Gas-Hydrate Storage of Natural Gas

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Abstract

Gas hydrate storage of gases occurs in nature. Recent core data from USGS deep ocean drilling endeavors form the basis of their estimates of more carbon stored in gas hydrates of ocean sediments than exist in all discoveries of coal, natural gas, and crude oil. Realizing the value of natural gas as a clean-burning, economical, abundant and efficient energy source for peak loads at electrical power plants, but realizing the major impediment of storage means, DOE granted our laboratory a study to determine feasibility of safely storing above-ground natural gas in synthetic gas hydrates. The research suggested a process that provided rapid hydrate formation, complete conversion of interstitial water, and packing of hydrate mass as it formed; 156 volumes of gas at standard temperature and pressure stored in 1 volume of the ice-like hydrate was accomplished. Subsequently, as a semester project, a group of five senior chemical engineering students were asked to put the hydrate research findings into an innovative large-scale plant design for their capstone design course; they were to select, size and cost the equipment; they were to create process flow charts, perform mass/energy balances, and perform an economic analysis of the prospective storage facility for a power plant. Their efforts in the preliminary design predicted that a 2.25 million standard cubic feet storage facility could be economically competitive with conventional natural gas storage if multiple cycles per year were involved. Their in-depth analysis and first-hand laboratory experience proved to be a unique learning experience in energy storage problems.

Community Service and Student Design

To teach engineering capstone design courses, there are many approaches available as to procedure and course content. One approach that we have found meritorious has been the inclusion of a community service component in the statement of the problem. By community service is meant an innovative design of a project that could benefit the community (local, state, or nation). For example, the project could improve the community's economic well being, address an environmental problem, or introduce the use or more efficient use of a natural resource. This might seem like too wide a swath to cut for senior engineering students, but consider some representative projects successfully incorporated in the senior chemical engineering design course at Mississippi State University. These examples served as precedents for the subject project of gas hydrate storage.

The following three projects assigned to our students, two [1] of which have been reported, are noteworthy: (1) Design a facility and perform an economic analysis for cleaning the soil and underlying water of one of Mississippi's abandoned industrial sites contaminated with trichloroethylene, perchloroethylene, and PCB; local newspapers had reported health problems in nearby communities. Data and lecture for the design was obtained from the Mississippi Department of Environmental Quality (DEQ). After submitting final bound reports and oral reports, the students presented their findings at the annual meeting of the Mississippi Academy of Sciences. (2) Design facilities for the recovery of platinum group metals from spent automobile catalysts based on two new processes: one process patented a few years earlier by the U.S. Bureau of Mines and a second process utilizing plasma arc extraction. (3) Design a coffee-bean decaffeination plant as a potential new industry for the state that would use supercritical CO_2 for extraction. With CO_2, decaffeination circumvents damaging solvents; supercritical CO_2 is a solvent selective of caffeine over flavor components. More importantly for community service, such a facility could utilize a unique and currently unexploited Mississippi natural resource in deep formations near the center of the state of 99.9+% pure carbon dioxide which may contain as much as 7 tcf (trillion cubic feet) of the supercritical fluid. Making use of published patents, the students designed a facility, specified a location in Mississippi, and showed its economic attractiveness. They were awarded 1st place in a regional paper contest that detailed the process.

A fourth project of our capstone design course will be mentioned. Richard Smalley in research at Rice University in 1985 discovered fullerenes, a 3rd configuration of carbon in addition to graphite and diamond. The discovery won him a Nobel prize in 1996. Since that relatively recent discovery, chemists have determined an amazing array of potential uses of the material. However, despite many proposed applications which promise to have profound impact on society, fullerenes have only been produced by chemists in small quantities at high cost. The students were required to design a process that could provide the fullerenes in commercial quantities. In order to fulfill the assignment, extensive literature searches of current research articles and patents were necessary; innovative thinking was especially required; it was necessary for students to study state-of-the-art equipment selections. Their calculations and conceptual design were an excellent treatise on solving the fullerene scale-up problem.

In each example cited, the design project emphasized a potential to impact the well-being of society. Likewise, the natural gas storage in hydrates has potential societal benefits.

Natural Gas Storage, DOE Statement of the Problem

The U.S. Department of Energy[2] in 1997 issued a call for proposals to alleviate a problem of power plants: how to safely store aboveground natural gas on-site for use at peak power demands. On-site storage is a limiting factor in the full utilization of natural gas. Natural gas is the cleanest burning of fossil fuels; it is abundant; it has a domestic source, not dependent on imports; an extensive pipeline infrastructure is in place for delivery; usually, it is relatively cheap. For these reasons, burning natural gas is desirable during those periods of the day when peak electrical loads occur, but a spike of pipeline withdrawal for a brief period is not possible. Some states near the Gulf of Mexico may have the option of storing gas in salt domes or, in producing states, the option may exist of storing in depleted gas reservoirs. However, some areas of high population density in the country have neither option.

