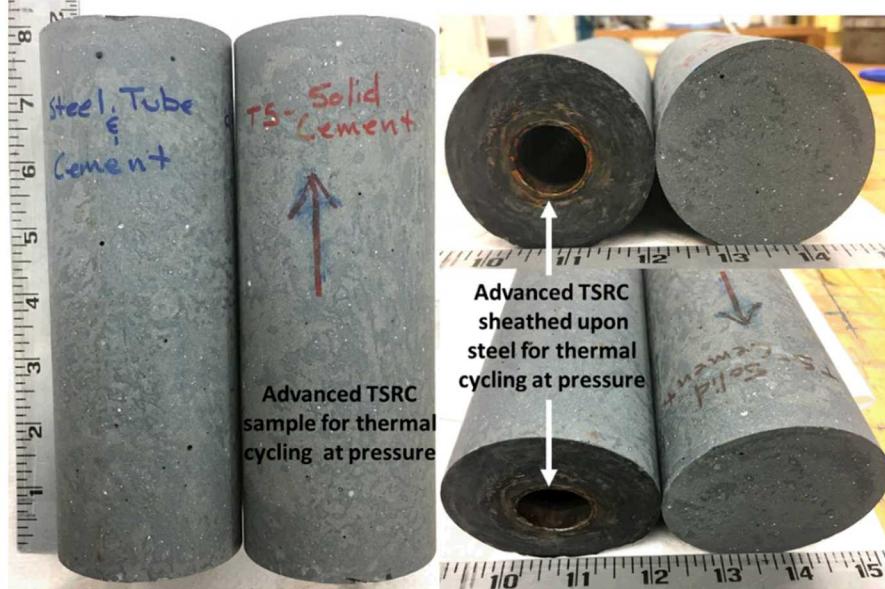


Figure 1: Images of TSR cement and TSR cement sheathed pipe considered in this study.

3.2. Laboratory Setup

To support understanding of material behavior of each sample at elevated temperature and pressure we have developed a laboratory-based test system which allows for high temperature sample displacement to determine strain, fluid flow through cement and fluid flow at high rates. The first allows us to estimate the thermal coefficient, the second allows us to estimate permeability, and the third allows us to create thermal gradients quickly in such a manner as to thermally shock the sample at elevated temperatures and pressure.

3.3 Test System

An experimental test system was developed which can be used to simulate reasonable downhole geothermal environmental conditions. It is capable of subjecting jacketed cement specimens to high temperature, elevated confining pressure, and differential stresses, and high pore-water pressures. Test conditions of 13.8 MPa confining pressure, 1.5 MPa differential stress, and 10.3 MPa pore water pressure were chosen as representative for this initial study; all tests were initialized to these conditions. The intent was to conduct the tests with no differential stress, however, the test system requires a small axial load. We chose 1.5 MPa; this load negated using the external linear voltage displacement transducers to measure displacement. The 10.3 MPa pore water pressure was the average; upstream and downstream pressures are varied to create flow through the specimen.

The test temperature ranged from 25°C to 220°C and was increased and decreased in approximately 50°C increments. Temperature estimates during the experiments are made at the (1) outer vessel top, (2) outer vessel bottom, (3) inside the vessel in the confining fluid (4) on the pore fluid tube entering the pressure vessel, and (5) on the pore fluid tube exiting the pressure vessel. The test system is monitored using (1), (2), (3) during heating and cooling and we use these temperatures to determine the sample temperature.

The test system needed to be able to achieve the test conditions stated and to maintain these conditions for extended times (weeks to months). This long test condition time was needed because we have limited samples, the test system was time consuming and laborious to set-up, achieve temperature, pressure, and stress conditions, and to conduct the tests. And, consequently, we desired to obtain as much data as possible from an individual sample.

We used an in-house built creep test system (Figure 2) already capable of maintaining the above temperature, stress, and pressure conditions, with recently added flow through pore pressure capability. The test system is controlled with a computer-based interfaced system and simultaneously controls the test and acquires test data at user specified time-based intervals. Data collection rates are high (1 sec) for test active testing and low (1 min) for quiescent times.

The testing system consists of a reaction frame (Figure 2B) that generates the axial force by reacting against a hydraulic cylinder located at the base of the frame, and a pressure vessel that houses specimens during testing. The reaction frame system can apply loads of up to 450 kN. The pressure vessel (Figure 2D) is rated to 70 MPa and is equipped with electrical band heaters (Figure 2D) capable of maintaining test temperatures up to approximately 250°C. Silicon oil is used as the confining medium. Fluid confining pressures are coarsely adjusted using an air-assisted pump and finely adjusted and maintained constant using a syringe pump (Figure 2E) that either injects or withdraws oil from the vessel. Vessel pressures are measured by a pressure transducer plumbed into the hydraulic line leading from the vessel to the syringe pump. Axial loads applied by the hydraulic cylinder are measured by a load cell located directly above the cylinder in line with the axial push-rod that extends into the pressure vessel and applies axial load to the ends of the specimen. Test temperature is recorded by three thermocouples, one located near the top of the pressure vessel, one near the vessel midheight, and one inside the pressure vessel. Pore-water temperatures are measured using thermocouples strapped to the high-pressure tubing leading into and out of the pressure vessel.

Pore fluid pressures (using tap water as the permeant) are created using two opposing ISCO pumps (maximum pressure 25.9 MPa) plumbed into the top and bottom of the sample (Figure 2C).

