(i) Project title: Below-zero saline fluid phase behavior in porous materials

(ii) Proposal team: Dr. Andrew Parsekian (proposal leader), Department of Geology & Geophysics *and* Department of Civil & Architectural Engineering & Construction Management; Dr. Morteza Dejam, Department of Energy & Petroleum Engineering & School of Computing

(iii) Total amount requested: $23,841

(iv) Description of the research problem to pursue and proposed long-term benefits:
The purpose of this project is to reveal the low-temperature phase change behavior on porous media saturated with brines. At low temperatures and ambient temperatures, flow through porous media can be restricted by the presence of ice. Depending on the pore size and chemical properties of the pore fluid, restriction in flow may occur before all pore fluid undergoes phase change to ice, meaning that the system may contain two materials with three thermal conductivities (i.e., mineral matrix, solid phase pore fluid, liquid phase pore fluid). The pore-scale transition from fully liquid pore fluid to fully ice pore fluid is of key importance for predicting fluid flow, particularly in materials with small pores such as silt or siltstone. While the case of low salinity brines in freezing porous media has been explored in the research literature, much less is understood about how the presence of brines influence this phase change behavior.

Although investigation of low-temperature phase changes in porous media is conceptually straightforward, in practice, measurement is challenging. This is one primary reason that knowledge gaps still exist. Two labs in CEPS are uniquely well suited to address this knowledge gap with measurement capability that is uncommonly available elsewhere. The Hydrogeophysical Material Properties Lab (SH Knight Building) run by Dr. Parsekian has a one-of-a-kind temperature-controlled nuclear magnetic resonance (NMR) instrument (Vista Clara, Mukilteo, WA) suited for core-sized samples, dubbed the 'CryoNMR,' that can hold samples at below-freezing temperatures during measurement. The key capability of NMR is that this instrument can directly measure the unfrozen water content in the sample and estimate change in solid-phase surface area as ice grows in the sample pore space. The Phase Change Behaviors Lab (EN4006) run by Dr. Dejam houses a BT 2.15 Low Temperature Calvet Calorimeter purchased from Setaram (see Figure 1). This instrument provides an independent measure of phase-change temperature in samples through analysis of time series temperature measurements. Dr. Dejam's lab is equipped with liquid nitrogen cooling to achieve sub-freezing temperatures, and a fluid injection system to introduce variable salinity pore fluids during the experiment. This independent measurement of phase change temperature is critical because it reveals the formation of ice in even the smallest nanopores that may be below the detection limit of the NMR.

The long-term benefits of this experiment include a new understanding of pore-scale properties of granular materials under a range of temperature. Results of this experiment have implications for engineering (e.g., extracting fluids from formations, stability of structures in cold regions with foundations in frozen materials) and natural sciences (infiltration into seasonally frozen soils, permafrost to degradation). The new fundamental understanding of pore ice accumulation is critical to enable additional lab experiments specifically imposing flow on partially ice-bonded sediments, as well as field-scale experiments to measure impacts of warming ground temperatures on structural properties of permafrost.

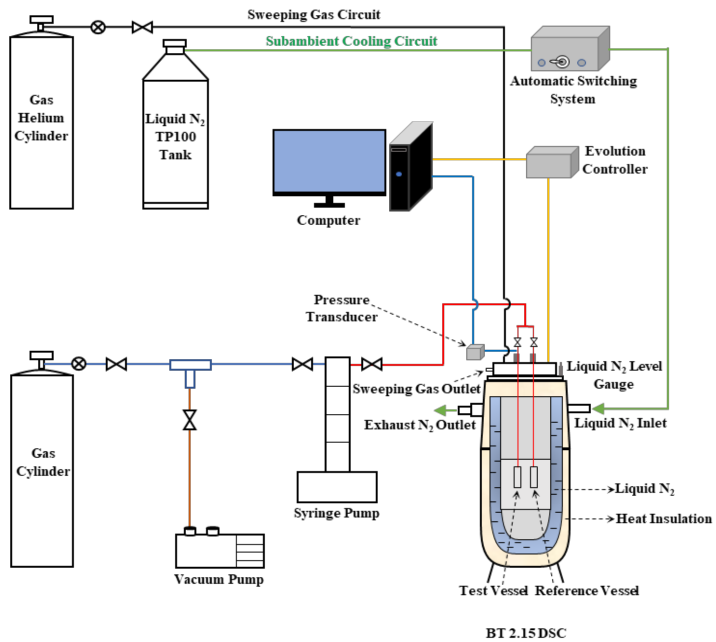

Figure 1 Schematic diagram of experimental setup for high pressure low temperature BT 2.15 differential scanning calorimeter (DSC).

(v) Short-term objectives & workplan:

Objectives: The primary short-term objective is to demonstrate how pore water salinity controls the phase transition temperature of partially saturated porous materials under both cooling and warming conditions. To accomplish this, we will work towards the following sub-objectives: 1) measure samples with controlled pore fluid salinity using NMR across a range of temperatures to determine ice volume and location of ice within the pore space (based on NMR relaxation parameters); 2) Observe differences in phase change depending on warming or cooling conditions, 3) independently determine phase change conditions using calorimetric measurements.

Workplan: The experiment that will be conducted will cover a range of pore fluid salinities and sample pore structures. We will explore five salinity conditions ranging from deionized freshwater to seawater (0, 100, 1000, 10,000, and 50,000 uS/cm) each in three different media porosity (5, 10 and 15% porosity by volume). Pore fluid will be created in the lab using sodium sulphate. The porous substrate will be created by washing and sieving granular media to achieve desired porosities and similar pore size distribution ranges. First, each sample will be analyzed by NMR in the range of +5 to -10C to characterize the relationship between temperature and remaining unfrozen water content. These experiments will be conducted both in the freezing and thawing directions, with equilibration pauses along the way to eliminate the effect of cooling rate, to observe possible hysteresis. Next, the material from the NMR experiment will be subsampled for calorimetric analysis that will reveal the phase transition temperature range. Using the NMR data, we can calculate the rate of change of liquid water content as a function of temperature. We can finally relate the rate of change in liquid water content with the phase transition temperature.

(vi) Potential future partners:

- Dr. Vladimir Alvarado, Chemical and Biomedical Eng. & Energy and Petroleum Eng.
- Dr. Noriaki Ohara, Civil and Architectural Eng. and Construction Management
- Dr. Hertanto Adidharma, Energy and Petroleum Eng. & Chemical and Biomedical Eng.

(vii) Funding sources and programs:

National Science Foundation (NSF), Hydrologic Sciences (NSF 22-540, rolling submission deadline). NSF, Arctic Natural Sciences (NSF 23-572, due January 15, 2025). Department of Energy (DoE) Office of Science (2025 FOA deadlines not posted yet).

Budget description:

1. Sample preparation and analysis costs: $400 per sample X 20 samples = $8,000
2. Technician time: 1 month salary @ $5,502 + $3,086 fringe = $8,588
3. MS Graduate student: 5 months salary @ $1,425/mo * 5 mo + $128 fringe = $7,253

Budget justification:

1. Sample preparation and analysis costs: This covers all expendable materials (Nickel O-ring, liquid nitrogen, helium gas cylinder, vacuum pump oil, tubing, fittings, and valves) in the Phase Change Behaviors lab.
2. Technician time: Each CryoNMR experiment takes approximately one day between sample preparation and measurement. Since there are approximately 20 working days in a month, the technician will be able to complete all NMR analysis in the budgeted time.
3. The MS-level graduate student will learn the experimental procedure from the technician during Fall 2024, support measurements, and will lead data analysis after the experimental work is complete.