Aboveground storage in these population-dense areas requires safety and economy. For example, compressed natural gas or liquefied natural gas (LNG) have high pressure or low temperature requirements, have an inherent danger associated with rupture of the storage tank, have the risk of ignition of suddenly-released gases, and have serious economic problems in achieving and maintaining storage pressure or temperature.

The author was awarded a grant by DOE to determine the feasibility of storing natural gas in gas hydrates, primarily for peak load use at electrical power plants. After all, in the last few years the U.S. Geological Survey has estimated that as much as twice the carbon is stored in gas hydrates occurring naturally in ocean sediments as is contained in all coal, crude oil, and conventional natural gas combined.[3] It is a national goal brought forward by DOE and funded by Congress to develop technology by the year 2015 to produce commercially the natural gas stored in ocean floor gas hydrates.[4] The author, as principal investigator, performed research under the grant and after significant laboratory breakthroughs, [5] a group in the senior design course was given the semester project to convert these breakthroughs into a meaningful storage facility design. All of the students assigned to the group had industry work experience through the Cooperative Work Program.

Establishing Feasibility of Gas Hydrate Storage

To understand the problems faced in an industrial storage of natural gas in gas hydrates, consider the following technical scenario. Gas hydrates are ice-like materials. As water is cooled under pressure of a natural gas (or other gases of similar molecular size), a 3-dimensional structure of hydrogen-bonded water develops similar in shape to a soccer ball, and the properly-sized gas molecules fit into its cavity to stabilize a crystal structure above the normal freezing point of water at a stabilization temperature dependent upon pressure. The faces of many 3-D structures meld to give occluded gas molecules in the crystals having a gas density approaching liquefied gas. As much as 180+ volumes of gas (measured at standard temperature and pressure) can be stored in 1 volume of the solid-phase gas hydrates. We found the optimum economical operating conditions would be 156 vol/vol of gas stored at 550 psi and 37°F.[6] From a safety standpoint, the stored gas is essentially encased in ice as a solid solution. If a hydrate storage tank were to be ruptured accidentally, gas would be released only as fast as latent heat of decomposition could be transferred. As an illustration, photographs show unconfined ice-like hydrates in air releasing natural gas at atmospheric pressure to burn at a slow, controlled rate.

At the beginning of the research, the four formidable problems for establishing a feasible gas hydrate storage process were the following: (1) Slow rate of hydrate formation. The formation rate is extremely slow in a non-stirred system because a hydrate film forms on the water surface to separate water and gas. (2) A quiescent system would be needed for scale up. It was anticipated that the attendant maintenance and operating problems of a stirred system would be economically prohibitive. (See results for substantiation of this estimate.) (3) Free water in the interstitial spaces of the hydrate particles can occupy up to 89% of the total volume, yet store practically no gas, causing excessive storage container costs. (4) Separating and packing hydrate particles from a chilled slurry under pressure would be impractical.

Prior to giving the design problem to the students, research [5,7] resolved the four problems: (1) Adding a surfactant to the water to form a solution at or above its critical micellar concentration (CMC) increased hydrate formation rate in a quiescent system >700 times. The surfactant's micelles acted as nuclei for hydrate crystal formation and the forming particles were transported rapidly with surfactant micelles to the stainless steel cell walls to be adsorbed, thus clearing the water surface of hydrate film and maintaining direct contact of gas and free water. (2) A non-stirred system could be achieved with a micellar solution. Non-stirred micellar solutions gave reaction rates approximating rates of stirred water systems. (3) Because surfactant micelles were excluded from the hydrate structure but existed in the free water of the interstitial spaces of the hydrates, interstitial water continued to react to completion, storing a full contingent of gas in the interstitial water–utilizing all the bulk volume of the container for gas storage. (4) The hydrate particles adsorbed on the test cell walls as they formed, building radially in a uniform manner until they filled the cell. A low surfactant concentration (CMC) of 242 ppm was sufficient.[4]

Given this background information, the students were required to design a hydrate-storage process with accompanying process flow charts, size/select/cost equipment, perform mass and energy balances calculations, and do an economic analysis comparing the proposed process with conventional processes.

Laboratory Work , WWW, Conferences

In the gas-storage design project, the students had the advantage of observing in the laboratory hydrate formation, storage, and decomposition. It was possible to collect specific data in the laboratory–for example, the efficacy of hydrate-surfactant adsorption on aluminum or copper surfaces versus stainless steel surfaces. Importantly, the observations helped generate and sustain project enthusiasm–always seemingly difficult to attain in an arduous assignment of semester duration.

In the gas hydrate project, as in the other community-based projects, the worldwide web facilitated background information searches that saved time.