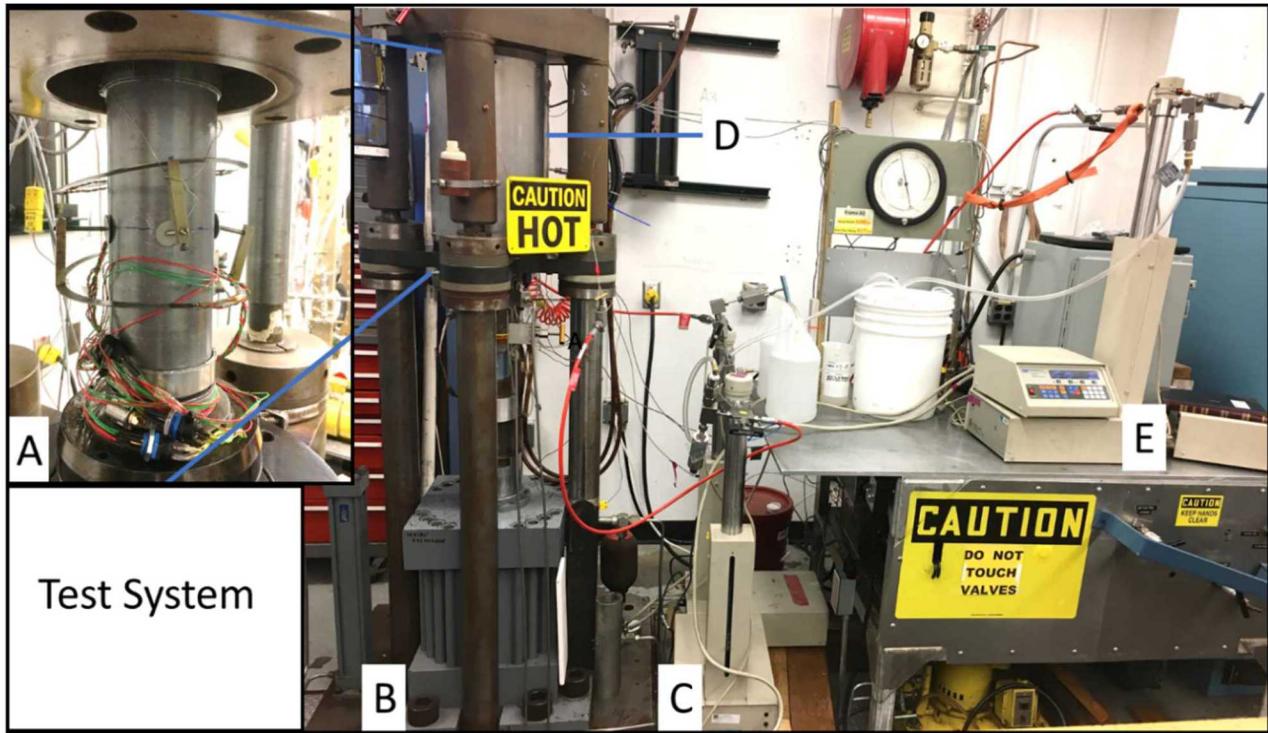


Figure 2: Test system. A: Assembled specimen prior to lowering the pressure vessel; B: Loading frame; C: Pore pressure generating syringe pumps; D: Pressure vessel encased in insulated heating furnace; E: Confining fluid controlling syringe pump.

3.4 Sample Assembly

The test specimen for this study is a right-circular-cylinder of steel, TSR Cement, and steel sheathed with TSR Cement. TSR Cement is a calcium-aluminate cement blend with fly ash, type F and sodium meta-silicate activator, prepared by Brookhaven National Laboratory.

The sample was kept in a water bath except when being end prepped. A metal mesh pad is placed on opposing ends of the sample between the cement and end cap. The sample is jacketed in a lead sleeve (Figure 3). The nippled coupling connects the sample to the pore fluid pumping system.

Sample displacements are measured using external displacement transducers (LVDTs) and internal high temperature lateral gages (Figure 3). The former measurements were not used, as discussed above.

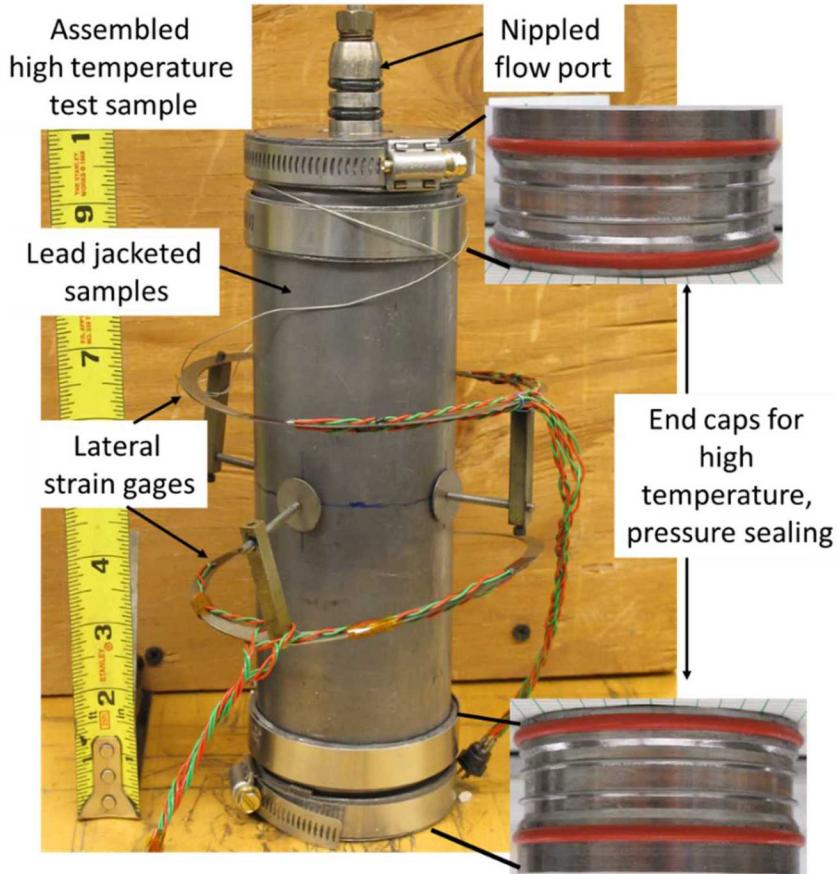


Figure 3: Assembled high temperature test sample showing specially designed high temperature end caps, lead jacketing, lateral strain gages and nipped flow ports.

