John Leeman, *B.S. Candidate, Geophysics/Meteorology, University of Oklahoma*
Megan Elwood Madden, *Assistant Professor, ConocoPhillips School of Geology and Geophysics*

COLLABORATIVE GAS HYDRATES RESEARCH AT OU

Gas hydrates (clathrates) are cages of water molecules surrounding guest molecules such as methane or carbon dioxide. Sir Humphry Davy first characterized hydrates in the early 1800's, but many things about the structure, formation, and dissociation of hydrates are not well understood. Hydrates have always been a concern to industry from a drilling safety standpoint and have even caused problems in pipelines by forming clathrate 'plugs' resulting in downtime. Gas hydrates also represent a massive reserve of methane, an estimated 6.4 trillion tones of methane (Buffett and Archer, 2004). This stored gas has inspired the 'Clathrate Gun Hypothesis' which suggests that a climate shift could destabilize gas hydrates releasing more greenhouse gas into the air in a positive feedback cycle (Kennett et al., 2003). Hydrate could also be an energy source as shown in the Prudhoe Bay and North Slope tests of recent years (Boswell, 2007). Dissociating one liter of clathrate will yield about 164 liters of gas!

Students and faculty at the University of Oklahoma are currently conducting clathrate experiments on a variety of scales to better characterize and monitor hydrates. At OU experiments are taking place in Dr. Megan Elwood Madden's lab using small (<1L) pressure vessels to study the rate at which hydrate forms and decomposes under various temperature and pressure conditions. These experiments are being performed with carbon dioxide as well as methane to allow application of the results from Earth to other planets (Leeman and Elwood Madden, 2010).

In collaboration with Oak Ridge National Laboratory, John Leeman has been working with the 72L Seafloor Process Simulator (SPS) for two years as a summer intern. This large pressure vessel is made of corrosion-resistant Hastelloy and cooled in a commercial cold room with an explosion-proof gas evacuation system. The SPS allows hydrate to be formed in an ocean floor environment under thousands of pounds per square inch pressure and just above the freezing point of water (Phelps et al., 2001). A sediment column is built within a PVC bucket, fit with instrumentation, and lowered into the SPS. The vessel is cooled and pressurized to form gas hydrates within the sediments.

Title Figure: Sealing the lid of the SPS with a hydraulic torque wrench.

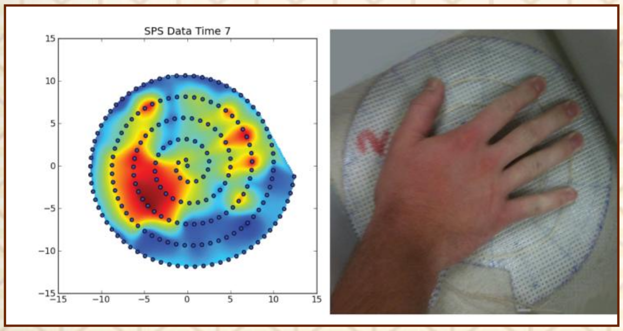

Figure 1 – A hand placed on a spiraled DSS fiber is easily resolved with the fiber optic sensing system.

Caption goes here

Leeman and Dr. Elwood Madden have worked with ORNL colleagues to develop a unique instrument to monitor hydrate formation and decomposition within the SPS. Fiber optic cables with Bragg gratings embedded every 1cm along their length are spiraled in the sediment. By sweeping a laser optical backscatter reflectometer through a range of wavelengths each grating is interrogated for changes in its characteristics. From this a 'Temperature Strain Value' (TS value) can be calculated and used as a combined proxy for temperature and physical forces at that location on the fiber (Hill and Meltz, 1997). John Leeman has developed software to estimate the position of each sensor in space given the orientation and vertical distribution of the fibers, grid the TS data, and show areas of high and low TS value (Leeman et al., in preparation). Shown in **Figure 1** is an experimenter's hand placed on a fiber and the output of the in house software.

A variety of experiments have been conducted in the SPS. A split column experiment has been conducted with sediment split vertically with a plastic mesh and filled with sand and silt. This experiment was conducted to investigate the effect of grain size on hydrate formation and to determine if the instrumentation in the sediments provided a pathway along which the gas was flowing**.** **Figure 2** shows the results of the experiment in which it is clear that the areas of hydrate (hot colors) are in the sand. In addition, a heat induced production test is currently underway. Hydrate is synthesized within a sand column; the hot water is pumped through a heat exchanger deep in the column to dissociate the hydrate and free the gas. Hydrate dissociation is endothermic, so it becomes colder leading to self-preservation. The effect of continuous heat flow on hydrate production rates will be determined by constantly pumping hot water through the system.

Experiments are also underway to determine fundamental properties of hydrates such as the bulk modulus. Claudia Rawn, an ORNL materials scientist, obtained beam time on a neutron diffractometer at the High Flux Isotope Reactor (HFIR). Hydrates were synthesized in the lab using deuterium and CO_2. The clath-rate was then cold loaded into a TiZr cell and neutron diffraction experiments conducted up to 100,000 psi. Samples were also taken to ORNL's Spallation Neutron Source (SNS) for analysis. Other samples were also loaded onto a computer controlled cold stage in a PANalytical X-ray diffractometer. With the Xcelerator detector diffraction patterns can be detected up to 100 times faster than conventional instruments allowing the evolution of the diffraction pattern to be examined increasing temperature of the sample stage decomposes hydrate.

Through collaboration with ORNL we are continuing to learn new things about clathrate formation and hazards. This research impacts natural gas production technology, climate modeling, risk assessment, and even planetary research.

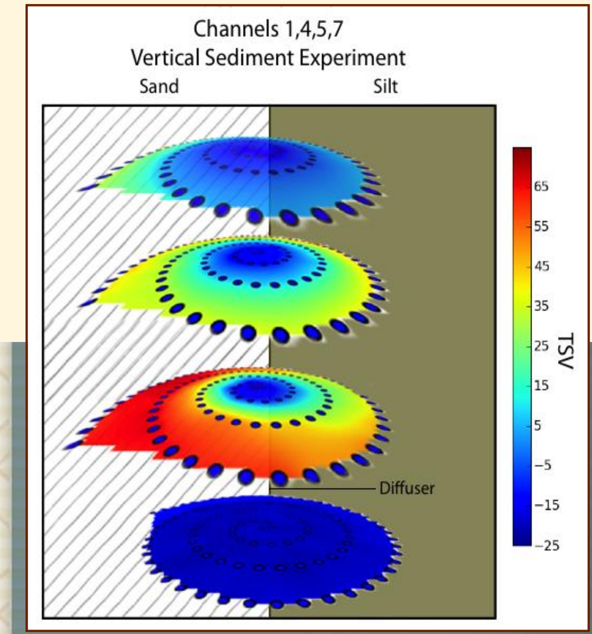

Figure 2 – Clathrate shows a clear formation preference in the sand, indicated by hot colors. The silt has some hydrate forming along the edges of the sediment column.