

PRF#: 59131-DNI9

Project Title: Connecting the Dynamics of Interfacial Gas Hydrate Films with Bulk Hydrate Rheology

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Co-PI: None

## Research Progress

Progress on the research plan has been strong. The project started as planned on the first of September 2018 when this funding began supporting my graduate student. The first task, which took two months, was to complete the fabrication of a novel double-wall ring interfacial geometry with sub-phase exchange capability. The experimental setup also required the development of a network of interconnected syringe pumps and integration into our commercial rheometer. Once completed, the nucleation of cyclopentane hydrates within this interfacial geometry

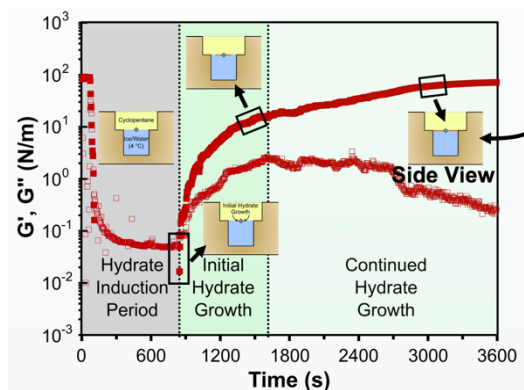


Figure 1. Dynamic moduli as measured in the custom double-wall ring geometry as a function of time. Different periods are shown, including a hydrate induction period, initial growth period, and a continued growth period.

proved to be reproducible and controllable, and within the first six months my student was able to observe the growth of cyclopentane hydrate films visually, track the growth with the rheometer, and also track the dissociation of the films with the rheometer by introducing thermodynamic hydrate inhibitors into the aqueous sub-phase. An example data set from the interfacial setup showing dynamic moduli as a function of time during hydrate induction and growth is shown in Fig. 1. The novel contribution that we have made thus far is in demonstrating the ability to use interfacial rheology to study the dissolution kinetics of hydrate films upon introduction of inhibitors. We now have data on the influence of methanol and ethylene glycol, separately, on the rate of dissolution of the cyclopentane hydrate film. Data showing the influence of the introduction of ethylene glycol on the dynamic moduli of an established hydrate film is shown in Fig. 2. At 2100 s ethylene glycol is introduced and by 3000 s the hydrate film has almost entirely dissociated as indicated by dynamic mechanical measurements. The data

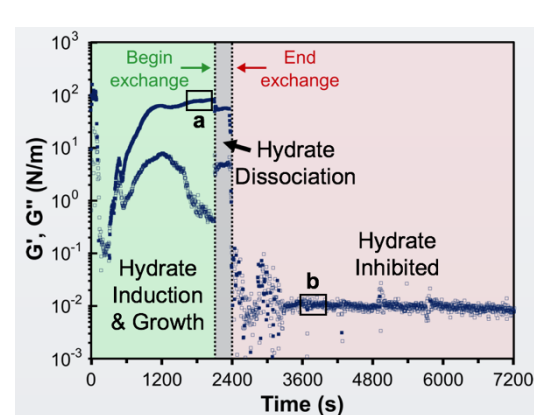


Figure 2. Dynamic moduli as a function of time with periods shown of hydrate induction and growth, introduction of ethylene glycol into the sub-phase (the exchange) and hydrate dissociation.

shown in Fig. 1 and Fig. 2, as well as other similar data sets have been presented at the ACS Colloids & Surface Science Symposium in Atlanta, GA in 2019, and at the ACS Fall Meeting in San Diego, CA in 2019. An additional presentation is forthcoming at the AIChE Annual Meeting in Orlando, FL, in 2019.

Considering the success we have had with the interfacial rheological setup that we have created, progress to this point deserves a publication, and we will prepare a manuscript while we work towards the final project goals. The overarching objective of the project is to link interfacial and bulk rheological properties of cyclopentane hydrates, and this requires the formation of complementary bulk cyclopentane hydrates to our interfacial hydrates. This aspect of the project will be the focus of the next calendar year, and it will take us through the completion of the project.

### Conference presentations supported by this grant

Goggin, D.M., J.R. Samaniuk, "Probing dynamics of hydrate film formation and dissociation using interfacial rheology with subphase exchange," ACS Colloids & Surface Science Symposium, Atlanta, GA, 2019.

Goggin, D.M., J.R. Samaniuk, "Interfacial rheology with sub-phase exchange used to investigate dynamics of cyclopentane hydrate film formation and dissociation," ACS Fall Meeting, San Diego, CA, 2019.

### **Impact on the PI's career**

The impact of this award on the PI's career is very significant. This project and the funding that comes with it is the first sole-PI awarded grant that the PI has received. The success of this proposal in the review process indicates to the PI's colleagues and the university administration that the PI can write compelling proposals to investigate important scientific phenomena. In addition, making tangible progress on a funded grant such as this one leads to the acquisition of new data that can give insight into poorly understood phenomena. The data we have obtained thus far has done that, and we have already prepared and given a number of conference presentations to disseminate the findings.

An additional impact on the PI's career is the opportunity with this grant to learn in depth about the fundamentals of gas hydrates. This will allow the PI to become an active participant in the ongoing efforts of multiple groups in the PI's department to investigate hydrates for both energy storage and flow assurance reasons. Gas hydrates are a major concern for energy producers, and theoretically a mechanism for storing natural gas and greenhouse gasses, and the ability to apply interfacial and bulk rheological tools to the investigation of them has created opportunity for the PI to have an impact in this area.

The PI also traveled to their first ACS National Meeting in San Diego, CA in 2019 to present on this work. This increased the network that the PI has access to for learning more about gas hydrate science.

### **Impact on the graduate student's career**

The graduate student on this project has been impacted in a number of ways. First, the construction of the interfacial geometry required knowledge of interfacial rheology, expertise in identifying the proper materials, and creativity in order to construct a relatively complex piece of laboratory equipment. This experience is highly valuable to other academic laboratories, and to industrial laboratories, so the time the student spent in this area will significantly improve their general opportunities for future employment as either a postdoc or a research and development scientist.

In addition, the student entered this project with no expertise in gas hydrate science, but will leave it with a great understanding of the problems surrounding gas hydrate formation in the energy industry, and of the solutions applied to fix those problems. In that way this project has opened a number of career paths for the student in the energy industry.

The impact of the financial support from this grant on this student is significant for advancing the students progress towards graduation with a PhD. As a direct consequence of this financial support this student does not need to act as a teaching assistant for these two years. This allows them to focus entirely on their thesis. Without this support progress towards their thesis would take significantly longer, negatively affecting the students employment opportunities and long-term career plans.

The graduate student traveled to their first ACS Colloids & Surface Science Symposium with financial support from this project. That travel increased their exposure to the broader research community surrounding this area, allowed them to practice their scientific presentation skills, and also facilitated networking that will be critical to their career.