Data collected in the experimental study included force, pressure, temperature, displacements, and volume change of water versus time. Typically, these data are acquired using electronic transducers in which the electrical output is proportional to the change in the measured variable. In all cases, the constants of proportionality were determined through calibration using standards traceable to the National Institute for Standards and Technology.

3.5. Test Conduct

Once in the pressure vessel, the sample is subjected to the small axial load. The axial load is maintained during application of confining pressure. After about 4 MPa confining pressure is applied, pore water pressure is introduced to the sample. Then confining and pore pressures are together increased to test conditions of 13.8 and 10.3 MPa, respectively, resulting in an effective pressure of ~ 3.5 MPa. Confining pressure is held constant at 13.8 MPa for the duration of the test. Once at these pressure conditions, temperature is ramped up and down to $\sim 200^\circ\text{C}$ in 50C or 100C increments and held for varying amounts of time. During the hold periods we circulated water through the sample by increasing the upstream pressure and decreasing the downstream pressure. For the steel sample tests, no water was moved through the sample at temperature, it was only done to check plumbing connections and pump functions.

The steel specimen was heated and cooled, and its dimensional change recorded. The steel was subjected to three 180-hour heating and cooling cycles. From this heating and cooling, thermal expansion of the cylinder at 13.8 MPa confining pressure was estimated.

The water-saturated cement specimen was heated and cooled, held at specific temperatures, and its dimensional change recorded. At specific temperatures, the upstream pressure increase coincided with a downstream pressure decrease of 0.345 MPa. The resultant water flow continued for a few hours, depending on the flow rate. This flow measurement allowed for permeability of the cement to be estimated.

The water-saturated cement sheathed steel specimen was heated to specific temperatures and after thermal equilibration was reached, room temperature water was rapidly flowed through the inner tubing. We believe temperature gradients of +100C were attained in 4 to 5 minutes. This created a thermal shock to the inner portion of the sample.

4. Results and discussion

4.1. Steel

The steel was cycled to ~220C three times, each cycle lasting about 180 hours, the first two times in steps, and the 3rd time in a single step to the maximum temperature; steel testing lasted about four weeks. An example of the heating and cooling is given in Figure 4. The sample, once pressurized, was heated in four steps, with a hold at each temperature. Displacement measurements on the sample are averaged to calculate strains and thermal expansion coefficient as a function of temperature. The coefficient of thermal expansion of the steel at 13.8MPa confining pressure varies slightly and estimated to be approximately $2 \text{ to } 5 \times 10^{-5}/\text{C}$ over this temperature range (Figure 5). The thermal expansion coefficient of steel should not be affected by pressure, and the thermal expansion of steel should be constant for this temperature range. The variability reflects measurement accuracy, instrument drift, etc. considerations, not that there is a difference in the two measurements (these are averaged for the calculations) and that the sample contracts to approximately the same position it begins at before heating.

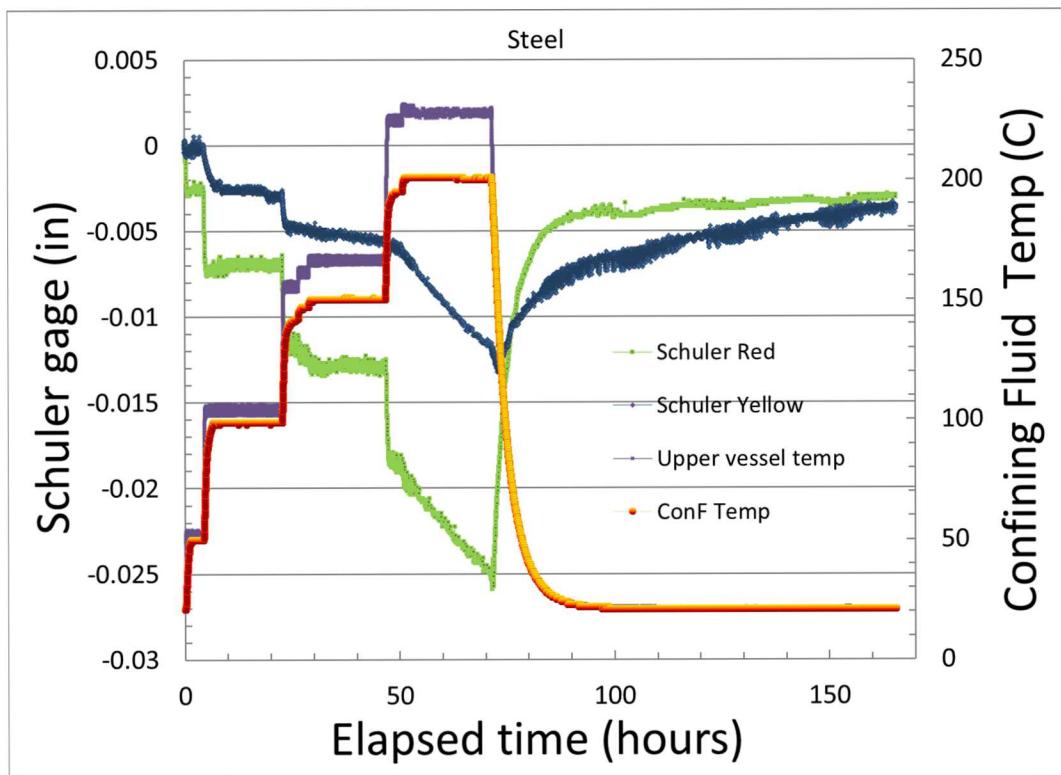


Figure 4. Displacement and temperature records for 1st heating cycle for steel.

