Clean Power at the Bottom of the Ocean

University of California, Irvine

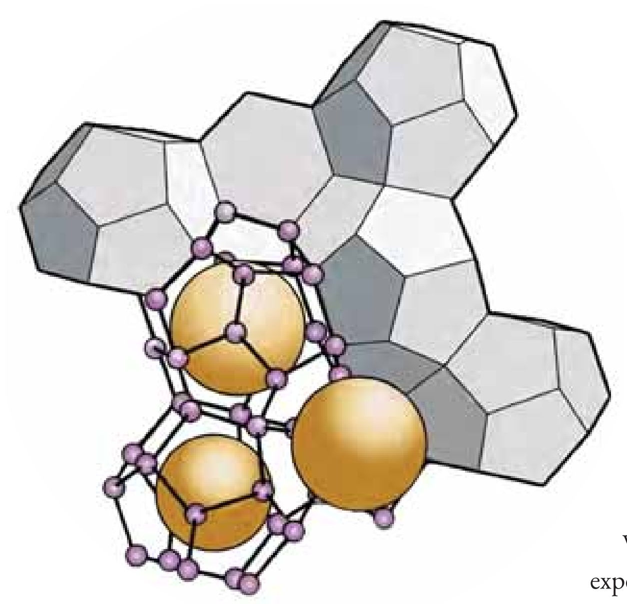
Imagine a power station that produces inexpensive energy with no pollution and lies at the bottom of the ocean. It sounds like the stuff of science fiction, but this was the guiding vision of a research project at the University of California, Irvine (UCI), funded by the Keck Foundation in 2012. With this award, Derek Dunn-Rankin and Peter Taborek, with project scientists Sunny Karnani and Yu-Chien (Alice) Chien, built the W. M. Keck Deep Ocean Power Science Laboratory, a unique facility that can recreate the pressures found at the bottom of the sea.

The visionary power station would be fueled using methane from hydrate clathrates, a form of ice that burns (Figure 1). As ice composed of methane hydrates (MH) melts, it releases over 160 times its volume of methane gas, making these fiery snowballs an attractive energy source. This drives global interest and research in using MH as an inexpensive, clean-burning fuel, especially in countries that need to import fossil fuels. The primary byproducts of combustion are water and carbon dioxide (CO_2).

Figure 1 ▲
A burning snowball. Water drips during methane hydrate combustion

Clathrates are a class of materials that trap one substance inside the matrix of another. In hydrate clathrates, water molecules freeze into a crystal with an open framework that can trap small molecules such as methane (CH_3 or natural gas) and CO_2 (Figure 2). Methane hydrates are naturally occurring forms of ice, found in abundance throughout the world's oceans and underground in permafrost (Figure 3). In fact, the world-wide volume of MH is comparable to all other fossil fuels combined. However, methane hydrates are a problem as they can form spontaneously in natural gas pipelines, where they interfere with valves and flow sensors and can block the flow of gas.

The Keck Deep Power Science Lab has focused on the formation of MH and their combustion at extreme pressures. To standardize the MH samples, they were grown in the laboratory. Surprisingly, the researchers found that adding sodium dodecyl sulfate, a common surfactant used in many home cleaning products, enhanced the growth rate by a factor of 100. Without surfactant, water forms a shell of normal ice, which is denser than the clathrate structure and slows the uptake of methane. The addition of a surfactant causes the MH to grow with a highly branched structure that looks like frost. This high surface area can more readily absorb methane. Conversely, the addition of salt significantly suppresses the formation of MH and is commonly used to prevent their formation in natural gas pipelines.



▲ **Figure 2**
Clathrate hydrate has a special chemical structure trapping methane in a crystallized water cage

So, how does a MH burn? Much like a candle. Once ignited, heat from the flame melts a bit of the ice, coating it in a liquid film. Methane and water vapor escape the liquid film, forming a second layer that feeds the flame, while excess liquid water drips from the bottom of the MH as it burns (Figure 4). For combustion to continue, most of the water from the hydrate must drain away. Unlike a candle, much of the heat of the burning methane is absorbed by the vaporization of water. The UCI group developed a test stand to investigate the behavior of water-laden methane flames. Not surprisingly, they found that the higher the water content, the lower the flame temperature. Importantly, their experiments measured the temperature profile of the flame and the distribution of hydroxide (OH), a reaction intermediate, in the flame. Their results matched theoretical predictions.