In addition to their usual collaboration on the project, the group of four students met twice each week for about an hour per meeting with the professor to discuss the project. Some sessions were brainstorming sessions for new ideas. Other sessions were group discussions of technical details or calculations. Individual assignments were made on calculations and library searches.

Results of Design Project

A process design resulted from the efforts that would store 2.25 million standard cubic feet of natural gas in gas hydrates per cycle.[8] A complete formation, storage, decomposition cycle could be accomplished in a 24-hour period. A semicontinuous process resulted in which the storage tank with water-surfactant solution could be pressurized to 550 psi with natural gas; hydrate formation and self-packing would proceed to fill the tank with hydrates within an 8-hour period. Banks of aluminum plates to collect the hydrates and to transfer latent heat during formation and decomposition would be situated on a removable rack. Water after decomposition would remain in the tank for reuse. (Some hydrogen-bonding structure of the hydrate crystal remains in the water after decomposition making hydrates easier to form on subsequent cycles.) Heat transfer tubes were designed to convey adequate chilling or heating water for formation/decomposition. Heat transfer rates, strengths of structure components, energy and mass balances, makeup water and makeup surfactant rates were calculated. No mechanical stirring would be needed– simply pressurize with natural gas, cool with a refrigeration unit, and the gas occludes in the self-packed hydrates. Emphasis was on making the simplest design possible for low capital investment and maintenance.

Despite simplification of the process, labor costs for the semi-continuous process remained the most expensive item of the operating costs; labor requirements were estimated by the method of Turton.[9] It becomes apparent that if additional costs from mechanical stirring and processing cold, pressurized slurry were imposed, the process would not be economically competitive–fortunately, micellar solutions obviate the need for agitation.

Cost comparisons were made with conventional storage in depleted reservoirs, salt caverns, and LNG.[10] Separate comparisons were made of total capital investment [11] and operating costs. In both comparisons, the hydrate process was found to be more economical than LNG, the most expensive conventional process, when more than 5- 15 cycles per year were required. The hydrate process was estimated to be more economical than the best conventional process, depleted reservoir storage, when more than 50- 125 cycles per year were required. Note that multiple cycles would be prevalent for power plant storage.

The complete details of the design and the calculations may be reviewed in the final reports on the project.[5,6,8] Potential uses for the process are suggested in Table I.

Table 1. Potential applications of process design

Application	Need
Peak-load use at electrical power plants	Cleaner burning fuel. Lack of safe, aboveground storage near populated regions of country.
Storage and transport of natural gas from future ocean-floor gas hydrate production	If national goal to produce seafloor hydrates realized by 2015, means to transport produced gas to shore is needed.
Storage and transport of natural gas from conventional gas produced offshore at depths beyond gas pipelines	Deepwater production that is planned lacks means to transport gas to shore. Depths are beyond pipeline infrastructure
Storage and transport of natural gas from Alaskan oil fields	20+ trillion cubic feet of gas at Prudhoe Bay available, but untransportable, as oil production declines
Storage and transport of natural gas to remote areas for small-scale applications	Remote areas on land beyond pipeline infrastructure. Small applications.
On-board storage of natural gas as alternative fuel for motor vehicles	Safe storage and capacity limits natural gas use as alternative fuel in vehicles

Perhaps the most important aspect of community-based projects, such as gas hydrate storage, was the enthusiasm and interest generated from knowing that their engineering knowledge when applied has a special meaning for dealing, even in a small way, with specific problems of society. Additionally, the student awareness of community problems and the student's capability to address them with specialized technical knowledge may remain with them throughout their careers in industry.

Conclusions

Incorporating community service in a capstone design course has proven to have advantages: (1) Students sustain deeper interest and enthusiasm for a rigorous, semester-long project, (2) Students see the application of their hard-earned engineering knowledge for the benefit, or potential benefit, of society. (3) The work instills an awareness of community service and the connection with the engineering profession which they carry into industry during their careers. (4) Applied, innovative projects open doors for student paper contests, technical presentations, community recognition. (4) The design projects may influence career paths or have particular influence with a recruiter.

The project to design a gas-hydrate storage facility for natural gas to be used by power plants at peak loads successfully presented a new and a novel approach to a national problem. The student's capability of meshing calculations with laboratory data obtained in their department independently of the course and the capability of going into the laboratory to see the characteristics of gas hydrate formation/storage/decomposition was extremely helpful. Through group meetings, the students and professor discussed an innovative design to arrive at a facility that could safely store 2.25 million SCF of natural gas per cycle in a minimum cycle time of 24 hours. Economic analysis predicted the new storage method to be economically competitive with conventional storage methods.

The student's approach to a national problem, as stated by DOE, established tangible results of an innovative design that could help alleviate the gas storage problem. Intangible results include the student's career awareness of the engineer's role in solving societal problems.

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Biography

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