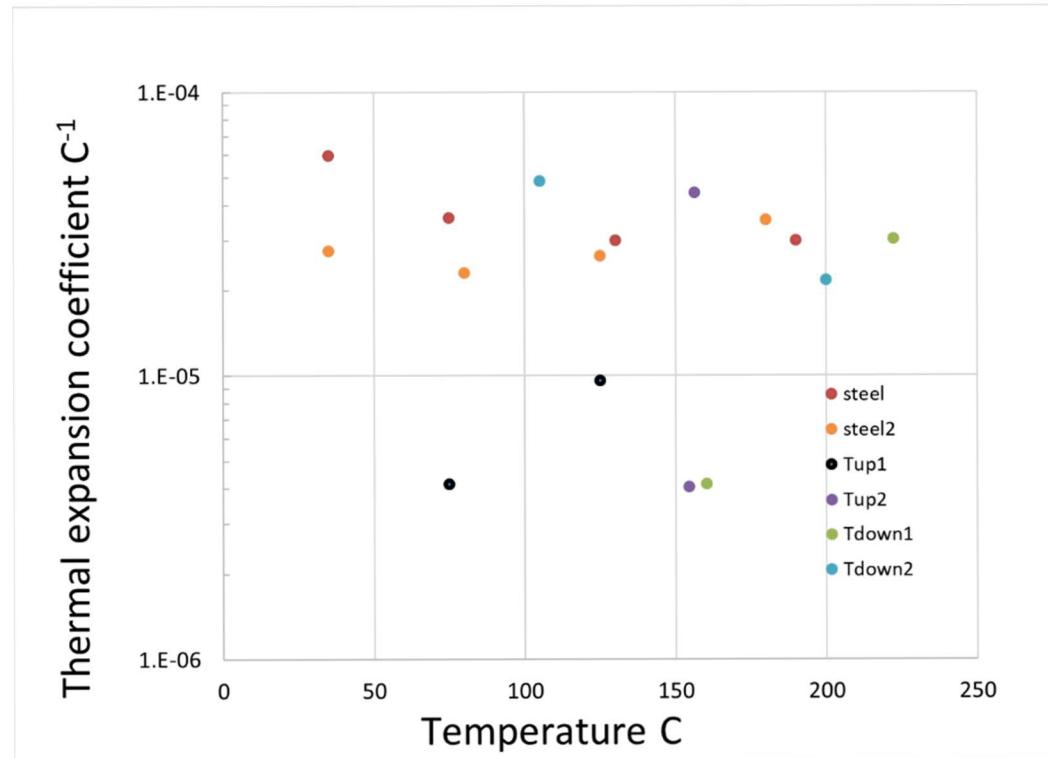


Figure 5. Thermal expansion coefficient of steel and water-saturated cement versus temperature.

4.2 Cement

The cement sample, after being subjected to 13.8 MPa confining pressure and 10.3 MPa pore pressure was subjected to thermal cycling and flow tests over the course of 16 days. Each work day the sample was heated to a test temperature, water flowed through it, and then the sample was sometimes cooled to reduce the high temperature exposure on the equipment. An example of sample cooling, and its compaction is given in Figure 6. Also shown is the 2-3-hour flow period for this test. During the flow period, flow rates were low, on the order of 0 to 0.1 cc/min. At these low flow rates, the flow meter jumped around. To estimate flow rates accurately, the volume in the pumps are noted at the start and the end of the flow. In this time, a hundred or more cc can flow, and the flow rate was then readily determined.