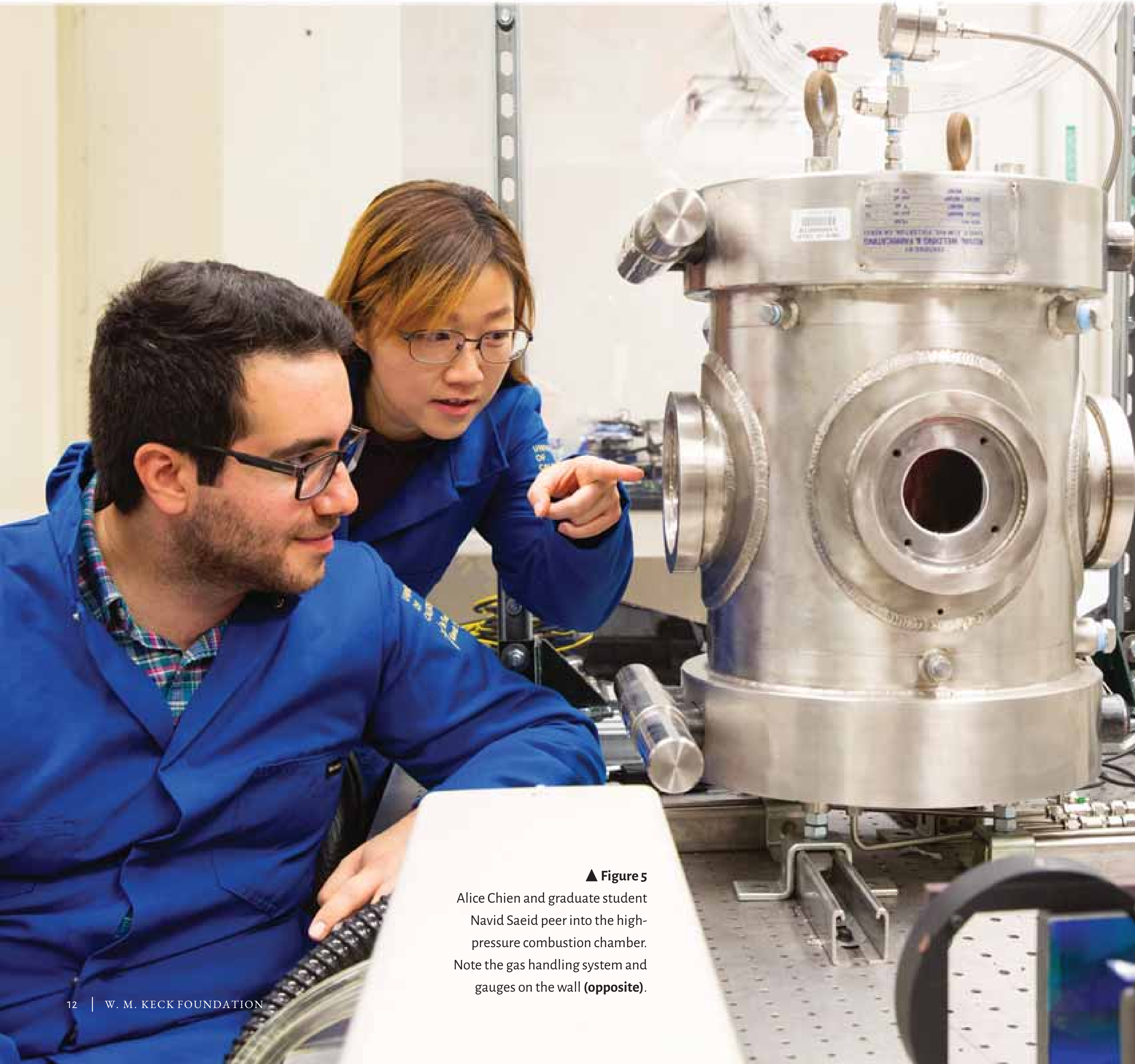
The team is now applying what it has learned about water-laden methane flames to the combustion of MH under pressure. Methane clathrates are found in the oceans at depths with pressures of 100-200 atmospheres, a new regime in combustion science. These enormous pressures necessitated the construction of a heavy-walled combustion chamber, which took several years to produce. The chamber has optical access for measurements and visual inspection of the combustion process (Figure 5). As part of the diagnostic system, the team developed a novel optical temperature sensor that can be moved through the flame to determine its temperature profile. The team also purchased a femtosecond laser to holographically image the combustion process.

The new research frontier of the Deep Power Sciences Lab is the sequestration of CO_2. Initial experiments worked with a two-step process of first burning MH, then refreezing the water released during combustion in a gas stream of CO_2 to form carbon dioxide hydrates. Just like the MH, the CO_2 hydrates contain over 160 times their volume of CO_2 gas and form a stable ice at the pressures and temperatures of the deep ocean. The CO_2 hydrate could safely be returned to the ocean floor as the only waste product of power generation. The UCI team is now pursuing a new strategy – direct replacement of methane with CO_2 without melting the MH. If successful, liberation of methane without first melting the MH would be a huge win for power generation on two fronts. First, the substantial amount of heat lost to the melting of MH and vaporization of water could instead be used to generate power. Second, the amount of water in the methane flame would be greatly reduced, leading to a much hotter flame, which is more efficient for power production.