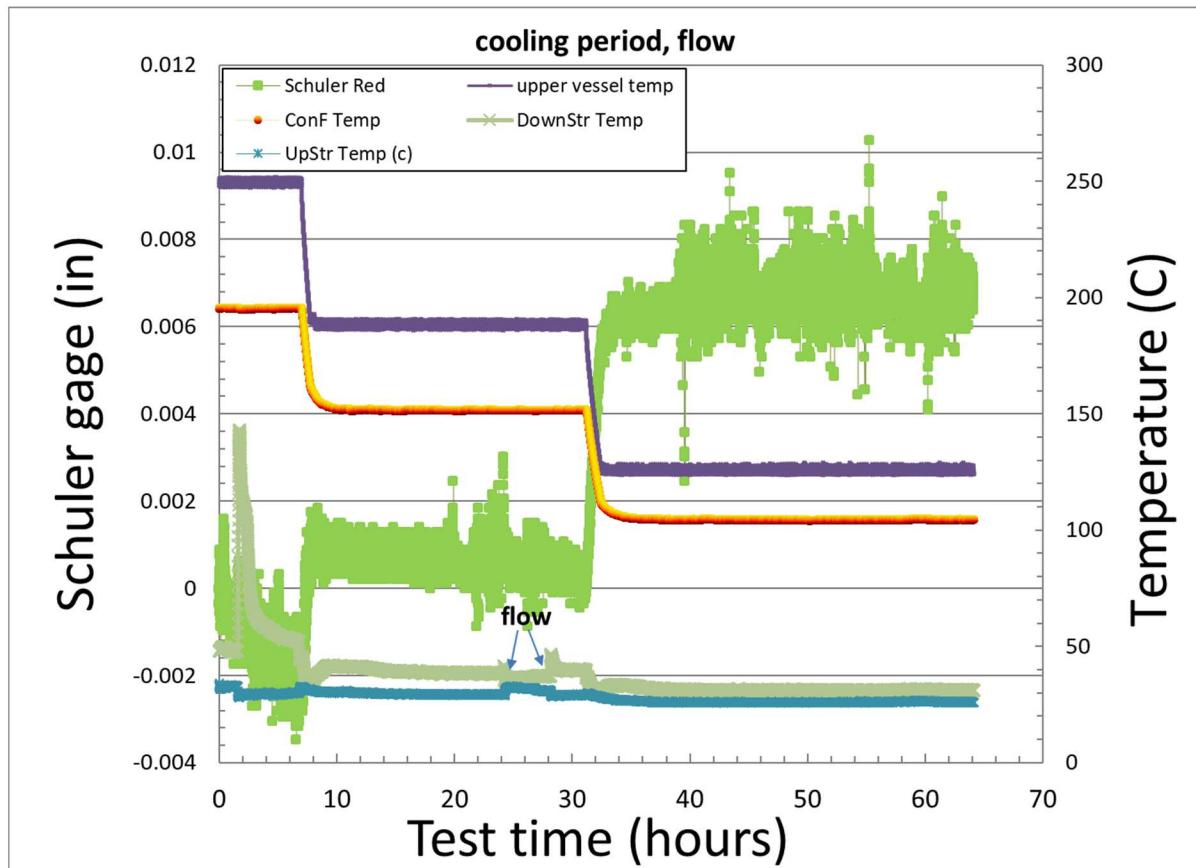


Figure 6. Example cooling temperature cycle, displacements, and flow period for cement sample.

Water flow rate versus temperature is displayed in Figure 7 (blue dots). The arrows indicate the direction of temperature increases and decreases. Generally, when temperature is increased, flow rate increases, and when temperature is decreased, flow rate decreases. The orange dots show the calculated flow rate for a material with a constant permeability of 0.05 mD, while considering the change in viscosity of water with increasing temperature.

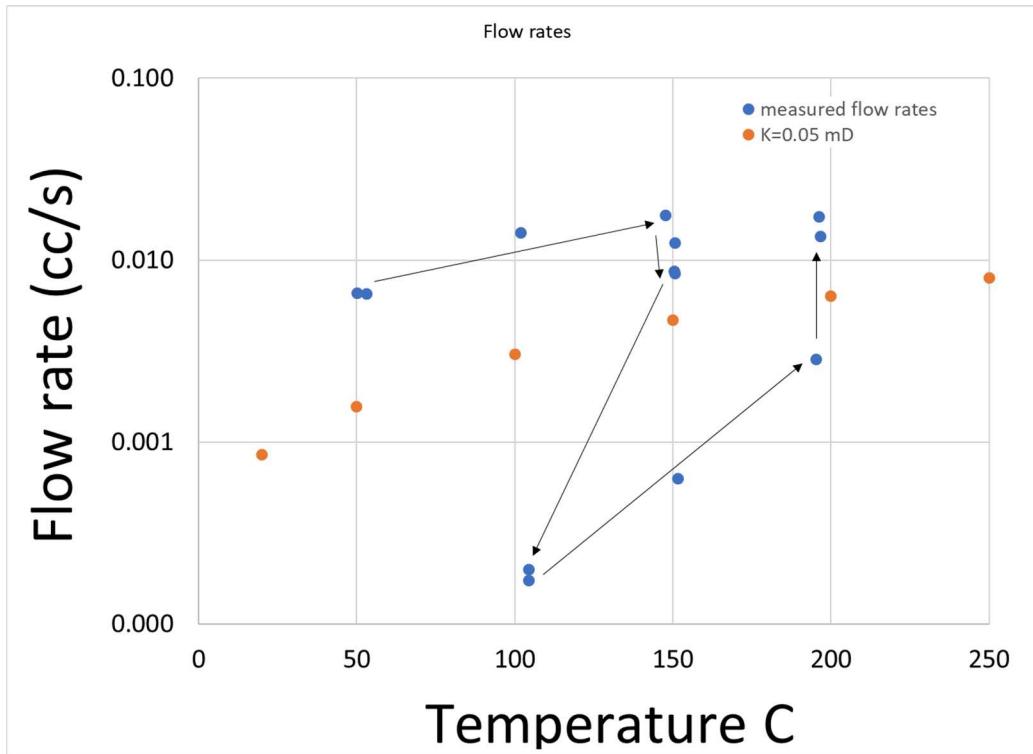


Figure 7: Flow rate versus temperature.

Permeability estimates are made from the water flow measurements. Permeability calculated using Darcy's law is expressed as the measured flow rate of fluid crossing a unit area and is proportional to the pressure differential measured across the ends of the specimen. The flow rate q and permeability k are related by the following equation:

$$q = \frac{k}{\mu} A \left(\frac{\Delta p}{L} \right) \quad (1)$$

where q , k , μ , A , L , Δp are volumetric fluid flow rate, absolute permeability, fluid viscosity, cross-sectional area, length and pressure drop over the length L , respectively.

Using the temperature-dependent water viscosity (Figure 8) and equation 1, we calculate the fluid flow rate variation in a non-temperature dependent permeability material (Figure 8).

The single sample was subjected to numerous thermal cycles over the course of sixteen days. The test was terminated because of a system leak.

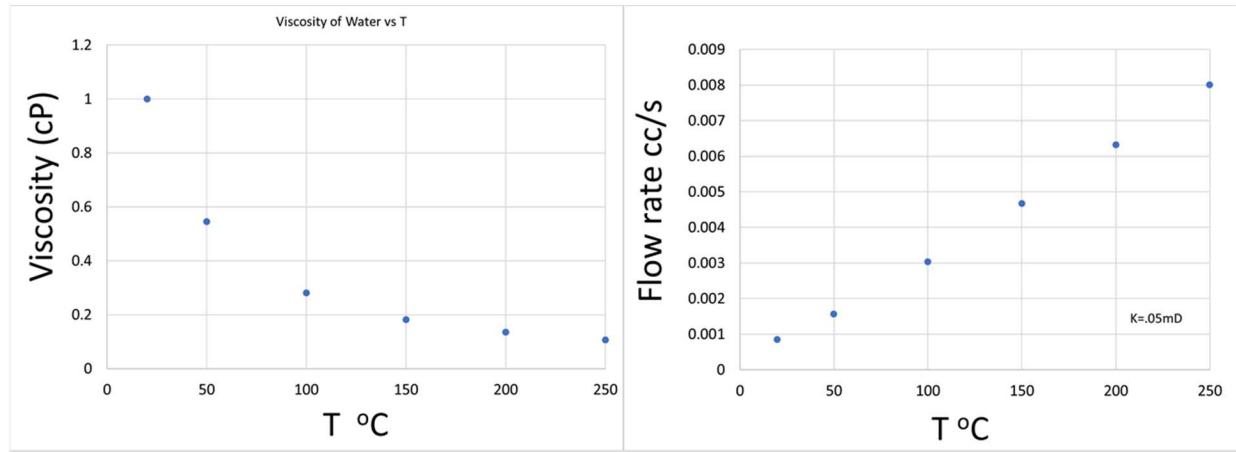


Figure 8. Viscosity of water versus temperature (left) and flow rate change for a 0.05 mD material considering viscosity of water change with increasing temperature.

Using equation 1 and the measured flow rates, we calculate the permeability of the cement versus time and temperature. The permeability of the cement is rather low, and we do not observe systematic changes in the permeability versus time or temperature (Figure 9).

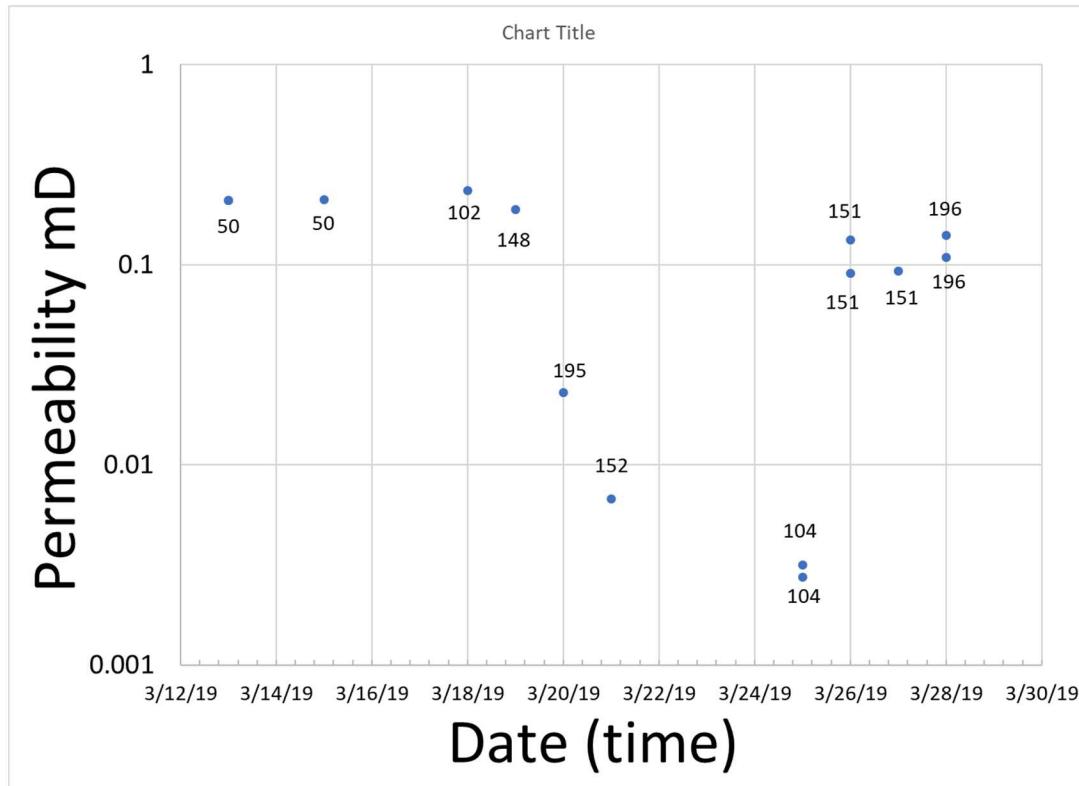


Figure 9: Permeability versus test time for cement sample

4.3 Cement sheathed steel

The primary purpose of this test configuration is to thermally shock the steel-cement interface. This was achieved by flowing chilled water into the inner sample tubing at high flow rates. Early in the testing we flowed at 20-40 cc/min, and later we were able to increase the flow rate to 100 cc/min. The limits of the flow were the size of the reservoir (500 cc), the tubing orifice temperature in the high-pressure tubing, and the chilling of the return water into the receiving pump. Using ice baths for the inlet water and exiting water, we were able to achieve approximately a 100C decrease in the core temperature of the water (and thus steel), and with the outer portion of the cement at +200C, a significant gradient was developed in 5 minutes of flow. A 25-hour test period is shown in Figure 10 (TOP), and an expanded time scale is shown in Figure 10 (BOTTOM).

In Figure 11, the Schuler gage displacement data is added to the plot. It appears that during the flow and quiescent periods, the sample expands. The details of the thermally driven behavior are complex during the flow, suggesting some complex interactions between the components.

The single sample was subjected to approximately twelve thermal shock cycles over the course of eight days. The test was terminated because of a jacket leak.