▲ **Figure 3**
Chunks of methane hydrate clathrate in a sample from the Gulf of Mexico

It turns out that CO_2 hydrates are thermodynamically more favorable than MH, so nature is on their side. However, natural exchange is too slow to be practical. The team is exploring ways to speed up the process by increasing the surface area of the MH exposed to CO_2 and exploring different pressure and temperature regimes.

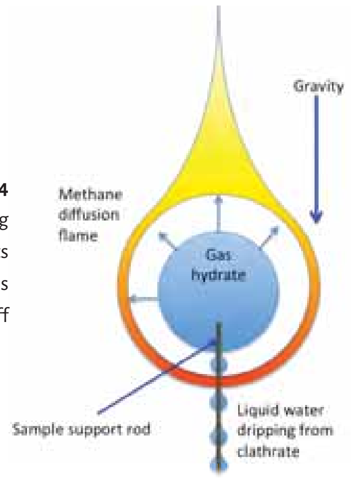
The scientific community questioned whether a deep power science laboratory like the one proposed by UCI could be built. We are pleased to have taken the risk to fund the Dunn-Rankin and Taborek team, which has not only successfully built the laboratory but continues to bring this cutting-edge science to the forefront while also engaging many students in the field of MH and combustion science.



▲ **Figure 5**
Alice Chien and graduate student Navid Saeid peer into the high-pressure combustion chamber. Note the gas handling system and gauges on the wall **(opposite)**.

▶ Figure 4

Schematic of a burning sphere of MH. Water coats the surface with the excess dripping off



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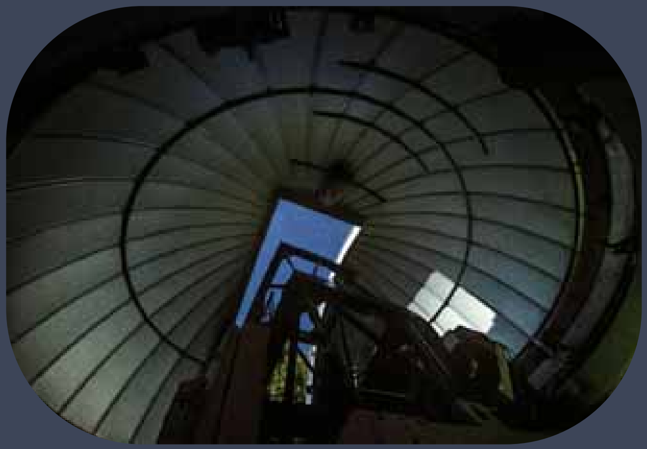
(Above) One of the six domes atop Mount Wilson that house the telescopes of the CHARA Array interferometer

(Right) Images of five stars based on observations with the CHARA Array



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Gazing out the dome of one of the six telescopes that make up the CHARA Array

Georgia State University

Enhancing Data and Imaging Capabilities

Over twenty years ago, Georgia State University began building the Center for High Angular Resolution Astronomy (CHARA) Array of telescopes atop Mount Wilson in Southern California. Mount Wilson is a geographically modest but historically important peak for the field of astronomy. Easily visible from the offices of the Keck Foundation in downtown Los Angeles, the summit is home to many record-breaking telescopes, including the CHARA Array, which has the highest resolution of any optical or infrared system ever built, allowing unprecedented views of the stars.

The CHARA Array began as an optical interferometric array of five one-meter telescopes whose five beams of light can be combined to provide the equivalent angular resolution of a single, giant telescope 330 meters in diameter. A Keck Foundation grant in 1998 enabled construction of a sixth telescope that provided data and imaging capability growth of over 50% – at an overall increase in cost of just 13% – a powerful example of leveraged funds.

The Array has proved spectacularly successful at studying stars "up close." Most telescopes see stars as points of light from which much can be measured and learned; but they collect almost no information about these stars' shapes and surface properties. Without interferometers and their high angular resolution, we have only our Sun to study for such important details. CHARA has also provided surprise after surprise about the diverse types and behaviors of stars in our neighborhood of the galaxy, including extremely fast rotators (with distorted shapes), as well as the first resolved images of binary star systems that reveal exotic aspects of their creation and destruction.

More recently, the CHARA Array has installed adaptive optical systems that use mirrors capable of changing shape many hundreds of times per second so they can correct for the image distortions introduced by the atmosphere.