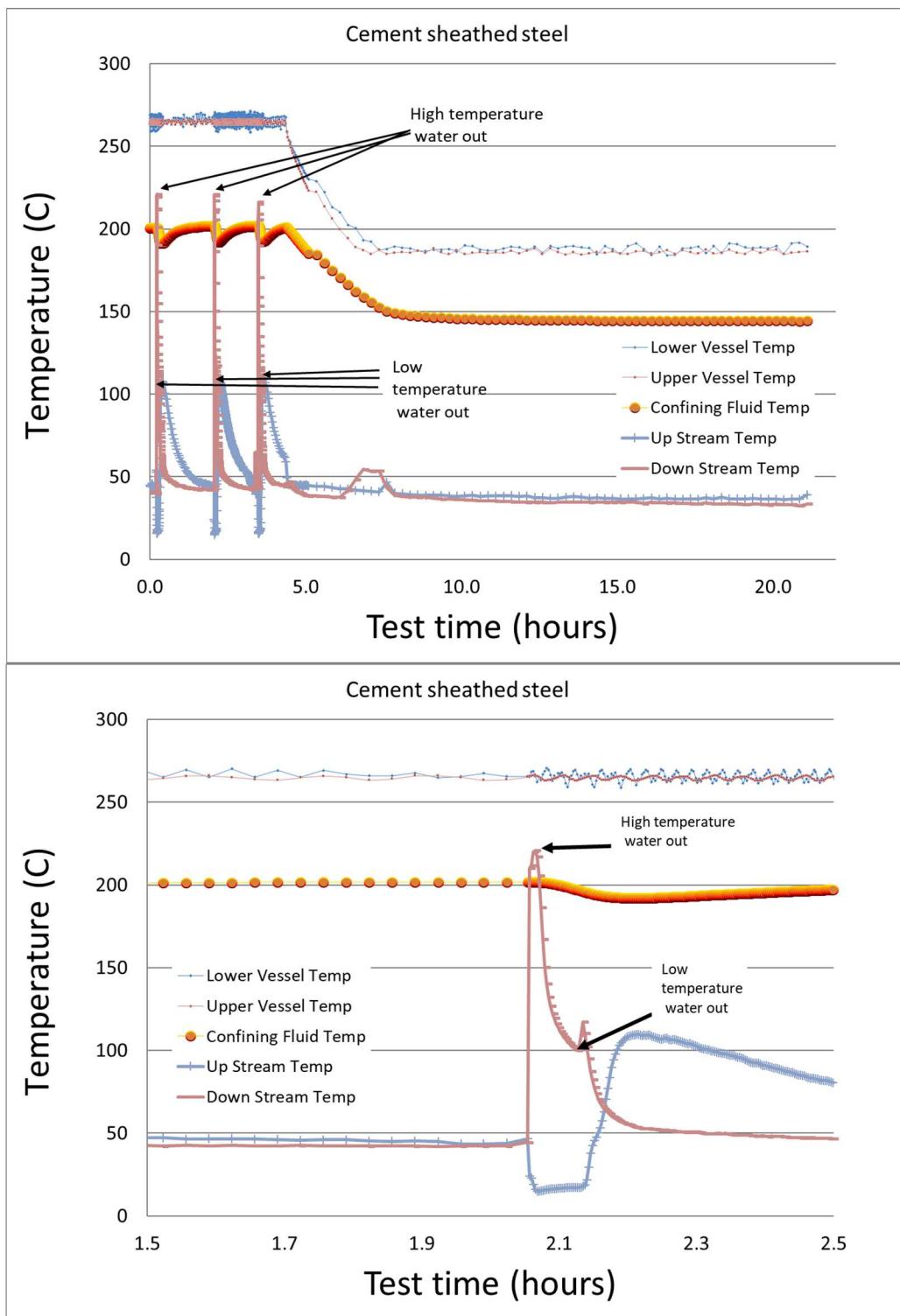


Figure 10. Test time versus temperature for components of the cement sheathed steel test (TOP). Test time versus temperature for components of the cement sheathed steel test with expanded time scale (BOTTOM).

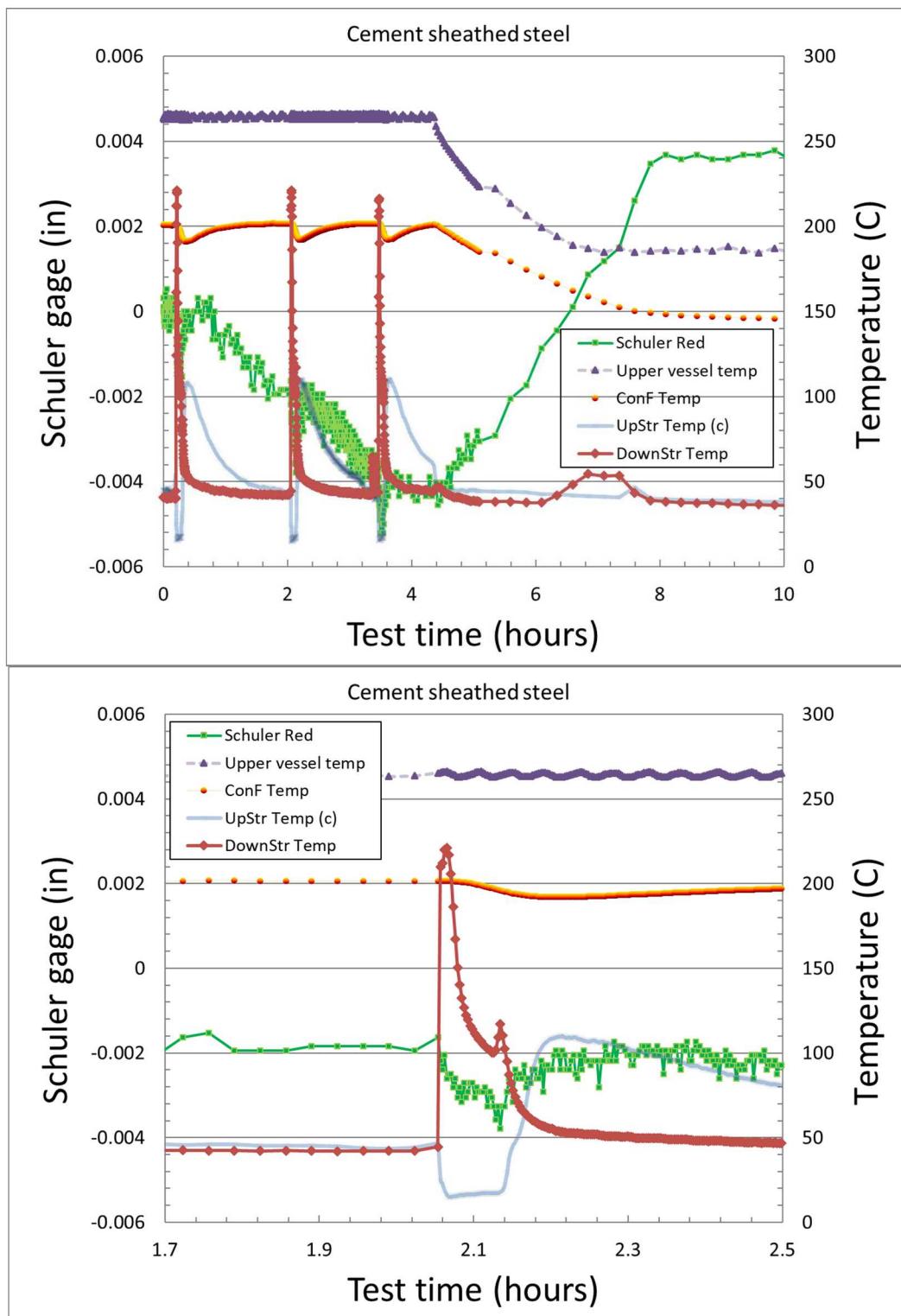


Figure 11. Test time versus sample displacement and temperature during flow periods for cement sheathed steel sample.

5. Observations

Observations of samples tested was limited to reflected light microscopy of sections cut through the samples. In Figure 12, viewing a slice parallel to the long axis, the cement sample looks unscathed by the hydrous thermal treatments. There are ever present round voids, occasionally the voids have white precipitate in them. At this scale, the sample looks relatively clean.

In Figure 13 is the cement sheathed steel sample sliced perpendicular to the long axis. In it, there is a small fracture (red arrow) from the steel which extends to a round pore and non-round pores, perhaps suggesting that these pores were slightly deformed (from round) during the thermal cycling. It appears that the steel is well adhered to the cement.



Figure 12. Cement sample sliced parallel to the long axis, reflected light.

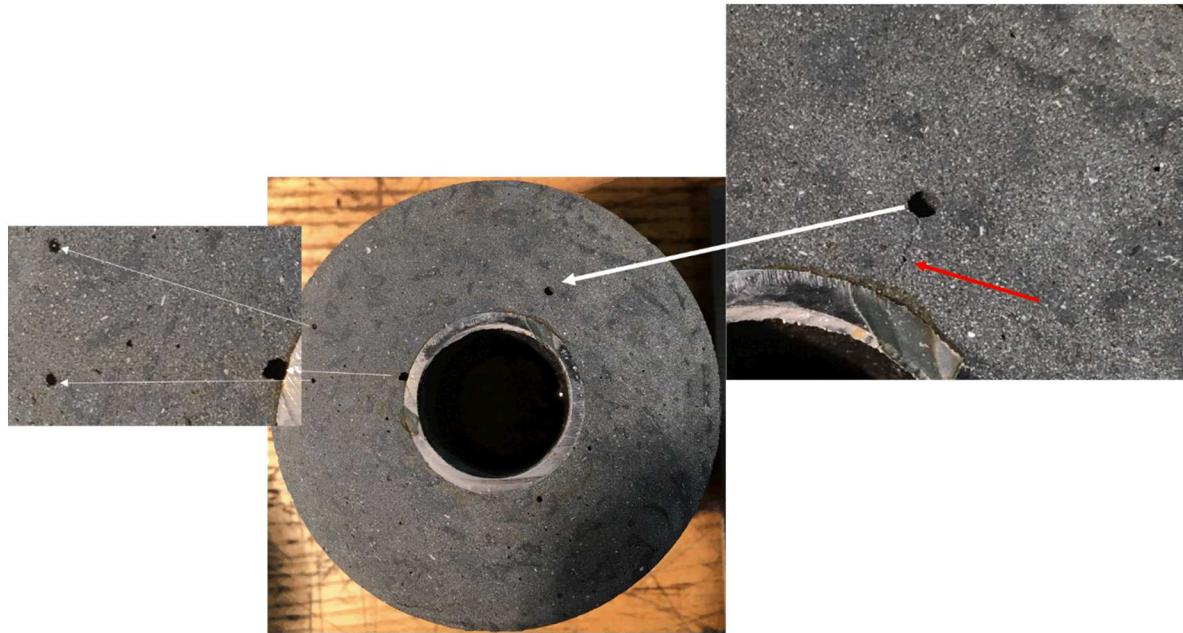


Figure 13. Cement sheathed steel sample sliced perpendicular to the long axis, reflected light.

6. Conclusions

This report documents additional evaluations of Thermal Shock-Resistant Cement (TSRC) developed by Brookhaven National Laboratory (BNL). The work focused on thermal expansion, and fluid flow through the TSRC, and the application of thermal shock to a steel/TSRC sheathed sample.

The key contributions of this work to the geothermal community are:

- 1-Development of a test system to make measurements of material properties at elevated temperature and pressure
- 2-Measurements of thermal expansion and permeability of TSRC at elevated temperature and pressure conditions relevant to in situ geothermal conditions.
- 3- Development of a test system to thermally shock a steel/TSRC sheathed sample at elevated temperature and pressure conditions relevant to in situ geothermal conditions.
- 4-The thermal expansion coefficient of the water-saturated TSRC is on the order of 4×10^{-5} to 3×10^{-6} /°C at 3.5 MPa effective confining pressure.
- 5-The permeability of the TSRC is temperature dependent and ranged from 0.002 to 0.2 mD.

7. Acknowledgements

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